# Concentration of Propagating Species and Rate of Propagation in Cationic Polymerization of Tetrahydrofuran

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*Received June 27, 1968*

ABSTRACT: Kinetic studies were carried out on the polymerization of tetrahydrofuran catalyzed by binary systems consisting of a Lewis acid and epichlorohydrin. As the Lewis acid component, boron trifluoride, tin tetrachloride and ethylaluminum dichloride were employed. At various times of polymerization, the propagating chain end was converted into phenyl ether by treatment with sodium phenoxide, and its concentration was determined by uv spectroscopy. It has been shown that in these polymerizations, [p*] is changed during the course of polymerization. From the time–[p*] curve and the time–conversion data, the rate constant of the propagation reaction $k_p$ was determined according to $\ln [([M]_{t_1} - [M]_e)/([M]_{t_2} - [M]_e)] = k_p\int_{t_1}^{t_2}[p^*]dt$, where $[M]_{t_1}$ and $[M]_t$ are the monomer concentrations at $t = t_1$ and $t_2$, respectively, and $[M]_e$ is the equilibrium monomer concentration. The cumulative value of [p*], $\int_{t_1}^{t_2}[p^*]dt$, is given by graph integration. The pattern of the [p*] change during the polymerization varied considerably with the Lewis acid catalyst. However, the $k_p$ value is little changed by the nature of Lewis acid catalyst.

Our previous studies have shown that the polymerization of tetrahydrofuran (THF) catalyzed by $AlEt_3$–$H_2O$ and epichlorohydrin (ECH) proceeds through a stepwise addition mechanism in which the propagating species continue to grow without being interrupted by chain transfer or termination.[1] In this polymerization, the concentration of the propagating species, [p*], corresponded to the concentration of the polymer molecule, which was determined according to

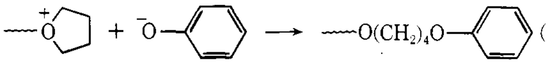
$$[p^*] = \left(\frac{\text{g of polymer}}{\text{mol wt}}\right)\left(\frac{1}{\text{vol of reaction system}}\right) \quad (1)$$

From [p*] thus obtained, the rate constant of the propagation $k_p$ can be calculated from

$$-d[M]/dt = k_p[p^*]([M] - [M]_e) \quad (2)$$

where [M] and $[M]_e$ are instantaneous and equilibrium concentrations of monomer, respectively.[1,2] The method of determination of [p*] by eq 1, however, is not applicable to those polymerization systems which involve chain transfer or termination.

In a recent paper, we have presented another method to determine [p*] in the THF polymerization, in which the propagating species at polymer end was converted into phenyl ether group by end capping with sodium phenoxide and the resulting phenyl ether group at the polymer end was quantitatively analyzed by determining its uv absorption.[3]


(3)

In the present study, the second method of [p*] determination was applied to the THF polymerizations by the binary catalyst system of a Lewis acid and ECH. Then the propagation rate constant, $k_p$, was determined from the time–[p*] curve and the time–conversion data.

Several kinetic studies on the THF polymerization with various catalyst systems have been reported.[4–8] However, the present study is the first specifically designed to determine directly the concentration of propagating species and to calculate the $k_p$ value on the basis of the time–[p*] relation.

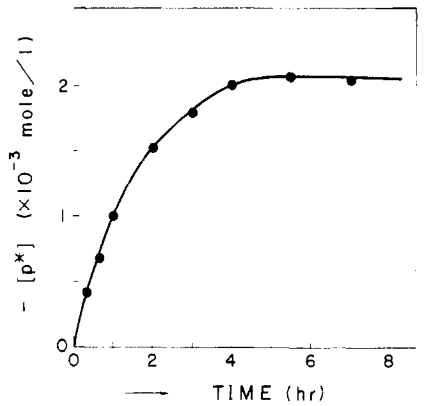


Figure 1. Polymerization of THF by $BF_3$–ECH: bulk polymerization at 0°; $[M]_0$, 12.6 mol/l.; $[BF_3]_0$, 0.011 mol/l.; $[ECH]_0$, 0.010 mol/l.

## Results and Discussion

**Concentration of Propagating Species.** The reaction conditions for the quantitative transformation of the propagating chain end into phenyl ether have been established (see Experimental Section). The course of bulk polymerization by $BF_3$–ECH system is shown in Figures 1 and 2. Figure 1 shows the variation of [p*] with time. It is observed that [p*] is increased slowly in the beginning of the polymerization, and then it

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(1) H. Imai, T. Saegusa, S. Matsumoto, T. Tadasa, and J. Furukawa, *Makromol. Chem.*, **102**, 222 (1967).

(2) T. Saegusa, H. Imai, and S. Matsumoto, *J. Polym. Sci., Part A-1*, **6**, 459 (1968).

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(4) B. A. Rozenberg, O. M. Chekhuta, E. B. Lyudvig, A. R. Gantmakher, and S. S. Medvedev, *Vysokomol. Soedin.*, **6**, 2030 (1964).

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(6) E. A. Ofstead, *Polym. Preprints*, **6**, 674 (1965).

(7) D. Vofsi and A. V. Tobolsky, *J. Polym. Sci., Part A*, **3**, 3261 (1965).

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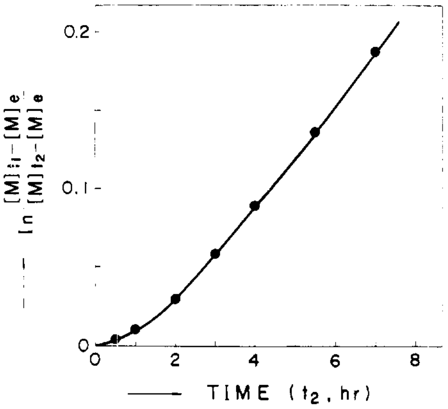


Figure 2. Polymerization of THF by $BF_3$–ECH: bulk polymerization at 0°; $[M]_0$, 12.6 mol/l.; $[BF_3]_0$, 0.011 mol/l.; $[ECH]_0$, 0.010 mol/l.; $[M]_e$, 1.7 mol/l.[6]; $t_1 = 0$.

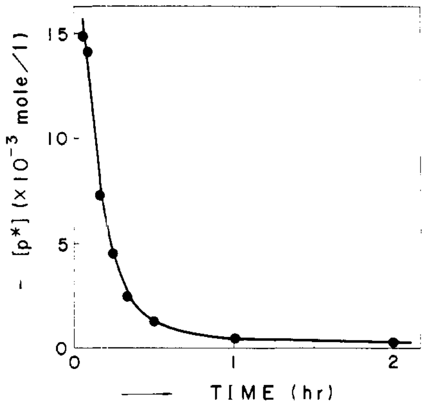


Figure 3. Polymerization of THF by $SnCl_4$–ECH: bulk polymerization at 0°; $[M]_0$, 12.6 mol/l.; $[SnCl_4]_0$, 0.055 mol/l.; $[ECH]_0$, 0.053 mol/l.

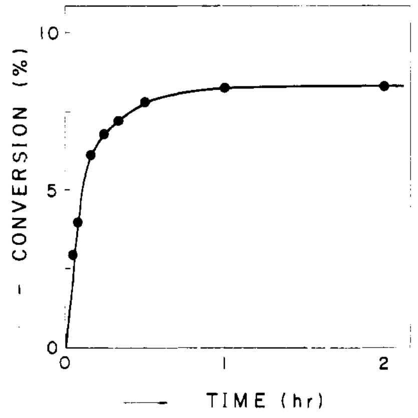


Figure 4. Polymerization of THF by $SnCl_4$–ECH: bulk polymerization at 0°; $[M]_0$, 12.6 mol/l.; $[SnCl_4]_0$, 0.055 mol/l.; $[ECH]_0$, 0.053 mol/l.

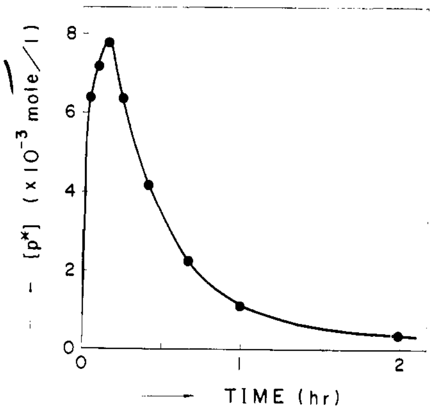


Figure 5. Polymerization of THF by $AlEtCl_2$–ECH: bulk polymerization at 0°; $[M]_0$, 12.6 mol/l.; $[AlEtCl_2]_0$, 0.054 mol/l.; $[ECH]_0$, 0.051 mol/l.

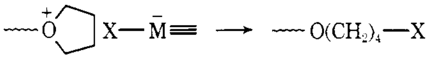
remains almost constant in the later stage (after 5 hr). Polymerization with this catalyst involves a slow initiation and it proceeds without termination. In the polymerization by the other two catalysts of the present study (Figures 3 and 5), the change of [p*] is more pronounced. These observations are in marked contrast to the [p*]-time course of the polymerization by $AlEt_3$–$H_2O$–ECH catalyst in which [p*] remains unchanged for the greater part of the polymerization.[1–3]

Figure 2 indicates a tentative plot of a first-order reaction rate law for the monomer concentration. Increase in polymerization rate is observed throughout the polymerization, corresponding to the increase of [p*] in Figure 1. A similar relationship between [p*] and time was also observed in the solution polymerization in methylene dichloride.

The time–[p*] relationship of the THF polymerization catalyzed by $SnCl_4$–ECH is shown in Figure 3. A very rapid initiation is indicated, *i.e.*, [p*] reaches quite a high value within a short initial stage of polymerization. Then [p*] is decreased immediately by termination reaction. Figure 4 shows the time–conversion curve of this polymerization. The rate of the monomer consumption is quite fast in the initial stage but is then decreased mainly by rapid termination reaction. Polymerization ceases at a very low conversion. Correspondingly, the polymer obtained with $SnCl_4$–ECH was an oily or a waxy product of low molecular weight.

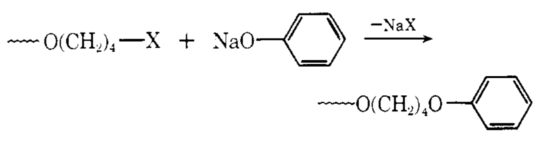
As shown in Figure 5, the course of the THF polymerization catalyzed by $AlEtCl_2$–ECH system was similar to that catalyzed by $SnCl_4$–ECH. In this case, however, a period for the increase of [p*] was observed at very early stage of polymerization, showing that the initiation is a little slower. The polymer obtained with this catalyst system was also of low molecular weights.

When a catalyst system containing a metal halide is employed, the carbon–halogen (C–X) bond may possibly be formed at the polymer chain end by a termination reaction, *e.g.*



(4)

The C–X group thus formed may in turn react with sodium phenoxide to form the phenyl ether group



(5)

A reference experiment, however, has shown that phenyl ether formation through reaction 5 can be neglected,

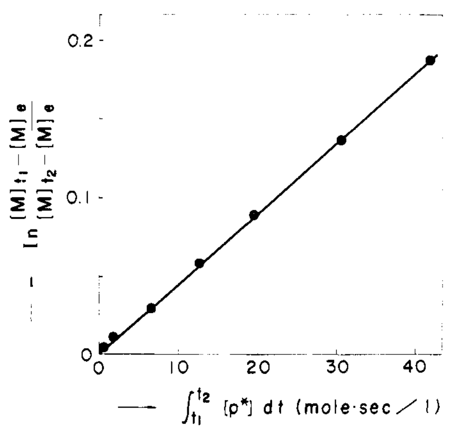


Figure 6. Polymerization of THF by $BF_3$–ECH: bulk polymerization at 0°; $[M]_e$, 1.7 mol/l.[6]; $t_1$, 0.

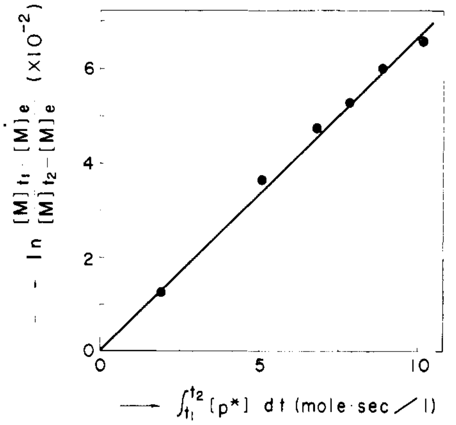


Figure 7. Polymerization of THF by $SnCl_4$–ECH: bulk polymerization at 0°; $[M]_e$, 1.7 mol/l.; $t_1$, 3 min.

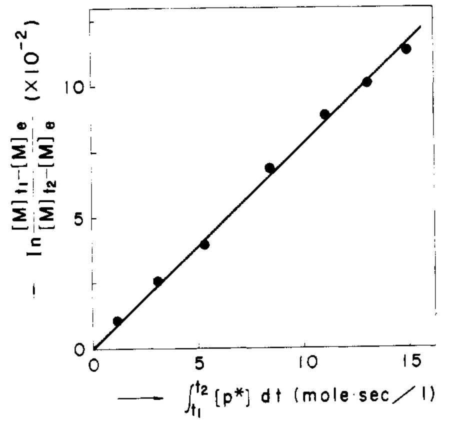
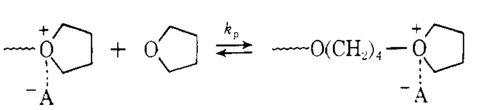


Figure 8. Polymerization of THF by $AlEtCl_2$–ECH: bulk polymerization at 0°; $[M]_e$, 1.7 mol/l.; $t_1$, 3 min.

even if it did occur, under the present experimental conditions. In the reference experiment, a model compound $CH_3O(CH_2)_4Cl$ was treated with excess sodium phenoxide under the same conditions, and the amount of phenyl ether formed, determined by uv spectroscopy, was found to be less than 1% of the amount of $CH_3O(CH_2)_4Cl$ used.

**Propagation Rate Constant.** In the cationic polymerization of THF, the propagation reaction can be expressed by

 (6)

On the basis of this mechanism the rate of polymerization is given by

$$-\frac{d[M]}{dt} = k_p[p^*]\{[M] - [M]_e\} \tag{7}$$

where [M] and $[M]_e$ are the instantaneous and equilibrium monomer concentrations, respectively, and $k_p$ is the rate constant of the propagation reaction. Here it is assumed that the chain transfer to monomer, if it occurs, is not important in the monomer consumption. Integration of eq 7 with respect to time gives

$$\ln \frac{[M]_{t_1} - [M]_e}{[M]_{t_2} - [M]_e} = k_p \int_{t_1}^{t_2} [p^*]dt \tag{8}$$

where $[M]_{t_1}$ and $[M]_{t_2}$ are the monomer concentrations at time $t_1$ and $t_2$, respectively. With the values of $\int_{t_1}^{t_2}$ [p*]d$t$ given by graphical integration in the time–[p*] curve, the $k_p$ value can be obtained from eq 8.

Figure 6 shows a plot of eq 8 ($t_1 = 0$, $t_2$ = variable) for the THF polymerization by $BF_3$–ECH. Here the integration of [p*] was made from $t_1 = 0$. The linear relationship in Figure 6 may be taken to support the assumption described above. The linear relationship was also found in solution polymerization by the same catalyst system. The $k_p$ values were obtained from the slope of the linear plot (Table I).

The linear relationship of eq 8 ($t_1$ = 3 min, $t_2$ = variable) for the polymerization by $SnCl_4$–ECH was obtained similarly (Figure 7), from which the $k_p$ value was calculated (Table I). The same procedure was applied also to the polymerization by $AlEtCl_2$–ECH ($t_1$ = 3 min, $t_2$ = variable) (Figure 8 and Table I).

No wide difference is seen among the $k_p$ values of these catalysts (Table I). In addition, these $k_p$ values are quite close to the $k_p$ value of the THF polymerization by $AlEt_3$–$H_2O$–ECH.[2] These three catalyst systems, however, differ from one another in the time–[p*] relationship. In other words, the rates of the initiation and termination reactions are much influenced by the nature of the catalyst. The formation of low molecular weight polymers with $SnCl_4$ and $AlEtCl_2$ are attributed to the rapid termination.

Further studies are necessary in order to elucidate the influence of the catalyst nature on the rates of elementary reactions in the THF polymerization.

Table I

Propagation Rate Constants of THF Polymerization[a]

| $[M]_0$, mol/l. | Catalyst | Concn, mol/l. | $[ECH]_0$, mol/l. | $10^3k_p$, l./mol sec |
|---|---|---|---|---|
| 12.6[b] | $BF_3$ | 0.011 | 0.010 | 4.5 |
| 12.6[b] | $BF_3$ | 0.021 | 0.020 | 4.6 |
| 6.3[c] | $BF_3$ | 0.025 | 0.020 | 4.1 |
| 12.6[b] | $SnCl_4$ | 0.028 | 0.029 | 5.8 |
| 12.6[b] | $SnCl_4$ | 0.055 | 0.053 | 6.7 |
| 12.6[b] | $AlEtCl_2$ | 0.054 | 0.051 | 7.8 |

[a] Polymerization at 0°. [b] Bulk polymerization. [c] Solution polymerization in methylene dichloride.

## Experimental Section

**Materials. THF and ECH.** Commercial reagents were purified as described in our previous paper.[1]

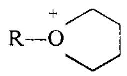
**Methylene Dichloride.** For uv measurements, commercial reagent was treated with concentrated sulfuric acid, washed with water, dried over calcium chloride and distilled. For use in polymerizations it was further dried over phosphorus pentoxide and finally distilled over calcium hydride, bp 40°.

**$SnCl_4$ and $AlEtCl_2$.** Commercial reagents were purified by distillation under reduced nitrogen pressure, bp 59° (112 mm) and 70° (8 mm), respectively.

**$BF_3$–THF.** The complex was synthesized by passing $BF_3$ gas into anhydrous THF at 0° and purified by distillation under reduced nitrogen pressure, bp 70° (4 mm) [lit.[9] bp 69° (4 mm)].

**Polymerization and Determination of [p*].** Polymerization was carried out at 0° under a nitrogen atmosphere. The reaction was initiated by the addition, by means of a syringe, of the Lewis acid catalyst to 10 ml of monomer containing ECH at 0°. $BF_3$ was added as its THF complex. After a desired time of reaction, the polymerization system was terminated by the addition of a THF solution of an equimolar amount (to the catalyst) of sodium phenoxide. The mixture was allowed to react for 1 min at 0° and then decomposed by an aqueous solution of sodium hydroxide. Then the uv analysis of the phenyl ether at the polymer end was carried out as described previously.[3]

It was shown by using $(C_2H_5)_3O \cdot BF_4$ that the reaction of sodium phenoxide with the trialkyloxonium ion proceeds quantitatively within a period of time less than 20 sec. The reactivity of cyclic trialkyloxonium ion of the type



toward phenoxide ion is considered to be even higher than that of $(C_2H_5)_3O^+$. Hence, the above result is taken to indicate that the reaction of sodium phenoxide with the propagating species, eq 3, proceeds very rapidly in comparison with the rate of the change of [p*] in the polymerization.

By reference experiments, it was also established that, under the present experimental conditions, no phenyl ether is formed by the reaction between sodium phenoxide and Lewis acid catalysts. Furthermore, the formation of phenyl ether by the reaction of sodium phenoxide with ECH was shown to be negligible under these conditions.

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[9] R. C. Osthoff, C. A. Brown, and J. A. Hawkins, *J. Amer. Chem. Soc.*, **73**, 5480 (1951).

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# Monomer Syntheses, Polymerization, and Copolymerization of Vinylthiazoles[1]

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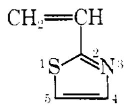
*Received May 29, 1968*

ABSTRACT: The syntheses of a number of vinyl and isopropenylthiazoles are described. Five of these monomers were found to undergo radical polymerization, and the 2-isopropenylthiazole monomer was found to polymerize readily anionically. The nmr spectra of the isopropenylthiazoles in the methyl group region show three distinct signals which are discussed. Reactivity ratios for the copolymerization of 2-vinyl- and 4-vinylthiazole have been determined. 2-Vinylthiazole is much more reactive than the 4-vinyl monomer, and reasons for this are discussed in terms of expansion of the sulfur octet.

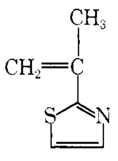
There is little literature concerning the synthesis and polymerization behavior of vinyl- or isopropenylthiazoles. This study was prompted by three factors: a desire to know more about the effect of the heterocyclic aromatic thiazole nucleus on monomer reactivity; the hope of determining polymer stereoregularity as a function of initiator type and other reaction variables by the use of nmr; and an interest in quaternized thiazole polymers as catalysts for reactions catalyzed by thiamine.[3] The first two aspects are commented on here, and the third is discussed in the following paper.

Literature reports of the polymerization of the known thiazole monomers are confined to the 2- and 5-vinyl derivatives. 4-Methyl-5-vinylthiazole is reported as yielding only viscous oils with benzoyl peroxide but hard copolymers with maleic anhydride.[4] The 2-vinyl-4-methyl- and 2-isopropenyl-4-methylthiazoles yield radical-initiated homopolymers[5] and radical-initiated copolymers with butadiene or styrene.[6] No reactivity ratios were reported.

**Monomer Syntheses.** Monomers I–VI were synthesized.



I



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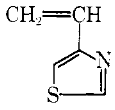

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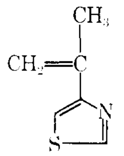

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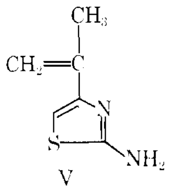
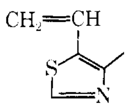


V



VI

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[1] A portion of this work was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; *Polym. Preprints*, 8 (1), 363 (1967).

[2] Continental Oil Co. Fellow, 1966–1967.

[3] The catalytic activity of thiamine is known to be due to the presence of the quaternized thiazole ring: R. Breslow and E. McNelis, *J. Amer. Chem. Soc.*, **81**, 3080 (1959).

[4] G. B. Bachman and L. V. Hersey, *ibid.*, 71, 1985 (1949).

[5] D. L. Schoene, *ibid.*, **73**, 1970 (1951).

[6] D. L. Schoene, U. S. Patent 2,515,318 (1950); *Chem. Abstr.*, **44**, 8699 (1950); U. S. Rubber Co., British Patent 609,467 (1949); *Chem. Abstr.*, **43**, 2805 (1949).