

Isomerization Polymerization of 2-Oxazoline. II. Propagating Species and Mechanism of Unsubstituted 2-Oxazoline Polymerization

Takeo SAEGUSA, Hiroharu IKEDA, and Hiroyasu FUJII

*Department of Synthetic Chemistry, Kyoto University,
Kyoto, Japan.*

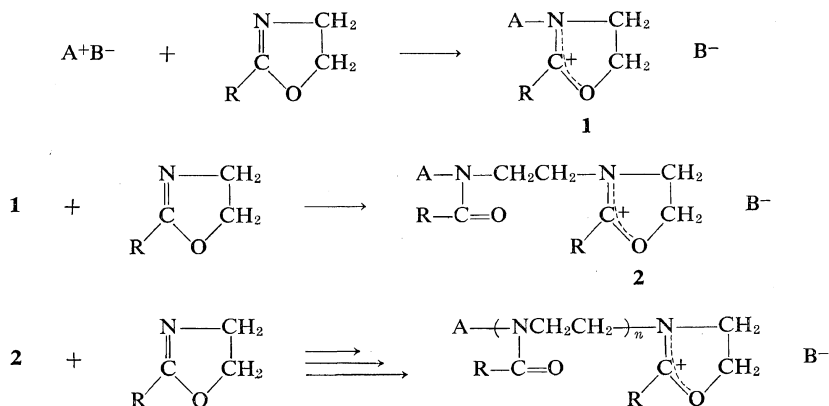
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ABSTRACT: The propagating species and the mechanism of the cationic polymerization of 2-oxazoline(OXZ) were investigated. Equimolar reactions of OXZ with polymerization catalysts were directly followed by NMR spectra. In the polymerization with methyl tosylate(MeOTs) catalyst, the propagating species was shown to be an oxazolinium ion. In the reaction of OXZ with BF_3OEt_2 in acetonitrile at 40°C , the $\text{BF}_3\text{-OXZ}$ complex was isolated in a quantitative yield. On the other hand, in the reaction of OXZ with CH_3I at 80°C , no oxazolinium ion was detected, but *N*-(β -iodoethyl)-*N*-methylformamide **3** was isolated. **3** was taken to have been derived from the ring-opening reaction of unstable oxazolinium iodide which was transiently formed by the reaction of OXZ with CH_3I . In addition, **3** itself caused the OXZ polymerization and gave a similar polymer yield to that of the polymerization by CH_3I . Thus, the propagating species of the OXZ polymerization by CH_3I was assumed to be $\sim\text{N}(\text{CHO})\text{CH}_2\text{CH}_2\text{N}(\text{CHO})\text{CH}_2\text{CH}_2\text{I}$. The initiating behavior of alkyl halides and the effect of solvents upon the OXZ polymerization demonstrated a close-relationship between the OXZ polymerization by alkyl halide catalyst and the Menshutkin reaction.

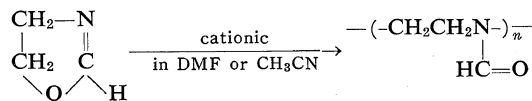
KEY WORDS 2-Oxazoline / Cationic Polymerization / Poly(*N*-formylethyleneimine) / Propagating Species / Oxazolinium Ion / *N*-(β -iodoethyl)-*N*-methylformamide / Menshutkin Reaction /

Cationic polymerization of 2-substituted-2-oxazolines has been widely studied,¹⁻⁴ and the following schemes involving the oxazolinium ion has been assumed without direct experimental support.

On the other hand, the polymerization of unsubstituted 2-oxazoline(OXZ) was not reported before our recent paper.⁵ We first succeeded in the cationic polymerization of OXZ by the isolation of the pure monomer and the use of



aprotic solvents such as dimethylformamide (DMF) and acetonitrile as the polymerization medium.⁵ The OXZ polymer is crystalline and has a structure of poly(*N*-formylethyleneimine).⁵



In the present studies, the nature of the propagating species and the mechanism of the OXZ polymerization initiated by several catalysts were examined on the basis of the equimolar reaction of OXZ with the polymerization catalysts.

EXPERIMENTAL

Reagents

OXZ was prepared and purified as before.⁵ BF_3OEt_2 , CH_3I , and methyl tosylate (MeOTs) were purified by distillation under nitrogen. DMF and acetonitrile were purified by distillation under nitrogen and dried by molecular sieves 4A. Commercial reagent of acetonitrile- d_3 (CD_3CN) was dried by molecular sieves 4A and distilled under nitrogen.

Polymerization

Polymerization was carried out in a glass tube under nitrogen. Firstly, the catalyst was added to a mixture of monomer and solvent at 0°C in a tube, and then the tube was sealed and heated. After polymerization methanol was

added to the reaction mixture, and the precipitated polymer was isolated by filtration and dried *in vacuo*. The washings were evaporated under reduced pressure and an oily oligomer was obtained as the residue.

Equimolar Reaction of OXZ with Catalyst

All operations were carried out under nitrogen.

NMR Study. The desired amount of catalyst was slowly added to a stirred solution of monomer in CD_3CN which had been cooled to -30°C . Then the mixture was kept at a constant temperature. After the reaction, the reaction mixture was immediately subjected to NMR measurement.

Reaction of OXZ with BF_3OEt_2 . To a solution of 7.5 mmol of OXZ in 3 ml of CH_3CN was added 7.5 mmol of BF_3OEt_2 at -30°C with stirring. The mixture was stirred at 40°C for 10 min. Then the evaporation of solvent under a reduced pressure gave a crystalline powder. The material was reprecipitated from the acetonitrile solution by ether to yield 1.02 g (98%) of crystalline powder: IR (Nujol) 1662 ($\text{C}=\text{N}$ —) 1218 ($\text{C}-\text{O}-\text{C}$), and 902, 867, 863 cm^{-1} (skeletal); NMR (CD_3CN) τ 2.08 (s, 1, $\text{N}=\text{CH}$ —), 5.15 (t, 2, $-\text{CH}_2-\text{O}$), and 6.07 ppm (t, 2, $-\text{CH}_2-\text{N}$).

Reaction of OXZ with CH_3I . In a glass tube, 60 mmol of CH_3I was added at 0°C with stirring to a 60 mmol of OXZ in 10 ml of acetonitrile. Then the solution was stirred at 80°C for 10 min in a sealed tube. By GLPC and NMR analyses, the conversion of OXZ was found to be quantitative and that of CH_3I was 81%.

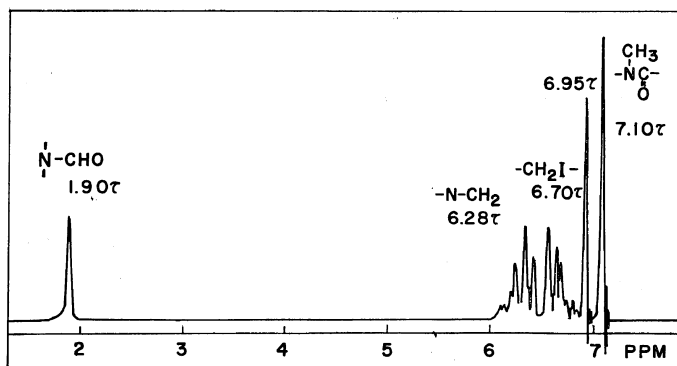


Figure 1. NMR spectrum of $\text{ICH}_2\text{CH}_2\text{NCHO}$ 3 (in CHCl_3).

CH_3

After the solvent and CH_3I were removed under vacuum at room temperature, the residue was extracted twice with 20 ml of anhydrous ether. The ether extract was distilled to give 6.47 g (30.4 mmol, 51%) of a fraction boiling at 67–74°C (0.1 mm), which was identified as *N*-(β -iodoethyl)-*N*-methylformamide **3**. *Anal.* Calcd for $\text{C}_4\text{H}_8\text{INO}$: C, 22.55; H, 3.79; I, 59.58; N, 6.58; O, 7.51; mol wt, 213. Found: C, 22.49; H, 3.93; I, 59.67; N, 6.89; O, 7.68; mol wt, 213 (mass spectroscopy), NMR (Figure 1, CDCl_3) agreed well with that of the authentic sample. The ether insoluble part was a reddish oil (3.32 g), which was shown by NMR to be a mixture of the OXZ oligomers.

Preparation of *N*-(β -chloroethyl)-*N*-methylformamide **4**

4 was prepared by the reaction of *N*-(β -hydroxyethyl)-*N*-methylformamide with thionyl chloride/pyridine in CHCl_3 : yield 65%; bp 97.5°C (3 mm); NMR (CDCl_3) τ 1.92 (s, 1, CHO), 6.32 (m, 4, CH_2), and 6.99 (d, 3, NCH_3). *Anal.* Calcd for $\text{C}_4\text{H}_8\text{ClNO}$: C, 39.52; H, 6.63; Cl, 29.16; N, 11.52. Found: C, 39.23; H, 6.91; Cl, 29.29; N, 11.40.

Preparation of *N*-(β -iodoethyl)-*N*-methylformamide **3**

3 was prepared by the reaction of **4** with NaI in acetone. The product was a slightly yellow liquid: yield 25%; bp 89°C (0.2 mm); IR 1667 cm^{-1} (amide $\text{C}=\text{O}$); NMR (CDCl_3) τ 1.90 (s, 1, CHO), 6.28 (m, 2, CH_2N), 6.70 (m, 2, CH_2I),

and 7.03 (d, 3, CH_3N); *Anal.* Calcd for $\text{C}_4\text{H}_8\text{INO}$: C, 22.55, H, 3.79; I, 59.58; N, 6.85; O, 7.51; mol wt, 213. Found: C, 22.62; H, 3.86; I, 58.74; N, 7.04; O, 7.87; mol wt, 213 (mass spectroscopy).

NMR Spectroscopy

NMR spectra were taken on Varian T-60 instrument using TMS as internal standard.

Molecular Weight

The molecular weight of the polymer was measured using a vapor pressure osmometer (Hitachi-Perkin-Elmer model 115) in water at 59°C.

RESULTS AND DISCUSSION

Equimolar reactions of OXZ with several polymerization catalysts⁵ were carried out in order to identify the real propagating species and to examine the polymerization mechanism.

Reaction of OXZ with MeOTs

An equimolar reaction mixture of OXZ with MeOTs in CD_3CN at 60°C for 10 min was examined by NMR spectrum (Figure 2). The peaks assignable to the oxazolinium salt were observed. In addition, the absorption peaks of oxazolinium tosylate were distinguished from the corresponding peaks of the unreacted OXZ and MeOTs. Therefore, the concentrations of the species in the reaction mixture were successfully determined. The percent conversion of the catalyst was 26%, which was calculated from

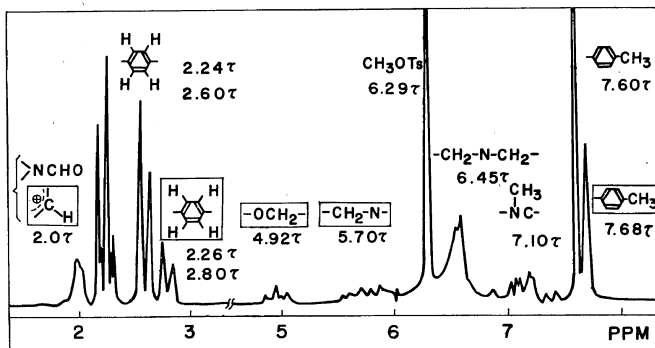
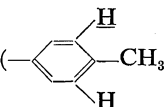


Figure 2. NMR spectrum of equimolar reaction of oxazoline with methyl tosylate in CD_3CN at 60°C: oxazoline, 2.29 mol/l; methyl tosylate, 2.29 mol/l. The groups in rectangles are those of the oxazolinium salt.

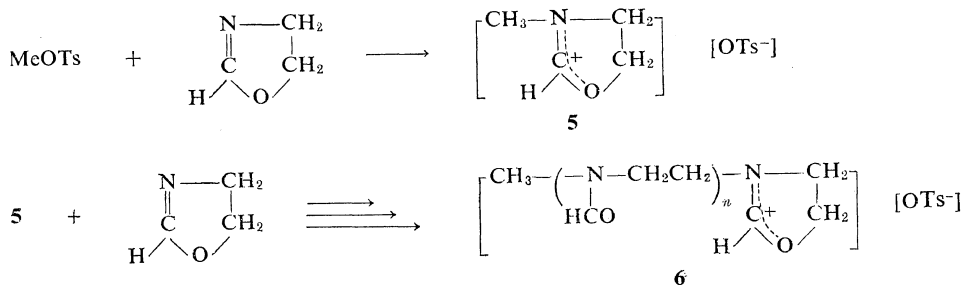
Mechanism of 2-oxazoline Polymerization

the peaks at τ 2.80 () of reacted

MeOTs) and τ 2.60 (unreacted MeOTs). The conversion of monomer was shown to be quantitative. No peak of monomer was observed and the peak area at τ 2.0 =NCHO— of oxazolinium salt and the formyl hydrogen, coincided with the stoichiometric amount of the fed monomer. The peak at τ 4.92 was reasonably assigned to the *O*-methylene protons of the oxazolinium ion at the growing polymer end, since the peaks of *O*-methylene protons of the oxazolinium salts derived from the reactions of 2-methyl- and 2-phenyl-2-oxazolines with MeOTs in ether, have appeared at similar regions (τ 5.20 and 4.93 ppm,

at 80°C, no oxazolinium ion was observed. Instead, **3** was obtained as the main product (conversion 51%). The structure of **3** was established by comparing the analytical data with those of an authentic sample prepared by a separate method (see Experimental section). The other product of this reaction was a linear oligomer of OXZ. These results suggest that in the reaction of OXZ with CH₃I, *N*-methyl-oxazolinium iodide **7** was transiently formed as an unstable intermediate, which was instantaneously converted to **3** by the ring-opening with isomerization. The oligomer **8** was formed by the repetition of the same type of process.

In an equimolar reaction at a lower temperature of 60°C, oxazolinium salt was not observed, either, in spite of the presence of a fairly



respectively).⁶ The concentration of oxazolinium salt determined by the peak area at τ 4.92 agreed with the value determined on the basis of the conversion percent of the MeOTs (tosylate anion) catalyst.

The concentration (0.59 mol/l) of tosylate anion determined by the peaks at τ 2.80 was almost the same as that (0.54 mol/l) of the terminal methyl group of —N—CH₃ at τ 7.10. Cor-

CHO

respondingly the peak of N—CH₃ of the oxazolinium ring (at τ 6.50) was very small. From these results it is clear that the reaction of OXZ with MeOTs initially gave *N*-methyl-2-oxazolinium tosylate **5** which promptly reacted with monomer to give oligomeric oxazolinium salt **6**.

Reaction of OXZ with CH₃I

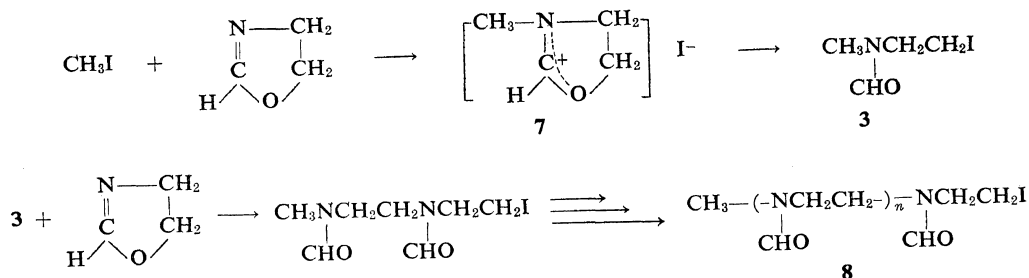
In an equimolar reaction of OXZ with CH₃I

large amount of unreacted monomer (conversion 41%).

Polymerization by Alkyl Halide Initiators

The polymerization of OXZ was carried out using **3** as well as various alkyl halide initiators. The results are shown in Table I. **3** gave a similar yield of polymer to that of polymerization by CH₃I. This fact supports the above assumption regarding the mechanism. No catalytic activity, however, was shown with **4**, which was the chlorine analogue of **3**. Similarly, butyl iodide was found to be active as catalyst, but butyl bromide showed much decreased activity and butyl chloride showed no catalytic activity at all.

Thus the species having the structure of ~N(CHO)CH₂CH₂I are taken to be the propagating species of the OXZ polymerization by CH₃I catalyst.



This finding provides a striking contrast to the equimolar reaction of 2-methyl-2-oxazoline with CH_3I , in which the formation of a considerable amount of the 2-methyl oxazolinium iodide species was suggested⁷ and observed by NMR.⁶

As to the effect of the solvent, the use of toluene instead of acetonitrile resulted in a poor yield, as observed in the polymerization by BF_3OEt_2 .⁵

Table I. Polymerization of 2-oxazoline by alkyl halides^a

| Alkyl halides | Polymer yield, % |
|---|------------------|
| CH_3I | 30 |
| $\text{HCON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{I}$ | 24 |
| $\text{HCON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Cl}$ | 0 |
| $n\text{-C}_4\text{H}_9\text{I}$ | 18 |
| $n\text{-C}_4\text{H}_9\text{Br}$ | 6.6 |
| $n\text{-C}_4\text{H}_9\text{Cl}$ | 0 |
| CH_3I^b | 4.0 |

^a 2-oxazoline, 3.2 mol/l; catalyst, 0.032 mol/l; solvent, CH_3CN ; 80°C, 5 hr.

^b Solvent, toluene.

All these reactions are interestingly compared with the reactivities of alkyl halides and the solvent effect in the Menshutkin reaction^{8,9} in which quarternary ammonium salt is formed by the reaction of tertiary amine with alkyl halide.



The reactivities of alkyl halides in the Menshutkin reaction have been shown to decrease in the order $\text{RI} > \text{RBr} \gg \text{RCl}$. In addition, the reaction rate was much influenced by the nature of the solvent. For example, in the re-

action of Et_3N with EtI , the rate constants at 70°C were in a ratio of 3.6 : 16 : 188 in toluene, ether, and benzonitrile, respectively. These observations suggest the similarity in the mechanism of this reaction to alkyl halide-catalyzed polymerization of OXZ.

Reaction of OXZ with BF_3OEt_2

A crystalline OXZ- BF_3 complex was isolated in a quantitative yield from an equimolar reaction of OXZ with BF_3OEt_2 in CH_3CN at 40°C, which was suggested by its NMR and IR spectra, and no other product was observed in the NMR spectrum search of the reaction mixture. Even when another equimolar amount of OXZ was added to the OXZ- BF_3 complex at 40°C, no reaction took place. But the reaction at 60°C gave a large amount of polymer. The initiating and propagating species of this case have not been examined.

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