Polymer Bulletin 11, 253-260 (1984)

Polymer Bulletin

Kinetics and Mechanism of Cationic Polymerization of 5-Methyl-2-Oxazoline. Concurrent Propagation Through Ionic and Covalent Species with Methyl Iodide Initiator

Shiro Kobayashi, Kenji Morikawa, Naoki Shimizu and Takeo Saegusa

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606, Japan

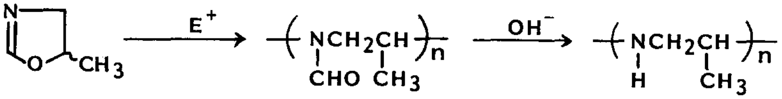
SUMMARY

Kinetic analysis of the cationic polymerization of 5-methyl-2-oxazoline (5-MeOZO) was performed with methyl tosylate(MeOTs) and methyl iodide(MeI) initiators by using ^{1}H NMR spectroscopy. With MeOTs the polymerization of 5-MeOZO proceeded through oxazolinium tosylate species 3 and 4 and the rate constant of propagation (k_p) was determined. With MeI, on the other hand, the propagating ends are present in equilibrium between alkyl iodide (covalent) species 7, 9 and 11 and oxazolinium(ionic) species 6, 8 and 10. Two model reactions enabled to determine the equilibrium constant (K) of 6/7 and to evaluate the reactivity of covalent species 9 (reflected by $k_{p(c)}$) and of ionic species 8 (reflected by $k_{p(i)}$). Both species 8 and 9 propagate concurrently and contribute to the whole propagation at comparative extents.

INTRODUCTION

Kinetic studies on the cationic ring-opening polymerization of 2-methyl-2-oxazoline(2-MeOZO) have been carried out extensively (1-3). With methyl tosylate(MeOTs) and methyl iodide(MeI) initiators in CD_3CN propagating species of 2-MeOZO were oxazolinium species in both cases. And the reactivities of the propagating ends with these two initiators are almost the same reflected by the rate constant of propagation; $k_p=1.17$ and 1.14×10^{-4} l/mol·sec at 40°C (1,2), respectively. The nature of the propagating species of 2-MeOZO polymerization, however, was dependent upon the counter anion derived from the initiator (3). With benzyl chloride initiator, the propagating end was of covalently-bonded alkyl chloride type. With benzyl bromide initiator, the propagating species consisting of ionic (~80%) and of covalent types (~20%) in CD_3CN has been suggested (3).

We have reported the cationic ring-opening polymerization of 5-methyl-2-oxazoline(5-MeOZO) to produce polymer 1 and the alkaline hydrolysis of 1 to give linear poly(propylenimine) 2 (4). The present paper deals with a kinetic study of the polymerization of 5-MeOZO. It has been found that



5-MeOZO 1 2

oxazolinium tosylates are propagating species in the polymerization with MeOTs initiator whereas the equilibrium between oxazolinium-covalent propagating species is involved with MeI initiator. This is the first clear-cut evidence in the polymerizations of 2-oxazoline and its derivatives that both ionic and covalent (neutral) species propagate concurrently.

RESULTS AND DISCUSSION

The polymerization of 5-MeOZO is unique in such a sense that the reaction site of the C-5 atom is a tertiary carbon. This situation is very rare in the ring-opening polymerization. Therefore, in order to examine the polymerizability kinetic study of the 5-MeOZO polymerization was carried out with the use of typical cationic initiators of MeOTs and MeI. Kinetic analysis was performed by means of ^1H NMR spectroscopy.

MeOTs-Initiated Polymerization

Figure 1 shows the ^1H NMR spectrum of the polymerization system initiated with MeOTs in CD_3CN, in which all MeOTs has already been consumed and the polymerization reached to a later stage. Signals around δ9.1-6.8 are assigned as follows. Peak A at δ9.1 is ascribed to methine proton at the C-2 position of oxazolinium species 3-5. Broad peak B at δ8.1 is due to formyl proton of polymer chain. A quartet signal C is due to aromatic protons of tosylate counter anion of 3-5. Peak D is due to methine proton of 5-MeOZO. These results clearly indicate that the propagation proceed through oxazolinium tosylate species 4. Therefore, the general course of the 5-MeOZO polymerization with MeOTs is given as follows.

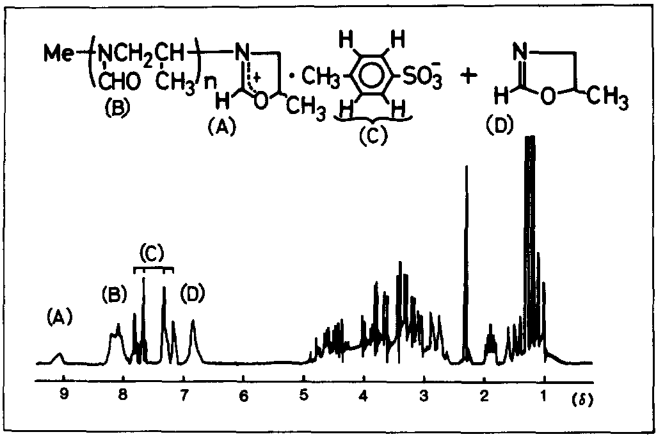
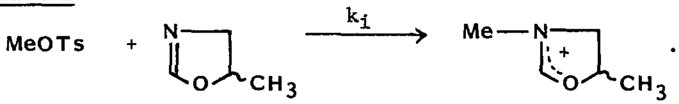


Figure 1. ^1H NMR spectrum of the MeOTs-initiated polymerization system of 5-MeOZO in CD_3CN at 90°C after 120 min.

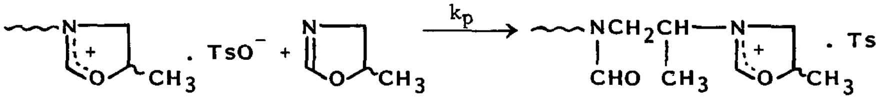
Initiation



(i)

3

Propagation



(ii)

4

5

A reference experiment of reaction (i) supported the above mechanism: A reaction of a slight excess amount of MeOTs over 5-MeOZO (MeOTs/5-MeOZO =1.14) in CD_3CN at 35°C gave quantitatively *N*-methyl oxazolinium tosylate **3**. The polymerization was not observed under these reaction conditions, indicating that the initiation is a fast reaction compared with the polymerization. Thus, it is concluded that the propagating ends are oxazolinium species like **3-5**.

The consumption rates of 5-MeOZO and MeOTs, and the production rates of polymer unit and oxazolinium species could be followed by ^1H NMR spectroscopy of the polymerization system. The kinetic analysis was therefore performed on the basis of S_N2 type reactions (i) and (ii). The rate equations are

$$\frac{-d[\mathrm{MeOTs}]}{dt} = k_i[\mathrm{MeOTs}][\text{5-MeOZO}] \qquad \text{(iii)}$$

and

$$\frac{-d[\text{5-MeOZO}]}{dt} = k_i[\mathrm{MeOTs}][\text{5-MeOZO}] + k_p[P^*][\text{5-MeOZO}] \qquad \text{(iv)}$$

where k_i and k_p are the rate constants of initiation and propagation, and $[P^*]$ denotes the total concentration of oxazolinium tosylate species. Values of k_i and k_p were obtained from the integrated form of equations (iii) and (iv). Kinetics were carried out at three temperatures and activation parameters were calculated (Table 1). The polymerizability of 5-MeOZO is compared with that of 2-MeOZO; the extraporated value of k_p of 5-MeOZO at 40°C is 0.9×10^{-5} l/mol.sec, which is about 1/12 of that of 2-MeOZO (1).

Table 1
Rate Constants and Activation Parameters in the Polymerization of 5-MeOZO with MeOTs Initiator in CD_3CN^a

	$k_i \times 10^4$ (l/mol.sec)	$k_p \times 10^4$ (l/mol.sec)
72°C	8.8	1.02
80°C	13.7	1.92
90°C	28.5	3.65
$\Delta H^{\ddagger}$ (kcal/mol)	18.7	14.8
$\Delta S^{\ddagger}$ (e.u.)	-21	-36

a) $[\text{5-MeOZO}]_0$ = 2.78 mol/l and $[\mathrm{MeOTs}]_0$ = 0.374 mol/l.

MeI-Initiated Polymerization

Figure 2 shows the ^1H NMR spectrum of the reaction system of 5-MeOZO polymerization initiated with MeI in CD_3CN. Three signals A(δ9.3-9.0), B(δ8.0), and C(δ6.8) are characteristic to those due to methine proton derived from 5-MeOZO. Signal C is assigned to methine proton of remaining 5-MeOZO. Peak A is ascribed to the methine proton of oxazolinium iodide species. The concentration of the oxazolinium, however, is lower than that of the initial feed amount of MeI. This is due to the existence of equilibrium between the oxazolinium **8** and alkyl iodide propagating species **9** as established also by a model reaction (*vide infra*). The signal due to the formyl proton of covalently-bonded propagating end **9** appears as peak B which also includes that of the monomeric unit of polymer chain. The general polymerization course with MeI initiator is shown as follows.

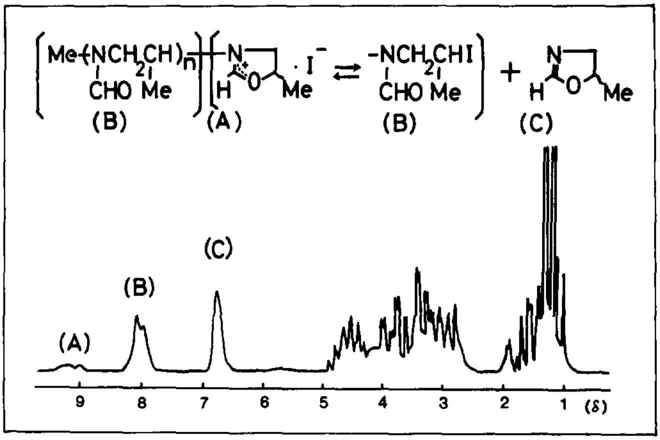
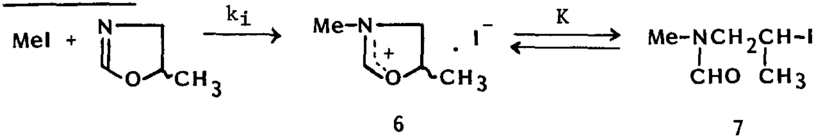


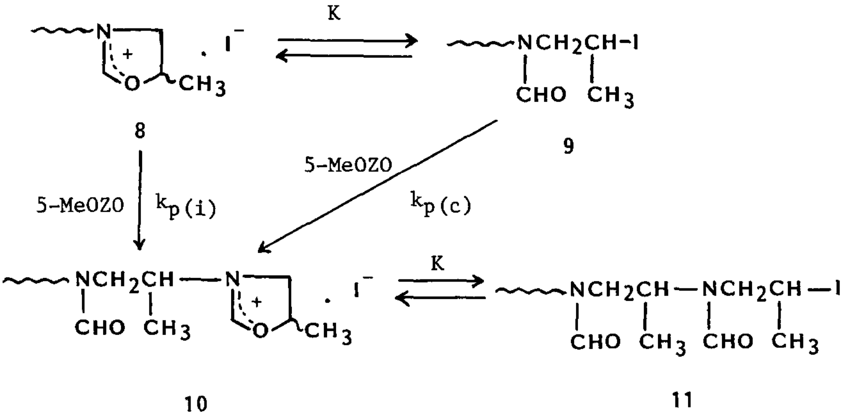
Figure 2. ^1H NMR spectrum of the MeI-initiated polymerization system of 5-MeOZO in CD_3CN at 80°C after 150 min.

Initiation



(v)

Propagation



(vi)

Kinetic analysis was carried out on the basis of the above scheme (vi). The following relationship holds

$$k_{p(ap)} = k_{p(i)} \cdot x_i + k_{p(c)} \cdot x_c \qquad \text{(vii)}$$

where $k_{p(ap)}$ is the apparent rate constant of propagation and $k_{p(i)}$ and $k_{p(c)}$ denote the rate constants of propagation due to ionic species 8 and covalent (alkyl iodide) species 9, respectively, and x_i and x_c are the molar fractions of ionic and covalent species, i.e., $x_i + x_c = 1$. Values of k_i and

k_p(ap) were obtained analogously to the MeOTs system based on eq (iii) and (iv) (Table 2). The polymerization of 5-MeOZO initiated by MeI proceeds slightly slower than that by MeOTs.

Table 2
Rate Constants and Activation Parameters in the Polymerization of 5-MeOZO with MeI Initiator in CD_3CN^a

	$k_i \times 10^4$(l/mol.sec)	$k_p(ap) \times 10^4$(l/mol.sec)
73°C	9.8	0.69
80°C	21	1.2
90°C		2.6
$\Delta H^{\ddagger}$ (kcal/mol)		16.6
$\Delta S^{\ddagger}$ (e.u.)		-32

a) $[5\text{-MeOZO}]_0$ = 2.94 mol/l and $[\text{MeI}]_0$= 0.588 mol/l.

Model Reactions

In order to examine the onium-covalent equilibrium of the propagating end, the first model reaction was undertaken. *N*-(2-Iodopropyl)-*N*-methylformamide 7 was prepared by an equimolar reaction of 5-MeOZO with MeI and was isolated by vacuum distillation. 7 corresponds to the smallest propagating species of covalent type in the polymerization of 5-MeOZO initiated by MeI. 7 was dissolved in a solvent in a sealed ^{1}H NMR sample tube. The ^{1}H NMR showed that 7 cyclizes to onium species 6 and finally reaches to an equilibrium. The concentrations of 6 and 7 could be determined since the methine proton at C-2 of 6 and formyl proton of 7 appear as different signals as shown in Figure 3. Temperature variation experiments showed that the interconversion, $6 \rightleftarrows 7$, is reversible. The equilibrium constant (K=6/7) was obtained at different temperatures in three solvents (Table 3). Changes of free-energy(ΔG), enthalpy(ΔH), and entropy(ΔS) values were also obtained on the basis of the following relationship

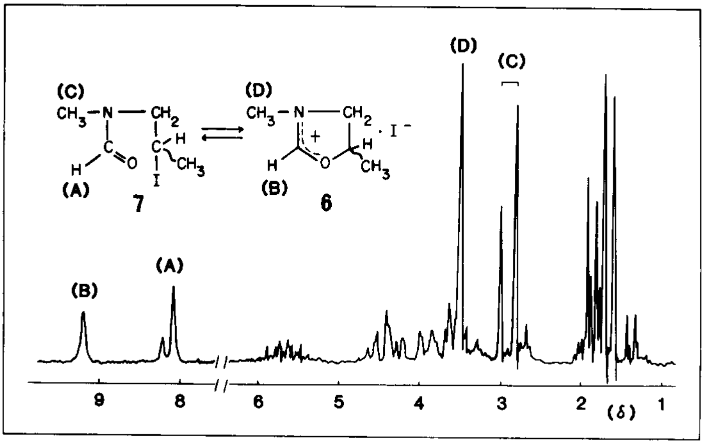


Figure 3. ^{1}H NMR spectrum of an equilibrium mixture 6 and 7 at 80°C (4.0 mol/l in CD_3CN).

$$\Delta G = -RT\ln K = \Delta H - T\Delta S$$

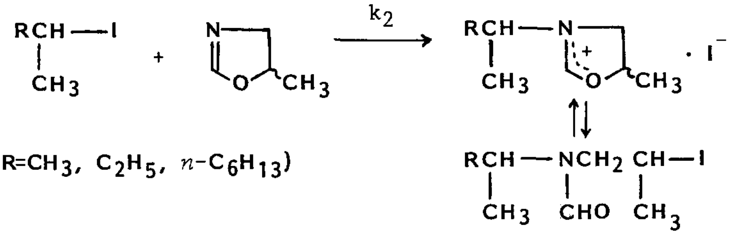
Ionic form 6 is favored in polar solvents and at a lower temperature.

Table 3
Values of K(=6/7), ΔG, ΔH, and ΔS in the
Equilibrium of 6 and 7 in Three Solvents

	$CDCl_3$		CD_3CN		CD_3NO_2	
	K	ΔG^a	K	ΔG^a	K	ΔG^a
35°C	0.49	0.43	1.12	-0.07	1.38	-0.20
60°C	0.28	0.85	0.82	0.14	1.08	-0.05
80°C	0.19	1.16	0.70	0.26	0.89	0.11
100°C			0.59	0.41	0.70	0.26
ΔH^a	-4.5		-2.4		-2.3	
ΔS(e.u.)	-16.1		-7.4		-6.9	

a) kcal/mol.

The second model reaction was undertaken to evaluate the polymerizability of the covalent propagating species 9. As a model of 9 three *sec*-alkyl iodides 12 were used. A bi-molecular reaction of 12 with 5-MeOZO in equimolar amount was examined and the rate constant (k_2) at an early stage of reaction was determined by ^1H NMR spectroscopy. In CD_3CN at 80°C,



12 ($R=CH_3$, C_2H_5, n-C_6H_{13})

(viii)

k_2(l/mol·sec) values for 12 were as follows: 8.72×10^{-5} for $R=CH_3$, 5.46×10^{-5} for $R=C_2H_5$, and 4.16×10^{-5} for $R=n-C_6H_{13}$. From these results it may be reasonable to take *sec*-butyl iodide ($R=C_2H_5$) as a suitable model of 9 and to take k_2 of reaction (viii) as $k_{p(c)}$ of reaction (vi).

Evaluation of $k_{p(i)}$ and $k_{p(c)}$ Values. Based on the above two model reactions an attempt was made to evaluate the reactivities of ionic 8 and covalent propagating species 9 reflected by $k_{p(i)}$ and $k_{p(c)}$, respectively. The K values of the model reaction (v) were applied to those of the propagating ends of reaction (vi). First, k_2 ($=k_{p(c)}$) values of reaction (viii) with *sec*-butyl iodide were determined under various conditions, and then, $k_{p(i)}$ values were calculated by employing K values in Table 3. These results indicate that ionic species are approximately several times more reactive in polymerizability than covalent species in three solvents (Table 4). For comparison, values of k_p ($=k_{p(i)}$) with MeOTs initiator are also cited in Table 4. The $k_{p(i)}$ values with both MeI and MeOTs initiators are not so much different, i.e., the polymerizability of the oxazolinium species of 5-MeOZO is little effected with a counter anion of I^- or TsO^-.

Table 4
Values of $k_{p(ap)}$, $k_{p(c)}$, $k_{p(i)}$ and k_p[a]

Solvent	Temp. (°C)	$k_{p(ap)}$	$k_{p(c)}(=k_2)$	$k_{p(i)}$	$k_p(=k_{p(i)})$[b]
$CDCl_3$	80	0.39	0.21	1.3	0.58
CD_3CN	73	0.69	0.33	1.2	~1.1
	80	1.2	0.55	2.2	1.92
	90	2.6	1.2	4.8	3.65
CD_3NO_2	80	1.6	0.70	2.6	2.2

a) All rate constants of propagation in $\times 10^4$ l/mol·sec.
b) Values with MeOTs initiator.

Since $k_{p(c)}$ and $k_{p(i)}$ values were separatedly evaluated, the contribution of the respective species to the propagation was calculated (Table 5). Covalent species contributed more in a less polar solvent of $CDCl_3$ than in a higher polar solvent such as CD_3CN or CD_3NO_2. Thus, it is concluded that in the MeI initiated polymerization of 5-MeOZO the propagating ends are present in equilibrium between two species of covalent (alkyl iodide) and ionic (oxazolinium iodide) type and that the propagations of both species take place in a comparable contribution to the whole propagation.

Table 5
Contribution of Covalent and Ionic Species to the Propagation of the MeI Initiated Polymerization of 5-MeOZO at 80°C

Solvent	Covalent Species(%)	Ionic Species(%)
$CDCl_3$	45	55
CD_3CN	25	75
CD_3NO_2	23	77

EXPERIMENTAL PROCEDURES

Materials

Monomer (5-MeOZO) was obtained as reported (4). All solvents, $CDCl_3$, CD_3CN, CD_3NO_2 and DMF, were commercial reagents and used after drying over molecular ceives. Initiators of MeOTs and MeI were distilled under nitrogen before use. *i*-PrI was used after distillation under nitrogen. *sec*-BuI and *sec*-octyl iodide were prepared by the bromide-iodide exchange reaction. A typical procedure is as follows: a mixture of *sec*-BuBr (11.9 g, 87 mmol) and NaI (19.5 g, 130 mmol) in 100 ml of acetone was kept at 70°C for 9 hr. Acetone was evaporated in vacuo and the residue was extracted with diethyl ether. The ether layer was dried over Na_2SO_4, concentrated and distilled to give *sec*-BuI, bp 53°C/82 mmHg. This fraction was purified further by preparative gas chromatography.

N-(2-Iodopropyl)-*N*-methylformamide 7 was prepared by the reaction of 5-MeOZO (14 mmol) with MeI (28 mmol) with refluxing for 1.5 hr. 7 was isolated by distillation in vacuo, bp 89 - 91°C / 0.25 mmHg.

Kinetics of the 5-MeOZO Polymerization

All kinetic runs were carried out in an NMR sample tube. A typical run is described. Into an NMR tube 1.50 mmol of MeOZO, 0.36 ml of CD_3CN and 0.30 mmol of MeI were introduced under nitrogen at 0°C. The tube was sealed and well shaken and the polymerization was monitored by ^1H NMR spectroscopy (60 MHz) at a desired reaction temperature.

Model Reaction of 5-MeOZO with *sec*-Alkyl Iodide

In an NMR tube 0.30 mmol of 5-MeOZO, 0.29 ml of CD_3CN and 0.30 ml of *sec*-BuI were placed under nitrogen. The tube was sealed at 0°C and well shaken. The reaction was then monitored by ^1H NMR spectroscopy. Only the disappearance rate of 5-MeOZO could be followed by ^1H NMR. It was reasonably assumed that the consumption rate of *sec*-BuI was equal to that of 5-MeOZO at an early stage of reaction. The k_2 values thus obtained were taken to indicate the values of $k_{p(c)}$.

REFERENCES

1. T. Saegusa, H. Ikeda and H. Fujii, Macromolecules **5**, 359 (1972).
2. T. Saegusa and H. Ikeda, Macromolecules **6**, 808 (1973).
3. T. Saegusa, S. Kobayashi and A. Yamada, Makromol. Chem. **177**, 2271 (1976).
4. S. Kobayashi, N. Shimizu and T. Saegusa, Polymer Bull. the preceding paper.

Accepted December 21, 1983