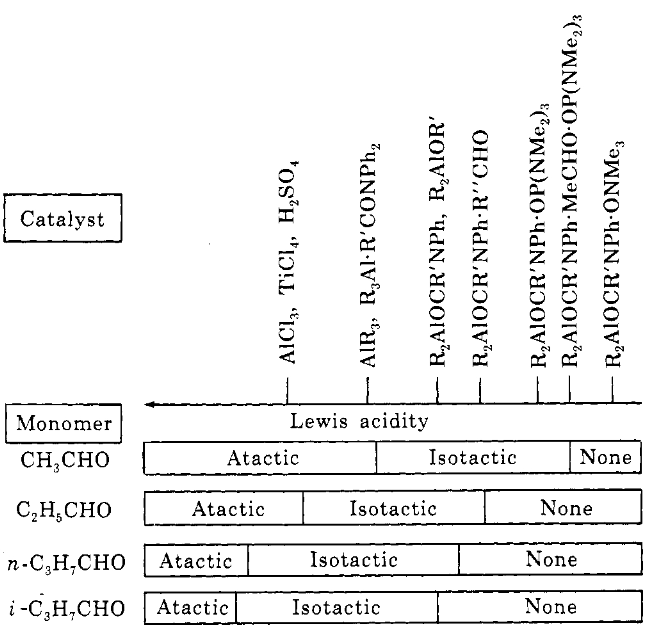
Scheme III



position using the fourth and fifth coordination sites of the aluminum atom, as mentioned above. Propionaldehyde and its higher homologs require no such assistance because of its alkyl groups being relatively large.

Therefore, the stereospecific polymerization of an aldehyde is interpretable more reasonably by a coordinate cationic mechanism than a coordinate anionic one. The presence of an optimum amount of a cocatalyst and the inhibition of the polymerization by a strong base are, in fact, quite similar to the well-known characteristic feature of cationic polymerizations in general.

Conclusion

In the stereospecific polymerization of an aliphatic monoaldehyde catalyzed by some organoaluminums, the bulkiness of the alkyl group of the aldehyde is the most important factor in the stereoregulation of the polymerization reaction; the catalyst enhances the degree of stereoregulation by controlling the mode of approach of the incoming monomer sterically through the coordination. Therefore, the structural requirement for the catalyst in relation to stereoregulation is the most severe for the lowest homolog, *i.e.*, acetaldehyde.

In general, the Lewis acidity of the catalyst suitable for each member the aldehyde series is resticted to a rather narrow range. When the Lewis acidity is too strong, only an amorphous polymer is obtained and when it is too weak no polymer is obtained. The same tendency is also observed for the Lewis basicity of the catalyst. These correlations are shown in Scheme III.

Although isotactic polyacetaldehyde cannot be obtained by strong acid or base, an isotactic polymer of a higher aldehyde can be obtained by strong acid or base.

Acknowledgment. We thank Professor N. Kasai, Professor M. Kakudo, Dr. N. Yasuoka, and Dr. Y. Kai of Osaka University for the X-ray structure determination of a series of organoaluminums.

Kinetic Studies on Ring-Opening Polymerization of Unsubstituted, 3-Methyl-, and 3,3-Dimethyloxacyclobutanes by Boron Trifluoride Catalyst. Methyl-Substituent Effects on Rate of Propagation

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ABSTRACT: The effect of the methyl substituent at the 3 position on the propagation rate constant, k_p, of the cationic ring-opening polymerization of oxacyclobutanes (oxetanes) was investigated. The rate constants and kinetic parameters of the propagation reaction were determined in the BF_3-catalyzed polymerizations of oxetane (1), 3-methyloxetane (2), and 3,3-dimethyloxetane (3) carried out in methylcyclohexane and methylene dichloride solvents. The kinetic analyses were made on the basis of the time–[P*] relationships, in which [P*], the concentration of propagating species, was determined by the phenoxyl end-capping method. At $-20°$, the k_p value of 1, 2, and 3 in methycyclohexane followed the relative ratio 1:5.1:19; *e.g.*, the introduction of the methyl group into the oxetane ring increased the rate. This result cannot be explained on the basis of ring strain or basicity. Examination of activation parameters showed that substitution of the methyl group decreased the negative value of the activation entropy (favorable for the k_p increase) whereas it increased the activation enthalpy (unfavorable for the k_p). These findings were interpreted mainly in terms of the solvation–desolvation phenomenon. The effects of the solvents methylcyclohexane and CH_2Cl_2 were found to be important for the polymerization kinetics, which were quite compatible with the S_N2 mechanism of propagation.

We have reported kinetic studies upon the cationic ring-opening polymerizations of cyclic ethers, oxacyclobutane (oxetane),[1] tetrahydrofuran (H_4furan),[2-5] and oxacycloheptane,[6] using the phenoxyl end-capping method. From these results, the correlation between the reactivity and the monomer ring size has been extensively discussed

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(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).

from the viewpoint of the propagation rate constants, k_p, and of the corresponding activation parameters.[7] The present study deals with the kinetics of the ring-opening polymerizations of unsubstituted (1), 3-methyl- (2), and 3,3-dimethyloxetanes (3) by BF_3 catalyst in methylcyclohexane and in CH_2Cl_2.


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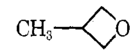
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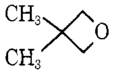
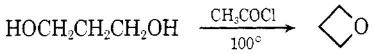

3

The ring-opening polymerization of oxetane by BF_3 catalyst was first reported by Rose.[8,9] Since then, no detailed kinetic study has been made except our recent report on the kinetic study of BF_3-catalyzed ring-opening polymerization of unsubstituted oxetane itself in CH_2Cl_2.[1] The purpose of the present study is to clarify the effect of the methyl substituent at the 3 position of oxetane on the propagation rate. In addition, the solvent effect was examined in which methylcyclohexane and CH_2Cl_2 were employed as one of typical nonpolar and polar solvents, respectively.

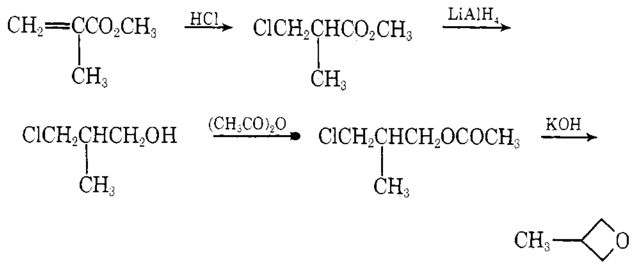
Results

Preparation of Monomers. The oxetane monomer was prepared from trimethylene glycol according to Rose.[8,9] 3-Methyloxetane was prepared starting from methyl

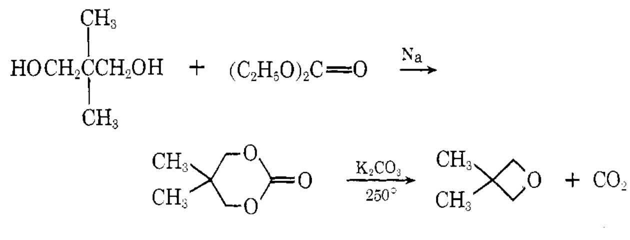


methacrylate as shown in Scheme I.[10] 3,3-Dimethyloxetane was prepared by catalytic decomposition of carbonate ester of 2,2-dimethyl-1,3-propanol (see Scheme II).[11]

Scheme I

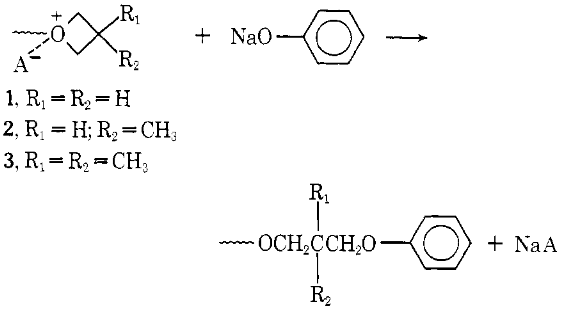


Scheme II



In all cases, the monomer was dried over sodium metal and purified by repeated distillation on spinning-band column under dry nitrogen. Three monomers showed purities higher than 99.9% by glpc analysis.

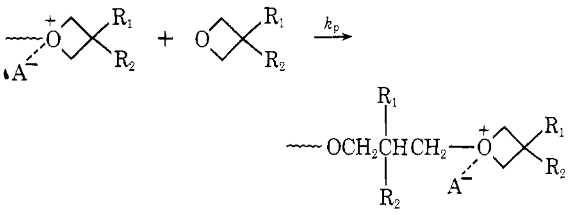
Determination of [P*] and Kinetic Analysis. The kinetic analysis was carried out on the basis of determination of the instantaneous concentration of propagating species, [P*], by means of our phenoxyl end-capping method, in which the propagating chain end was quantitatively converted into the corresponding phenyl ether by treatment with excess sodium phenoxide and the phenyl ether group at the polymer end was determined by uv spectroscopy (eq 1). The phenoxyl end-capping method has already been established in the case of oxetane polymerization, in which the extinction coefficient, ϵ (1.93×10^3 l./(mol cm)), was used to determine the concentration of phenyl ether group.



(1)

λ_{max} 272 mμ (ϵ 1.93×10^3 l./(mol cm))

In the cationic polymerization of oxetane, the propagation reaction can be expressed by the S_N2 mechanism (eq 2). On the basis of this mechanism the rate of polymerization is given by



(2)

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{P}^*][\mathrm{M}] \qquad (3)$$

where [M] is the monomer concentration, k_p is the propagation rate constant, and [P*] is the instantaneous concentration of propagating species determined by the phenoxyl end-capping method. Integration of eq 3 with respect to time gives

$$\ln \frac{[\mathrm{M}]_{t_2}}{[\mathrm{M}]_{t_2}} = k_p \int_{t_1}^{t_2} [\mathrm{P}^*]\mathrm{d}t \qquad (4)$$

where $[\mathrm{M}]_{t1}$ and $[\mathrm{M}]_{t2}$ are the monomer concentrations at time t_1 and t_2, respectively. With the value of $\int[\mathrm{P}^*]\mathrm{d}t$ given by graphical integration in the time-[P*] curve, the k_p value can be obtained from eq 4.

Polymerization of Oxetane. As a typical nonpolar solvent methylcyclohexane was used for the polymerization of oxetane. Figure 1 shows [P*] *vs.* time curve of the oxetane polymerization by $BF_3 \cdot H_4$furan catalyst at −40.0° in methylcyclohexane solvent. It is seen that the increase of [P*] ceased within 10 min and then [P*] decreased slowly. The [P*] concentrations during polymerization are between 28 and 36% of the initial molar concentration of the $BF_3 \cdot H_4$furan catalyst. Similar [P*]-time relation-

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(3) T. Saegusa and S. Matsumoto, *Macromolecules*, 1, 442 (1968).
(4) T. Saegusa and S. Matsumoto, *J. Macromol. Sci., Chem.*, 4, 873 (1970).
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(6) T. Saegusa, T. Shiota, S. Matsumoto, and H. Fujii, *Macromolecules*, 5, 34 (1972).
(7) T. Saegusa, Presented at IUPAC Symposium on Macromolecular Chemistry, Boston, Mass., 1971.
(8) J. B. Rose, *J. Chem. Soc.*, 542 (1956).
(9) J. B. Rose, *J. Chem. Soc.*, 546 (1956).
(10) M. Bartok, B. Kozma, and N. I. Shuikin, *Isv. Akad. Nauk, Kaz. SSSR, Ser Khim.*, 1241 (1966).
(11) S. Seales, D. G. Hummel, S. Nukina, and P. E. Throckmorton, *J. Amer. Chem. Soc.*, 82, 2928 (1956).

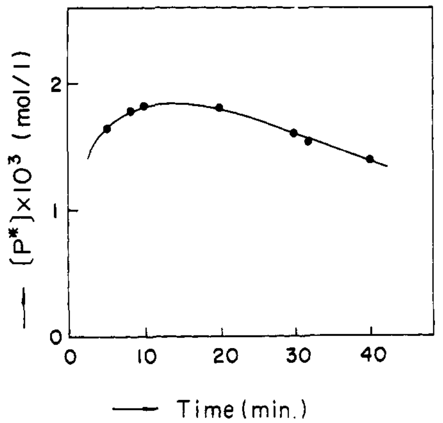


Figure 1. Polymerization of oxetane by $BF_3 \cdot H_4$furan in $CH_3C_6H_{11}$ solution at −40.0°: $[M]_0$ = 0.61 mol/l.; $[BF_3]_0$ = 5.0 × 10^{-3} mol/l.

ships were observed in a series of polymerizations at −9.0, −20.0, −30.0, and −50.0°. Figure 2 shows a linear plot of eq 4, where the experimental data have been afforded from Figure 1. The slope of the straight line passing through the origin gave the k_p value of 0.054 l./(mol sec) at −40.0°. Table I summarizes the k_p values of the oxetane polymerization at five temperatures in methylcyclohexane along with those previously obtained in CH_2Cl_2.[1]

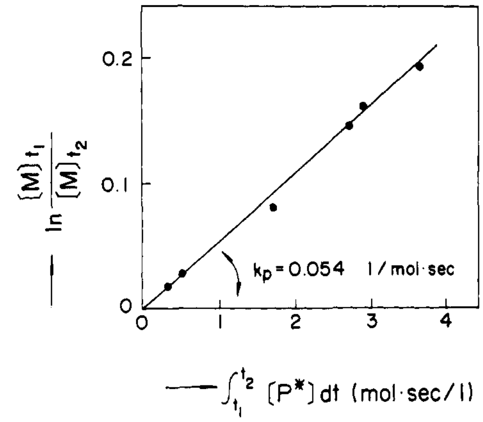


Figure 2. Polymerization of oxetane by $BF_3 \cdot H_4$furan in $CH_3C_6H_{11}$ solution at −40.0°: t_1 = 5 min.

Polymerization of 3-Methyloxetane. 3-Methyloxetane was found to be polymerized in a same manner as the unsubstituted oxetane by BF_3 catalyst.[10] Therefore, the kinetic analysis was successfully carried out using the same procedure as that of oxetane.

Figure 3 shows the [P*] *vs.* time relationships of the polymerization of 3-methyloxetane in methylcyclohexane, a nonpolar solvent, at −30.0, −40.0, and −50.0°, respectively. It is seen that at these temperatures the active species P* was formed immediately after the addition of catalyst and then diminished gradually probably due to the termination reaction. It is also interesting to note that the catalyst efficiency is dependent upon the reaction temperature, *e.g.*, the higher the reaction temperature the less the concentration of P*. At −30° the average [P*] value is about 5% of the initial catalyst concentration, whereas at −50° it is about 20%. At −20°, the phenomenon of the [P*]-time relation was similar to that of −30°.

A plot of ln $([M]_{t1}/[M]_{t2})$ *vs.* $\int_{t1}^{t2}[P^*]dt$ of the 3-methyloxetane polymerization at −30° has given a straight line passing through the origin as shown in Figure 4, which seems to support S_N2 mechanism in the 3-methyloxetane polymerization. From eq 4, the slope of the straight line gave k_p value of 0.45 l./(mol sec). The k_p values at other temperatures were obtained in a similar way (Table II).

As a polar solvent, CH_2Cl_2 was used also in the 3-methyloxetane polymerization. Figure 5 shows the [P*]-time relationships of the polymerization of 3-methyloxetane in CH_2Cl_2 solution at −20.0, −30.0, and −40.0°. At −20.0 and −30.0°, the active species was formed almost instantaneously and then decreased slowly. At −40.0°, however, P*'s were produced in the early stages (about 1 hr) and then diminished slowly. The catalyst efficiency at −20° was about 20% of the initial catalyst employed. The k_p value of 0.11 l./(mol sec) at −20° was obtained from a

Table I
Propagation Rate Constants of Oxetane Polymerization by $BF_3 \cdot H_4$furan Catalyst

In Methylcyclohexane		In CH_2Cl_2	
Temp (°C)	$10^2 k_p$ (l./(mol sec))[a]	Temp (°C)	$10^2 k_p$ (l./(mol sec))[b]
−9.0	69	0	14
−20.0	18	−10.4	5.7
−30.0	9.8	−22.6	1.3
−40.0	5.4	−27.8	0.75
−50.0	0.96		

[a] This work. [b] Taken from ref 1.

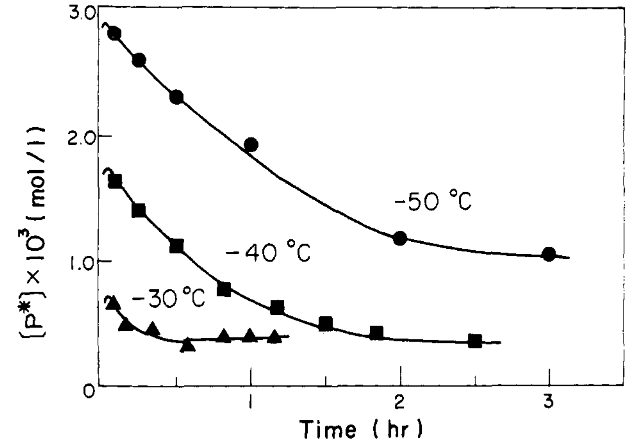


Figure 3. Polymerization of 3-methyloxetane by $BF_3 \cdot H_4$furan in $CH_3C_6H_{11}$ solution at −30.0, −40.0, and −50.0°: $[M]_0$ = 1.16 mol/l.; $[BF_3]_0$ = 1.0 × 10^{-2} mol/l.

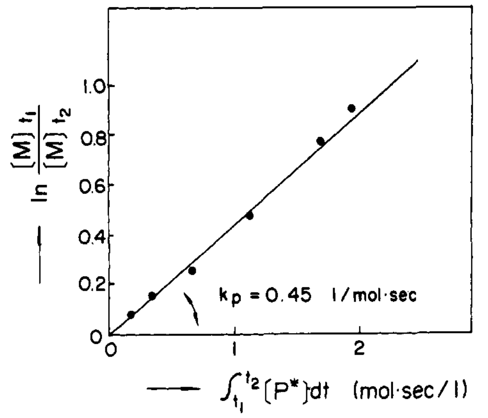


Figure 4. Polymerization of 3-methyloxetane by $BF_3 \cdot H_4$furan in $CH_3C_6H_{11}$ at −30.0°: t_1 = 0

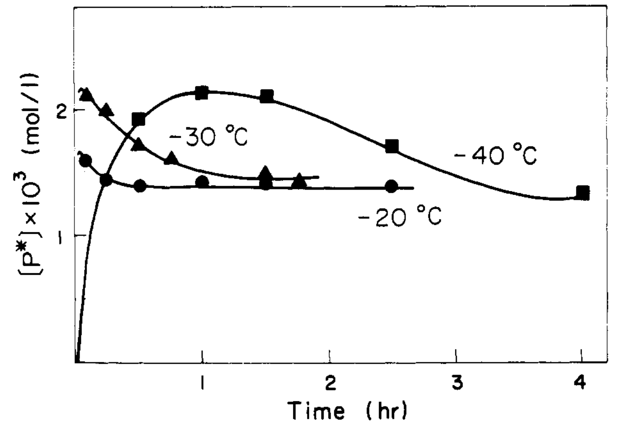


Figure 5. Polymerization of 3-methyloxetane by $BF_3\cdot H_4$furan in CH_2Cl_2 solution at −20.0, −30.0, and −40.0°: $[M]_0$ = 1.16 mol/l.; $[BF_3]_0 = 0.8 \times 10^{-2}$ mol/l.

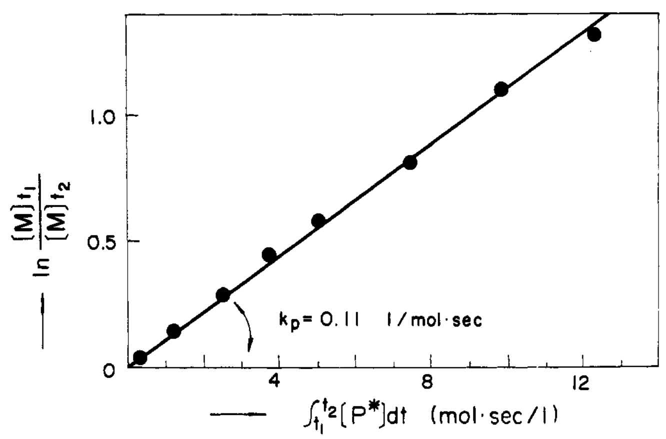


Figure 6. Polymerization of 3-methyloxetane by $BF_3\cdot H_4$furan in CH_2Cl_2 solution at −20.0°: t_1 = 0.

Table II
Propagation Rate Constants of 3-Methyloxetane Polymerization by $BF_3\cdot H_4$furan Catalyst

In Methylcyclohexane		In CH_2Cl_2	
Temp (°C)	$10k_p$ (l./(mol sec))	Temp (°C)	$10k_p$ (l./(mol sec))
−20.0	9.2	−20.0	1.1
−30.0	4.5	−30.0	0.28
−40.0	1.2	−40.0	0.068
−50.0	0.48		

linear relationship between $\int_{t_1}^{t_2}[P^*]dt$ *vs.* ln $([M]_{t_1}/[M]_{t_2})$ as shown in Figure 6. The k_p values at other temperatures in CH_2Cl_2 are given in Table II along with those obtained in methylcyclohexane.

Polymerization of 3,3-Dimethyloxetane. It seems to be interesting to study further how the introduction of two methyl groups at the 3 position of oxetane ring affects the rate of propagation. Therefore, the kinetics of the polymerization of 3,3-dimethyloxetane was examined. In methylcyclohexane the kinetic analysis was successfully performed. The $[P^*]$ *vs.* time relationship is illustrated in Figure 7 for the polymerization at −20.0°. As shown in Figure 7, the active species was generated in the initial 5 min. The concentration of P^* remained almost constant during polymerization. It should be noted that the catalyst efficiency is only 0.7% of the initial catalyst concentration. The k_p value, 3.4 l./(mol sec), at −20.0° was obtained from the slope of the straight line in Figure 8. The k_p values thus obtained at four temperatures are given in Table III.

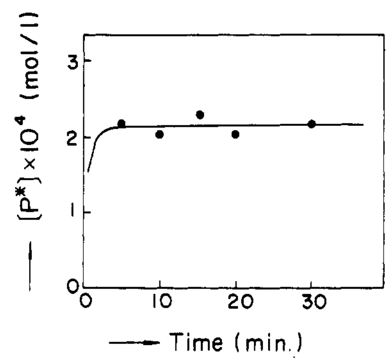


Figure 7. Polymerization of 3,3-dimethyloxetane by $BF_3\cdot H_4$-furan in $CH_3C_6H_{11}$ solution at −20.0°: $[M]_0$ = 0.405 mol/l.; $[BF_3]_0 = 3.0 \times 10^{-2}$ mol/l.

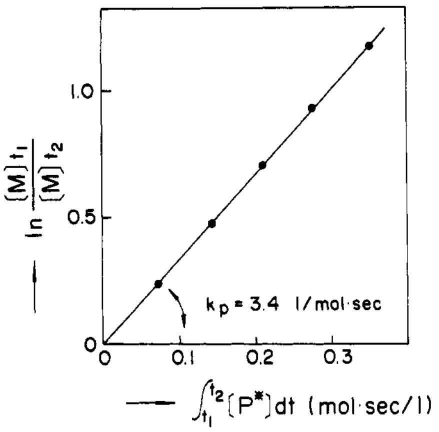


Figure 8. Polymerization of 3,3-dimethyloxetane by $BF_3\cdot H_4$-furan in $CH_3C_6H_{11}$ solution at −20.0°: t_1 = 0.

Table III
Propagation Rate Constants of 3,3-Dimethyloxetane Polymerization by $BF_3\cdot H_4$furan Catalyst

In Methylcyclohexane	
Temp (°C)	k_p (l./(mol sec))
−9.3	6.8
−20.0	3.4
−30.0	1.0
−40.0	0.25

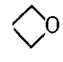
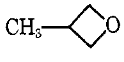
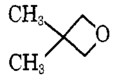
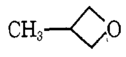
In CH_2Cl_2, however, the kinetic analysis was found to be difficult since the reaction system became heterogeneous at reaction temperatures due to a small solubility of the product polymer in CH_2Cl_2.

Discussion

Kinetic Parameters. The k_p values in Tables I, II, and III in methylcyclohexane solution were plotted according to the Arrhenius equation, eq 5 (Figure 9), from which the following values of activation parameters were obtained: $\Delta E_p\ddagger$ = 11.2 kcal/mol, $A_p = 1.3 \times 10^9$ l./(mol sec) for **1**; $\Delta E_p\ddagger$ = 11.8 kcal/mol, $A_p = 1.5 \times 10^{10}$ l./(mol sec) for **2**; $\Delta E_p\ddagger$ = 12.6 kcal/mol, $A_p = 2.3 \times 10^{11}$ l./(mol sec) for **3**.

$$k_p = A_p e^{-\Delta E_p^{\dagger}/RT} \quad (5)$$

Table IV
Kinetic Parameters of Polymerization in Methylcyclohexane and CH_2Cl_2 Solution

	In Methylcyclohexane			In CH_2Cl_2	
	 1	 2	 3	 1	 2
k_p at −20° (l./(mol sec))	0.18	0.92	3.4	0.019[a]	0.11
ΔE_p‡ (kcal/mol)	11.2	11.8	12.6	14.2	16.1
A_p (l./(mol sec))	1.3×10^9	1.5×10^{10}	2.3×10^{11}	5.3×10^{10}	8.3×10^{12}
ΔF_p‡ (kcal/mol)	15.4	14.7	14.2	17.0	15.7
ΔH_p‡ (kcal/mol)	10.7	11.3	12.1	13.7	15.6
ΔS_p‡ (eu)	−18.6	−14.6	−8.5	−12.1	−1.3

[a] Calculated from the data at other temperatures.

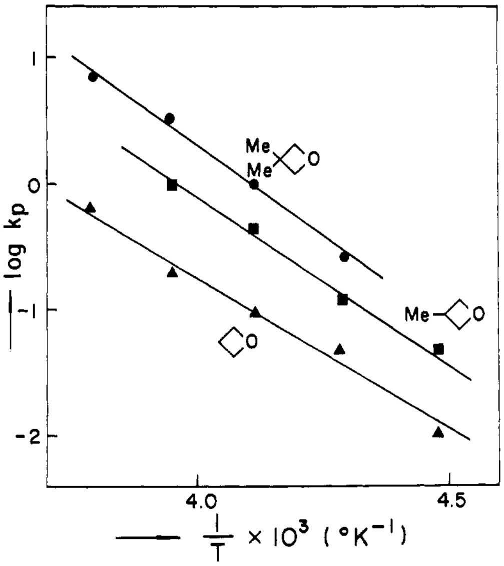


Figure 9. Arrhenius plots of k_p in the polymerization of 1, 2, and 3 in methylcyclohexane solution.

In the same way the activation parameters in CH_2Cl_2 were calculated: ΔE_p‡ = 14.2 kcal/mol, $A_p = 5.3 \times 10^{10}$ l./(mol sec) for 1; ΔE_p = 16.1 kcal/mol, $A_p = 8.2 \times 10^{12}$ l./(mol sec) for 2.

According to the transition-state theory,[12] the k_p can be expressed by

$$k_p = \frac{k^*T}{h} e^{-\Delta F_p{}^\dagger/RT} \tag{6}$$

where k^* is the Bolzmann constant and h is the Planck constant and

$$\Delta F_p\ddagger = \Delta H_p\ddagger - T\Delta S_p\ddagger \tag{7}$$

therefore

$$k_p = \frac{k^*T}{h} e^{-\Delta H_p{}^\dagger/RT} e^{\Delta S_p{}^\dagger/R} \tag{8}$$

$$\Delta H_p\ddagger = \Delta E_p\ddagger - RT \tag{9}$$

According to eq 6–9, the kinetic parameters were determined (Table IV). The k_p values at −20° are cited again in Table IV for the purpose of comparison.

At −20°, the relative reactivities of 1, 2, and 3 in methylcyclohexane are 1:5.1:19, and those of 1 and 2 in CH_2Cl_2 are 1:5.8, respectively, *e.g.*, the methyl group at the 3 position of oxetane ring enhances the polymerization reactivity in both solvents. Correspondingly, ΔF_p‡ increases in the order, 1 > 2 > 3.

Since the activation energy, the ΔE_p‡ (or ΔH_p‡) value, is in the order 3 > 2 > 1, opposite to that of the k_p value, the reactivity difference cannot be understood in terms of the ΔE_p‡ values. Consequently, the difference in reactivity is attributed to the frequency factor, the A_p value, *e.g.*, the entropy factor governs predominantly the reactivity.

Ring Strain and Basicity of Monomers. The reactivities of cyclic monomers were once compared on the basis of the apparent values of the so-called monomer reactivity ratios in the cationic copolymerization, and these relative reactivities were tentatively interpreted by two parameters of the ring strain and basicity of monomer.[13-15] The ring strain of cyclic ether monomer is quantified by the thermodynamic parameter of the free energy of polymerization, ΔF, which has been considered to be close to the corresponding value of the hypothetical polymerization of the corresponding cycloalkane.[16] The ΔF values of the unsubstituted and methyl-substituted cycloalkanes have been given[17] (Table V). It has been indicated that substitution by either one or two methyl groups on the same carbon atom decrease the ΔF value. The ΔF value is taken as a measure of the ring strain of monomer, which decreases in the following order, 1 > 2 > 3. This is the opposite order of the k_p values obtained in the present study. If the ring strain were the most influential in the ring-opening polymerization of 1, 2, and 3, the relative reactivity would be expected to be the order, 3 < 2 < 1. Thus the ring strain of monomer is not an influential element for the control of the kinetic reactivity of monomer of k_p. The next possible factor for the SN2 propagation rate might be the nucleophilic reactivity of monomer. Sometimes the nucleophilic reactivity is taken to be in parallel with the basicity, although the parallelism is not always valid. The basicity of cyclic ether is conveniently determined by ir spectroscopy.[15] The $\Delta\nu_{OD}$ value, the difference of ν_{OD} of methanol-*O*-*d* in benzene and ν_{OD} of

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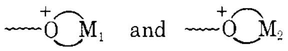
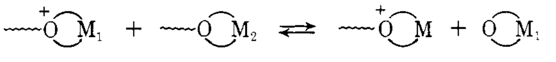
(16) P. A. Small, *Trans. Faraday Soc.*, 51, 1717 (1955).

(17) F. S. Dainton, T. R. E. Devlin, and P. A. Small, *Trans. Faraday Soc.*, 51, 1710 (1955).

methanol-*O-d* and monomer in benzene, has been taken as a measure of basicity of monomer. The $\Delta\nu_{OD}$ values thus obtained are given in Table V. The basicities of **1**, **2**, and **3** are in a narrow range, which are in the order, **3** < **1** < **2**. Again, the basicity does not explain the kinetic reactivity of k_p, too.

Unlike in the case of copolymerization of vinyl monomer, the apparent values of the monomer reactivity ratios in the cationic copolymerization of cyclic ethers do not indicate the kinetic reactivity of monomer in the S_N2 process of eq 2. The monomer reactivity ratios are determined on the basis of the copolymer composition. In the cationic copolymerization of cyclic ether, an oxonium exchange reaction may occur rapidly to change the molar fractions of the two kinds of propagating species

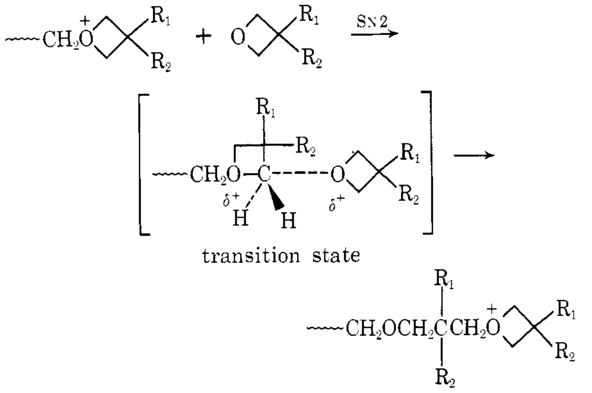




(10)

The apparent values of the monomer reactivity ratios in this case may be much influenced by the above exchange of oxonium and hence they do not show the kinetic reactivity of the ring-opening process of eq 2.

Solvent Effects. Methylene dichloride has a dipole moment of 1.14 D, whereas methylcyclohexane has no dipole moment.[18] The k_p value in methylcyclohexane is higher than that in CH_2Cl_2, *e.g.*, its relative ratio is 9.5:1 for **1** and 8.3:1 for **2** at −20°. Reduction of the solvent polarity attends the increase of the reaction rate. The solvent effect of this kind has been observed in a S_N2 reaction between an ionic species of electrophile and a neutral molecule of nucleophile.[19] The solvent effect of the present study is quite compatible with the proposed reaction scheme of S_N2 mechanism. The transition state may be formulated as a nucleophilic attack of monomer onto the α carbon of cyclic trialkyloxonium (eq 11). The initial state is more strongly solvated than the transition state, since the positive charge is more dispersed in the latter than in the former. Such solvation should be more profound in a more polar solvent than in a less polar solvent. It follows that the extent of solvation is greater in CH_2Cl_2 than in methylcyclohexane, which increased the activation energy and consequently caused the rate decrease in CH_2Cl_2.



(11)

$R_1, R_2 = H$ or methyl

Methyl Substituent Effects. As mentioned above, the activation entropy $\Delta S_p\ddagger$ is quite influential for the kinetic reactivity of polymerization of oxetanes. The $\Delta S_p\ddagger$ values are −18.6, −14.6, and −8.5 eu for **1**, **2**, and **3** in methylcyclohexane. Substitution of the methyl group at the 3 position of oxetane ring made the activation entropy increased by more than enough to govern the rates, notwithstanding the countervailing effect of the activation energy. A similar tendency was observed also in CH_2Cl_2.

Table V
Thermodynamic and Basicity Data for Oxetane Monomers

	1	2	3
ΔF^a (kcal/mol)	21.5	17.7	14.0
$\Delta\nu_{OD}{}^b$ (cm^{-1})	103	106	99

^{a}Taken from ref 17. The values of cyclobutane, methylcyclobutane and 1,1-dimethylcyclobutanes were used for **1**, **2**, and **3** monomers. ^{b}This work. Measured according to ref 15. See Experimental Section.

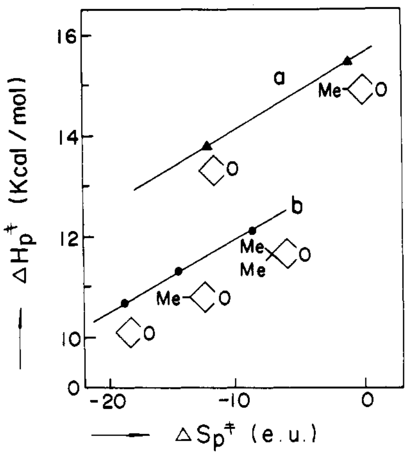


Figure 10. The $\Delta H_p\ddagger - \Delta S_p\ddagger$ relationship: (a) in methylcyclohexane; (b) in methylene dichloride.

Various kind of factors can be considered to interpret the present findings. Among them, solvation effect seems to give one of plausible explanations. In the course from the initial state to the transition state, the methyl-substituted monomer **3** suffers from the unfavorable entropy effect to a much less extent in comparison with the unsubstituted monomer **1**, because the desolvation in the transition state of the propagation of **3** is facilitated by the steric hindrance due to the two methyl groups. Thus the entropy change from the solvated initial state to the desolvated transition state in the propagation of **3** is less unfavorable than that of **1**. The monomer **2** is the intermediate case.

The plot of $\Delta H_p\ddagger$ *vs.* $\Delta S_p\ddagger$ gave a linear relationship in the series of polymerizations in methylcyclohexane (Figure 10). The so-called compensation effect between $\Delta H_p\ddagger$ and $\Delta S_p\ddagger$ is seen. Furthermore, it may be assumed that the effect of the methyl substitution is the same in the polymerization in two the different solvents, since a straight line connecting the two points of the polymerizations of **1** and **2** in CH_2Cl_2 is parallel with the line for the polymerization series in methylcyclohexane.

Finally, it is seen that the concentrations of propagating species [P*] varied depending greatly upon monomers **1-3** and upon the reaction temperatures. The larger the k_p value became, the smaller the so-called catalyst efficiency for both solvents. Maximum [P*] values observed for monomers **1**, **2**, and **3** among all runs were 3.1×10^{-3}, 2.7×10^{-3}, and 5.0×10^{-4} mol per l., respectively. The [P*] value is closely related with the initiation mechanism. Taking it

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(18) J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, New York, N. Y., 1970.

(19) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 457.

Table VI
Position of ν_{OD} (cm^{-1})^a

	ν_{OD} (cm^{-1})	$\Delta\nu_{OD}$ (cm^{-1})^b
MeOD	2664	0
MeOD + 1	2561	103
MeOD + 2	2558	106
MeOD + 3	2565	99

^{a}In benzene solution. $^b\Delta\nu_{OD} = \nu_{OD}$ (benzene) − ν_{OD} (monomer).

into account that the BF_3-catalyzed oxetane polymerization does not occur when water or hydroxy compounds were removed completely from the reaction system[20], and that the purification procedure of the monomer and solvent in this work can hardly assure higher purity of the reaction system than the magnitude ot the [P*] value, then the initiating species may be formed by the aid of water cocatalysis in the way as Rose[9] first proposed.

Rose used the initial catalyst concentration, $[BF_3]_0$ of 0.1 mol/l.[9] which was much higher than those of this work. Thus, he could show the critical effect of water on the oxetane polymerization. In the present study, however, the main purpose was to perform the kinetics of the propagation reaction on the basis of the instantaneous [P*], which was obtained by means of the phenoxyl end-capping method. Therefore, little attention was paid to elucidate the behavior of water present in the reaction system probably due to incomplete drying.

Conclusions. The effect of methyl substitution of the oxetane monomer in the cationic ring-opening polymerization has revealed that the activation entropy is more influential in the determination of the propagation rate. A methyl substituent on the oxetane ring made the activation entropy increased enough to counteract the activation enthalpy which became greater as a result of the methyl group. The rate order, 1 < 2 < 3, was accounted for on the basis of the difference of ease of desolvation in going from the solvated initial state to the desolvated transition state. The activation energy is a minor contributor in this case. It should be emphasized again that the entropy term can in some cases be a predominating factor to determine the propagation rate as presented in this work. The ring strain and the basicity of monomer seem to be less important in the cationic ring-opening homopolymerization of oxetanes, although they are believed to be important factors to determine the monomer reactivity ratios of the cationic ring-opening copolymerization of cyclic ethers.[13-15]

Experimental Section

Materials. The oxetane monomer was prepared from trimethylene glycol using the procedure of Rose.[8] It was purified and dried by repeated distillation using spinning-band columns over sodium metal under dry nitrogen, bp 47.2°; nmr ($CDCl_3$) δ 2.7 (m, 2 H, $-CH_2-$), 4.75 (t, 4 H, $-CH_2OCH_2-$). 3-Methyloxetane was prepared from methyl methacrylate according to Bartok *et al.*[10] The same procedure above was taken to purify it, bp 67.0–67.5° (lit.[9] bp 68°); nmr ($CDCl_3$) δ 1.30 (d, 3 H, CH_3), 3.1 (m, 1 H, $-CH(CH_3)$), 4.6 (m, 4 H, $-CH_2OCH_2-$). 3,3-Dimethyloxetane was prepared by catalytic decomposition of carbonate ester of 2,2-dimethyl-1,3-propanol according to Seales *et al.*[11] It was distilled three times on spinning-band columns over sodium metal under dry nitrogen, bp 78.0–78.5° (lit.[11] bp 78°); nmr ($CDCl_3$) δ 1.37 (s, 6 H, $-(CH_3)_2$), 4.30 (s, 4 H, $-CH_2OCH_2-$). Methylcyclohexane was commercial reagent which was treated with concentrated sulfuric acid for 1 day, washed successively with an aqueous solution of sodium hydroxide and with water, dried over calcium chloride, and distilled repeatedly under dry nitrogen, bp 101°. CH_2Cl_2 was purified and dried as described in a previous paper.[3] $BF_3 \cdot H_4$furan complex was prepared and purified as described previously.[3] Methanol-*d* was purchased from the commercial source and distilled before use, bp 64.0–65.0°.

Polymerization Procedure and Determination of [P*]. Polymerization was carried out in methylcyclohexane of CH_2Cl_2 solution under a dry nitrogen atmosphere. At the polymerization temperature, a solution of $BF_3 \cdot H_4$furan complex was added to a monomer solution to initiate the reaction. At a desired time of reaction, three-times excess sodium phenoxide in H_4furan was added to stop the polymerization. After stirring for 30 min, the short-stopped mixture was treated with a large excess of 1 *N* aqueous sodium hydroxide solution. The decomposition mixture was extracted with CH_2Cl_2. The uv measurement was performed in CH_2Cl_2 solution for the determination of [P*], the procedure of which was the same as reported previously.[3] Conversions were determined from the amount of product polymer.

Measurement of Monomer Basicity. The procedure of ir measurement was same as that of Iwatsuki *et al.*[15] in which the O–D band of methanol-*d* was determined with a Hitachi grating ir spectrometer, Model EPI-G3. The cell was of 0.010 cm thick. The concentration of methanol-*d* was 0.1 mol/l. of benzene solution. The results of measurement are shown in Table VI.

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(20) A. C. Farthing, *J. Chem. Soc.*, 3648 (1955).