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Polymerization of 2-Oxazolines. III. Influence of Polymerization Media on the Propagation Reaction in the Cationic Polymerization of 2-Phenyl-2-oxazoline

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ABSTRACT

The influence of solvent on the cationic polymerization of 2-phenyl-2-oxazoline initiated with 2-phenyl-2-oxazolinium perchlorate was studied in connection with the physical properties of the solvents used. The polymerizations in all solvents used proceeded successively with little termination and transfer reactions. The propagation rate constant in polar solvents was larger than in nonpolar solvents. The propagation rate constant increased with a decrease in nucleophilicity of the solvent used. In binary solvent systems composed of components with similar nucleophilicities and with different dielectric constants, the propagation rate constant increased with an amount of the polar solvent. In binary solvent systems composed of components with similar dielectric constants and with different nucleophilicities, the propagation rate constant decreased with the amount of the

solvent having more nucleophilicity. The activation energy (E_a) of the propagation reaction was about 17~27 kcal/mole, and the activation entropy (ΔS^\ddagger) was about -29~-2 E.U. The E_a and ΔS^\ddagger values in polar solvents were larger than those in nonpolar ones. On the basis of these results, the role of the solvent on the propagation reaction was discussed.

INTRODUCTION

In the kinetic study of the solution polymerization of 2-phenyl-2-oxazoline in *N,N*-dimethylacetamide initiated with 2-phenyl-2-oxazolinium perchlorate (Part II of this series [1]), it was found that the polymerization proceeded successively without termination and transfer reactions.

It has been known that the rate of ionic polymerization is affected markedly by the natures of the solvent used, such as the dielectric constant and the nucleophilicity of the solvent [2-11].

The purpose of this study was to investigate the influence of the solvent on the propagation reaction in the cationic ring-opening polymerization of 2-phenyl-2-oxazoline with 2-phenyl-2-oxazolinium perchlorate in connection with the physical properties of the solvent used.

EXPERIMENTAL

The preparation and purification of 2-phenyl-2-oxazoline (monomer) and 2-phenyl-2-oxazolinium perchlorate (initiator), and the procedures of the solution polymerization, were carried out by the same methods as described in previous papers [1, 12] (monomer concentration, 3.00 mole/liter; the initial molar ratio of the initiator to monomer is 1.00×10^{-2}).

The commercially available solvents for polymerization (G.R. grade), nitroethane, nitrobenzene, acetonitrile, ethyl acetate, anisole, and di-*n*-propyl ether, were purified by several careful distillations under reduced pressure according to the method reported by Weisberger et al. [13].

Kinetic Feature of the Polymerization of 2-Phenyl-2-Oxazoline Initiated with 2-Phenyl-2-oxazolinium Perchlorate

The solution polymerization of 2-phenyl-2-oxazoline initiated with 2-phenyl-2-oxazolinium perchlorate at constant temperature over the 105 to 150°C range were carried out in two groups of solvents; one was polar solvents with high dielectric constant ($\epsilon = 28\sim 38$) such as nitroethane ($\epsilon = 28.1$), nitrobenzene ($\epsilon = 34.8$), and acetonitrile ($\epsilon = 37.5$), and the other was nonpolar solvents with low dielectric constant ($\epsilon = 3\sim 6$) such as di-n-propyl ether ($\epsilon = 3.4$), anisole ($\epsilon = 4.3$), and ethyl acetate ($\epsilon = 6.0$).

As shown in Figs. 1 and 2, the rate of monomer consumption is expressed by a first-order rate equation with respect to monomer concentration. The deviation from the first-order plot in nonpolar solvents, which appeared in the advanced stage of polymerization (about 70% conversion), may be due to the precipitation of polymer.

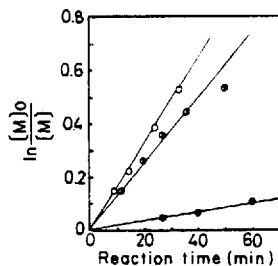


FIG. 1. The first-order plots for nonpolar solvents at 120°C. Anisole (○), ethyl acetate (◐), and di-n-propyl ether (●).

The number-average degree of polymerization of the resulting polymer is almost proportional to the conversion of polymerization, independent of the kind of the solvent used (Fig. 3). The slope of the straight line leads to the conclusion that the moles of the polymer formed are nearly equal to that of the catalyst initially charged.

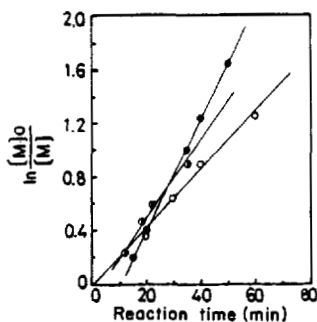


FIG. 2. The first-order plots for polar solvents at 120°C. Nitroethane (●), nitrobenzene (●), and acetonitrile (○).

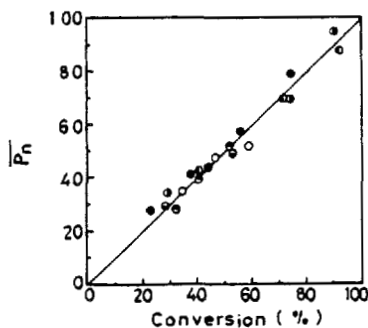


FIG. 3. The relation between the number-average degree of polymerization and the conversion in various solvents at 120°C. Nitroethane (●), nitrobenzene (●), acetonitrile (●), Anisole (⊖), ethyl acetate (○), and di-n-propyl ether (⊖).

It means that the initiation coefficient of the catalyst, which is defined by Eq. (1), is almost unity:

$$\alpha = \frac{[M]_0/[I]_0}{\bar{P}_n} = 1.0 \quad (1)$$

where $[M]_0$ and $[I]_0$ denote the moles of monomer and of the catalyst initially charged, respectively, and \bar{P}_n is the number-average degree of polymerization.

These results may indicate that the solution polymerization in the solvents used proceed successively without termination and transfer reactions, the same as in *N,N*-dimethylacetamide media [1]. Accordingly, the propagation rate constant (k_p) can be evaluated from the following equation (2), as has been described in the previous paper [1].

$$\ln ([M]_0/[M]) = k_p \int [P^*] dt = k_p [I]_0 (t - t') \quad (2)$$

where $[M]$ and $[P^*]$ are the concentrations of remaining monomer and of the active propagating polymer chain, respectively, and t and t' are the reaction time and the period of the complete conversion of the catalyst to the active propagating species

$$\int_0^{t'} [P^*] dt = [I]_0$$

It was found that the solvents used in the present polymerization have the main influence on the propagation reaction. The values of k_p are summarized in Table 1, together with the physical properties of the solvent used.

Relation between the Physical Properties of Solvent and Propagation Rate Constant

The propagation rate constants (k_p) thus obtained in two different groups of solvents with high and low dielectric constant were plotted against the magnitude of the nucleophilicity ($\Delta\nu_D$) of the solvents used (Fig. 4), where $\Delta\nu_D$ is a measure of the magnitude of nucleophilic solvation to a deuterium atom of a methanol-*d* molecule [14]. (In the quantitative studies on the electron-donating power of liquid organic compounds, Kagiya et al. [14] proposed that the magnitude of the shift of the O-D band of a methanol-*d*, which was caused by

TABLE 1. Cationic Polymerization of 2-Phenyl-2-oxazoline Initiated by 2-Phenyl-2-oxazolium Perchlorate in Various Solvents

Run No.	Solvent	Dielectric constant (ϵ ; 25°C)	Nucleophilicity ($\Delta\nu$; D; cm^{-1})	Propagation rate constant ^a		
				105°C	120°C	135°C 150°C
1	Polar	28.1	8	0.70	1.52	4.24 -
2	Nitrobenzene	34.8	21	0.34	0.82	2.09 -
3	Acetonitrile	37.5	49	0.22	0.71	1.75 -
4	N,N-Dimethylacetamide ^b	36.7	113	-	0.25	0.69 2.39
5	Nonpolar Anisole	3.4	26	-	0.50	1.04 2.70
6	Ethyl acetate	6.0	39	-	0.40	0.85 1.81
7	Di-n-propyl ether	4.3	73	-	0.06	0.14 0.30

^a Liter/mole min.

^b Measured in Part II of this series (see Ref. 1).

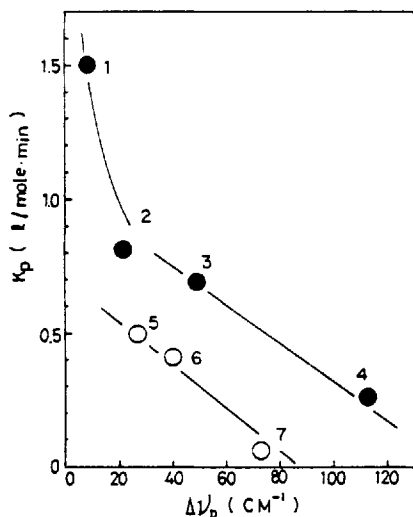


FIG. 4. Variations in the propagation rate constant with changes in the nucleophilicity of the solvent at 120°C. $\Delta\nu_D$ is the O-D shift of methanol-d in the solvent (reference: benzene). Polar (●) and nonpolar (○) solvent. The numbers are the same as in Table 1.

the nucleophilic coordination [counted as wave number], $\Delta\nu_D$, was a measure of the strength of the organic compounds.

$$\text{Electron-donating power: } \Delta\nu_D = \nu_D [\text{benzene}] - \nu_D [\text{compound}]$$

Figure 4 indicates that k_p in both groups of solvents with similar dielectric constant decreased with an increase in the nucleophilicity of the solvent. This fact may indicate that the solvent with large nucleophilicity coordinates to the cationic end group of the propagating species, and that solvation prevents the coordination of the incoming monomer.

The propagation rate constant in polar solvents is larger than in nonpolar solvents. This fact may mean that the dissociation of the propagating ion-pair is promoted by the solvents with high dielectric constants and enhances the propagation rate [8, 9].

Polymerization in Binary Solvent Systems

The polymerizations of 2-phenyl-2-oxazoline were carried out in two groups of binary solvent systems; the first group (A-1, A-2) contained components with similar nucleophilicities and different dielectric constants, and the second group (B-1, B-2) contained similar dielectric constants and different nucleophilicities, as shown in Table 2. The propagation rate was determined from the first-order plot with respect to monomer concentration according to the procedure as mentioned above.

TABLE 2. The Physical Properties of the Solvent in the Binary Solvent System

Binary solvent system		Dielectric constant (ϵ)	Nucleophilicity ($\Delta\nu$; cm^{-1})
A-1	Nitrobenzene	34.8	21
	Anisole	4.3	26
A-2	Acetonitrile	37.5	49
	Ethyl acetate	6.0	39
B-1	Nitrobenzene	34.8	21
	N,N-Dimethylacetamide	36.7	113
B-2	Anisole	4.3	26
	Di-n-propyl ether	3.4	73

The relations between the propagation rate constant and the solvent composition are shown in Figs. 5 and 6. In the binary solvents with similar nucleophilicities and different dielectric constants (A-1, nitrobenzene-anisole; A-2, acetonitrile-ethyl acetate), the propagation rates decreased with an increase in the amount of the solvent with low dielectric constant. These facts suggest that, in binary solvent systems with similar abilities for nucleophilic solvation, the propagation reaction is mainly dependent on the degree of ionic dissociation of the propagating species.

On the other hand, in binary solvent system with similar

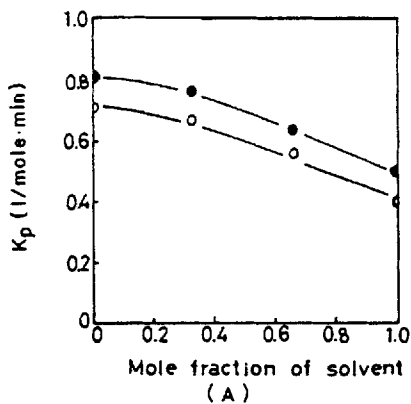


FIG. 5. The propagation rate constant in binary solvent systems at 120°C. (●) Nitrobenzene-anisole (A-1). (○) Acetonitrile-ethyl acetate (A-2).

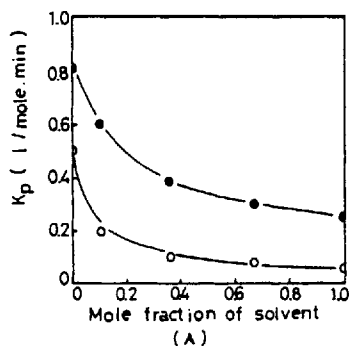


FIG. 6. The propagation rate constant in binary solvent system at 120°C. (●) Nitrobenzene-N,N-dimethylacetamide (B-1). (○) Anisole-di-n-propyl ether (B-2).

dielectric constants and different nucleophilicities (B-1, anisole-di-n-propyl ether; B-2, N,N-dimethylacetamide-nitrobenzene), propagation rates are depressed by the addition of a small amount of the solvents with larger nucleophilicity (N,N-dimethylacetamide,

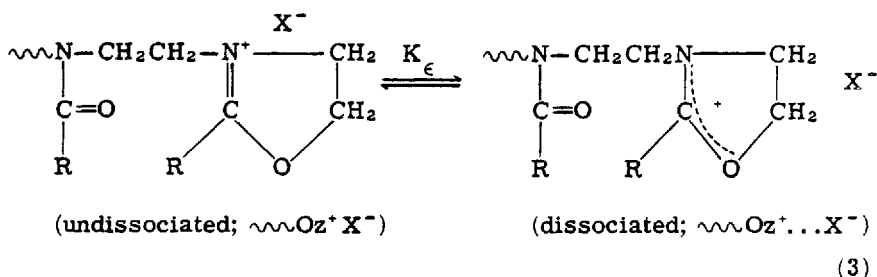
di-n-propyl ether). Since solvent and monomer competitively coordinates to the cationic propagation end, and the coordination of the solvents increases with larger nucleophilicity, the preferential coordination of the solvent with the larger nucleophilicity depressed the monomer coordination to the growing end. This is in accord with the fact that the propagation rate in single solvent systems decreases with an increase in the nucleophilicity of the solvent used.

Quantitative Expression of the Influence of the Solvent

It has been proposed in previous papers [1, 12] that the incorporation reaction of monomer proceeds through the nucleophilic attack on the active propagating oxazolinium perchlorate. The following scheme is proposed for the interpretation of the influence of the solvent on the propagation reaction based on the experimental results mentioned in this report.

The solvent with a high dielectric constant may promote the dissociation of the propagating ion-pair and facilitate the delocalization in the positively-charged oxazolinium end as follows.

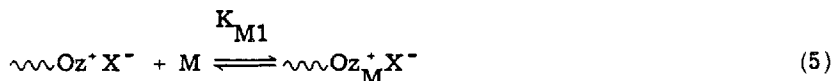
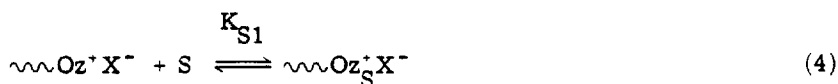
Dissociation of the Propagating Oxazolinium Perchlorate:



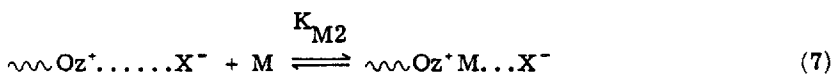
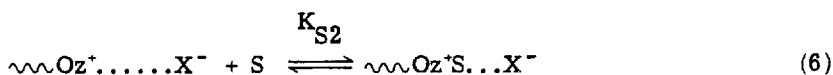
where X^- denotes the counterion, ClO_4^- . The equilibrium constant (K_ϵ) is considered to increase with an increase in the dielectric constant (ϵ) of the solvent.

Both dissociated and undissociated species would be coordinated nucleophilically by the solvent (S) and the monomer (M) according to the following competitive reactions (Eqs. 4-7), where the nucleophilic coordination or solvation is considered to increase with an increase in their nucleophilicities.

Nucleophilic Coordinations of Undissociated Propagating Species
($\sim\text{Oz}^+\text{X}^-$):



Nucleophilic Coordinations to Dissociated Propagating Species
($\sim\text{Oz}^+\text{X}^-$):

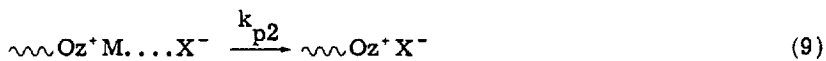


where K_{S1} , K_{S2} , K_{M1} , and K_{M2} are equilibrium constants. Since the coordination of the solvent to both the propagating species and methanol-d is nucleophilic solvation, the equilibrium constant (K_S) is considered to increase with an increase in the $\Delta\nu_D$ value of the solvent [9, 14].

The incorporation of the monomer into the polymer chain in reactions of the coordinated monomer with the undissociated and dissociated propagating species to generate the oxazolinium heterocycle are as follows;



(P₁)



(P₂)

The net propagation rate constant in Eq. (9), k_{p2} , is considered to be larger than k_{p1} in Eq. (8) because the free-ion character of the propagating species enhances the reaction rate.

On the basis of the above considerations, the propagation rate (R_p) is represented as

$$R_p = -d[M]/dt = k_{p1}[P_1^*] + k_{p2}[P_2^*] \quad (10)$$

where $[P_1^*]$ and $[P_2^*]$ denote the concentrations of the undissociated and the dissociated propagating species coordinated with monomer, respectively. By combining Eqs. (3)-(7), and considering that the concentration of the propagating species ($[P^*]$) is almost equal to that of the initiator initially charged ($[I]_0$), $[P_1^*]$ and $[P_2^*]$ are expressed as

$$[P_1^*] = \frac{K_{M1}[I]_0[M]}{1 + K_{M1}[M] + K_{S1}[S] + K_\epsilon(1 + K_{M2}[M] + K_{S2}[S])} \quad (11)$$

$$[P_2^*] = \frac{K_\epsilon K_{M2}[I]_0[M]}{1 + K_{M1}[M] + K_{S1}[S] + K_\epsilon(1 + K_{M2}[M] + K_{S2}[S])} \quad (12)$$

Accordingly, by substituting Eqs. (11) and (12) into Eq. (10):

$$\begin{aligned} R_p &= -\frac{d[M]}{dt} \\ &= \frac{(K_{M1}k_{p1} + K_\epsilon K_{M2}k_{p2})[I]_0[M]}{1 + K_{M1}[M] + K_{S1}[S] + K_\epsilon(1 + K_{M2}[M] + K_{S2}[S])} \end{aligned} \quad (13)$$

Since the rate of monomer consumption is expressed by a first-order equation with respect to the monomer concentration, $K_{M1}[M]$ and $K_{M2}[M]$ may be much smaller than unity. Accordingly, the rate

of monomer consumption and the observed propagation rate constant may be expressed as

$$-\frac{d[M]}{dt} = \frac{K_{M1}k_{p1} + K_{\epsilon}K_{M2}k_{p2}}{1 + K_{S1}[S] + K_{\epsilon}(1 + K_{S2}[S])} [I]_0[M] \quad (14)$$

$$k_p = \frac{K_{M1}k_{p1} + K_{\epsilon}K_{M2}k_{p2}}{1 + K_{S1}[S] + K_{\epsilon}(1 + K_{S2}[S])} \quad (15)$$

The influence of the solvent on the propagation reaction would be expressed by Eq. (15). That is, in solvents with similar nucleophilicities, k_p remains constant in the range of small K_{ϵ} value:

$$k_p = \frac{K_{M1}k_{p1}}{1 + K_{S1}[S]} \quad (K_{\epsilon} \ll 1) \quad (16)$$

then increases gradually with an increase in K_{ϵ} value, and reaches a constant value in the range of large K_{ϵ} value

$$k_p = \frac{K_{M2}k_{p2}}{1 + K_{S2}[S]} \quad (K_{\epsilon} \gg 1) \quad (17)$$

and k_p in solvents with similar dielectric constants decreases with an increase in the nucleophilicity of the solvent, irrespectively of dielectric constant. Equations (16) and (17) may express the influence of solvent on the propagation rate constant in nonpolar and polar solvents, respectively (Fig. 4). Considering that k_p increases with an increase in the dielectric constant and with a decrease in the nucleophilicity of the solvent, the observed k_p value can be satisfactorily given by the following empirical equation in the range of the present experiment:

$$k_p = (-7 \times 10^{-3} \Delta\nu) + (1.0 \times 10^{-2}\epsilon) + 0.66 \quad (18)$$

Activation Energy and Entropy of the Propagation Reaction

The Arrhenius plots of the logarithm of the propagation rate constant and the reciprocal of the absolute reaction temperature are shown in Fig. 7. The activation energy (E_a) and entropy (ΔS^\ddagger) thus obtained are tabulated in Table 3. The activation energies are about 17 ~ 27 kcal/mole, which are considerable larger as compared with those in cationic polymerization of five-membered heterocyclic compounds such as tetrahydrofuran (10 ~ 14 kcal/mole) [15]. This may be due to the large energy required for the bond-rearrangement process of the C=N bond to the C-N bond, and the C-O bond to the C=O bond.

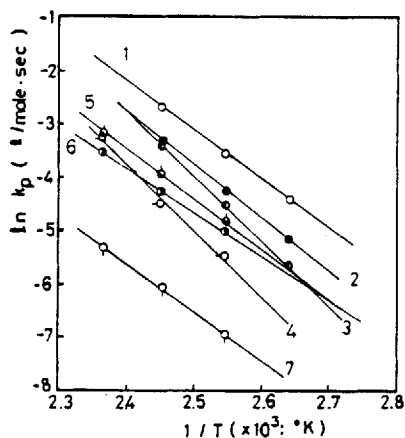


FIG. 7. Arrhenius plot for the propagation reaction in various solvents. The numbers are the same as in Table 3.

There appeared to be an approximate compensation rule between the E_a and ΔS^\ddagger values, as shown in Fig. 8. The E_a value in polar solvents is larger than that in nonpolar ones, despite the increasing propagation rate constant in polar solvents. This indicates that the activation energy is overcompensated for by the gain in the activation entropy.

The activation energy and entropy in polar solvents increases with an increase in the nucleophilicity of the solvent, whereas those in nonpolar ones decrease, as shown in Figs. 9 and 10. These facts may suggest the difference in the mode of solvation for the initial and transition state between polar and nonpolar solvents. The tentative representation for the mode of solvation is given in Fig. 11. In highly polar solvents in which the growing chain end would be largely dissociated, the oxazolinium cation in the initial state is tightly solvated nucleophilically due to the enhanced free-ion character. In the transfer process from initial to transition state,

TABLE 3. Activation Energies and Entropies for Propagation Reaction in Various Solvents

Run No.	Solvent	Activation energy (kcal/mole)	Activation entropy ^a (E.U.)
1	Nitroethane	19.2	-16.8
2	Nitrobenzene	19.1	-19.5
3	Acetonitrile	23.1	-10.8
4	N,N-Dimethylacetamide	27.4	-2.0
5	Anisole	18.8	-22.4
6	Ethyl acetate	17.0	-27.4
7	Di-n-propyl ether	17.8	-29.0

^aThe standard state for ΔS^\ddagger is 1 mole/liter. The activation entropy was calculated from

$$\Delta S^\ddagger = R \left(\ln A - \ln \frac{ekT}{h} \right)$$

where A is the frequency factor in the Arrhenius equation (liter/mole sec), and k and h are, respectively, Boltzmann's and Planck's constant.

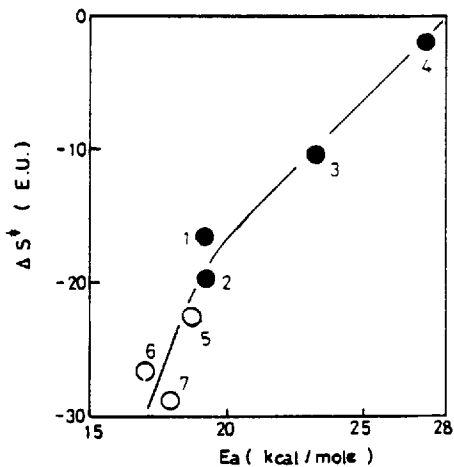


FIG. 8. The relation between activation energy and entropy for the propagation reaction in various polar (●) and nonpolar (○) solvents. The numbers are the same as in Table 3.

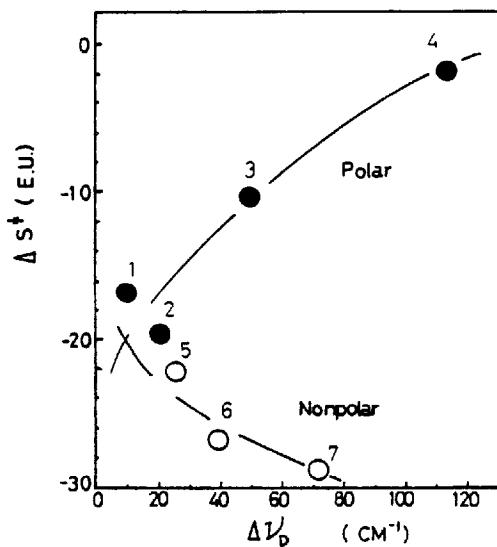


FIG. 9. The relation between activation entropy and the nucleophilicity of the solvent: polar (●) and nonpolar (○) solvents. The numbers are the same as in Table 3.

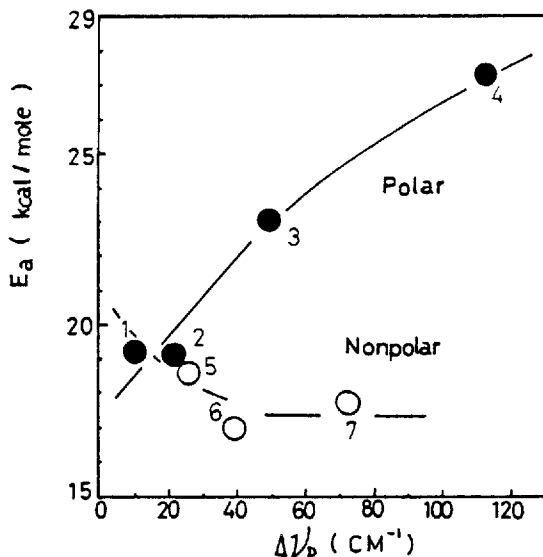


FIG. 10. The relation between activation energy and the nucleophilicity of the solvent: polar (●) and nonpolar (○) solvents. The numbers are the same as for Table 3.

the solvation shell and solvent molecules frozen around a cation would be destroyed or released by the coordination of monomer, and by the dispersal of charge at the transition state. The desolvation in the transfer to transition state would result in an increase in the ΔS^\ddagger and E_a values with an increase in the nucleophilicity of the solvent used, because E_a increased in proportion to the desolvation energy [16].

On the other hand, in nonpolar solvents in which the growing chain end is scarcely dissociated, the ion-pairs in the transition state would be more solvated nucleophilically than those in the initial state, because the ion-pairs in the transition state would be separated by the insertion or coordination of monomer into the ion-pair. Accordingly, the nucleophilic solvation in the transition state would result in an increase in E_a and ΔS^\ddagger with a decrease in the nucleophilicity of the solvent due to the loss of the freedom of solvent and the gain in the solvation energy at the transition state.

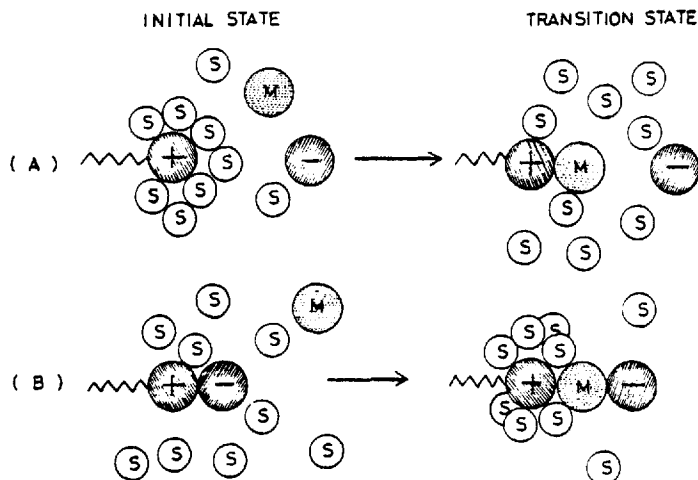


FIG. 11. The tentative representation for the mode of solvation at the initial and transition states. (A) Dissociated ion-pair. (B) Undissociated ion-pair. (S) Solvent molecule. (M) Monomer molecule.

These considerations seem to be in accord with the results given in Figs. 9 and 10.

From these results it may be suggested that the influence of the polar solvent on the propagation reaction through the dissociated ion-pair would be predominantly controlled by the nucleophilic solvation at the initial state (activation energy control), whereas that of the nonpolar solvent through the undissociated ion-pair would be controlled at the transition state (activation entropy control).

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