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Initiation and Propagation in the Copolymerization of *N*-Phenylethylenimine with β-Propiolactone

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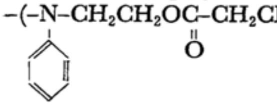
In the copolymerization of *N*-phenylethylenimine with β-propiolactone, the mechanisms of the initiation and propagation reactions were investigated. The rate of the copolymerization was markedly increased by the addition of propionic acid. When a mixture of triethylamine and propionic acid was used as additive, the rate decreased with an increase in the amount of triethylamine, while with an equimolar mixture the rate was almost equal to that without any catalyst. No polymer was obtained with an excess of triethylamine. With Brönsted acid, the composition of the copolymer was independent of the concentration of the catalyst, but it varied with the pK_a value. The monomer reactivity ratio of *N*-phenylethylenimine increased with a decrease in the pK_a value. While that of β-propiolactone decreased.

We have reported in a previous paper that *N*-phenylethylenimine and β-propiolactone copolymerized without any catalyst at 0°C in an acetonitrile solution, giving a powdery or a resinous polymer.[1] The copolymer had the ester structure of  $-(-\underset{C_6H_5}{N}-CH_2CH_2O\underset{O}{\overset{\|}{C}}-CH_2CH_2-)_n-$ in the mainchain, and the monomer reactivity ratios of *N*-phenylethylenimine (r_I) and β-propiolactone (r_L) were estimated to be $r_I=7.5$ and $r_L=0.15$ respectively.

In this paper, the initiation mechanism of the copolymerization without any addition of the catalyst was first studied. Secondly, in order to elucidate the role of the catalyst in the propagation reaction, copolymerization by various acids was studied.

Experimental

Reagents. The method of the synthesis of *N*-phenylethylenimine, and that of the purification of β-propiolactone and acetonitrile, have been described in our previous paper.[1] Guaranteed reagents of acids and dimethylaniline were used without further purification. Triethylamine was purified by the usual method.

Copolymerization Procedure. Measured amounts of a catalyst and a solvent were placed into a glass ampule under a nitrogen atmosphere, β-propiolactone and *N*-phenylethylenimine were then added to this system at −78°C. The ampule was sealed and maintained at 0—1°C for the duration of the reaction. The products were then washed with chloroform and diethylether, separated by a centrifuge, and dried *in vacuo*.

Determination of the Composition of the Copolymer. The composition of the copolymer was determined by the method described in the previous paper.[1]

Results and Discussion

Initiation Mechanism in the Polymerization Without any Catalyst. The copolymerization was carried out in acetonitrile without any catalyst and at 0°C. The relation between the total conversion and the mole per cent of β-propiolactone in the monomer feed is shown in Fig. 1. The conversion of each monomer was obtained from the data of the total conversion and the composition of the copolymer. In Fig. 2 the rates of the consumption of the two monomers, defined as the ratio of the conversion of each monomer to the

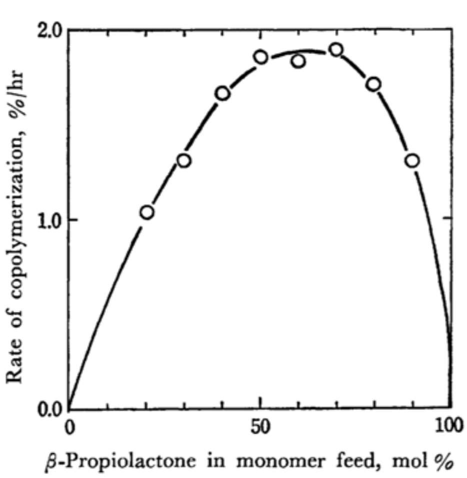


Fig. 1. Copolymerization of *N*-phenylethylenimine and β-propiolactone without any catalyst.

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[1] "Copolymerization of *N*-phenylethylenimine and β-propiolactone," T. Kagiya, T. Kondo, S. Narisawa and K. Fukui, This Bulletin, **41**, 172 (1968).

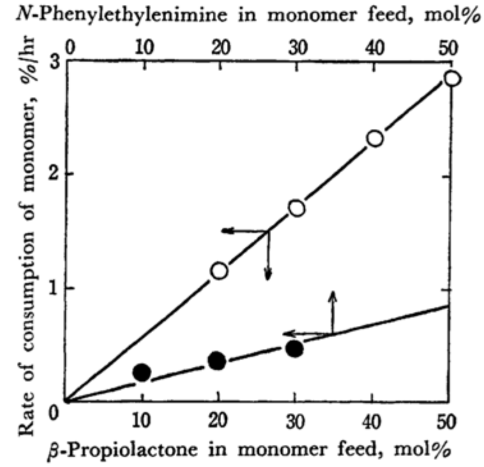


Fig. 2. Rates of the consumption of *N*-phenylethylenimine and *β*-propiolactone in the copolymerization.
○: *N*-phenylethylenimine ●: *β*-propiolactone

reaction time, are plotted against the amount of the comonomer in the monomer feed. The rate of the consumption of *N*-phenylethylenimine or *β*-propiolactone increased proportionately with an increase in the amount of the comonomer. Furthermore, Fig. 2 shows that the rate of the consumption of *N*-phenylethylenimine was about three times larger than that of *β*-propiolactone. From these results, it may be concluded that the effect of *β*-propiolactone on the polymerization of *N*-phenylethylenimine is greater than that of *N*-phenylethylenimine on the polymerization of *β*-propiolactone.

In order to elucidate the effect of the *β*-propiolactone on the polymerization of *N*-phenylethylenimine, and that of *N*-phenylethylenimine on the polymerization of *β*-propiolactone, the copolymerization was carried out using propionic acid or dimethylaniline respectively as substances analogous to the hydrolyzed compound of *β*-propiolactone and *N*-phenylethylenimine. The rate of the copolymerization was slightly increased by the addition of dimethylaniline, while the rate was remarkably increased by the addition of propionic acid (Fig. 3). The above facts suggest that the copolymerization without any catalyst was initiated by the acid present in *β*-propiolactone.

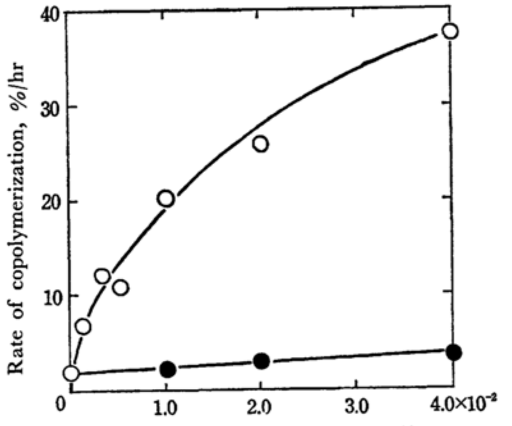


Fig. 3. Rates of copolymerization with propionic acid or dimethylaniline as additive.
○: propionic acid
●: dimethylaniline

Moreover, in order to study the role of the acid in the polymerization, the copolymerization was carried out using a mixture of triethylamine and propionic acid. As is shown in Fig. 4, the rate of the copolymerization markedly decreased with an increase in the amount of triethylamine, while in the case of an equimolar mixture of triethylamine and propionic acid the rate was almost equal to that without any catalyst. No polymer was obtained with an excess of triethylamine. This fact may be due to the neutralization of the acid present in *β*-propiolactone with triethylamine. These results are consistent with the initiation mechanism described above.

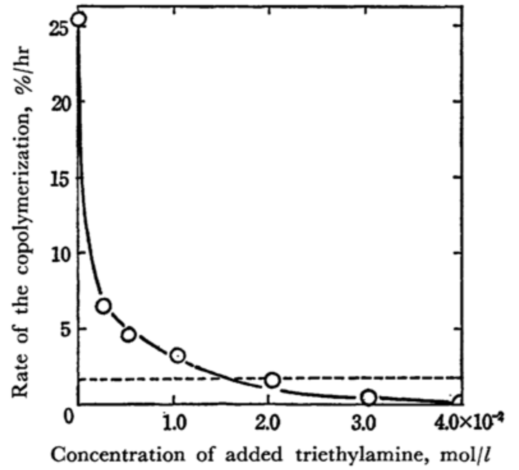


Fig. 4. Copolymerization with the mixture of propionic acid and triethylamine.
Concentration of propionic acid: 2.0×10^{-2} mol/*l*
----: Rate of copolymerization without any catalyst.

The Role of Various Brönsted Acids. Copolymerization was carried out by using various Brönsted acids as catalysts ($pK_a=2.85$—15.7). The relationship between the logarithm of the rate of copolymerization and the pK_a of the acids is shown in Fig. 5. Because the rate increased with a decrease in the pK_a of the catalyst, it has been concluded that the copolymerization was initiated by proton acids and that it proceeded by a cationic mechanism.

The relation between the rate of the consumption of *N*-phenylethylenimine (or *β*-propiolactone) and the pK_a of the acids is shown in Fig. 6. The rates

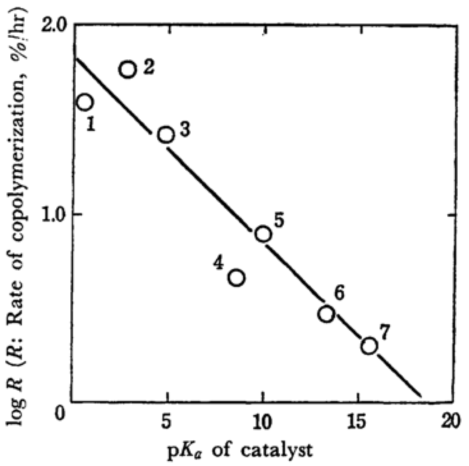


Fig. 5. Plots of rate of copolymerization against the pK_a of the catalyst.
Catalyst 1: Trichloroacetic acid, 2: Monochloroacetic acid, 3: Propionic acid, 4: Nitroethane, 5: Phenol, 6: Diethyl malonate, 7: Water

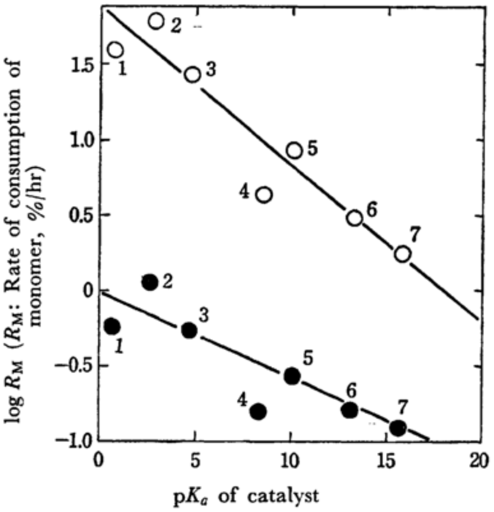


Fig. 6. Plots of rates of consumption of *N*-phenylethylenimine and β-propiolactone against pK_a of the catalyst in copolymerization.
○: *N*-phenylethylenimine
●: β-propiolactone
The number of the catalyst is the same as shown in Fig. 5.

of the consumption of both monomers decreased with an increase in the pK_a of the catalyst. The slopes of the lines in Fig. 6 show that the effect of the pK_a of the catalyst on the rate of the consumption of *N*-phenylethylenimine was greater than that of β-propiolactone. The cause of the lower dependency of the consumption rate of β-propiolactone than that of *N*-phenylethylenimine on the pK_a of the acid is not clear, but it may be that, as will be discussed below, the separation of the counter anion from the propagating oxonium ion is restricted by the electrophilic action of the carbonyl carbon of β-propiolactone on the counter anion.

The composition of the copolymer was independent of the concentration of the catalyst, but it varied with the pK_a of the acid, and the composition of *N*-phenylethylenimine in the copolymer decreased with an increase in its pK_a value (Fig. 7). This fact indicates that the rate of the propagation was influenced by the electronic nature of the counter anion.

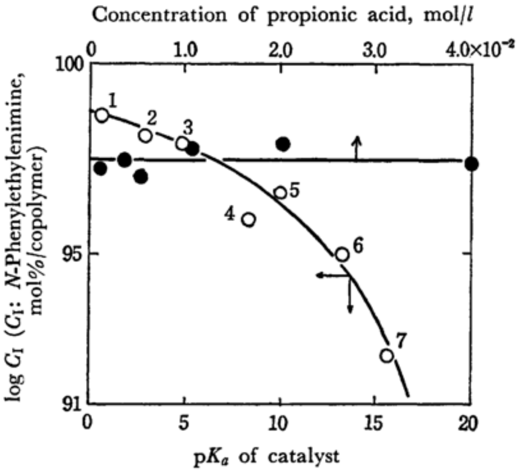


Fig. 7. Relation between composition of *N*-phenylethylenimine in copolymer and the pK_a of the catalyst or concentration of propionic acid.
The number of the catalyst is the same as shown in Fig. 5.

In order to investigate the role of the counter anion of the catalyst in the propagation reaction, the copolymerization was carried out using water, phenol, or propionic acid. The relation between the mole per cent of β-propiolactone in the copolymer and that in the monomer feed is shown in Fig. 8. The monomer reactivity ratios of *N*-phenylethylenimine (r_I) and β-propiolactone (r_L) were

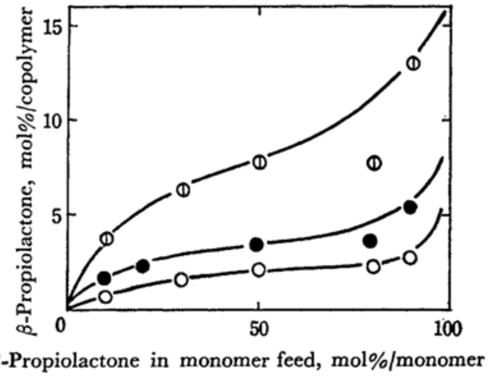


Fig. 8. Relation between the composition of β-propiolactone in the copolymer and in the monomer feed.
○: Propionic acid, ●: Phenol, ⦶: Water

Table 1. Monomer reactivity ratios of *N*-phenylethylenimine and β-propiolactone in the copolymerization with various Brönsted acid catalysts

Catalyst	pK_a	Monomer reactivity ratio	
		N-phenylethylenimine	β-propiolactone
Propionic acid	4.87	16.7	0.103
Phenol	9.98	9.10	0.106
Water	15.7	3.60	0.115

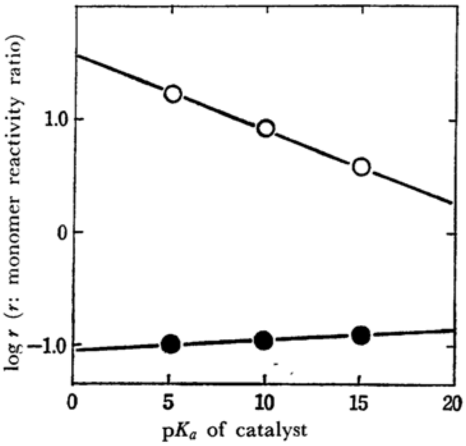
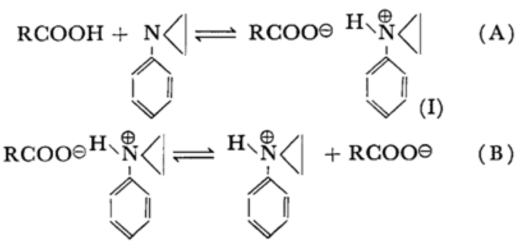


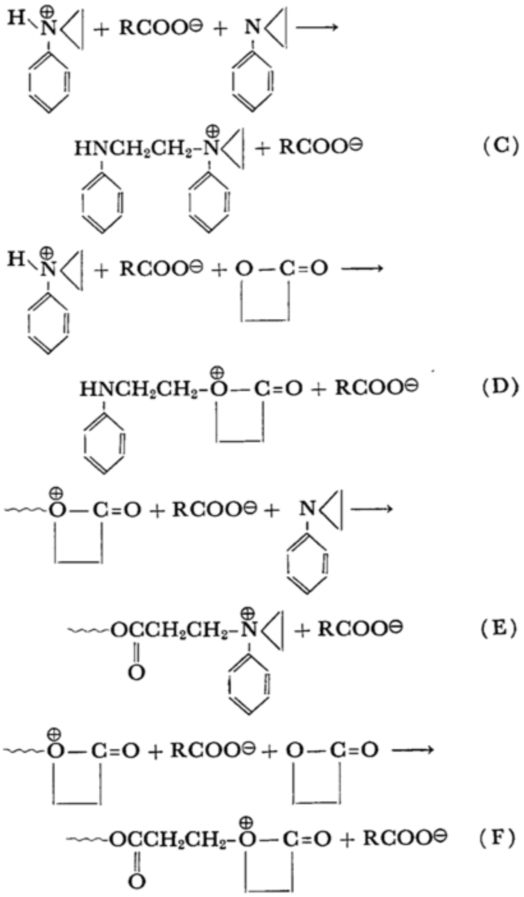
Fig. 9. Relation between monomer reactivity ratios and the pK_a of the catalyst.
○: *N*-phenylethylenimine
●: β-propiolactone

estimated from these curves by the method described in the previous paper[1] (Table 1). The relations between $\log r_{\rm I}$ (or $\log r_{\rm L}$) and the pK_a of the acid are plotted in Fig. 9. The monomer reactivity ratio of *N*-phenylethylenimine increased with a decrease in the pK_a of the catalyst, but, on the contrary, that of β-propiolactone decreased. The fact that the slope of the line for *N*-phenylethylenimine was larger than that for β-propiolactone shows that the effect of the pK_a of the acid on the monomer reactivity ratio of *N*-phenylethylenimine is much larger than that of β-propiolactone.

The Mechanism of the Copolymerization. From these experimental facts, the copolymerization mechanism was postulated to be as follows:
Initiation:



Propagation:



The initiation reaction is considered to be the reaction of the acid with *N*-phenylethylenimine to produce compound (I). The counter anion is separated from the immonium ion as shown in Eq. (B). It is considered that the equilibrium constant of the reaction (B) increases with a decrease in the pK_a of the catalyst, similar to the dissociation of the acid in water.

In the propagation, each monomer attacks a dissociated quarternary immonium ion or an oxonium ion. The rates of the consumption of the two monomers are expressed by the following equations:

$$-\frac{d[\mathrm{I}]}{dt} = (k_{\rm II}[\mathrm{I}\oplus] + k_{\rm LI}[\mathrm{L}\oplus])[\mathrm{I}] \qquad (1)$$

$$-\frac{d[\mathrm{L}]}{dt} = (k_{\rm IL}[\mathrm{I}\oplus] + k_{\rm LL}[\mathrm{L}\oplus])[\mathrm{L}] \qquad (2)$$

where [I], [L], [I⊕], and [L⊕] are the concentrations of *N*-phenylethylenimine, β-propiolactone, dissociated immonium ions, and oxonium ions respectively. The monomer reactivity ratios, $r_{\rm I}$ and $r_{\rm L}$ are given by Eqs. (3) and (4) respectively:

$$r_{\rm I} = k_{\rm II}/k_{\rm IL} \qquad (3)$$

$$r_{\rm L} = k_{\rm LL}/k_{\rm LI} \qquad (4)$$

Since r_I is larger, and r_L, smaller than unity, and since the immonium ion (three-membered ring) is more reactive than oxonium ion (four-membered ring), the rate constant in the propagation reaction is considered to decrease in the order:

$$k_{II} > k_{IL} > k_{LI} > k_{LL} \tag{5}$$

Furthermore, the propagating species is almost entirely the immonium ion, because the amount of β-propiolactone consumed is less than that of N-phenylethylenimine. Therefore, Eqs. (1) and (2) may be approximated as Eqs. (6) and (7) respectively:

$$-\frac{d[I]}{dt} \fallingdotseq k_{II}[I\oplus][I] \tag{6}$$

$$-\frac{d[L]}{dt} \fallingdotseq k_{IL}[I\oplus][L] \tag{7}$$

Taking the logarithm of Eqs. (6) and (7), and subtracting the latter from the former, Eq. (8) is derived:

$$\begin{aligned}\log r_I &= \log k_{II} - \log k_{IL} \\ &= \log(-d[I]/dt) - \log(-d[L]/dt) \\ &\quad + \log([I]/[L])\end{aligned} \tag{8}$$

From Fig. 6, the two empirical equations (9) and (10) are obtained:

$$\log(-d[I]/dt) = 1.7 - 0.102\,pK_a \tag{9}$$

$$\log(-d[L]/dt) = 0.04 - 0.042\,pK_a \tag{10}$$

substituting Eqs. (9) and (10) into Eq. (8), we obtain:

$$\log r_I = 1.66 - 0.06\,pK_a + \log([I]/[L]) \tag{11}$$

Considering that the concentration of N-phenylethylenimine is almost equal to that of β-propiolactone during the initial period of the copolymerization, Eq. (11) is approximately expressed by Eq. (12):

$$\log r_I \fallingdotseq 1.66 - 0.06\,pK_a \tag{12}$$

Equation (12) interprets the experimental finding that the monomer reactivity ratio of N-phenylethylenimine increases with a decrease in the pK_a value of the acid.

On the other hand, the empirical equation (13) is obtained from Fig. 9:

$$\log r_I = 1.51 - 0.06\,pK_a \tag{13}$$

The agreement of Eq. (13) with Eq. (12) indicates that the postulated mechanism of copolymerization and the method of approximation are suitable.

In the monomer reactivity ratio of β-propiolactone, the empirical equation (14) is obtained from Fig. 9:

$$\log r_L = -1.30 + 0.01\,pK_a \tag{14}$$

This result may be explained in the following way. If linear relations exist between $\log k_{LI}$ (and $\log k_{LL}$) and the pK_a of the acid as with k_{II} and k_{IL}, these relations may be expressed as:

$$\log k_{LI} = C_1 - C_2\,pK_a \tag{15}$$

$$\log k_{LL} = C_3 - C_4\,pK_a \tag{16}$$

where C_1, C_2, C_3, and C_4 are positive constants; C_2 is larger than C_4 since the effect of the pK_a value of the acid on the rate of the consumption of N-phenylethylenimine is greater than that of β-propiolactone. Subtracting Eq. (15) from Eq. (16), we obtain:

$$\begin{aligned}\log r_L &= \log k_{LL} - \log k_{LI} \\ &= (C_3-C_1) + (C_2-C_4)pK_a \\ &= C_5 + C_6\,pK_a \quad (C_6>0)\end{aligned} \tag{17}$$

where C_5 and C_6 are constants. Equation (17) interprets the fact that $\log r_L$ decreases with a decrease in the pK_a of the catalyst.

Further work on the effect of the solvent on the copolymerization will be reported in a subsequent paper.