BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1634—1640 (1969)

Effect of the Binary Solvent System on the Copolymerization of *N*-Phenylethylenimine with β-Propiolactone

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(Received October 17, 1968)

The effect of the binary solvent system on the copolymerization of *N*-phenylethylenimine with β-propiolactone has been studied quantitatively. The copolymerization was carried out in three kinds of binary solvent systems, each consisting of components with similar dielectric constants (ε) and with very different nucleophilicities: (1) the nitrobenzene - *N,N*-dimethylacetamide system, $\varepsilon \fallingdotseq 36$, (2) the ethylene dichloride - tetrahydrofuran system, $\varepsilon \fallingdotseq 10$, (3) the toluene-anisole system, $\varepsilon \fallingdotseq 3$. In the binary solvent system with the highest dielectric constant, the copolymerization rate decreased with an increase in the content of the nucleophilic solvent. In the nitrobenzene - *N,N*-dimethylacetamide system, the copolymerization rate markedly decreased upon the addition of a small amount of *N,N*-dimethylacetamide in nitrobenzene. On the other hand, in the ethylene dichloride - tetrahydrofuran binary solvent system, with a lower dielectric constant than the nitrobenzene and *N,N*-dimethylacetamide system, the rates decreased in proportion to the tetrahydrofuran content. The β-propiolactone content in the copolymer increased with the amount of the larger nucleophilic solvents, and the dependency of the copolymer composition on the nucleophilicity of the solvents was much larger in the binary solvents with high dielectric constants than in the binary solvents with low dielectric constants. In the toluene - anisole system, which has a very low dielectric constant, the copolymerization rate and the composition of the copolymer were almost constant, independent of the composition of the solvents.

We have studied the solvent effect in the copolymerization of *N*-phenylethylenimine with β-propiolactone. It has been reported[1] that, in the copolymerization of *N*-phenylethylenimine with β-propiolactone in various solvents, the copolymerization rate and the composition of the copolymer were much affected by the nucleophilicity, the electrophilicity, and the dielectric constant of the solvents. The dependency of the rate and the composition of the copolymer on the nucleophilicity and electrophilicity of the solvent increased with an increase in the dielectric constant of the solvent. On the basis of the kinetic study, the roles of the solvent in the copolymerization could be quantitatively explained.

In this paper, the effect of the binary solvent system on the copolymerization of the *N*-phenylethylenimine with β-propiolactone will be quantitatively investigated.

Experimental

Material. The methods of the purification of the materials were described in a previous paper.[1]

Copolymerization Procedure. Measured amounts of β-propiolactone (0.005 mol) and the binary solvents (total volume: 2 m*l*) were placed in a glass ampule under a 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 solid 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 was described in a previous paper.[2]

Results and Discussion

The copolymerization of *N*-phenylethylenimine with β-propiolactone was carried out in the binary solvent system without the addition of any catalyst. Three binary solvent systems, each consisting of components with similar dielectric constants and very different nucleophilicities, were used, as is shown in Table 1.

The Effect of the Solvent on the Copolymerization Rate. The relations between the copolymerization rate and the mole fraction of the solvents are show in Fig. 1 (A, B, C). In the binary solvent system A, with the highest dielectric constant, the copolymerization rate in nitrobenzene was much larger than that in *N,N*-dimethylacetamide, and the rate was markedly depressed by the addition of small amounts of *N,N*-dimethylacetamide. According to

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[1] T. Kagiya, T. Kondo and K. Fukui, This Bulletin, **42**, 1628 (1969).

[2] T. Kagiya, T. Kondo, S. Narisawa and K. Fukui, *ibid.*, **41**, 172 (1968).

Table 1. The physical properties of the solvent in the binary solvent systems

	Solvent	Dielectric constant ε	Nucleophilicity[3] $\Delta\nu_{O-D}$	Electrophilicity[3] $\Delta\nu_{C=O}$
Binary solvent system (A)	Nitrobenzene	34.8	21	8.0
	N,N-Dimethylacetamide	36.7	113	—
Binary solvent system (B)	Ethylene dichloride	10.4	2	−1.5
	Tetrahydrofuran	7.4	90	0.2
Binary solvent system (C)	Toluene	2.38	2	−0.9
	Anisole	4.33	26	1.4

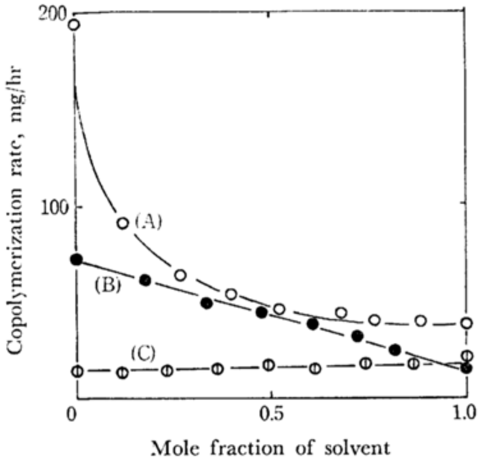


Fig. 1. Relations between copolymerization rates and mole fraction of the solvents in the binary solvent systems.

○: (A) Nitrobenzene ↔ *N,N*-Dimethylacetamide

●: (B) Ethylene dichloride ↔ Tetrahydrofuran

⦶: (C) Toluene ↔ Anisole

Abscissa is mole fraction of *N,N*-dimethylacetamide, tetrahydrofuran and anisole.

the mechanism postulated in the previous paper, that the competitive coordination of the nucleophilic solvent to the cationic growing end of the polymer depresses the reaction of the monomers, this fact indicates that *N, N*-dimethylacetamide, with a larger nucleophilicity, coordinates selectively to the cationic growing end of the polymer.

On the other hand, in the ethylene dichloride-tetrahydrofuran binary solvent system B, with a lower dielectric constant than A, the copolymerization rate decreased in proportion to the amount of tetrahydrofuran. In view of this fact, the coordination of the solvent to the cationic polymer end may be considered to increase proportionally with the amount of tetrahydrofuran. The effect of the nucleophilicity of the solvent on the copolymerization rate in A is larger than that in B. This finding is in accord with the finding that the dependency of the rate on the nucleophilicity of the solvent increased with the dielectric constant of the solvent.

In the binary solvent system C, consisting of components with low dielectric constants, the effect of the solvents on the copolymerization rate is small compared with that of the solvent with a high dielectric constant. This fact may lead to a consideration that the propagation mechanism in the solvent with a low dielectric constant differs from that in the solvents with high dielectric constants. It is considered that, in the solvent with a low dielectric constant, the propagation proceeds mainly by means of undissociated ions, whereas that in the solvents with high dielectric constants proceeds by means of dissociated ions, and that coordination of the solvent to the undissociated ions is small.

The Effect of the Solvent on the Copolymer Composition. The plots of the β-propiolactone content (mol%) in the copolymer (conversion 6.5—17.8%) against the mole fraction of the solvent are shown in Fig. 2. It may be seen that, in the solvents with high dielectric constants, A and B, the β-propiolactone content increased with an incerase in the amounts of nucleophilic solvents. Moreover, Fig. 2

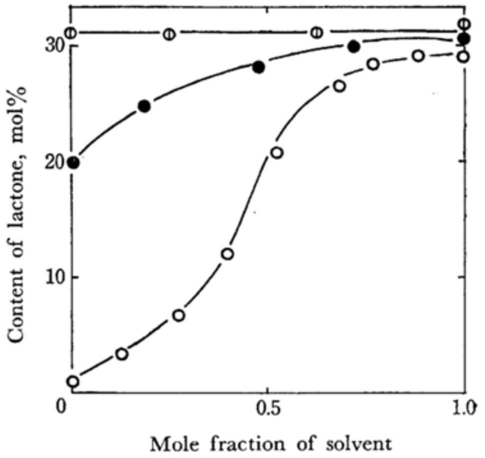


Fig. 2. Relations between contents of β-propiolactone and mole fraction of the solvent in the binary solvent systems.

○: (A) Nitrobenzene ↔ *N,N*-Dimethylacetamide

●: (B) Ethylene dichloride ↔ Tetrahydrofuran

⦶: (C) Toluene ↔ Anisole

Abscissa is mole fraction of *N,N*-dimethylacetamide, tetrahydrofuran and anisole.

shows that the dependency of the copolymer composition on the nucleophilicity of the solvent in A is larger than that in B. In view of this fact and the results obtained previously, it may be considered that the degree of the effect of the nucleophilic solvent on the copolymer composition increases with the dielectric constant of the solvent. On the other hand, in the solvent with a low dielectric constant (the toluene - anisole system), the solvent has no effect on the copolymer composition.

The Effect of the Solvent on the Reaction Rates of Monomers. The reaction rates of the monomers were obtained from the copolymerization rate and the composition of the copolymer as shown in Fig. 1 and Fig. 2. The relations between the reaction rate of *N*-phenylethylenimine and the mole fraction of the solvent are shown in Fig. 3. In A, with the highest dielectric constant, the effect of the nucleophilic solvent on the reaction rate of *N*-phenylethylenimine is larger than that in the ethylene dichloride - tetrahydrofuran system.

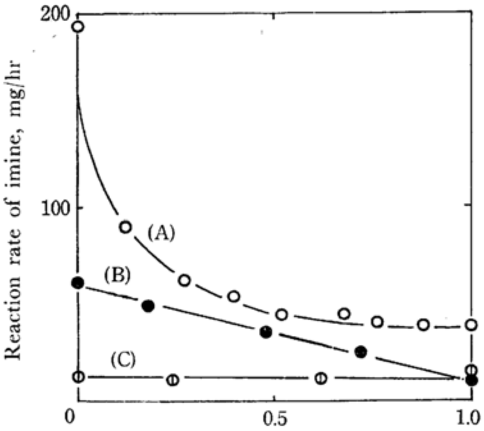


Fig. 3. Relations between reaction rate of *N*-phenylethylenimine and mole fraction of solvent in the binary solvent systems.

○: (A) Nitrobenzene ↔ *N*,*N*-Dimethylacetamide

●: (B) Ethylene dichloride ↔ Tetrahydrofuran

⦶: (C) Toluene ↔ Anisole

Abscissa is mole fraction of *N*,*N*-dimethylacetamide, tetrahydrofuran and anisole.

In C, with its low dielectric constant, the reaction rate of *N*-phenylethylenimine remains almost constant, independent of the mole fraction of the solvent. In comparison with Fig. 1, it is found that the relations of the apparent copolymerization rate and the reaction rate of *N*-phenylethylenimine to the mole fraction of the solvent resemble each other, whereas the plots of the reaction rate of β-propiolactone against the mole fraction (Fig. 4) differ, in Fig. 1 and Fig. 3. These facts may indicate that the copolymerization rate is much more affected by the reaction rate of *N*-phenylethylenimine with the propagating species than by that of β-propiolactone, considering that the reaction rate of β-propiolactone is very small. Therefore, it may be suggested that the propagating species consist mainly of immonium ions and a few oxonium ions.

The relations between the reaction rate of β-propiolactone and the mole fraction of the solvent are shown in Fig. 4. In A and B, the reaction rate of β-propiolactone decreases with an increases in the amounts of nitrobenzene and tetrahydrofuran respectively. Considering that, in a solvent with a high dielectric constant, the reaction of β-propiolactone is much depressed by the electrophilic solvent, as has been described in a previous paper, this fact may be due to the larger electrophilicities, of nitrobenzene and tetrahydrofuran than of *N*,*N*-dimethylacetamide and ethylene dichloride respectively. In the nonpolar solvent, C, there is no effect of the solvent on the reaction rate of β-propiolactone.

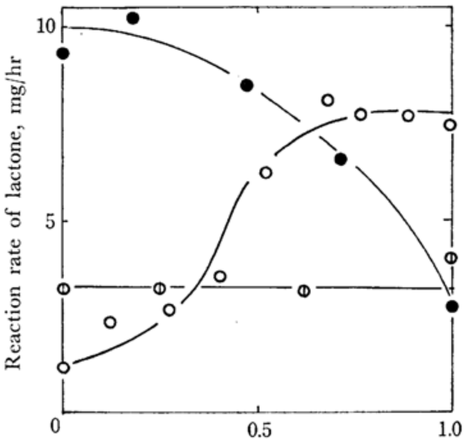


Fig. 4. Relations between reaction rate of β-propiolactone and mole fraction of solvents in the binary solvent systems.

○: (A) Nitrobenzene ↔ *N*,*N*-Dimethylacetamide

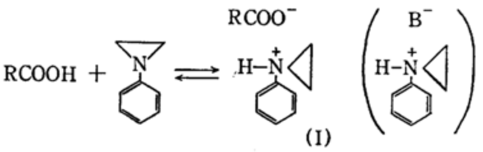
●: (B) Ethylene dichloride ↔ Tetrahydrofuran

⦶: (C) Toluene ↔ Anisole

Abscissa is mole fraction of *N*,*N*-dimethylacetamide, tetrahydrofuran and anisole.

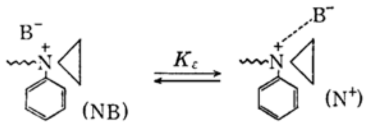
Mechanism of the Copolymerization. From these experimental facts, the following mechanism of the copolymerization was postulated:

Initiation

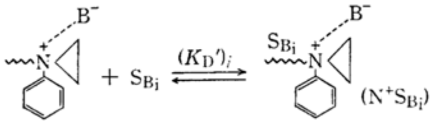


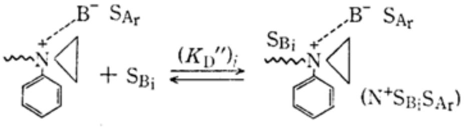
(1)

Propagation

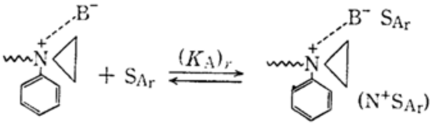

(2)

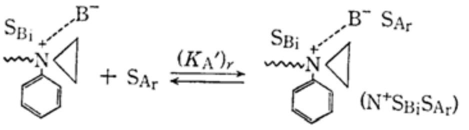
Nucleophilic solvation


(3)


(4)

Electrophilic solvation

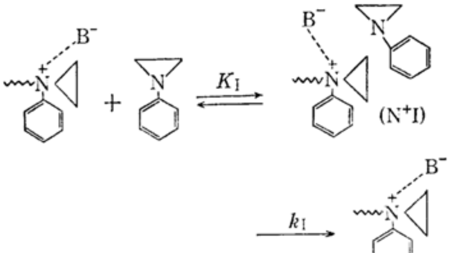

(5)


(6)

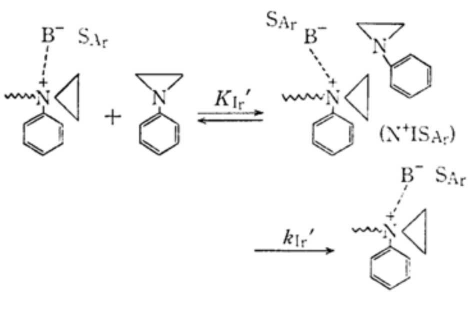
S_B; nucleophilic solvent, S_A; electrophilic solvent, i; 1, 2. r; 1, 2.

Reaction of N-Phenylethylenimine in propagation

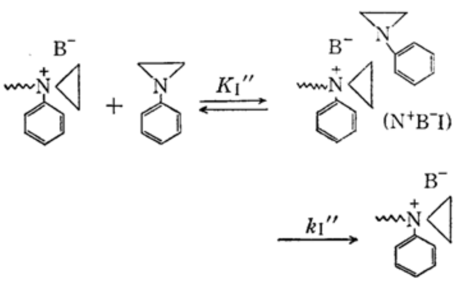
Reaction with dissociated immonium ion; Nonsolvated


(7)

Solvated

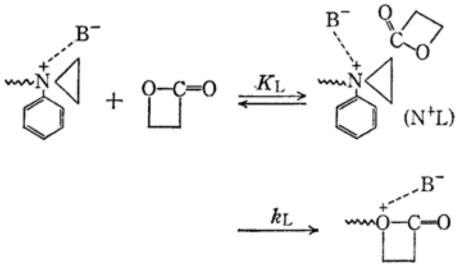

(8)

Reaction with undissociated immonium ion;

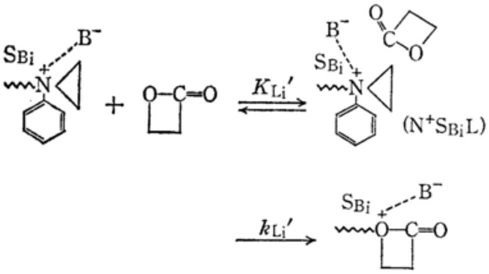

(9)

Reaction of β-propiolactone in propagation

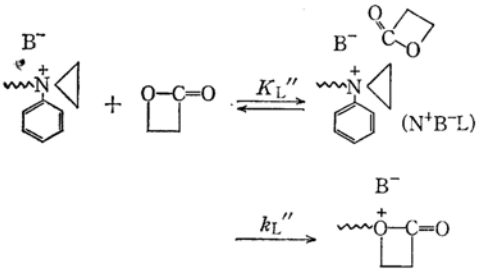
Reaction with dissociated immonium ion; Nonsolvated


(10)

Solvated


(11)

Reaction with undissociated immonium ions;


(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. This compound dissociates partially to the immonium ion, and the reaction is in equilibrium. The equilibrium constant (K_s) is considered to increase with an increase in the dielectric constant of the solvent. Equations (3) and (4) show the nucleophilic solvation of the solvents to the immonium ion. Since the coordinations of the solvent to both the propagating species and methanol-d are nucleophilic reactions, the equilibrium constants (K_D' and K_D'') are considered to increase with an increase in the $\Delta\nu_{O-D}$ (or K_D) value.[3] Equations (5) and (6) show the electrophilic solvation of the solvent to the polymer end. Since the coordination of the solvent to both the counter-anion and acetophenone are electrophilic reactions, it seems reasonable to assume that K_A and K_A' are larger in the solvents with larger $\Delta\nu_{C=O}$ values.[3] 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 may be considered that the coordination of the solvent to the undissociated immonium ion is small.

In the propagation reaction, both immonium ions 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. From the fact that, in the solvent with high dielectric constants, the reaction rate of *N*-phenylethylenimine was depressed with an increase in the nucleophilicity of the solvent, the reaction of *N*-phenylethylenimine is considered to occur by means of nonsolvated immonium ions, as is shown in Eqs. (7) and (8). Since, in the solvents with high dielectric constants, the reaction rate of β-propiolactone decreased with an increase in the electrophilicity of the solvent, the reaction of β-propiolactone may proceed by means of dissociated immonium ions whose counter ions are not solvated by the solvent, as is shown by Eqs. (10) and (11). On the other hand, the propagation can proceed in a solvents with a low dielectric constant; therefore, it is assumed to occur by means of the reaction of the undissociated immonium ions with monomers (Eqs. (9) and (12)).

Kinetics. On the basis of the mechanism postulated, the effects of the solvent on the copolymerization rate and the copolymer composition were quantitatively investigated. From the fact that the amount of β-propiolactone consumed is 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 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 the constant $(0<\alpha<1)$:

$$\begin{aligned}\alpha[C]_0 = {} & [N^+] + [N^+B^-] + \sum_{i=1}^{2}[N^+S_{B_i}] \\ & + \sum_{r=1}^{2}[N^+S_{A_r}] + \sum_{i=1}^{2}\sum_{r=1}^{2}[N^+S_{B_i}S_{A_r}] \\ & + [N^+I] + [N^+L] + \sum_{r=1}^{2}[N^+IS_{A_r}] \\ & + \sum_{i=1}^{2}[N^+S_{B_i}L] + [N^+B^-I] + [N^+B^-L]\end{aligned} \tag{13}$$

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

$$[N^+]/[N^+B^-] = K_\varepsilon \tag{14}$$

$$[N^+S_{B_i}]/([N^+][S_i]) = (K_D')_i \tag{15}$$

$$[N^+S_{A_r}]/([N^+][S_r]) = (K_A)_r \tag{16}$$

$$[N^+S_{A_r}S_{B_i}]/([N^+S_{A_r}][S_i]) = (\mathrm{K}_D'')_i \tag{17}$$

$$[N^+S_{A_r}S_{B_i}]/([N^+S_{B_i}][S_r]) = (K_A')_r \tag{18}$$

$$[N^+I]/([N^+][I]) = K_I \tag{19}$$

$$[N^+L]/([N^+][L]) = K_L \tag{20}$$

$$[N^+IS_{A_r}]/([N^+S_{A_r}][I]) = (K_I')_r \tag{21}$$

$$[N^+S_{B_i}L]/([N^+S_{B_i}][L]) = (K_D')_i \tag{22}$$

$$[N^+B^-I]/([N^+B^-][I]) = K_I'' \tag{23}$$

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

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, $N^+IS_{A_r}$, $N^+S_{B_i}$, N^+B^-I, and N^+B^-L may be represented as in Eqs. (25), (26), (27), (28), (29), and (30) respectively:

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

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

$$[N^+IS_{A_r}] = K_\varepsilon (K_I')_r (K_A)_r \alpha[C]_0[I][S_r]/f(K,M,S) \tag{27}$$

$$[N^+S_{B_i}L] = K_\varepsilon (K_L')_i (K_D')_i \alpha[C]_0[L][S_i]/f(K,M,S) \tag{28}$$

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

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

where $f(K,M,S) = 1 + K_I''[I] + K_L''[L] + K_\varepsilon(1 + K_I[I] + K_L[L] + \sum_{i=1}^{2}(K_D')_i[S_i] + \sum_{r=1}^{2}(K_A)_r[S_r] + \sum_{r=1}^{2}\sum_{i=1}^{2}(K_D')_i(K_A')[S_i][S_r])$.

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

$$\begin{aligned}-\mathrm{d}[I]/\mathrm{d}t = {} & k_I[N^+I] + \sum_{r=1}^{2}k_{I_r}'[N^+IS_{A_r}] \\ & + k_I''[N^+B^-I]\end{aligned} \tag{31}$$

$$\begin{aligned}-\mathrm{d}[L]/\mathrm{d}t = {} & k_L[N^+L] + \sum_{i=1}^{2}k_{L_i}'[N^+S_{B_i}L] \\ & + k_L''[N^+B^-L]\end{aligned} \tag{32}$$

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

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

$$-\mathrm{d}[\mathrm{I}]/\mathrm{d}t = (K_\varepsilon K_\mathrm{I}k_\mathrm{I} + K_\varepsilon \sum_{r=1}^{2} (K_\mathrm{I}')_r(K_\mathrm{A})_r k_{\mathrm{I}r}'[\mathrm{S}_r] + K_\mathrm{I}''k_\mathrm{I}'')\alpha[\mathrm{C}]_0[\mathrm{I}]/f(\mathrm{K,M,S}) \tag{33}$$

$$-\mathrm{d}[\mathrm{L}]/\mathrm{d}t = (K_\varepsilon K_\mathrm{L}k_\mathrm{L} + K_\varepsilon \sum_{i=1}^{2} (K_\mathrm{L}')_i(K_\mathrm{D}')_i k_{\mathrm{L}i}'[\mathrm{S}_i] + K_\mathrm{L}''k_\mathrm{L})\alpha[\mathrm{C}]_0[\mathrm{L}]/f(\mathrm{K,M,S}) \tag{34}$$

Since the propagation in the solvents with high dielectric constants is considered to occur mainly with the dissociated immonium ions, Eqs. (33) and (34) may be approximately expressed by Eqs. (35) and (36):

$$-\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = \frac{K_\varepsilon(K_\mathrm{I}k_\mathrm{I} + \sum_{r=1}^{2}(K_\mathrm{I}')_r(K_\mathrm{A})_r k_{\mathrm{I}r}'[\mathrm{S}_r])\alpha[\mathrm{C}]_0[\mathrm{I}]}{\mathrm{C}_1 + K_\varepsilon(\mathrm{C}_2 + \sum_{i=1}^{2}(K_\mathrm{D}')_i[\mathrm{S}_i] + \sum_{r=1}^{2}(K_\mathrm{A})_r[\mathrm{S}_r] + \sum_{i=1}^{2}\sum_{r=1}^{2}(K_\mathrm{D}'')_i(K_\mathrm{A}')_r[\mathrm{S}_i][\mathrm{S}_r])} \tag{35}$$

$$-\frac{\mathrm{d}[\mathrm{L}]}{\mathrm{d}t} = \frac{K_\varepsilon(K_\mathrm{L}k_\mathrm{L} + \sum_{i=1}^{2}(K_\mathrm{L}')_i(K_\mathrm{D}')_i k_{\mathrm{L}i}'[\mathrm{S}_i])\alpha[\mathrm{C}]_0[\mathrm{L}]}{C_1 + K_\varepsilon(C_2 + \sum_{i=1}^{2}(K_\mathrm{D}')_i[\mathrm{S}_i] + \sum_{r=1}^{2}(K_\mathrm{A})_r[\mathrm{S}_r] + \sum_{i=1}^{2}\sum_{r=1}^{2}(K_\mathrm{D}'')_i(K_\mathrm{A}')_r[\mathrm{S}_i][\mathrm{S}_r])} \tag{36}$$

where $C_1 = 1 + K_\mathrm{I}''[\mathrm{I}] + K_\mathrm{L}''[\mathrm{L}]$, $C_2 = 1 + K_\mathrm{I}[\mathrm{I}] + K_\mathrm{L}[\mathrm{L}]$.

Considering that the nucleophilic equilibrium constants of *N,N*-dimethylacetamide ($(K_\mathrm{D}')_\mathrm{DMA}$ and $(K_\mathrm{D}'')_\mathrm{DMA}$) are much larger than those of nitrobenzene ($(K_\mathrm{D}')_\mathrm{NB}$ and $(K_\mathrm{D}'')_\mathrm{NB}$), the following relationships may be obtained, even in the case of $[\mathrm{S}]_\mathrm{DMA} \gg [\mathrm{S}]_\mathrm{NB}$: $(K_\mathrm{D}')_\mathrm{DMA}[\mathrm{S}]_\mathrm{DMA} \gg (K_\mathrm{D}')_\mathrm{NB}[\mathrm{S}]_\mathrm{NB}$, $(K_\mathrm{D}'')_\mathrm{DMA}[\mathrm{S}]_\mathrm{DMA} \gg (K_\mathrm{D}'')_\mathrm{NB}[\mathrm{S}]_\mathrm{NB}$. Therefore, since the selective solvation of *N,N*-dimethylacetamide to the cationic end of the polymer brings on an increase in the terms containing K_D' and K_D'' in a denominator of Eq. (35), the reaction rate of *N*-phenylethylenimine may markedly decrease upon the addition of *N,N*-dimethylacetamide. On the other hand, in the ethylene dichloride - tetrahydrofuran system, considering that the equilibrium constants of tetrahydrofuran ($(K_\mathrm{D}')_\mathrm{THF}$ and $(K_\mathrm{D}'')_\mathrm{THF}$) are much larger than those of ethylene dichloride ($(K_\mathrm{D}')_\mathrm{EDC}$ and $(K_\mathrm{D}'')_\mathrm{EDC}$), the terms containing K_D' and K_D'' in a denominator of Eq. (35) may be approximately expressed by Eqs. (37) and (38):

$$\sum_{i=1}^{2}(K_\mathrm{D}')_i[\mathrm{S}_i] = (K_\mathrm{D}')_\mathrm{THF}[\mathrm{S}]_\mathrm{THF} \tag{37}$$

$$\sum_{i=1}^{2}\sum_{r=1}^{2}(K_\mathrm{D}'')_i(K_\mathrm{A})_r[\mathrm{S}_i][\mathrm{S}_r] = \sum_{r=1}^{2}(K_\mathrm{D}'')_\mathrm{THF}[\mathrm{S}]_\mathrm{THF}(K_\mathrm{A})_r[\mathrm{S}_r] \tag{38}$$

Equations (37) and (38) indicate that the terms containing $(K_\mathrm{D}')_\mathrm{THF}$ and $(K_\mathrm{D}'')_\mathrm{THF}$ increase in proportion to the amounts of tetrahydrofuran. Therefore, considering that these terms are larger than the other terms in the denominator of Eq. (35), the experimental finding that the reaction rate of *N*-phenylethylenimine decreased in proportion to the amount of tetrahydrofuran can be explained.

Equation (36) explains the fact that, in the solvents with high dielectric constants, the reaction rate of *β*-propiolactone decreased with an increase in the amounts of the electrophilic solvents, such as nitrobenzene and tetrahydrofuran.

On the other hand, in the solvents with low dielectric constants, the terms containing K_ε in Eqs. (33) and (34) are considered to be negligible. Therefore, the rate equations of monomers may be approximately expressed by Eqs. (39) and (40):

$$-\mathrm{d}[\mathrm{I}]\mathrm{d}t = K_\mathrm{I}''k_\mathrm{I}''\alpha[\mathrm{C}]_0[\mathrm{I}] \tag{39}$$

$$-\mathrm{d}[\mathrm{L}]/\mathrm{d}t = K_\mathrm{L}''k_\mathrm{L}''\alpha[\mathrm{C}]_0[\mathrm{L}] \tag{40}$$

According to Eqs. (39) and (40), we can explain the experimental finding that, in the solvent with low dielectric constants, the nucleophilicity and electrophilcity of the solvent has no effect on the reaction rates of the monomers.

Since the *N*-phenylethylenimine content 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 will be:

$$R_p = \frac{K_\varepsilon(K_\mathrm{I}k_\mathrm{I} + \sum_{r=1}^{2}(K_\mathrm{I}')_r(K_\mathrm{A})_r k_{\mathrm{I}r}'[\mathrm{S}_r])\alpha[\mathrm{C}]_0[\mathrm{I}]}{C_1 + K_\varepsilon(C_2 + \sum_{i=1}^{2}(K_\mathrm{D}')_i[\mathrm{S}_i] + \sum_{r=1}^{2}(K_\mathrm{A})_r[\mathrm{S}_r] + \sum_{i=1}^{2}\sum_{r=1}^{2}(K_\mathrm{D}'')_i(K_\mathrm{A}')_r[\mathrm{S}_i][\mathrm{S}_r])} \tag{41}$$

Considering that $C_1 > C_2 + \sum_{i=1}^{2}(K_\mathrm{D}')_i[\mathrm{S}_i] + \sum_{r=1}^{2}(K_\mathrm{A})_r[\mathrm{S}_r] + \sum_{i=1}^{2}\sum_{r=1}^{2}(K_\mathrm{D}'')_i(K_\mathrm{A}')_r[\mathrm{S}_i][\mathrm{S}_r]$, Eq. (41) explains the following experimental facts: in the solvents with high dielectric constants, the copolymerization rate increased with the K_ε value, while in the solvents with similar dielectric constants, the rate decreased with an increase in the amounts of the nucleophilic solvents.

In the solvents with low dielectric constants, the *β*-propiolactone content in the copolymer is larger than in the solvents with high dielectric constants. Therefore, the copolymerization rate in a solvent with a low dielectric constant should be represented by the sum of Eqs. (39) and (40):

$$\begin{aligned} R_p &= -\mathrm{d}[\mathrm{I}]/\mathrm{d}t + -\mathrm{d}[\mathrm{L}]/\mathrm{d}t \\ &= (K_\mathrm{I}''k_\mathrm{I}''[\mathrm{I}] + K_\mathrm{L}''k_\mathrm{L}''[\mathrm{L}])\alpha[\mathrm{C}]_0 \end{aligned} \tag{42}$$

This equation shows 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. (43):

$$C_\mathrm{L} = [\mathrm{Y}]_\mathrm{L}/([\mathrm{Y}]_\mathrm{I} + [\mathrm{Y}]_\mathrm{L}) \tag{43}$$

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 the fact $[\mathrm{Y}]_\mathrm{I} \gg [\mathrm{Y}]_\mathrm{L}$, the *β*-propiolactone content may be approximately expressed by Eq. (44):

$$C_\mathrm{L} \fallingdotseq [\mathrm{Y}]_\mathrm{L}/[\mathrm{Y}]_\mathrm{I} \tag{44}$$

By combining Eqs. (35), (36) and (44), and by assuming $[\mathrm{I}] \doteqdot [\mathrm{L}]$ in the early stages of the copolymerization, Eq. (45) is derived:

$$C_\mathrm{L} \fallingdotseq \frac{K_\mathrm{L}k_\mathrm{L} + \sum_{i=1}^{2} (K_\mathrm{L}')_i (K_\mathrm{D}')_i k_{\mathrm{L}i}'[\mathrm{S}_i]}{K_\mathrm{I}k_\mathrm{I} + \sum_{r=1}^{2} (K_\mathrm{I}')_r (K_\mathrm{A})_r k_{\mathrm{I}r}'[\mathrm{S}_r]} \tag{45}$$

This approximate equation can explain the experimental fact that the *β*-propiolactone content increased with an increase in the amounts of the nucleophilic solvents. On the other hand, in the solvents with low dielectric constants, the *β*-propiolactone content can be approximately expressed by Eq. (46), which is derived from Eqs. (39), (40), and (43):

$$C_\mathrm{L} = K_\mathrm{L}''k_\mathrm{L}''/(K_\mathrm{L}''k_\mathrm{L}'' + K_\mathrm{I}''k_\mathrm{I}'') \tag{46}$$

This equation (46) explains the fact that, in the solvents with low dielectric constants, the *β*-propiolactone content is almost constant, regardless of both the electric natures and the dielectric constants of the solvents.