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Mechanism of the Solvent Effect in a Binary Solvent System on the Cationic Polymerization of *N*-Phenylethylenimine

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The effect of the binary solvent systems on the polymerization of *N*-phenylethylenimine with a formic acid catalyst was studied quantitatively. In an acetonitrile - acetone system composed of components with similar nucleophilicities but with very different dielectric constants, the polymerization rate increases with an increase in the dielectric constant of the binary solvent system. In an acetonitrile - *N,N*-dimethylacetamide system composed of components with very different nucleophilicities but with similar dielectric constants, on the other hand, the rate was markedly depressed by the addition of a small amount of *N,N*-dimethylacetamide with a large nucleophilicity. On the basis of these results, a mechanism of the solvent effect in a binary solvent system was proposed; the rate equation of the polymerization was expressed empirically as a function of both the dielectric constant of the binary solvent mixture and the nucleophilic equilibrium constant, and the concentration of the component.

It has been well known that the reaction rate is dependent on the nature of the solvent in an ionic polymerization. Little attention has, however, been paid to the quantitative study of the solvent effect on the ionic polymerization. It has been previously reported by the present authors[1] that, in the polymerization of *N*-phenylethylenimine with a formic acid catalyst in various solvents, the polymerization rate depended upon the nucleophilicity and the dielectric constant of the solvent, and that the initiation rate was not very much influenced by the nature of the solvent, whereas that of the propagation was remarkably affected.

As a continuation of our quantitative study of the solvent effect in the cationic polymerization of *N*-phenylethylenimine, we focused on the binary solvent system in the polymerization. The purpose of this report is to determine quantitatively the solvent effect in a binary mixture of the solvent on the polymerization of *N*-phenylethylenimine.

Experimental

The method of preparing and purifying *N*-phenylethylenimine has been described in our previous paper.[1] Guaranteed-reagent-grade formic acid was used without further purification. The acetonitrile, acetone, and *N,N*-dimethylacetamide were purified by the usual method.[2] The method of polymerization was also described in the previous paper.[1] The polymerization was carried out under the following conditions: monomer, 0.005 mol; catalyst, formic acid (4 mol% for monomer); total volume of solvent, 3 m*l*; temperature, 0°C. The measurement of the dielectric constant of the solvent was carried out at 25°C by the use of a Kikusui Electronic Industry 231 A-type LC meter.

Results and Discussion

Polymerization in Binary Solvent Systems. Both acetonitrile and acetone have similar nucleophilic equilibrium constants to methanol-d (K_D),[3,4] and a very different dielectric constant, (acetonitrile, K_D; 0.4,[*1] ε; 37.5 and acetone, K_D; 0.6,[*1] ε;

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[1] T. Kagiya, T. Kondo, K. Nakao and K. Fukui, This Bulletin, **42**, 1049 (1969).

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

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

[4] T. Kagiya, Y. Sumida and T. Inoue, *ibid.*, **41**, 773 (1968).

[*1] The nucleophilic equilibrium constants of acetonitrile, acetone, and *N,N*-dimethylacetamide were obtained by the method of literature[4] on the basis of the $\Delta\nu_D$ values shown in Ref. 3.

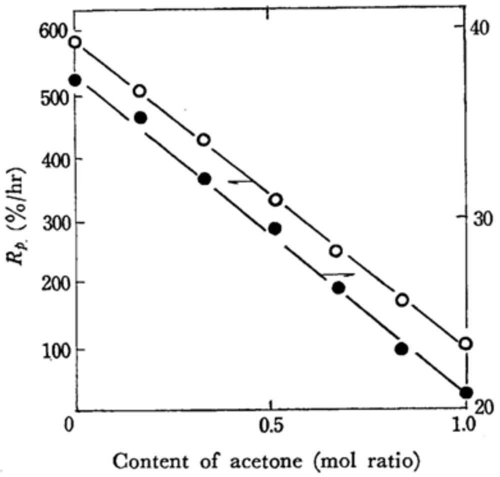


Fig. 1. Plots of polymerization rate (R_p) and the dielectric constant (ε) of the mixed solvent against the composition of the solvent in the acetonitrile - acetone binary solvent system.

20.7). As is shown in Fig. 1, the polymerization rate, defined as the ratio of the polymer yield ($<20\%$) to the reaction time, and the dielectric constant of the binary solvent both decrease with an increase in the amount of acetone in the acetonitrile - acetone system. The rate increases with an increase in the dielectric constant of the binary solvent (Fig. 2). This fact suggests that, in the binary solvent system with a similar ability for nucleophilic solvation, the polymerization is mainly dependent upon the degree of ionic dissociation of the propagating species.

On the other hand, in the acetonitrile - *N,N*-dimethylacetamide (K_D*1, 1.6; ε, 36.7) binary system, the dielectric constant of the mixed solvent remains constant on varying the ratio of the two components, while the rate of polymerization is markedly depressed by the addition of a small amount of *N,N*-dimethylacetamide (Fig. 3). This fact suggests that the solvent and monomer coordinate competitively to the cationic growing end, and that coordination of the solvents increases with the amounts of *N,N*-dimethylacetamide with a larger nucleophilicity than that of acetonitrile and so depresses the monomer addition to the growing end. This is in accord with the finding that the rate decreased with an increase in the nucleophilicity of the solvent.[1)]

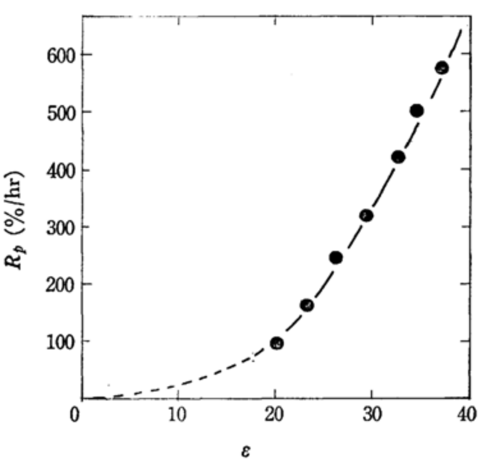


Fig. 2. Relation between the polymerization rate (R_p) and the dielectric constant (ε) of the mixed solvent in the acetonitrile-acetone binary solvent system.

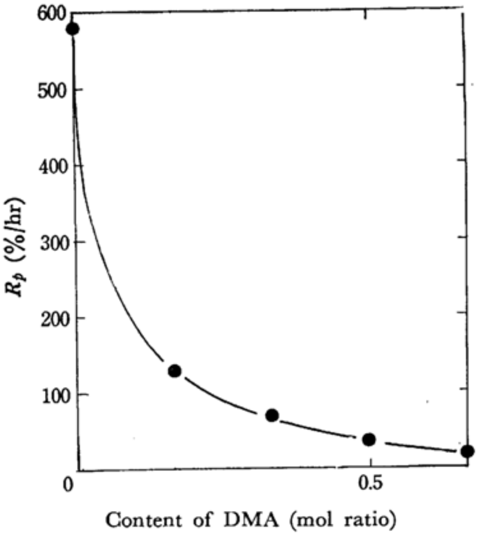
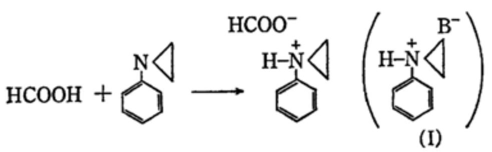


Fig. 3. Relation between polymerization rate (R_p) and the composition of the solvent in the acetonitrile - *N,N*-dimethylacetamide (DMA) binary solvent system.

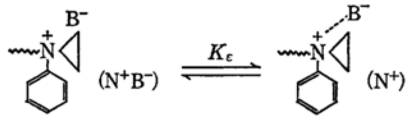
Mechanism of the Solvent Effect of the Polymerization. On the basis of these experimental facts and the results obtained previously,[1)] the mechanism of the polymerization and the role of the solvent were postulated as follows:

Initiation:



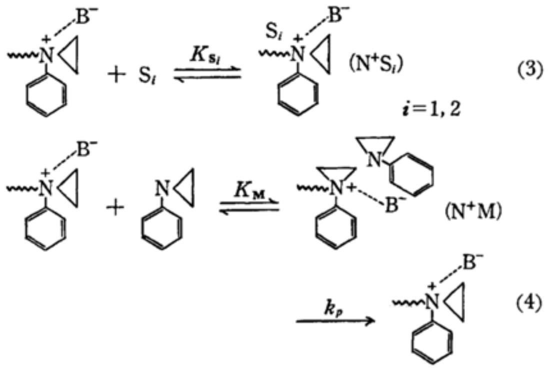
(1)

Propagation:

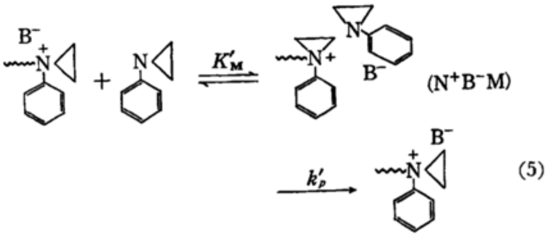


(2)

Propagation by the dissociated immonium ion:



Propagation by the undissociated immonium ion:



where K_ε, K_{S_i}, K_M, and K_M' are equilibrium constants and where k_p and k_p' are rate constants.

The initiation reaction is the reaction of formic acid with *N*-phenylethylenimine to produce Compound I. This compound dissociates partially to 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. Equation (3) shows the nucleophilic solvation of the solvent to the dissociated immonium ion. Since the coordination of the solvent to both the propagating species and methanol-d are nucleophilic reactions, the equilibrium constant (K_{S_i}) is considered to increase with an increase in the K_D value. From the fact that, in the solvent with a high dielectric constant, the polymerization rate decreased with an increase in the nucleophilicity of the solvent, the propagation is considered to occur by means of the reaction of the monomer and nonsolvated immonium ion, as is shown in Eq. (4). On the other hand, the propagation can also proceed in the solvents with a low dielectric constant. Therefore, the reaction of the undissociated immonium ions with the monomer (Eq. (5)) is also probable.

Kinetics. On the basis of the mechanism postulated, the effect of the solvent on the polymerization rate was quantitatively investigated. As was established in the previous paper,[1] the concentration of the propagating species was constant regardless of both the reaction time and the nature of the solvent. Therefore, the concentration of Compound I, $\alpha[C]_0$, may be expressed by Eq. (6), where $[C]_0$ is the initial concentration of the catalyst and where α is the constant ($0<\alpha<1$):

$$\alpha[C]_0 = [N^+] + [N^+B^-] + \sum_{i=1}^{2}[N^+S_i] + [N^+M] + [N^+B^-M] \tag{6}$$

On the other hand, according to Eqs. (2), (3), (4), and (5), the equilibrium equations will be:

$$[N^+]/[N^+B^-] = K_\varepsilon \tag{7}$$

$$[N^+S_i]/([N^+][S_i]) = K_{S_i} \tag{8}$$

$$[N^+M]/([N^+][M]) = K_M \tag{9}$$

$$[N^+B^-M]/([N^+B^-][M]) = K_M' \tag{10}$$

where [M] is the concentration of *N*-phenylethylenimine. By combining Eqs. (6), (7), (8), (9), and (10), the concentrations of N^+B^-M and N^+M may be represented by Eqs. (11) and (12) respectively:

$$[N^+B^-M] = \frac{\alpha[C]_0K_M'[M]}{1+K_M'[M]+K_\varepsilon\{1+K_M[M]+\sum_{i=1}^{2}(K_S[S])_i\}} \tag{11}$$

$$[N^+M] = \frac{K_\varepsilon K_M\alpha[C]_0[M]}{1+K_M'[M]+K_\varepsilon\{1+K_M[M]+\sum_{i=1}^{2}(K_S[S])_i\}} \tag{12}$$

The polymerization rate is represented by Eq. (13):

$$R_p = -\mathrm{d}[M]/\mathrm{d}t = k_p[N^+M] + k_p'[N^+B^-M] \tag{13}$$

Then, by substituting Eqs. (11) and (12) into Eq. (13), Eq. (14) is derived:

$$R_p = \frac{(K_\varepsilon K_M k_p + K_M' k_p')\alpha[C]_0[M]}{1+K_M'[M]+K_\varepsilon\{1+K_M[M]+\sum_{i=1}^{2}(K_S[S])_i\}} \tag{14}$$

Since, in the solvents with high dielectric constants, propagation may occur mainly with the dissociated immonium ions, Eq. (14) may be approximately expressed by Eq. (15):

$$R_p \fallingdotseq \frac{K_\varepsilon K_M K_p\alpha[C]_0[M]}{1+K_\varepsilon\{1+K_M[M]+\sum_{i=1}^{2}(K_S[S])_i\}} \tag{15}$$

The reciprocal of Eq. (15) is:

$$1/R_p \fallingdotseq \frac{1}{K_M k_p\alpha[C]_0[M]}\{(1+K_M[M]) + \sum_{i=1}^{2}(K_S[S])_i + 1/K_\varepsilon\} \tag{16}$$

By considering that, in an acetonitrile-acetone binary solvent system (K_D is almost constant, while ε varies from 20.7 to 37.5), the value of $\sum_{i=1}^{2}(K_S[S])_i$ is constant regardless of the composition of the solvent, it can be interpreted by means of Eq. (16) that the polymerization rate increases with an increase in the K_ε value (that is, the dielectric constant of the solvent). On the other hand, in the case of the acetonitrile - *N,N*-dimethylacetamide system having a similar dielectric constant ($\varepsilon \fallingdotseq 37$), the term of K_ε is constant. Therefore, Eq. (16) explains the fact that the rate decreases with the $\sum_{i=1}^{2}(K_S[S])_i$ value or with the amont of *N,N*-dimethylacetamide.

The empirical equations of the polymerization rate were obtained as follows. On the assumptions that $K_{S_i}=aK_{D_i}{}^m$ and $K_\varepsilon=(1/b)\varepsilon^n$, where m, n, a, and b are constants, Eq. (16) may be written in this form:

$$1/R_p \fallingdotseq \frac{1}{K_M k_p \alpha[C]_0[M]}\{(1+K_M[M]) + a\sum_{i=1}^{2}(K_D{}^m[S])_i + b(1/\varepsilon)^n\} \tag{17}$$

Taking the logarithm of Eq. (17) gives Eq. (18):

$$\log(1/R_p) \fallingdotseq \log\{1/(K_M k_p \alpha[C]_0[M])\} + \log\{(1 + K_M[M] + a\sum_{i=1}^{2}(K_D{}^m[S])_i + b(1/\varepsilon)^n\} \tag{18}$$

In the acetonitrile - acetone binary solvent system, it is found that the plot of $\log(1/R_p)$ against $\log(1/\varepsilon)$ gives a straight line whose slope is 2.5. This fact indicates that the value of $(1+K_M[M] + a\sum_{i=1}^{2}(K_D{}^m[S])_i)$ is much smaller than that of the $b(1/\varepsilon)^n$ in Eq. (17).

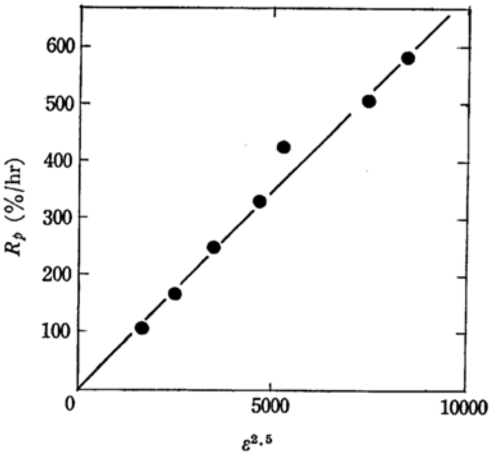


Fig. 4. Plots of R_p against $\varepsilon^{2.5}$ (ε : the dielectric constant of the mixed solvent) in the acetonitrile - acetone binary solvent system.

From the slope in the linear relation between R_p and $\varepsilon^{2.5}$ (Fig. 4), the value of $(K_M k_p \alpha[C]_0[M])/b$ is obtained as 0.07:

$$(K_M k_p \alpha[C]_0[M])/b = 0.07 \tag{19}$$

Therefore, the polymerization rate in the acetonitrile - acetone system can be approximately expressed by:

$$R_p \fallingdotseq \frac{K_M k_p \alpha[C]_0[M]}{b}\varepsilon^{2.5} = 0.07\varepsilon^{2.5} \tag{20}$$

On the other hand, in the acetonitrile - *N,N*-dimethylacetamide binary solvent system (K_D varies from 0.3 to 1.6, while ε is almost constant, 37), the empirical equation of the rate was obtained as follows. If it takes $m=2$, Eq. (17) is written:

$$1/R_p = \frac{1+K_M[M]}{K_M k_p \alpha[C]_0[M]} + \frac{a\sum_{i=1}^{2}(K_D{}^2[S])_i}{K_M k_p \alpha[C]_0[M]} + \frac{b(1/\varepsilon)^{2.5}}{K_M k_p \alpha[C]_0[M]} \tag{21}$$

By substituting the values of $b/(K_M k_p \alpha[C]_0[M])=14$ and $\varepsilon=37$ into Eq. (21), one obtaines:

$$1/R_p = \frac{1+K_M[M]}{K_M k_p \alpha[C]_0[M]} + \frac{\sum_{i=1}^{2}(K_D{}^2[S])_i}{(1/a)K_M k_p \alpha[C]_0[M]} + 5.4\times10^{-4} \tag{22}$$

A plot of the $1/R_p$ against $\sum_{i=1}^{2}(K_D{}^2[S])_i$ gives a straight line (Fig. 5), this straight line is written in form:

$$1/R_p = 0.33\sum_{i=1}^{2}(K_D{}^2[S])_i \tag{23}$$

By comparing Eq. (23) with Eq. (22), we discover that the value of 5.4×10^{-4} is much smaller than the term of K_D in Eq. (22), and that:

$$(1+K_M[M])/(K_M k_p \alpha[C]_0[M]) \fallingdotseq 0 \tag{24}$$

$$1/\{(1/a)K_M k_p \alpha[C]_0[M])\} \fallingdotseq 0.33 \tag{25}$$

By combining Eqs. (21) and (24), the rate equation in the solvent with a high dielectric constant can be expressed generally as:

$$R_p \fallingdotseq \frac{K_M k_p \alpha[C]_0[M]}{a\sum_{i=1}^{2}(K_D{}^2[S])_i + b(1/\varepsilon)^{2.5}} \tag{26}$$

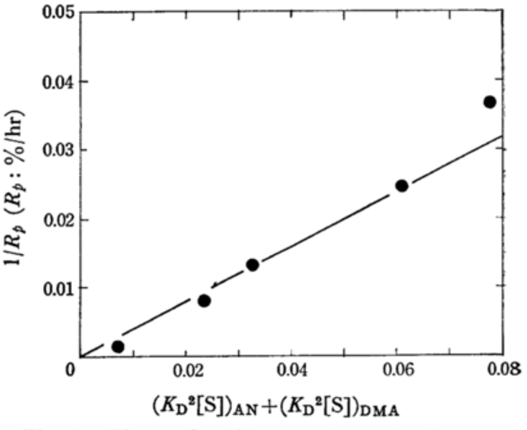


Fig. 5. Plot of $1/R_p$ against $(K_D{}^2[S])_{AN} + (K_D{}^2[S])_{DMA}$ in the acetonitrile (AN) - *N,N*-dimethylacetamide (DMA) binary solvent system.

Then:

$$R_p \fallingdotseq \frac{K_M k_p(\alpha/a)[C]_0[M]}{\sum_{i=1}^{2}(K_D{}^2[S])_i + (b/a)(1/\varepsilon)^{2.5}} \tag{27}$$

By substituting the value of $b/a \doteqdot 40$ obtained from Eqs. (19) and (25) into Eq. (27), Eq. (27) may be written in the form:

$$R_p \fallingdotseq \frac{K_M k_p(\alpha/a)[C]_0[M]}{\sum_{i=1}^{n}(K_D{}^2[S])_i + 40(1/\varepsilon)^{2.5}} \tag{28}$$

Eq. (28) can then be applied to the results obtained in the single solvent system ($10<\varepsilon<37.5$). As is shown in Fig. 6, although the polymerization rate, R_p, increases with an increase in the dielectric constant of the solvent, the order can not necessarily be explained by the dielectric constant of the solvent. The plot of R_p against $\{(K_D{}^2[S])+40(1/\varepsilon)^{2.5}\}^{-1}$ gives a straight line through the point of origin (Fig. 7). This fact indicates that Eq. (29) can be applied as an empirical equation of the polymerization rate to both the single and the binary solvent system.

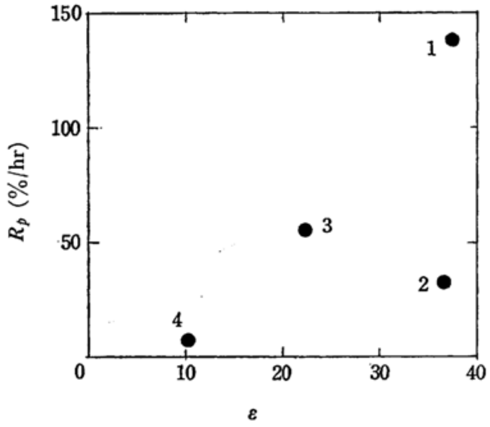


Fig. 6. Plot of polymerization rate (R_p) against the dielectric constant (ε) of the solvent in the single solvent system.

1, Acetonitrile; 2, *N,N*-Dimethylacetamide; 3, Epichlorohydrin; 4, Ethylene dichloride

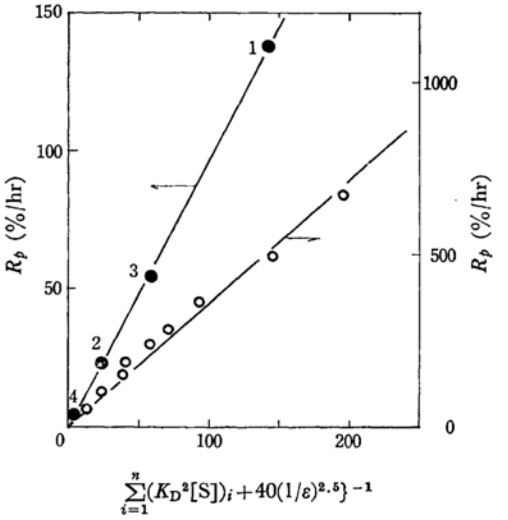


Fig. 7. Plots of R_p against $\{\sum_{i=1}^{n}(K_D{}^2[S])_i + 40(1/\varepsilon)^{2.5}\}^{-1}$ in the single and binary solvent systems.

● Single solvent system, notes are the same as Fig. 6.

○ Binary solvent system.