# Isomerization Polymerization of 1,3-Oxazine. II.[1] Kinetic Studies of the Ring-Opening Isomerization Polymerization of Unsubstituted 5,6-Dihydro-4*H*-1,3-oxazine

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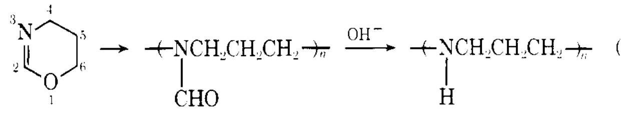
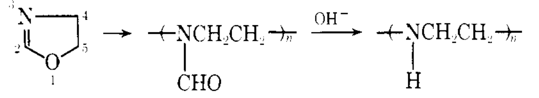
ABSTRACT: This paper deals with kinetic studies of the ring-opening isomerization polymerization of unsubstituted 5,6-dihydro-4*H*-1,3-oxazine (OZI), by means of high-resolution nmr spectroscopy. Initiators were methyl tosylate (MeOTs), methyl iodide (MeI), methyl methanesulfonate, methyl *o*- and *p*-nitrobenzenesulfonates, ethyl trifluoromethanesulfonate, and 2,4,6-trinitrophenetole. As polymerization solvents $CD_3CN$ was mainly employed; nitrobenzene also was used for the purpose of comparison. Kinetic analyses were carried out on the basis of the direct determination of the instantaneous concentrations of propagating species, monomer, and initiator. The polymerization of OZI was found to proceed *via* an oxazinium propagating species regardless of the initiator employed. The propagation rate constants ($k_p$) with the above initiators were in a narrow range of 1.9 to 5.8 × $10^{-5}$ l./(mol sec) at 35° in $CD_3CN$. The $k_p$ values did not change according to the reaction medium, in $CD_3CN$ or nitrobenzene. These findings were taken to suggest a propagation mechanism of free ion character with solvation. The initiation rate constants ($k_i$), however, changed according to the initiator and solvent. The reactivities of OZI were compared with those of a corresponding five-membered cyclic ether of 2-oxazoline (OZO). In the MeOTs-initiated polymerization, OZI was 43 times less reactive than OZO. This was due to a smaller frequency factor of OZI. The reactivity difference was explained by the steric hindrance in the transition states as well as by the solvation–desolvation phenomena in the course from the initial to the transition state. In the MeI-induced polymerization, OZI was 6.7 times more reactive than OZO, which was ascribed to a different mechanism of polymerization. Finally, the nucleophilic reactivity of OZI reflected by $k_i$ values was 12 times as high as that of OZO.

Recently we have reported the ring-opening isomerization polymerization of unsubstituted 5,6-dihydro-4*H*-1,3-oxazine (OZI)[1] and 2-oxazoline (OZO)[3] giving respectively poly(*N*-formyltrimethylenimine) and poly(*N*-formylethylenimine). Alkaline hydrolyses of the product polymers gave linear poly(trimethylenimine) (eq 1)[1] and poly(ethylenimine) (eq 2),[4] respectively.



(1)

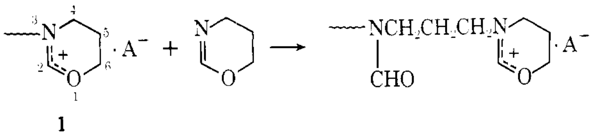
OZI



(2)

OZO

Furthermore, the kinetic study on the OZO polymerization has been successfully performed by us.[5] As to the mechanism of the OZI polymerization, we have proposed the following $S_N2$ reaction (eq 3) in which an oxazinium ion **1** is opened by a nucleophilic attack at its C-6 carbon atom by OZI.[1]



(3)

**1**

The present paper deals with kinetic studies on the ring-opening isomerization polymerization of OZI by a variety of initiators. Initiators were methyl tosylate (MeOTs), methyl iodide (MeI), *N*-methyl-*N*-(3-iodopropyl)formamide, methyl *o*- and *p*-nitrobenzenesulfonates (*o*- and *p*-$NO_2C_6H_4SO_3Me$), methyl methanesulfonate ($MeSO_3Me$), ethyl trifluoromethanesulfonate ($CF_3SO_3Et$), and 2,4,6-trinitrophenetole ($(NO_2)_3C_6H_2OEt$). Kinetic analyses were performed on the basis of the direct determination of the concentrations of monomer, propagating species, and polymer by means of nmr spectroscopy. Thus, the rate constants of propagation ($k_p$) and initiation ($k_i$) were determined for these initiators. It was also of great interest to compare the reactivities between unsubstituted six-membered (OZI) and five-membered (OZO) cyclic imino ethers.

## Experimental Section

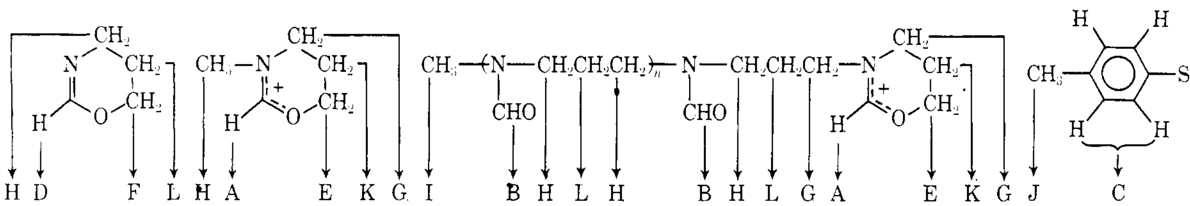
**Reagents.** OZI was prepared and purified as reported previously.[1] The purity of OZI was higher than 99.9% according to the gas chromatographic analysis. $CD_3CN$, a polymerization solvent, was a commercial reagent, which was dried on molecular sieves Linde 4A (Union Carbide) and distilled under nitrogen. Nitrobenzene, also a polymerization solvent, was dried with $P_2O_5$ and distilled *in vacuo* under nitrogen. This purification procedure was repeated twice. MeOTs, MeI, and $MeSO_3Me$ were commercial reagents, which were distilled under nitrogen before use. $CF_3SO_3Et$ was prepared by the reaction of $Et_2SO_4$ with $CF_3SO_3H$, bp 115° (lit.[6] bp 115°). *o*- and *p*-$NO_2C_6H_4SO_3Me$ were prepared by reactions of MeONa with *o*- and *p*-$NO_2C_6H_4SO_2Cl$ mp of the former, 60° (lit.[7] mp 60°) and of the latter, 92–93° (lit.[8] mp 90–91°). $(NO_2)_3C_6H_2OEt$ was obtained by reaction of picryl chloride with EtONa in ethanol according to Dyall,[9] mp 79–80° (lit.[10] mp 78°).

*N*-Methyl-*N*-(3-iodopropyl)formamide (**2**), $CH_3N(CHO)CH_2CH_2CH_2I$, was prepared by the following reaction. A mixture of OZI (75 mmol) and MeI (100 mmol) in 15 ml of $CH_3CN$ was allowed to react at 80° for 3 hr. Compound **2** was isolated in 43% yield by vacuum distillation, bp 88–90° (0.1 mm). Nmr spectrum of **2** (in $CCl_4$) shows two singlets at $\delta$ 8.00 and 7.94 (>NCHO, 1 H), two triplets at $\delta$ 3.47 and 3.43 (>$NCH_2$–, 2 H), a triplet at $\delta$ 3.18 (–$CH_2I$, 2 H), two singlets at $\delta$ 2.98 and 2.80 (>$NCH_3$, 3 H), and a quintet at $\delta$ 2.07 ($CCH_2C$, 2 H), which confirms the structure of **2**.

*Anal.* Calcd for $C_5H_{10}INO$: C, 26.45; H, 4.44; N, 6.17. Found: C, 26.73; H, 4.53; N, 6.01.

**Polymerization Procedures and Nmr Measurement.** The whole operations were carried out under nitrogen. A typical run of polymerization was as follows. Into a 2.0-ml measuring flask containing 1.0 ml of $CD_3CN$, 3.34 mmol of OZI and 0.80 mmol of MeOTs were introduced at room temperature. $CD_3CN$ was further added until the total volume reached to 2.00 ml. Then, a small portion of the solution mixture was transfered into an nmr sample tube. The tube was sealed. Until this moment, no polymerization was observed although the initiation somewhat took place. However, this does not interfere with the kinetic analysis for the determination of $k_p$. Then, the polymerization was allowed to start at 53°. The polymerization system was monitored by recording nmr spectra at several reaction times on Hitachi

### Table I
### Signal Assignments in the Polymerization of OZI by MeOTs in $CD_3CN$



| Signal | Chemical Shift[a] | Signal | Chemical Shift[a] |
|---|---|---|---|
| A | 8.62 (bs) | G | 3.56 (t) |
| B | 8.01 (bs) | H | 3.26 (t) |
| C | 7.39 (q) | I | 2.76, 2.88 (two s) |
| D | 6.93 (s) | J | 2.35 (s) |
| E | 4.53 (t) | K | 2.22 (m) |
| F | 4.12 (t) | L | 2.3 to 1.4 (m) |

[a] In ppm from $Me_4Si$. Multiplicity: bs = broad singlet, s = singlet, t = triplet, q = quartet, and m = multiplet.

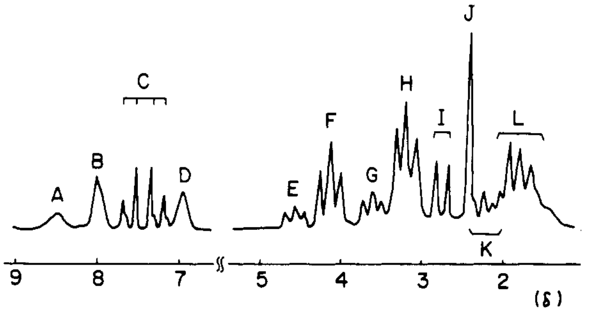


**Figure 1.** Nmr spectrum of the OZI polymerization by MeOTs in $CD_3CN$ (after 100 min at 53°), $[M]_0$ = 1.67 mol/l., $[I]_0$ = 0.40 mol/l.

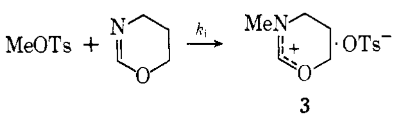
R-20B (60 MHz) nmr spectrometer. A typical example for the kinetic analysis of initiation is as follows. In a 2.0-ml measuring flask containing 1.0 ml of $CD_3CN$, 1.48 mmol of OZI and 1.06 mmol of MeOTs initiator were placed at 0°. $CD_3CN$ was further added to the mixture until its total volume became 2.00 ml. A small portion of the mixture was placed in an nmr sample tube. The tube was sealed. Then, the tube was inserted into the sample probe at 35°. The initiation reaction was taken to start at the insertion where the extent of the reaction was negligible. The experimental error of the nmr integration is within ±2%.

## Results and Discussion

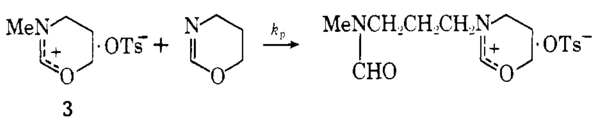
**Kinetics of the Polymerization of OZI by MeOTs. 1. Propagation in $CD_3CN$.** Figure 1 shows an example nmr spectrum of the polymerization system initiated by MeOTs in $CD_3CN$ taken at 100 min after the start of the reaction at 53°. The initial concentrations of monomer and initiator were 1.67 and 0.40 mol per 1., respectively. The concentrations of OZI and propagating species were successfully determined by the integration of respective peaks, since they appeared at different chemical shifts. As to the signals relevant to C-2 methine proton of OZI ring, three kinds of peaks, A, B, and D, appeared, which were respectively due to the C-2 methine proton of the propagating oxazinium ring at $\delta$ 8.62 (peak A), the *N*-formyl group of the product polymer units at $\delta$ 8.01 (peak B), and the C-2 proton of monomer itself at $\delta$ 6.93 (peak D). The instantaneous monomer concentration, [M], was calculated from its fraction among these species and the initial feed concentration of monomer, $[M]_0$. The instantaneous concentration of the propagating species, [P*], was calculated from the area of peak A. After the initiator was consumed in an early stage of polymerization at 53°, [P*] remained constant which was equal to the initial feed concentration of initiator, $[I]_0$, throughout the polymerization. Furthermore, [P*] could be determined by several peaks; *i.e.*, peak A, peak C at $\delta$ 7.39 (4 H, $A_2B_2$ type quartet) due to aromatic protons of tosylate anion, peak E at $\delta$ 4.53 (2 H, triplet) due to C-6 methylene protons of oxazinium ring, and peak J at $\delta$ 2.35 (3 H, singlet) due to methyl protons of tosylate anion. The stoichiometry of the integrated values of these signals was found to be valid during a kinetic run. In addition to the above mentioned signals several other peaks appeared in Figure 1. Their assignments are given in Table I.

Now, the kinetic analyses were carried out on the basis of the nmr spectroscopy. The following scheme of reactions will explain the course of the OZI polymerization initiated by MeOTs.

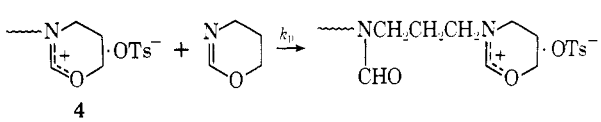
Initiation


(4)

Propagation


(5)

Generally


(6)

Then, kinetic equations for initiation and propagation are given as follows.

$$-(d[I]/dt) = k_i[I][M] \quad (7)$$

$$-(d[M]/dt) = k_i[I][M] + k_p[P^*][M] \quad (8)$$

where [I], [M], and [P*] denote, respectively, the concentrations of initiator, monomer, and propagating species (3 and 4).

Integration of eq 8 with respect to time from $t_1$ to $t_2$ gives

$$\ln \frac{[M]_{t_1}}{[M]_{t_2}} = k_i \int_{t_1}^{t_2} [I]dt + k_p \int_{t_1}^{t_2} [P^*]dt \quad (9)$$

where $t_1$ and $t_2$ are longer than the time required for the

**Table II**
**Rate Constants and Activation Parameters of OZI Polymerization by MeOTs Initiator**

| | Propagation[a] | | | Initiation[b] | |
|---|---|---|---|---|---|
| | In $CD_3CN$ | In Nitrobenzene | | In $CD_3CN$ | In Nitrobenzene |
| $k_p \times 10^4$ (l./(mol sec)) | 0.23 (35°)<br>0.83 (45°)<br>1.6 (53°)<br>3.4 (60°) | 1.7 (53°)<br>6.5 (65°) | $k_i \times 10^4$ (l./(mol sec)) | 9.0 (35°)<br>14.8 (45°)<br>18.2 (51°) | 2.9 (35°) |
| $\Delta E_p^*$ (kcal/mol) | 20 | | $\Delta E_i^*$ (kcal/mol) | 9.5 | |
| $A_p$ (l./(mol sec)) | $3.6 \times 10^9$ | | $A_i$ (l./(mol sec)) | $5.5 \times 10^3$ | |

[a] $[M]_0 = 1.67$ mol/l., $[I]_0 = 0.40$ mol/l. [b] $[M]_0 = 0.74$ mol/l., $[I]_0 = 0.53$ mol/l.

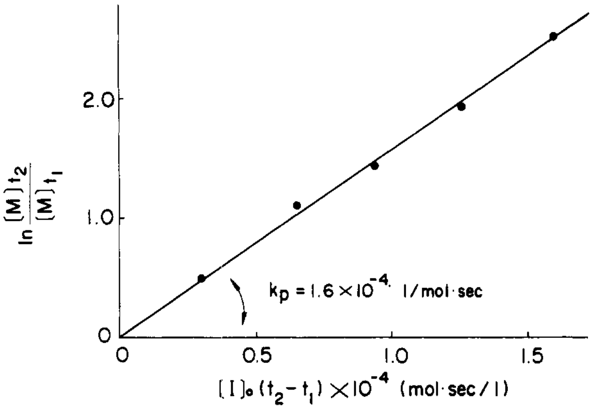


**Figure 2.** Plot of eq 10 in the polymerization of OZI by MeOTs in $CD_3CN$ at 53°, $t_1$ = 21 min.

complete consumption of MeOTs. After MeOTs was consumed completely

$$k_i \int_{t_1}^{t_2} [I]dt$$

was taken to be null. Furthermore, [P*] was found to be equal to the initial feed of initiator, $[P^*] = [I]_0$. Then, eq 9 becomes

$$\ln ([M]_{t_1}/[M]_{t_2}) = k_p[I]_0(t_2 - t_1) \qquad (10)$$

A linear plot of eq 10 is shown in Figure 2. The slope of the straight line gives a $k_p$ value of $1.6 \times 10^{-4}$ l./(mol sec) at 53°. The $k_p$ values were determined at several other temperatures by a similar procedure. Arrhenius plot of $k_p$ values is linear (Figure 3) and activation parameters were calculated (Table II).

In order to examine the relationship between the polymer molecular weight and the initiator concentration, the polymerization system of Figure 1 was allowed to react further at 53° for a sufficient long time of 20 hr until the monomer was completely polymerized. On the basis of the peak assignment described above, the amounts of the polymer repeating units and the propagating species were calculated, respectively, from peak B and peak A, to give the degree of polymerization ($\bar{P}_n$) of 4.2. This value coincides well with the feed molar ratio of monomer/initiator = 4.2. Furthermore, a polymer sample was prepared by the polymerization of the ten times larger scale than that of nmr kinetics, at 53° for 20 hr. Its molecular weight was obtained as 570 by vapor pressure osmometry,[1] which was very close to the calculated value of 543 for $\bar{P}_n$ of 4.2. This result agrees to our previous observations[1] that in all cases of initiators examined, $\bar{P}_n$ was roughly represented as

$$\bar{P}_n = \frac{\text{monomer moles}}{\text{initiator moles}} \times \frac{\text{conversion (\%)}}{100}$$

These findings are taken to support the view that every

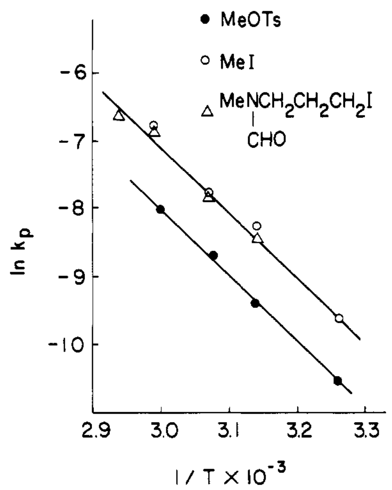


**Figure 3.** Arrehnius plots of $k_p$ values by three initiators.

molecule of MeOTs initiates the polymerization and the all propagating species continue to grow throughout the polymerization, which is quite compatible with the present kinetic results.

**2. Initiation in $CD_3CN$.** As described above, the initiation reaction was very fast under the polymerization conditions. In order to obtain more reliable data, kinetics of initiation was studied separately in an equimolar reaction of eq 4. In the aromatic proton region (δ 7–8) of the nmr spectrum of the reaction mixture there appeared two $A_2B_2$-type quartets centered at δ 7.62 (peak B) and 7.39 (peak C) as shown in Figure 4. They are assigned to aromatic protons of MeOTs and of tosylate anion, respectively. From the relative intensity of these two quartets the concentration of MeOTs was determined. In an alternative way, the instantaneous initiator concentration was calculated from the relative peak area of a sharp singlet at δ 3.70 (peak G) and a triplet at δ 4.53 (peak E). Peak G is assigned to *p*-tolyl methyl protons (3 H) of MeOTs and peak E is due to the C-6 methylene protons (2 H) of the oxazinium ring. Both ways of determination of the initiator concentration gave identical values. The concentration of monomer was calculated from the relative integration value of the C-2 methine proton of monomer at δ 6.93 (peak D) and of oxazinium ring proton peak at δ 8.62 (peak A). During kinetic runs no polymer production was observed. This shows that the reaction of eq 4 took place exclusively.

The rate equation of initiation is given (eq 11) by integration of eq 7 with respect to time

$$\ln \frac{[I]_0}{[I]_t} = k_i \int_0^t [M]dt \qquad (11)$$

In all cases plots of eq 11 were linear. An example is shown in Figure 5. Thus, $k_i$ values were determined at

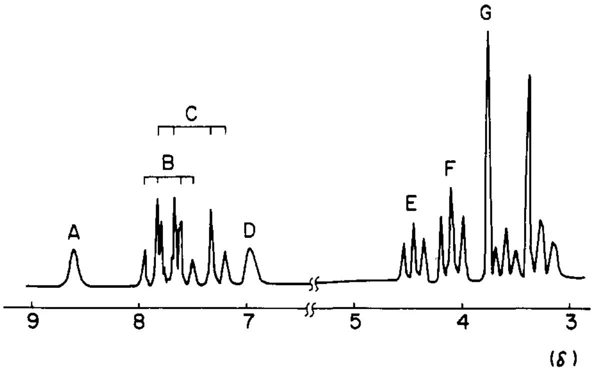


**Figure 4.** Nmr spectrum of the molar reaction of OZI with MeOTs in $CD_3CN$ (after 32 min at 35°), $[M]_0$ = 0.74 mol/l., $[I]_0$ = 0.53 mol/l.

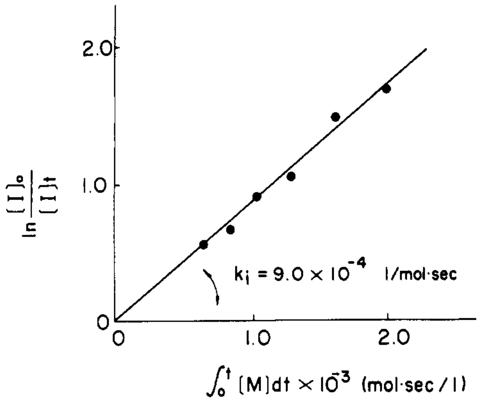


**Figure 5.** A linear plot of eq 11 in the molar reaction of OZI with MeOTs in $CD_3CN$ at 35 °.

three temperatures. Activation parameters for $k_i$ were also calculated. These data are listed in Table II.

**3. Propagation in Nitrobenzene.** The kinetic analyses of the MeOTs-initiated polymerization of OZI were attempted in a polymerization solvent of nitrobenzene. Figure 6 shows an nmr spectrum of the polymerization system by MeOTs initiator in nitrobenzene at the reaction time of 92 min at 53°. $[P^*]$ was determined from the integration value of the triplet peak A at δ 4.92 due to C-6 methylene portons (2 H) of the propagating oxazinium ring because the peak region of C-2 methine proton of OZI is overlapping with aromatic proton peaks of nitrobenzene solvent. After the complete consumption of the initiator, $[P^*]$ was found to be equal to the initial concentration of the initiator, $[MeOTs]_0$.

For the determination of the instantaneous monomer concentration the triplet signal B was used. Peak B at δ 4.17 due to C-6 methylene protons of the unreacted monomer overlapped with the signals due to two kinds of methylene protons (total 4 H) adjacent to nitrogen atom of the oxazinium in nitrobenzene solvent. The peak area of one of them, *e.g.*, the C-4 methylene protons of the oxazinium ring, should be equal to that of peak A (2 H). The peak area of the other (2 H), *e.g.*, the open-chain α-methylene protons of the oxazinium nitrogen atom, was estimated from that of signal E (3 H) at δ 3.06 due to the terminal *N*-methyl protons. Thus, the instantaneous concentration of monomer $[M]_{t_2}$ was obtained from the following relationship of the peak integration

$$[M]_{t_2} = [M]_{t_1} \frac{\{B - A - (2/3)E\}_{t_2}}{\{B - A - (2/3)E\}_{t_1}}$$

where *B*, *A*, and *E* represent the integrated values of peaks B, A, and E at time $t_1$ and $t_2$, respectively. Since the integrated value of peak A was strictly constant during the kinetic run, the relationship above was found to be valid for the determination of $[M]_{t_2}$.

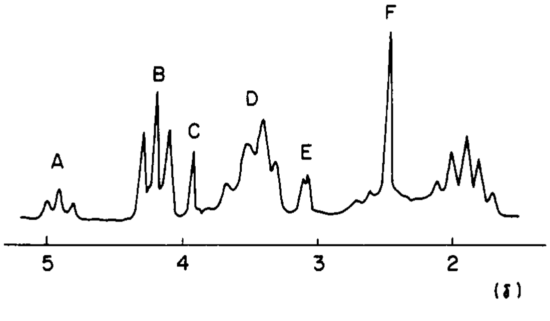


**Figure 6.** Nmr spectrum of the OZI polymerization by MeOTs in nitrobenzene (after 92 min at 53°), $[M]_0$ = 1.67 mol/l., $[I]_0$ = 0.40 mol/l.

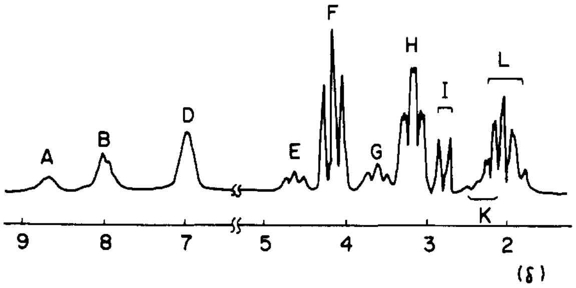


**Figure 7.** Nmr spectrum of the OZI polymerization by MeI in $CD_3CN$ (after 60 min at 53°), $[M]_0$ = 1.67 mol/l., $[I]_0$ = 0.40 mol/l.

The kinetic analysis was carried out on the basis of eq 10. A linear relationship was observed in plotting eq 10 and a $k_p$ value of 1.7 × $10^{-4}$ l./(mol sec) at 53° was obtained. Similarly, kinetics was run at 65°. These kp values are also included in Table II.

**4. Initiation in Nitrobenzene.** In the initiation of an equimolar reaction at 35°, no polymer production was observed, *i.e.*, the reaction of eq 4 exclusively took place. Therefore, the corresponding peaks A, D, and F of Figure 6 appeared as single peaks. Peaks A (a triplet at δ 4.92), D (a triplet like at δ 3.40), and F (a sharp singlet at δ 2.43) were assigned respectively to C-6 methylene protons (2 H) of the oxazinium, to C-4 methylene protons (2 H) of the unreacted monomer, and to *p*-tolyl methyl protons (3 H) of tosylate anion and MeOTs. The instantaneous monomer concentration was obtained from the relationship

$$[M] = [M]_0 \left\{ \frac{D}{A + D} \right\}$$

where *A* and *D* represent the integration values of peaks A and D, respectively. The instantaneous MeOTs concentration was calculated from the relationship

$$[MeOTs] = [MeOTs]_0 \left\{ \frac{F - (3/2)A}{F} \right\}$$

where *A* and *F* are the integration values of peaks A and F.

The kinetic analysis was made on the basis of eq 11. Then, the $k_i$ value was obtained as 2.9 × $10^{-4}$ l./(mol sec) at 35° in nitrobenzene. This is also given in Table II.

**Kinetics of the Polymerization of OZI by MeI and *N*-Methyl-*N*-(3-iodopropyl)formamide Initiators in $CD_3CN$. 1. Propagation.** Figure 7 shows an nmr spectrum of the polymerization system of OZI by MeI at a

**Table III**
**Rate Constants and Activation Parameters of OZI Polymerization Initiated by MeI and 2 in $CD_3CN$**

| | Propagation[a] | | Initiation[b] | |
|---|---|---|---|---|
| | MeI | $CH_3N(CHO)CH_2CH_2CH_2I$ (**2**) | | MeI |
| $k_p \times 10^4$ (l./(mol sec) | 0.58 (35°) | | $k_i \times 10^4$ (l./(mol sec)) | 6.1 (23°) |
| | 2.7 (45°) | 2.4 (45°) | | 12.1 (35°) |
| | 3.9 (53°) | 4.2 (53°) | | 20.6 (43°) |
| | 11.1 (61°) | 10.4 (61°) | | |
| | | 14.8 (67°) | | |
| $\Delta E_p$* (kcal/mol) | 20 | 20 | $\Delta E_i$* (kcal/mol) | 12 |
| $A_p$ (l./(mol sec)) | $1.0 \times 10^{10}$ | $1.0 \times 10^{10}$ | $A_i$ (l./(mol sec)) | $3.6 \times 10^5$ |

[a] $[M]_0 = 1.67$ mol/l., $[I]_0 = 0.40$ mol/l. [b] $[M]_0 = 0.74$ mol/l., $[I]_0 = 0.53$ mol/l.

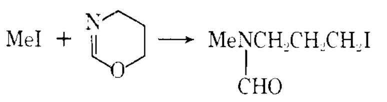
**Table IV**
**Rate Constants of OZI Polymerization by Various Initiators in $CD_3CN$ at 35°**

| Initiator | $k_p \times 10^5$[a] (l./(mol sec) | $k_i \times 10^4$ (l./(mol sec)) |
|---|---|---|
| MeOTs | 2.3 | 9.0[b] |
| MeI | 5.8 | 12.1[b] |
| $MeSO_3Me$ | 2.8 | 2.8[a,c] |
| $CF_3SO_3Et$ | 2.9 | Very fast |
| o-$NO_2C_6H_4SO_3Me$ | 1.9 | |
| p-$NO_2C_6H_4SO_3Me$ | 2.7 | |
| $(NO_3)_3C_6H_2OEt$ | 4.5[d] | 0.20[a,c,d] |

[a] $[M]_0 = 1.67$ mol/l., $[I]_0 = 0.40$ mol/l. [b] $[M]_0 = 0.74$ mol/l., $[I]_0 = 0.53$ mol/l. [c] Obtained in the polymerization kinetic run. [d] Extrapolated value from the data at 52 and 61°.

reaction time of 60 min at 53°. The spectrum is almost the same as that of OZI–MeOTs system (Figure 1) except for the signals due to p-tolyl group. Signal assignments of peaks A–L in Figure 7 are corresponding to those of respective peaks as given in Table I, although chemical shifts are not always identical. It is shown by the presence of peaks A (δ 8.70) and E (δ 4.61) that the propagating species are oxazinium ions. The initiator of MeI was consumed very rapidly. After the consumption of MeI, [P*] was constant and equal to the initial concentration of MeI. Therefore, the rate eq 10 was applied. The $k_p$ values thus obtained at four temperatures are given in Table III.

N-Methyl-N-(3-iodopropyl)formamide (2) was prepared from MeI and OZI (eq 12), which was isolated by distillation.



2 (12)

Kinetics of the OZI polymerization by 2 was carried out at four temperatures. Propagation of OZI proceeded via oxazinium iodide species. The $k_p$ values of 2 initiator agreed with those of MeI initiator within experimental errors (Table III). In both systems of MeI and 2 initiators, Arrhenius plots gave the same straight line (Figure 3) from which activation parameters were calculated (Table III).

2. **Initiation.** As in the case of MeOTs initiator $k_i$ values were obtained at lower temperatures than in the reaction of MeI with OZI. Arrhenius plot was linear and activation parameters were calculated (Table III).

**Kinetics of the Polymerization of OZI by Other Initiators.** Kinetic studies with the other initiator systems were further carried out. Four initiators of sulfonate esters of $MeSO_3Me$, o-$NO_2C_6H_4SO_3Me$, p-$NO_2C_6H_4SO_3Me$, and $CF_3SO_3Et$ were used for kinetic runs of OZI at 35°. The $k_p$ values were determined in similar kinetic analyses to those of MeOTs initiator. The $k_i$ value of $MeSO_3Me$ initiator was obtained in the polymerization kinetic run, since the initiation rate was fairly slow. Among the other three initiators, the initiation by $CF_3SO_3Et$ was very fast. These data are given in Table IV.

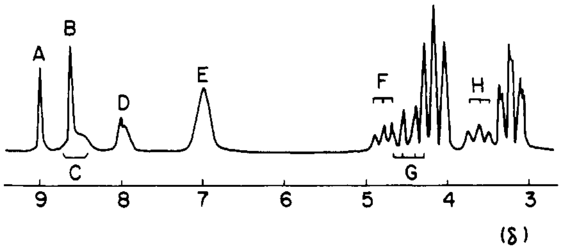
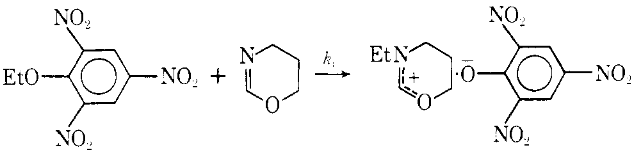


**Figure 8.** Nmr spectrum of the OZI polymerization by 2,4,6-trinitrophenetole in $CD_3CN$ (after 60 min at 61°), $[M]_0 = 1.67$ mol/l., $[I]_0 = 0.40$ mol/l.

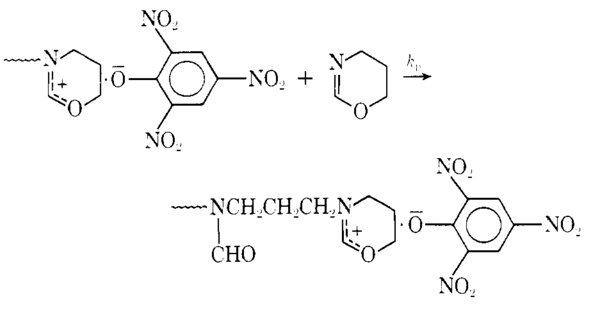
Kinetic runs with $(NO_2)_3C_6H_2OEt$ were carried out at higher temperatures of 52 and 61°, since the initiation process was very slow at 35°. Therefore, it was possible to determine both the $k_p$ and $k_i$ values in the same kinetic run. Figure 8 shows an nmr spectra of the OZI polymerization system at the reaction time of 60 min at 61°, in which $[M]_0$ and $[I]_0$ were 1.67 and 0.40 mol per l. The course of the polymerization is formulated as follows

Initiation



5 (13)

Propagation



(14)

Sharp singlets of peaks A at δ 8.92 and B at δ 8.62 are assigned respectively to aromatic protons of $(NO_2)_3C_6H_2OEt$ and of 2,4,6-trinitrophenoxide anion. Among peaks C, D, and E relevant to C-2 methine proton, peak C at δ 8.60 due to the oxazinium ring is overlapping with peak B. Peaks D and E are ascribed to N-formyl proton of polymer and C-2 methine proton of OZI, respectively. Signals of C-4 methylene protons and of the open-chain α-methylene protons of the oxazinium appeared as a triplet

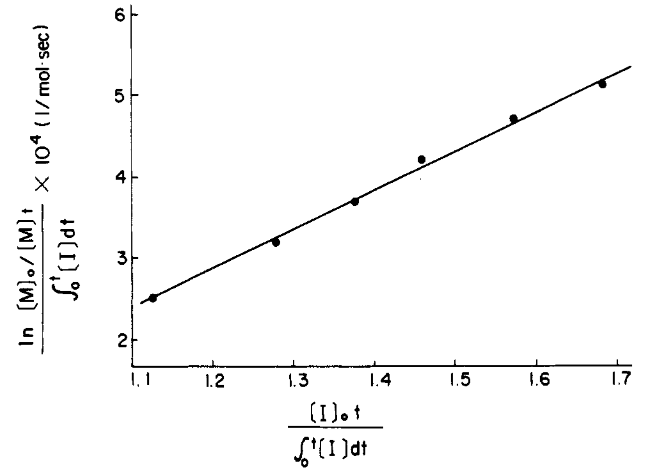


**Figure 9.** A linear plot of eq 18 in the OZI polymerization by 2,4,6-trinitrophenetole in $CD_3CN$ at 61°.

(peak H) at $\delta$ 3.70. Thus, [P*] was determined from the peak area of peaks B plus C. In addition to these peaks, a triplet (peak F) at $\delta$ 4.65 and a quartet (peak G) appeared with partly overlapping. They are assigned respectively to C-6 methylene protons of oxazinium ions and methylene protons of ethoxy group of the initiator.

The consumption of OZI is given by eq 8. Since [P*] was found by nmr to be equal to the decrease of the concentration of $(NO_2)_3C_6H_2OEt_7$.

$$[P^*] = [I]_0 - [I] \tag{15}$$

Therefore, eq 8 becomes

$$-(d[M]/dt) = (k_i - k_p)[I][M] + k_p[I]_0[M] \tag{16}$$

Integration of eq 16 gives

$$\ln\frac{[M]_0}{[M]} = (k_i - k_p)\int_0^t [I]dt + k_p[I]_0 t \tag{17}$$

hence

$$\frac{\ln\dfrac{[M]_0}{[M]_t}}{\displaystyle\int_0^t [I]dt} = (k_i - k_p) + k_p\frac{[I]_0 t}{\displaystyle\int_0^t [I]dt} \tag{18}$$

The value of [I]d$t$ (from 0 to $t$) was obtained by graphical integration on the [I]–time curve. Figure 9 shows a linear plot of eq 18 whose slope gave a $k_p$ value of 4.6 × $10^{-4}$ l./(mol sec) at 61°. A similar kinetic run was carried out at another temperature. Another $k_p$ value obtained was 1.9 × $10^{-4}$ l./(mol sec) at 52°.

For the determination of $k_i$ eq 11 was adopted. Plots of eq 11 are shown in Figure 10. A $k_i$ value was calculated from the slope to be $k_i$ = 1.5 × $10^{-4}$ l./(mol sec) at 61°. At 52°, a $k_i$ value was 0.73 × $10^{-4}$ l./(mol sec). In Table IV rate constants of OZI polymerization at 35° in $CD_3CN$ are summarized.

**Reaction Mechanism of the OZI Polymerization.** All the above findings support that the polymerization of OZI proceeds *via* an $S_N2$ mechanism between oxazinium propagating species 1 and monomer (eq 3). The propagating species was in all cases an oxazinium ion 1 regardless of the initiator employed. The $k_p$ values by several initiators (Table IV) lie in a range of 1.9 to 5.8 × $10^{-5}$ l./(mol sec) at 35° in $CD_3CN$, *i.e.*, the nature of the counteranion, $A^-$, affects very little the $k_p$ value. This suggests that the propagation process of eq 3 is of free ion character of the oxazinium propagating species in $CD_3CN$ solvent. Coincidentally, $k_p$ values in nitrobenzene solvent were not different from those in $CD_3CN$. The initiation, however, was about three times slower in nitrobenzene than in $CD_3CN$ (Table II). In addition, examination of activation parameters (Tables II and III) supports the idea that both the MeOTs- and MeI-initiated polymerizations proceed by a similar mechanism since activation parameters ($\Delta E_p^*$ = 20 kcal/mol, $A_p$ = $10^9$–$10^{10}$ l./(mol sec)) are very close in both systems.

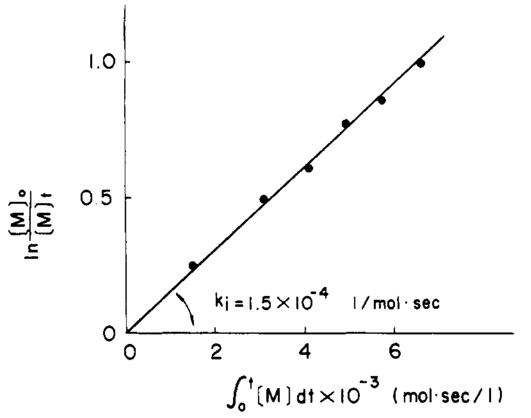
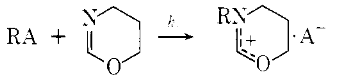


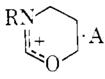
**Figure 10.** A linear plot of eq 11 in the OZI polymerization by 2,4,6-trinitrophenetole in $CD_3CN$ at 61°.

On the other hand the $k_i$ values of several initiators (Table IV) differ very much depending upon the initiator employed, since the initiation is a dipole-dipole $S_N2$ reaction between initiator and monomer (eq 19). Thus, the $k_i$



(19)

value of the initiator, RA, indicates an electrophilic reactivity of RA toward a base of OZI. Among the initiators examined, the initiation of $CF_3SO_3Et$ was so fast that the $k_i$ value could not be determined by nmr. This is not surprising since it has been already known that the same type of sulfonate, ethyl fluorosulfate ($FSO_3Et$), is about $10^5$ times more reactive than ethyl tosylate in the Menschutkin reaction of alkyl halide alkylation of triethylamine base.[11] In the polymerization systems by MeI or sulfonate esters the initiation process was much faster than the propagation (Table IV). Therefore, in these systems the first propagation species 6 was detected at the beginning of polymerization. In the system of $(NO_2)_3C_6H_2OEt$ initiator, however, the propagation was faster than the initiation (Table IV), and hence the first propagating species 5 was not detected during the kinetic run.



6. R = Me, Et

**Comparison of the Reactivities of OZI and OZO.** It seems to be of great interest to compare the reactivities of unsubstituted six- and five-membered cyclic imino ethers, OZI and OZO, respectively. For such purpose, Table V summarizes the rate constants and activation parameters in the polymerizations of OZI and OZO initiated by MeOTs and MeI.

In the MeOTs-initiated polymerization OZI is 43 times less reactive than OZO in comparison with $k_p$ values at 40° in $CD_3CN$ (Table V). It has been already established that OZO also propagates *via* oxazolinium propagating species in the MeOTs-initiated system.[5] Comparing the activation parameters of OZI and of OZO the reactivity

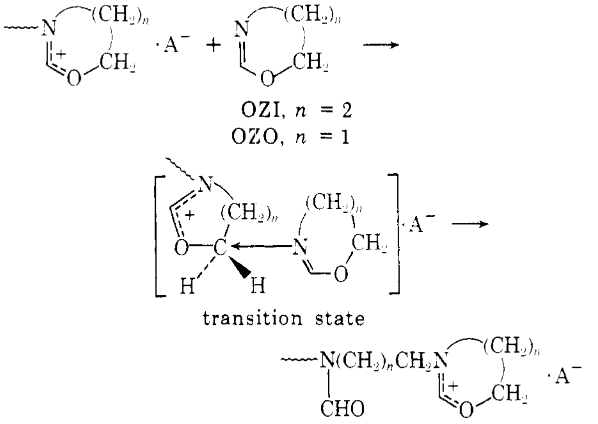
**Table V**
**Comparison of the Reactivities and Activation Parameters in the Polymerizations of OZI and OZO by MeOTs and MeI Initiators in $CD_3CN$**

| | OZI[a] | | OZO[b] | |
|---|---|---|---|---|
| | MeOTs | MeI | MeOTs | MeI |
| $k_p \times 10^{4c}$ (l./(mol sec)) | 0.44[d] | 1.2[d] | 19 | 0.18 |
| $\Delta E_p^*$ (kcal/mol) | 20 | 20 | 25 | 13.5 |
| $A_p$ (l./mol sec)) | $3.6 \times 10^9$ | $1.0 \times 10^{10}$ | $7.5 \times 10^{14}$ | $5.0 \times 10^4$ |
| $k_i \times 10^{4c}$ (l./(mol sec)) | 11.8[d] | 17.5[d] | 0.98 | 1.6 |
| $\Delta E_i^*$ (kcal/mol) | 9.5 | 12 | | |
| $A_i$ (l./(mol sec)) | $5.5 \times 10^3$ | $3.6 \times 10^5$ | | |

[a] Present work. [b] Taken from ref 5. [c] Data at 40°. [d] Calculated values at 40° from the data in Tables II and III.

difference is ascribed to the frequency factor, $A_p$, but not to the activation energy, $\Delta E_p^*$, *i.e.*, the lower reactivity of OZI is due to the lower $A_p$ value ($3.6 \times 10^9$ l./(mol sec)) although the $\Delta E_p^*$ value of OZI is lower (more favorable) by 5 kcal/mol than that of OZO.

As we have pointed out in our studies on the ring-opening polymerization of cyclic ethers,[12] polymerization reactivity of cyclic monomers is governed by two factors, *e.g.*, the ring-opening reactivity of the propagating cyclic onium species and the nucleophilic reactivity of monomer. Since OZI is 11–12 times more reactive in nucleophilicity than OZO as shown by $k$ values (*vide infra*), the lower $k_i$ value of OZI must be ascribed to the lower reactivity of the propagating oxazinium ion. The following explanations may give a plausible interpretation. The transition state of OZI or OZO propagation may be formulated as a nucleophilic attack of monomer onto the C-6 or C-5 carbon atom of the oxazinium or the oxazolinium (eq 20).



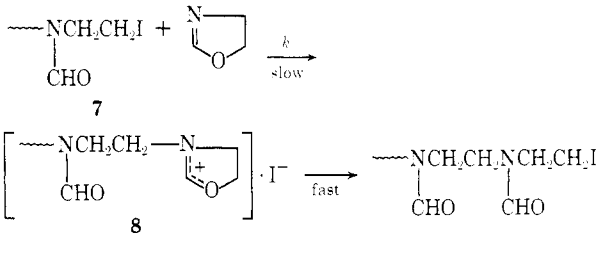
(20)

The structure of the propagating species of OZI is not a planar one, *i.e.*, the C-5 carbon atom is flipped out of the ring plane on which the other five atoms lie (Figure 11A). On the other hand, the five-membered cyclic onium of the propagating species of OZO is planar as shown in Figure 11B. Thus, the Newman projection reveals the difference of conformations in the transition state of the OZI and OZO polymerizations as shown in the bottom of A and B (Figure 11). The structure of the propagating species of the former is a staggered conformation whereas that of the latter is a eclipsed conformation. When monomer OZI (nucleophile) attacks the C-6 carbon atom of the oxazinium (electrophile), monomer suffers steric hindrance due to the eclipsed hydrogen attached to the C-5 carbon atom as seen in the Newman projection. In the case of OZO, however, such a steric hindrance is not present, since the vicinal hydrogen at the C-4 carbon stands gauche to the attacking monomer (nucleophile). This may be one of the reasons that the reactivity of the propagating oxazolinium is much enhanced.

As described above, the polymerization of OZI proceeds in free ion character. Therefore, the propagating species must be much solvated[13] since the solvent $CD_3CN$ is a typical dipolar solvent. In the initial state, the solvation should be more profound for a rigid planar oxazolinium than for a nonplanar larger molecule of oxazinium. In the transition state, however, the solvation decreases to a great extent in both cases, because the positive charge is dispersed in the transition state. This probably explains the higher activation energy ($\Delta E_p^* = 25$ kcal/mol) for desolvation in the OZO polymerization than that ($\Delta E_p^* = 20$ kcal/mol) in the OZI polymerization. Going from the initial state to the transition state, OZO suffers desolvation to the greater extent, which means the greater entropy gain (more favorable for $k_p$) of the OZO polymerization. This desolvation (entropy or frequency factor) seems to play the most important role to determine the $k_p$ values in the polymerizations of OZI and OZO.

In the MeI-initiated polymerization, the reactivity of OZI is higher than that of OZO; OZI being 6.7 times more reactive than OZO as reflected by $k_p$ values at 40° in $CD_3CN$ (Table V). The present result provides an interesting example that a six-membered cyclic monomer is polymerized faster than a five-membered one as in the case of the polymerization of lactones.[14] The reactivity difference is due to the difference of mechanism between the OZI and OZO polymerizations.[5] Among the initiators examined the largest $k_p$ value was obtained by MeI initiator. The iodide counteranion ($A^- = I^-$ in eq 3) is the most favorable for the OZI polymerization rate.

In the OZO case, it has been established already that the propagation species of the OZO polymerization is a covalent alkyl iodide species 7.[5] The rate-determining step is a formation of oxazolinium iodide 8 which is followed by the fast nucleophilic attack of the counteranion to produce a covalent alkyl iodide as shown in eq 21. The oxazolinium salt formation from alkyl iodide with OZO resembles the Menschutkin reaction between alkyl halide and tertiary amine producing the corresponding ammonium salt (eq 22). The mechanism of eq 21 was further supported by a close resemblance of activation parameters between the MeI-initiated polymerization ($\Delta E_p^* = 13.5$ kcal/mol, $A_p = 5.0 \times 10^4$ l./(mol sec)) and a Menschutkin reaction.[5]



(21)

$$R_3N + RX \longrightarrow R_4N^+X^- \qquad (22)$$

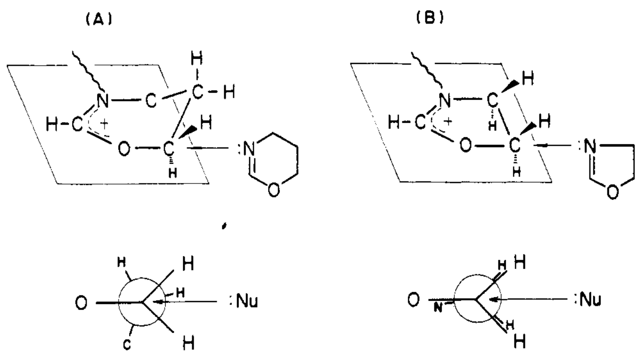


**Figure 11.** Schematic views of the transition state in the polymerization of (A) OZI and of (B) OZO. The bottoms show the Newman projections of (A) the C-6 carbon atom of the oxazinium and of (B) the C-5 carbon atom of the oxazolinium.

When $k_i$ values are compared OZI is more reactive than OZO (Table V), *i.e.*, the $k_i$ value of OZI is about 12 times larger than that of OZO for both MeOTs and MeI initiators. The initiation (eq 19) is similar to the Menschutkin reaction (eq 22) in terms of the onium formation by a dipole-dipole reaction. A specific feature of the Menschutkin reaction of low $\Delta E^*$ and $A$ values is clearly observed also in the initiations of OZI by MeOTs and by MeI (Table V).

## References and Notes

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# Isomerization Polymerization of 1,3-Oxazine. III.[1] Kinetic Studies on the Ring-Opening Polymerization of 2-Phenyl-5,6-dihydro-4*H*-1,3-oxazine by Methyl Tosylate and Methyl Iodide Initiators

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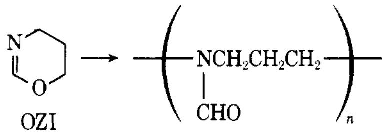
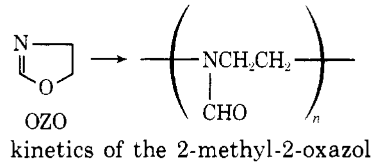
ABSTRACT: Kinetics of the isomerization polymerization of 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (PhOZI) by methyl tosylate (MeOTs) and methyl iodide (MeI) initiators in nitrobenzene were carried out on the basis of the direct determination of the instantaneous concentrations of monomer, initiator, and the propagating species by using nmr spectroscopy. The mechanisms of the two polymerizations by MeOTs and by MeI were different from each other. The MeOTs-initiated polymerization proceeded *via* the propagating species of oxazinium tosylate **1** which is opened by the nucleophilic attack of PhOZI (eq 8). The MeI-initiated polymerization, on the other hand, involved convalent-bonded alkyl iodide **2** as propagating species in the polymerization conditions, *e.g.*, reaction temperatures above 100°, in which **2** was identified and quantified directly by nmr spectroscopy (eq 14). Rate constants ($k_p$) and activation parameters of propagation were determined. Kinetic data were quite compatible with two different mechanisms. Rate constants of initiation ($k_i$) were determined separately. In the initiation reaction of PhOZI with MeI at a lower temperature of 35°, however, both species of alkyl iodide **5** and oxazinium iodide **6** were simultaneously formed (eq 12).

We have recently reported the kinetic studies on the polymerization of unsubstituted six- and five-membered cyclic imino ethers, 5,6-dihydro-4*H*-1,3-oxazine (OZI)[1,3] and 2-oxazoline (OZO),[4] respectively, by using nmr spectroscopy.

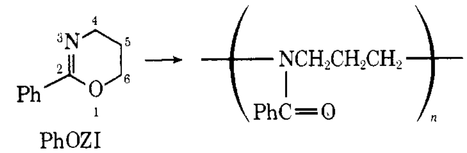


(1)



(2)

In addition, kinetics of the 2-methyl-2-oxazoline polymerization has successfully been carried out to see the effect of the 2-methyl substituent of OZO ring on the polymerization reactivities.[5] The present study deals with the kinetics of the polymerization of 2-phenyl-5,6-dihydro-4*H*-1,3-oxazine (PhOZI) initiated by methyl tosylate (MeOTs) and methyl iodide (MeI) in nitrobenzene, in which the effect of the 2-phenyl group on the reaction rate and mechanism of polymerization were examined. The progress of polymerization was monitored by using nmr spectroscopy.



(3)

Before the present study, the polymerization of PhOZI had been carried out by Levy and Litt[6] with dimethyl sul-