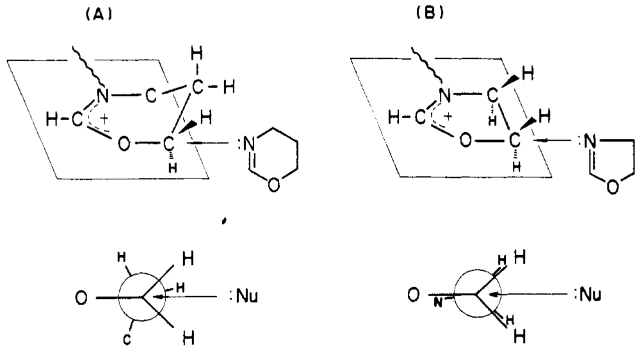


Figure 11. Schematic views of the transition state in the polymerization of (A) OZI and of (B) OZO. The bottoms show the Newman projections of (A) the C-6 carbon atom of the oxazinium and of (B) the C-5 carbon atom of the oxazolinium.

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 ΔE^* and A values is clearly observed also in the initiations of OZI by MeOTs and by MeI (Table V).

References and Notes

(1) For Part I, see T. Saegusa, Y. Nagura, and S. Kobayashi, *Macromolecules*, **6**, 495 (1973).
(2) Research Laboratory, Central Glass Co., Ltd., Kawagoe, Saitama, Japan.
(3) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, **3**, 35 (1972).
(4) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 108 (1972).
(5) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **6**, 315 (1973).
(6) T. Gramstad and R. N. Haszeldine, *J. Chem. Soc.*, 173 (1956).
(7) A. I. Kiprianov and A. I. Tolmachev, *Zh. Obshch. Khim.*, **29**, 2868 (1959).
(8) R. Kuhn and H. W. Ruelius, *Chem. Ber.*, **83**, 420 (1950).
(9) L. K. Dyall, *J. Chem. Soc.*, 5160 (1960).
(10) R. Foster and R. K. Mackie, *J. Chem. Soc.*, 3796 (1963).
(11) M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Commun.*, 1533 (1968).
(12) T. Saegusa, Y. Kimura, H. Fujii, and S. Kobayashi, *Macromolecules*, **6**, 657 (1973).
(13) T. Kagiya, T. Matsuda, and R. Hirata, *J. Macromol. Sci. Chem.*, **6**, 451 (1972).
(14) R. D. Lundberg and E. F. Cox in "Ring-Opening Polymerization," K. C. Frisch and S. L. Reegen, Ed., Marcel Dekker, Inc., New York, N. Y., 1969, Chapter 6.

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

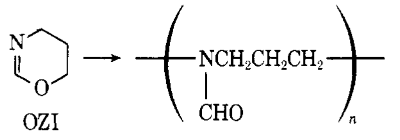
Takeo Saegusa,*,[2] Shiro Kobayashi, and Yoshitomi Nagura

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan.

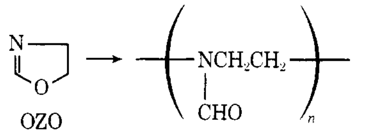
Received December 31, 1973

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.

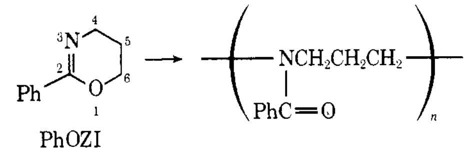


OZI (1)



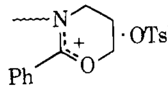
OZO (2)

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.

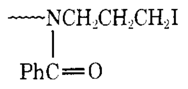


PhOZI (3)

Before the present study, the polymerization of PhOZI had been carried out by Levy and Litt[6] with dimethyl sulfate initiator. However, no kinetic study on the PhOZI polymerization has been made so far. Here it was found that the polymerization proceeded *via* an oxazinium propagating species **1** by MeOTs initiator, whereas *via* covalent alkyl iodide propagating species **2** by MeI initiator. Introduction of phenyl group at the 2 position of OZI decreased remarkably the reactivities of both initiation and propagation reactions in comparison with the case of the unsubstituted monomer.



1



$$\begin{array}{l}\sim\!\!\sim\mathrm{NCH_2CH_2CH_2I}\\ \quad|\\ \mathrm{PhC{=}O}\end{array}$$

2

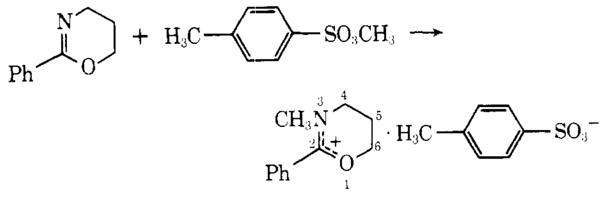
Experimental Section

Reagents. 2-Phenyl-5,6-dihydro-4*H*-1,3-oxazine (PhOZI) was prepared by cyclodehydration of *N*-(3-hydroxypropyl)benzamide with concentrated H_2SO_4 according to the literature method:[6] bp 80° (0.2 mm) (lit.[6] bp 80-81° (0.2 mm)); nmr ($CDCl_3$) δ 8.1-7.1 (m, 5 H, C_6H_5-), 4.10 (t, 2 H, -OCH_2), 3.43 (t, 2 H, -NCH_2), 1.70 (q, 2 H, -CCH_2C-). MeOTs and MeI were commercial reagents which were purified by distillation under nitrogen. Nitrobenzene was dried on phosphorus pentoxide and distilled under nitrogen *in vacuo*.[7] This procedure was repeated twice.

Polymerization Kinetics and Nmr Measurement. The whole operation was carried out under nitrogen. A typical run for the kinetics of the polymerization was as follows. To a mixture of 0.274 g (1.70 mmol) of PhOZI and 0.50 ml of nitrobenzene in a 1.0-ml measuring flask 0.058 g (0.31 mmol) of MeOTs was added at room temperature, and then, nitrobenzene was added to a total volume of 1.0 ml. A portion of this solution was transfered into an nmr sample tube and it was sealed. The polymerization was allowed to continue in the tube at a desired temperature and monitored directly by recording nmr spectra on Hitachi R-20B spectrometer. For the kinetics of the initiation, 0.068 g (0.36 mol) of MeOTs was added to a mixture of 0.120 g (0.72 mmol) of PhOZI and 0.5 ml of nitrobenzene in a 1.0-ml measuring flask at 0°, and the mixture was diluted with nitrobenzene to a total volume of 1.0 ml. A portion of the solution was placed in an nmr sample tube and it was sealed. During the preparation of the sample the extent of the reaction was not detected. Then, the reaction in the tube was followed at 35° by using nmr spectroscopy.

Results and Discussion

Polymerization of PhOZI by MeOTs Initiator. 1. Initiation. At first, kinetics of the initiation was carried out independently because the initiation was a much faster process than the propagation. Figure 1 shows an nmr spectrum of the initiation reaction system in nitrobenzene at a reaction time of 30 hr at 35°. The initial concentrations of PhOZI, $[M]_0$, and of MeOTs initiator, $[I]_0$, were $[M]_0 = 0.72$ and $[I]_0 = 0.36$ mol per l., respectively. Under these reaction conditions, neither the polymer formation nor ring-opening reaction were observed. The reaction of initiation can be formulated by eq 4. Peak A at δ 5.16 is due to 6-methylene protons (2 H) of *N*-methyl-2-phenyl-5,6-dihydro-4*H*-1,3-oxazinium tosylate (**3**). Signal of 4-methylene protons (2 H) of **3** is overlapping with 6-methylene protons (2 H) signal of PhOZI of peak B at δ 4.43. Sharp singlets of peaks C at δ 3.88 and D at δ 3.75 are ascribed to methoxy protons (3 H) of MeOTs and *N*-methyl protons (3 H) of **3**, respectively. A quintet of peak F centered at δ 2.72 is due to 5-methylene protons (2 H) of **3**, which is overlapping partly with peak G. A singlet peak G is assigned to *p*-tolylmethyl protons (3 H) of both MeOTs and tosylate anion. Since phenyl proton signals derived from PhOZI and MeOTs are overlapping with those of nitrobenzene solvent, the aromatic proton region is not given in Figure 1.



(4)

3

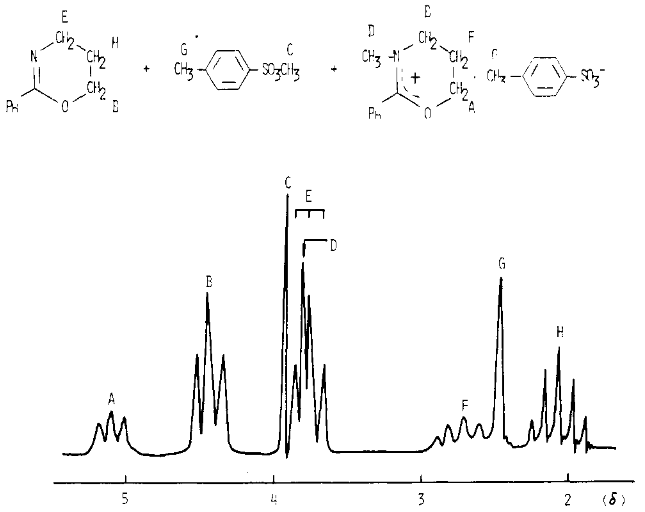


Figure 1. Nmr spectrum of the PhOZI-MeOTs reaction system in nitrobenzene after 30 hr at 35°, $[M]_0 = 0.72$ mol/l., $[I]_0 = 0.36$ mol/l.

Now, it is possible to determine the instantaneous concentrations of monomer, [M], and initiator, [I], on the basis of the above assignments. They could be obtained from the following relationships

$$[M] = [M]_0\left\{\frac{B - 2A}{B}\right\}$$

$$[I] = [I]_0\left\{\frac{C}{F + G - A}\right\}$$

where the peak sign in the braces represents the integration values of the respective peak.

Kinetic equation of the initiation is given according to the scheme of eq 4

$$-\mathrm{d}[I]/\mathrm{d}t = k_i[I][M] \tag{5}$$

Integration of eq 5 gives

$$\ln([I]_0/[I]_t) = k_i\int_0^t[M]\mathrm{d}t \tag{6}$$

where k_i denotes the rate constant of initiation. The value of $[M]\mathrm{d}t$ (from 0 to t) was calculated by graphical integration of the [M]-time relationship. Plots of

$$\ln [I]_0/[I] \textit{ vs. } \textstyle\int_0^t[M]\mathrm{d}t$$

of eq 6 showed a straight line passing through the origin whose slope gave a value of $k_i = 1.8 \times 10^{-5}$ l./(mol sec) at 35° in nitrobenzene.

2. Propagation. Next, kinetics of the propagation was carried out at higher temperatures. Figure 2 shows an nmr spectrum of the PhOZI polymerization system initiated by MeOTs at a reaction time of 46 min at 111° in nitrobenzene solvent. The initial concentration of $[M]_0$ and $[I]_0$ were 1.70 and 0.31 mol per l., respectively. At 111° MeOTs initiator was consumed completely at an early stage of the polymerization, *e.g.*, within 13 min and hence, the unreacted MeOTs was not detected anymore in Figure 2. Nmr signals of Figure 2 look more complicated than those of Figure 1 owing to the production of polymer.

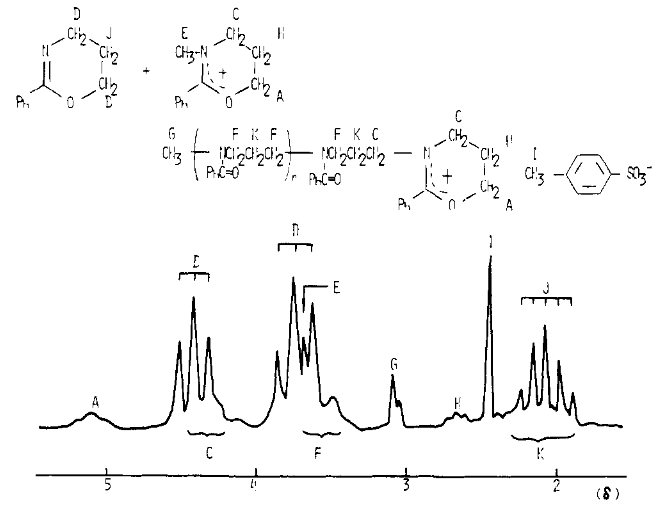
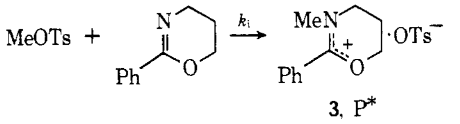


Figure 2. Nmr spectrum of the polymerization system by MeOTs initiator in nitrobenzene after 46 min at 111°, $[M]_0$ = 1.70 mol/l., $[I]_0$ = 0.31 mol/l.

As is clear in the signal assignments below, the following schemes of eq 4, 7, and 8 seem to explain the reactions.

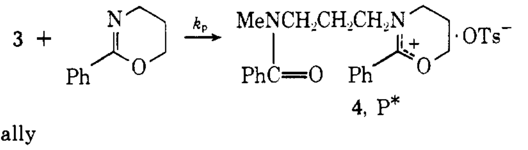
Initiation



3, P*

(4)

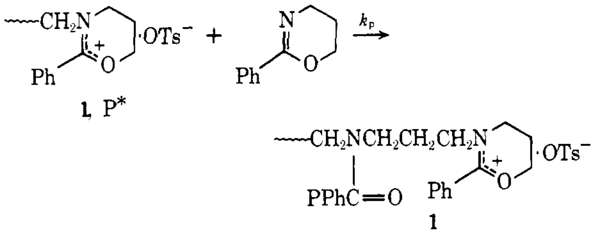
Propagation



4, P*

(7)

generally



1, P*

1

(8)

Peak A at δ 5.12 is assigned to 6-methylene protons (2 H) of propagating oxazinium, **3** and **1**. A triplet signal B at δ 4.43 is due to 6-methylene protons (2 H) of PhOZI monomer. In C region, both signals of 4-methylene protons (2 H) and open-chain α-methylene protons (2 H) of the propagating oxazinium, **4** and **1**, appear with overlapping. Of two kinds of signals in C region the concentration of the signal due to open-chain α-methylene protons (2 H) should be equal to two-thirds of that of the signal (peak G) due to *N*-methyl protons (3 H) at the polymer end of **4** and **1**. The presence of a singlet (peak E) at δ 3.66 due to *N*-methyl protons of oxazolinium ion indicates that the first propagating species of **3** still remained after 46 min at 111°. Other peaks' assignments may be found in Figure 2.

Based on the above assignments the instantaneous monomer concentration $[M]_{t2}$ could be calculated from the integration ratio of the peaks derived from 6-methylene protons of PhOZI

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

where the peak sign in the braces represent the integration values of the respective peak and t_1 denotes the time when the initiator has been consumed completely, t_2 being a longer time than t_1. Since the relationships of

$$[M]_{t_1} = [M]_0 - [I]_0$$

and

$$\{B + C - A - (2/3)G\}_{t_1} = \{J + K\}$$

were found to be valid when t_1 was taken a time immediately after the complete consumption of the initiator, *e.g.*, t_1 = 13 min, the above relationship becomes

$$[M]_{t_2} = ([M]_0 - [I]_0)\frac{\{B + C - A - (2/3)G\}_{t_2}}{\{J + K\}}$$

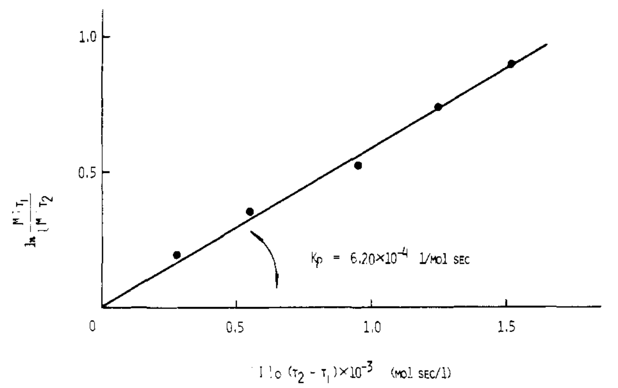


Figure 3. Plot of eq 11 in the PhOZI polymerization by MeOTs at 111°, t_1 = 13 min.

After t_1 the total concentration of propagating oxazinium ions, **3**, **4**, and **1**, was constant throughout kinetic runs, *i.e.*, the polymerization system was of living character. Furthermore, the concentration of propagating species, $[P^*]$, was equal to $[I]_0$, which means that the initiator charged for the polymerization converted quantitatively into propagating species. The stoichiometry of oxazinium ion and the counteranion was found to hold from the integration values of peak A (2 H) and *p*-tolyl methyl protons (3 H) of peak I.

The following kinetic equation is given for the polymerization (eq 4, 7, and 8)

$$-d[M]/dt = k_i[I][M] + k_p[P^*][M] \tag{9}$$

where k_p denotes the propagation rate constant. Integration of eq 9 with respect to time t_1 to t_2 gave

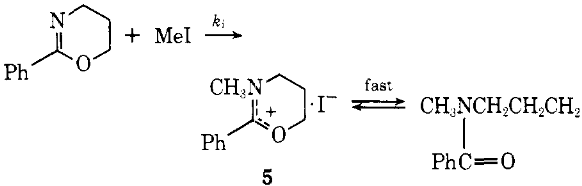
$$\ln [M]_{t_1}/[M]_{t_2} = k_p[P^*](t_2 - t_1) \tag{10}$$

where t_1 is the time required for the complete consumption of the initiator. Since it was found to be $[P^*] = [I]_0$ after t_1, eq 10 becomes

$$\ln [M]_{t_1}/[M]_{t_2} = k_p[I]_0(t_2 - t_1) \tag{11}$$

A plot of eq 11 is shown to be a straight line passing through the origin as shown in Figure 3, whose slope gave a value of $k_p = 6.20 \times 10^{-4}$ l./(mol sec) at 111°. Similarly, kinetic runs were carried out at other temperatures. These data are given in Table I.

Polymerization of PhOZI by MeI Initiator. 1. Initiation. Kinetics of initiation was carried out separately from that of propagation. Figure 4 shows an nmr spectrum of the reaction system of PhOZI with MeI after 24 hr at 35°. The initial concentrations of PhOZI monomer and MeI initiator were $[M]_0$ = 0.97 and $[I]_0$ = 0.64 mol per l., respectively. In this reaction system, two kinds of products were formed at 35° as shown in signal assignments below, *i.e.*, one was *N*-methyl-2-phenyl-5,6-dihydro-4*H*-1,3-oxazinium iodide (**5**) and the other was *N*-methyl-*N*(γ-iodopropyl)benzamide (**6**).



(12)

5 **6**

A triplet signal (peak A) at δ 5.20 is due to 6-methylene protons (2 H) of oxazinium ion **5**. A signal of 4-methylene protons (2 H) of **5** appears at δ 4.38 as a triplet (peak C) overlapping with a triplet peak B at δ 4.43 due to 6-methylene protons (2 H) of PhOZI. A sharp singlet (peak D) at δ 3.80 is ascribed to *N*-methyl protons (3 H) of **5**. Signals E and F due respectively to 4-methylene protons (2 H) of PhOZI and to *N*-methylene protons of **5** are overlapping with peak D. A triplet peak G at δ 3.32 and a sharp singlet peak H at δ 3.14 are assigned respectively to α-methylene protons of iodide (2 H) and *N*-methyl protons (3 H) of **6**. A quintet peak I at δ 2.86 is ascribed to 5-methylene protons (2 H) of **5**. At a region of δ 2 unreacted MeI appears as a sharp singlet, peak K (3 H) at δ 2.17 overlapping with signals J at δ 2.30 and L at δ 2.02 due respectively to C-methylene protons (2 H) of **5** and to 5-methylene protons (2 H) of PhOZI.

Thus, the determination of the instantaneous concentration of monomer [M] was made on the basis of the integration values relevant to 6-methylene protons of PhOZI

$$[\mathrm{M}] = [\mathrm{M}]_0\left\{\frac{\mathrm{B} + \mathrm{C} - \mathrm{A}}{\mathrm{B} + \mathrm{C} + (2/5)(\mathrm{G} + \mathrm{H})}\right\}$$

The instantaneous initiator concentration [I] should be obtained in principle from the following relationship

$$[\mathrm{I}] = [\mathrm{I}]_0\left\{\frac{\mathrm{K}}{\mathrm{D} + \mathrm{H} + \mathrm{K}}\right\}$$

All of these peaks, D, H, and K relevant to methyl protons of initiator are overlapping with other peaks. Integration values of their peaks, however, were successfully calculated from following relationships

$$\mathrm{D} = (\mathrm{D} + \mathrm{E} + \mathrm{F}) - (\mathrm{B} + \mathrm{C} - \mathrm{A}) - (2/5)(\mathrm{G} + \mathrm{H})$$
$$\mathrm{H} = (3/5)(\mathrm{G} + \mathrm{H})$$
$$\mathrm{K} = (\mathrm{J} + \mathrm{K} + \mathrm{L}) - (\mathrm{B} + \mathrm{C} - \mathrm{A}) - (2/5)(\mathrm{G} + \mathrm{H})$$

Then, the above relationship becomes

$$[\mathrm{I}] = [\mathrm{I}]_0\left\{\frac{(\mathrm{J} + \mathrm{K} + \mathrm{L}) - (\mathrm{B} + \mathrm{C} - \mathrm{A}) - (2/5)(\mathrm{G} + \mathrm{H})}{(\mathrm{D} + \mathrm{E} + \mathrm{F}) - (\mathrm{B} + \mathrm{C} - \mathrm{A}) - (2/5)(\mathrm{G} + \mathrm{H}) + (3/5)(\mathrm{G} + \mathrm{H}) + (\mathrm{J} + \mathrm{K} + \mathrm{L}) - (\mathrm{B} + \mathrm{C} - \mathrm{A}) - (2/5)(\mathrm{G} + \mathrm{H})}\right\}$$

Plots of eq 6 gave a straight line passing through the origin and k_i was determined from its slope to be a value of $k_i = 7.5 \times 10^{-5}$ l./(mol sec) at 35°. The ratio of peak area of D (due to **5**) to that of H (due to **6**) did not change throughout the kinetic run and the value was D/H = 47/53 at 35° in nitrobenzene. This indicates that the interconversion of **5** ⇄ **6** was a rapid process as shown in eq 12 and a fraction of **5** and **6** was controlled thermodynamically.

2. **Propagation** Figure 5 shows an nmr spectrum of the polymerization system by MeI initiator after 66 min at 110° in nitrobenzene, where $[\mathrm{M}]_0$ and $[\mathrm{I}]_0$ were 1.82 and 0.39 mol per l., respectively. It should be noted that no peak due to 6-methylene protons of the oxazinium was observed in an area of δ 5. This demonstrates that the oxazinium iodide species **7** was not involved in the system,

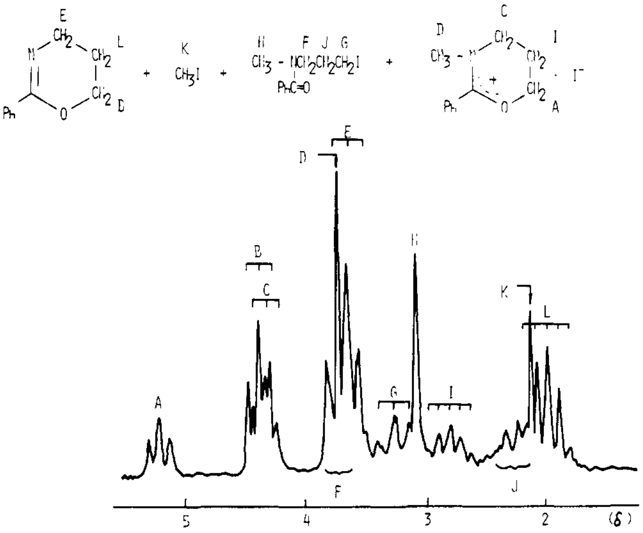


Figure 4. Nmr spectrum of the PhOZI-MeI reaction system in nitrobenzene after 24 hr at 35°, $[\mathrm{M}]_0$ = 0.97 mol/l., $[\mathrm{I}]_0$ = 0.64 mol/l.

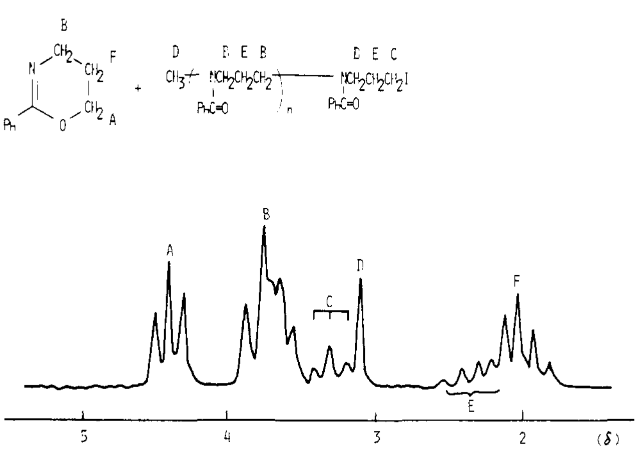
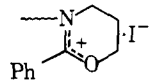
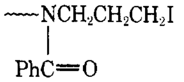


Figure 5. Nmr spectrum of the polymerization system by MeI initiator in nitrobenzene after 66 min at 110°, $[\mathrm{M}]_0$ = 1.82 mol/l., $[\mathrm{I}]_0$ = 0.39 mol/l.



7



$$\text{—NCH}_2\text{CH}_2\text{CH}_2\text{I} \atop {|\atop \text{PhC=O}}$$

2

under the polymerization conditions, which is strikingly different from the MeOTs-initiated polymerizations (Figures 1 and 2) and even from the initiation by MeI at 35° (Figure 4). Instead, a triplet peak C due to α-methylene protons (2 H) of iodide **2** is seen at δ 3.32. Other peaks assignments are as follows. Peak A at δ 4.43 is ascribed to 6-methylene protons (2 H) of PhOZI. In peak B signals due to methylene protons adjacent to nitrogen atom of PhOZI and polymer are included. A singlet peak D at δ 3.14 is assigned to *N*-methyl protons (3 H) at the polymer end. Peaks E and F are due to C-methylene protons (2 H) of polymer and PhOZI, respectively.

Now, the following scheme of reactions will explain the course of polymerization involving alkyl iodide (**6**, **8**, and **2**) as propagating species.

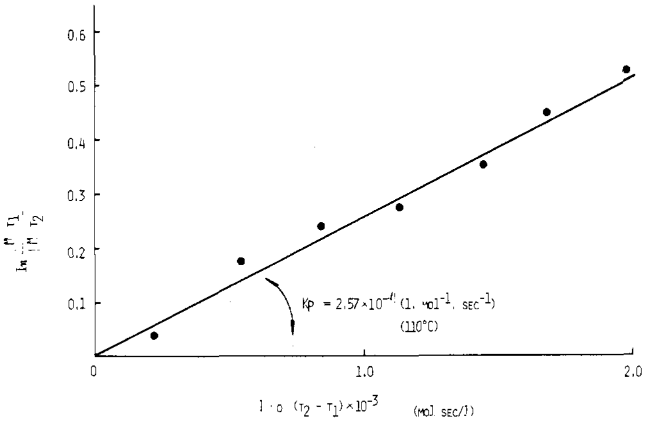
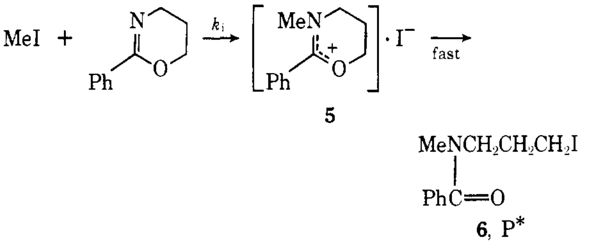


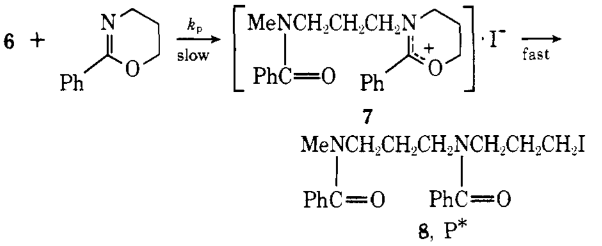
Figure 6. Plot of eq 11 in the PhOZI polymerization by MeI at 110°, t_1 = 16 min.

Initation



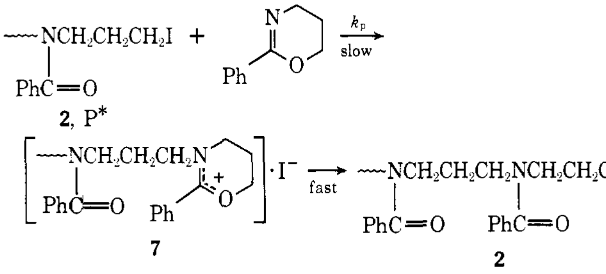
(12)

Propagation



(13)

Generally



(14)

After the initiator has completely been consumed (within 16 min at 110°) the concentration of propagating alkyl iodide species [P*] was found to be equal to the initial concentration of the initiator $[I]_0$ by nmr spectroscopy. Peaks E and F are all signals derived originally from 5-methylene protons of PhOZI. Peak A is due to the unreacted PhOZI. Thus, the instantaneous concentration of monomer [M] was obtained from the following relationship of the peak areas.

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

Therefore, a plot of eq 11 was made (Figure 6) and its slope gave a value of $k_p = 2.57 \times 10^{-4}$ l./(mol sec) at 110°. Similarly, k_p values were obtained at other temperatures. In addition, an Arrhenius plot was made and activation parameters were calculated. These data are given in Table II.

Table I
Propagation Rate Constants (k_p) and Activation Parameters in the Polymerization of PhOZI with MeOTS Initiator in Nitrobenzene[a]

$k_p \times 10^4$ (l./(mol sec))	2.53 (100°)
	6.20 (111°)
	10.0 (120°)
	19.4 (129°)
ΔE_p^* (kcal/mol)	21
A_p (l./(mol sec))	3.6×10^8

[a] $[M]_0$ = 1.70 mol/l., $[I]_0$ = 0.31 mol/l.

Table II
Propagation Rate Constants (k_p) and Activation Parameters in the Polymerization of PhOZI with MeI Initiator in Nitrobenzene[a]

$k_p \times 10^4$ (l./(mol sec))	1.41 (100°)
	2.57 (110°)
	3.40 (119°)
	7.56 (131°)
ΔE_p^* (kcal/mol)	16
A_p (l./(mol sec))	6.2×10^5

[a] $[M]_0$ = 1.82 mol/l., $[I]_0$ = 0.39 mol/l.

Table III
Comparison of Rate Constants and Activation Parameters in the Polymerization of PhOZI and OZI by MeOTS and MeI Initiators in Nitrobenzene

	PhOZI[a]		OZI[b]	
	MeOTs	MeI	MeOTs	MeI[c]
$k_i \times 10^5$ (l./(mol sec) at 35°)	1.8	7.5	29	121
$k_p \times 10^4$ (l./(mol sec) at 100°)	2.53	1.41	110[d]	250[d]
ΔE_p^* (kcal/mol)	21	16		20
A_p (l./(mol sec))	3.6×10^8	6.2×10^5		1.0×10^{10}

[a] This work. [b] Taken from ref 1. [c] Data in acetonitrile solvent. [d] Calculated value.

Polymerization Mechanism. As shown in Tables I and II, k_p values of MeOTs initiator were 1.7 times at 100° and 2.7 times at 120° as high as those of MeI initiator. The reactivity difference is attributed to the higher frequency factor of the MeOTs-initiated system (3.6×10^8 l./(mol sec)) than that of the MeI-initiated system (6.2×10^5 l./(mol sec)), although the activation energy was higher (less favorable) in the former system (21 kcal/mol) than in the latter one (16 kcal/mol). These results also indicate that the mechanism is different in the two series of PhOZI polymerization by MeOTs and by MeI in accordance with the above observations by nmr spectroscopy.

In the MeOTs-initiated polymerization, the rate-determining step of propagation is the ring-opening process of oxazinium ion by the attack of PhOZI monomer as shown in eq 8. In the MeI-initiated polymerization, however, the production of oxazinium iodide species 7 from alkyl iodide propagating species 2 and PhOZI is the rate-determining step, followed by a rapid nucleophilic attack of iodide anion on to the 6-carbon atom of 7 to produce alkyl iodide propagating species 2 (eq 14). With this respect the propagation process (eq 14) resembles the Menschutkin reaction (eq 15) producing a quaternary ammonium salt from amine and alkyl halide.

$$R_3N + RX \longrightarrow R_4N^+X^- \qquad (15)$$

It is well known that the Menschutkin reaction is characterized by an S_N2 process exhibiting low values of activation energy and frequency factor,[8] *e.g.*, ΔE^* = 13 kcal/

mol and $A = 4.0 \times 10^6$ l./(mol sec) at 100° in the reaction of pyridine with MeI in nitrobenzene.[9] Those values in the MeI-initiated polymerization are very close to those of the Menschutkin reaction.

Similar results have already been observed in the polymerization of OZO by MeOTs and MeI initiators.[4] The propagating species of the OZO polymerization was an oxazolinium ion by MeOTs initiator and a covalent-bonded alkyl iodide by MeI initiator.[4] It should be added here, however, that in the present study propagating species of covalent-bonded alkyl iodide was directly observed by nmr spectroscopy for the first time in the MeI-initiated polymerization of PhOZI.

Phenyl Substituent Effects. It should be worth while to compare the reactivities and activation parameters between PhOZI and OZI with respect to the effect of 2-phenyl group of OZI monomer (Table III). First, the nucleophilic reactivity of PhOZI is about 16 times decreased by the phenyl group being reflected by k_i value with MeOTs initiator at 35°. Second, the polymerization reactivity (k_p) of PhOZI is 44 times less than that of OZI in the MeOTs-initiated system in which both PhOZI and OZI proceeded *via* oxazinium tosylate propagating species. Third, the introduction of phenyl group altered polymerization mechanism in the MeI-initiated polymerization at temperatures higher than 100°. Since k_p was almost the same in nitrobenzene and acetonitrile solvents for the OZI polymerization involving oxazinium propagating species,[1] a k_p value of OZI, 2.5×10^{-2} l./(mol sec) at 100° in acetonitrile, was roughly taken to represent that in nitrobenzene. Then, the k_p of PhOZI is about 180 times smaller than that of OZI with MeI initiator in nitrobenzene. Finally, it should be mentioned here that OZI was 43 times less reactive than OZO in CD_3CN by MeOTs initiator.[1] Consequently, PhOZI must be about 1.9×10^3 times less reactive than unsubstituted five-membered cyclic imino ether of OZO.

References and Notes

(1) For Part II, see T. Saegusa. S. Kobayashi, and Y. Nagura, *Macromolecules*, **7**, 264 (1974).

(2) Address correspondence to this author.

(3) T. Saegusa, Y. Nagura, and S. Kobayashi, *Macromolecules*, **6**, 495 (1973).

(4) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **6**, 315 (1973).

(5) T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, **5**, 359 (1972).

(6) A. Levy and M. Litt, *J. Poly. Sci., Part B*, **5**, 881 (1967).

(7) J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, New York, N.Y., 1970, p 795.

(8) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1963, p 379.

(9) N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936).

Plasma Polymerization of Saturated and Unsaturated Hydrocarbons

H. Kobayashi, A. T. Bell, and M. Shen*

Department of Chemical Engineering, University of California, Berkeley, California 94720.

Received December 11, 1973

ABSTRACT: A series of nine saturated and unsaturated hydrocarbons were polymerized by subjecting them to a radiofrequency glow discharge at reduced pressures. It was found that acetylene polymerizes most rapidly, followed by ethylene and butadiene, then by propylene, *cis*-2-butene and isobutylene. The saturated alkanes: methane, ethane, and propane polymerize most slowly. As shown by previous work, the form of the polymer depends upon the rate of polymer deposition. Thus very high deposition rates produce only a powder, intermediate rates produce either a powder or a film, and low rates produce only a film. It was found from carbon–hydrogen analysis that polymers prepared from the alkanes exhibited a greater loss of hydrogen than did those from olefinic monomers. The polymer prepared from acetylene exhibited the least loss of hydrogen. Infrared spectra of the polymers made of ethane, ethylene, and acetylene showed that with increasing monomer unsaturation the polymer contained more double bonds, fewer methylene groups, and a greater tendency to be oxidized after preparation. An examination of the mechanism of ethylene polymerization led to the conclusion that a significant amount of oligomerization occurs in the gas phase. In addition it is hypothesized that an important initial step is the partial conversion of ethylene to acetylene. This hypothesis can also be extended to the other monomers to explain their relative rates of polymer deposition.

There has recently been an increasing interest in the use of low pressure electric discharges for the polymerization of organic and organometallic compounds.[1-5] The formation of a polymer by this means is a complex process which is initiated by collisions between energetic free electrons, present in the plasma formed by the discharge, and molecules of the monomer. The products of these collisions are ions, excited molecules, and free radicals.[6] Once formed these species can react with themselves as well as with additional ground-state molecules to produce polymers both in the gas phase as well as on solid surfaces placed in the plasma. Because of its complexity, the mechanism of plasma polymerization is not well understood. In our previous publications[7,8] dealing with the plasma polymerization of ethylene, a mechanism was proposed to explain the dependence of polymer deposition rate and the type of polymer formed on the reaction conditions. In the present work, the investigation is broadened to include a number of saturated and unsaturated hydrocarbon gases. On the basis of their relative rates of polymer deposition and the characteristics of the corresponding polymers, additional information has been obtained relating to the plasma polymerization of hydrocarbons.

Experimental Section

Monomer gases (CP grade) were purchased from Matheson Gas Products, and were used as received. The detailed experimental arrangement for plasma polymerization has been described previously.[7] The apparatus consists of an evacuable bell jar housing a parallel pair of disc electrodes. An International Plasma Corporation Model PM 401 radiofrequency generator was used to sustain the discharge. The generator operates at 13.56 MHz and has a maximum power output of 150 W. The lower electrode was water cooled. The rate of polymer deposition was determined by