Group Interactions in Polyelectrolytes. VI.[1] Amination Kinetics of Chloromethylated Polystyrene in *N,N*-Dimethylformamide and Dimethyl Sulfoxide

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(Received May 2, 1972)

Although the apparent second-order rate constant of the amination of chloromethylated polystyrene with *n*-butylamine or with 2-aminobutanol decreased or increased, respectively, during the course of the amination in dioxane, as has been reported previously, both aminations as well as the aminations of benzyl chloride have been found to conform to the ordinary second-order kinetics in DMF and DMSO. The viscometric measurements have indicated that the viscosity of the reaction mixture decreased during the amination with *n*-butylamine and increased slightly during the amination with 2-aminobutanol, but no relation between the kinetic behavior and the viscometric changes in the reaction mixtures could be found. The magnitude of the rate constants was comparable to that of the amination of benzyl chloride, and it increased with an increase in the dielectric constant of the solvents in this order: dioxane$\ll$DMF$<$DMSO. The effects of the solvents on both the kinetic behavior in the aminations of the polymer and the magnitude of the rate constants have been discussed in terms of the interactions between the solvent and the solute molecules.

The quaternization of chloromethylated polystyrene (CMPS) with tertiary amines in various solvents was studied by Noda and Kagawa.[2] They reported that the initial rate of the quaternization with triethylamine increased with an increase in the dielectric constant of the solvents, like in ordinary Menschutkin reactions; they also reported that the rate in *N,N*-dimethylformamide (DMF) conformed completely to the ordinary second-order equation. Kawabe and Yanagita[3,4] investigated the aminations of CMPS with some primary and secondary amines in dioxane and found that the aminations apparently did not obey the second-order rate law. In the amination with *n*-butylamine or di-*n*-butylamine, the apparent second-order rate constant decreased as the amination proceeded, whereas it increased in the amination with 2-aminobutanol. In these cases, the amination kinetics could be expressed by rate equations which were derived by assuming that the reaction is subjected to the steric hindrance or "hydrophilic effect" of the already-aminated neighboring groups.

In the present study, the authors will deal with the amination of CMPS with *n*-butylamine in DMF and with that with 2-aminobutanol in DMF and dimethyl sulfoxide (DMSO); they will show that the rates conform to the second-order equation and that the rate constants in these solvents are markedly higher than those in dioxane. The effects of the solvents on the kinetic behavior in the aminations of CMPS, and also the dependence of the rate constants on the polarity of the solvents, will be discussed.

Experimental

Materials. The polystyrene and chloromethylated polystyrene (CMPS) were prepared and purified by the procedures described in previous papers.[3,4] The chlorine contents and the molecular weights of CMPS used in the present study are tabulated in Table 1. The 2-aminobutanol was prepared by the procedure described in a previous paper.[4] The other amines, benzyl chloride and the solvents, all of a reagent grade, were distilled before use; they were proved to be pure by their refractive indices. All the other chemicals were of a reagent grade, and de-ionized, de-carbonized water was used throughout the experiments.

TABLE 1. CHLOROMETHYLATED POLYSTYRENE

Code	Content of Cl %	Degree of Chloromethylation	Molecular weight
SC-4	22.04	0.93	7.3×10^4
SC-5	21.15	0.87	10.3×10^4
SC-6	18.76	0.74	—

Kinetic Measurements. As has been described in the previous papers,[3,4] 150 m*l* of a solution containing one gram of CMPS or benzyl chloride and a large excess of amine (about twenty times as many moles as the chloromethyl group) was stirred at a constant temperature (within ±0.1°). At appropriate intervals, aliquots were taken out, poured into dilute nitric acid, and titrated with 0.1 N silver nitrate. The experimental conditions in the aminations of CMPS are listed in Table 2, where a denotes the initial concentration of an amine, and b, the initial concentration of the chloromethyl group of CMPS. In the amination of benzyl chloride, a was 1.06 mol/*l* and b was 0.053 mol/*l*. All the reaction except the amination of CMPS with di-*n*-butylamine, which was accompanied by the emulsification of the reaction mixture, were homogeneous and reached completion.

Viscometric Measurements. In the amination of CMPS, the viscosity change in the reaction mixture was also checked. After the reaction mixture had been prepared, a 10 m*l* portion of the solution was taken out and put into an Ostwald-type viscometer, while the temperature was kept constant (within ±0.1°). At appropriate intervals, the flow times were measured, and the relative viscosity ($\eta_{\rm rel}$) and the reduced viscosity ($\eta_{\rm sp}/c_{\rm p}$) were determined:

$$\eta_{\rm rel} = \rho_{\rm p}t/\rho_0 t_0, \quad \eta_{\rm sp} = \eta_{\rm rel} - 1$$

where $c_{\rm p}$ is the concentration of CMPS expressed by g/100 m*l* where ρ_0 and $\rho_{\rm p}$ are the densities of a pure solvent and a CMPS solution of the same concentration as the reaction mixture

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[1] Part V; H. Kawabe and M. Yanagita, This Bulletin, **44**, 896 (1971).

[2] I. Noda and I. Kagawa, *Kogyo Kagaku Zasshi*, **66**, 857 (1963).

[3] H. Kawabe and M. Yanagita, This Bulletin, **41**, 1518 (1968).

[4] H. Kawabe and M. Yanagita, *ibid.*, **44**, 896 (1971).

TABLE 2. AMINATION OF CHLOROMETHYLATED POLYSTYREHE

Run	Amine[a)]	Solvent	Temp °C	CMPS	a[b)] mol/l	b[c)] mol/l	a/b
1	A	Dioxane	50	SC-4	0.8353	0.0415	20.1
2	A	Dioxane	55	SC-4	0.8480	0.0421	20.1
3	A	Dioxane	60	SC-4	0.8304	0.0414	20.1
4	A	Dioxane	65	SC-4	0.8346	0.0414	20.2
5	A	Dioxane	70	SC-4	0.8470	0.0416	20.9
6	A	DMF	18	SC-5	0.8211	0.0397	20.7
7	A	DMF	30	SC-5	0.7523	0.0375	20.1
8	A	DMF	40	SC-5	0.8205	0.0399	20.6
9	A	DMF	50	SC-5	0.8236	0.0400	20.6
10	B	DMF	30	SC-5	0.8046	0.0409	19.7
11	C	DMF	20	SC-4	0.8853	0.0422	21.0
12	C	DMF	30	SC-4	0.8862	0.0464	19.1
13	C	DMF	40	SC-4	0.8580	0.0409	21.0
14	C	DMF	50	SC-4	0.8852	0.0437	20.3
15	C	DMSO	20	SC-6	0.7123	0.0341	20.9
16	C	DMSO	25	SC-6	0.7005	0.0339	20.7
17	C	DMSO	30	SC-6	0.7070	0.0339	20.9
18	C	DMSO	35	SC-6	0.7077	0.0339	20.9
19	C	DMSO	40	SC-6	0.7100	0.0341	20.8
20	C	DMSO	20	SC-6	0.3557	0.0355	10.0
21	C	DMSO	20	SC-6	0.1800	0.0355	5.1
22	C	DMSO	20	SC-6	0.0362	0.0355	1.0

a) Amine A: *n*-butylamine; Amine B: di-*n*-butylamine;Amine C: 2-aminobutanol
b) a: Initial concentration of amine
c) b: Initial concentration of the polymer expressed in moles of chloromethyl group per litre

respectively, and where t_0 and t are the flow times of a pure solvent and the reaction mixture respectively. The values of c_p were 0.67—0.69, and those of ρ_p/ρ_0 were lower than 1.01 in the present experiments. The observed viscosity change in the reaction mixture was expressed in terms of the viscosity ratio (H), defined by the following equation:

$$H \equiv (\eta_{sp}/c_p)/(\eta_{sp}/c_p)_{\beta\to 0}$$

where β is the fractional conversion of the chloromethyl group. The numerical values of $(\eta_{sp}/c_p)_{\beta\to 0}$, which are the extraporated values of η_{sp}/c_p to $\beta=0$, are as follows:

n-butylamine: 0.5 (dioxane, 50°C), 0.46 (DMF, 50°C)
2-aminobutanol: 0.67 (dioxane, 40°C), 0.8 (DMF, 40°C), 0.51 (DMSO, 30°C)

Results

Amination with n-*Butylamine*. As has been reported previously,[3)] the amination of benzyl chloride with *n*-butylamine in dioxane obeyed the second-order rate law, and the rate constant, k, was given by:

$$kt = \frac{1}{(a-b)} \ln \frac{b(a-x)}{a(b-x)} \equiv \overline{kt} \qquad (1)$$

where a and b are the initail concentrations of an amine and the chloromethyl group respectively, while x is the concentration of chloride ions after time t. The dependence of k on the temperature was expressed by:

$$k = A \exp\,(-E_a/RT) \qquad (2)$$

where A is the frequency factor and E_a, the activation energy.

In the amination of CMPS with *n*-butylamine in dioxane, the rate constant computed by Eq. (1) was not constant, but decreased as the amination proceeded, and the plot of $\overline{kt}$ against t could be expressed approximately by two lines which intersected near the half-amination.[3)] This behavior can be explained by the assumption that the amination of the chloromethyl group situated between two already-aminated neighboring groups is sterically obstructed, and the over-all kinetics in the presence of a large excess of the amine ($a \gg b$) can be expressed by Eq. (3):

$$\beta = x/b = 1 - \frac{k_1-k_2}{2k_1-k_2} e^{-2k_1at} - \frac{k_1}{2k_1-k_2} e^{-k_1at} \qquad (3)$$

$$k_1 = \frac{1}{[(2-k_2/k_1)a-b]t} \ln \frac{1-\beta}{1-(2-k_2/k_1)\beta} \qquad (4)$$

$$k_2 = \frac{1}{(a-b)(t-\tau)}\left(\ln\frac{1-\alpha}{1-\beta} - \ln\frac{1-\chi/a}{1-\chi/b}\right) \qquad (5)$$

where k_1 and k_2 are the rate constants of the elementary reactions which are independent of the neighboring groups and under this influence respectively. In Eqs. (4) and (5), $\alpha = x/a$, τ and χ are the values of t and x respectively when $x_1 \simeq b/2$, and x_1 is the concentration of the group which is aminated independently of its neighbors.

TABLE 3. AMINATION OF CHLOROMETHYLATED POLYSTYRENE WITH *n*-BUTYLAMINE IN DIOXANE

Temp °C	$k_1\times 10^3$ l/mol·min	$k_2\times 10^3$ l/mol·min	E_a kcal/mol	$A\times 10^{-6}$ l/mol·min
50	6.59	3.84		
55	8.66	6.27	(k_1) 12.1±0.1	1.01
60	11.4	7.82		
65	15.0	9.44	(k_2) 12.1±0.9	0.601
70	19.8	12.2		

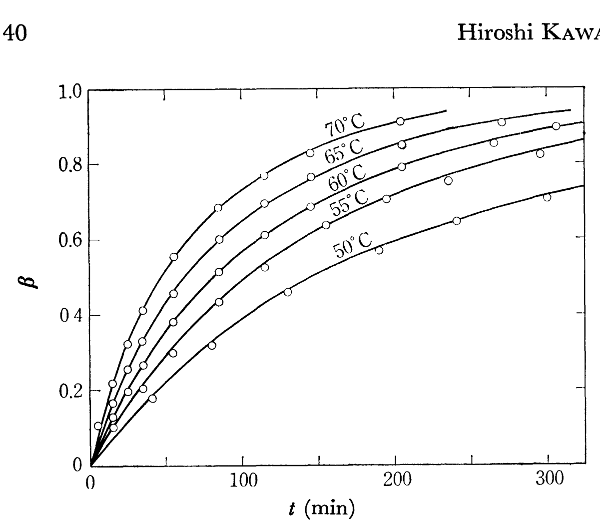

Fig. 1. Amination of chloromethylated polystyrene with n-butylamine in dioxane.
——: calculated values, ○: observed values

The rate of the amination of CMPS with n-butylamine in dioxane has been re-mesaured in the present study in order to obtain a more accurate value for E_a; the results are shown in Fig. 1 and Table 3. The solid lines in Fig. 1, calculated on the basis of Eq. (3) by using the numerical values for k_1 and k_2 listed in Table 4, are in good agreement with the observed values of β, represented by the white circles. The values of E_a and A, computed by the least-squares method on the basis of Eq. (2), are also listed in Table 3.

TABLE 4. AMINATION OF CHLOROMETHYLATED POLYSTYRENE AND BENZYL CHLORIDE WITH n-BUTYLAMINE IN DMF

Temp °C	k_P[a] × 10^2 l/mol·min	k_B[b] × 10^2 l/mol·min	E_a kcal/mol	$A\times10^{-6}$ l/mol·min
18	1.26	—	(k_P) 11.4±0.1	4.89
20	—	1.61		
30	2.78	3.21		
40	5.24	6.10	(k_B) 11.6±0.2	7.42
50	8.89	10.2		

a) k_P: Rate constant of chloromethylated polystyrene
b) k_B: Rate constant of benzyl chloride

In DMF, on the other hand, the aminations of both CMPS and benzyl chloride have turned out to obey the second-order law; their rate constants can be determined on the basis of Eq. (1). The rate constants are tabulated in Table 4. The figures of E_a and A are also listed in Table 4. The rate constants in DMF are much higher than those in dioxane.

In contrast to the amination of CMPS with n-butylamine, the amination of CMPS with di-n-butylamine in DMF showed a kinetic behavior similar to that in dioxane.[3] The results of the amination in DMF at 30°C are shown in Fig. 2. The $\overline{kt}$-t plot can be expressed approximately by two lines which intersect near β=0.5, and k_1 and k_2 are given by Eqs. (4) and (5) as follows:

$$k_1 = 1.83\times10^{-2},\ k_2 = 4.98\times10^{-3}\ l/\text{mol}\cdot\text{min}$$

In Fig. 2, the solid line was calculated on the basis of Eq. (3), and the observed values, represented by the white circles, fall substantially on the line.

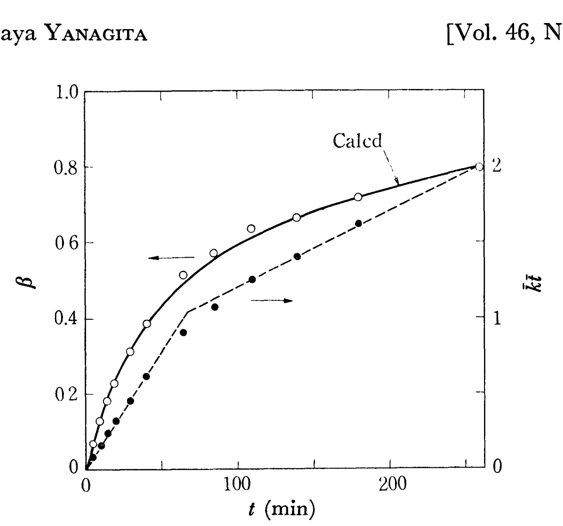

Fig. 2. Amination of chloromethylated polystyrene with di-n-butylamine in DMF.

The amination rates of CMPS with these amines could not be determined in DMSO, because the polymer was precipitated in the initial stage of the amination with n-butylamine and di-n-butylamine was not dissolved in DMSO.

Amination with 2-Aminobutanol. Although self-acceleration was observed during the amination of CMPS with 2-aminobutanol in dioxane,[4] in DMF or DMSO the amination of CMPS as well as that of benzyl chloride has been found to conform to the second-order rate equation. The rate constants computed by Eq. (1) are tabulated in Tables 5 and 6. The rate constants in DMF are much higher than those in dioxane,[4] and the rate constants in DMSO are even higher than those in DMF. The numerical values for E_a and A are also listed in Tables 5 and 6.

As has been mentioned above, the aminations of CMPS with n-butylamine and 2-aminobutanol, which show abnormal kinetic behavior in dioxane, are normal

TABLE 5. AMINATION OF CHLOROMETHYLATED POLYSTYRENE AND BENZYL CHLORIDE WITH 2-AMINOBUTANOL IN DMF

Temp °C	k_P[a] × 10^3 l/mol·min	k_B[b] × 10^3 l/mol·min	E_a kcal/mol	$A\times10^{-7}$ l/mol·min
20	2.73	3.35		
30	6.18	7.20	(k_P) 13.1±0.2	1.53
40	11.6	14.7	(k_B) 13.3±0.1	2.93
50	22.3	28.1		

a) k_P: Rate constant of chloromethylated polystyrene
b) k_B: Rate constant of benzyl chloride

TABKE 6. AMINATION OF CHLOROMETHYLATED POLYSTYRENE AND BENZYL CHLORIDE WITH 2-AMINOBUTANOL IN DMSO

Temp °C	k_P[a] × 10^2 l/mol·min	k_B[b] × 10^2 l/mol·min	E_a kcal/mol	$A\times10^{-7}$ l/mol·min
20	1.06	1.40		
25	1.55	1.97	(k_P) 12.2±0.2	1.24
30	2.06	2.75		
35	2.97	3.89	(k_B) 12.5±0.2	3.08
40	4.08	5.56		

a) k_P: Rate constant of chloromethylated polystyrene
b) k_B: Rate constant of benzyl chloride

in DMF and DMSO; that is, their rates, like those of benzyl chloride, are fully represented by the ordinary second-order equation. In these cases, therefore, even the amination of CMPS is considered to be controlled by the bimolecular reaction of chloromethyl groups and amine molecules, and the rate constants are considered to be independent of the initial concentrations of these amines. This has been confirmed in the amination of CMPS with 2-aminobutanol in DMSO. The rate constants computed by Eq. (1), which are shown in Table 7, are much the same over a wide range of amine concentrations.

TABLE 7. DEPENDENCE OF RATE CONSTANTS ON INITIAL CONCENTRATION OF AMINE IN THE AMINATION OF CHLOROMETHYLATED POLYSTYRENE WITH 2-AMINOBUTANOL IN DMSO (20°C)

a/b	21	10	5	1
a, mol/l	0.712	0.356	0.180	0.036
$k\times 10^2$, l/mol·min	1.06	1.13	1.13	1.43 (1.46)[a]

a) The figure in parenthesis was computed by the equation, $kt=x/b(b-x)$.

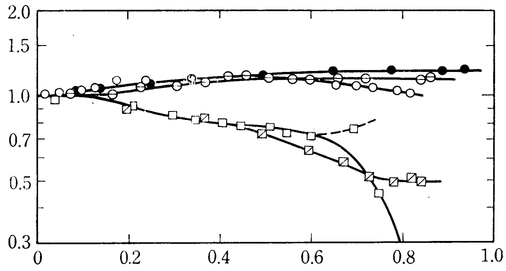

Fig. 3. Viscosity change of reaction mixture in the aminations of chloromethylated polystyrene.
□: n-butylamine in dioxane, ▨: n-butylamine in DMF
○: 2-aminobutanol in dioxane, ⊖: 2-aminobutanol in DMF, ●: 2-aminobutanol in DMSO

Viscosity Change in the Reaction Mixture During the Amination of Chloromethylated Polystyrene. The viscosity change in the reaction mixture in the amination of CMPS ($a/b=20$) is shown in Fig. 3, where the viscosity ratio, $H\equiv(\eta_{sp}/c_p)/(\eta_{sp}/c_p)_{\beta\to 0}$, is plotted against β.

In the amination with n-butylamine, H decreases with an increase in β ($H<1$), whereas H increases slightly with an increase in β ($H>1$) in the amination with 2-aminobutanol. On the other hand, the influence of the solvent is less marked. These results show that there is no relation between the kinetic behavior in the amination of CMPS and the viscometric changes in the reaction mixtures.

Discussion

The apparent second-order rate constant of the amination of CMPS with n-butylamine in dioxane decreases as the amination proceeds, but the rate in DMF conforms to the ordinary second-order equation. This difference is considered to be related to the expansion and contraction of butylamine molecules in the two solvents, which are present as reagent molecules and also as substituents of the polymer. The Hildebrand solubility parameter, δ, is an index of cohesive interaction among molecules in a solution, and the calculated values of δ at 25°C are as follows: 9.15 (n-butylamine), 9.98 (dioxane), and 12.11 (DMF).[5] Since DMF is a poorer solvent for n-butylamine than dioxane, it may be possible that the relatively long molecule of n-butylamine contracts in DMF because of the attraction among segments of the molecule. On the other hand, in the amination of CMPS with di-n-butylamine ($\delta=8.42$[5]), a decrease in the rate constant with an increase in β has been observed even in DMF. In this case, however, di-n-butylamine is a secondary amine of a larger molecular weight than n-butylamine, and so the former is more bulky than the latter. The contraction of n-butylamine molecules in DMF may not be pronounced, but it seems to be sufficient to cancel a small steric obstruction of the neighboring groups, because no such steric effect has been observed in the amination of CMPS with i- or s-butylamine in dioxane.[7]

Although the rate of the amination of CMPS with 2-aminobutanol is self-accelerated in dioxane as a result of the "hydrophilic effect" of the neighboring hydroxyl group,[4] it conforms to the ordinary second-order kinetics in DMF and DMSO. The effect of the solvents on the kinetic behavior may be explained in terms of interactions between 2-aminobutanol molecules and solvent molecules. The additional solubility parameters of the related substances are: 16.17 (2-aminoethanol) and 13.31 (DMSO).[5] Dioxane must be a poorer solvent for 2-aminobutanol than DMF and DMSO. Not only are DMF and DMSO better solvents for aminoalcohol, but also these dipolar aprotic solvents are hydrogen-bond acceptors; therefore, they may interact with the hydroxyl groups to obstruct the accelerating effect of the neighboring hydroxyl group on the polymer.

The enthalpy of activation, $\Delta H^{\neq}$, the entropy of activation, $\Delta S^{\neq}$, and the free energy of activation, $\Delta G^{\neq}$, are computed by these equations:

$$\left\{\begin{array}{l} \Delta H^{\neq} = E_a - RT \\ A/60 = e(kT/h)\exp(\Delta S^{\neq}/R) \\ \Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \end{array}\right.$$

The numerical values for these thermodynamic quantities at 25°C, obtained on the basis of the E_a and A values, are summarized in Table 8.

The value of the rate constant of CMPS is about the same as that of benzyl chloride in any solvent; this is indicated by the $\Delta G^{\neq}$ values in Table 8. Provided that benzyl chloride is a proper model for DMPS, this fact suggests that the intrinsic reactivity of the functional group of CMPS may be essentially independent of its molecular weight.

The rate constant of the amination with 2-aminobutanol is lower than that of the amination with n-butyl-

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[5] The δ values are calculated at 25°C on the basis of the data given in Ref. 6.

[6] J. A. Riddrick and W. B. Banger, "Organic Solvents," third edition, Wiley-Interscience (1970).

[7] The present author's unpublished data.

Table 8. Thermodynamic quantities at 25°C in the amination of chloromethylated polystyrene ahd benzyl chloride

Amine	Solvent	Chloride	ΔH^{*} kcal/mol	ΔS^{*} e. u.	ΔG^{*} kcal/mol
n-Butylamine	Dioxane	CMPS, k_1	11.5	−41.2	23.8
		k_2	11.5	−42.2	24.1
		Benzyl[a]	12.0	−41.5	24.3
	DMF	CMPS	10.8	−38.1	22.2
		Benzyl	11.0	−37.2	22.1
2-Aminobutanol	Dioxane[b]	CMPS, k_1	13.0	−40.3	25.0
		k_2	13.0	−38.2	24.4
		Benzyl	12.8	−40.3	24.8
	DMF	CMPS	12.5	−35.8	23.1
		Benzyl	12.7	−34.5	23.0
	DMSO	CMPS	11.6	−36.2	22.4
		Benzyl	11.9	−34.4	22.2

a) Calculated on the basis of the data given in Ref. 3.
b) Calculated on the basis of the data given in Ref. 4.

amine; *e.g.*, in DMF the former is about 20% of the latter, corresponding to a difference in ΔG^{*} of 0.9 kcal, and the ΔH^{*} of the former reaction is about 1.7 kcal higher than the latter. Accordingly, the lower rate in the amination with 2-aminobutanol seems to be related to the inductive effect of the hydroxyl group; however, it is necessary for a strict interpretation to compare 2-aminobutanol with 2-aminobutane.

On the other hand, the magnitude of the rate constants is greatly influenced by the solvents. The approximate values for the relative rate, expressed on the basis of the rate constant of benzyl chloride or CMPS in dioxane, are as follows:

n-butylamine (benzyl chloride): dioxane(1)<DMF(40)

2-aminobutanol (benzyl chloride and CMPS): dioxane(1) <DMF(20)<DMSO(80)

In the amination of both CMPS and benzyl chloride with 2-aminobutanol in dioxane, the rate constant is somewhat influenced by the initial concentration of the amine;[7] the relative rates, expressed on the basis of the rate constant extrapolated to a zero concentration of the amine, are:

2-aminobutanol (benzyl chloride and CMPS): dioxane(1) <DMF(40)<DMSO(160)

The order of the rate constants is in agreement with that of the dielectric constants of the solvents, D: dioxane (2.21)<DMF (36.71)<DMSO (46.68). It should be noted, however, that the plot of log k against $1/D$ is not linear.

In the amination with *n*-butylamine, the change of solvent from dioxane to DMF lowers the ΔH^{*} and increases the ΔS^{*}. The lower ΔH^{*} in DMF may be explained principally in terms of the solvation of the transition state in this dipolar aprotic solvent. This solvation, however, is considered to be accompanied by a lowering of ΔS^{*}. The observed enhancement of ΔS^{*} must be caused by some other factors, one of which may be the change in the configurational entropy of the solvent in the reaction mixture. The solubility parameter of benzyl chloride ($\delta=9.79$[8]) is almost the same as that of dioxane, but the transition state is rather ionic and may have a considerably higher value for δ. The formation of the transition state may thus be accompanied by a decrease in the entropy of the solvent, dioxane. Since the δ value of DMF is much higher than that of dioxane, its entropy change may be relatively small.

In the amination with 2-aminobutanol, the lowering of the ΔG^{*} from dioxane to DMF is principally ascribable to the increase in the ΔS^{*}, and the lowering of the ΔH^{*} is not so marked as in the case of *n*-butylamine. This discrepancy cannot be explained at the present time; further investigation is needed, especially in order to establish the dependence of the rate constant on the initial concentration of 2-aminobutanol in dioxane. On the other hand, the lowering of the ΔG^{*} from DMF to DMSO is substantially caused by the lowering of the ΔH^{*}. This small entropy change can be understood if we assume that both DMF and DMSO are dipolar aprotic solvents and that their δ values are approximately the same. The lowering of the ΔH^{*} is brought about by the lowering of the potential energy of the activation complex, which may be more strongly solvated in DMSO than it is in DMF, for the former is more polar than the latter.

The authors wish to express their thanks to Mr. Masayuki Takahashi, Mr. Akihiro Kishi, and Mr. Sachio Fukushima for their helpful assistance in preparing the polymer and in carrying out the measurements.

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[8] The δ value is calculated on the basis of the data given in the book: Kirk-Othmer "Encyclopedia of Chemical Technology," second edition, Vol. 5, Interscience Publishers (1964), p. 282.