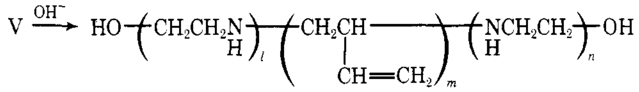
analysis, because the OXZ–BD block copolymer was quite insoluble and could not be well analyzed. The OXZ–BD block copolymer was hydrolyzed in aqueous alkaline solution at 100° for 4 hr. A swollen product was washed by water and dried *in vacuo* at room temperature to give a powdery material. This became a rubbery polymer by treating at 90° *in vacuo*. The rubbery product was soluble in $CHCl_3$ having $[\eta]$ of 0.33 which is larger than that of polybutadiene tosylate ($[\eta] = 0.13$).

As shown in Figure 6b, the ir spectrum of the product has no absorption of amide group, but it has bands characteristic of the polybutadiene structure, as well as the bands at 3260 cm^{-1} (NH), 1122 cm^{-1} (C–N) and 784 cm^{-1}, which are attributable to the polyethylenimine structure.[8] The nmr spectrum of the polymer taken in $CDCl_3$ (Figure 7a) shows peaks at τ 4.65, 5.03, and 8.03 due to the protons of polybutadiene and peaks at τ 7.27 and 7.94, which are assignable to *N*-methylene protons ($(-CH_2)_2N-$) and amine proton (>NH), respectively. D_2O treatment of the nmr sample solution decreased the combined areas of the peaks at τ 7.8–8.2. The decrease corresponded to the number of the secondary amine proton. This observation is taken to confirm the structure of the block copolymer (Figure 7b). The peak intensity ratio of *N*-methylene protons to amine proton is 4:1. No peak due to amide structure ($-CH_2N(HCO)CH_2-$) was observed in the spectrum, which shows complete hydrolysis. These results indicate that the product of the alkaline hydrolysis is an ABA-type block copolymer (VI) with El block (A) and



$$V \xrightarrow{OH^-} HO\left(CH_2CH_2\underset{H}{N}\right)_l\left(\underset{CH=CH_2}{CH_2\overset{}{CH}}\right)_m\left(\underset{H}{N}CH_2CH_2\right)_n OH$$

VI

BD block (B). The EI unit content in the block copolymer (VI) was found to be 63 mol % by nmr. This value was in good agreement with that of OXZ–BD block copolymer (61 mol %). The molecular weight of polyEI block was calculated to be 4700 ($l + n \sim 109$ in VI). The degree of polymerization of polyEI block agreed fairly well with that of polyOXZ block before hydrolysis.

(8) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 5, 108 (1972).

Isomerization Polymerization of 2-Oxazoline. VI. Kinetic Study on the Polymerization of 2-Methyl-2-oxazoline Initiated by Methyl Iodide

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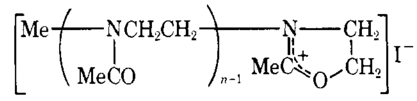
ABSTRACT: A kinetic study of the isomerization polymerization of 2-methyl-2-oxazoline (MeOXZ) initiated by methyl iodide (MeI) was made on the basis of the determination of the instantaneous concentrations of MeI, MeOXZ, and the propagating species of oxazolinium salt by means of nmr spectroscopy. The rate was expressed by the equation $-d[M]/dt = k_i[MeI][M] + k_{p1}[P_1^*][M] + k_{pn}[M]\Sigma_{n=2}[P_n^*]$, where k_i, k_{p1}, and k_{pn} are the rate constants for the initiation, the first propagation step and the subsequent propagation steps, respectively. $[P_1^*]$ and $[P_n^*]$ ($n \geq 2$) are the instantaneous concentrations of the propagating species of two types having $n = 1$ and $n \geq 2$, respectively, of the formula



The values of k_{p1} and k_{pn} were in good agreement with the respective values of the MeOXZ polymerization initiated by the isolated species of $[P_1^*]$. The activation parameters were obtained from the Arrhenius plots of rate constants at different temperatures. The difference in the polymerization mechanism between the unsubstituted 2-oxazoline (OXZ) and MeOXZ by a common MeI initiator was discussed.

This paper deals with a kinetic study on the isomerization polymerization of 2-methyl-2-oxazoline (MeOXZ) initiated by methyl iodide (MeI). As to the kinetics of the polymerization of 2-substituted 2-oxazolines, two studies have already been made by Tomalia *et al.*,[2] and by Kagiya *et al.*[3] In our previous kinetic studies on the polymerizations of substituted and unsubstituted oxazolines[4,5] a convenient method has been established in which each of the instantaneous concentrations of monomer, initiator, and propagating species is directly determined by means of nmr spectroscopy. In the MeI-initiated polymerization of unsubstituted 2-oxazoline (OXZ), the propagating species was shown to be a covalent-bonded alkyl iodide species.[5] In the present study, the MeOXZ polymerization by MeI has been shown to proceed through a different mechanism.

Experimental Section

Reagents. MeOXZ was prepared and purified as before.[4] MeI, a commercial reagent, was purified by distillation under nitrogen. Trideuterioacetonitrile (CD_3CN) was a commercial reagent which was dried by molecular sieves 4A (Union Carbide) and distilled under nitrogen.

Preparation of *N*-Methyl-2-methyl-2-oxazolinium Iodide (2). To a stirred solution of MeI (8.52 g, 60 mmol) in ether (10 ml) was slowly added MeOXZ (1.28 g, 15 mmol) at 5°. The solution

[1] Tokyo Research Laboratories, Japan Synthetic Rubber Co., Kawasaki, Japan.

[2] D. A. Tomalia and D. P. Sheetz, *J. Polym. Sci., Part A-1*, 4, 2253 (1966).

[3] T. Kagiya and T. Matzuda, Presented at 19th Polymer Symposium, Kyoto, 1970, Abstr., p 155.

[4] T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 5, 539 (1972).

[5] T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 6, 315 (1973).

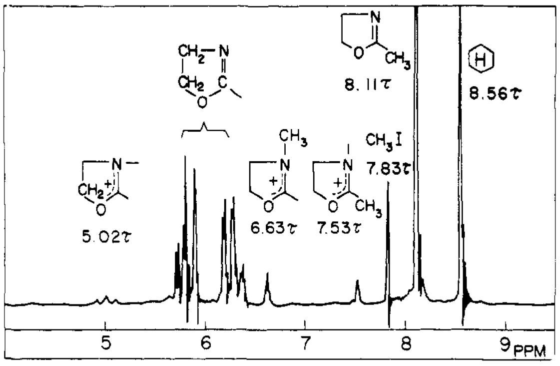
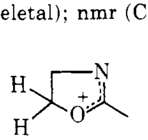


Figure 1. Nmr spectrum of the MeOXZ polymerization system initiated by MeI in CD_3CN (after 27 min at 30°).

was stirred at 20° for 1 hr to give a white precipitate, which was isolated by filtration and washed with ether. The solid was further purified by reprecipitation by means of a solvent-nonsolvent combination of acetonitrile and ether to give 0.79 g (23%) of white crystal: mp 145-146°; ir (Nujol) 1683 (C=N-), 1282 (C-O-C), and 982 (skeletal); nmr (CD_3CN) τ 5.06 (t, 2, i), 5.80 (t, 2, ii), 6.67 (s,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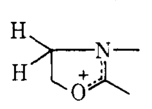
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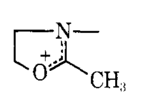

iii

3, N^+-CH_3), 7.55 ppm (s, 3, iii). *Anal.* Calcd for $C_5H_{10}INO$: I, 55.89. Found: I, 55.62.

Polymerization and Nmr Measurement. The whole operation was carried out under nitrogen. Polymerization was commenced by adding the MeI initiator to a stirred solution of MeOXZ in CD_3CN containing small amounts of benzene and cyclohexane as the internal standard of nmr measurement. The composition of the mother solution was as follows: MeI, 1.60 mmol; MeOXZ, 8.03 mmol; CD_3CN, 1.44 ml; benzene, 0.1 ml; cyclohexane, 0.1 ml. Then, a small portion of the reaction mixture was placed in an nmr tube, and the polymerization system was directly subjected to nmr analysis. The instantaneous concentrations of [M] (monomer, [MeI] (initiator), and [P*] (propagating species) were determined from nmr spectra taken at several reaction times on a JNM 4H 100 nmr spectrometer (Jeol).

Results and Discussion

Polymerization of MeOXZ Initiated by MeI. Figure 1 shows an example of the nmr spectrum of the polymerization system initiated by MeI in CD_3CN taken at a reaction time of 27 min at 30°. The initial concentrations of monomer and initiator were 3.33 and 0.667 mol per l., respectively, the molar ratio being 5:1. The concentrations of MeOXZ, MeI, and the propagating species were successfully determined by the areas of the respective peaks. As to the monomer concentration, the concentrations of the relevant three species were determined from the areas of their peaks, *i.e.*, the 2-methyl group of the propagating oxazolinium ring at τ 7.53, the *N*-acetyl group of the product polymer units at τ 8.02, and the 2-methyl group of the monomer itself at τ 8.11. The instantaneous monomer concentration, [M], was calculated from its fraction among three species and the initial monomer concentration. The peaks at τ 6.63 and 7.83 were assigned respectively to the *N*-methyl group of oxazolinium ring derived from MeI and the methyl group of MeI, whose areas were conveniently utilized to calculate the instantaneous initiator concentration, [I]. The peak at τ 7.53 gave the combined concentrations of propagating species, P_1* and P_n* ($n \geq 2$) which are defined by eq 1-3 in the subsequent section. The fraction of [P_1*] and [P_n*] ($n \geq 2$) in the total propagating species ([P*]) are known from the peak area of *N*-methyl protons of oxazolinium ring (P_1*) and that of the terminal *N*-methyl group of the longer propagating polymer molecule at τ 7.03. The stoichiometric relation among the combined concentrations of *N*-methyl group, the 2-methyl group of oxazolinium ring, and the initial and instantaneous concentrations of MeI was found to hold during the polymerization. Figure 2 shows the nmr spectrum of the reaction system at the complete polymerization of monomer after 30 hr at 40°. According to the peaks' assignments described above, the amount of the polymer units and the propagating species were determined separately, from which the degree of polymerization was calculated at 5. This value was in good agreement with the feed ratio of monomer/initiator = 5. These results are taken to support that the polymerization proceeds through a living mechanism.

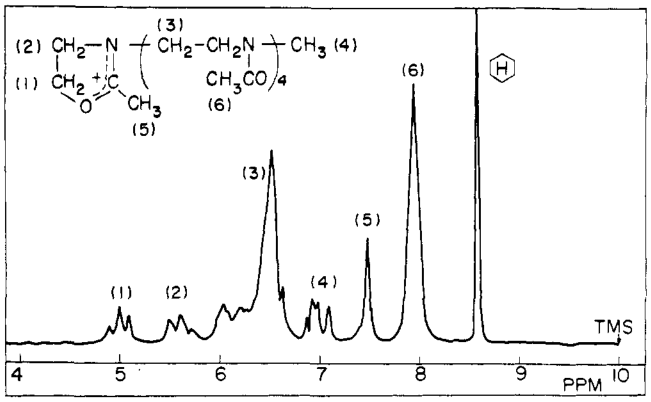
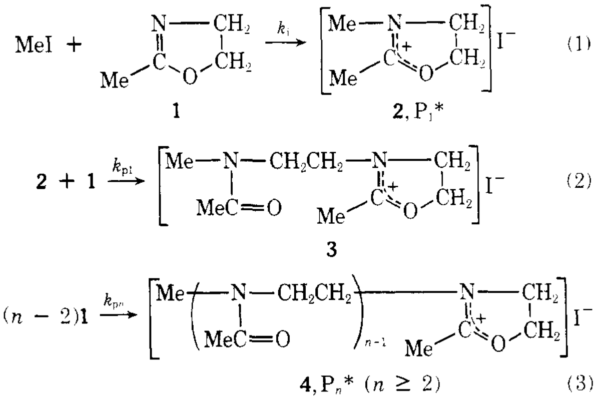


Figure 2. Nmr spectrum of the MeOXZ polymerization system initiated by MeI in CD_3CN (after 30 hr at 40°).

Kinetics. Figure 3 shows the time-conversion curves for monomer and initiator at 40°. MeI was consumed in an early stage of polymerization. It was observed by nmr that [P*] increased with the consumption of MeI in an early period of the polymerization, and then it remained almost constant after all MeI was consumed. The stoichiometry between the total [P*] at the later stage of polymerization and the initial feed concentration of MeI was satisfactory.

Now, the following scheme of reactions will explain the course of the MeOXZ polymerization initiated by MeI.



(1)

(2)

(3)

Then, the kinetic equation is expressed as follows.

$$-d[M]/dt = k_i[MeI][M] + k_{p1}[P_1^*][M] + k_{pn}[M]\sum_{n=2}[P_n^*] \quad (4)$$

Assuming that k_{p1} is equal to k_{pn} in eq 4, the rate equation becomes

$$-d[M]/dt = k_i[MeI][M] + k_p[P^*][M] \quad (5)$$

where $k_p = k_{p1} = k_{pn}$ and $[P^*] = [P_1^*] + \Sigma_{n=2}[P_n^*]$. Since [P*] was found by nmr to be equal to the amount of the consumption of MeI.

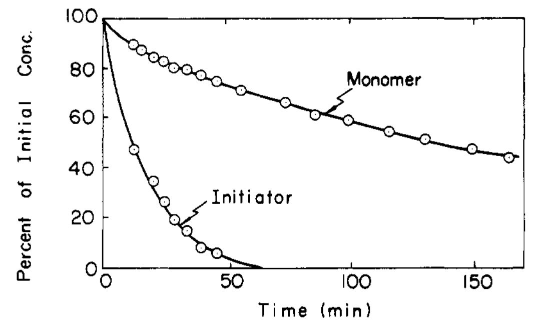


Figure 3. Time-conversion curves of the MeOXZ polymerization initiated by MeI in CD_3CN at 40°: [MeOXZ], 3.33 mol; [MeI], 0.667 mol.

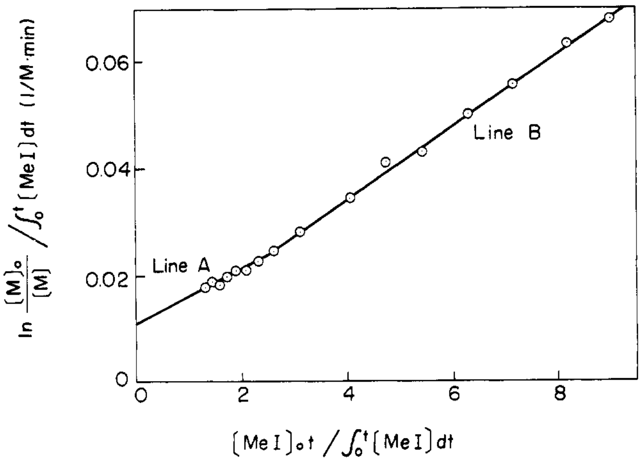


Figure 4. Plot of eq 8 in the MeOXZ polymerization by MeI at 40°.

$$[P^*] = [MeI]_0 - [MeI]$$

where $[MeI]_0$ is the initial concentration of MeI. Then

$$-d[M]/dt = (k_i - k_p)\int_0^t [MeI][M] + k_p[MeI]_0[M] \quad (6)$$

Integration of eq 6 gives

$$\ln [M]_0/[M] = (k_i - k_p)\int_0^t [MeI]dt + k_p[MeI]_0 t \quad (7)$$

Therefore

$$\frac{\ln [M]_0/[M]}{\int_0^t [MeI]dt} = (k_i - k_p) + k_p \frac{[MeI]_0 t}{\int_0^t [MeI]dt} \quad (8)$$

The integrated value of [MeI] in eq 8 was obtained by graphical integration on the [MeI]-time curve. A plot of eq 8 shown in Figure 4 consists of two straight lines, A and B. The difference between the slopes of these two lines are small but definite, which may be due to the difference between k_{p1} and k_{pn} ($n > 2$) in eq 4. The slope and the intercept of line A were utilized to determine k_i and k_{p1}, since $[P_n^*]$ ($n \geq 2$) was found to be quite low by the nmr spectra in an initial stage of the polymerization; $k_{p1} = 0.90 \times 10^{-4}$ and $k_i = 2.68 \times 10^{-4}$ l./(mol sec) at 40°. In the later stage of the polymerization, $[P_1^*]$ was found to be very small and k_p in eq 5 is regarded as k_{pn} ($n \geq 2$) in the period of corresponding to the line B. From the slope of B, k_{pn} was determined, $k_{pn} = 1.14 \times 10^{-4}$ l./(mol sec).

The rate of initiation was also determined by the rate of consumption of MeI according to the equation

$$-d[MeI]/dt = k_i[MeI][M] \quad (9)$$

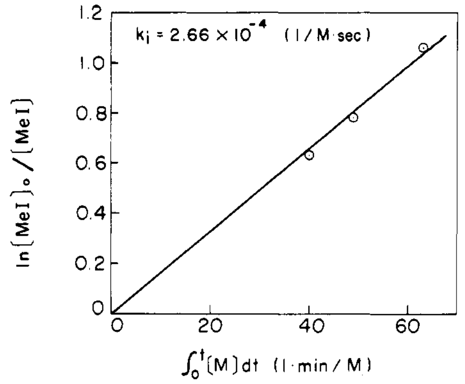


Figure 5. Plot of eq 10 in the MeOXZ polymerization by MeI at 40°.

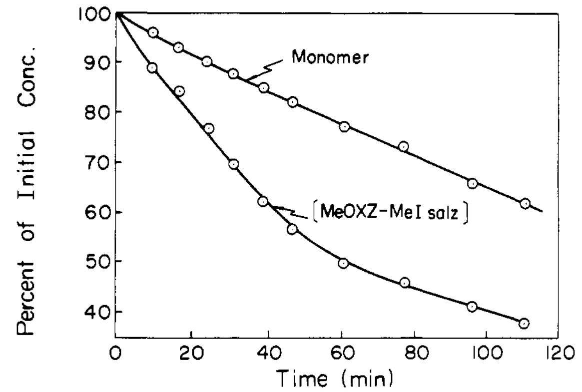


Figure 6. Time-conversion curves of the MeOXZ polymerization initiated by *N*-methyl-2-methyl-2-oxazolinium salt 2 in CD_3CN at 40°: [MeOXZ], 2.67 mol; $[2]_0$, 0.667 mol.

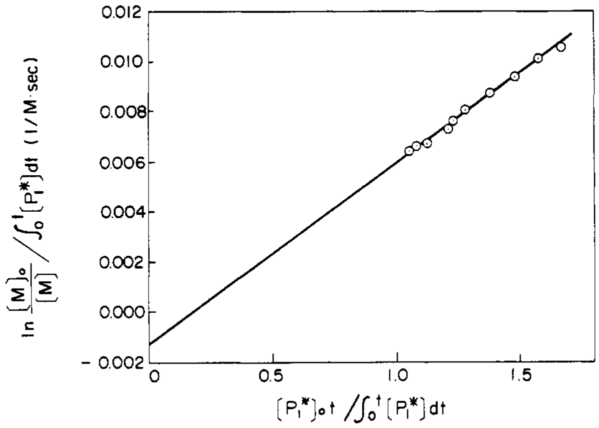


Figure 7. Plot of eq 13 in the polymerization by MeOXZ-MeI salt at 40°.

Integration of eq 9 gives

$$\ln [MeI]_0/[MeI] = k_i\int_0^t [M]dt \quad (10)$$

The integrated value of [M] in eq 10 was given by graphical integration of the [M]-time curve. A linear plot of eq 10 is shown in Figure 5, whose slope corresponds to k_i, $k_i = 2.66 \times 10^{-4}$ l./(mol sec) at 40°. The two k_i values by eq 8 and eq 10 agreed well with each other.

Kinetics of Polymerization Initiated by Oxazolinium Salt (P_1^*). An oxazolinium salt of 2 was prepared by the reaction of MeOXZ with excess MeI in ether, which was used as the polymerization initiator. In this case, the polymerization commences directly from the first propagation step of k_{p1}. Figure 6 shows the time-conversion curves for monomer and initiator at 40° in the polymeriza-

Table I
Rate Constants of the MeOXZ Polymerization Initiated by MeI in CD_3CN^a (10^{-4} l./(mol sec))

Temp (°C)	k_i	k_{p1}	k_{pn}
30	0.98	0.38	0.47
40	2.68	0.90	1.14
50			2.85

[a] Polymerization conditions: $[MeOXZ]_0$ = 3.33 mol/l.; $[MeI]_0$ = 0.667 mol/l.

Table II
Activation Parameters of the MeOXZ Polymerization Initiated by MeI in CD_3CN^a

	MeOXZ	OXZ^b
k_i (40°) (l./(mol sec))	2.7×10^{-4}	1.6×10^{-4}
k_p (40°) (l./(mol sec))	1.14×10^{-4}	0.18×10^{-4}
ΔE^* (kcal/mol)	17.4	13.5
A (l./(mol sec))	1.7×10^8	5.0×10^4

[a] Polymerization conditions: $[MeOXZ]_0$ = 3.33 mol/l.; $[MeI]_0$ = 0.667 mol/l. [b] The data of the OXZ polymerization from ref 5.

tion initiated by **2**. The changes of concentrations of monomer, initiator (P_1^*), and propagating species (P_n^*, $n \geq 2$) were followed by the nmr spectra in the same manner as described in the previous section. The stoichiometry between the amount of the P_1^* consumption and the P_n^* production held during the polymerization.

The rate of polymerization by **2** is expressed by

$$-d[M]/dt = k_{p1}[P_1^*][M] + k_{pn}[M]\sum_{n=2}[P_n^*] \quad (11)$$

Since the decrease of $[P_1^*]$ was found by nmr to be equal to $\Sigma_{n=2}[P_n^*]$, *i.e.*, $\Sigma_{n=2}[P_n^*] = [P_1^*]_0 - [P_1^*]$, eq 11 becomes

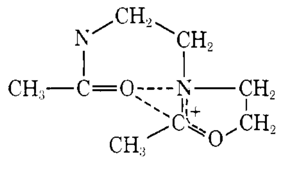
$$-d[M]/dt = (k_{p1} - k_{pn})[P_1^*][M] + k_{pn}[P_1^*]_0[M] \quad (12)$$

where $[P_1^*]_0$ is the initial feed concentration of **2**. The integrated form is

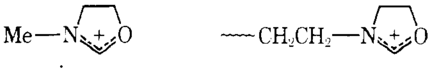
$$\frac{\ln [M]_0/[M]}{\int_0^t [P_1^*]dt} = (k_{p1} - k_{pn}) + k_{pn}\frac{[P_1^*]_0 t}{\int_0^t [P_1^*]dt} \quad (13)$$

The integrated value of $[P_1^*]$ in eq 13 was obtained by graphical integration on the $[P_1^*]$-time curve. The linear plot of eq 13 is shown in Figure 7, in which the slope corresponds to k_{pn} and the intercept is ($k_{p1} - k_{pn}$). The rate constants at 40° were $k_{p1} = 0.98 \times 10^{-4}$ and $k_{pn} = 1.20 \times 10^{-4}$ l./(mol sec). These values are in good agreement with the respective values obtained in the polymerization initiated by MeI.

The difference between the rate constants of the first propagation step and the subsequent steps has been observed also in the polymerization of MeOXZ initiated by methyl tosylate as previously reported.[4] This difference may be taken to suggest an interaction between the oxazolinium ring and the *N*-acetyl group of the penultimate unit in $[P_n^*]$ ($n \geq 2$).



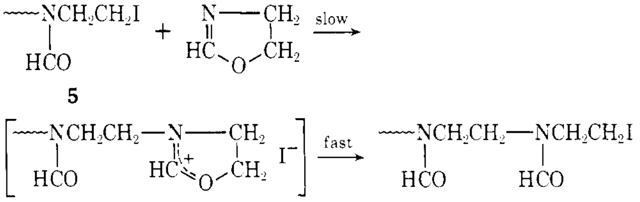
In addition, it may be attributable also to the difference of the inductive effect between iv and v on the oxazolinium ion character at the growing end.


iv v

Activation Parameters. By the same procedure, kinetic analysis was made for the MeOXZ polymerization initiated by MeI at varying temperatures. The rate constants are listed in Table I. From the linear Arrhenius plot of the propagation rate constant, k_{pn}, the activation parameters were successfully obtained. In Table II, the values of activation energy and frequency factor are compared with the corresponding values[5] of the polymerization of unsubstituted 2-oxazoline (OXZ) by the same initiator.

The initiation is a bimolecular process between MeI and monomer, where k_i is governed by the relative nucleophilic reactivity of monomer toward the common MeI electrophile. The larger k_i value of MeOXZ in comparison with that of OXZ may be taken to show the higher nucleophilicity of MeOXZ.

The propagation mechanism is definitely different between OXZ and MeOXZ. The higher value of k_p for MeOXZ is attributed to the higher frequency factor value. On the other hand, the activation energy for MeOXZ is much higher than that for OXZ. The rate determining steps of the propagations of these two monomers are different from each other. As previously reported,[5] the rate-determining step of propagation of the OXZ polymerization by MeI is the formation of the unstable oxazolinium iodide **6** from OXZ and covalent-bonded alkyl iodide **5**. The intermediate species of **6** rearranges quickly to the covalent species of **7**. In the MeOXZ polymerization by the same initiator, however, the ring-opening process of oxazolinium iodide by the nucleophilic attack of monomer (see eq 3) is the rate-determining step.



5
6
7

The difference in mechanism between these two polymerizations may be explained by assuming the order of the nucleophilic reactivity, MeOXZ > I^- > OXZ. In the polymerization system, there are two nucleophiles, iodide and the monomer. In the case of OXZ, the attack of the stronger nucleophile of iodide at the oxazolinium ring leads to the covalent-bonded species. In the case of MeOXZ, however, the nucleophilic attack of the monomer at the oxazolinium ring reproduces an oxazolinium ring. The higher nucleophilic reactivity of MeOXZ in comparison with OXZ has been shown by the higher value of k_i of MeOXZ in the reaction with the common MeI electrophile. In addition, a previous study by us has shown that MeOXZ is more reactive than OXZ in the reaction with the common 2-phenyloxazolinium tosylate electrophile.[6]

The ring-opening reactivity of 2-methyloxazolinium is lower than that of oxazolinium.[6] The lower ring-opening reactivity of 2-methyloxazolinium explains the nmr spectrum of the complete polymerization mixture (Figure 2) in which 2-methyloxazolinium iodide remained unchanged after all monomer was consumed.

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