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Radical Copolymerization of 2-Isopropenyl-2-oxazoline with Styrene in the Presence of Lewis Acids

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ABSTRACT

Free-radical copolymerization of 2-isopropenyl-2-oxazoline (IPOZ) with styrene (ST) and methyl methacrylate (MMA) was carried out at 60°C. The reactivity of IPOZ (Q = 0.81 and e = 0.35) was nearly equal to that of MMA. In the radical polymerization of IPOZ in the presence of $ZnCl_2$, the initial polymerization rate and the specific viscosity of the resulting polymer increased with an increase in the concentration of $ZnCl_2$. The tacticities of the polymer determined by the NMR spectrum of the polymer obtained by radical polymerization showed that the content of syndiotactic triads of the polymer obtained in the absence of $ZnCl_2$ was greater than that in the presence of $ZnCl_2$. In the radical copolymerization of IPOZ (M_1) and styrene (M_2) in the presence of $ZnCl_2$, the apparent reactivity ratio r_1 increased with an increase in the $ZnCl_2$ molar content, whereas r_2 decreased. The apparent Q and e values of IPOZ increased markedly by the addition of $ZnCl_2$. The radical copolymerizations in the presence of Lewis acids such as $SnCl_4$, BF_3, and

$HgCl_2$ gave copolymerization behaviors similar to those in $ZnCl_2$. The white solid complexes isolated from IPOZ and Lewis acids were identified by spectroscopic (IR and NMR spectra) and elemental analyses. On the basis of these results, the reactivities of the complexed IPOZ monomer with Lewis acid and the radical derived from the complexed monomer are discussed.

INTRODUCTION

2-Isopropenyl-2-oxazoline (IPOZ) is a polar vinyl monomer containing the oxazoline heterocycle, and it is known that IPOZ undergoes free-radical polymerization to give poly(2-isopropenyl-2-oxazoline) due to vinyl-type polymerization [1-3].

2-Substituted-2-oxazoline reacts easily with strong Brönsted acids such as perchloric or hydroiodic acid to form the oxazolinium salts [4] because of its considerable basicity due to the imino-ether linkage. Therefore, it is thought that the complex formation between the oxazoline heterocycle of the IPOZ molecule and Lewis acid takes place by the electron donor-acceptor interaction.

In recent years it has been found by several groups of workers [5-17] that the rate of radical polymerization of such polar vinyl monomers as methyl methacrylate, acrylonitrile, and vinylpyridine and the composition of the copolymers were affected by the addition of Lewis acids such as zinc chloride. From these studies it was concluded that the Lewis acid-base interaction decisively induced to enhancement of the inherent monomer reactivities of the polar vinyl monomers.

In the present paper the radical copolymerization of IPOZ with styrene (ST) in the presence of Lewis acids such as zinc chloride ($ZnCl_2$) are investigated. From the results of spectroscopic analyses of the complexes isolated from IPOZ and Lewis acid and the apparent reactivity ratios, the role of Lewis acid on the propagating step is discussed.

EXPERIMENTAL

Materials

2-Isopropenyl-2-oxazoline was synthesized by the isomerization reaction of N-methacryloyl ethylenimine, prepared from ethylenimine and methacryloyl chloride with the use of sodium iodide catalyst according to a previous paper [3] and purified by several distillations under reduced pressure (bp 50.5-51.5°C/17 Torr). Styrene and methyl methacrylate were commercially available guaranteed grade materials. These vinyl comonomers were distilled before use. The initiator, α,α'-azobisisobutyronitrile (G. R. Grade, AIBN), was used without further purification. The Lewis acids, anhydrous zinc chloride, stannic chloride, and anhydrous mercuric chloride (commercially available guaranteed or extra-reagent grade materials), were used without further purification, and commercial boron trifluoride etherate was redistilled before use; bp 125-126°C.

Polymerization Procedure

A definite amount of zinc chloride was placed in a glass ampoule, and then 1.00 g of pure IPOZ and 2 ml of benzene solution containing 0.5 mole % of AIBN initiator was introduced. The ampoule, degassed under high vacuum by the usual freezing and thawing technique, was sealed off. Polymerizations were carried out in a thermostat kept at constant temperature in the 0-120°C range. After a given time the ampoule was removed from the thermostat and the content of the ampoule was dissolved in a methanol solution containing hydrochloric acid. The resulting polymer was isolated by reprecipitation from methanol solution into n-hexane and purified repeatedly. The polymer thus obtained was dried and weighed. The resulting polymer contained no zinc chloride as confirmed by ash analysis.

The specific viscosities of N,N-dimethylacetamide solutions of the resulting polymer (0.50 g/l) were measured at 35°C by the use of an Ubbelohde-type viscometer.

Copolymerization Procedure

A given amount of Lewis acid and pure IPOZ were added to the polymerization ampoule containing 3 ml of benzene solution of AIBN initiator (0.5 mole % of monomer). Copolymerizations were carried out in a manner similar to that described above. After the treatment with the methanol solution containing hydrochloric acid, the polymer was isolated from a large amount of n-hexane, and purified repeatedly by dissolving with chloroform and reprecipitating into n-hexane. The lack of a methanol-soluble portion proved that no cationic polymerization of ST by Lewis acid catalyst had taken place.

Preparation of the Complexes of IPOZ with Lewis Acids

With a molar feed ratio of IPOZ to $ZnCl_2$ of 10:1, the toluene solution of IPOZ was gradually added to the mixture of toluene and powdery

$ZnCl_2$ with vigorous stirring at -10 to -20° C. After the excess $ZnCl_2$ was removed by filtration, the filtrate was introduced into a large amount of stirred diethyl ether cooled to 0° C. The precipitated white powdery product was dried under reduced pressure, and purified by several dissolution-reprecipitation-evacuation cycles. The complexes with $SnCl_4$ and BF_3 were prepared in n-hexane solution at -10 to -20° C, the complex with $HgCl_2$ by dissolving $HgCl_2$ in IPOZ directly at -50° C. The removal of the excess IPOZ was by distillation under reduced pressure at room temperature. In all cases, 0.10 mole of IPOZ and 0.01 mole of Lewis acid were used.

Determination of the Tacticities of Polymers

Proportions of isotactic, heterotactic, and syndiotactic triads were calculated from the relative heights of the respective α-methyl proton signals in NMR spectra according to the method of Bovey et al. [18].

Spectral Measurement

Infrared spectra were recorded on a JASCO Grating Infrared Spectrometer, Model DS-403G by the potassium bromide technique. The NMR spectra were run at room temperature on a Varian H-100 Spectrometer (100 MHz) and Japan Electron Optics 60 MHz Spectrometer (JNM-3H-60) with tetramethylsilane as an internal standard.

RESULTS AND DISCUSSION

Free-Radical Copolymerization of 2-Isopropenyl-2-oxazoline

Free-radical copolymerizations of IPOZ, with ST and methyl methacrylate (MMA) were carried out at 60° C in benzene solution with the use of AIBN as initiator. The IR spectra of the white, powdery products showed that these products were copolymers of IPOZ without the ring-opening reaction of oxazoline heterocycle in copolymers. The results of copolymerizations with different monomer pairs are shown in Fig. 1, in which the IPOZ-MMA pair shows the azeotropic copolymer composition. Figure 2 represents the Fineman-Ross plots [19] for different monomer pairs with IPOZ monomer. The monomer reactivity ratios r_1 and r_2 were calculated from the intersect and slope, and are given in Table 1. The Q-e value [20] of IPOZ was calculated by assuming $Q = 1.0$ and $e = -0.80$ for St [20] and $Q = 0.74$ and $e = 0.40$ for

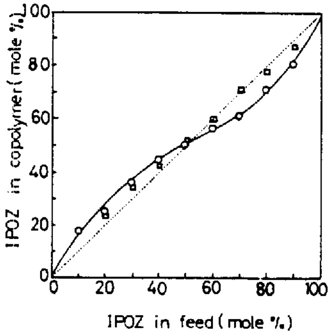


FIG. 1. Copolymerizations of 2-isopropenyl-2-oxazoline (IPOZ) with styrene and methyl methacrylate in benzene solution at 60° C: IPOZ-ST (O) and IPOZ-MMA (□).

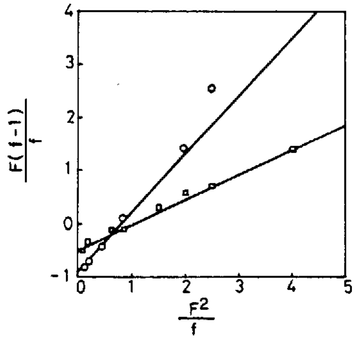


FIG. 2. Reactivity ratios for IPOZ(M_1)-ST and IPOZ(M_1)-MMA by the Fineman-Ross equation: $F(f - 1)/f = r_1(F^2/f) - r_2$, $F = m_1/m_2$ where m_1 and m_2 are the concentrations of the monomers units incorporated into the polymer, and f is the ratio of monomer M_1 to M_2 initially. IPOZ-ST (□) and IPOZ-MMA (O).

MMA [21] (Table 1). The Q-e value of IPOZ is almost equal to that of MMA. This may indicate that the oxazoline group in the IPOZ molecule acts as an electron-withdrawing group toward the vinyl group, as does the ester group in MMA.

TABLE 1. Reactivity Ratios and Copolymerization Parameters in the Free-Radical Polymerization of IPOZ (M_1)[a]

M_2 (comonomer)	r_1	r_2	Q_1	e_1
Styrene	0.55	0.49	0.81[b]	0.35[b]
Methyl methacrylate	1.12	0.89	0.76[c]	0.40[c]

[a] Reaction temperature 60° C.

[b] Calculated from $Q_2 = 1.0$ and $e = -0.80$ for styrene.

[c] Calculated from $Q_2 = 0.7$ and $e_2 = 0.40$ for methyl methacrylate.

Influence of Zinc Chloride on the Free-Radical Polymerization of 2-Isopropenyl-2-oxazoline

The radical polymerization of IPOZ in benzene solution in the presence of $ZnCl_2$ was carried out at 60° C. The polymer yield at the initial stage of polymerization increased linearly with reaction time up to almost 20% conversion (Fig. 3). The results obtained by varying the concentration of $ZnCl_2$ are shown in Table 2. Figure 4 shows the linear relation between the initial polymerization rate (R_p) and

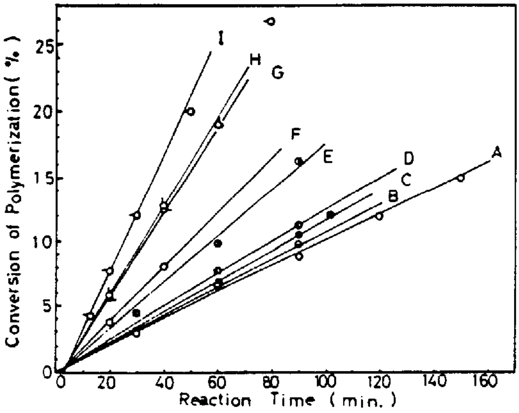


FIG. 3. Polymerization of IPOZ in the presence of $ZnCl_2$ at 60° C. The initial molar ratios of $ZnCl_2$ to IPOZ monomer were: A (none), B (0.01), C (0.02), D (0.03), E (0.09), F (0.20), G (0.32), H (0.38), and I (0.50).

TABLE 2. The Relative Ratio of the Initial Polymerization Rate $(R_p)_c$ in the Presence of $ZnCl_2$ to That of $(R_p)_f$ in the Absence of $ZnCl_2$

The feed molar ratio of $ZnCl_2$ to IPOZ monomer	$(R_p)_c/(R_p)_f$ [a]
0.01	1.1
0.02	1.2
0.03	1.3
0.09	1.8
0.20	2.5
0.32	3.7
0.38	3.8
0.50	4.8

[a] $(R_p)_f = 0.10\%/\text{min}$. Polymerizations were carried out at 60°C with the use of AIBN (0.50 mole % to monomer) as radical initiator.

the charged molar ratio of $ZnCl_2$ to monomer, and the remarkable increase in the specific viscosity of the resulting polymer at low conversion, measured in N,N-dimethylacetamide solution at 35° C, with an increase in the $ZnCl_2$ molar content. Furthermore, the specific viscosity results of the experiment with a definite amount of $ZnCl_2$ were constant, independent of conversion (Fig. 5). The increase in the degree of polymerization, independent of conversion, may be attributed to an increase in the propagation rate or a decrease in the transfer rate, and the enhanced initial polymerization rate is attributable to an increase in the propagation rate or a decrease in the termination rate.

It has been reported by Imoto et al. [10] that the decomposition rate of AIBN as a radical initiator is not affected by the addition of $ZnCl_2$. According to the results reported by Bamford et al. [5, 6], in the radical polymerization of MMA and acrylonitrile by the use of the rotating sector technique, the propagation rate constant increases by the addition of zinc chloride or lithium chloride, whereas the termination reaction is hardly affected. In the radical polymerization of vinylpyridines, Tazuke et al. [14] showed that the addition of zinc salts enhanced the propagation rate constant, based of a linear

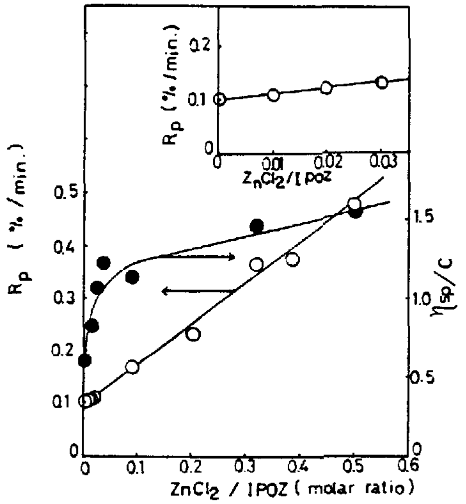


FIG. 4. The variation of the initial polymerization rate (R_p) and specific viscosity of the resulting polymer with the changes in the initial molar ratio of $ZnCl_2$ to IPOZ. η_{sp}/C; specific viscosity in N,N-dimethylacetamide solution (0.50 g/l) at 35°C.

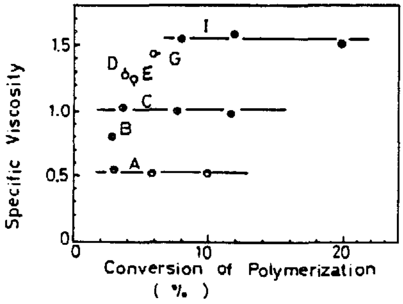


FIG. 5. The relation between the conversion of polymerization and the specific viscosity of the resulting polymer. The reaction conditions were the same as for Fig. 4. The initial molar ratios of $ZnCl_2$ to IPOZ were: A (none), B (0.01), C (0.02), D (0.03), E (0.09), G (0.32), and I (0.50).

relationship between an increase in rate and the degree of polymerization.

In considering these results, it seems reasonable that the increase in the rate of radical polymerization of polar vinyl monomers by the addition of $ZnCl_2$ would be predominantly caused by the enhancement of the propagation rate constant.

Tacticities of Poly(2-isopropenyl-2-oxazoline)

The NMR spectrum of the polymer (Poly-IPOZ) resulting from the free-radical polymerization of IPOZ indicates three signals at 8.6-8.9T, as shown in Fig. 6. By analogy to the signals of the α-methyl protons of poly(methyl methacrylate) [18], peaks at 8.64, 8.80, and 8.91 were attributed to α-methyl protons of monomeric units in isotactic(I), heterotactic(H), and syndiotactic(S) triads, respectively.

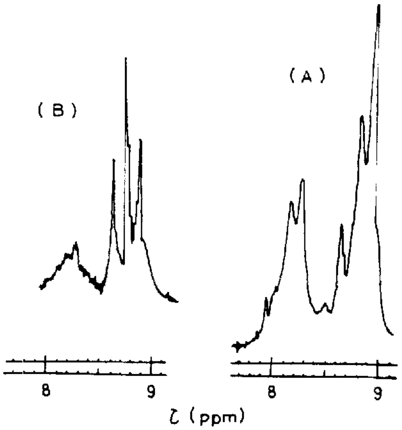


FIG. 6. The NMR spectra of the polymers recorded in the absence and presence of $ZnCl_2$, measured in 10% $CDCl_3$ solution at room temperature (100 MHz). (A) The polymer obtained in the absence of $ZnCl_2$ at 70°C. (B) The polymer obtained in the presence of $ZnCl_2$ (50 mole % to monomer) at 60°C.

As can be seen in Table 3, triads tacticities calculated from the relative heights of α-methyl absorption split into three peaks, indicating that the Poly-IPOZ obtained by free-radical polymerization in the absence of $ZnCl_2$ possesses a larger S percentage, whereas

Poly-IPOZ obtained in the presence of $ZnCl_2$ (50 mole % to IPOZ monomer) has a smaller S percentage.

In addition, the tacticities of the polymer obtained in the absence of $ZnCl_2$ changed markedly with the polymerization temperature, favoring the syndiotactic triad addition at lower polymerization temperatures. On the other hand, the tacticities of the polymer obtained in the presence of $ZnCl_2$ were hardly dependent on the polymerization temperature over the 0 to 120°C range (Table 3).

Isotactic and syndiotactic diad propagation steps can be expressed by the absolute rate theory, as proposed by Bovey et al. [18]:

$$k_i = (\kappa T/h) \exp\{\Delta S_i^{\ddagger}/R) - (\Delta H_i^{\ddagger}/RT)\} \tag{1}$$

$$k_s = (\kappa T/h) \exp\{(\Delta S_s^{\ddagger}/R) - (\Delta H_s^{\ddagger}/RT)\} \tag{2}$$

where the subscripts i and s indicate isotactic and syndiotactic, respectively. The ratio of isotactic diad probability to syndiotactic diad probability, P_i/P_s, is written as

$$\ln(P_i/P_s) = \ln(k_i/k_s) = \{(\Delta S_i^{\ddagger} - \Delta S_s^{\ddagger})/R - (\Delta H_i^{\ddagger} - \Delta H_s^{\ddagger})/RT\} \tag{3}$$

Therefore, the difference in activation enthalpies $[\Delta(\Delta H_p^{\ddagger})]$ and entropies $[\Delta(\Delta S_p^{\ddagger})]$ between the isotactic and syndiotactic diad addition can be estimated from

$$\Delta(\Delta H_p^{\ddagger}) = \Delta H_i^{\ddagger} - \Delta H_s^{\ddagger} = -R\,\delta \ln(P_i/P_s)(1/T) \tag{4}$$

$$\Delta(\Delta S_p^{\ddagger}) = \Delta S_i^{\ddagger} - \Delta S_s^{\ddagger} = R \ln(P_i/P_s) + \Delta(\Delta H_p^{\ddagger})/T \tag{5}$$

From the slope of the relationship between $\ln(P_i/P_s)$ and $1/T$ (Fig. 7), the activation entropies and enthalpies can be calculated, and are listed in Table 3. The preference of the syndiotactic diad addition observed in the free-radical polymerization in the absence of $ZnCl_2$ is entirely ascribable to the activiation enthalpy difference $[\Delta(\Delta H_p^{\ddagger}) = 0.8$ kcal/mole, $\Delta(\Delta S_p^{\ddagger}) = 0.2$ e.u.]. On the other hand, $\Delta(\Delta H_p^{\ddagger})$ in polymerization in the presence of $ZnCl_2$ (50 mole %) was nearly equal to zero, and the probability of isotactic diad addition was

TABLE 3. Comparison of Tacticities of the Polymers Resulting from Free-Radical Polymerization in the Absence and Presence of $ZnCl_2$

Monomer	Temperature (°C)	Conversion (%)	Tacticity (%)[c]			P_s[d]	$\Delta(\Delta H_p)$[e] (kcal/mole)	$\Delta(\Delta S_p)$[e] (e.u.)
			I	H	S			
IPOZ	5[b]	4	8.0	40.6	51.3	0.71_6		
	40	6.2	10.2	46.2	46.2	0.66_8	0.8 ± 0.1	0.2 ± 0.02
	70	19.5	11.4	44.5	44.3	0.66_5		
	120	10.2	16.5	48.3	35.2	0.59_4		
IPOZ-$ZnCl_2$[a]	0[b]	4.8	22.8	49.9	27.3	0.52_2		
	40	25	23.0	50.0	27.0	0.52_0	0.06 ± 0.01	-1.2 ± 0.3
	60	19	23.9	49.2	26.9	0.50_5		
	100	28	23.4	50.0	26.6	0.51_6		

[a] Feed ratio of IPOZ to $ZnCl_2$ = 2:1 (molar).

[b] Polymerization was effected with the use of AIBN as photosensitizer by irradiation with a high-pressure mercury lamp.

[c] The proportions of syndiotactic (S), heterotactic (H), and isotactic (I) triads.

[d] The probability of syndiotactic diad P_s is calculated from the equation: $P_s = (S + H/2)/100$.

[e] Enthalpy difference $\Delta(\Delta H_p)$ and entropy difference $\Delta(\Delta S_p)$ between isotactic and syndiotactic diad addition.

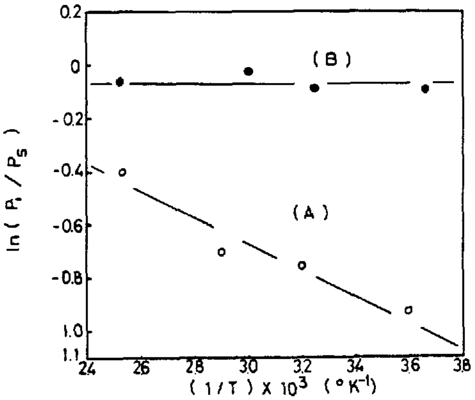
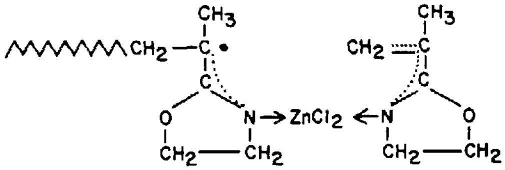


FIG. 7. The relation between ln (P_i/P_s) and the reciprocal polymerization temperature, where P_i and P_s denote the probabilities of the isotactic and syndiotactic diad addition, respectively. (A) and (B) were the same as for Fig. 6.

governed only by the magnitude of the difference in activation entropy $[\Delta(\Delta S_p^{\ddagger}) = -1.2$ e.u.].

These facts suggest that the stereoregular addition of monomer in the propagation process can be controlled by the electron donor-acceptor interaction between zinc chloride and both oxazoline heterocycles in the growing terminal unit and the incoming monomer in the transition state:



The cyclic addition mentioned above could be supported by the isolation of the 2:1 complex $[(IPOZ)_2ZnCl_2]$ of IPOZ and $ZnCl_2$ as described below.

Radical Copolymerization of 2-Isopropenyl-2-oxazoline with Styrene in the Presence of Lewis Acids

In order to study the reactivity change of IPOZ by Lewis acid, the radical copolymerizations of IPOZ with styrene in the presence of Lewis acids such as $ZnCl_2$, stannic chloride ($SnCl_4$), mercuric chloride ($HgCl_2$), and boron trifluoride (BF_3) were carried out at 60°C in benzene solution. No homopolymers of IPOZ and styrene by Lewis acid catalysts were obtained under the present reaction conditions, and hydroquinone (1 mole % to monomer) effectively inhibited the polymerization.

As can be seen in Fig. 8, with an increase in the $ZnCl_2$ molar content, the incorporation of IPOZ in the resulting copolymer was promoted markedly. The apparent monomer reactivity ratios r_1 and r_2 (M_1: IPOZ, M_2: ST) in the presence of $ZnCl_2$, estimated from the method of Fineman-Ross [19], showed that r_1($= k_{11}/k_{12}$) increased with an increase in the concentration of $ZnCl_2$, whereas r_2($= k_{22}/k_{21}$) decreased (Table 4). The apparent Q and e values of IPOZ as listed in Table 4 increased markedly by the addition of $ZnCl_2$. By the use of the Alfrey-Price equation [20], the relative value of the reactivity ratio $(r)_c$ in the presence of $ZnCl_2$ to that of $(r)_f$ in the absence of $ZnCl_2$ can be expressed as

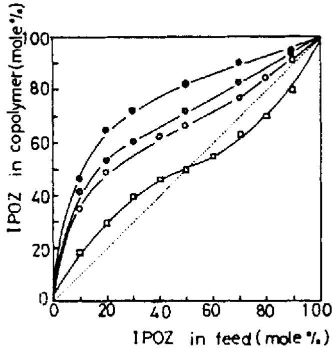


FIG. 8. Copolymerizations of IPOZ with styrene in the presence of $ZnCl_2$ at 60°C. The initial molar ratio of $ZnCl_2$ were none (□), 0.02 (○), 0.10 (◐), and 0.50 (●).

TABLE 4. Apparent Reactivity Ratios and Q-e values of the IPOZ (M_1) - ST (M_2) Copolymerization in the Presence of $ZnCl_2$.

$ZnCl_2$/IPOZ (molar ratio)	Reactivity ratio		Q_1	e_1
	r_1	r_2		
0	0.55	0.49	0.81	0.35
0.02	1.50	0.10	3.32	0.58
0.10	1.75	0.07	4.5	0.65
0.50	4.50	0.02	14.8	0.80
1.00[a]	4.60	0.009	~28	~1.0

[a] Estimated by extrapolating in Fig. 12.

$$\frac{(r_1)_c}{(r_1)_f} = \frac{(Q_1)_c}{(Q_1)_f} \exp\{(e_{1c} - e_{1f})(e_2 - e_{1f} - e_{1c})\} \tag{7}$$

$$\frac{(r_2)_c}{(r_2)_f} = \frac{(Q_1)_f}{(Q_1)_c} \exp\{(e_2(e_{1c} - e_{1f})\} \tag{8}$$

where the subscripts c and f denote the presence and absence of $ZnCl_2$, respectively. Accordingly, the increase in r_1 value and the decrease in r_2 value by the addition of $ZnCl_2$ may be caused by the marked increase in Q_1 value, in spite of the decrease in the exponential term in Eq. (7) and (8) ($e_{1c} > e_{1f} > 0$, and $e_2 = -0.80$).

The relative ratio of the apparent monomer reactivity ratios in the radical copolymerizations of IPOZ (M_1) and ST (M_2) in the presence and absence of $ZnCl_2$ are

$$\frac{(r_1)_c}{(r_1)_f} = \frac{(k_{11})_c}{(k_{11})_f} \times \frac{(k_{12})_f}{(k_{12})_c} \tag{9}$$

$$\frac{(r_2)_c}{(r_2)_f} = \frac{(k_{22})_c}{(k_{22})_f} \times \frac{(k_{21})_f}{(k_{21})_c} \tag{10}$$

where the subscripts c and f denote the presence and absence of $ZnCl_2$, respectively, and k is a propagation reaction constant of four elementary propagation reactions. Assuming that the propagation step in homopolymerization of styrene is not affected by the addition of $ZnCl_2$,

$$(k_{22})_c/(k_{22})_f = 1 \tag{11}$$

Accordingly, the relative ratio of the cross-propagation rate constants (k_{21}) in the presence and absence of $ZnCl_2$ can be calculated by

$$(r_2)_c/(r_2)_f = (k_{21})_f/(k_{21})_c \tag{12}$$

As can be seen in Table 5, the apparent cross-propagation rate constant (k_{21}) increases proportionally with an increase in the concentration of $ZnCl_2$). This means that the reactivity of IPOZ monomer toward the propagating styryl radical increased markedly by the addition of $ZnCl_2$.

On the basis of the results of the increase in initial polymerization rate and the specific viscosity of the resulting polymer, independent of conversion, with an increase in $ZnCl_2$ molar content in radical polymerization of IPOZ, the following relation can be assumed approximately:

$$(k_{11})_c/(k_{11})_f \doteqdot (R_p)_c/(R_p)f \tag{13}$$

where $(R_p)_c$ and $(R_p)_f$ denote the initial polymerization rate in the presence and absence of $ZnCl_2$, respectively. Accordingly, from Eqs. (9) and (13), using the initial polymerization rates (Table 2), the apparent relative ratios of the cross-propagation rate constant (k_{12}) in the presence and absence of $ZnCl_2$ were estimated (Table 5). With an increase in the $ZnCl_2$ molar content, the apparent cross-propagation rate constant of the propagating radical derived from IPOZ monomer was reduced approximately to one-half of that in the absence of $ZnCl_2$. These results may imply that IPOZ monomer in the presence of $ZnCl_2$ is more reactive than in the absence of $ZnCl_2$, whereas the reactivity of the radical derived from the former monomer is less than that from the latter.

The radical copolymerizations of IPOZ with ST in the presence of other kinds of Lewis acids ($SnCl_4$, BF_3, and $HgCl_2$; 2 mole % to IPOZ monomer; Fig. 9) are summarized in Table 6. The apparent reactivity ratios r_1 increased by the addition of the Lewis acids of $SnCl_4$ and $HgCl_2$, but r_2 decreased by the addition of the above three kinds of Lewis acids. Copolymerization behaviors in the presence of the three

TABLE 5. Apparent Relative Ratio of Cross-Propagation Rate Constants in the Polymerization of IPOZ (M_1) and ST (M_2) in the Presence and Absence of $ZnCl_2$.

$ZnCl_2$/IPOZ (molar ratio)	Reactivity ratio		$\frac{(r_1)_c}{(r_1)_f}$[b]	$\frac{(r_2)_c}{(r_2)_f}$	$\frac{(k_{21})_c}{(k_{21})_f}$	$\frac{(k_{11})_c}{(k_{11})_f}$	$\frac{(k_{12})_c}{(k_{12})_f}$
	r_1	r_2					
0	0.55	0.49	-	-	-	-	-
0.02	1.50	0.10	2.72	0.202	4.9	1.2	0.59
0.10	1.75	0.07	3.18	0.142	7.0	1.8	0.56
0.50	4.5	0.02	8.20	0.041	25	4.8	0.48
1.00[a]	4.6	0.009	8.38	0.018	54	-	-

[a] Estimated by the use of Q = 28 and e = 1.0.

[b] Subscripts c and f denote the presence and absence of $ZnCl_2$, respectively.

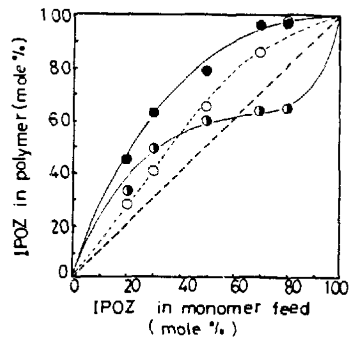


FIG. 9. Copolymerizations of IPOZ with styrene in the presence of Lewis acids at 60° C. The initial molar ratio of Lewis acid to IPOZ was 0.02. $SnCl_4$ (●), $HgCl_2$ (○), and BF_3 (◑).

Lewis acids are similar to those in $ZnCl_2$. Accordingly, the role of Lewis acids on the radical copolymerization of IPOZ with ST is considered to be mainly the enhancement of the reactivity of IPOZ monomer.

Isolation and Spectroscopic Analyses of the IPOZ-Lewis Acid Complexes

The products obtained immediately from the mixture of IPOZ and Lewis acid under the feed molar ratio of $[ZnCl_2]/[IPOZ] \leq 0.1$, at -20 to -10° C were white, powdery solids except for BF_3, which was a colorless, crystalline needle. The elemental analysis showed a

TABLE 6. Monomer Reactivity Ratios and Copolymerization Parameters in the Copolymerization of IPOZ (M_1) and Styrene (M_2) in the Presence of Lewis Acid[a]

Lewis acid[b]	r_1	r_2	Q	e
$ZnCl_2$	1.50	0.10	3.3	0.58
$SnCl_4$	2.76	0.36	$[r_1 \times r_2 =$	$1.0]$
$HgCl_2$	2.60	0.62	$[r_1 \times r_2 =$	$1.61]$
BF_3	0.60	0.32	1.1	0.48

[a] Copolymerizations were carried out at 60° C in benzene solution.
[b] Initial molar ratio of Lewis acid to IPOZ monomer was 0.02.

TABLE 7. Properties of IPOZ-Lewis Acid Complexes

Complex	Composition[a]	mp (°C)	State at room temperature	Solvent[b]
$(IPOZ)_2ZnCl_2$	2.0	55-56	White powder	Bz, Tol, Acet, MeOH, DMAc
$(IPOZ)_2SnCl_4$	1.8 1.9	91-92	White powder	MeOH, DMAc, Bz[c]
$(IPOZ)_2HgCl_2$	2.0	101-102	White powder	MeOH, DMAc, Bz[c]
$(IPOZ)BF_3$	1.0	~60 (decomp)	Colorless, crystalline needles	Acet, MeOH, DMAc, Bz[c]

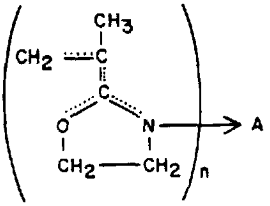
[a] Mole ratio of IPOZ to Lewis acid.

[b] Bz, benzene; Tol, toluene; Acet, acetone; MeOH, methanol; DMAc, N,N-dimethylacetamide.

[c] Slightly soluble in benzene.

composition of 2(IPOZ):1 (Lewis acid) except for the equimolar composition of IPOZ-BF_3 (Table 7). The values of the composition of $(IPOZ)_2SnCl_4$, which were somewhat scattered from 1.78 to 1.92, were close to the 2:1 composition.

The IR and NMR spectra showed the characteristic absorptions of the IPOZ molecule (Figs. 10 and 11), which indicated the ring-opening reaction did not occur. The evidence thus obtained leads to the conclusion that the products are 2:1 or 1:1 complexes of IPOZ with Lewis acids, due to the coordination of N-atom in IPOZ to Lewis acid:



where n = 1 or 2, and A denotes Lewis acid. The complex formation is probably caused by the Lewis acid-base interaction due to the strong

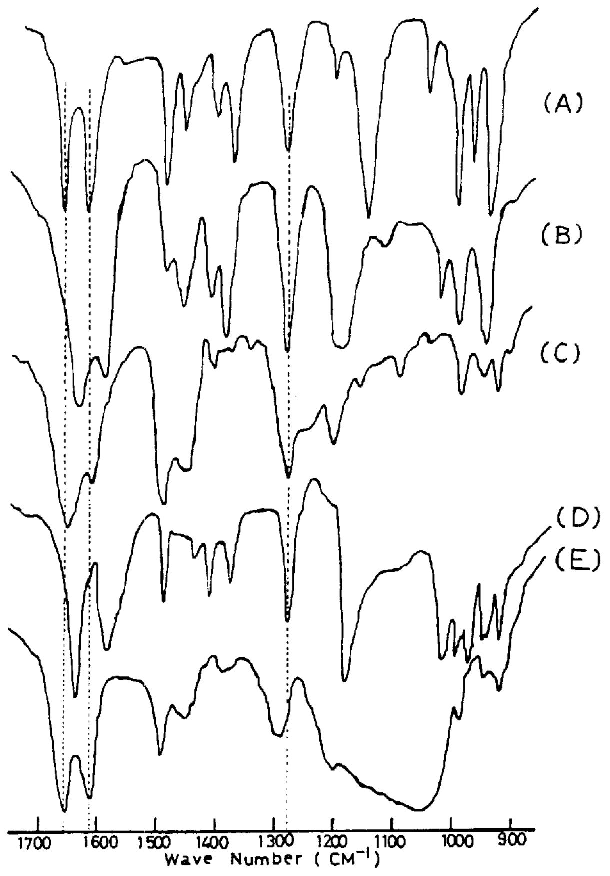


FIG. 10. The infrared spectra of the uncomplexed IPOZ and the complexed IPOZ with Lewis acids. (A) Uncomplexed IPOZ. (B) $(IPOZ)_2ZnCl_2$. (C) $(IPOZ)_2SnCl_4$. (D) $(IPOZ)_2HgCl_2$. (E) IPOZ-BF_3.

electron donating power of oxazoline heterocycle because of its considerable basicity. The properties of IPOZ-Lewis acid complexes are shown in Table 7.

Characteristic IR and NMR spectral data of the complexes are summarized in Table 8. The imino-stretching frequency at 1655 cm^{-1} and the vinyl-stretching vibration at 1610 cm^{-1} in uncomplexed IPOZ monomer [3] were shifted toward lower frequencies by the complexation, whereas the ether-stretching frequency shifted toward higher frequencies.

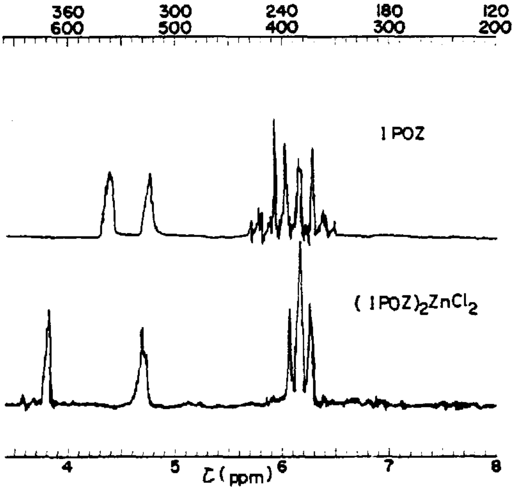


FIG. 11. The NMR spectra of the uncomplexed IPOZ and the complexed IPOZ with ZnCl$_2$. (IPOZ)$_2$ZnCl$_4$ was measured in 5% benzene solution at room temperature (60 MHz).

TABLE 8. Changes in Infrared Spectra and Proton Chemical Shift of IPOZ on Complex Formation

Complex	IR shift (cm^{-1})[a]			NMR shift (ppm)[b]	
	$\Delta\nu_{C=N}$	$\Delta\nu_{C-O}$	$\Delta\nu_{C=CH_2}$	$\Delta\tau_{H_t}$[c]	$\Delta\tau_{H_c}$[c]
(IPOZ)$_2$ZnCl$_2$	-27	+1	-16	-0.08	-0.47
(IPOZ)$_2$SnCl$_2$	-5	+1	-2	-0.06	-0.36
(IPOZ)$_2$HgCl$_2$	-17	+2	-25	-0.07	-0.31
(IPOZ)BF$_3$	-2	+12	0	-0.01	-0.08

[a] Characteristic absorption of IPOZ monomer: $\nu_{C=N}$, 1655 cm^{-1}; $\nu_{C=O}$, 1610 cm^{-1}; ν_{C-O}, 1278 cm^{-1}.

[b] Chemical shift (τ) is referred to tetramethylsilane (τ = 10.00 ppm) at 100 MHz. For pure monomer; τ (H$_c$) at 4.28 ppm and τ(H$_t$) at 4.59 ppm. H$_c$ and H$_t$ are vinyl protons cis and trans to the oxazoline group, respectively.

[c] Shift value Δ = (complexed) - (free).

On the other hand, the chemical shifts of vinyl protons of the complexed IPOZ were observed in lower magnetic fields compared with those of the uncomplexed IPOZ molecule. This fact might suggest that the electron density of the carbon-carbon double bond of the IPOZ-Lewis acid complex was lower than that of the uncomplexed IPOZ. From these observations it might be indicated that the interaction between the positively charged metal of the Lewis acid and the nitrogen atom of the oxazoline ring would decrease the electron density around the nitrogen, and then the effect would be transferred to the vinyl group by an inductive or resonance effect.

Accordingly, the observed e value increase with an increase in the concentration of Lewis acid may be caused by the major participation of the complexed IPOZ monomer with Lewis acid, in which the electron density on the vinyl group is lower than that of uncomplexed IPOZ molecule. The marked increase in Q value might be resulted from the contribution of the expansion of the conjugative system.

A distinct relationship between the acid-strength [22] of Lewis acid based on the carbonyl-shift in the complexed xanthone with Lewis acid and the observed shift in values in the characteristic absorption frequency or chemical shift values between uncomplexed and complexed IPOZ molecule did not appear to exist. This may be due to the difference in the stereochemical structure of the complexes and the back-donation of the metal atom to the oxazoline molecule.

Reactivity of the Complexed IPOZ with $ZnCl_2$

The IPOZ complex with $ZnCl_2$ would play an important role in the radical copolymerization of IPOZ with ST. The complex formation between IPOZ and $ZnCl_2$ in the copolymerization may be established by the following reversible equilibriums:

$$\text{IPOZ} + \text{ZnCl}_2 \rightleftharpoons \text{IPOZ-ZnCl}_2 \tag{14}$$

$$\text{IPOZ} + \text{IPOZ-ZnCl}_2 \rightleftharpoons (\text{IPOZ})_2\text{ZnCl}_2 \tag{15}$$

Suppose that the present copolymerization is composed of three component monomers (uncomplexed IPOZ, equimolar complex IPOZ-$ZnCl_2$ and ST), then the nine possible elementary reactions at the propagating step in the present copolymerization are assumed to be

$$M_i\cdot + M_j \xrightarrow{k_{ij}} M_j\cdot \tag{16}$$

where $M_i\cdot$ represents the growing polymer radical having the monomer

M_i as the terminal, free-radical-bearing unit, and k is the propagating rate constant.

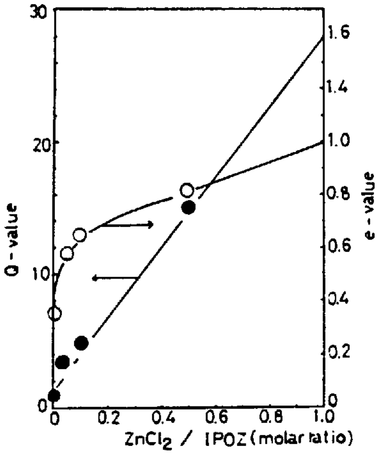


FIG. 12. The variation of Q-e values of IPOZ monomer in radical copolymerization with styrene at 60°C with changes in the initial molar ratio of $ZnCl_2$ to IPOZ monomer.

TABLE 9. Estimated Reactivity Ratios in the Copolymerizations of IPOZ-$ZnCl_2$ Complex (1:1)

Run No.[a]	M_1	M_2	r_1	r_2
1	IPOZ	ST	0.55	0.49
2	IPOZ-$ZnCl_2$	ST	4.6	0.009
3	IPOZ-$ZnCl_2$	IPOZ	18	0.04

[a] Run No. 1 is calculated from the copolymerization data, run Nos. 2 and 3 are estimated by the use of Q = 28 and e = 1.0 for the equimolar complexed IPOZ with $ZnCl_2$.

In the radical copolymerizations of the equimolar complex IPOZ-$ZnCl_2$ (M_3) with ST (M_2) and uncomplexed IPOZ (M_1), the monomer reactivity ratios with different monomer-pairs are predicted approximately

TABLE 10. Relative Rate Constants at the Propagation Step in the Polymerization of IPOZ and ST in the Presence of $ZnCl_2$

Elementary reaction at the propagation step[a]	Relative propagation rate constant	
$M_1\cdot + M_1 \longrightarrow M_1\cdot$	1.00	0.56
$M_1\cdot + M_2 \longrightarrow M_2\cdot$	1.8	1.00
$M_1\cdot + M_3 \longrightarrow M_3\cdot$	25	14
$M_2\cdot + M_1 \longrightarrow M_1\cdot$	1.00	2.00
$M_2\cdot + M_2 \longrightarrow M_2\cdot$	0.50	1.00
$M_2\cdot + M_3 \longrightarrow M_3\cdot$	54	108
$M_3\cdot + M_1 \longrightarrow M_1\cdot$	1.00	0.26
$M_3\cdot + M_2 \longrightarrow M_2\cdot$	3.8	1.00
$M_3\cdot + M_3 \longrightarrow M_3\cdot$	18	4.7

[a] M_1 (free uncomplexed IPOZ), M_2 (ST), M_3 (the equimolar complexed IPOZ with $ZnCl_2$), and $M\cdot$ (the corresponding growing polymer radical).

from the Alfrey-Price equation [20] by using the estimated copolymerization parameters $Q_3 = 28$ and $e_3 = 1.0$, which were obtained by extrapolating to unity the relationship between Q,e-values and the molar ratio of $ZnCl_2$ to IPOZ (Fig. 12). Accordingly, by the use of the corresponding pairs of reactivity ratios tabulated in Table 9, the relative propagation rate constants of nine possible elementary reactions in the copolymerization were estimated approximately as shown in Table 10. The additions of the growing polymer radicals $M_1\cdot$, $M_2\cdot$, and $M_3\cdot$ to the complexed monomer (M_3) are markedly faster than those to the uncomplexed IPOZ (M_1) and ST (M_2). This result indicates that the complexed IPOZ monomer with $ZnCl_2$ is a more reactive monomer than is the uncomplexed.

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