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A Study of the Solvent Effect on the Polymerization of *N*-Phenylethyleneimine

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The effect of solvents on the cationic polymerization of *N*-phenylethyleneimine with formic acid catalyst has been studied quantitatively. The polymerization rates in the various solvents used increase in the following order: diethyl ether≃tetrahydrofuran<toluene≃carbon tetrachloride<anisole<methyl acetate<ethylene dichloride<*N*,*N*-dimethylacetamide<dimethyl sulfoxide<epichlorohydrin<acetonitrile. In polar solvents with high dielectric constants, the rates are much larger than those in nonpolar solvents with low dielectric constants. However, in the solvents with similar dielectric constants, such as acetonitrile and *N*,*N*-dimethylacetamide, ethylene dichloride, methyl acetate and tetrahydrofuran, and anisole and diethyl ether, the rates decreased with an increase in the nucleophilicity of the solvents, and the dependence of the polymerization rate on the nucleophilicity of the solvents is much larger in polar solvents than in nonpolar solvents. The propagation rate was markedly influenced by the nature of the solvent, whereas the initiation rate was only a little influenced.

A number of instances have been reported in which the polymerization rate was markedly influenced by the solvents used. No quantitative study of the solvent effect on the polymerization has yet been reported, however. It has been pointed out by many authors that the difference in the rate can not be explained only by the magnitude of the dielectric constant of the solvent, and that the characteristic features of the solvation also affect the reaction rate. As a part of the investigation of the electric nature of the molecule in the liquid phase, we have previously made a quantitative study of the nucleophilic solvation to a deuterium atom of the methanol-d molecule by using the infrared spectroscopic method, and have determined the equilibrium constant, K_D, of various solvents.[1]

The purpose of this paper is to investigate quantitatively the effect of the solvent on the polymerization of *N*-phenylethyleneimine by using the equilibrium constants thus obtained.

Experimental

The methods used in the preparation and purification of *N*-phenylethyleneimine have been described in a previous paper.[2] Formic acid and dimethyl sulfoxide of a guaranteed grade were used without further purification. The acetonitrile, epichlorohydrin, anisole, diethyl ether, methyl acetate, *N*,*N*-dimethylacetamide, carbon tetrachloride, toluene and ethylene dichloride were purified by the conventional method.[3] The tetrahydrofuran was distilled in the presence of sodium

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

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

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

naphthalene after drying over potassium hydroxide and calcium hydride. The methods of the polymerization and molecular-weight determination of the polymer were described in the previous paper. The polymerization was carried out under the following conditions: monomer, 0.005 mol; solvent, 1 m*l*; catalyst, 2 mol% on monomer; temperature, 0°C.

Results and Discussion

The polymerization of *N*-phenylethyleneimine was carried out in various solvents using formic acid as the catalyst. The plots of the polymer yield against the reaction period are shown in Fig. 1 and Fig. 2. These figures show that the polymerization rate varies markedly with the kind of solvent used. As is shown in Fig. 3 and Fig. 4, the rate of the monomer consumption is expressed by a first-order rate equation with respect to the monomer concentration in the early stages of the polymerization. Considering the fact that the steady-state method is applicable in the polymerization with formic acid in acetonitrile, as has been described in the previous paper, Figs. 3 and 4 may indicate that the concentrations of the propagating species, [P*], are almost constant in the early stages of the polymerization. Moreover, from the fact that the plot of the number-average degree of polymerization is almost proportional to

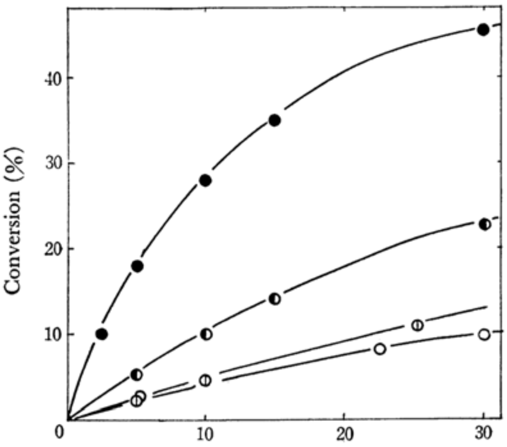


Fig. 1. Polymer yield *vs.* reaction time.
●: Acetonitrile, ◐: Epichlorohydrin
⦶: Dimethyl sulfoxide
○: *N,N*-Dimethylacetamide

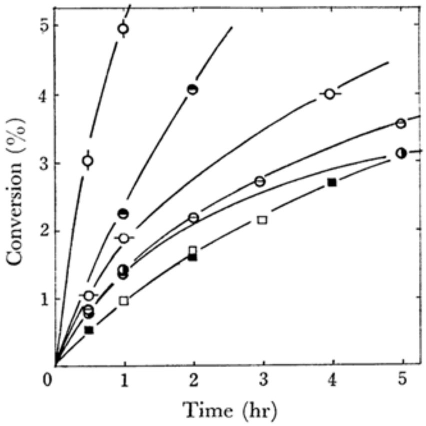


Fig. 2. Polymer yield *vs.* reaction time.
⌽: Ethylene dichloride, ◓: Methyl acetate
-○-: Anisole, ⊖: Carbon tetrachloride
◑: Toluene, □: Diethyl ether
■: Tetrahydrofuran

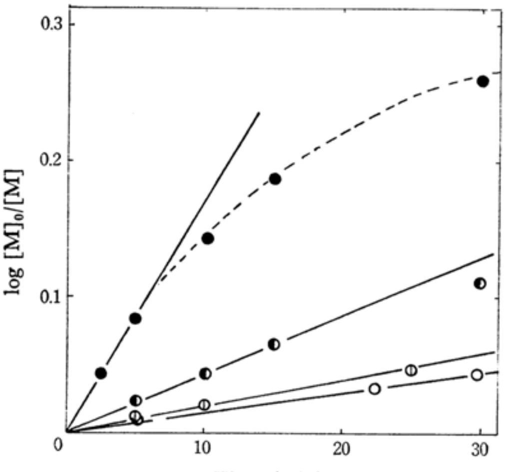


Fig. 3. The plots of log $[M]_0/[M]$ against reaction time.
Notes are the same as in Fig. 1.

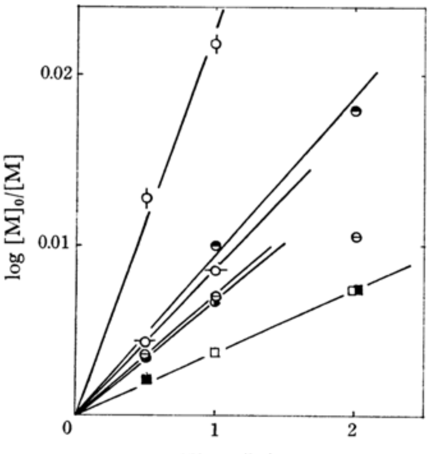


Fig. 4. The plots of log $[M]_0/[M]$ against reaction time.
Notes are the same as in Fig. 2.

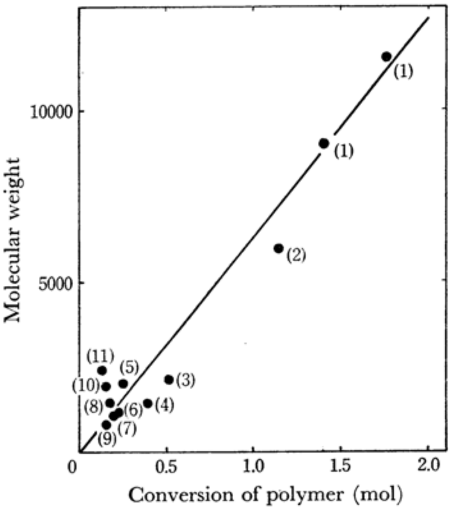


Fig. 5. Plots of molecular weight against conversion of polymer.

Experimental conditions are the same as in Fig. 1 and Fig. 2. (1) Acetonitrile, (2) Epichlorohydrin, (3) Dimethyl sulfoxide, (4) *N,N*-Dimethylacetamide, (5) Ethylene dichloride, (6) Methyl acetate, (7) Anisole, (8) Carbon tetrachloride, (9) Toluene, (10) Tetrahydrofuran, (11) Diethyl ether.

the polymer yield in the solvent used (Fig. 5), the concentration of the propagating species may be constant independently of the kind of solvent. The difference in the slopes of the line in Fig. 3 and Fig. 4 may, then, be due to the differences in the propagation rate between solvents.

From the slopes of the straight line in Fig. 3 and Fig. 4, the products of the rate constant of the propagation reaction, k_p, and the concentrations of the propagating species were obtained. The values of $k_p[\mathrm{P}^*]$ are summarized in Table 1, along with the physical properties of the solvents. Figure 6 shows the result of plotting the $\log k_p[\mathrm{P}^*]$ value against the dielectric constant of the solvent. Although the polymerization rate tends to increase with an increase in the dielectric constant of the solvent, there was a great difference in the rates, even in solvents with similar dielectric constants, *e. g.*, acetonitrile and *N,N*-dimethylacetamide.

TABLE 1. THE POLYMERIZATION RATES AND THE PHYSICAL PROPERTIES OF THE SOLVENTS

No.	Solvent	$k_p[\mathrm{P}^*]$ 1/min	Dielectric constant ε	K_D
1	Acetonitrile	1720×10^{-5}	37.5	0.352
2	Epichlorohydrin	450	22.6	0.307
3	Dimethyl sulfoxide	210	48.9	2.79
4	*N,N*-Dimethyl acetamide	153	36.7	1.61
5	Ethylene dichloride	43.3	10.4	0.035
6	Methyl acetate	16.7	6.68	0.213
7	Anisole	14.2	4.33	0.136
8	Carbon tetrachloride	11.7	2.24	0.0051
9	Toluene	11.0	2.38	0.0348
10	Tetrahydrofuran	6.25	7.4	1.153
11	Diethyl ether	6.25	4.34	0.854

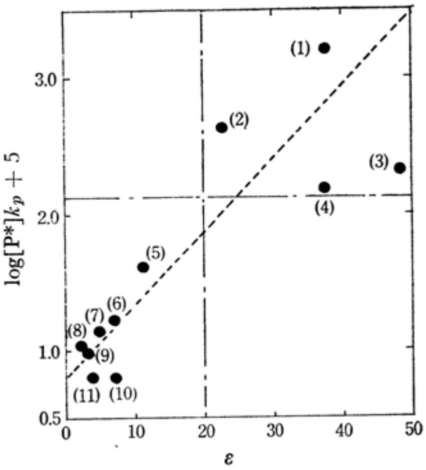


Fig. 6. Relation between $\log k_p[\mathrm{P}^*]$ and dielectric constant of solvents. The numbers of the solvent are the same as in Table 1.

In order to investigate the effect of the electric nature of the solvent on this polymerization, $\log k_p[\mathrm{P}^*]$ was plotted against K_D,[1] where K_D is the nucleophilic equilibrium constant of the solvent in the nucleophilic solvation to a deuterium atom of a methanol-d molecule (Fig. 7). Figure 7 shows

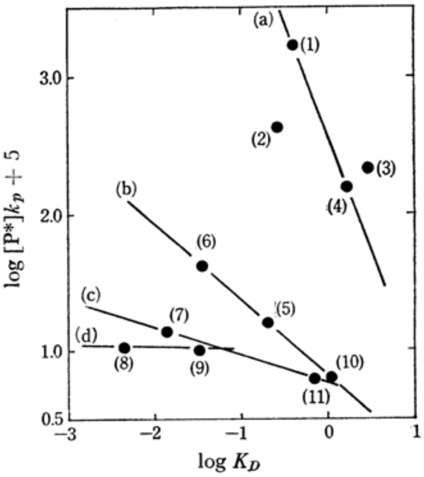
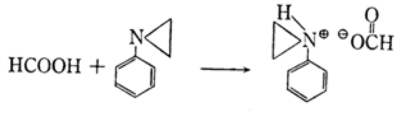


Fig. 7. Relation between $\log k_p[\mathrm{P}^*]$ and $\log K_D$. Solvents: (a) Acetonitrile and *N,N*-Dimethylacetamide, (ε; 36.6—37.5), (b) Ethylene dichloride, Methyl acetate and Tetrahydrofuran, (ε; 6.68—10.4), (c) Anisole and Diethyl ether, (ε; 4.33—4.34), (d) Carbon tetrachloride and Toluene, (ε; 2.24—2.38). The numbers of the solvent are the same as in Table 1.

that in solvents with similar dielectric constants ((a), (b), (c) and (d)), $k_p[\mathrm{P}^*]$ decreased with an increase in the nuculeophilicity of the solvent. This fact indicates that the solvents coordinate competitively to the cationic end group of the polymer and that they depress the propagation rate. Moreover, from the fact that the slope of the straight line increases with an increase in the dielectric constant of the solvent, it is found that the dependency of $k_p[\mathrm{P}^*]$ on the nucleophilicity of the solvent is larger in a solvent with high dielectric constant than in one with a low dielectric constant. As has been mentioned in the previous paper, the propagating species are considered to be the dissociated immonium ion and the undissociated immonium ion, which are in equilibrium in a solvent, and the polar solvent is considered to have a larger dissociation constant than the nonpolar solvent. Therefore, the higher dependency of the rate on the electron donability of the polar solvent than on that of the nonpolar solvent may indicate that the solvation of the solvent to the dissociated immonium ion is much larger than that to the undissociated immonium ion.

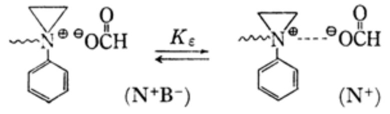
Mechanism of the Polymerization. From these experimental facts, the mechanism of the polymerization was postulated, with due consideration taken of the solvent effect.

Initiation:



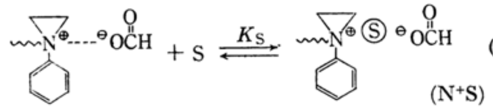
(1)

Propagation:



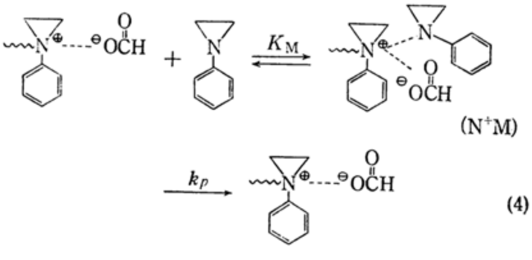
(2)

Propagation by the dissociated immonium ion:



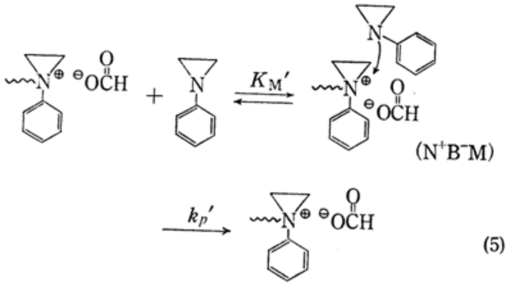
(3)

S: Solvent



(4)

Propagation by the undissociated immonium ion:



(5)

The initiation reaction is considered to be the reaction of formic acid with *N*-phenylethyleneimine to produce the compound (I). This compound dissociates partially to the immonium ion, and the reaction is in equilibrium. The equilibrium constant is considered to increase with an increase in the dielectric constant of the solvent. Equation (3) shows the solvation of the solvents to the dissociated immonium ion. Since the coordinations of solvents to both propagating species and methanol-d are nucleophilic reactions, the equilibrium constant (K_s) is considered to increase with an increase in K_D. From the facts that, in polar solvents, the propagation rates decrease with an increase in the electron donability of the solvent, propagation is considered to occur by means of a non-solvated immonium ion (Eq. (4)). On the other hand, since in nonpolar solvents, the propagation rate was constant independently of the kind of solvent, it is considered that the coordination of the solvent to the undissociated immonium ion is little, and that propagation occurs as is shown in Eq. (5).

Kinetics. On the basis of the mechanism postulated, the effect of the solvent on the rate of the polymerization (R_p) was quantitatively investigated. When the concentration of compound (I) is expressed by $\alpha[\mathrm{C}]_0$, where $[\mathrm{C}]_0$ is the initial concentration of the catalyst and whose α is the constant ($0<\alpha<1$), $\alpha[\mathrm{C}]_0$ is expressed by Eq. (6):

$$\alpha[\mathrm{C}]_0 = [\mathrm{N}^+] + [\mathrm{N}^+\mathrm{B}^-] + [\mathrm{N}^+\mathrm{S}] + [\mathrm{N}^+\mathrm{M}] + [\mathrm{N}^+\mathrm{B}^-\mathrm{M}] \tag{6}$$

On the other hand, from Eqs. (2), (3), (4) and (5), Eqs. (7), (8), (9) and (10) were obtained:

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

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

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

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

By combining Eqs. (6), (7), (8), (9) and (10), the concentrations of ($\mathrm{N}^+\mathrm{B}^-\mathrm{M}$) and ($\mathrm{N}^+\mathrm{M}$) are expressed in Eqs. (11) and (12) respectively:

$$[\mathrm{N}^+\mathrm{B}^-\mathrm{M}] = \frac{\alpha[\mathrm{C}]_0 K'_\mathrm{M}[\mathrm{M}]}{1 + K'_\mathrm{M}[\mathrm{M}] + K_\varepsilon(1+K_\mathrm{M}[\mathrm{M}] + K_\mathrm{S}[\mathrm{S}])} \tag{11}$$

$$[\mathrm{N}^+\mathrm{M}] = \frac{\alpha[\mathrm{C}]_0 K_\varepsilon K_\mathrm{M}[\mathrm{M}]}{1 + K'_\mathrm{M}[\mathrm{M}] + K_\varepsilon(1+K_\mathrm{M}[\mathrm{M}] + K_\mathrm{S}[\mathrm{S}])} \tag{12}$$

The rate of the propagation is expressed in Eq. (13):

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

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

$$R_p = \frac{(K_{\varepsilon}K_{\mathrm{M}}k_p + K'_{\mathrm{M}}k'_p)\alpha[\mathrm{C}]_0}{1 + K'_{\mathrm{M}}[\mathrm{M}] + K_{\varepsilon}(1 + K_{\mathrm{M}}[\mathrm{M}] + K_{\mathrm{S}}[\mathrm{S}])}[\mathrm{M}] \tag{14}$$

Considering that K_{M} and K'_{M} are much smaller than unity, Eq. (14) may be expressed by Eq. (15):

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t \fallingdotseq \frac{(K_{\varepsilon}K_{\mathrm{M}}k_p + K'_{\mathrm{M}}k'_p)\alpha[\mathrm{C}]_0}{1 + K_{\varepsilon}(1 + K_{\mathrm{S}}[\mathrm{S}])}[\mathrm{M}] \tag{15}$$

Equation (15) shows that the rate of the monomer consumption is expressed by a first-order rate equation with respect to the monomer concentration.

Since, in polar solvents, it is considered that propagation occurs mainly by the dissociated immonium ion, and that k_p is much larger than k_p', Eq. (14) may be expressed approximately by Eq. (16):

$$R_p \fallingdotseq \frac{K_{\varepsilon}K_{\mathrm{M}}K_p\,\alpha[\mathrm{C}]_0}{1 + K'_{\mathrm{M}}[\mathrm{M}] + K_{\varepsilon}(1 + K_{\mathrm{M}}[\mathrm{M}] + K_{\mathrm{S}}[\mathrm{S}])} \tag{16}$$

By assuming $0 < K_{\varepsilon} < 1$, Equation (16) explains the experimental facts that, in polar solvents, the polymerization rate increases with an increase in the K_{ε} value (that is, the dielectric constant of the solvent), and that, in a solvent with a similar dielectric constant, the rate decreases with an increase in the K_{D} (the nucleophilicity of the solvents). Moreover, it can be interpreted by Eq. (16) that the dependency of the rate on the electron donability of the solvent increases as the dielectric constant of the solvent increases. In nonpolar solvents, it is reasonable to consider that the terms of $K_{\varepsilon}K_{\mathrm{M}}K_p$ and $K_{\varepsilon}(1+K_{\mathrm{M}}[\mathrm{M}]+K_{\mathrm{S}}[\mathrm{S}])$ are negligible. Therefore, the rate equation with the use of the nonpolar solvents may be approximately expressed by Eq. (17):

$$R_p \fallingdotseq K'_{\mathrm{M}}\,k'_p\,\alpha[\mathrm{C}]_0[\mathrm{M}]/(1 + K'_{\mathrm{M}}[\mathrm{M}]) \tag{17}$$

According to Eq. (17), we can explain the experimental finding that, in a nonpolar solvent, the nucleophilicity of the solvent has no effect on the polymerization rate.