

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polymerization of 2-Oxazolines. I. Cationic Polymerization of 2-Phenyl-2-oxazoline Initiated by Various Oxazolinium Salts of Monomer with Brønsted Acids

Tsutomu Kagiya^a; Takehisa Matsuda^a

^a Department of Hydrocarbon Chemistry Faculty of Engineering, Kyoto University, Kyoto, Japan

To cite this Article Kagiya, Tsutomu and Matsuda, Takehisa(1971) 'Polymerization of 2-Oxazolines. I. Cationic Polymerization of 2-Phenyl-2-oxazoline Initiated by Various Oxazolinium Salts of Monomer with Brønsted Acids', *Journal of Macromolecular Science, Part A*, 5: 8, 1265 – 1285

To link to this Article: DOI: 10.1080/00222337108061106

URL: <http://dx.doi.org/10.1080/00222337108061106>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polymerization of 2-Oxazolines. I. Cationic Polymerization of 2-Phenyl-2-oxazoline Initiated by Various Oxazolinium Salts of Monomer with Brönsted Acids*

TSUTOMU KAGIYA and TAKEHISA MATSUDA

*Department of Hydrocarbon Chemistry
Faculty of Engineering
Kyoto University
Kyoto, Japan*

SUMMARY

Various kinds of the complexes of 2-phenyl-2-oxazoline with various Brönsted acids were prepared. From the elementary analysis and spectroscopic analysis of the complex, it was identified to be an equimolar oxazolinium salt. The monomer could be polymerized with the oxazolinium salt to give N-benzoyl-polyethylenimine. The polymer yield in bulk polymerization was linearly proportional to the reaction time, and the number-average degree of polymerization of the polymer obtained at the complete conversion was proportional to the initial molar ratio of the monomer to the complex. The catalytic activities of the oxazolinium salts increased with a decrease in the pK_a value of Brönsted acid in water. The results of the infrared spectroscopy and nuclear magnetic resonance spectroscopy of the oxazolinium salt at room temperature and elevated temperature indicated that the change of the double bond character of the imino and ether linkages is brought about by the complexation. On the basis of these results, the mechanism of the polymerization was proposed.

*Presented at the 19th Annual Meeting of the Society of Polymer Science, Japan, Tokyo, on May, 1970.

1265

Copyright © 1971 by Marcel Dekker, Inc. *NO PART of this work may be reproduced or utilized in any form or by any means, electronic or mechanical, including xerography, photocopying, microfilm, and recording, or by any information storage and retrieval system, without the written permission of the publisher.*

INTRODUCTION

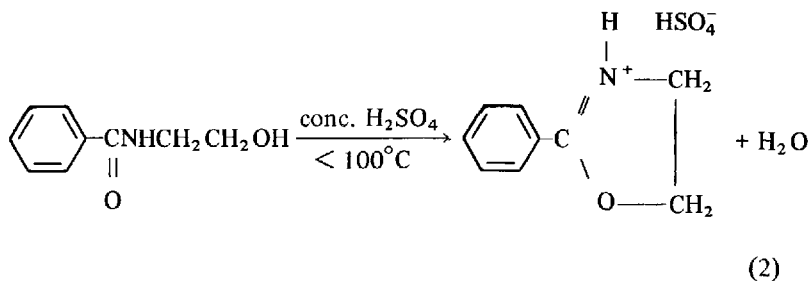
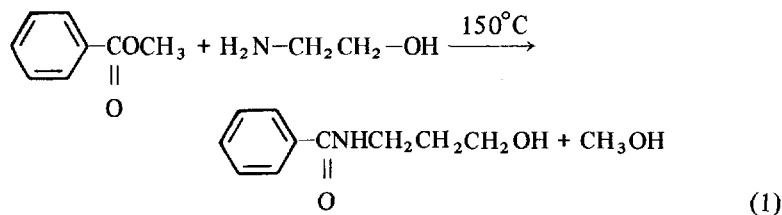
It has been found by the present authors [1] and several other investigators [2-4] that the ring-opening polymerization of 2-substituted-2-oxazoline takes place by a typical cationic catalyst such as trifluoroboron etherate or stannic chloride to give N-acyl- or N-aryroyl-polyethylenimine. However, no detailed investigation on the mechanism of this polymerization reaction has been reported.

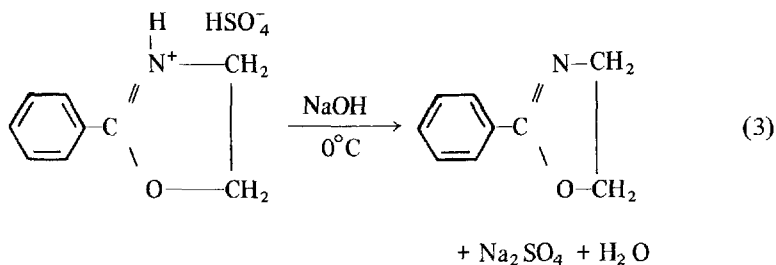
In this paper, structural studies of the complex of 2-phenyl-2-oxazoline with Brønsted acid and the polymer obtained by the complex catalyst are made. The catalytic activity of the complex and the mechanism of this polymerization are discussed on the basis of kinetic behavior of the polymerization and spectroscopic studies of the complex.

EXPERIMENTAL

Preparation of 2-Phenyl-2-oxazoline

2-Phenyl-2-oxazoline can be prepared from monoethanolamine and methyl benzoate according to the literatures [5-8]. In order to obtain higher yield of the product, the present authors used concentrated sulfuric acid instead of phosphorous pentoxide [8] as a dehydrating agent in the cyclization reaction step (2).





A mixture of monoethanolamine (1.5 mole, G. R. Grade) and methyl benzoate (1.0 mole, G. R. Grade) was refluxed for several hours at 150°C in a flask equipped with the reflux condenser. Then the produced methanol and the excess monoethanolamine were removed from the reaction mixture by distillation under reduced pressure. The residue gave a white crystalline mass when kept standing overnight at room temperature.

The crude reaction product was identified to be N-hydroxyethylbenzamide by measuring the melting point and the infrared spectrum of the product (mp 60-62°C; Ref. 8, 61-62°C: IR, the secondary amide bands at 1540 and 1640 cm⁻¹).

Concentrated sulfuric acid (150 ml) was poured gradually into 80 g of liquid N-hydroxyethylbenzamide at about 80°C with vigorous stirring. The reaction vessel had to be kept at a temperature below 100°C because the reaction was exothermic. When no temperature rise of the mixture was observed upon successive addition of concentrated sulfuric acid, the transparent viscous reaction mixture was gradually dissolved in an ice water-sodium hydroxide solution, and the oily base that precipitated was extracted with diethyl ether. The ethereal extract was dried with magnesium sulfate powder and distilled under reduced pressure. 2-Phenyl-2-oxazoline was yielded as a colorless oil (bp 128-128.5°C/13 torr; Ref. 6, 69°C/0.2 torr). The conversion of methyl benzoate to 2-phenyl-2-oxazoline was about 93%.

The purification of 2-phenyl-2-oxazoline was carried out by several careful fractionations after successive treatments with potassium hydroxide powder, metallic sodium, and phthalic anhydride. The purified monomer thus obtained gave no polymer when heated for 4 hr at 150°C in the absence of catalyst.

Preparation of the Complex

A cooled ethanol solution of Brönsted acid was gradually poured into

Table 1. Elementary Analysis of the Oxazolium Salt of 2-Phenyl-2-oxazoline with Brönsted Acid

Run No.	OX · HX ^a	Found (%)				Calculated (%)			
		C	N	Others	C	N	Others	Others	
1	OX · HClO ₄	43.68	5.65	Cl, 14.42	43.64	5.71	Cl, 14.36		
2	OX · p-C ₇ H ₇ SO ₃ H ^b	60.09	4.52	S, 9.99	60.15	4.49	S, 10.00		
3	OX · H ₂ SO ₄	43.98	5.77	S, 12.99	44.08	5.74	S, 12.99		
4	OX · HIO ₄	31.72	4.29	I, 37.72	31.87	4.18	I, 37.44		
5	OX · H ₃ PO ₄	44.25	5.57	P, 12.41	44.08	5.70	P, 12.61		
6	OX · HI	39.03	5.13	I, 46.04	39.30	5.13	I, 46.18		
7	OX · HBr	47.37	6.21	Br, 35.31	43.58	6.18	Br, 35.12		
8	OX · HCl	58.65	7.73	Cl, 19.49	58.90	7.65	Cl, 19.31		
9	OX · HNO ₃	51.38	13.33	-	51.43	13.30	-		
10	OX · CCl ₃ COOH	42.20	4.65	Cl, 35.07	42.53	4.69	Cl, 35.63		

^aOX · HX is the oxazolium salt of 2-phenyl-2-oxazoline (OX; C₉H₉NO) with Brönsted acid (HX).

^bp-C₇H₇SO₃H (p-toluenesulfonic acid).

the diethyl ether solution of 2-phenyl-2-oxazoline with vigorous stirring. The precipitated white mass was filtered and recrystallized from anhydrous diethyl ether-ethanol solution twice. The white powder thus obtained was identified to be the equimolar complex of 2-phenyl-2-oxazoline with Brönsted acid by means of the elementary analysis as shown in Table 1.

Polymerization Procedure

2-Phenyl-2-oxazoline (1.503×10^{-2} mole) and a precise amount of the complex of 2-phenyl-2-oxazoline with Brönsted acid were charged into a glass ampoule. After several freeze-evacuate-thaw cycles at liquid nitrogen temperature, the ampoule was placed into an oil bath kept at a constant temperature of $150 \pm 0.2^\circ\text{C}$. After a set time of polymerization, the ampoule was removed from the bath and immediately cooled to -78°C by the Dry Ice-methanol mixture and opened. The reaction mixture was dissolved in a small amount of chloroform. The chloroform solution was gradually poured with rapid stirring into a large amount of n-hexane. The precipitated material was filtered, washed with diethyl ether, dried in vacuo at 60°C , and weighed. The polymer sample for the measurement of number-average molecular weight was reprecipitated from a chloroform-n-hexane solution twice and dried by the above treatments.

Thermal Rearrangement Reaction of the Complexes of 2-Phenyl-2-oxazoline

The thermal rearrangement reaction of the complex of 2-phenyl-2-oxazoline with Brönsted acid was carried out in a sealed glass ampoule under nitrogen atmosphere at 150°C for 2 hr. The reaction product was isolated from acetone-ethanol solution and reprecipitated from diethyl ether-methanol. The isolated product was identified by infrared analysis and its melting point. N-Bromoethylbenzamide; $\text{C}_9\text{H}_{10}\text{NOBr}$: mp $105-106^\circ\text{C}$ (Ref. 9, $105-106^\circ\text{C}$). N-Chloroethylbenzamide; $\text{C}_9\text{H}_{10}\text{NOCl}$: mp $102-103^\circ\text{C}$ (Ref. 9, 102°C); Ref. 10, $106-108^\circ\text{C}$). N-Benzamidoethyl trichloroacetate; $\text{C}_{11}\text{H}_{10}\text{NO}_3\text{Cl}_3$: mp $88-89^\circ\text{C}$.

Physical Analyses of the Oxazolinium Salts of Monomer with Various Brönsted Acid and the Polymer

The infrared spectrum was obtained by the use of the potassium bromide technique on a JASCO Grating Infrared Spectrometer, Model DS-403G. The shifts ($\Delta\nu$) of characteristic absorption peaks of the oxazoline heterocycle by the complexation with a Brönsted acid were obtained by

measuring the difference in the wavelength of the peak maxima for the free and complexed characteristic bands (with the scale-up): $\Delta\nu = \nu_{\text{free}} - \nu_{\text{complexed}}$.

The nuclear magnetic resonance spectra were measured by a Japan Electron Optics 60 MHz Spectrometer (JNM-3H-60) and a Varian H-220 Spectrometer (220 MHz) with tetramethylsilane as an internal standard.

The molecular weight of the polymer was measured with a vapor-pressure osmometer (Mechrolab Model 302) at $37.0 \pm 0.05^\circ\text{C}$ in chloroform.

The melting point of the polymer and oxazolinium salts was measured visually under nitrogen atmosphere in a capillary with a Yanagimoto melting point measuring apparatus, Model MP-S2, equipped with a microscope ($\times 10$).

RESULTS AND DISCUSSION

Characterization of the Oxazolinium Salts and Polymer of 2-Phenyl-2-oxazoline

The infrared spectrum of 2-phenyl-2-oxazoline by the potassium bromide film technique showed the characteristic absorptions of oxazoline heterocycle (imino stretching vibration $\nu_{\text{C=N}}$ 1650 cm^{-1} ; ether stretching vibration $\nu_{\text{C-O}}$ 1262 cm^{-1} ; and ring skeletal vibrations ν_{ring} 975 , 945 , and 897 cm^{-1}). The infrared spectrum of the white powdery compound obtained

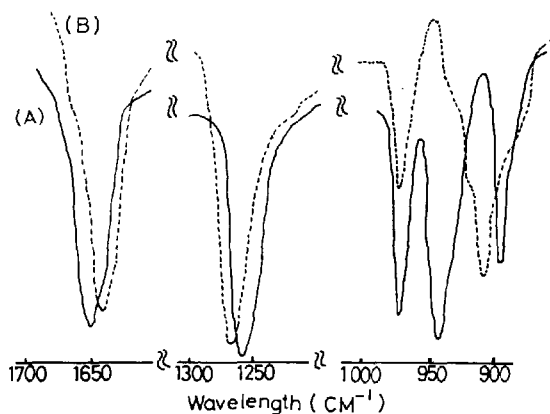


Fig. 1. Infrared spectra of 2-phenyl-2-oxazoline and the oxazolinium salt of 2-phenyl-2-oxazoline with perchloric acid.

Table 2. Several Physical Properties and Catalytic Activity of the Oxazolium Salt with Brönsted Acid

Run No.	OX · HX ^a	mp (°C)	$\Delta\nu$ (cm ⁻¹) ^b		ν_{ring}	pK _a of HX in water ^c	PR ^d × 10 ²	log PR	Thermal re- arrangement ^e
			$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$					
1	OX · HClO ₄	150-151	+7	-9	-13	-8	ca. 10	-1.0	X
2	OX · p-C ₇ H ₇ ·SO ₃ H	112-113	+8	-16	-12	.	ca. 8.8	-1.06	X
3	OX · H ₂ SO ₄	138-139	+3	-8	-8	-3	0.78	-2.11	X
4	OX · HIO ₄	141-142	+6	-7	-9	1.55	0.70	-2.16	X
5	OX · H ₃ PO ₄	138-139	+1	-11	-7	1.78	0.28	-2.55	X
6	OX · HI	102-103	+6	-6	-7	-11	0.60	-2.22	X
7	OX · HBr	92-93	0	-5	-2	-9	0.12	-2.92	0
8	OX · HCl	80-81	-2	-3	-4	-7	0	.	0
9	OX · HNO ₃	101-102	-2	-3	-1	-1.64	0	.	0
10	OX · CCl ₃ COOH	129-130	-1	-3	-2	0.66	0	.	0

^aThe oxazolium salt with Brönsted acid (HX).

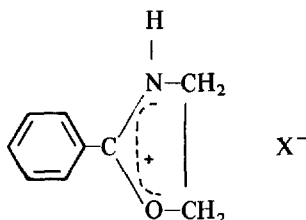
^bThe shift between the free and complexed oxazoline ($\Delta\nu = \nu_{\text{free}} - \nu_{\text{complexed}}$). $\nu_{\text{free}} = 1650$ (C=N), 1262 (C-O), and 897 (ring) cm⁻¹.

^cpK_a of Brönsted acid in water.

^dPropagation rate per mole of catalyst (mole min⁻¹).

^eThe characteristic absorption of the secondary amide by the thermal rearrangement reaction.

from 2-phenyl-2-oxazoline and a Brönsted acid showed almost the same peaks as the characteristic absorptions of the oxazoline heterocycle (Fig. 1). The fact mentioned above and the results of elementary analysis lead to the conclusion that the compound is an equimolar complex of 2-phenyl-2-oxazoline with Brönsted acid without the occurrence of the ring-opening reaction. Therefore the general structure of the complex is illustrated by the following oxazolinium salt structure, where X is the anion part of a Brönsted acid.



The N-atom of 2-oxazoline would be the center of basicity in the heterocycle because of the enhanced nucleophilicity of the imino group due to the neighboring ether linkage. Several physical properties of these oxazolinium salts are summarized in Table 2.

2-Phenyl-2-oxazoline could be polymerized by using the oxazolinium salt as catalyst to give a white powdery solid with a melting point of 205-206°C. The infrared spectrum of this polymer displayed the characteristic absorptions at 1630 cm^{-1} , assignable to the tertiary amide linkage, and at 1600 cm^{-1} , assignable to the monosubstituted benzene nucleus, and the disappearance of the characteristic peaks of the oxazoline heterocycle. The polymer obtained is identified from these results to be N-benzoyl-polyethylenimine as expected.

The polymer was soluble in chloroform, acetone, and dipolar aprotic solvents such as N,N-dimethylacetamide, but insoluble in water and common hydrocarbon solvents such as benzene or n-hexane. The nuclear magnetic resonance spectrum of the polymer, as shown in Fig. 2, showed a broad peak centered at $\tau 6.8$ and a complex multiplet at $\tau 2.8$. The former peak is assignable to the nitrogen-linked methylene protons, and the latter to phenyl protons. The breadth of the former may be caused by the hindered rotation around the amide band due to the partial double bond character of the linkage between the carbonyl and the nitrogen. The integration of these resonance peaks gives the proton ratio of 4 (ethylene):5 (phenyl) which is consistent with the proposed structure.

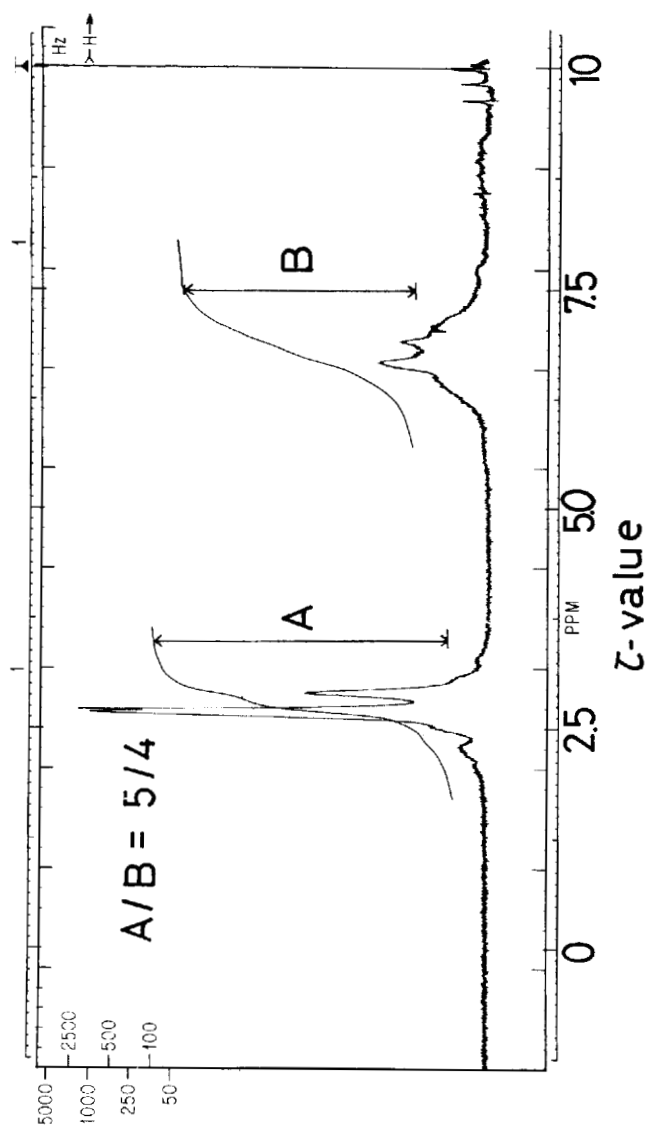


Fig. 2. Nuclear magnetic resonance spectrum of N-benzoyl polyethylenimine. Conditions: 10% CDCl_3 solution, 70°C , 220 MHz/sec, tetramethylsilane as an internal standard.

Catalytic Behavior of the Oxazolinium Salts of Monomer with Brönsted Acids

The system of polymerization carried out in bulk at 150°C was homogeneous and became a highly viscous liquid at the latter stage of polymerization. As shown in Fig. 3, the polymer yield is linearly proportional to the reaction time in the polymerizations which use various kind of oxazolinium salts.

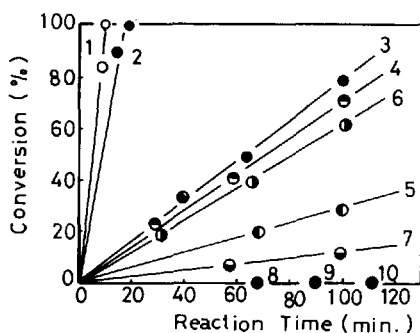


Fig. 3. Time-conversion curve of the polymerization of 2-phenyl-2-oxazoline. Conditions: monomer = 1.503×10^{-2} mole, catalyst = 1.503×10^{-4} mole. Polymerizations were carried out at 150°C in bulk. The numbers have the same meaning as in Table 2.

The number-average degree of polymerization of the polymer obtained at the complete conversion, as shown in Fig. 4, is proportional to the initial molar ratio of the monomer to the salt with perchloric acid used as catalyst. The slope of the straight line leads to the conclusion that the moles of the polymer is nearly equal to that of the catalyst initially charged. It means that the initiation coefficient of the catalyst, α , which is defined by the equation (4), is almost unity:

$$\alpha = \frac{[M]_0/[I]_0}{\bar{P}_n} \doteq 1.0 \quad (4)$$

where $[M]_0$ and $[I]_0$ denote the moles of monomer and of the catalyst initially charged, respectively, and \bar{P}_n is the number-average degree of polymerization.

From the fact that the over-all polymerization rate was constant during

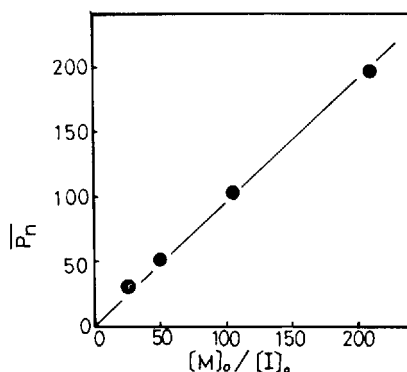


Fig. 4. Relation between the number-average degree of polymerization (\bar{P}_n) at complete conversion and the initial molar ratio of monomer ($[M]_0$) to catalyst ($[I]_0$). Same conditions as in Fig. 3.

polymerization (Fig. 3) and the moles of the polymer chain is approximately equal to that of the catalyst initially charged, it can be said that the long-lived propagating species exist without termination and transfer reactions. From these considerations, the over-all polymerization rate per mole of the catalyst in bulk polymerization is almost equal to the propagation rate, and the catalytic activities of various kinds of oxazolinium salts can be compared by the use of their values. As shown in Table 2, the salts of monomer with perchloric acid and with p-toluenesulfonic acid exhibited excellent catalytic activity, whereas the salts with hydrogen chloride, with trifluoroacetic acid, and with nitric acid could not initiate polymerization.

In order to investigate the effect of the counter-ion on polymerization, the logarithm of the propagation rate was plotted against the pK_a value of Brönsted acid in water (Fig. 5). There are two series of relationships between the values obtained. This is discussed in a later section in connection with the mechanism of polymerization. Both relationships indicated that the propagation rate increased with a decrease in the pK_a value of Brönsted acid. There is a positive relationship between the change of the free energy of the dissociation equilibrium of Brönsted acid in aqueous solution and that of the active propagating species in bulk. Figure 5 may indicate that the free ion character of the active propagating species brought about the increase in the propagation rate.

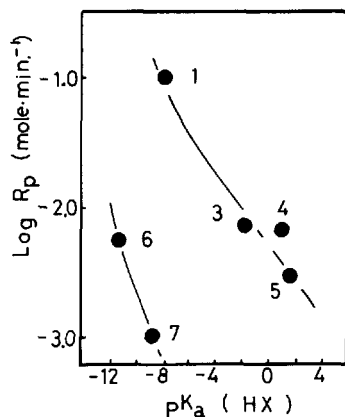
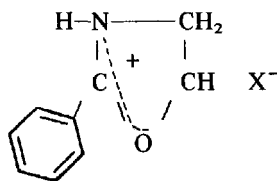


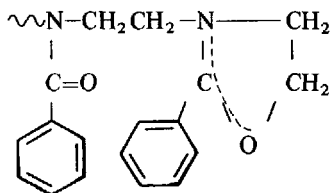
Fig. 5. Relation between the logarithm of the propagation rate per mole of catalyst and pK_a of Brønsted acid (HX) in water. The numbers have the same meaning as in Table 2.

Infrared Spectroscopy of the Oxazolinium Salts of Monomer with Brønsted Acids and Its Thermal Rearrangement Reaction

The salt with a Brønsted acid, such as perchloric acid or sulfuric acid, is thermally stable even at elevated temperature (150°C). The active propagating species in this polymerization may therefore be a kind of oxazolinium salt, the structure of which is similar to that of the salt of the monomer with Brønsted acid as catalyst. For example, the oxazolinium salt of monomer with Brønsted acid:



The active propagating species:



In order to elucidate the mechanism of this polymerization, the infrared spectra of the salts of monomer with various Brönsted acids were compared with that of monomer. These results are shown in Fig. 1 and summarized in Table 2. The characteristic absorption peaks of 2-oxazoline heterocycle were shifted by the complexation with Brönsted acid. The peak assignable to the carbon-nitrogen double bond (imino linkage) stretching vibration was generally shifted toward lower frequency, whereas those assignable to the ether stretching vibration and the ring skeletal vibrations shifted toward higher frequency.

As shown in Table 2, there is a general tendency for both absolute shift values $|\Delta\nu|$ ($= |\nu_{\text{free}} - \nu_{\text{complexed}}|$) of the ether stretching vibration and the ring skeletal vibrations to increase with an increase in that of the imino stretching vibration. On the basis of these observations, it seems reasonable to assume that the lower frequency shift of the imino linkage and the higher shift of the ether linkage indicate that the complexation with Brönsted acid brings about some appreciable change of the bonding state in the oxazoline heterocycle which induces a weakening of the double bond character of the imino linkage and a strengthening of that of the ether linkage.

The logarithm of the propagation rate was plotted against the absolute shift $|\Delta\nu|$ of the oxazolinium salt, as shown in Fig. 6. Since these points lay on a broad band of a positive slope, it is considered that the catalytic activity of the salt increased with an increase in the absolute shift value of the characteristic absorption of oxazoline heterocycle due to the complexation. The change of the double bond character in the oxazoline heterocycle by the complexation with Brönsted acid may facilitate ring-opening polymerization, based on the consideration that this polymerization would proceed via the conversion process of the imino linkage (C=N) to carbonyl-nitrogen single bond and of the ether linkage to the carbonyl linkage.

Figure 7 shows that the characteristic absorption bands of the complex of monomer with perchloric acid were broadened and shifted largely without the ring-opening reaction because the scanning temperature increased almost up to the reaction temperature. On the other hand, this complex underwent the thermal changes exhibited by the original shifts when it was cooled to room temperature. The shifts of the characteristic absorptions of the salt of monomer with various other Brönsted acids were also increased by increasing the scanning temperature, and these salts were thermally stable without the ring-opening reaction under these experimental conditions, as shown in Table 2.

On the other hand, the infrared spectra of the salts of monomer with

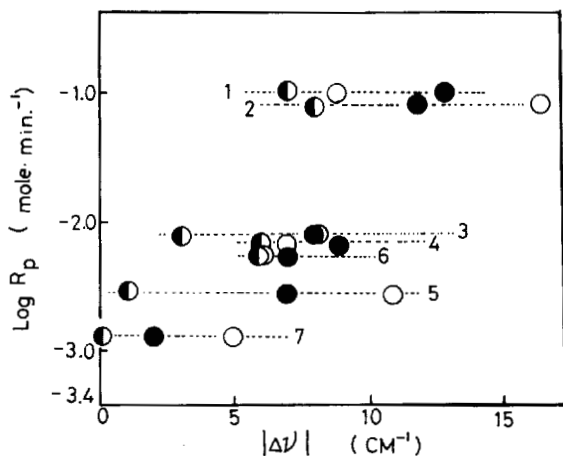


Fig. 6. Relation between the logarithm of the propagation rate per mole of catalyst and the absolute shift ($|\Delta\nu|$) of the characteristic absorption of the oxazolinium salt: (●) C=N stretching vibration, (●) C-O ether stretching vibration, (○) ring skeletal vibration. The numbers have the same meaning as in Table 2.

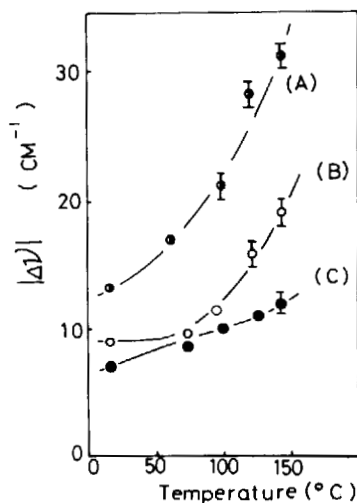
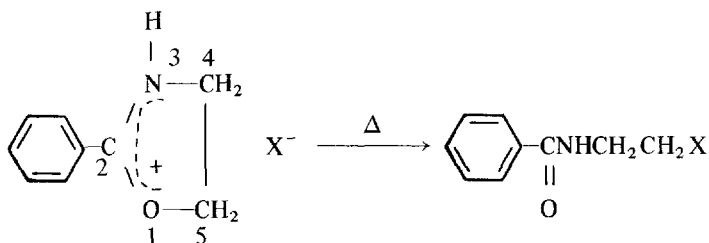


Fig. 7. Influence of temperature on the absolute shift value ($|\Delta\nu|$) of the characteristic absorption of the oxazolinium salt with perchloric acid: (●) C=N stretching vibration, (○) C-O stretching vibration, (●) ring skeletal vibration.

hydrogen bromide, with hydrogen chloride, with trifluoroacetic acid, and with nitric acid at a temperature over 100°C showed a new absorption peak at $1540\text{--}1550\text{ cm}^{-1}$, assignable to the characteristic absorption of the secondary amide. These salts, when heated at 150°C for 2 hr under nitrogen atmosphere, gave an almost quantitative amount of an amide derivative by the following ring-opening reaction due to the thermal rearrangement reaction:



Nuclear Magnetic Resonance Spectra of Monomer and the Salts of Monomer with Perchloric Acid

As is shown in Fig. 8, the methylene-methylene protons in the monomer heterocycle exhibited the symmetrical pattern (A_2B_2 type) centered at $\tau 5.78$ at room temperature and shifted only slightly toward a lower magnetic field at an elevated temperature (135°C). On the other hand, those of the salt of the monomer with perchloric acid at either room or elevated temperature displayed the complex multiplet pattern. The methylene protons attached to the 5-position (neighboring oxygen atom) in the oxazoline heterocycle were shifted toward a lower magnetic field when the scanning temperature was raised.

Since the chemical shift parameter is in general a function of the electron density around the nucleus for comparable protons in a common solvent [11], it is suggested that the carbon atom at the 5-position in the oxazoline heterocycle became positively charged by the complexation with perchloric acid and that its cationic character could be enhanced by raising the temperature.

On the basis of the consideration that the complexation with perchloric acid induces the loosening of the double bond of the imino linkage and the strengthening of the double bond character of the ether linkage, the conclusion follows that the bonding state in oxazoline heterocycle would be influenced by the complexation with perchloric acid, and that the change

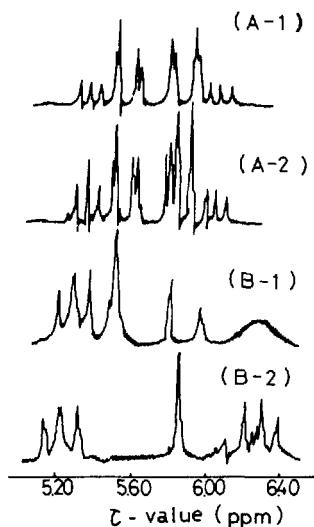
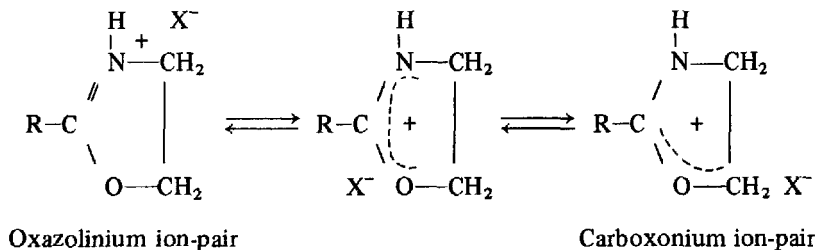


Fig. 8. Nuclear magnetic resonance spectra of monomer and the oxazolinium salt with perchloric acid. 2-Phenyl-2-oxazoline (A-1, 20°C; A-2, 135°C). The oxazolinium salt with perchloric acid (B-1, 20°C; B-2, 135°C). Conditions: 10% solution of *N,N*-dimethylacetamide, 60 MHz/sec, tetramethylsilane as an internal standard.

of the electronic state in the oxazoline heterocycle may be brought about to give some cationic character at the 5-position. Therefore, the complexation may enhance the nucleophilic attack on the electron-deficient center of the oxazoline heterocycle.

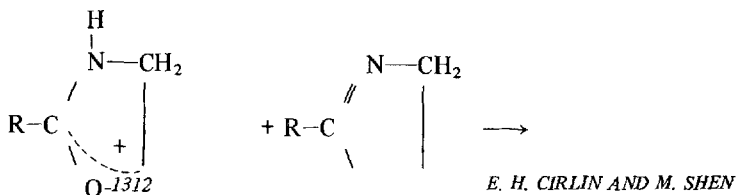
Mechanism of Polymerization

From the results mentioned above, it is considered that this polymerization proceeds through the following two routes:



Route 1.

Initiation reaction:



and deformation [3]. In this note we shall report the results on our thermoelastic measurements for a number of acrylic polymers with different side-chain structures in order to examine the effect of intramolecular forces on f_e/f by changing the molecular constitution of polyacrylates.

In previous publications from this laboratory, we have proposed a new equation for the calculation of the relative energy contribution to the elasticity of polymers in the rubbery state [1, 5]:

$$\frac{f_c}{f} = 1 - \frac{d \ln G}{d \ln T} - \beta_L^0 T \tag{1}$$

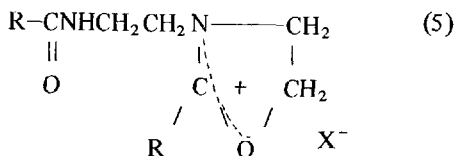
Where f is the total force, f_c is the energetic component of the elastic force, T is absolute temperature, β_L^0 is the linear thermal expansion coefficient of unstrained rubber, and G is the shear modulus. The latter is defined by the equation of state for rubber elasticity:

$$f = GA_0(\lambda - V/V_0\lambda^2) \tag{2a}$$

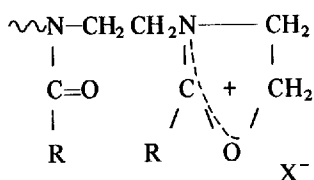
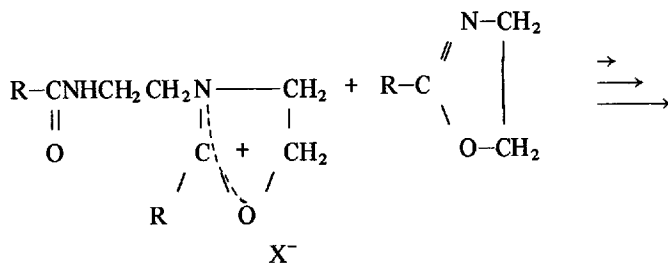
and

$$G = (NRT/V_0) (\bar{r}_1^2/\bar{r}_f^2) \tag{2b}$$

In Eqs. (2), λ is the extension ratio, L/L_0 ; L_0 , A_0 , and V_0 are the length, cross-sectional area, and volume of the rubber at zero pressure, zero force, respectively; and L and V are the length and volume at force f , and pressure



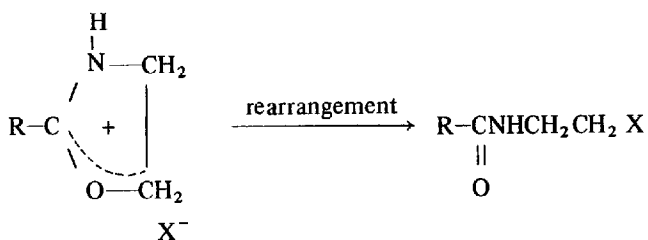
Propagation reaction:



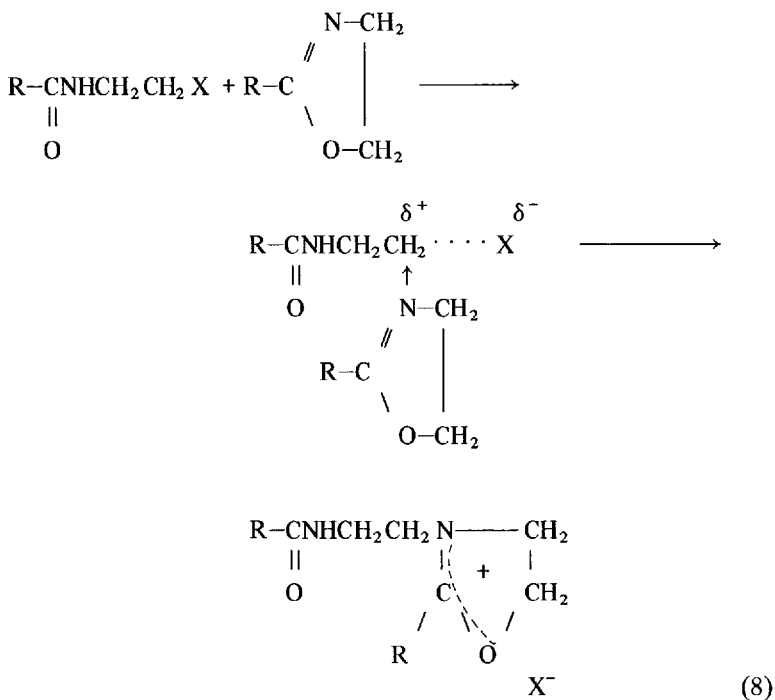
(6)

Route 2.

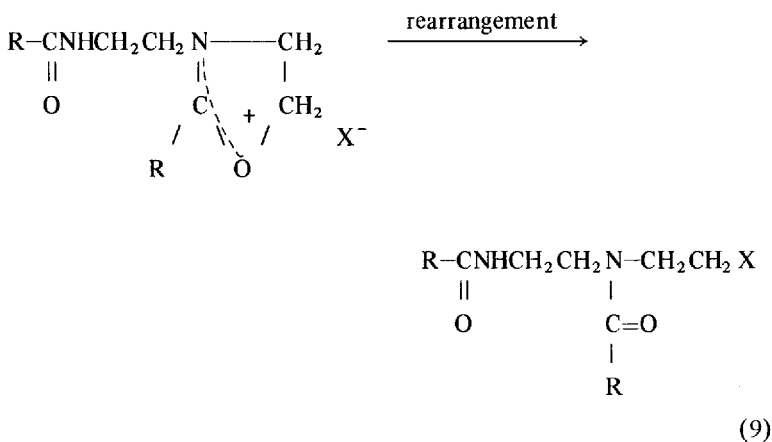
Initiation reaction:

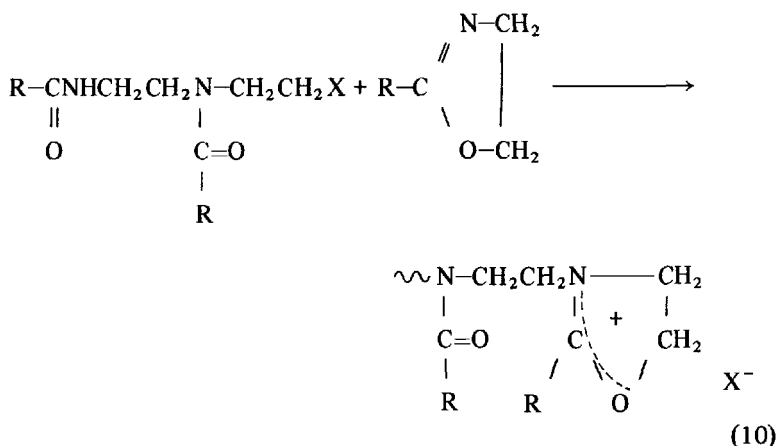


(7)



Propagation reaction:





Route 1, shown schematically by Eqs. (5) and (6), is the direct quaternization reaction of the incoming monomer by the oxazolinium salt, and Route 2, Eqs. (7)-(10), is composed of the ring-opening rearrangement reaction of the oxazolinium salt and the quaternization reaction of the incoming monomer by the rearrangement product.

In the former route, the oxazolinium salt, which is stable thermally without the occurrence of ring-opening reaction, would effectively decrease the electron density in the oxazoline heterocycle due to the change of the bonding state by the complexation. The nucleophilic attack of monomer on the electron-deficient 5-position of the oxazolinium salt generates a quaternary nitrogen on the incoming heterocycle. On the basis of experimental results that the propagation rate increased with a decrease in the pK_a value of Brønsted acid in aqueous solution and with an increase in the absolute shift values of the characteristic absorption of the oxazoline heterocycle, it is considered that the catalytic activity of the oxazolinium salt may increase with an increase in the free ion character of the ion-pair of the active propagating end and that the delocalization in the positively charged oxazolinium heterocycle may facilitate the nucleophilic attack of monomer.

In the latter route, the oxazolinium salt, which is thermally unstable, is rearranged easily to give the straight chain derivative, $\text{R}-\text{CNHCH}_2\text{CH}_2\text{X}$.

$$\begin{array}{c}
 \text{R}-\text{CNHCH}_2\text{CH}_2\text{X} \\
 || \\
 \text{O}
 \end{array}$$

If the ionic bond dissociation energy of the C-X bond of the derivative is small, the derivative would quaternize the incoming monomer to aid polymerization, whereas if that of the derivative is larger, polymerization would not occur.

The two series of relationships between the propagation rate and the pK_a value of Brønsted acid in aqueous solution (Fig. 5) and the result of the thermal rearrangement reaction of the oxazolinium salt may indicate that the polymerization with ClO_4^- or HSO_4^- as the counter-ion of the active propagating species proceeds through Route 1, whereas by the use of I^- or Br^- it proceeds through Route 2. These different mechanisms may be caused by the nature of the covalency of the counter-ion. The role of the counter-ion on the elementary reactions will be discussed in a future paper.

ACKNOWLEDGMENT

Thanks are given to Mr. T. Shimada for his assistance in the experimental work.

REFERENCES

- [1] T. Kagiya, S. Narisawa, T. Manabe, and K. Fukui, *J. Polym. Sci., Part B*, **4**, 441 (1966).
- [2] D. A. Tomalia and D. P. Sheetz, *J. Polym. Sci.*, **A4**, 2253 (1966).
- [3] W. Seeliger and W. Thier, *Angew. Chem.*, **78**, 613 (1966).
- [4] T. G. Bassiri, A. Levy, and M. Litt, *J. Polym. Sci., Part B*, **5**, 871 (1967).
- [5] R. H. Wiley and L. L. Bennett, Jr., *Chem. Rev.*, **44**, 447 (1949).
- [6] W. Seeliger and W. Thier, *Justus Liebigs Ann. Chem.*, **698**, 158 (1966).
- [7] H. Wenker, *J. Amer. Chem. Soc.*, **57**, 1079 (1947).
- [8] A. P. Phillips and R. Balzly, *J. Amer. Chem. Soc.*, **69**, 200 (1947).
- [9] S. Gabriel and T. Heymann, *Chem. Ber.*, **23**, 2493 (1890).
- [10] A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, **1948**, 1919.
- [11] J. D. Robert, *Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, p. 22.

Accepted by editor March 31, 1971

Received for publication July 6, 1971