Isomerization Polymerization of 2-Oxazoline. V. Kinetic Studies on the Polymerization of 2-Oxazoline

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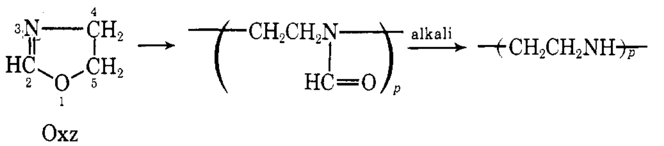
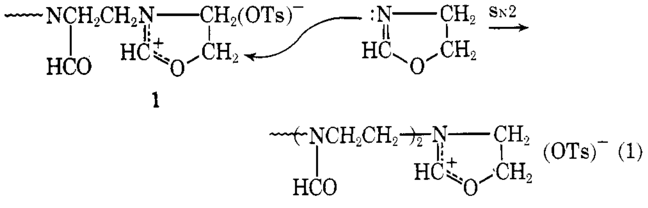
ABSTRACT: Kinetic analysis of the isomerization polymerization of 2-oxazoline (Oxz) producing poly(*N*-formylethylenimine) was made on the basis of the instantaneous concentrations of monomer, unreacted initiator, and the growing species. As the initiator, methyl tosylate (MeOTs) and methyl iodide (MeI) were used. The polymerization proceeds through cationic mechanism, but the rate-determining step of propagation was different between the two initiators. The MeOTs-initiated polymerization propagates through the growing species of oxazolinium tosylate 1 which is opened by the nucleophilic attack of monomer (eq 2–3). In the MeI-initiated polymerization, however, the propagation occurs between the species of covalent-bonded alkyl iodide 2 and Oxz (eq 10–12). The rate constants of initiation and propagation as well as the activation parameters of propagation were determined for the two series polymerizations. The reaction schemes were well rationalized by the kinetic data.

The present paper describes kinetic studies on the isomerization polymerization of 2-oxazoline (Oxz). The polymerization of Oxz was recently performed by us to produce poly(*N*-formylethylenimine), from which crystalline polyethylenimine having a linear structure was prepared for the first time.[2,3]

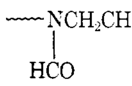


Oxz

As to the mechanism of the propagation, we have presented two different mechanisms depending upon the nature of initiator.[4] In the Oxz polymerization by methyl tosylate (MeOTs), the species at the propagating end is an oxazolinium tosylate **1**, which is opened by an S_N2 attack at C-5 atom by the monomer nucleophile.



On the other hand, the Oxz polymerization by methyl iodide (MeI) proceeds through a covalent-bonded species having a terminal structure of β-(*N*-formylamino)ethyl iodide **2**.



$$\sim\!\!\sim\underset{\displaystyle \mathrm{HCO}}{\mathrm{N}}\mathrm{CH_2CH_2I}$$

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In the present study, the Oxz polymerizations induced by these two initiators were characterized definitely by kinetic analysis using nmr spectroscopy. The polymerization reaction was done in an nmr sample tube, and the kinetic analysis was successfully performed by the direct determination of the instantaneous concentrations of the initiator, propagating species, and Oxz monomer.

Experimental Section

Reagents. Oxz was prepared and purified as previously reported.[2] MeOTs and MeI were commercial reagents, which were distilled under nitrogen. Trideuterioacetonitrile (CD_3CN), the polymerization solvent, was a commercial reagent, which was dried by Linde molecular sieves 4A and distilled under nitrogen. *N*-(β-Iodoethyl)-*N*-methylformamide, $CH_3N(CHO)CH_2CH_2I$, **3**, was prepared as reported previously[4] by the equimolar reaction of Oxz with MeI. Cyclohexane, 1,1,2,2-tetrachloroethane, and benzene were purified by distillation under nitrogen and treated with Linde molecular sieves 4A.

Polymerization and Nuclear Magnetic Resonance Measurement. The whole procedure was carried out under nitrogen. First, a mother solution of polymerization mixture was prepared by adding the initiator to an Oxz solution in CD_3CN containing small amounts of cyclohexane and 1,1,2,2-tetrachloroethane. The compositions of the mother solutions for two initiators were as follows: MeOTs initiator—0.988 mmol of MeOTs, 4.94 mmol of Oxz, 0.84 ml of CD_3CN, 0.15 ml of 1,1,2,2-tetrachloroethane (internal standard of nmr measurement), 0.03 ml of cyclohexane; MeI initiator—0.96 mmol of MeI, 4.82 mmol of Oxz, 1.03 ml of CD_3CN, 0.03 ml of cyclohexane. Then a small portion of the mother solution was placed in an nmr tube, and the polymerization was continued in the tube. At several reaction times, the polymerization system was subjected directly to nmr analysis by using a JNM 4H100 nmr spectrometer (Jeol). In the MeI initiated polymerization at 55 and 70°, the nmr measurement was carried out after the complete consumption of initiator at 40°.

Results and Discussion

MeOTs Initiated Polymerization. 1. Nmr Spectroscopy. Figure 1 illustrates the nmr spectrum of the polymerization system initiated by MeOTs, which was taken at a reaction time of 109 min at 31°. The molar ratio of initiator to monomer is 1:5. The concentrations of Oxz, unreacted initiator and the propagating species were successfully determined on the basis of the following assignment of the spectrum. The peaks at τ 2.48 and 2.72 are respectively due to the two ortho hydrogens of MeOTs and tosylate anion of the propagating species. The peak at τ 3.12 is assigned to 2-methine hydrogen of Oxz. The instantaneous concentration of monomer was determined from the peak area ratio between 2-methine hydrogen (τ 3.12) and hydrogens of 1,1,2,2-tetrachloroethane (τ 3.50), the internal standard. The peak at τ 4.93 is due to the 5-methylene protons of the oxazolinium salt at the growing end, whose area indicates the concentration of the propagating species. The stoichiometric relation between the tosylate anion (τ 2.72) and the oxazolinium salt (τ 4.93) hold during the polymerization. In addition, the decrease of the MeOTs concentration was equal to the concentration of the propagating oxazolinium salt.

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[2] T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, 3, 35 (1972).

[3] T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 5, 108 (1972).

[4] T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, 3, 176 (1972).

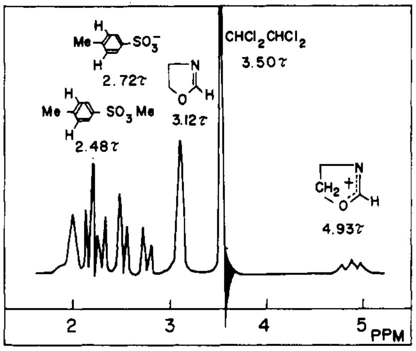


Figure 1. Nmr spectrum of the Oxz polymerization system initiated by MeOTs in CD_3CN (after 109 min at 31°).

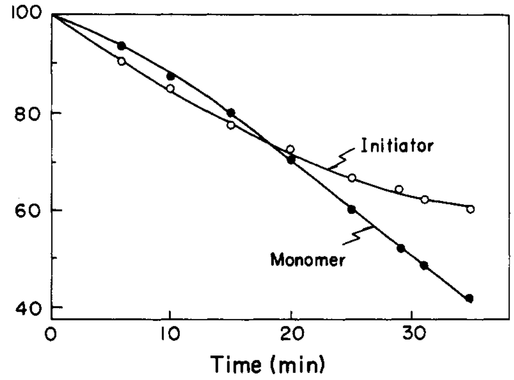
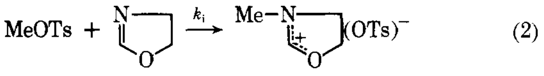


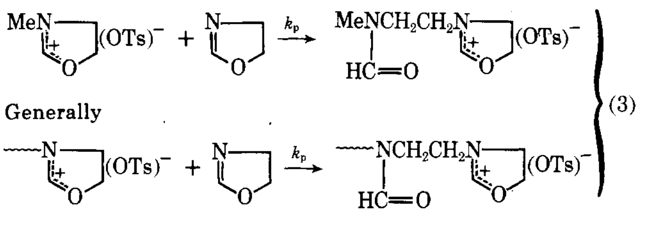
Figure 2. Decrease rates of the concentrations of the initiator and monomer in the Oxz polymerization initiated by MeOTs in CD_3CN at 40°; [Oxz], 3.33 mol/l.; [MeOTs], 0.667 mol/l.

2. Kinetics. Figure 2 shows the time-conversion curves for Oxz and MeOTs at 40°, which have been drawn on the basis of the time change of nmr spectrum. Now, the following scheme of reactions will explain the course of polymerization.

Initiation



Propagation



The rate of initiation is

$$-\frac{d[I]}{dt} = k_i[I][M] \qquad (4)$$

where [I] and [M] are the concentrations of MeOTs and Oxz, respectively. Integration of eq 4 gives

$$\ln [I]_0/[I] = k_i \int_0^t [M]dt \qquad (5)$$

where $[I]_0$ is the initial feed concentration of MeOTs. The integrated value of [M] in eq 5 was given by graphical integration on the [M]-time curve. A linear plot of eq 5 is shown in Figure 3, whose slope corresponds to k_i, $k_i = 0.98 \times 10^{-4}$ l./(mol sec) at 40°.

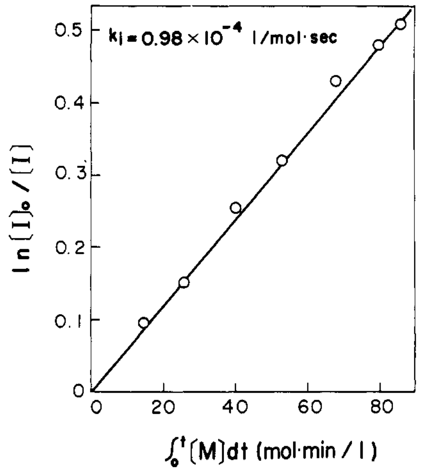


Figure 3. Plot of eq 5 in the Oxz polymerization by MeOTs at 40°.

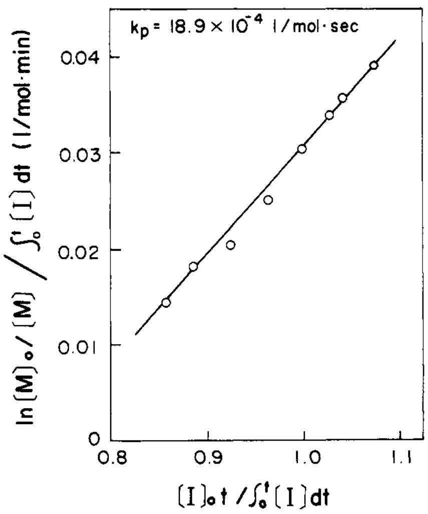


Figure 4. Plot of eq 9 in the Oxz polymerization by MeOTs at 40°.

The consumption rate of Oxz is given by

$$-\frac{d[M]}{dt} = k_i[I][M] + k_p[P^*][M] \qquad (6)$$

where $[P^*]$ is the concentration of propagating species and k_p is the propagation rate constant. Since $[P^*]$ was found by nmr to be equal to the decrease of the MeOTs concentration

$$[P^*] = [I]_0 - [I] \qquad (7)$$

Therefore

$$-\frac{d[M]}{dt} = (k_i - k_p)[I][M] + k_p[I]_0[M] \qquad (8)$$

Integration of eq 8 gives

$$\ln [M]_0/[M] = (k_i - k_p)\int_0^t [I]dt + k_p[I]_0 t$$

therefore

$$\frac{\ln [M]_0/[M]}{\int_0^t [I]dt} = (k_i - k_p) + k_p\frac{[I]_0 t}{\int_0^t [I]dt} \qquad (9)$$

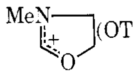
The integrated value of [I] in eq 9 was given by graphical integration on the [I]-time curve. Figure 4 shows a linear plot of eq 9, whose slope gives k_p, $k_p = 19 \times 10^{-4}$ l./(mol sec) at 40°.

Table I
Rate Constants of Oxz Polymerization in CD_3CN [10^{-4} l./(mol sec)]

	MeOTs[a]			MeI[a]	
°C	k_i	k_p	°C	k_i	k_p
24	0.14	1.9	40	1.6	0.18
31	0.29	4.6	55		0.42
40	0.98 (1.8)[b]	19 (1.2)[b]	70		1.2

[a] Polymerization conditions; $[Oxz]_0$ = 3.33 mol/l., initiator = 0.667 mol/l. [b] The rate constants of the polymerization of 2-methyl-2-oxazoline from ref 5.

In Table I, the values of k_i and k_p of the Oxz polymerization (40°) are compared with the corresponding values of the polymerization of 2-methyl-2-oxazoline (MeOxz) by the same initiator.[5] In the case of Oxz, k_i is much smaller than k_p, and therefore the concentration of the first propagating species 4 is assumed to be very small. In fact, the



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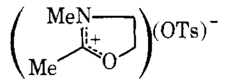
methyl group linked to the oxazolinium nitrogen was not detected by nmr even in an early polymerization mixture. In the case of MeOxz, however, k_i is larger than k_p. As was reported previously, the first propagating species 5 was actually detected by nmr spectroscopy.[5] As to the reactivities of Oxz and MeOxz, the rate constant values in Table I bear an interesting significance. Oxz is less nucleophilic than MeOxz, because the rate of reaction of Oxz with the common electrophile of MeOTs is smaller than that of MeOxz.[6] Therefore, the larger k_p value of Oxz in comparison with that of MeOxz may be attributed to the higher ring-opening reactivity of unsubstituted oxazolinium salt in comparison with that of 2-methyloxazolinium salt, since the propagation is a bimolecular process between oxazolinium salt and the nucleophile of monomer.



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MeI-Initiated Polymerization. 1. Nuclear Magnetic Resonance Spectroscopy. Figure 5 shows the nmr spectrum of the polymerization mixture with MeI initiator in CD_3CN at a reaction time of 57 min at 40°. The feed molar ratio of MeI to Oxz is 1:5. A striking difference from the MeOTs-initiated polymerization (Figure 1) is the absence of the nmr peak due to 5-methylene protons of oxazolinium salt in Figure 5. Even in an equimolar reaction mixture of MeI and Oxz, the peak due to oxazolinium salt was not detected.[4] The MeI-initiated polymerization is assumed to proceed through an active species of 2. In fact, N-(β-iodoethyl)-N-methylformamide (3) was isolated in a yield of 51% in the equimolar reaction of MeI and Oxz.[4]

The peak at τ 7.87 is due to the unreacted MeI. The two peaks at τ 7.08 and 7.19 are assigned to N-methyl group at the polymer chain end, which is derived from MeI in the initiation. The stoichiometry between the decrease of MeI (τ 7.87) and the increase of the N-methyl chain end (τ 7.08 and 7.19) was quite satisfactory. For the determination of the Oxz, the peak at τ 3.18 due to 2-methine hydrogen of Oxz as well as the peak at τ 2.0 due to the formyl hydrogen of polymer (the monomer consumption) were conveniently utilized.

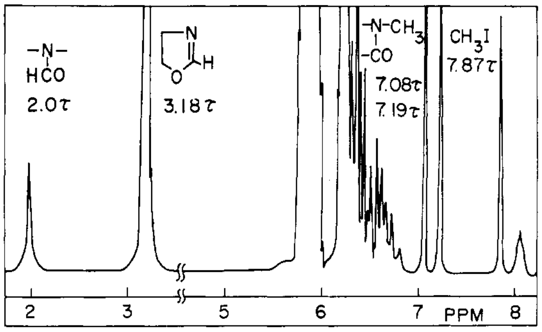


Figure 5. Nmr spectrum of the Oxz polymerization system initiated by CH_3I in CD_3CN (after 57 min at 40°).

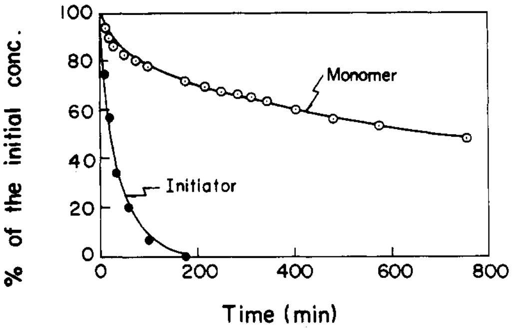
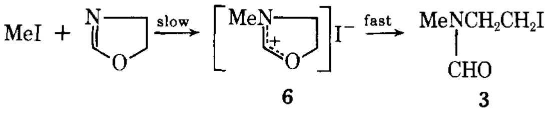


Figure 6. Decrease rates of the concentrations of the initiator and monomer in the Oxz polymerization initiated by CH_3I in CD_3CN at 40°; [Oxz], 3.33 mol/l.; [CH_3I], 0.667 mol/l.

2. Kinetics. Figure 6 shows the time-conversion curves for Oxz and MeI, which have been constructed on the basis of the time change of the nmr spectrum of the polymerization mixture at 40°. It is indicated that MeI is consumed in an early stage of polymerization.

The polymerization may be expressed by the following scheme.

Initiation



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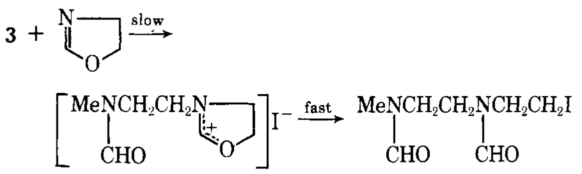
Propagation



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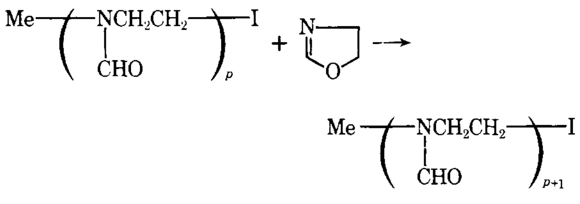

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(5) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 5, 359 (1972).
(6) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, 4, 87 (1973).

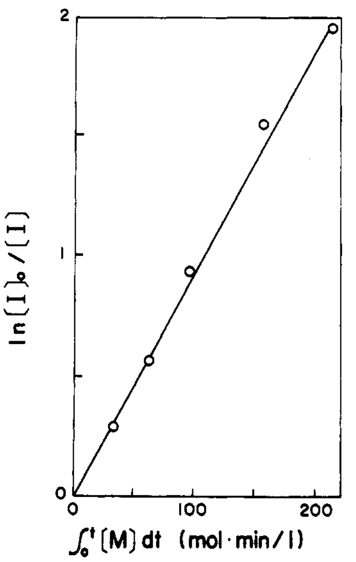

Figure 7. Plot of eq 14 in the Oxz polymerization by CH_3I at 40°.

The initiation is the reaction of MeI with Oxz, which gives 3 through an unstable intermediate of 6. The rate-determining step is the formation of 6. The propagation is the successive reaction of Oxz with a propagating species of covalent-bonded alkyl iodide, which proceeds through unstable intermediates of oxazolinium iodides such as 7. Some experimental supports to the above scheme will be given later.

The rate of initiation is

$$-\frac{d[I]}{dt} = k_i[I][M] \qquad (13)$$

Integration of eq 13 gives

$$\ln [I]_0/[I] = k_i \int_0^t [M]dt \qquad (14)$$

As in the case of the MeOTs-initiated polymerization, the value of integrated [M] was obtained by graphical integration. Figure 7 shows a linear plot of eq 14, from which k_i has been determined, $k_i = 1.6 \times 10^{-4}$ l./(mol sec) at 40°.

After all MeI has been converted into the propagating species (174 min in Figure 6), the rate of the monomer consumption is expressed by

$$-\frac{d[M]}{dt} = k_p[P^*][M] \qquad (15)$$

In eq 15, [P*], the concentration of propagating species, is taken as being equal to the initial concentration of MeI, because the stoichiometric formation of propagating species has been established on the basis of nmr data in which the amount of $-N(CHO)CH_3$ group at polymer end is equal to the amount of the reacted MeI. Then, eq 15 becomes

$$-\frac{d[M]}{dt} = k_p[I]_0[M] \qquad (16)$$

Integration of eq 16 with respect to time gives

$$\ln \frac{[M]_{t'}}{[M]_t} = k_p[I]_0(t - t') \qquad (17)$$

where t and t' are longer than the time required for the complete consumption of MeI, *e.g.*, 174 min in Figure 6, and $[M]_t$ and $[M]_{t'}$ are the Oxz concentrations at time t and t', respectively. Figure 8 shows a plot of eq 17 at 40°. From the slope of the straight line passing the origin, the value of k_p was determined, $k_p = 0.18 \times 10^{-4}$ l./(mol sec). By similar procedure, the k_p value was determined at 55 and 70° (Table I). In the polymerization at 55 and 70°, the change of the Oxz concentration was examined by nmr after all MeI had been consumed at 40°.

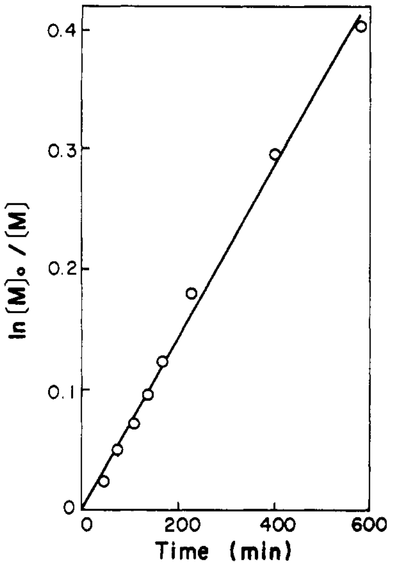

Figure 8. Plot of eq 17 in the Oxz polymerization by CH_3I at 40°.

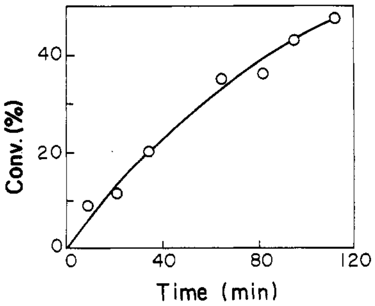

Figure 9. Time-conversion curve of the Oxz polymerization initiated by 3 in CD_3CN at 70°.

Polymerization Initiated by $CH_3N(CHO)CH_2CH_2I$ (3). According to the scheme of the MeI-initiated polymerization, 3 is the smallest species of propagation. The kinetics of the polymerization by 3 was then studied. In this case, the polymerization commences directly from the first propagation step. By nmr spectroscopy, the instantaneous Oxz concentration was determined from the peak area ratio between 2-methine proton and aromatic hydrogens of the internal standard of benzene. Figure 9 shows the time-conversion curve for Oxz at 70°.

The rate of polymerization by 3 is expressed by

$$-\frac{d[M]}{dt} = k_p[3][M] \qquad (18)$$

which has no term of initiation. The integrated form is

$$\ln \frac{[M]_0}{[M]} = k_p[3]_0 t \qquad (19)$$

where $[3]_0$ is the initial feed concentration of 3. Figure 10 shows the linear plot of eq 19, whose slope corresponds to k_p, $k_p = 1.4 \times 10^{-4}$ l./(mol sec) at 70°. The k_p value of the MeI-initiated polymerization has been determined to be $k_p = 1.2 \times 10^{-4}$ l./(mol sec) at 70°, which is in good agreement with that given in Figure 10. These findings

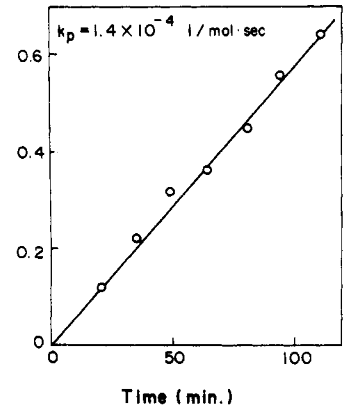

Figure 10. Plot of eq 19 in the Oxz polymerization initiated by $ICH_2CH_2N(CH_3)CHO$ at 70°.

are taken to support the mechanism of propagation which proceeds through the species of covalent-bonded iodides such as **2**, **3**, and **8**. Oxazolinium iodide species (**6** and **7**) are quite unstable, and are converted rapidly into the covalent iodide species.

Activation Parameters and Difference of Mechanism. The k_p values of the two series of Oxz polymerization by MeOTs and MeI at varying temperatures are summarized in Table I. The Arrhenius plots of the two polymerizations were linear, from which the activation energies and frequency factors for the two initiators could be determined (Table II). An interesting observation is that the activation parameters are different between the two polymerizations. The k_p of the MeI-initiated polymerization at 40° is about one-hundredth of that of the MeOTs-initiated one. The small k_p value for MeI is ascribed to the exceptionally small value of the frequency factor. As to the activation energy, the value for MeI is about a half of that for MeOTs. These results clearly show that the rate-determining steps of the propagations of polymerizations by these two initiators are different from each other.

In the MeOTs-initiated polymerization, the rate-determining step of propagation is the ring-opening process of oxazolinium ion by the attack of Oxz (see eq 3). In the MeI-initiated polymerization on the other hand, the formation of the unstable oxazolinium iodide from covalent-bonded alkyl iodide and Oxz is the rate-controlling step (see eq 11 and 12). In addition, the oxazolinium salt formation from alkyl iodide with Oxz resembles the Menschutkin reaction between alkyl halide and tertiary amine to produce the corresponding quaternary ammonium salt. Table II shows the activation parameters of a typical Menschutkin reaction between Et_3N and EtI in a polar solvent of nitrobenzene.[7] It is seen that the activation parameters of the propagation of the MeI-initiated polymerization are quite similar to those of the Menschutkin reaction. This similarity may be taken to support the scheme of the MeI-initiated polymerization (eq 10–12). The mechanistic difference between the two polymerizations may possibly be explained by the difference of the so-called nucleophilic reactivity between the two counteranions of tosylate and iodide. According to Swain–Scott–Hine,[8] the nucleophilic constants (n) of iodide ($n = 5.04$) is much higher than tosylate ($n < 1.0$). A strong nucleophile of iodide rapidly opens the oxazolinium salt to produce the species of covalent alkyl iodide (eq 10–12), whereas a weak nucleophile of tosylate does not. In the MeOTs-initiated polymerization of Oxz, the oxazolinium salt is opened by Oxz which is a stronger nucleophile than tosylate. In the polymerizations of MeOxz and 2-phenyloxazoline by MeI, however, the intermediates of the corresponding 2-substituted oxazolinium iodide are not very unstable, and they are isolable under suitable conditions.[9]

$$R_3N + RX \longrightarrow R_4N^+X^-$$

Table II
Activation Parameters of Oxz Polymerization in CD_3CN [a]

Initiator	MeOTs	MeI	Et_3N + EtI in $PhNO_2$ (40°)[7]
k_p (40°)	19×10^{-4}	0.18×10^{-4}	4.8×10^{-4}
ΔE^*	25	13.5	11.6
A	7.5×10^{14}	5.0×10^{4}	7.9×10^{4}

[a] Polymerization conditions; $[Oxz]_0 = 3.33$ mol/l., initiator = 0.667 mol/l.

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(7) H. G. Grimn, H. Ruf, and H. Wolff, *Z. Phys. Chem., Abt. B*, **13**, 301 (1973).

(8) C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).

(9) T. Saegusa, H. Ikeda, and H. Fujiii, Presented at the 24th Annual Meeting of Chemical Society, Osaka, Japan, April 1971.