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Ring-Opening Polymerization of Oxacyclobutane by Boron Trifluoride. Concentration of Propagating Species and Rate of Propagation

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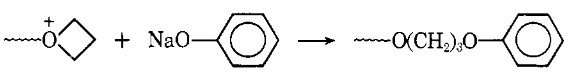
ABSTRACT: This paper reports a kinetic study on the polymerization of oxacyclobutane catalyzed by BF_3–tetrahydrofuran complex. The concentration of propagating species, [P*], during polymerization was determined at various times of polymerization by the phenoxyl end-capping method, *i.e.*, the propagating chain end was quantitatively converted into the corresponding phenyl ether by treatment with excess sodium phenoxide and the amount of resulting phenyl ether was determined by uv spectroscopy. In the polymerization at $-27.8°$, the [P*] value was almost constant throughout the polymerization and was about 80% of the initial catalyst concentration. On the basis of the time–[P*] and the time–conversion data, the rate constant of the propagation reaction, k_p, was calculated from eq 5 in which $[M]_t$'s are the instantaneous monomer concentration and $\int[P^*]dt$ (from t_1 to t_2) was obtained by graphical integration. From the k_p values at -27.8, -22.6, -10.4, and 0°, the activation parameters of propagation reaction were determined, $\Delta E_p^{\ddagger} = 14.0$ kcal/mol and $A_p^{\ddagger} = 5.3 \times 10^{10}$ l./mol sec. These values were compared with those of tetrahydrofuran polymerization.

The present paper describes a kinetic study on the BF_3-catalyzed polymerization of oxacyclobutane (oxetane), a four-membered cyclic ether. The kinetic analysis was made on the basis of the determination of the instantaneous concentration of propagating species [P*] by means of phenoxyl end-capping method, in which the propagating species is quantitatively transformed 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.



(1)

The BF_3-catalyzed polymerization of oxetane was studied first by Rose.[1,2] Since then, no detailed kinetic study has been made. The present study is mainly concerned with the propagation reaction. The propagation rate constant has been determined from the concentration of propagating species during the polymerization. Using the same procedure, the polymerization of tetrahydrofuran (THF), a five-membered cyclic ether, has already been examined by us.[3-5] Comparisons of the propagation rate constants and the activation parameters of the polymerizations of these two cyclic ether monomers having different ring sizes have been made.

Results and Discussion

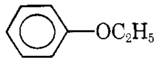
Determination of [P*] by Phenoxyl End-Capping Method. The phenoxyl end-capping method has already been established in the case of the THF polymerization.[3] In the present study, the method was applied to the polymerization of oxetane. Before the determination of [P*] by this method, the following three requisites must be satisfied.

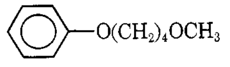
(a) The molar extinction coefficient of the phenyl ether group at polymer end should be known.

(b) The conversion of the propagating chain end into phenyl ether should be quantitative and instantaneous.

(c) Any side reaction producing phenyl ether group should be absent.

The molar extinction coefficient (ϵ_{max}) of the phenyl ether group at the polymer end has reasonably been estimated from the ϵ_{max} of two phenyl alkyl ethers, phenetole and ω-methoxybutyl phenyl ether.[3] In





methylene dichloride and in diethyl ether, the two phenyl ethers showed the same absorption spectra with λ_{max} at 272 mμ and with the same ϵ_{max}. The presence of ether linkage in the alkyl group does not affect the

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(1) J. B. Rose, *J. Chem. Soc.*, 542 (1956).

(2) J. B. Rose, *ibid.*, 546 (1956).

(3) T. Saegusa and S. Matsumoto, *J. Polym. Sci., Part A-1*, **6**, 1559 (1968).

(4) T. Saegusa and S. Matsumoto, *Macromolecules*, **1**, 442 (1968).

(5) T. Saegusa, S. Matsumoto, and Y. Hashimoto, *Polym. J.*, **1**, 31 (1970).

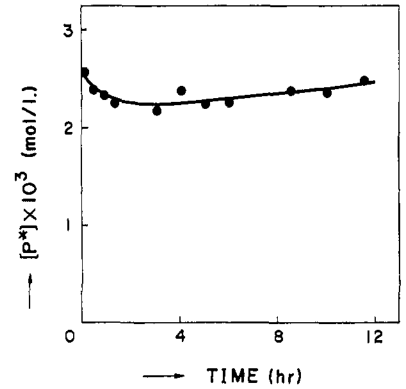
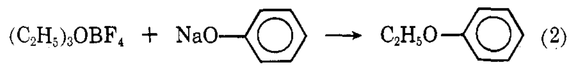


Figure 1. Polymerization of oxetane by $BF_3 \cdot THF$: solution polymerization at −27.8°; solvent CH_2Cl_2; $[M]_0$, 3.1 mol/l.; $[BF_3]_0$, 3.0×10^{-3} mol/l.

ϵ_{max} of a phenyl alkyl ether. In addition, the uv spectrum of the phenoxyl end-capped polyoxetane strongly resembled the spectra of these two phenyl ethers as well as that of phenoxyl end-capped polytetrahydrofuran. From these findings, the ϵ_{max} of these two model compounds, 1.93×10^3 l./mol cm, has reasonably been assigned to the phenyl ether group at the oxetane polymer end.

Quantitative reaction of cyclic oxonium ion at the oxetane propagating chain end with sodium phenoxide is a reasonable assumption since the reaction of triethyloxonium tetrafluoroborate with sodium phenoxide (eq 2) under the same conditions is instantaneous and quantitative.[3] Cyclic trialkyloxonium species at the propagating chain end is more strained and its reactivity toward phenoxide ion is considered to be even higher than that of the cyclic trialkyloxonium ion.


(2)

The absence of side reactions leading to the formation of phenyl ether was established by a series of reference experiments. When the mixture of oxetane and methylene dichloride was treated with sodium phenoxide under the same conditions, no phenyl ether was formed. In addition, no phenyl ether was formed when the polymerization system was first terminated by a small amount of aqueous sodium hydroxide and then treated with phenoxide.

Polymerization of Oxetane. The [P*] change in the course of the oxetane polymerization was examined by means of the phenoxyl end-capping method. Figure 1 shows the [P*] *vs.* time curve of the polymerization by $BF_3 \cdot THF$ at −27.8°. It is seen that [P*] remains almost constant during the polymerization. The average [P*] value is about 80% of the initial concentration of $BF_3 \cdot THF$. Thus every molecule of $BF_3 \cdot THF$ catalyst does not furnish a propagating species. Similar [P*]–time relationships were observed in polymerizations at −22.6, −10.5, and 0°.

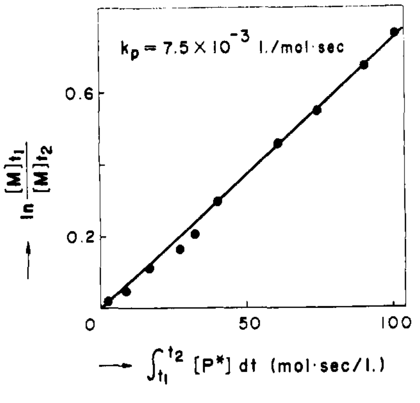
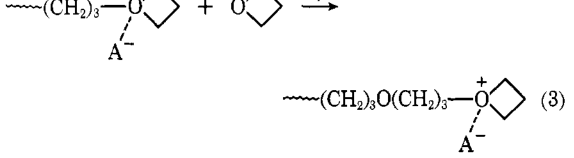


Figure 2. Polymerization of oxetane by $BF_3 \cdot THF$: solution polymerization at −27.8°; solvent CH_2Cl_2; t_1, 55 min.

The rate constant of propagation, k_p, of the oxetane polymerization was determined from the [P*]–time curve.

The propagation of the oxetane polymerization has been formulated as a nucleophilic attack of monomer on the growing oxonium end according to an SN2 mechanism (eq 3).[2] In this equation, A^- represents the counteranion derived from the initiator. On the basis of this scheme, a bimolecular rate equation is given


(3)

$$-\frac{d[M]}{dt} = k_p[P^*][M] \qquad (4)$$

where [M] is the monomer concentration, k_p is the rate constant, and [P*] is the instantaneous concentration of propagating species. Integration of eq 4 with respect to time gives

$$\ln \frac{[M]_{t_1}}{[M]_{t_2}} = k_p \int_{t_1}^{t_2} [P^*]dt \qquad (5)$$

where $[M]_{t_1}$ and $[M]_{t_2}$ are the monomer concentrations at time t_1 and t_2, respectively. The cumulative value of [P*] in eq 5 can be obtained by graphical integration of the time–[P*] curve. In every run of polymerizations at four different temperatures, a plot of ln ($[M]_{t_1}/[M]_{t_2}$) *vs.* the integrated value of [P*] from t_1 to t_2 gave a straight line passing through the origin. Figure 2 illustrates the linear relationship, which has been obtained in the polymerization at −27.8°.

From the slope of the straight line, the rate constant of propagation reaction k_p was obtained. Table I shows the k_p values of the oxetane polymerizations by $BF_3 \cdot THF$ catalyst at four temperatures.

Table I

Propagation Rate Constants[c]

Temp, °C	10^3k_p, l./mol sec
Oxetane (catalyst $BF_3 \cdot THF$)	
0	140
−10.4	57
−22.6	13
−27.8	7.5
THF (catalyst $BF_3 \cdot THF$–ECH)[a]	
0	4.1[b]

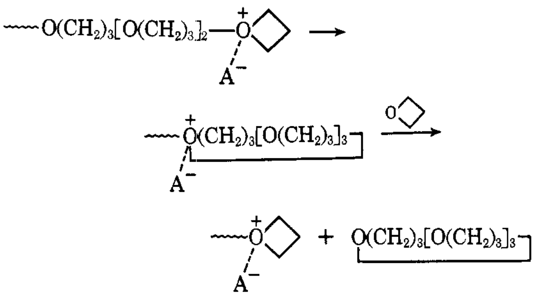
[a] ECH, epichlorohydrin. [b] See ref 4. [c] Solution polymerization in CH_2Cl_2.

TABLE II
ACTIVATION PARAMETERS

Catalyst	Oxetane/ $BF_3 \cdot THF$	THF $(C_2H_5)_3OSbCl_6$	THF $BF_3 \cdot O(C_2H_5)_2$–ECH	THF $Al(C_2H_5)_3$–H_2O–ECH
$\Delta E_p{}^{\ddagger}$, kcal/mol	14	15[a]	13[a]	12[b]
$A_p{}^{\ddagger}$, l./mol sec	5.3×10^{10}			5.2×10^{7}

[a] B. A. Rozenberg, E. B. Lyudvig, and N. V. Desyatoba, *Vysokomol. Soedin.*, **7**, 1010 (1965). [b] T. Saegusa, H. Imai, and S. Matsumoto, *J. Polym. Sci., Part A-1*, **6**, 459 (1968).

The cationic polymerization of oxetane suffers from a complication from the formation of cyclic tetramer, a 16-membered cyclic ether. The formation of this tetramer has been formulated as the so-called back-biting of the growing chain end,[2] *i.e.*


(6)

In the present study, the rate of polymerization was determined from the amount of polymeric product containing tetramer. This treatment does not cause any considerable error in the kinetic analysis of the present study. The relative rates of the formation of tetramer and of propagation is dependent on the relative basicities of the ether linkages of polymer chain and of the monomer. Because the basicity of oxetane is much larger than that of open-chain ethers, the formation of tetramer may be considered to be unimportant unless the polymerization is performed to a very high conversion. Furthermore, the present study was carried out at lower temperatures, where the extent of the formation of tetramer has been shown to be small.[1] The k_p value of the oxetane polymerization is interestingly compared with that of the polymerization of tetrahydrofuran, a five-membered cyclic ether, with the catalyst of $BF_3 \cdot THF$–epichlorohydrin system. It has been found by us that the propagation rate constant of THF polymerization varies very little according to the nature of initiator.[4,5] Therefore, a comparison of the k_p value of oxetane at 0° with that of THF is informative as to the reactivities of these two cyclic ethers.

Qualitatively, oxetane has been known to be more reactive than THF in cationic ring-opening polymerization. However, the quantitative comparison was given for the first time in the present study. At 0°, oxetane is about 35 times as reactive as THF.

Arrhenius plot of these k_p values of the oxetane polymerization gives a straight line (Figure 3), from which the activation energy and frequency factor were calculated. The activation parameters of the oxetane polymerization are compared with those of the THF polymerization in Table II. The activation energy values ($\Delta E_p{}^{\ddagger}$) are quite similar to each other, but the frequency factor values ($A_p{}^{\ddagger}$) differ considerably. Thus, the difference of propagation rate constant between oxetane and THF is mainly due to the difference of frequency factor.

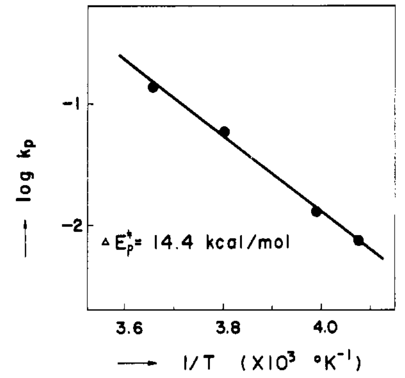
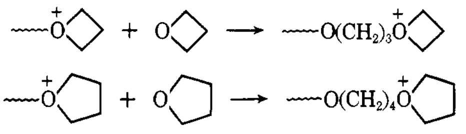


Figure 3. Arrhenius plot of propagation rate constant in the polymerization of oxetane: solution polymerization in CH_2Cl_2.

The propagation reactions of both of the oxetane and THF polymerizations have been shown to be of SN2 type, *i.e.*, the nucleophilic attack of monomer upon the cyclic oxonium propagating end. The smaller value of frequency factor of the THF polymerization is taken as suggesting a closer and highly oriented approach of monomer to the oxonium species in the transition state. On the other hand, the ring opening of the cyclic oxonium ion of the oxetane polymerization is caused by a less close approach of the monomer. This difference may be ascribed to the cyclic oxonium ion of oxetane being more strained than that of THF.



Experimental Section

Materials. The oxetane monomer was prepared from trimethylene glycol according to the method of Rose.[1] It was purified and dried by repeated distillation over sodium metal under dry nitrogen, bp 47.2°. Methylene dichloride and tetrahydrofuran were commercial reagents which were purified and dried as described in a previous paper.[4] BF_3–tetrahydrofuran complex was synthesized and purified as described previously.[4]

Polymerization Procedure and Determination of [P*]. Polymerization was carried out in solution in methylene dichloride under a nitrogen atmosphere. The reaction was initiated by the addition, at polymerization temperature, of a solution of BF_3–THF complex to a monomer solution. After a desired time of reaction, the polymerization system was short-stopped by the addition of a solution of sodium phenoxide in THF. The procedure for the determination of [P*] was the same as that for the THF polymerization.[3,4] Conversions were determined from the amount of polymeric product.