Polymerization of Tetrahydrofuran by the AlEt₃-H₂O-Promoter System
Function of Promoter in Polymerization Kinetics

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ABSTRACT: A Kinetic study on the polymerization of tetrahydrofuran catalyzed by the system AlEt₃–H₂O(2: 1)-promoter was carried out. Epichlorohydrin, propylene oxide and β-propiolactone were employed as the promoter. The concentration of propagating species [P*] was determined at several times during polymerization by means of a new method in which the propagating species at polymer chain end was converted into the corresponding phenyl ether by end-capping with sodium phenoxide, and the phenyl ether group was analyzed by UV spectroscopy. On the basis of the plot of [P*] *vs.* time, the rate constant of propagation k_p was calculated according to

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

where $[M]_t$'s and $[M]_e$ are the instantaneous and equilibrium monomer concentrations, respectively, and $\int_{t_1}^{t_2}[P^*]\,dt$ was obtained by graphical integration. It has been concluded that the nature of the promoter does not affect the rate of propagation reaction, although it does affect the overall rate and the initiation reaction. These results support the concept of the promoter's function, *i.e.*, the promoter is responsible mainly for the formation of propagating species.

KEY WORDS   Promoter / Polymerization / Tetrahydrofuran / Active Species Concentration / End-Capping / Phenyl Ether Group / Propagation Rate Constant / Initiation Efficiency /

This paper reports the kinetic studies made on the function of reactive, small ring compounds in the polymerization of tetrahydrofuran (THF) by the AlEt₃–H₂O system. Our previous studies have shown that the cationic polymerization of THF by AlEt₃–H₂O system can be achieved in the presence of a small ring compound.[1,2] Effective small ring compounds are three- and four-membered cyclic ethers and four-membered lactones. As to the functions of small ring compounds it has been assumed that the cationic ring-opening of reactive cyclic compound constitutes the initiation reaction, in which the cyclic trialkyloxonium ion, the propagating species, is formed.[3]

In the THF polymerization with the AlEt₃–H₂O (2: 1)-epichlorohydrin (ECH) system, the formation of the genetic species (2a or 2b) was shown by isolating its end-capped derivative in a mixture of an early polymerization system treated with sodium methoxide.[4]

The ring-opening reaction of these cyclic compounds is essential for the initiation reaction. Their functions are generally observed in the THF polymerization with various Lewis acid catalysts, and they are differentiated by the term "promoter" from the so-called "cocatalyst" such as active halogen compounds and protic compounds.[3]

The purpose of the present study was to examine the effect of the promoter on the kinetics of the THF polymerization catalyzed by AlEt₃–H₂O (2: 1)-promoter. The concentration of propagating species [P*] was determined at various times during polymerization from the amount of phenyl ether group formed on treatment with

sodium phenoxide.[5] On the basis of the time-[P*] relation, the rate constant of propagation k_p was calculated.[6] As promoter, ECH, propylene oxide (PO) and β-propiolactone (BPL) were employed.

RESULTS AND DISCUSSION

Figure 1 shows the variation of [P*] in the course of the THF polymerization catalyzed by AlEt₃–H₂O(2:1)–ECH. The [P*] increased in an initial stage and then remained almost constant.
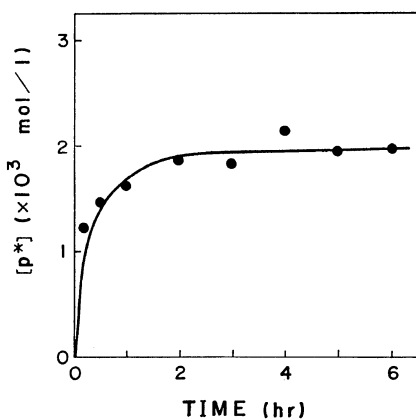
Figure 1. Polymerization of THF by AlEt₃–H₂O-(2:1)-ECH: bulk polymerization at 0°C; [M]₀ 12.6 mol/l; [AlEt₃]₀ 0.18 mol/l; [ECH]₀ 0.020 mol/l.

This observation is in general agreement with our previous finding that polymerization using this catalyst system proceeds by means of a stepwise addition mechanism without chain transfer or termination.[7]

On the basis of the equilibrium polymerization mechanism, the rate of polymerization is expressed by

$$- \frac{d[M]}{dt} = k_p[P^*]\{[M] - [M]_e\} \qquad (3)$$

in which [M] and [M]ₑ are the instantaneous and equilibrium monomer concentrations, respectively.[8] By means of the time-[P*] relationship in Figure 1, the k_p value was calculated by the following equation:

$$\ln \frac{[M]_{t_1} - [M]_e}{[M]_{t_2} - [M]_e} = k_p \int_{t_1}^{t_2} [P^*] dt \qquad (4)$$

in which $[M]_{t_1}$ and $[M]_{t_2}$ are the monomer concentrations at time t_1 and t_2, respectively. A plot of Eq. 4 for this polymerization is shown in Figure 2. Here, $\int_{t_1}^{t_2} [P^*] dt$ was obtained by graphical integration. From the slope of the linear plot, k_p was calculated (Table I).
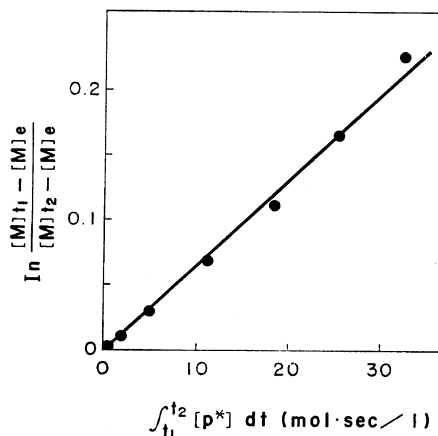
Figure 2. Polymerization of THF by AlEt₃–H₂O-(2:1)-ECH: bulk polymerization at 0°C; [M]ₑ 1.7 mol/l[8]; t_1 0.

Polymerization by PO as the promoter was then examined. Figure 3 shows the time-[P*] relationship of the polymerization catalyzed by the AlEt₃–H₂O(2:1)–PO system. In this case, the procedure for the [P*] determination had to be modified because a reference experiment had indicated that the extent of the reaction of PO with sodium phenoxide to generate the phenyl ether group was not negligible under the end-capping conditions. In this polymerization, therefore, the excess PO was removed by vacuum distillation from the system after 10 minutes' reaction (see Experimental Section). As can be seen in Figure 3, [P*] is decreased slowly with time, showing the occurrence of a slow termination reaction. A plot of the first-order rate law for the monomer concentration (Figure 4) also indicates the presence of termination. Using Eq. 4, the k_p value was obtained from the slope of the linear plot
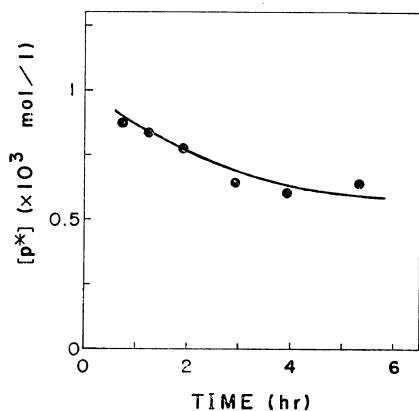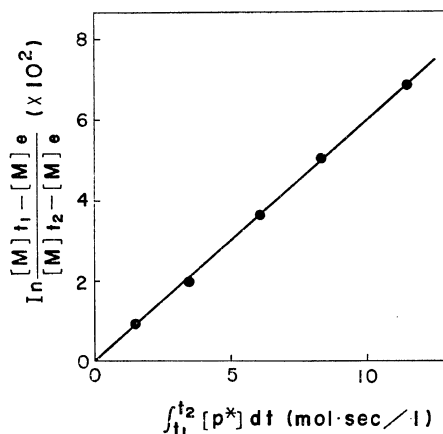
Figure 3. Polymerization of THF by $AlEt_3$–H_2O-(2:1)–PO: bulk polymerization at $0°C$; $[M]_0$ 12.6 mol/l; $[AlEt_3]_0$ 0.15 mol/l; $[PO]_0$ 0.030 mol/l.

Figure 5. Polymerization of THF by $AlEt_3$–H_2O-(2:1)–PO: bulk polymerization at $0°C$; $[M]_e$ 1.7 mol/l^8; t_1, 45 min.
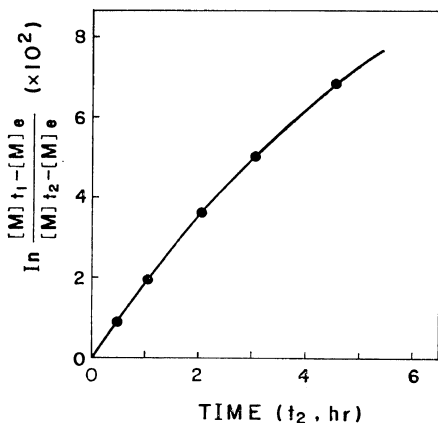
Figure 4. Polymerization of THF by $AlEt_3$–H_2O-(2:1)–PO: bulk polymerization at $0°C$; $[M]_e$ 1.7 mol/l^8; t_1 45 min.
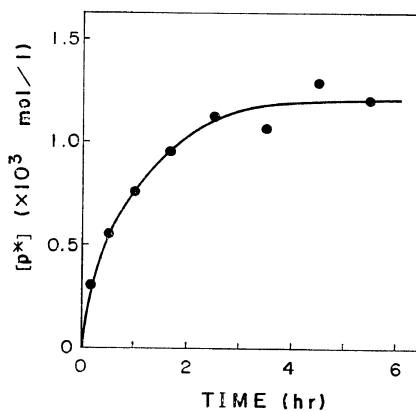
Figure 6. Polymerization of THF by $AlEt_3$–H_2O-(2:1)–BPL: bulk polymerization at $0°C$; $[M]_0$ 12.6 mol/l; $[AlEt_3]_0$ 0.30 mol/l; $[BPL]_0$ 0.005 mol/l.

(Figure 5 and Table I).

Figure 6 shows the time-[P*] profile of the polymerization catalyzed by $AlEt_3$–$H_2O(2:1)$–BPL. By a reference experiment, phenyl ether formation by the reaction of sodium phenoxide with BPL was shown to be negligible. As in the polymerization by $AlEt_3$–$H_2O(2:1)$–ECH, [P*] increased in the initial stage and then remained

unchanged. The curve of a first order plot for the monomer concentration (Figure 7) is consistent with the time-[P*] profile. Here it is shown that polymerization by this catalyst system also proceeds without termination. However, the rate of [P*] increase in the initial stage is slower in comparison with the cases of ECH and PO. The k_p value was obtained by the
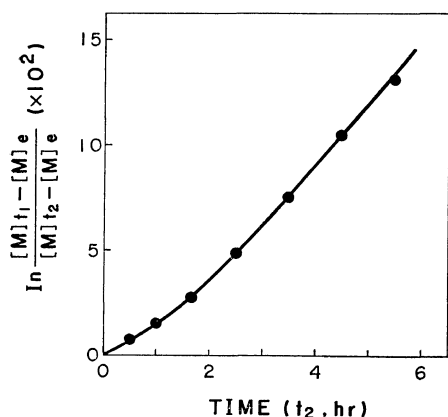
Figure 7. Polymerization of THF by AlEt₃–H₂O-(2:1)–BPL: bulk, polymerization at 0°C; [M]ₑ 1.7 mol/l[8]; t₁ 0.
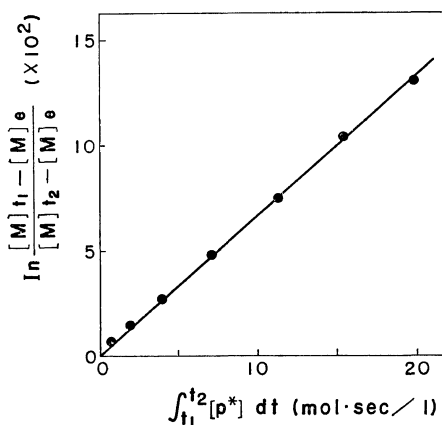
Figure 8. Polymerization of THF by AlEt₃–H₂O-(2:1)–BPL: bulk polymerization at 0°C; [M]ₑ 1.7 mol/l[8]; t₁ 0.

Table I. Propagation rate constants of THF polymerization by AlEt₃–H₂O(2:1)-promoter system[a]

Promoter	Concn. (mol/l)	[AlEt₃]₀[b] (mol/l)	$10^3 k_p$ (l/mol·sec)
ECH	0.02	0.18	6.6
PO	0.03	0.15	6.0
BPL	0.005	0.30	6.7

[a] Bulk polymerization at 0°C; [M]₀, 12.6 mol/l

[b] Amount of AlEt₃ used in the preparation of the catalyst.

to the nature of the promoter can be attributed mainly to the difference in the efficiency of formation of the propagating species from the catalyst components. These findings essentially support the concept that the promoter is chiefly responsible for the formation of the propagating species.

In the case of PO, the occurrence of termination reaction is also responsible for a slower rate of conversion as compared with the rates in the cases of ECH and BPL.

EXPERIMENTAL

Materials

THF, ECH and AlEt₃

Commercial reagents were purified and dried as described in the previous paper.[7]

PO

Commercial reagent was refluxed over potassium hydroxide pelletts and dried by repeated distillations over calcium hydride.

BPL

Commercial reagent was dried by refluxing and distilling twice over calcium hydride.

AlEt₃–H₂O(2:1) System

The catalyst was prepared as described previously.[7]

Procedure

Polymerizations were carried out in bulk at 0°C in a nitrogen atmosphere.

The reaction was initiated by the addition of a THF solution of promoter to a solution of AlEt₃–H₂O catalyst in THF at 0°C. The determination of [P*] was performed as described in the previous paper.[5,6] A modified procedure of [P*] determination in the polymerization by AlEt₃–H₂O (2:1)–PO system was as follows: the polymerization was performed as usual for 10 min, when the

same procedure as before (Figure 8 and Table I).

It is quite significant that k_p values for these three promoters (Table I) are almost the same, *i.e.*, the nature of promoter has no appreciable effect on the rate of propagation reaction. The overall conversion rate of polymerization, however, is known to be dependent upon the nature of the promoter to a considerable extent.[1-3] It has become clear from the present studies that the difference in the overall conversion rate due

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reaction was stopped by cooling in a Dry Ice-methanol bath. Any excess PO that may have been present was then removed *in vacuo* (1–2 mm) at −40∼−50°C. Distillation was continued until a small amount of THF was distilled (*ca.* 3 hr). Polymerization was then resumed at 0°C and [P*] determined.

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