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**Polymerization of 2-Oxazolines. IV.
The Structure and the Reactivity of
2-Substituted-2-oxazolines and
Oxazolinium Perchlorates***

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ABSTRACT

In order to elucidate the structure and the stability of the growing cationic end in the polymerization of 2-oxazolines, the reactions of 2-bromoethylbenzamide with silver salts such as silver perchlorate, tetrafluoroborate, nitrate, nitrite, cyanate, and acetate were investigated. The reactions with silver perchlorate and tetrafluoroborate gave the 2-phenyl-2-oxazolinium salt (intramolecular O-alkylation product) quantitatively, whereas the reaction with silver nitrate gave the corresponding alkyl nitrate (straight-chain product). For the reactions with silver nitrite, cyanate and acetate, both products were obtained. In order to elucidate the ring-opening reactivity of the

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oxazolinium cation, the ring-opening addition reaction of N-methyl-2-oxazolinium perchlorates with pyridine was investigated. It was found that N-methyl-2-phenyl-2-oxazolinium perchlorate was more reactive toward the nucleophilic ring-opening reaction than was N-methyl-2-methyl-2-oxazolinium perchlorate. The mutual copolymerization of 2-phenyl-2-oxazoline with the other 2-substituted-2-oxazoline such as 2-methyl-, 2-isopropyl-, and 2-benzyl-2-oxazoline indicated that the monomer reactivity ratio r_2 was much larger than unity, whereas r_1 was very much smaller. Based on these results, the influence of the structure and the reactivity of the monomer and the growing cationic end of the polymerizability of 2-oxazolines are discussed.

INTRODUCTION

In the previous papers of this series the ring-opening polymerizations of 2-phenyl-2-oxazoline initiated with oxazolinium perchlorate have been investigated in connection with references to the mechanism of polymerization [1], the kinetics of the solution polymerization [2], and the influence of the polymerization media on the propagation reaction [3]. From these investigations it was suggested that the active propagating species is a kind of N-alkyl-2-oxazolinium perchlorate.

It has been well known that the cationic polymerizability of heterocyclic monomers such as cyclic ethers is controlled by the power of nucleophilic coordination of monomer toward a growing cationic end, and by the cationic ring-opening and bond-forming power of the growing cationic heterocycle; that is, its stability [4, 5].

To the best knowledge of the present authors, however, little attention has been paid to the reactivity of 2-oxazolines and the stability of the growing cationic end, except the recent work reported by Saegusa and his co-workers [6].

In the present paper a novel preparative method for the formation of 2-oxazolinium cation and the cationic mutual copolymerization of 2-phenyl-2-oxazoline with the other 2-substituted-2-oxazoline are investigated in order to elucidate the structure and the reactivity of 2-substituted-2-oxazolines and oxazolinium perchlorates.

EXPERIMENTAL

Materials2-Bromoethylbenzamide

2-Bromoethylbenzamide was obtained by the simultaneous addition of benzoyl chloride (G.R. grade, 0.27 mole) and 5-N sodium hydroxide (110 ml) to a stirred ice-cooled solution of 2-bromoethylamine hydrobromide (G.R. grade, 0.26 mole) in water (110 ml). After stirring for 2 hr, the precipitated white solid was collected, washed with water, and dried in vacuo; yield 92%, mp 100-102°C (Ref. 7; 100-102°C).

Analysis: Calculated for $C_9H_{10}NOBr$: C, 47.39; N, 6.14; Br, 35.03. Found: C, 47.28; N, 6.02; Br, 35.25.

2-Bromoethyl-N-methylbenzamide

2-Bromoethyl-N-methylamine hydrobromide was prepared from N-methylethanamine (G.R. grade) and hydrobromic acid (sp gr, 1.42) according to the method of Cortese [8]: mp 69-71°C.

Analysis: Calculated for $C_3H_9NBr_2$: C, 16.46; N, 6.40; Br, 73.00. Found: C, 16.61; N, 6.36; Br, 72.81.

2-Bromoethyl-N-methylbenzamide was obtained from the Schotten-Baumann reaction of 2-bromoethyl-N-methylamine hydrobromide and benzoyl chloride in ice-cooled acetone solution with the use of sodium hydroxide in methanol solution as an acid acceptor in a manner similar to that mentioned above. The white solid soluble in acetone and methanol, but insoluble in diethyl ether, is identified as N-methyl-2-bromoethylbenzamide by IR spectrum. The isolated product was used without further purification.

N-Methyl-2-oxazolinium Iodides

N-Methyl-2-phenyl- and N-methyl-2-methyl-2-oxazolinium iodides were prepared from the quaternization reactions of the corresponding 2-oxazolines with methyl iodide at 60°C in dark (feed molar ratio of methyl iodide to 2-oxazoline: 3.0). These were purified by several reprecipitations from methanol-diethyl ether solution.

N-Methyl-2-phenyl-2-oxazolinium iodide: mp 106-108°C.

Analysis: Calculated for $C_{10}H_{12}NOI$: C, 41.64; N, 4.84; I, 43.89. Found: C, 41.54; N, 4.90; I, 43.16.

N-Methyl-2-methyl-2-oxazolinium iodide: hygroscopic yellowish solid. Analysis: Calculated for $C_5H_{10}NOI$: C, 26.45; N, 6.14; I, 55.89. Found: C, 26.51; N, 6.11; I, 54.27.

Anion Exchange Reaction of N-Methyl-2-oxazolinium Iodides with Silver Perchlorate

N-Methyl-2-phenyl- and N-methyl-2-methyl-2-oxazolinium perchlorates were prepared from the anion exchange reactions of the corresponding N-methyl-2-oxazolinium iodides with silver perchlorate (G.R. grade) in nitrobenzene at room temperature in the dark. The white solids isolated from diethyl ether were identified to be N-methyl-2-phenyl- and N-methyl-2-methyl-2-oxazolinium perchlorates, respectively, by elementary analysis (Table 2) and spectroscopic analyses (Figs. 4 and 5).

Reaction of 2-Bromoethylbenzamides with Silver Salts

The equimolar reaction of 2-bromoethylbenzamide or 2-bromoethyl-N-methylbenzamide with silver salts such as silver perchlorate, nitrate, tetrafluoroborate, nitrite, cyanate, and acetate in nitrobenzene at room temperature in the dark was carried out with vigorous stirring (the feed molar concentration of the reactants: 0.220 mole/liter). For the reactions with silver perchlorate, tetrafluoroborate, and nitrate, the white powdery solid precipitated from diethyl ether was obtained after filtration of the silver bromide formed.

Ring-Opening Reaction of N-Methyl-2-oxazolinium Perchlorates with Pyridine

The equimolar reactions of N-methyl-2-phenyl- and N-methyl-2-methyl-2-oxazolinium perchlorates with pyridine were carried out in nitrobenzene at 70°C (the feed molar concentration of the oxazolinium perchlorate and pyridine; 0.200 mole/liter). The white solid was obtained by precipitation from diethyl ether.

N-Methyl-2-benzamidoethyl pyridinium perchlorate: mp 116°C. Analysis: Calculated for $C_{15}H_{17}N_2O_5Cl$: C, 52.87; N, 8.22; Cl, 10.40. Found: C, 53.06; N, 8.28; Cl, 10.22.

N-Methyl-2-acetamidoethyl pyridinium perchlorate: hygroscopic solid. Analysis: Calculated for $C_{10}H_{15}N_2O_5Cl$: C, 43.10; N, 10.05; Cl, 12.72. Found: C, 43.41; N, 10.71; Cl, 12.65.

Preparation of 2-Oxazolines

2-Phenyl-2-oxazoline(Ph-Oz) was prepared by the same method as described previously [1]. 2-Methyl-2-oxazoline(Me-Oz), 2-isopropyl-2-oxazoline(Ip-Oz), and 2-benzyl-2-oxazoline(Bz-Oz) were prepared from the isomerization reaction of the corresponding N-acylethylenimine with the use of sodium iodide as catalyst at 70°C: N-acylethylenimines were prepared from Schotten-Baumann reactions of ethylenimine and the corresponding acid chlorides in acetone at -30°C. The monomers were purified by several fractionations under reduced pressure (Ph-Oz: 129°C/13 Torr; Me-Oz: 110°C, Ref. 9, 110-111°C; Ip-Oz: 136°C, Ref. 9, 136-139°C; Bz-Oz: 94°C/15 Torr).

Copolymerization Procedures

Copolymerization was carried out at 120°C in a sealed ampoule under reduced pressure, according to the manner described previously [1, 2] (total oxazoline monomer: 1.54×10^{-2} mole; 2-phenyl-2-oxazolinium perchlorate as an initiator: 1.54×10^{-4} mole; and N,N-dimethylacetamide as solvent: 3.0 ml). The copolymer was precipitated from a large amount of n-hexane, dried at 60°C in vacuo, and weighed.

Physical Analysis

The IR spectrum was measured by a JASCO Grating Infrared Spectrometer, Model DS-403G. The shift value of the O—D stretching vibration of methanol-d in various monomers in IR spectra was carried out according to the method reported in Ref. 10.

The NMR spectrum was measured by a Varian H-100 Spectrometer (100 MHz) with tetramethylsilane as an internal standard at room temperature.

The copolymer composition was determined by elementary analysis and NMR spectrometry.

RESULTS AND DISCUSSION

Formation of the Oxazolinium Cation

In a previous paper [1], it was suggested that the polymerization of 2-oxazolines initiated by the oxazolinium salts proceeds through two routes: one is the direct quaternization reaction of the oxazolinium cation and monomer (Fig. 1, Route 1), and the other is composed of the rearrangement reaction of the oxazolinium cation and the subsequent quaternization reaction (Fig. 1, Route 2), and that these different mechanisms may be caused by the kind of the counterion used. (See Fig. 1, where X^- denotes the counterion.)

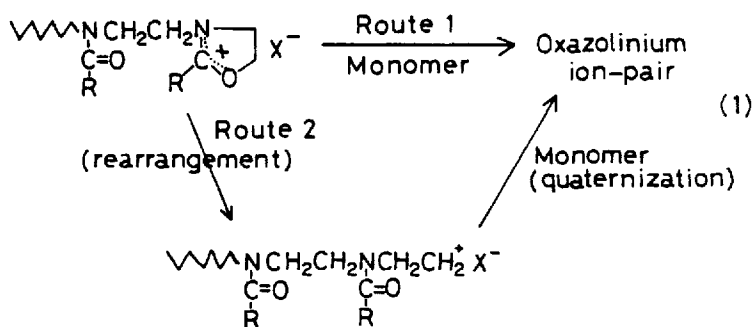


FIG. 1. The possible routes of the ring-opening polymerization of 2-oxazolines.

In order to elucidate the more detailed mechanism of the incorporation of monomer into a growing cationic end, the influence of the anionic group of the salts in the reaction of 2-bromoethylbenzamide or 2-bromoethyl-N-methylbenzamide with silver salts such as silver perchlorate, tetrafluoroborate, nitrate, nitrite, cyanate, and acetate was investigated. As can be seen in Table 1, the reactions of 2-bromoethylbenzamide with silver salts gave the quantitative amount of silver bromide in nitrobenzene in the dark. Table 1 shows that the different types of reaction products depend on the kind of the anionic group of silver salt used as mentioned below.

TABLE 1. The Reactions of 2-Bromoethylbenzamide with Silver Salts in Nitrobenzene

Run No.	Silver salt	AgBr (%)	Product			IR spectrum (cm ⁻¹)
			2-Phenyl-2-oxazolinium salt	2-Phenyl-2-oxazoline	Open-chain derivative	
1	AgClO ₄	95.0	0	-	-	1637 ($\nu_{C=N^+}$)
2	AgBF ₄	93.4	0	-	-	1648 ($\nu_{C=N^+}$)
3	AgNO ₃	95.1	-	-	0	Amide II 1630, 845 (ν_{ONO_2} , ν_{N-O})
4	AgNO ₂	99.3	-	0	0	Oxazoline amide II 1635 (ν_{NO_2})
5	Ag(CH ₃ COO)	98.6	-	0	0	Oxazoline amide II 1754 (ν_{COO-C})
6	AgCN	99.2	-	0	0	Oxazoline amide II ca 2100 ($\nu_{C=N}$ or $\nu_{N=C}$)

For the reactions with silver perchlorate (AgClO_4) or tetrafluoroborate (AgBF_4), the IR spectra of the white powdery solids precipitated from diethyl ether displayed the disappearance of the characteristics of the secondary amide linkage, whereas they showed the characteristic absorption bands attributed to the oxazolinium cation ($\nu_{\text{C}=\text{N}}$, $1635\text{--}1648\text{ cm}^{-1}$; $\nu_{\text{C}-\text{O}}$, ca 1270 cm^{-1}); and the ring skeletal vibrations, $900\text{--}1000\text{ cm}^{-1}$), as shown in Fig. 2. The NMR spectra of the reaction mixtures showed the

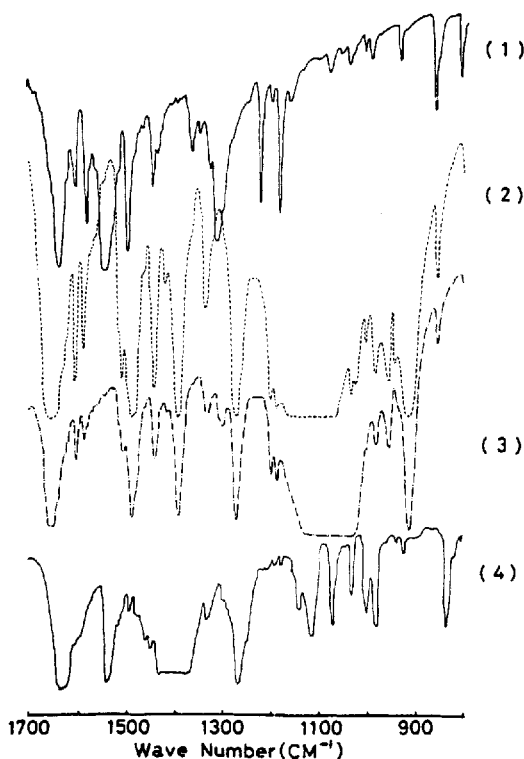


FIG. 2. The IR spectra of the reaction products from 2-bromoethylbenzamide and silver salts. (1) 2-Bromoethylbenzamide, (2) 2-phenyl-2-oxazolinium perchlorate, (3) 2-phenyl-2-oxazolinium tetrafluoroborate, and (4) 2-benzamidoethyl nitrate.

disappearance of proton signals attributed to methylene-methylene in 2-bromoethylbenzamide, and displayed two triplets attributable to oxazolinium heterocycle (Fig. 3). In addition, the elementary

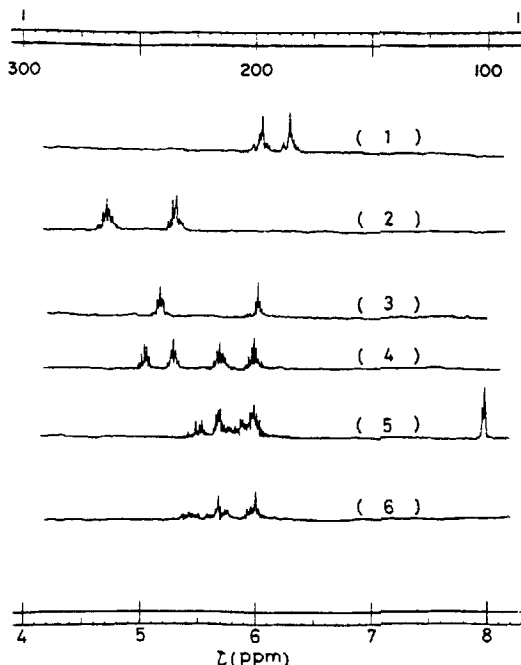


FIG. 3. The NMR spectra of the reaction mixtures of 2-bromoethylbenzamide with silver salts. (1) 2-Bromomethylbenzamide (BA), (2) BA + AgBF_4 , (3) BA + AgNO_3 , (4) BA + AgNO_2 , (5) BA + $\text{Ag}(\text{CH}_3\text{COO})$, (6) BA + AgCN (measured in nitrobenzene).

analysis of these products indicated the equimolar composition of 2-phenyl-2-oxazoline and perchloric acid or hydrofluoroboric acid (Table 2), respectively. The reaction products from 2-bromoethyl-N-methylbenzamide and AgClO_4 or AgBF_4 are identical with the reaction products of the anion exchange reaction of N-methyl-2-phenyl-2-oxazolinium iodide with AgClO_4 or AgBF_4 (Fig. 5 and Table 2).

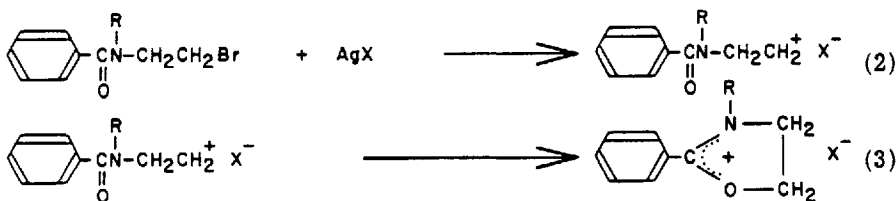
From these results the products from the reactions of

TABLE 2. The Elementary Analysis of the Reaction Products from 2-Bromoethylbenzamidates and Silver Salts

Run No.	Product	Melting point (°C)	Formula	Calculated (%)			Found (%)		
				C	N	Cl	C	N	Cl
1	2-Phenyl-2-oxazolinium perchlorate	150-151	$C_9H_{10}NO_5Cl$	43.65	5.66	14.32	43.68	5.75	14.43
2	2-Phenyl-2-oxazolinium tetrafluoroborate	115-116	$C_9H_{10}NOBF_4$	46.00	5.96	-	45.25	6.26	-
3	2-Benzamido-ethyl nitrate	122-123	$C_9H_{10}N_2O_4$	51.07	13.33	-	49.95	12.80	-
4	N-Methyl-2-phenyl-2-oxazolinium perchlorate	180-182	$C_{10}H_{12}NO_5Cl$	45.90	5.35	13.55	45.62	5.39	13.28
5	N-Methyl-2-methyl-2-oxazolinium perchlorate	^a	$C_5H_{10}NO_5Cl$	30.09	7.02	17.76	29.90	7.12	17.23

^aHygroscopic white solid at room temperature.

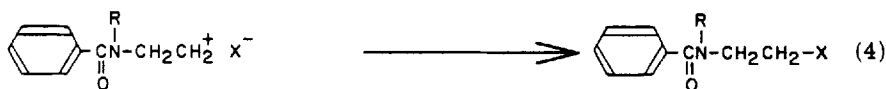
2-bromoethylbenzamide with AgClO_4 and AgBF_4 are identified as the corresponding 2-phenyl-2-oxazolinium salts. These facts indicate that the oxazolinium salts are produced by the ring-closure reactions



where X denotes a perchlorate or tetrafluoroborate ion, and R denotes a proton or methyl group.

This means that the unstable carbonium ion produced by the reaction of the corresponding alkyl bromide with silver salts (Eq. 2) was attacked nucleophilically by the oxygen atom with large electronegativity to give a more stable oxazolinium cation (intramolecular O-alkylation product).

On the other hand, for the reaction with silver nitrate (AgNO_3), the IR spectrum of the white powdery product displayed no characteristic absorptions attributed to the oxazoline and oxazolinium heterocycles, but instead the characteristic absorptions attributed to the secondary amide linkage (1640 and 1550 cm^{-1}) and alkyl nitrate (ν_{ONO_2} , 1630 cm^{-1} ; $\nu_{\text{N-O}}$, 845 cm^{-1} ; and ν_{NO_2} , 1275 cm^{-1}), as shown in Fig. 2. The NMR spectrum of the reaction mixture displayed the two triplets at $\tau 5.20$ and 6.03 , not assignable to the proton signals of oxazoline, oxazolinium, and 2-bromoethylbenzamide (Fig. 3). Considering that silver nitrate is often used as a test of alkyl halides [11], these results indicate that the reaction with AgNO_3 gave 2-benzamidoethyl nitrate quantitatively due to the strong covalency of the carbon-nitrate bond:

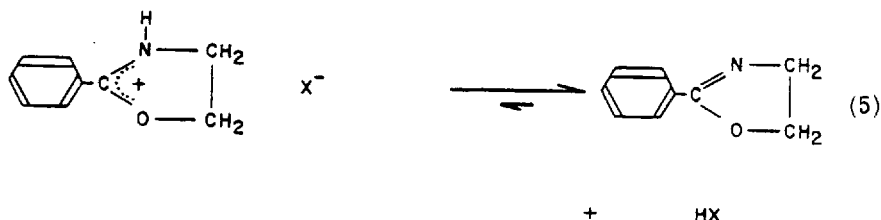


where X^- denotes a nitrate ion.

For the reactions with silver nitrite (AgNO_2), cyanate (AgCN), and

acetate (CH_3COOAg), the IR spectra of the residue obtained after filtration of silver bromide and removal of the solvent (nitromethane) displayed the characteristic absorption bands attributed to 2-phenyl-2-oxazoline ($\nu_{\text{C=N}}$, 1650 cm^{-1} ; $\nu_{\text{C-O}}$, 1262 cm^{-1} ; and the ring skeletal vibrations, 975 , 945 , and 897 cm^{-1}) and, in addition, showed the characteristic absorptions assignable to nitrite or nitro groups, cyanate or isonitrile groups (these may be caused by the ambident-ion character of nitrite or cyanate ion), and ester linkage, respectively, as shown in Table 1. The NMR spectra of these reaction mixtures (Fig. 3) displayed the proton signals attributed to 2-phenyl-2-oxazoline (τ 5.68 and 6.00), and methylene protons at τ 5-6, not assignable to 2-bromoethylbenzamide, respectively.

From these results it can be said that the reactions with AgNO_2 , AgCN , and $\text{Ag}(\text{CH}_3\text{COO})$ gave the corresponding straight-chain derivatives according to Eq. (4), 2-phenyl-2-oxazoline which may be produced by the intramolecular O-alkylation reaction (Eq. 3), and the subsequent dissociation reaction of the oxazolinium salts (Eq. 5) due to the weakly conjugated acid of the anionic group of the silver salt:



where X denotes NO_2^- , CN^- and CH_3COO^- , respectively.

Summing up these results, the unstable carbonium ion produced in Eq. (2) converts preferentially to a more stable intramolecular O-alkylation product (oxazolinium cation) by the use of the anionic groups, such as ClO_4^- or BF_4^- , to give the weakly covalent alkyl-hetero linkage ($\text{R}-\text{ClO}_4$ or $\text{R}-\text{BF}_4$) Eq. 3), to the corresponding straight-chain product by the use of NO_3^- to give the strongly covalent $\text{R}-\text{ONO}_2$ (Eq. 4), and to both reaction products by the use of NO_2^- , CN^- , or CH_3COO^- . These results lead to the conclusion that polymerization with ClO_4^- or BF_4^- as the counterion of the active propagating species proceeds through the oxazolinium cation (Route 1 in Fig. 1), whereas with the use of NO_3^- or carboxylate ion it hardly proceeds due to the formation of the more stable straight-chain derivative by the rearrangement reaction of

the oxazolinium salt at the growing chain end. These are consistent with the experimental facts described in the previous paper [1], in which 2-phenyl-2-oxazolinium nitrate and trifluoroacetate did not initiate polymerization.

Nucleophilic Ring-Opening Reactivity of N-Methyl-2-oxazolinium Perchlorate

In order to elucidate the nucleophilic ring-opening reactivity of N-methyl-2-oxazolinium perchlorates which are very similar to the structure of the active propagating end, the reactions of N-methyl-2-methyl-2-oxazolinium perchlorate (MO) and N-methyl-2-phenyl-2-oxazolinium perchlorate (PO) with pyridine as the attacking nucleophile were carried out in nitrobenzene.

The NMR spectra of the reaction mixtures at complete conversion (Runs 1 and 4 in Table 3) displayed the disappearance of proton signals of the oxazolinium heterocycle at τ 5-6 that are attributed to the methyl group attached to the quaternary nitrogen (N^+-CH_3) at \sim 6.1, whereas they displayed the appearance of methylene protons and the methyl protons attributed to $N-CH_3$ and $C-CH_3$ in higher magnetic fields (Fig. 4).

The IR spectra of the product isolated from diethyl ether showed the characteristic absorptions attributed to the tertiary amide linkage (\sim 1630 cm^{-1}) and the disappearance of the characteristic absorptions of the oxazolinium heterocycle (Fig. 5). In addition, elementary analysis of the white powdery product indicated the equimolar composition of the oxazolinium perchlorate and pyridine. Accordingly, these results indicate that the reactions of N-methyl-2-oxazolinium perchlorate (PO and MO) with pyridine gave N-methyl-2-benzamidoethyl pyridinium perchlorate or N-methyl-2-aceto-amidoethyl pyridinium perchlorate, respectively, by the following ring-opening quaternization reaction due to the nucleophilic attack of pyridine on the 5-position of the oxazolinium heterocycle:

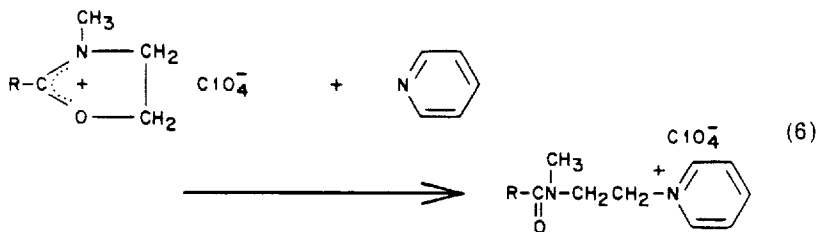


TABLE 3. The Reaction of N-Methyl-2-oxazolinium Perchlorates with Pyridine in Nitrobenzene

Run No.	Oxazolinium perchlorate	Reaction temperature (°C)	Reaction time (hr)	Unreacted oxazolinium perchlorate (%)	Product	
					CPPa (%)	SPPb (%)
1	N-Methyl-2-phenyl-	70	0.75	0	0	100
2	2-Oxazolinium	50	2.00	7	35	58
3	Perchlorate	50	24.00	0	0	100
4	N-Methyl-2-methyl-	70	0.75	0	0	100
5	2-Oxazolinium	50	2.00	12	62	26
6	Perchlorate	50	24.00	0	0	100

^aCyclic pyridinium perchlorate (shown in Eq. 7).

^bStraight-chain pyridinium perchlorate (shown in Eq. 6). The conversion was calculated from the relative ratios of the integration of N⁺-CH₃ and N-CH₃ in NMR spectrum.

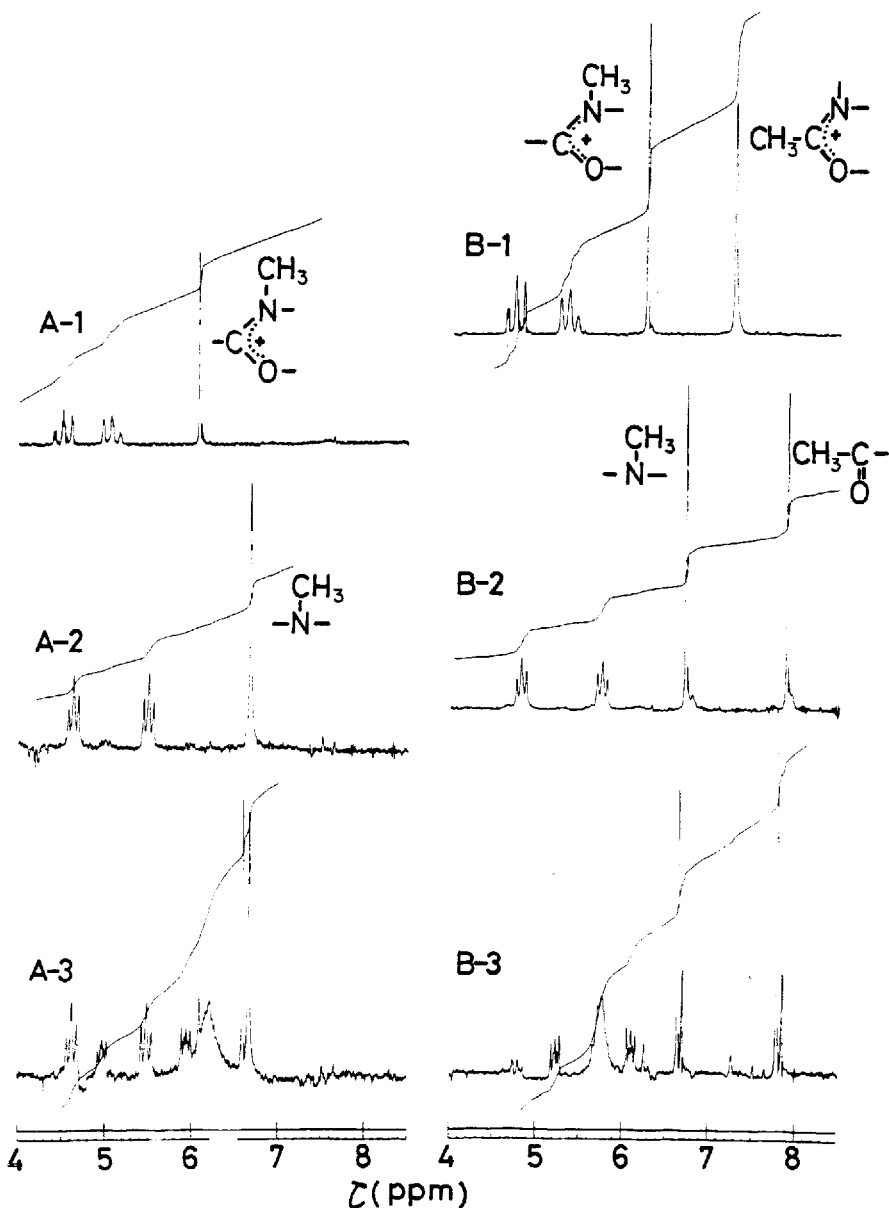


FIG. 4. The NMR spectra of the reaction mixtures of N-methyl-2-oxazolinium perchlorates and pyridine in nitrobenzene. (A-1) and (B-1) are N-methyl-2-phenyl-2-oxazolinium perchlorate and N-methyl-2-methyl-2-oxazolinium perchlorate, respectively. (A-2), (A-3), (B-2), and (B-3) correspond to Run nos. 1, 2, 4, and 5 in Table 3, respectively.

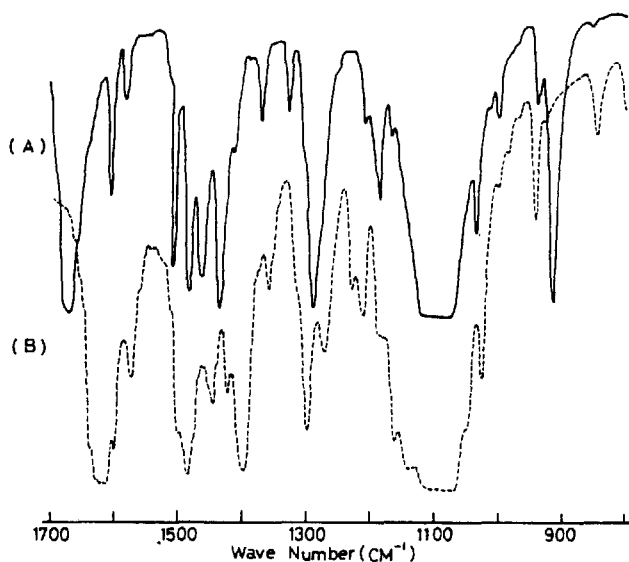
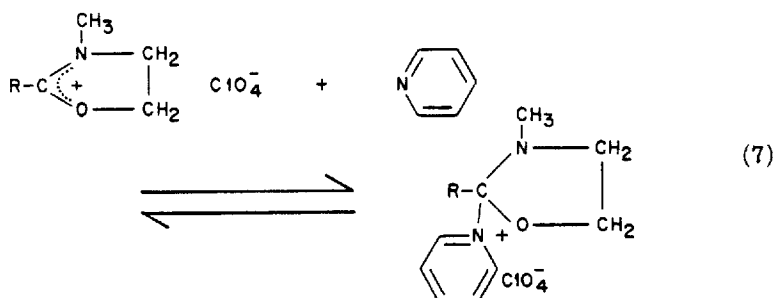


FIG. 5. The IR spectra of *N*-methyl-2-phenyl-2-oxazolinium perchlorate (A) and *N*-methyl-2-benzamidoethyl pyridinium perchlorate (B).

On the other hand, the NMR spectrum of these reaction mixtures at incomplete conversion (Fig. 4, A-3 and B-3) showed the characteristic protons signals attributed to the unreacted *N*-methyl-2-oxazolinium perchlorate and the above-mentioned straight-chain pyridinium perchlorate and, in addition, displayed the proton signals attributed to another species at a slightly lower magnetic field than that of the straight-chain derivative, which cannot be observed at the complete conversion. Considering the ambident-ion character of 2-oxazolinium heterocycle having two cationic centers at the 2- and 5-positions [12, 13], it is suggested that the other species is the cyclic pyridinium adduct resulting from the nucleophilic attack of pyridine on the cationic center at the 2-position of the oxazolinium heterocycle according to the following reversible reaction:



As can be seen in Table 3, the reactions of N-methyl-2-oxazolinium perchlorate with pyridine afforded only the straight-chain derivatives, respectively, and the ring-opening reaction were promoted by increasing the reaction temperature. Accordingly, it can be said that the reaction with pyridine proceeds through two competitive reactions (Eqs. 6 and 7) to give the straight-chain and cyclic pyridinium perchlorates, and that the former is a thermodynamically stable product, and the latter is a kinetically controlled product. These may suggest that the cationic polymerization of 2-oxazolines is thermodynamically controlled. The detailed mechanism of the reaction of N-methyl-2-oxazolinium perchlorate with pyridine will be described in a subsequent paper.

The relative nucleophilic ring-opening reactivity of N-methyl-2-oxazolinium perchlorates can be evaluated from the relative ratios of the integrations of N^+-CH_3 and $\text{N}-\text{CH}_3$ in NMR spectra of the reaction mixture. The results, shown in Table 3 may indicate that N-methyl-2-phenyl-2-oxazolinium perchlorate is more reactive toward the nucleophilic ring-opening reaction than is N-methyl-2-methyl-2-oxazolinium perchlorate. This is in accord with the result reported by Saegusa and his co-workers [6] in which 2-phenyl-2-oxazolinium tosylate is more effective as an initiator in the polymerization of 2-oxazolines than is 2-methyl-2-oxazolinium tosylate. Considering that the methylene protons at the 5-position of PO ($\tau 4.51$) is located at a lower magnetic field than that of MO ($\tau 4.73$) (Fig. 4), it is suggested that the nucleophilic ring-opening reactivity of N-methyl-2-oxazolinium perchlorate is primarily governed by the electrophilicity at the 5-position of the oxazolinium heterocycle.

Copolymerization of Equimolar Mixture of 2-Phenyl-2-oxazoline and the Other 2-Substituted-2-oxazoline

In order to elucidate the cationic polymerizability of 2-oxazolines, the mutual copolymerization of equimolar amounts of 2-phenyl-2-oxazoline (Ph-Oz) with 2-substituted-2-oxazoline derivatives such as 2-methyl-(Me-Oz), 2-isopropyl-(Ip-Oz), and 2-benzyl-2-oxazoline (Bz-Oz) were carried out at 135°C in *N,N*-dimethylacetamide with the use of 2-phenyl-2-oxazolinium perchlorate as an initiator. The white powdery solid obtained were insoluble in *n*-hexane and diethyl ether, but very soluble in methanol and chloroform.

As shown in Fig. 6, the time-conversion curves of copolymerizations indicate that the copolymerization rates are larger than the homopolymerization rate of 2-phenyl-2-oxazoline which has been determined previously [2]. The relationship between the conversion of comonomer and that of Ph-Oz indicates that the mole fraction of comonomer in the copolymer is markedly larger than that of Ph-Oz (Fig. 7). These experimental facts indicate that the incorporation of monomer into copolymer is facilitated according to the following order:

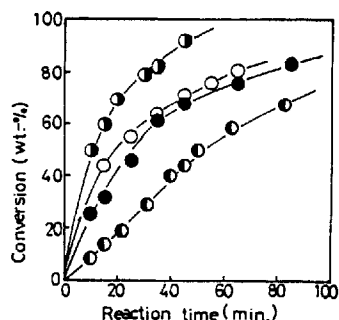
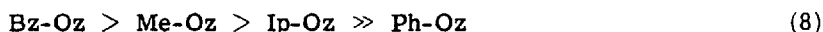


FIG. 6. The time-conversion curves in the mutual copolymerization of 2-phenyl-2-oxazoline in *N,N*-dimethylacetamide at 135°C. (●) Ph-Oz-Ip-Oz, (○) Ph-Oz-Me-Oz, (●) Ph-Oz-Bz-Oz (equimolar monomer concentration; 1.50 mole/liter), (○); Ph-Oz (monomer concentration; 3.00 mole/liter).

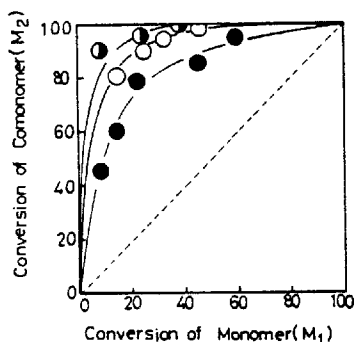


FIG. 7. The relation between the conversion of comonomer (M_2) and that of 2-phenyl-2-oxazoline (M_1): (●) Ip-Oz, (○) Me-Oz, (◐) Bz-Oz.

The order of incorporation into polymer is in accord with that of the copolymerization rate, as can be seen from Fig. 6.

From the curves in Fig. 7, the monomer reactivity ratios were calculated according to the Fineman-Ross-Sakurada equation:

$$\frac{[M_1]}{[M_2]} - \frac{1}{\alpha} = r_1 \frac{1}{\alpha} \frac{[M_1]}{[M_2]} - r_2 \quad (9)$$

where α is given by

$$\alpha = \frac{d[M_1]}{d[M_2]} \bigg/ \frac{[M_1]}{[M_2]}$$

and $d[M_1]/d[M_2]$ denotes the ratio of the instantaneous concentration of monomer incorporated into polymer chains, and $[M_1]/[M_2]$ denotes the concentration of monomer unreacted. By plotting $[M_1]/[M_2] - (1/\alpha)$ against $[M_1]/\alpha[M_2]$, the reactivity ratios r_1 and r_2 are obtained from the slope and the intercept of the straight line, respectively. This is shown in Fig. 8, where M_1 and M_2 represent Ph-Oz and comonomer, respectively.

As tabulated in Table 4, it was found that r_1 was very much

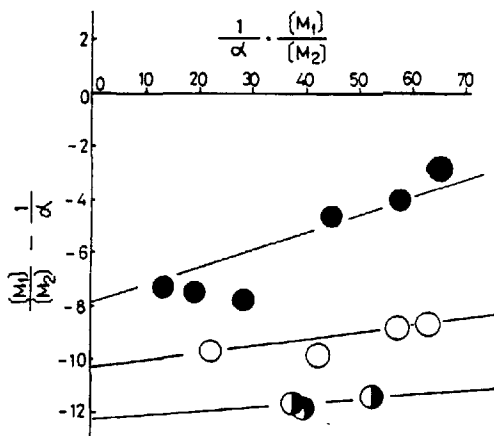


FIG. 8. The Fineman-Ross-Sakurada plot: (●) Ph-Oz-Ip-Oz, (○) Ph-Oz-Me-Oz, (◐) Ph-Oz-Bz-Oz.

TABLE 4. The Monomer Reactivity Ratios in the Mutual Copolymerization of 2-Phenyl-2-oxazoline (M_1) and the Other 2-Oxazolines (M_2)^a

Comonomer (M_2)	r_1	r_2
2-Isopropenyl-2-oxazoline	0.07 ± 0.01	7.9 ± 1.0
2-Methyl-2-oxazoline	0.02 ± 0.02	10.2 ± 1.0
2-Benzyl-2-oxazoline	0.01 ± 0.005	12.2 ± 1.0

^aThe copolymerizations were carried out at 135°C in *N,N*-dimethylacetamide. r_1 and r_2 were calculated from the Finemann-Ross-Sakurada equation.

smaller than unity, whereas r_2 was markedly larger. This means that comonomers (Ip-Oz, Me-Oz, and Bz-Oz) are more reactive than Ph-Oz. Considering that *N*-methyl-2-methyl-2-oxazolinium perchlorate is less reactive toward the nucleophilic ring-opening reaction than is *N*-methyl-2-phenyl-2-oxazolinium perchlorate, these facts strongly indicate that the polymerizability of

2-oxazolines depends predominantly on the reactivity of monomer, but hardly on the nucleophilic ring-opening reactivity of the oxazolinium heterocycle derived from the corresponding monomer at the growing chain end, or its stability.

Relation between the Polymerizability and the Reactivity of the Oxazolinium Perchlorate and Monomer

The cationic polymerizability of heterocycle monomers depends on the nucleophilicity of monomer and the power of ring-opening of the growing cationic heterocycle, as stated in the introduction. The nucleophilicity of 2-oxazolines used was estimated from the relative basicity which could be evaluated by the shift of the O—D stretching vibration of methanol-d in the monomer due to the nucleophilic coordination. As shown in Table 5, the order of the nucleophilicity of monomer is in agreement with that of the reactivity of the monomer.

TABLE 5. Physical Properties of Monomer and N-Methyl-2-oxazolinium Perchlorate

2-Oxazolines	Shift value of the O-D of methanol-d (cm^{-1})	The methylene protons at the 5-position (τ ; ppm)	
		2-Oxazoline ^a	N-Methyl-2-oxazolinium perchlorate ^b
2-Phenyl-2-oxazoline	148	5.57	4.51
2-Isopropenyl-2-oxazoline	168	5.82	-
2-Methyl-2-oxazoline	176	5.79	4.73
2-Benzyle-2-oxazoline	191	5.91	-

^a Measured in CDCl_3 .

^b Measured in nitrobenzene.

On the other hand, the order of the electrophilicity of the oxazolinium perchlorate as the active propagating species, which may be evaluated from the methylene protons at the 5-position of the heterocycles by their NMR spectrum (Table 5), indicates the reverse order of the nucleophilicity or the reactivity of monomer. Accordingly, the results mentioned above lead to the conclusion that the oxazolinium cation derived from the more reactive monomer has less ring-opening reactivity, and that the polymerizability of 2-oxazolines is predominantly controlled by the nucleophilic attack which depends on the basicity of the monomer.

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