Macromolecules

Volume 7, Number 6 November–December 1974

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Isomerization Polymerization of 1,3-Oxazine. IV.¹ Kinetic Studies on the Polymerization of 2-Methyl-5,6-dihydro-4H-1,3-oxazine

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ABSTRACT: This paper describes the kinetics of the isomerization polymerization of 2-methyl-5,6-dihydro-4H-1,3-oxazine (MeOZI) initiated by methyl tosylate (MeOTs) and by methyl iodide (MeI) in nitrobenzene. The kinetic analysis was made on the basis of the direct determination of the concentrations of monomer, initiator, and propagating species by nmr spectroscopy. In both cases the polymerization of MeOZI proceeded by an SN2 reaction between the propagating oxazinium species (4 and 6) and MeOZI monomer (eq 3 and 11). The rate constants of initiation (k_i) and propagation (k_p) as well as the activation parameters of propagation were determined. The reactivity of MeOZI was compared with the reactivities of other six- and five-membered cyclic imino ethers. The effect on the rate of polymerization of the methyl group at the 2 position of the 1,3-oxazine ring was demonstrated in k_i and k_p values.

This paper describes a study of the kinetics of the polymerization of 2-methyl-5,6-dihydro-4H-1,3-oxazine (MeOZI, 1), which is an important extension of a series of our investigations¹⁻³ on the polymerizations of 5,6-dihydro-4H-1,3-oxazine (OZI, 2) and its substituted derivatives. Previously, we have performed kinetic studies on the polymerizations of OZI² and 2-phenyl-5,6-dihydro-4H-1,3-oxazine¹ (PhOZI, 3). We have found that the polymerization of

$$\begin{array}{cccc} & & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

PhOZI initiated with MeOTs occurred via an oxazinium tosylate as the propagating species and via a covalent bonded alkyl iodide with MeI initiator, whereas that of OZI proceeded via an oxazinium propagating species regardless of the nature of the initiator (e.g., MeOTs, MeI, trinitrophenetole, etc.²). The introduction of a phenyl group at the 2 position of OZI changed monomer reactivities as well as the polymerization mechanism. It is of interest, therefore, to examine the effect of a methyl group at the 2 position. This paper reports the kinetics of the MeOZI polymerization by MeOTs and MeI initiators in nitrobenzene. Polymerization and reference reactions were carried out in nmr sample tubes, and the progress of the reaction was monitored by nmr spectroscopy.

Experimental Section

Reagents. MeOZI was prepared in 23% yield according to Levy and Litt⁴ by the vapor-phase cyclodehydration of N-(3-hydroxypropyl)acetamide on activated silica-alumina at 250–270°.⁵ It was purified by fractional distillation under nitrogen, bp 58–60° (56 mm) (lit.⁴ 131-132°). N-(3-Hydroxypropyl)acetamide was obtained in 71% yield by the reaction of *n*-propanolamine (1 mol) with ethyl acetate (2 mol) in toluene (500 ml) at 120° for 2 hr, bp 124-126° (0.3 mm). MeOTs, MeI, and nitrobenzene were purified as previously reported.²

Kinetic Procedures and Nmr Measurement. All operations were carried out under nitrogen. In a kinetic run of the initiation reaction with MeOTs, the sample was prepared as follows. To a mixture of 0.93 mmol of MeOZI and 0.70 ml of nitrobenzene in a 1.0 ml measuring flask, 0.40 mmol of MeOTs was added at 0°. This mixture was diluted with nitrobenzene to a total volume of 1.00 ml. A portion of this mixture was sealed in an nmr tube. The reaction was allowed to continue in the tube at 35° and monitored by recording the nmr spectrum at several times on a Hitachi R-20B nmr spectrometer. A typical run for kinetics of the MeOTs-initiated polymerization was as follows. In a 1.0-ml measuring flask were placed 1.51 mmol of MeOZI and 0.70 ml of nitrobenzene. To this mixture was added 0.30 mmol of MeOTs at 0° and the mixture was diluted with nitrobenzene to a total volume of 1.00 ml. A portion of this mixture was sealed in an nmr sample tube. No polymerization was observed before recording the nmr spectrum. The polymerization was followed by nmr spectroscopy.

Results and Discussion

Polymerization by MeOTs. The rate constant of propagation (k_p) was determined as follows. Figure 1 shows an nmr spectrum of the polymerization system at a reaction time of 52 min at 77° in nitrobenzene, in which MeOTs has already been consumed. The initial concentrations of MeOZI and MeOTs were 1.51 and 0.30 mol/l., respectively. The signal assignments may be found in Figure 1. The propagating species of the MeOTs initiator is clearly shown to be 2-methyl-5,6-dihydro-4H-1,3-oxazinium tosylate, 4. At a higher polymerization temperature, *e.g.*, 77°, the initiator





Figure 1. Nmr spectrum of the polymerization mixture of MeOZI initiated with MeOTs in nitrobenzene after 52 min at 77°: $[M]_0 = 1.51 \text{ mol/l.}$, $[I]_0 = 0.30 \text{ mol/l}$.

was converted at a very early stage into the propagating species 4. The following scheme of reactions will explain the course of the MeOZI polymerization (eq 1-3).

Initiation

$$Me \xrightarrow{N} OTs^{-} (1)$$

Propagation

Generally

The propagation rate is given by

$$-d[\mathbf{M}]/dt = k_{p}[\mathbf{P}^{*}][\mathbf{M}]$$
(4)

where $[P^*]$ and [M] are the concentrations of the propagating species (4 and 5) and of monomer, respectively. The integrated form of eq 4 is

$$\ln [\mathbf{M}]_{t_1} / [\mathbf{M}]_{t_2} = k_p \int_{t_1}^{t_2} [\mathbf{P}^*] dt$$
 (5)

where t_1 represents a time longer than that required for the complete conversion of MeOTs into the propagating species, *e.g.*, it is 7 min in Figure 1, and t_2 is longer than t_1 . After t_1 the following relationship (eq 6) was found to be valid by nmr spectroscopy

$$[\mathbf{P}^*] = [\mathbf{I}]_0 \tag{6}$$

Table IRate Constants and Activation Parameters in thePolymerization of MeOZI by MeOTs and MeI Initiatorsin Nitrobenzene

	MeOTs	MeI
$\overline{k_i \times 10^4, l./(\text{mol sec})}$	6.10 (35°) ^a	25.8 (35°)°
$k_{\rm p} \times 10^4$, l./(mol sec)	$1.61 (66^{\circ})^{b}$	$1.33(56^{\circ})^{d}$
	4.24 $(77^{\circ})^{b}$	$2.87 (66^{\circ})^{d}$
	9.44 $(90^{\circ})^{b}$	$7.02 (77^{\circ})^{d}$
	$19.3 (100^{\circ})^{b}$	$17.4 \ (90^{\circ})^{d}$
$\Delta E_{\rm p}$, kcal/mol	17.9	17.3
A_{p} , $l./(mol sec)$	$2.2 imes 10^8$	$4.5 imes10^7$

^a [MeOZI]₀ = 0.93 mol/l., [MeOTs]₀ = 0.40 mol/l. ^b [MeOZI]₀ = 1.51 mol/l., [MeOTs]₀ = 0.30 mol/l. ^c [MeOZI]₀ = 0.95 mol/l., [MeI]₀ = 0.50 mol/l. ^d [MeoZI]₀ = 1.70 mol/l., [MeI]₀ = 0.25 mol/l.

then, eq 5 becomes

$$\ln \frac{[\mathbf{M}]_{t_1}}{[\mathbf{M}]_{t_2}} = k_{\mathfrak{p}}[\mathbf{I}]_0(t_2 - t_1)$$
(7)

The monomer concentration ratio, $[M]_{t_1}/[M]_{t_2}$, was obtained from the following equation (the peak assignment in Figure 1)

$$\frac{[\mathbf{M}]_{t_1}}{[\mathbf{M}]_{t_2}} = \frac{\{B + C - A - 2/3G\}_{t_1}}{\{B + C - A - 2/3G\}_{t_2}}$$
(8)

where $\{B + C - A - \frac{2}{3}G\}_{t_1}$ and $\{B + C - A - \frac{2}{3}G\}_{t_2}$ represent the integrated values of the noted peaks at times t_1 and t_2 , respectively. The area of peak A remained strictly constant during a kinetic run, and, hence, the validity of the above calculation was justified. A plot of eq 7 was linear, the slope of which gave $k_p = 4.24 \times 10^{-4} \text{ l./(mol sec)}$ at 77°. Similar kinetic analyses were made at other temperatures (Table I).

The rate of initiation (k_i) was so fast at polymerization temperatures that k_i was determined by a separate reaction of MeOZI with MeOTs at a lower temperature of 35°. The nmr spectrum clearly showed the occurrence of the initiation reaction (eq 1). According to the bimolecular reaction of eq 1 the rate of initiation is expressed by

$$-d[I]/dt = k_i[I][M]$$
(9)

Integration of eq 9 gives

$$\ln \left[\mathbf{I}\right]_{0} / \left[\mathbf{I}\right]_{t} = k_{i} \int_{0}^{t} \left[\mathbf{M}\right] \mathrm{d}t$$
 (10)

where $[I]_0$ is the initial concentration of MeOTs. A plot of eq 10 was linear, whose slope gave a value of $k_i = 6.10 \times 10^{-4}$ l./(mol sec) at 35° (Table I).

Polymerization by MeI. Figure 2 shows an nmr spectrum of the polymerization system initiated by MeI after 29 min at 77°, in which $[M]_0$ and $[I]_0$ were 1.70 and 0.25 mol/l., respectively. The presence of peak A at δ 4.97 characteristic of the 6-methylene protons (2 H) of the oxazinium ion indicates that the polymerization proceeded *via* an oxazinium iodide 6 propagating species. At 77° MeI was



consumed within 5 min and converted quantitatively into the propagating species, *i.e.*, $[P^*] = [I]_0$. In the region of peak B centered at δ 4.15 due to the 6-methylene protons (2 H) of the unreacted MeOZI, peak C appeared which was

Imino Ethers by MeOTS Initiator in Nitrobenzene or in CD ₃ CN						
	Me		Ph		Me	
$\overline{k_{ m i}} imes 10^4 \; ({ m l.}/({ m mol \; sec}))$	6.10ª	2.9^{a} 11.8 ^b	0.18ª	0.98	1.82^{b}	
$k_{ m p} imes10^4~({ m l./mol~sec})$	19 .3°	110° 0.44 ^b	2.53°	$(13,000)^d$ 19 ^b	$(120)^{d} \ 1 . 17^{b}$	
$\Delta E_{ m p}^{*} ~({ m kcal/mol}) \ A_{ m p} ~({ m l}./({ m mol}~{ m sec})$	$rac{17.9}{2.2 imes10^8}$	$rac{20}{3.6 imes10^9}$	$rac{21}{3.6 imes10^8}$	${25 \atop 7.5 imes10^{14}}$	$rac{19.1}{1.9 imes10^9}$	

 Table II

 Rate Constants and Activation Parameters in the Polymerizations of Cyclic

 Imino Ethers by MeOTS Initiator in Nitrobenzene or in CD₃CN

^a Data at 35° in nitrobenzene. ^b Data at 40° in CD₃CN. ^c Data at 100° in nitrobenzene. ^d Calculated values at 100° in CD₃CN. ^e T. Saegusa, H. Ikeda, and H. Fujii, *Macromolecules*, 6, 315 (1973).

due to the 4-methylene protons (2 H) of 6 and to openchain N-methylene protons (2 H) of 6. The integrated value of the latter methylene protons of 6 should be equal to two-thirds of that of peak G at δ 3.12 due to the N-methyl protons (3 H) at the nonpropagating chain end. Therefore, the same relationship as eq 8 could be employed.

The course of the MeI-initiated polymerization of MeOZI is similarly given as that of the MeOTs-initiated one (eq 1-3) involving an oxazinium ion propagating species 6; *i.e.*, the propagation is generally shown by



Therefore, the rate equation of propagation according to eq 4 can be applied. A linear plot of eq 7 was made, and a value of $k_{\rm p} = 7.02 \times 10^{-4}$ l./(mol sec) at 77° was obtained. Analogously, $k_{\rm p}$ values were determined at other temperatures (Table I).

The kinetics of the initiation was also carried out by a separate experiment at 35° in nitrobenzene. In this case a reaction of eq 12 took place exclusively in which $[M]_0$ and $[I]_0$ were 0.95 and 0.50 mol/l., respectively. A plot of eq 10

$$\underbrace{\overset{N}{\underset{Me}{\longrightarrow}}}_{Me} + \underbrace{MeI} \longrightarrow \underbrace{\overset{Me}{\underset{Me}{\longrightarrow}}}_{Me} \cdot I^{-} \quad (12)$$

was linear, and a value of $k_i = 25.8 \times 10^{-4}$ l./(mol sec) at 35° was obtained (Table I).

Activation Parameters of Propagation. The Arrhenius plots of k_p in Table I were all linear in both systems of MeOTs and MeI initiators, from which the activation parameters were calculated (Table I). The values of the activation parameters are very similar in both cases and compatible with the polymerization mechanism (eq 3 and 11) of an SN2 reaction between ionic propagating species (4 and 6) and MeOZI monomer.

The k_p values by the MeI initiator are somewhat larger than those of the MeOTs initiator, *e.g.*, 1.84 times larger at 90°. This kind of phenomena has often been observed in the polymerization of cyclic imino ethers where propagations proceeded *via* cyclic cationic propagating species. Namely, k_p values of the iodide counteranion were slightly bigger than those of the tosylate counteranion.^{1,6,7} This may be ascribed to the greater contribution of the free ion character in the case of the iodide counteranion than in that of the tosylate one.



Figure 2. Nmr spectrum of the polymerization mixture of MeOZI initiated with MeI in nitrobenzene after 29 min at 77°: $[M]_0 = 1.70$ mol/l., $[I]_0 = 0.25$ mol/l. Peak signs A, B, C, ... correspond to those of Figure 1.

Comparison of the Reactivity of MeOZI with Those of Other Cyclic Imino Ethers. In a series of kinetic studies on the polymerizations of cyclic imino ethers the reactivities of several monomers have been determined. With MeOTs as initiator, all the polymerizations of these monomers proceeded *via* an onium propagating species. Their reactivities, therefore, can be compared on the same basis (Table II).

The k_i values can be taken to represent nucleophilic reactivities of monomers toward a common electrophile of

$$\begin{array}{c}
\overset{N}{\underset{R}{\longrightarrow}} (CH_2)_n + MeOTs \xrightarrow{k_1} \\
MeOZI, R = CH_3; n = 3 \\
OZI, R = H; n = 3 \\
PhOZI, R = C_6H_5; n = 3 \\
OZO, R = H; n = 2 \\
MeOZO, R = CH_3; n = 2 \\
MeOZO, R = CH_3; n = 2 \\
Me \xrightarrow{N} (CH_2)_n \cdot OTs^{-} (13)
\end{array}$$

MeOTs (eq 13). From the k_i values in Table II, the nucleophilic reactivities are in the order of MeOZI > OZI > MeOZO > PhOZI > OZO; i.e., six-membered monomersare by far more nucleophilic than the five-membered ones. The polymerization reactivities reflected by k_p values, however, are in the following order: OZO > MeOZO > OZI > MeOZI > PhOZI. It is believed in the cationic ring-opening polymerization that the k_{p} value is governed mainly by two factors, *i.e.*, the nucleophilicity of the monomer and the tendency of the propagating species to open.8 The order of the k_p values is not parallel to that of the former factor reflected by k_i values and therefore it is not unreasonable to conclude that the ring-opening tendency of the propagating species determines the value of k_{p} . It follows that in the polymerization of 1,3-oxazine monomers the ring-opening reactivity of the propagating species is in the following order: ~~OZI+ > ~~PhOZI+ > ~~MeOZI+. A similar order of the reactivity has already been noted in the series of 2-oxazolines,⁹ e.g., $\sim OZO^+ > \sim PhOZO^+ > \sim MeOZO^+$. In addition, the entropy factor (or the frequency factor, A_p) seems to be important as well. It has been established that k_p values were not much affected by changing of the solvent from nitrobenzene to CD_3CN . Therefore, it is meaningful to compare k_p values at 100° in nitrobenzene and CD_3CN in Table II. These values of five monomers are in the range of 0.00025–1.3 l./(mol sec).

Finally, the effect of a methyl group on k_i and k_p values is another point of interest. Introduction of a methyl group at the 2 position of the OZI ring made the k_i value more than double but made the k_p value decrease by 5.7 times (Table II). From the above discussion, this behavior may be ascribed to the decreased ring-opening tendency of 2methyl-5,6-dihydro-4H-1,3-oxazinium ion (4 and 6) in comparison to that of unsubstituted 5,6-dihydro-4H-1,3-oxazinium ion.

References and Notes

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Poly(2-vinylfluorenone). I. Synthesis and Polymerization of 2-Vinylfluorenone

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ABSTRACT: The synthesis and polymerization characteristics of the new monomer, 2-vinylfluorenone, are reported. Previous attempts to prepare 2-vinylfluorenone polymers by oxidation of poly(2-vinylfluorene) were unsuccessful, leading to low yields of soluble copolymer products containing approximately 50 mol % of fluorenone units. Using an improved oxidation procedure we have succeeded in increasing the degree of oxidation of fluorene to fluorenone groups to 90% without any loss of solubility. The monomer synthesis and polymerization, however, provide the only unequivocal route to homopolymers of 2-vinylfluorenone. 2-Vinylfluorenone can be readily polymerized and copolymerized by free-radical techniques to give high molecular weight, $M_n > 10^5$, soluble polymers. The monomer does not polymerize by cationic or anionic methods. Free-radical polymerization of 2-vinylfluorenone in solution exhibits a very unusual concentration effect which remains unexplained.

Vinyl polymers containing aliphatic and aromatic carbonyl groups have been widely studied in recent years because of their relevance to photodegradation and photostabilization phenomena. Guillet and his coworkers have reported the photochemical behavior of a variety of poly(ethylene-co-carbon monoxide) materials¹ and poly(alkyl and aryl vinyl ketones).^{2,3} Geuskens, *et al.*, have also studied energy-transfer processes and photolytic reactions in carbonyl containing polymers such as poly(methyl vinyl ketone),⁴ poly(phenyl vinyl ketone),⁵ and poly(vinylbenzophenone).⁶

Braun first proposed⁷ a synthetic procedure for preparing a fluorenone-containing vinyl polymer: amyl nitrite oxidation of poly(2-vinylfluorene) to the corresponding poly(2vinylfluorenone). Gipstein, Hewett, and Need⁸ investigated this synthetic route and developed a more direct oxidation procedure using chromium trioxide in glacial acetic acid. Oxidation of poly(2-vinylfluorene) using these conditions gave a product from which a soluble fraction could be extracted. Analysis of the polymer showed it to be an approximately 50:50 copolymer of 2-vinylfluorene and 2vinylfluorenone. The insoluble fraction gave a chemical analysis more consistent with a higher degree of oxidation, *i.e.*, a poly(2-vinylfluorenone) homopolymer. Similarly, oxidation of copolymers containing 2-vinylfluorene gave soluble and insoluble product mixtures, the soluble fractions consisting of terpolymers resulting from partial oxidation.

The very appreciable changes in the polymer molecular weights and molecular weight distributions, and the high yields of insoluble products, clearly indicate the severity of these oxidation procedures. Using much milder oxidation conditions, e.g., benzyltrimethylammonium hydroxide:oxygen in pyridine at 0°, we have been able to oxidize poly(2vinylfluorene) to a much higher degree (80–90%) in high yield and without any appreciable molecular weight variations and insolubilization. However, even under optimum conditions it was not possible to achieve complete oxidation, *i.e.*, a homopolymer of 2-vinylfluorenone. This was achieved, however, *via* synthesis and polymerization of the new monomer, 2-vinylfluorenone.



Experimental Section

2-Vinylfluorene (1) was synthesized from fluorene-2-carboxaldehyde (Aldrich) using the Wittig procedure. Triphenylmethylphosphonium bromide (36 g; 0.1 mol) in 500 ml of dry THF was