for χ_1 than given in eq 4. If the calculations are made as before, but with the higher value of χ_1, the CPC are displaced to higher temperatures, in better agreement with experiment. We conclude that the Flory model with the Flory–Huggins critical value of χ_1 predicts the phase behavior semiquantitatively, but that further experiments may show a modification of the theory to be warranted.

Acknowledgment. We acknowledge with gratitude the award of the Newell P. Beckwith Fellowship of the Paint Research Institute to one of us (K. S. S.) and the support of the National Research Council of Canada.

Appendix. Correspondence of the Prigogine and Flory Expressions for χ_1

The theory of Flory and collaborators gives (*cf.* eq 49–51 of ref 20)

$$\chi_1 = \frac{P_1^* V_1^*}{RT\tilde{V}_1}\left[\left(\frac{s_2}{s_1}\right)^2 \frac{X_{12}}{P_1^*} + \frac{\alpha_1 T}{2}\left\{\frac{P_2^*}{P_1^*}\tau - \frac{s_2}{s_1}\frac{X_{12}}{P_1^*}\right\}^2\right] \quad (10)$$

If one neglects the third order of differences in the starred reduction parameters

$$\chi_1 = \frac{P_1^* V_1^*}{RT\tilde{V}_1}\left[\left(\frac{s_2}{s_1}\right)^2 \frac{X_{12}}{P_1^*} + \frac{\alpha_1 T}{2}\tau^2\right] \quad (11)$$

In the model used by the theory, $-U_1 = P_1^* V_1^*/\tilde{V}_1$ and $TC_{p,1} = P_1^* V_1^* \alpha_1 T/\tilde{V}_1$, whence eq 11 and the Prigogine eq 5 are identical if ν_2 is replaced by $(s_2/s_1)^2(X_{12}/P^*)$. The (s_2/s_1) parameter is the ratio of the surface to volume ratios for polymer and solvent. In deriving[21b] eq 5, this was set equal to unity, surface and segment fractions being made equal, and so does not appear in eq 5.

Kinetic Study of Ring-Opening Polymerization of Oxepane

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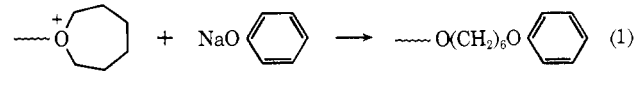
ABSTRACT: Kinetics of the cationic polymerization of oxepane, a seven-membered cyclic ether, by the initiator system BF_3·THF–epichlorohydrin (promoter) in CH_2Cl_2 was examined. The kinetic analysis was based on the determination of the concentration of propagating species, [P*], by the phenoxyl end-capping method. On the basis of SN2 reaction mechanism, the rate constant of propagation reaction, k_p, was calculated from the integrated equation, $\ln [([M]_{t_1} - [M]_e)/([M]_{t_2} - [M]_e)] = k_p \int_{t_1}^{t_2} [P^*]dt$, where the $[M]_t$'s and $[M]_e$ are respectively the instantaneous and equilibrium concentrations of monomer, and the $\int_{t_1}^{t_2} [P^*]dt$ value is obtained by graphical integration on the time–[P*] curve. From the k_p values at five temperatures in a range from −10 to 30°, the activation parameters of this polymerization were determined: $\Delta E_p^{\ddagger} = 18$ kcal/mol, $A_p^{\ddagger} = \times 10^9$ l./(mol sec).

In ring-opening polymerization, the relationship between the ring sizes and the polymerization reactivities of a series of cyclic monomers is one of the most fundamental problems. As to cyclic ethers, the propagation rate constants, k_p, of the polymerizations of four- (oxetane)[1] and five- (THF)[2–5] membered cyclic ethers have been determined by us on the basis of the determination of the concentration of propagating species, [P*]. This paper is concerned with a seven-membered cyclic ether, oxepane.

Previously we reported general features of the oxepane polymerization and characterization of the oxepane polymer as well as the monomer–polymer equilibrium.[6] In the present study, the kinetic studies of the oxepane polymerization by the BF_3·THF–epichlorohydrin (ECH) system were performed on the basis of the concentration of propagating species determined by means of the phenoxyl end-capping method.[2] BF_3·THF–ECH catalyst is among the most suitable systems for the analysis of our phenoxyl end-capping method because of the stability of BF_3·THF complex and the absence of side reactions such as phenetole formation in the case of the oxonium ion salt system.[5] Our studies on polymerizations of other cyclic ethers have systematically been performed with the same counterion derived from the BF_3·THF–ECH system. The k_p values were successfully determined in a temperature range between −10 and 30°, and the activation parameters were obtained. The kinetic data of the oxepane polymerization were interestingly compared with the corresponding data of four- and five-membered cyclic ethers.

Results and Discussion

Determination of [P*] by the Phenoxyl End-Capping Method. The [P*] determination by the phenoxyl end-capping method has been established in the polymerizations of oxetane[1] and THF.[2] In the present study, the same method was applied to the oxepane polymerization, *i.e.*, the active species at the propagating chain end was converted into the corresponding phenyl ether (eq 1) and its concentration was analyzed by uv absorption at 272 mμ. As to the phenoxyl end capping, the molar extinction coefficient value



(1)

(1) T. Saegusa, Y. Hashimoto, and S. Matsumoto, *Macromolecules*, 4, 1 (1971).
(2) T. Saegusa and S. Matsumoto, *J. Polym. Sci., Part A-1*, 6, 1559 (1968).
(3) T. Saegusa and S. Matsumoto, *Macromolecules*, 1, 442 (1968).
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(6) T. Saegusa, T. Shiota, S. Matsumoto, and H. Fujii, *Polym. J.*, 2 (1971).

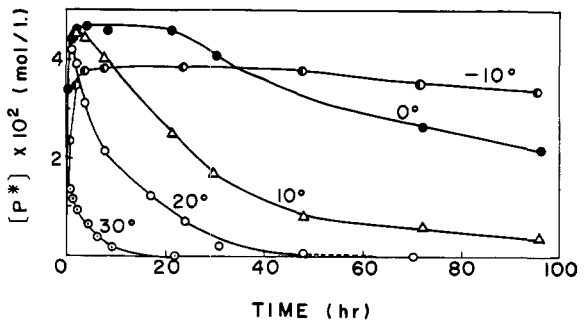
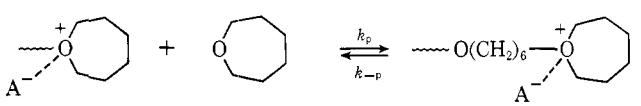


Figure 1. Time *vs.* [P*] curves of oxepane polymerization by BF_3.THF–ECH in CH_2Cl_2; $[M]_0$, 2.87 *M*; $[cat.]_0$, 0.057 *M* (−10–20°), 0.029 *M* (30°).

(ϵ_{max}) of the phenyl ether at the oxepane polymer end was reasonably assumed to be the same as the ϵ_{max} values (1.93×10^3 l./(mol cm) at 272 mμ) of two model phenyl ethers, phenetole and ω-methoxybutyl phenyl ether.[2] The quantitative reaction of the propagating end with sodium phenoxide was assumed according to a reference reaction of $Et_3O^+BF_4^-$ with sodium phenoxide, and the absence of a side reaction leading to the formation of phenyl ether was also established by reference experiments.[2]

Time–[P*] Curve and Propagation Rate Constants. The [P*] change in the oxepane polymerization by the BF_3·THF–epichlorohydrin system was examined by means of the phenoxyl end-capping method. Figure 1 shows the time–[P*] curves at five temperatures between −10 and 30°. It is demonstrated that the [P*] decreases considerably in a long period of polymerization. Especially at temperatures above 20°, [P*] decreases rapidly.

Similar to the polymerizations of oxetane and THF, the rate constant of propagation, k_p, of the oxepane polymerization was determined on the basis of the time–[P*] curve. The propagation of the oxepane polymerization is considered as a nucleophilic attack of monomer onto the propagating species of cyclic oxonium by an SN2 mechanism.



(2)

In the above equation, A^- represents the counteranion derived from the initiator. On the basis of eq 2, the following integral rate equation can be given, as in the cases of the polymerizations of THF[3] and oxetane[1]

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

where $[M]_e$ is the equilibrium monomer concentration and $[M]_{t_1}$ and $[M]_{t_2}$ are the monomer concentrations at times t_1 and t_2, respectively. The integrated value of [P*] can be obtained by graphical integration of the time–[P*] curve. The value of $[M]_e$ is very small, *i.e.*, 8×10^{-2} *M* at 30° and 6×10^{-2} *M* at 10°,[6] and this term can be eliminated in practical calculations. In the polymerizations at −10, 0, 10, 20, and 30°, the plot of eq 3 always gave a straight line passing through the origin. Figure 2 is the plot of eq 3 in the polymerization at 0°. The slope of the linear plot of eq 3 gives the values of k_p. The Arrhenius plot of k_p values at five temperatures was linear (Figure 3), from which the activation parameters were obtained. The rate constant data and the activation parameters are given in Table I.

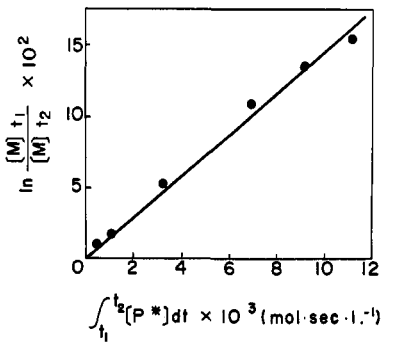


Figure 2. Linear plot of eq 3 in oxepane polymerization at 0°; t_1 = 1 hr.

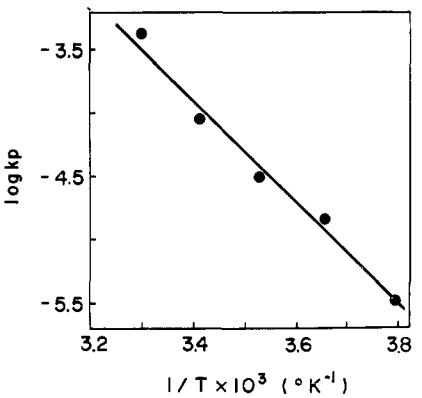


Figure 3. Arrhenius plot of propagation rate constant in the oxepane polymerization.

TABLE I
PROPAGATION RATE CONSTANTS AND ACTIVATION PARAMETERS OF CYCLIC ETHER POLYMERIZATIONS[a]

	 [b]	 [c]	
$k_p \times 10^3$, l./(mol sec)			
−28°	7.5		
−23°	13		
−10°	57	1.7	0.0033
0°	140	4.1	0.015
10°		8.4	0.031
20°			0.091
30°			0.43
$\Delta F^{\neq}$, kcal/mol at 0°	17	22	27
$\Delta E_p^{\neq}$, kcal/mol	14	12	18
$10^{-7}A_p^{\neq}$, l./(mol sec)	5300	1.1	190

[a] Solution polymerization in CH_2Cl_2. The initial feeds were as follows: oxetane $[M]_0$ 3.1 *M*, BF_3·THF 0.003 *M*; THF $[M]_0$ 6.3 *M*, BF_3·THF and ECH each 0.01 *M*; oxepane $[M]_0$ 2.9 *M*, BF_3·THF and ECH each 0.057 *M*. [b] Reference 1. [c] Reference 7.

Termination Rate Constants. A kinetic analysis of termination was made also on the basis of the time–[P*] curve. The termination of the THF polymerization has been assumed to be a unimolecular reaction.[5,7,8] On the assumption that

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(8) P. Dreyfuss and M. P. Dreyfuss, *Advan. Chem. Ser.*, **No. 91**, 335 (1969).

TABLE II
TERMINATION RATE CONSTANTS OF OXEPANE POLYMERIZATION[a]

Temp, °C	k_t, $sec^{-1} \times 10^6$
0	2.9
10	11
20	24
30	72
10 (THF)[b]	21

[a] Solution polymerization in CH_2Cl_2. $[M]_0$ 2.9 *M*, BF_3·THF and ECH each 0.057 *M*. [b] THF polymerization in CH_2Cl_2. $[M]_0$ 6.3 *M*, BF_3·THF and ECH each 0.01 *M*.

the termination of the oxepane polymerization is similarly unimolecular, the following rate equation is derived

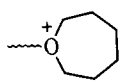
$$-d[P^*]/dt = k_t[P^*] - R_i \quad (4)$$

where R_i is the rate of production of [P*] and k_t is the rate constant of termination. At the very beginning of polymerization, the production of [P*] sometimes prevails over its disappearance by termination, and [P*] increases (Figure 1). In the latter stage of polymerization, however, the production of [P*] ceases and [P*] decreases monotonously; thus

$$-d[P^*]/dt = k_t[P^*]$$

$$\therefore -d(\ln [P^*])/dt = k_t \quad (5)$$

The plot of ln [P*] *vs.* time was linear in the latter stages at four temperatures except for −10°. At −10°, the conditions for eq 5 were not satisfied, because the [P*] production continued to the latter stage. From the slope of the ln [P*] *vs.* time plot, k_t was determined (Table II). It is interestingly noted that the k_t value of oxepane at 10° is even smaller than that of THF at the same reaction temperature. In other words, the seven-membered cyclic oxonium (**1**) of the oxepane polymerization is more stable than the five-membered one (**2**)



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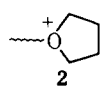
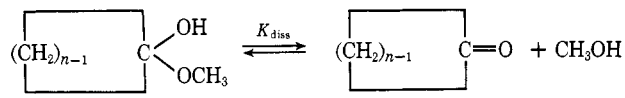


2

of the THF polymerization. The higher stability of **1** might be in conflict with the noticeable decrease of [P*] during the oxepane polymerization as shown in Figure 1. The considerable decrease of [P*], however, was observed because of the long period of reaction due to the slow propagation of oxepane polymerization.

Polymerization Reactivities and Ring Sizes of Cyclic Ethers. Table I summarizes the rate constants and the activation parameters of the propagation of four-, five-, and seven-membered cyclic ethers. All of these rate constants were determined by the phenoxyl end-capping method. At 0°, oxetane is 35 times as reactive as THF and THF is about 270 times as reactive as oxepane. Examination of the activation parameters of the propagation gives information on the difference of reactivity among three cyclic ethers. It is to be noted that the nature of the difference between the reactivities of oxetane and THF is quite dissimilar from that between THF and oxepane. Between the oxetane and THF polymerizations, the $\Delta E_p^{\neq}$ values do not differ very much from each other, whereas the $A_p^{\neq}$ values differ considerably. The higher reactivity of oxetane comes from a higher value of the frequency factor. In contrast to this, much decreased reactivity of oxepane in comparison with that of THF is ascribed mainly to the larger activation energy. One of possible explanations for the higher activation energy of the oxepane polymerization may be given on the basis of the higher stability (lower reactivity) of the seven-membered cyclic oxonium. The seven-membered ring takes a puckered form, and the strain caused by the conversion of monomer ether to the corresponding cyclic oxonium will be relieved by small deformations of the angles of other bonds. On the other hand, oxetane and THF rings are quite rigid, and the strains of their cyclic oxoniums are not relieved; hence, their oxoniums are highly reactive. In relation to the ease of relief of the strain caused by the bond-angle deformation in a seven-membered ether, the dissociations of cyclic hemiacetal[9] (**3**) and cyclic cyanohydrin[10] (**4**) into the corresponding cyclic ketones is to be mentioned.



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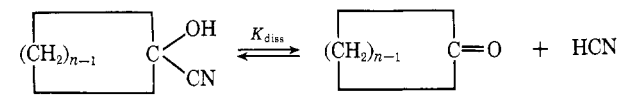

4

In both of the above dissociations, the sp^3 carbon atoms of the adducts of **3** and **4** are converted into the sp^2 carbons of carbonyl groups, and the dissociation constants of the seven-membered adducts are much higher than those of the respective five-membered ones. These facts have been explained as follows: the strain caused by the conversion of the sp^3 carbon atom to an sp^2 one is relieved more easily in the seven-membered adducts than in the five-membered ones.

Experimental Section

Materials. The oxepane monomer was prepared from hexamethylene glycol as previously reported[6] and purified by repeated fractional distillations over sodium metal after treatment with bromine water, bp 120.5°. Methylene dichloride, THF, and epichlorohydrin were commercial reagents which were purified and dried as described in a previous paper.[3] BF_3·THF complex was synthesized and purified as described previously.[3]

Polymerization Procedure and Determination of [P*]. Polymerization was carried out in solution in CH_2Cl_2 under nitrogen. 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 stopped short 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.[2,3]

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(10) H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).