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A Study of the Solvent Effect in the Copolymerization of *N*-Phenylethylenimine with *β*-Propiolactone

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The effect of the solvent on the copolymerization of *N*-phenylethylenimine with *β*-propiolactone has been studied quantitatively. The copolymerization rates for the various solvents used increase in the order: diethyl ether < toluene < carbon tetrachloride < methyl acetate < *N,N*-dimethylacetamide < anisole < dioxane < acetone < ethylene dichloride < acetonitrile < acetophenone < nitrobenzene < dimethyl sulfoxide < nitroethane. The rates in solvents with high dielectric constants are much larger than those in solvents with low dielectric constants. However, in the case of solvents with similar dielectric constants, the rates decrease with an increase in the nucleophilicity of the solvent; moreover, the dependency of the copolymerization rate on the nucleophilicity of the solvents is much larger in the solvents with high dielectric constants than in those with low dielectric constants. The rate of the consumption of *N*-phenylethylenimine is markedly affected by the nucleophilicity of the solvents in solvents with high dielectric constants, but it is little affected in solvents with low dielectric constants. Although there is no effect of the nucleophilicity of the solvents on the consumption rate of *β*-propiolactone, the rate of the consumption of *β*-propiolactone varies with the electrophilicity of the solvent in solvents with high dielectric constants. On the other hand, the *β*-propiolactone content in the copolymer increases in proportion to the nucleophilicity of the solvents with high dielectric constants, whereas the *β*-propiolactone content in solvents with low dielectric constants is almost constant regardless of the electric nature of the solvents.

We have studied the copolymerization of *N*-phenylethylenimine with *β*-propiolactone. As has been mentioned in a previous paper, *N*-phenylethylenimine and *β*-propiolactone copolymerized with the acid present in the *β*-propiolactone without the addition of any catalyst,[1] while in the copolymerization with various Brönsted acids, the composition of the copolymer varied with the kind of acid.[2] On the other hand, it has been reported that, in the polymerization of *N*-phenylethylenimine with formic acid, the polymerization rates were markedly affected by the nucleophilicity and the dielectric constant of the solvents.[3]

In the ionic copolymerization, a number of instances have been reported in which the rate and the composition of the copolymer were markedly influenced by the solvents. No quantitative study of the solvent effect on the polymerization has, however, yet been reported.

The purpose of this paper is to investigate quantitatively the solvent effect on the rate and the composition of the copolymer in the copolymerization of *N*-phenylethylenimine with *β*-propiolactone.

Experimental

Materials. The method of the preparation and purification of *N*-phenylethylenimine and purification of *β*-propiolactone were described in a previous paper.[1] The acetonitrile, anisole, diethyl ether, methyl acetate, *N,N*-dimethylacetamide, carbon tetrachloride, toluene, ethylene dichloride, acetone, nitrobenzene, nitroethane, and acetophenone were purified by the usual methods.[4] Dimethyl sulfoxide of a guaranteed reagent grade was used without further purification.

Copolymerization Procedure. Measured amounts of *β*-propiolactone (0.005 mol) and a solvent (5 m*l*) were placed into a glass ampule under nitrogen atmosphere, and then *N*-phenylethylenimine (0.005 mol) was added to this system at −78°C. After the ampule had been sealed and maintained at 0—1°C for a definite period of time, the products were washed with chloroform and diethyl ether, separated by a centrifuge, and dried *in vacuo*. The method of the determination of the copolymer composition has already been described.[1]

Results and Discussion

The copolymerization was carried out without the addition of any catalyst in various kinds of

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[1] T. Kagiya, T. Kondo, S. Narisawa and K. Fukui, This Bulletin, **41**, 172 (1968).

[2] T. Kagiya, T. Kondo and K. Fukui, *ibid.*, **41**, 1682 (1968).

[3] T. Kagiya, T. Kondo, K. Nakao and K. Fukui, *ibid.*, **42**, 1094 (1969).

[4] A. Weissberger *et al.*, "Technique of Organic Chemistry, Vol VII, Organic Solvents," Interscience Publishers, Inc., New York (1955).

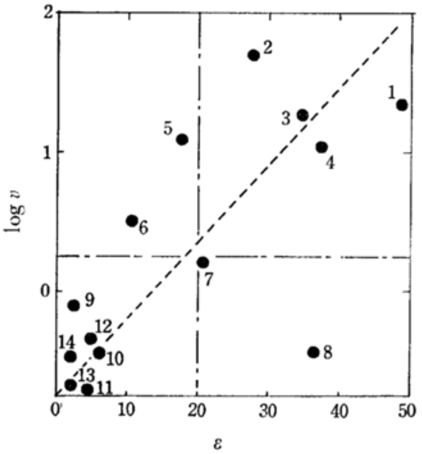

Fig. 1. The plots of the copolymerization rate against the dielectric constant of the solvents.
1, dimethyl sulfoxide; 2, nitroethane;
3, nitrobenzene; 4, acetonitrile;
5, acetophenone; 6, ethylene dichloride;
7, acetone; 8, *N,N*-dimethylacetamide;
9, dioxane; 10, methyl acetate;
11, diethyl ether; 12, anisole; 13, toluene;
14, carbon tetrachloride.

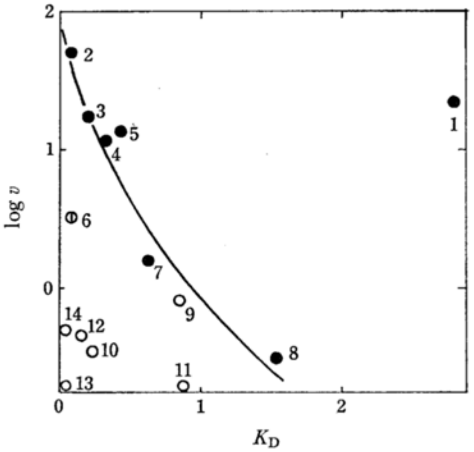

Fig. 2. The plots of the copolymerization rate against the K_D value of the solvents.
●, high dielectric constant ($\varepsilon > 10$)
⦶, ethylene dichloride ($\varepsilon \fallingdotseq 10$)
○, low dielectric constant ($\varepsilon < 10$)
The number of a solvent is same as Fig. 1.

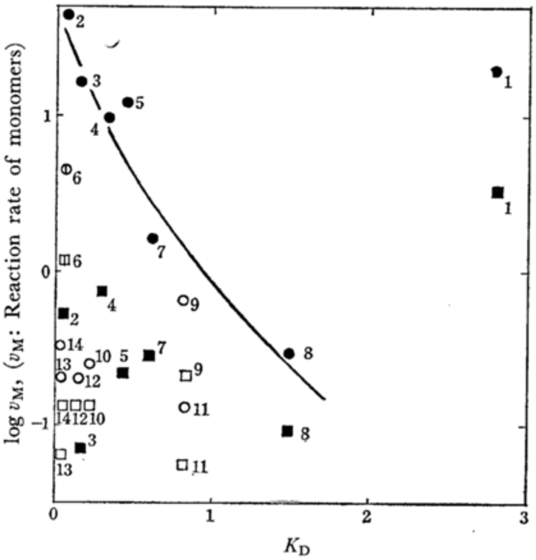

Fig. 3. The relations between the reaction rates of the monomers and the K_D value of the solvents.
Reaction rate of *N*-phenylethylenimine
●, high dielectric constant ($\varepsilon > 10$)
⦶, ethylene dichloride ($\varepsilon \fallingdotseq 10$)
○, low dielectric constant ($\varepsilon < 10$)
Reaction rate of β-propiolactone
■, high dielectric constant ($\varepsilon > 10$)
◫, ethylene dichloride ($\varepsilon \fallingdotseq 10$)
□, low dielectric constant ($\varepsilon < 10$)
The number of a solvent is same as Fig. 1.

solvents. The plots of the copolymerization rate against the dielectric constant of the solvent (ε) are shown in Fig. 1. Although the rates tend to increase with an increase in the dielectric constant of the solvent, there are great differences in the rate, even in the solvents with similar dielectric constants, *i. e.*, nitrobenzene, acetonitrile, and *N,N*-dimethylacetamide.

In order to investigate the effect of the electric nature of the solvent, the rate was plotted against K_D, where K_D is the nucleophilic equilibrium constant of a solvent in the nucleophilic solvation to a deuterium atom of a methanol-d molecule[5] (Fig. 2). It was found that the effects of the solvents on the copolymerization rate may be classified into two large groups, that is, solvents with high dielectric constants ($\varepsilon > 10$) and those with low dielectric constants ($\varepsilon < 10$).

In solvents with high dielectric constants, the rates decrease markedly with an increase in the nucleophilicity of the solvent, while in solvents with low dielectric constants the rates are almost constant, regardless of the nucleophilicity of the solvent. Ethylene dichloride ($\varepsilon \fallingdotseq 10$) shows the intermediate behavior in these groups. The cause of the great deviation of dimethyl sulfoxide from the other solvents with high dielectric constants may be due to its much larger electrophilicity.

The relation between the consumption rates of the monomers and the K_D values is shown in Fig. 3. The consumption rate of *N*-phenylethylenimine in the solvents with high dielectric constants decreased markedly with an increase in the nucleophilicity of the solvents, while in the solvents with low dielectric constants the consumption rate was almost

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[5] T. Kagiya, Y. Sumida and T. Inoue, This Bulletin, **41**, 767 (1968).

constant, regardless of the nucleophilicity of the solvents. On the other hand, the consumption rate of β-propiolactone is much smaller than that of *N*-phenylethylenimine, and the effect of the nucleophilicity of the solvent on the rate of the consumption of β-propiolactone was small. These facts show that, in the solvents with high dielectric constants, the consumption rate of *N*-phenylethylenimine is more affected by the nucleophilicity of the solvents than is the consumption rate of β-propiolactone.

Moreover, in order to investigate the effect of the electrophilicity of the solvent on the consumption rates of each monomer, the rates were plotted against the $\Delta\nu_{C=O}$ values of the solvents (Fig. 4), where $\Delta\nu_{C=O}$ was defined as the relative difference between the C=O absorption band of acetophenone observed in solution and the C=O absorption band of acetophenone in benzene.[5] As is shown in Fig. 4, although the effect of the electrophilicity of the solvent on the consumption rate of *N*-phenylethylenimine is small, the consumption rate of β-propiolactone decreased markedly with an increase in the $\Delta\nu_{C=O}$ value of the solvents in the case of the solvents with high dielectric constants. On the other hand, in the solvents with low dielectric constants, the rate consumption of β-propiolactone is not affected by the $\Delta\nu_{C=O}$ value of the solvents.

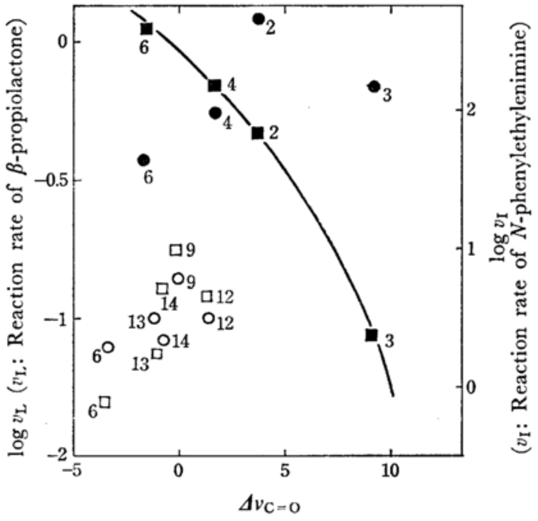


Fig. 4. The relations between the reaction rates of the monomers and $\Delta\nu_{C=O}$ value of the solvents.
The notes are the same as Fig. 3.
The number of a solvent is same as Fig. 1.

In view of these facts, it may be assumed that, although the solvents with low dielectric constants have no effect on the propagation reaction, in the solvent with high dielectric constants, the propagation reaction of *N*-phenylethylenimine is much affected by the nucleophilicity of the solvent, and that of β-propiolactone, by the electrophilicity. These results may lead to the explanation that *N*-phenylethylenimine (large nucleophilicity) directly attacks the cationic end group of the polymer, whereas β-propiolactone (large electrophilicity) coordinates electrophilically with the counter-anion and then reacts with the cationic end group. Therefore, in the solvents with high dielectric constants the competitive coordination of the solvents with the cationic end group (or the counter-anion) may depress the reaction of *N*-phenylethylenimine (or β-propiolactone).

The relation between the β-propiolactone content in the copolymer and the K_D values of the solvents is shown in Fig. 5. In the solvent with high dielectric constants the β-propiolactone content is much smaller than in the solvents with low dielectric constants, and it increases in proportion to the K_D value of the solvent. On the other hand, in the solvents with low dielectric constants, the β-propiolactone content is almost constant (32%). The variation in the copolymer composition with the kind of solvent also indicates that the effect of the solvent on the reaction of *N*-phenylethylenimine differs from that of β-propiolactone.

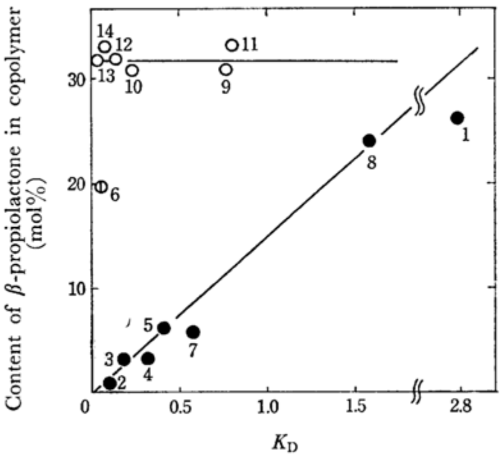
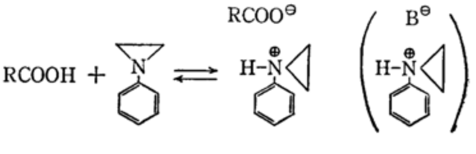


Fig. 5. The relations between the composition of the copolymer and K_D value of the solvents.
The notes are the same as Fig. 2.
The number of a solvent is same as Fig. 1.

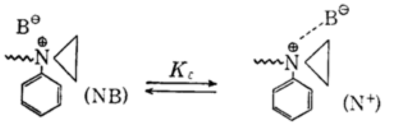
Mechanism of the Copolymerization. From these experimental facts, the mechanism of the copolymerization may be postulated as follows:

Initiation



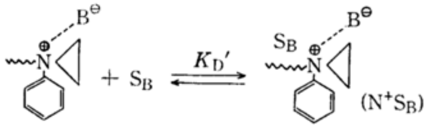
(1)

Propagation

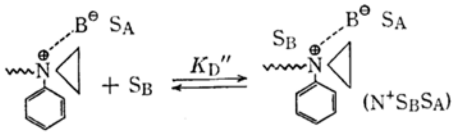


(2)

Nucleophilic solvation

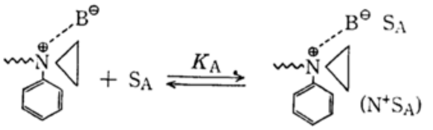


(3)

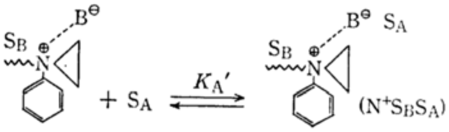


(4)

Electrophilic solvation



(5)

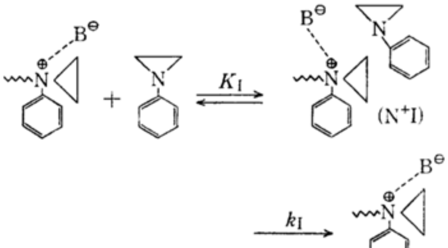


(6)

S_B; nucleophilic solvent, S_A: electrophilic solvent.

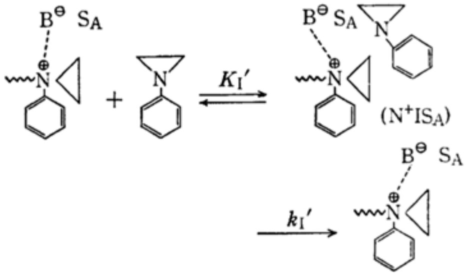
Reaction of N-phenylenimine in propagation

Reaction with dissociated immonium ion:
Nonsolvated



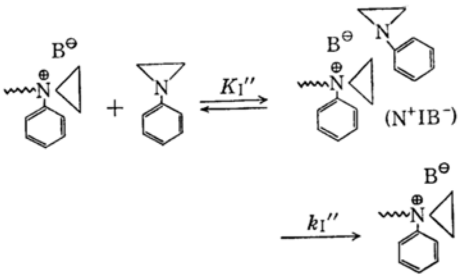
(7)

Solvated



(8)

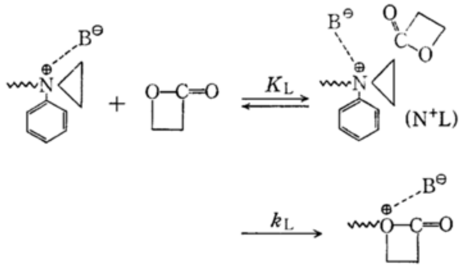
Reaction with undissociated immonium ion:



(9)

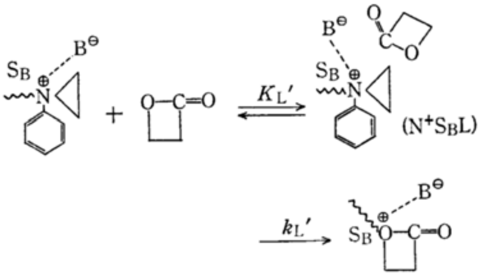
Reaction of β-propiolactone in propagation

Reaction with dissociated immonium ion:
Nonsolvated



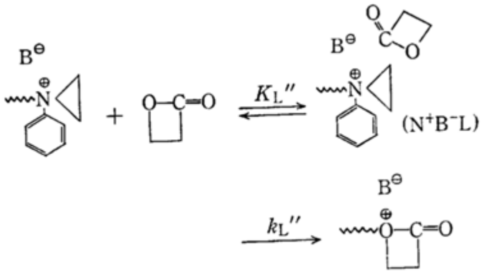
(10)

Solvated



(11)

Reaction with undissociated immonium ion:



(12)

The initiation reaction is considered to be the reaction of the acid present in β-propiolactone with N-phenylethylenimine to produce compound I as has been described in a previous paper.[2] This compound dissociates partially from the immonium ion, and the reaction is in equilibrium. The equilibrium constant (K_ε) is considered to increase with an increase in the dielectric constant of the solvent. Equations (3) and (4) show the nucleophilic solvation of the solvent to the immonium ion. Since the coordinations of the solvents with both propagating species and methanol-d are nucleophilic reactions, the equilibrium constants (K_D' and K_D'') are considered to increase with an increase in K_D. Equations (5) and (6) show the electrophilic solvation of the solvent to the counter-anion of the polymer end. The coordination of the solvent with both the counter-anion and acetophenone are considered to be electrophilic reactions. Therefore it seems reasonable to assume that K_A and K_A' are larger in the solvents with larger $\Delta\nu_{C=O}$ values. On the other hand, on the basis of the fact that there is no effect on the propagation reaction in the solvents with low dielectric constants, it is considered that the coordination of the solvent with the undissociated immonium ion is small.

In the propagation reaction, immonium and oxonium ions are considered to react with the monomers by the same mechanism. Therefore, the propagation reactions of immonium ions with monomers are shown as an example. The reaction rate of *N*-phenylethylenimine decreases with an increase in the nucleophilicity of the solvent; *i. e.*, in a low-nucleophilic solvent such as the nitro compound, the reaction rate of *N*-phenylethylenimine is much larger than in a nucleophilic solvent such as dimethylacetamide. Since these facts may indicate that the competitive coordination of the nucleophilic solvent with the cationic end group depresses the coordination of *N*-phenylethylenimine, the reaction of *N*-phenylethylenimine is considered to occur by means of a nonsolvated immonium ion, as is shown by Eqs. (7) and (8). From the fact that the reaction rate of β-propiolactone decreases with an increase in the electrophilicity of the solvent in the solvents with high dielectric constants, the reaction of β-propiolactone may proceed by means of a dissociated immonium ion whose counter ion is not solvated by the solvent, as is shown by Eqs. (10) and (11). On the other hand, the propagation in the solvents with low dielectric constants is assumed to occur by means of the reaction of the undissociated immonium ion with monomers (Eqs. (9) and (12)).

Kinetics. On the basis of the mechanism postulated, the effect of the solvent on the copolymerization rate and the copolymer composition was kinetically investigated. From the fact that the amount of β-propiolactone consumed is much less than that of *N*-phenylethylenimine, the quantity of immonium ions is considered to be much larger than that of oxonium ions. Therefore, the concentration of the compound I, $\alpha[C]_0$, may be approximately expressed by Eq. (13), where $[C]_0$ is the initial concentration of the catalyst and where α is a constant ($0<\alpha<1$):

$$\begin{aligned}\alpha[C]_0 = {} & [N^+] + [N^+B^-] + [N^+S_B] + [N^+S_A] \\ & + [N^+I] + [N^+L] + [N^+S_BL] + [N^+IS_A] \\ & + [N^+B^-I] + [N^+B^-L] + [N^+S_AS_B] \qquad (13)\end{aligned}$$

On the other hand, according to Eqs. (2), (3), ⋯, (11) and (12), the equilibrium equations will be:

$$[N^+]/[N^+B^-] = K_\varepsilon \qquad (14)$$

$$[N^+S_B]/([N^+][S]) = K_D' \qquad (15)$$

$$[N^+S_A]/([N^+][S]) = K_A \qquad (16)$$

$$[N^+S_AS_B]/([N^+S_A][S]) = K_D'' \qquad (17)$$

$$[N^+S_AS_B]/([N^+S_B][S]) = K_A' \qquad (18)$$

$$[N^+I]/([N^+][I]) = K_I \qquad (19)$$

$$[N^+IS_A]/([N^+S_A][I]) = K_I' \qquad (20)$$

$$[N^+B^-I]/(N^+B^-][I]) = K_I'' \qquad (21)$$

$$[N^+L]/([N^+][L]) = K_L \qquad (22)$$

$$[N^+S_BL]/([N^+S_B][L]) = K_L' \qquad (23)$$

$$[N^+B^-L]/([N^+B^-][L]) = K_L'' \qquad (24)$$

where [I] and [L] are the concentrations of *N*-phenylethylenimine and β-propiolactone respectively. By combining Eqs. (13), (14), ⋯, (23) and (24), the concentrations of N^+I, N^+L, N^+S_BL, N^+IS_A, N^+B^-I, and N^+B^-L are represented by Eqs. (25), (26), (27), (28), (29) and (30) respectively:

$$[N^+I] = K_\varepsilon K_I\alpha[C]_0[I]/f(K,M,S) \qquad (25)$$

$$[N^+L] = K_\varepsilon K_L\alpha[C]_0[L]/f(K,M,S) \qquad (26)$$

$$[N^+S_BL] = K_\varepsilon K_L'K_D'\alpha[C]_0[L][S]/f(K,M,S) \qquad (27)$$

$$[N^+IS_A] = K_\varepsilon K_I'K_A\alpha[C]_0[I][S]/f(K,M,S) \qquad (28)$$

$$[N^+B^-I] = K_I''\alpha[C]_0[I]/f(K,M,S) \qquad (29)$$

$$[N^+B^-L] = K_L''\alpha[C]_0[L]/f(K,M,S) \qquad (30)$$

where $f(K,M,S) = 1+K_I''[I]+K_L''[L]+K_\varepsilon(1+K_I[I]+K_L[L]+K_D'[S]+K_A[S]+K_L'K_D'[S][L]+K_AK_I'[S][I]+K_A'K_D'[S]^2)$.

The reaction rates of *N*-phenylethylenimine and β-propiolactone are represented by Eqs. (31) and (32) respectively:

$$-d[I]/dt = k_I[N^+I] + k_I'[N^+IS_A] + k_I''[N^+B^-I] \qquad (31)$$

$$-d[L]/dt = k_L[N^+L] + k_L'[N^+S_BL] + k_L''[N^+B^-L] \qquad (32)$$

By substituting Eqs. (25), ⋯, (29) and (30) into Eqs. (31) and (32), Eqs. (33) and (34) are derived:

$$-\frac{d[I]}{dt} = \frac{(K_\varepsilon K_Ik_I+K_\varepsilon K_I'K_Ak_I'[S]+K_I''k_I'')\alpha[C]_0}{f(K,M,S)}[I] \qquad (33)$$

$$-\frac{d[L]}{dt} = \frac{(K_\varepsilon K_Ik_L+K_\varepsilon K_L'K_D'k_L'[S]+K_L''k_L'')\alpha[C]_0}{f(K,M,S)}[L] \qquad (34)$$

Since the propagations in the solvents with high dielectric constants occur mainly by the reaction of the dissociated immonium ion and the monomers, Eqs. (33) and (34) may be expressed approximately by Eqs. (35) and (36):

$$-\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}=\frac{K_{\varepsilon}(K_{\mathrm{I}}k_{\mathrm{I}}+K_{\mathrm{A}}K_{\mathrm{I}}k_{\mathrm{I}}'[\mathrm{S}])\alpha[\mathrm{C}]_0}{f(\mathrm{K,M,S})}[\mathrm{I}] \qquad (35)$$

$$-\frac{\mathrm{d}[\mathrm{L}]}{\mathrm{d}t}=\frac{K_{\varepsilon}(K_{\mathrm{L}}k_{\mathrm{L}}+K_{\mathrm{D}}'K_{\mathrm{L}}'k_{\mathrm{L}}'[\mathrm{S}])\alpha[\mathrm{C}]_0}{f(\mathrm{K,M,S})}[\mathrm{L}] \qquad (36)$$

Because of $[\mathrm{S}]\gg 1$, $K_{\mathrm{A}}K_{\mathrm{I}}'k_{\mathrm{I}}'[\mathrm{S}]$ and $K_{\mathrm{D}}'K_{\mathrm{L}}'k_{\mathrm{L}}'[\mathrm{S}]$ *are considered to be much larger than* $K_{\mathrm{I}}k_{\mathrm{I}}$ and $K_{\mathrm{L}}k_{\mathrm{L}}$ respectively. Therefore, Eqs. (35) and (36) may be approximately expressed by Eqs. (37) and (38) respectively:

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t=(K_{\varepsilon}K_{\mathrm{A}}K_{\mathrm{I}}'k_{\mathrm{I}}'[\mathrm{S}]\alpha[\mathrm{C}]_0[\mathrm{I}])/f(\mathrm{K,M,S}) \qquad (37)$$

$$-\mathrm{d}[\mathrm{L}]/\mathrm{d}t=(K_{\varepsilon}K_{\mathrm{D}}'K_{\mathrm{L}}'k_{\mathrm{L}}'[\mathrm{S}]\alpha[\mathrm{C}]_0[\mathrm{L}])/f(\mathrm{K,M,S}) \qquad (38)$$

Taking the reciprocal of Eqs. (37) and (38), and considering that the concentration of the solvent is much larger than unity, two approximate equations, Eqs. (39) and (40), may be obtained:

$$1/(-\mathrm{d}[\mathrm{I}]/\mathrm{d}t)\fallingdotseq\frac{K_{\mathrm{D}}'(1+K_{\mathrm{L}}'[\mathrm{L}])}{K_{\mathrm{A}}K_{\mathrm{I}}'k_{\mathrm{I}}'\alpha[\mathrm{C}]_0[\mathrm{I}]}+\frac{(1+K_{\mathrm{I}}'[\mathrm{I}]+K_{\mathrm{D}}''[\mathrm{S}])}{K_{\mathrm{I}}'k_{\mathrm{I}}'\alpha[\mathrm{C}]_0[\mathrm{I}]} \qquad (39)$$

$$1/(-\mathrm{d}[\mathrm{L}]/\mathrm{d}t)\fallingdotseq\frac{K_{\mathrm{A}}(1+K_{\mathrm{I}}'[\mathrm{I}])}{K_{\mathrm{D}}'K_{\mathrm{L}}'k_{\mathrm{L}}'\alpha[\mathrm{C}]_0[\mathrm{L}]}+\frac{(1+K_{\mathrm{L}}'[\mathrm{L}]+K_{\mathrm{A}}'[\mathrm{S}])}{K_{\mathrm{L}}'k_{\mathrm{L}}'\alpha[\mathrm{C}]_0[\mathrm{L}]} \qquad (40)$$

Equations (39) and (40) explain the experimental results that, in the polar solvents with similar dielectric constants, the reaction rate of *N*-phenylethylenimine (or *β*-propiolactone) decreases with an increase in the K_{D}' (or K_{A}). On the other hand, considering that the terms containing K_{ε} in Eqs. (33) and (34) are negligible in the solvents with low dielectric constants, the rate equations of the monomers may be approximately expressed by Eqs. (41) and (42) respectively:

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t=K_{\mathrm{I}}''k_{\mathrm{I}}''\alpha[\mathrm{C}]_0[\mathrm{I}] \qquad (41)$$

$$-\mathrm{d}[\mathrm{L}]/\mathrm{d}t=K_{\mathrm{L}}''k_{\mathrm{L}}''\alpha[\mathrm{C}]_0[\mathrm{L}] \qquad (42)$$

According to Eqs. (41) and (42), we can explain the experimental finding that, in the solvents with low dielectric constants, there was no effect of the electric nature of the solvent on the reaction rates of the monomers.

Since the scale of the reaction of *N*-phenylethylenimine is much larger than that of *β*-propiolactone in the solvents with high dielectric constants, the copolymerization rate may be almost equal to the reaction rate of *N*-phenylethylenimine. Therefore the copolymerization rate (R_p) in the solvents with high dielectric constants is:

$$\begin{aligned}R_p \fallingdotseq\ & K_{\varepsilon}(K_{\mathrm{I}}k_{\mathrm{I}}+K_{\mathrm{A}}K_{\mathrm{I}}'k_{\mathrm{I}}'[\mathrm{S}])\alpha[\mathrm{C}]_0[\mathrm{I}]/\\ & \{1+K_{\mathrm{I}}''[\mathrm{I}]+K_{\mathrm{L}}''[\mathrm{L}]+K_{\varepsilon}(1+K_{\mathrm{I}}[\mathrm{I}]\\ & +K_{\mathrm{L}}[\mathrm{L}]+K_{\mathrm{D}}'[\mathrm{S}]+K_{\mathrm{A}}[\mathrm{S}]+K_{\mathrm{L}}'K_{\mathrm{D}}'[\mathrm{S}][\mathrm{L}]\\ & +K_{\mathrm{A}}K_{\mathrm{I}}'[\mathrm{S}][\mathrm{I}]+K_{\mathrm{A}}'K_{\mathrm{D}}'[\mathrm{S}]^2)\}\end{aligned} \qquad (43)$$

By assuming $0<K_{\varepsilon}<1$, Eq. (43) explains the experimental facts that, in solvents with high dielectric constants, the copolymerization rate increased with an increase of the K_{ε} value, while in solvents with similar dielectric constant the rate decreased with an increase in the K_{D}'. The copolymerization rate in solvents with low dielectric constants is represented by the sum of Eqs. (41) and (42);

$$\begin{aligned}R_p &\fallingdotseq -\mathrm{d}[\mathrm{I}]/\mathrm{d}t + -\mathrm{d}[\mathrm{L}]/\mathrm{d}t\\ &=(K_{\mathrm{I}}''k_{\mathrm{I}}''[\mathrm{I}]+K_{\mathrm{L}}''k_{\mathrm{L}}''[\mathrm{L}])\alpha[\mathrm{C}]_0\end{aligned} \qquad (44)$$

This equation shows that there is no effect of the solvents with low dielectric constants on the copolymerization rate.

The *β*-propiolactone content in the copolymer (C_{L}) is given by Eq. (45):

$$C_{\mathrm{L}}=[\mathrm{Y}]_{\mathrm{L}}/([\mathrm{Y}]_{\mathrm{I}}+[\mathrm{Y}]_{\mathrm{L}}) \qquad (45)$$

where $[\mathrm{Y}]_{\mathrm{I}}$ and $[\mathrm{Y}]_{\mathrm{L}}$ are the amounts of *N*-phenylethylenimine and *β*-propiolactone respectively present in the copolymer. In the solvents with high dielectric constants, by considering that $[\mathrm{Y}]_{\mathrm{I}}\gg[\mathrm{Y}]_{\mathrm{L}}$ because the *β*-propiolactone content in the copolymer is smaller than 26%, as is shown in Fig. 5, the *β*-propiolactone content may be approximately expressed by Eq. (46):

$$C_{\mathrm{L}}\fallingdotseq[\mathrm{Y}]_{\mathrm{L}}/[\mathrm{Y}]_{\mathrm{I}} \qquad (46)$$

By combining Eqs. (35), (36) and (46), and by assuming that $[\mathrm{I}]\fallingdotseq[\mathrm{L}]$ in the early stage of the copolymerization, Eq. (47) is derived:

$$C_{\mathrm{L}}\fallingdotseq(K_{\mathrm{L}}k_{\mathrm{L}}+K_{\mathrm{D}}'K_{\mathrm{L}}'k_{\mathrm{L}}'[\mathrm{S}])/(K_{\mathrm{I}}k_{\mathrm{I}}+K_{\mathrm{A}}K_{\mathrm{I}}'k_{\mathrm{I}}'[\mathrm{S}]) \qquad (47)$$

This approximate equation can explain the experimental fact that the *β*-propiolactone content increases in proportion to the K_{D}' value of the solvent. On the other hand, in the solvents with low dielectric constants, *β*-propiolactone content is approximately expressed by Eq. (48), which is derived from Eqs. (41), (42) and (45):

$$C_{\mathrm{L}}\fallingdotseq K_{\mathrm{L}}''k_{\mathrm{L}}''/(K_{\mathrm{L}}''k_{\mathrm{L}}''+K_{\mathrm{I}}''k_{\mathrm{I}}'') \qquad (48)$$

Equation (48) explains the fact that, in the solvents with low dielectric constants, the *β*-propiolactone content is almost constant, independent of the characteristic nature of the solvents.