Group Interactions in Polyelectrolytes. VIII.[1] The Amination of Chloromethylated Polystyrene with Secondary Amines and the Quaternization of the Aminated Polymer

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The amination of chloromethylated polystyrene (CMPS) and benzyl chloride with diethyl amine, diethanolamine, and di-*n*-butylamine was investigated kinetically in *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or dioxane. The apparent second-order rate constant decreased as the amination proceeded in the amination of CMPS with diethylamine and di-*n*-butylamine in DMF as well as in dioxane. Although a similar deceleration was also observed in the amination of CMPS with diethanolamine in DMF and DMSO, acceleration was observed during the course of the amination in dioxane. It is assumed that the deceleration and the acceleration are due to the steric obstruction and to the formation of a hydrogen bond by the neighboring groups in the transition state respectively. The intrinsic rate constants of the amination of CMPS were almost the same as those of benzyl chloride. The rate of the amination with diethanolamine was lower than that of the amination with diethylamine because of the inductive effect of the hydroxyl group. The rate constants in different solvents were in this order; DMSO$>$DMF$\gg$dioxane. The aminated CMPS with diethanolamine ($pK_0=7.37$) was quaternized with methyl iodide or bromoacetic acid in 50% aq. DMF. The deceleration due to the electrostatic effect of the neighboring groups was observed in the quaternization.

The effect of the species of amines and solvents on the kinetics in the amination of chloromethylated polystyrene (CMPS) was previously investigated by Kawabe and Yanagita.[1-4] Although most of the amination with primary amines such as butylamine isomers conformed to the ordinary second-order rate equation, deceleration was observed during amination with such secondary amines as diethylamine and di-*n*-butylamine. On the other hand, acceleration was observed during amination with 2-aminobutanol in dioxane, though the amination with the amine in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) obeyed the ordinary second-order kinetics.

In the above reactions, charged groups were not formed on the polymer molecules, because CMPS was aminated with a large excess of primary or secondary amine. On the other hand, in the Menschutkin reaction of polymers, during which quaternary ammonium groups are formed on polymer molecules, the following two different kinetic behaviors were reported; one was an ordinary second-order kinetics, while the other was modified by the deceleration because of the electrostatic repulsion among the charged groups. Noda and Kagawa[5] found that the amination of CMPS with triethylamine in DMF conformed to the second-order kinetics. Fouss *et al.*[6] observed that the rate of the quaternization of poly-4-vinyl-pyridine with *n*-butylbromide in tetramethylene sulfon or propylene carbonate decreased rapidly beyond half-quaternization.

In the present study, the kinetics of the aminations of CMPS and benzyl chloride with diethanolamine has been compared with that of the aminations with diethylamine, and also the quaternization of the CMPS aminated with diethanolamine has been investigated kineticcally.

Experimental

Chloromethylated polystyrene (CMPS). The CMPS was prepared and purified by the procedures described in previous papers.[2-4] The chlorine contents and the molecular weights of the CMPS used in the present study are tabulated in Table 1.

Table 1. Chlorine content and molecular weight of CMPS

Code	Content of Cl %	Degree of chloromethylation	Molecular weight
SC-5	21.15	0.874	10.3×10^4
SC-7	19.53	0.782	
SC-8	22.11	0.931	9.2×10^4
SC-11	21.75	0.909	12.4×10^4

Aminated Chloromethylated Polystyrene (AMPS). Five grams of CMPS (SC-5) were dissolved in 200 ml of DMF, and to the solution we then added 300 ml of a DMF solution containing 60 g of diethanolamine. The reaction mixture thus obtained was kept at 50 °C for 2 days. After it was ascertained that the reaction had proceeded quantitatively, the reaction mixture was cooled to room temperature and was poured into water to precipitate the aminated polymer. The polymer, which was dried *in vacuo*, was easily soluble in DMF, but less soluble in dioxane, methyl ethyl ketone, and benzene. The polymer was dissolved in 25 ml of DMF, and a 45-ml portion of benzene was added to the solution. This solution was poured into 350 ml of ligroin to precipitate the polymer. After two reprecipitations, the polymer was dried *in vacuo* to give a yield of 4.6 g. Elementary analysis and acid-base titration were carried out with this dried sample. The nitrogen content of the sample was found to be 6.10%, and no chlorine was found. The content of amine combined with CMPS was found, by titration, to be 4.23 mmol/g. The value of the nitrogen content calculated from the degree of the amination on the basis of Eq. (1) and the value calculated from the titration data both agreed with that of elementary analysis, as is shown in Table 2.

Table 2. Nitrogen contents of AMPS

Elementary analysis %	Calculated from titration %	Calculated from conversion %
6.10	5.96	5.93

$$[\mathrm{N}\%] = \frac{14.01xy\times 100}{221.99xy+152.61x(1-y)+104.14(1-x)} \qquad (1)$$

In Eq. (1), x is the degree of the chloromethylation of polystyrene, and y is the degree of the amination of the chloromethyl group; $x=0.874$ and $y=1.00$ in this experiment. The figures in the denominators are molecular weights of *N,N*-bis(2-hydroxyethyl)-aminomethyl styrene, chloromethyl styrene, and styrene respectively.

Other Chemicals. The amines, the solvents, and the other liquid chemicals, 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 deionized, decarbonized water was used.

Kinetic Measurements. *Amination of CMPS and Benzyl Chloride*: The rate of the amination was measured as has been described in a previous paper.[4] The experimental conditions in the amination of CMPS are listed in Table 3. In Run 7, since the reaction mixture was emulsified during the reaction, it was distributed in test tubes dipped in a thermostat to avoid uneven sampling, as has been described in another previous paper.[1]

Quaternization of AMPS: AMPS (N content: 6.10%) was quaternized with mthyl iodide and bromoacetic acid in 50% aq. DMF in a vessel protected from light. The rates of the reactions were measured by the same procedures as those used for the amination. The experimental conditions are shown in Table 4.

Viscometric Measurements. In the amination of CMPS, the viscosity change in the reaction mixture was also checked for Runs 4, 6, 11, and 13 by the procedure described in a previous paper.[4]

Acid-base Titration of AMPS. A portion of AMPS (0.1185 g) was dissolved in 18 ml of DMF, and the solution was diluted to 50 ml by adding water. This solution was titrated first with 8 ml of 0.0989 M HCl; after the addition of 5 g of sodium chloride (about a 1.5 M concentration), the solution was back-titrated with 0.1008 M NaOH. The pH of the solution was measured with glass and calomel electrodes by means of a Beckman Model G pH meter. In the back-titration, 15.6 ml of DMF in all was added to avoid the precipitation of the polymer.

Results

Amination with Diethylamine in DMF. As has been described in a previous paper,[1] the amination of benzyl chloride could be expressed by Eq. (2), and the over-all kinetics of the amination of chloromethylated polystyrene (CMPS) in the presence of a large excess of diethylamine ($a\gg b$) could be expressed by Eq. (3):

$$kt = \frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(a-b)} \equiv \overline{kt} \qquad (2)$$

$$\beta = x/b = 1 - \frac{k_1-k_2}{2k_1-k_2}\mathrm{e}^{-2k_1at} - \frac{k_1}{2k_1-k_2}\mathrm{e}^{-k_2at} \qquad (3)$$

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

$$\overline{kt} = k_2t + C \qquad (5)$$

where a and b are the initial concentrations of an amine and the chloromethylgroup respectively, and where x is the concentration of chloride ions after time t; k_1 and k_2 are the rate constants of the elementary reactions which are independent of the neighboring groups and which are dependent on their steric effect respectively. C in Eq. (5) is a constant in a given system: $C=\ln[(1-$

Table 3. Conditions of amination of CMPS

Run	Amine[a]	Solvent	Temp.[b] °C	CMPS	a,[c] mol/l	b,[d] mol/l	a/b
1	A	DMF	10	SC-8	0.8315	0.0416	20.0
2	A	DMF	15	SC-8	0.8353	0.0417	20.0
3	A	DMF	20	SC-8	0.8289	0.0413	20.0
4	A	DMF	25	SC-8	0.8321	0.0416	20.0
5	A	DMF	30	SC-8	0.8319	0.0416	20.0
6	B	DMF	25	SC-8	0.8312	0.0416	20.0
7	C	dioxane	40	SC-11	0.8648	0.0439	19.7
8	C	DMF	10	SC-11	0.8628	0.0401	21.5
9	C	DMF	20	SC-11	0.8667	0.0411	21.1
10	C	DMF	30	SC-11	0.8671	0.0536	19.9
11	C	DMF	40	SC-11	0.8625	0.0413	20.9
12	C	DMSO	20	SC-7	0.7667	0.0382	20.1
13	C	DMSO	25	SC-7	0.7395	0.0367	20.1
14	C	DMSO	30	SC-7	0.7339	0.0367	20.0

a) A: diethylamine, B: di-*n*-butylamine, C: diethanolamine. b) Temp. was maintained constant within ±0.1°. c) a: Initial concentration of amine. d) b: Initial concentration of CMPS expressed in moles of chloromethyl group per liter of the solution.

Table 4. Conditions of quaternization of AMPS

Halide	Solvent	Temp.,[a] °C	a,[b] mol/l	b,[c] mol/l	a/b
Methyl iodide	50% aq. DMF	30	0.3797	0.0362	10.5
Bromoacetic acid	50% aq. DMF	30	0.2877	0.0228	12.6

a) Temp. was maintained constant within ±0.1 °C. b) a: Initial concentration of halide. c) b: Initial concentration of AMPS expressed in moles of amino group per liter of the solution.

$\chi/a)/(1-\chi/b)]-k_2(a-b)\tau$.1)

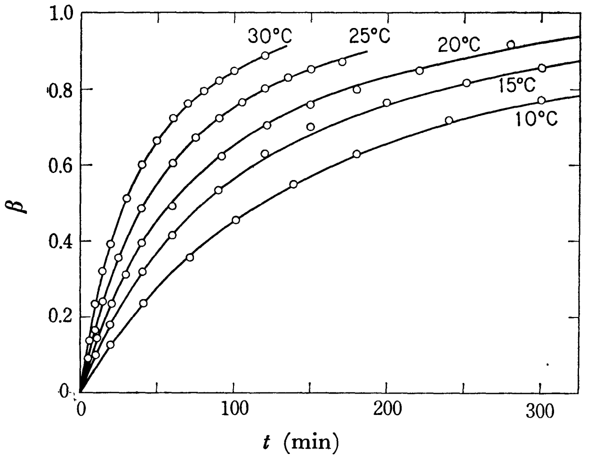

Fig. 1. Amination of CMPS with diethylamine in DMF.
——: calculated on the basis of Eq. (3).

The results of the amination of CMPS with diethylamine at different temperatures are shown in Fig. 1, where the solid lines are these calculated on the basis of Eq. (3). The observed values, represented by the white circles, substantially fall on the calculated lines. The rate constants of the amination of benzyl chloride and CMPS, as computed by Eqs. (2), (4), and (5), are listed in Table 5. The values of E_a, the activation energy, and A, the frequency factors, computed by the mean-squares method are also listed in Table 5.

It was shown in a previous paper4) that deceleration was observed during the amination of CMPS with di-*n*-butylamine in DMF and that the kinetics could be described by Eq. (3). In the present study, the rate of CMPS at 25 °C has been compared with that of benzyl chloride. The results were:

(Benzyl Chloride) $k_B=1.19\times10^{-2}$ l/mol min
(CMPS $k_1=1.26\times10^{-2}$, $k_2=3.98\times10^{-3}$ l/mol min
$k_2/k_1=0.31$, $k_1/k_B=1.06$

Amination with Diethanolamine in DMF and DMSO. Deceleration such as that described in the preceding section was also observed in the amination of CMPS with diethanolamine. The courses of the aminations in DMF and DMSO could be fully expressed on the basis of Eq. (3). The rate constants of CMPS are listed in Tables 6 and 7, along with the rate constants of benzyl chloride, k_B. In the table are also listed the values of E_a and A, which were computed by the least-squares method.

Amination of CMPS with Diethanolamine in Dioxane. The results of kinetic measurements in the amination of CMPS with diethanolamine in dioxane at 40 °C are shown in Fig. 2. The plot of β against t is represented by a sigmoid curve, which indicates the acceleration during the reaction. The plot of kt against t is nearly represented by two straight lines which intersect at

TABLE 5. THE AMINATION OF CMPS AND BENZYL CHLORIDE WITH DIETHYLAMINE IN DMF

Temp. °C	Rate const. ×10² l/mol·min				E_a kcal/mol	log A c)
	k_1 a)	k_2 a)	k_B b)			
5			0.457			
10	0.861	0.430	0.645	(k_1)	11.7±0.2	6.93±0.16
15	1.29	0.612	0.950			
20	1.75	0.861	1.36	(k_2)	12.2±0.2	7.05±0.12
25	2.38	1.24	1.93			
30	3.48	1.81	2.82	(k_B)	12.1±0.1	7.18±0.06
35			3.71			

a) k_1 and k_2: Rate constants of CMPS. b) k_B: Rate constants of benzyl chloride. c) A is expressed in l/mol·min.

TABLE 6. THE AMINATION OF CMPS AND BENZYL CHLORIDE WITH DIETHANOLAMINE IN DMF

Temp. °C	Rate const. ×10², l/mol·min				E_a kcal/mol	log A c)
	k_1 a)	k_2 a)	k_B b)			
10	0.285	0.210	0.331	(k_1)	12.8±0.3	7.33±0.18
20	0.659	0.429	0.724	(k_2)	12.8±0.1	7.15±0.13
30	1.36	0.900	1.52	(k_B)	12.8±0.1	7.38±0.04
40	2.50	1.83	2.90			

a) k_1 and k_2: Rate constants of CMPS. b) k_B: Rate constants of benzyl chloride. c) A is expressed by l/mol·min.

TABLE 7. THE AMINATION OF CMPS AND BENZYL CHLORIDE WITH DIETHANOLAMINE IN DMSO

Temp. °C	Rate const. ×10², l/mol·min				E_a kcal/mol	log A c)
	k_1 a)	k_2 a)	k_B b)			
20	3.25	2.58	3.92	(k_1)	11.7±0.1	7.27±0.09
25	4.58	3.67	5.46	(k_2)	12.0±0.1	7.35±0.06
30	6.33	5.10	7.66	(k_B)	11.7±0.1	7.35±0.08

a) k_1 and k_2: Rate constants of CMPS. b) k_B: Rate constants of benzyl chloride. c) A is expressed in l/mol·min.

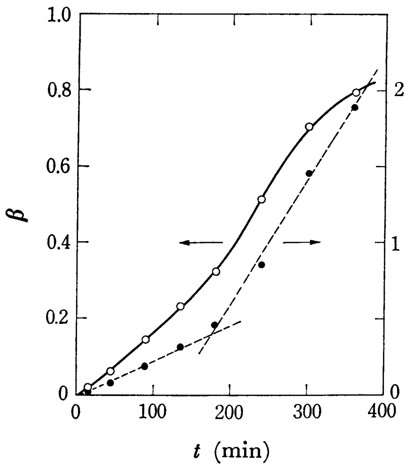

Fig. 2. Amination of CMPS with diethanolamine in dioxane at 40 °C.

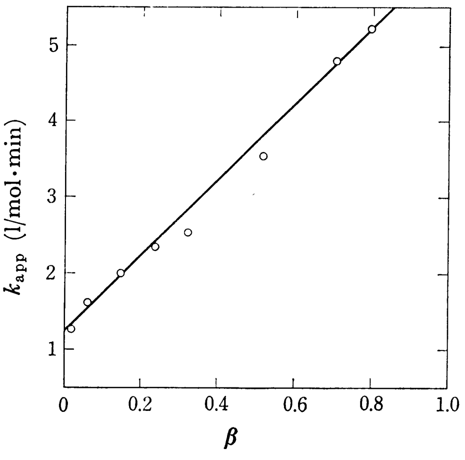

Fig. 3. Plot of k_{app} *vs.* β in the amination of CMPS with diethanolamine in dioxane at 40 °C.

$\beta\approx1/3$. The rate constant calculated on the basis of Eq. (2) is not constant, but increases with β. The plot of this apparent rate constant, k_{app}, against the β shown in Fig. 3 is represented by a straight line. Such kinetic behavior is analogous to that exhibited in the amination of CMPS with 2-aminobutanol in dioxane, and the line in Fig. 3 may be expressed by this equation:[3]

$$k_{app} = k_0(1+m\beta) \tag{6}$$
$$k_0 = 1.25\times10^{-3}$$
$$m = 4.0$$

Viscosity Change During the Amination of CMPS. The viscosity ratios $(H\equiv(\eta_{sp}/C_p)/(\eta_{sp}/C_p)_{\beta\to0})$[4] in the amination of CMPS in DMF and DMSO are plotted against β in Fig. 4. The *H* value decreases with β in the amination with alkyl amines, while it increases with β in the amination with aminoalcohols.

Acid-base Titration of Aminated Chloromethylated Polystyrene (AMPS). AMPS (N%=6.10), which was obtained by the amination of CMPS with diethanolamine, is analogous in its chemical structure to poly[bis-(2-hydroxyethyl)aminomethyl styrene] (N%=6.33). An aq. DMF solution of AMPS was titrated first with hydrochloric acid and then with a sodium hydroxide solution in the presence of 1.5 M NaCl. The titration curves are shown in Fig. 5, where β_i is the degree of ionization of the base and where α_i $(=1-\beta_i)$ is the degree of dissociation of the conjugated acid.

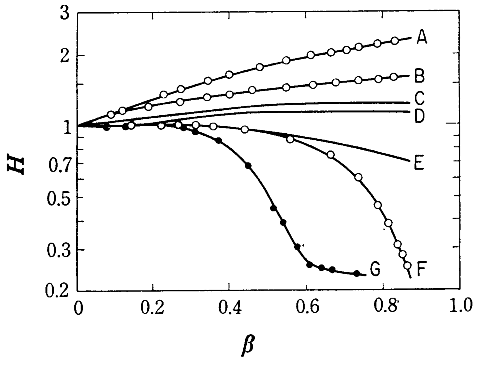

Fig. 4. Viscosity change of a reaction mixture in the amination of CMPS.
A: with diethanolamine in DMSO at 25 °C. B: with diethanolamine in DMF at 40 °C. C: with 2-aminobutanol in DMSO at 30 °C.[4] D: with 2-aminobutanol in DMF at 40 °C.[4] E: with *s*-butylamine in DMF at 50 °C.[1] F: with diethylamine in DMF at 25 °C. G: with di-*n*-butylamine in DMF at 25 °C.

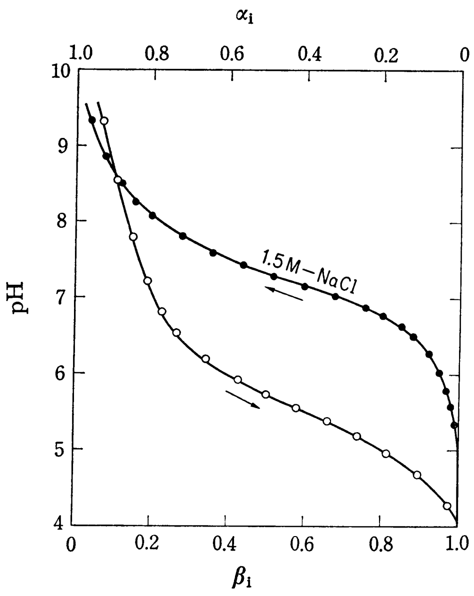

Fig. 5. Titration curve of AMPS.

It has been established that the titration data of some polyelectrolytes can be expressed by a modification of the Henderson-Hasselbach equation:[7]

$$\mathrm{pH} = \mathrm{p}K_a-n'[(1-\alpha_i)/\alpha_i] \tag{7}$$

where $\mathrm{p}K_a$ and n' are empirical constants. This relation is, in general, hard to apply to polymeric bases such as polyethyleneimine and polyvinylamine.[8] However, the titration data of AMPS fit Eq. (7); $\mathrm{p}K_a=5.76$ and $n'=1.25$ in the absence of salt, and $\mathrm{p}K_a=7.37$ and $n'=1.0$ in the presence of added salt. Accordingly, the $\mathrm{p}K_a$ value of 7.37 is considered to represent the intrinsic dissociation constant of AMPS ($\mathrm{p}K_0$), and this value is close to the dissociation constant of bis(2-hydroxypropyl)benzylamine ($\mathrm{p}K=7.5$) reported by Boivin.[9]

Quaterinization of AMPS. AMPS could be *N*-methylated easily and completely with methyl iodide in 50% aq. DMF. AMPS was unreactive to chloroacetic acid, while it was quantitatively *N*-carboxymethylated with bromoacetic acid. In both the quaternizations, the deceleration was marked beyond the half-quaternization point. The kinetics of the two reactions can be described by Eqs. (3), (4), and (5), where a is the initial concentration of methyl iodide or bromoacetic acid, b is that of the amine groups of AMPS, and x is the concentration of halogen ions after time t. The courses of these reactions are shown in Fig. 6, where the white circles indicate the observed values and where the solid lines indicate those calculated on the basis of Eq. (3). The course of the latter reaction could also be expressed by Eq. (3). The rate constants of these reactions are tabulated in Table 8.

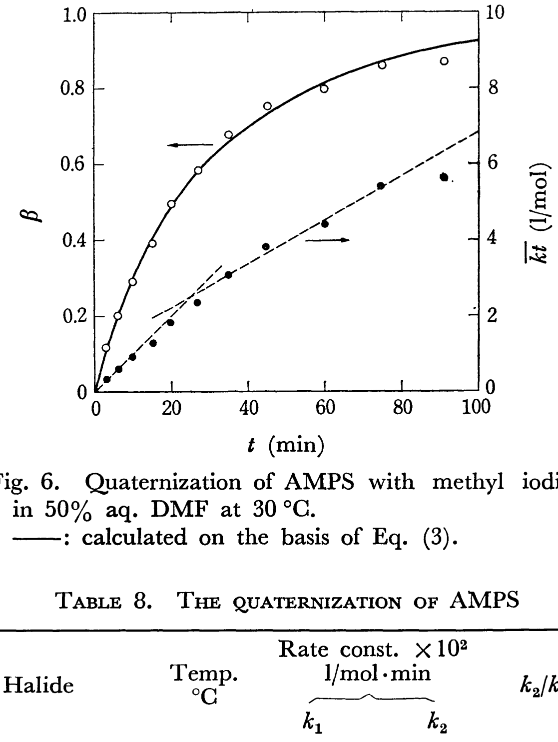

Fig. 6. Quaternization of AMPS with methyl iodide in 50% aq. DMF at 30 °C.
——: calculated on the basis of Eq. (3).

TABLE 8. THE QUATERNIZATION OF AMPS

Halide	Temp. °C	Rate const. $\times 10^2$ l/mol·min k_1	Rate const. $\times 10^2$ l/mol·min k_2	k_2/k_1
Methyl iodide	30	10.4	5.89	0.57
Bromoacetic acid	30	3.54	2.05	0.58

Discussion

Acceleration and Deceleration during the Amination of CMPS. We observed a stronger acceleration during the amination of CMPS with diethanolamine in dioxane than in amination with 2-aminobutanol.[3] On the other hand, deceleration was observed during the amination of CMPS with diethanolamine in DMF and DMSO, while the kinetics of the amination with 2-aminobutanol obeyed the ordinary second-order kinetics in both the solvents.[4] Comparing this kinetic behavior in the amination with aminoalcohols with that in the amination with the corresponding alkylamines, it was found that the amination with *s*-butylamine (2-aminobutane) conformed to the second-order rate equation in dioxane and DMF and that the amination with diethylamine was decelerated in both dioxane and DMF.[1] Therefore, the hydroxyl groups of the aminoalcohols are obviously involved in the acceleration phenomena in dioxane. It is reasonable to presume that the hydroxyl groups of the already-aminated neighbors form the hydrogen bond with the chlorine of the chloromethyl groups in the transition state of the amination and that the formation of this hydrogen bond is obstructed in dipolar aprotic solvents, such as DMF and DMSO.

The slope of the $\overline{kt}$ *vs.* t plot beyond $\beta \approx 1/3$, which is shown in Fig. 2, is considered to be a rate constant of the chloromethyl group under the accelerating effect of the neighboring groups (k_2);[3] it will be given by $\Delta\overline{kt}/\Delta t$ on the basis of Eq. (5); $k_2 = 8.25 \times 10^{-3}$ l/mol min, $k_2/k_0 = 6.6$ (40 °C).

Comparison between the Rates of CMPS and Benzyl Chloride. In the present study, a comparison of the intrinsic amination rate constant of CMPS (k_p) and the corresponding rate constant of benzyl chloride (k_B), showed that $k_p < k_B$ with diethanolamine ($k_1/k_B = 0.88$ (DMF), $k_1/k_B = 0.83$ (DMSO)), while $k_p > k_B$ with diethylamine ($k_1/k_B = 1.23$ (DMF)) and with di-*n*-butylamine ($k_1/k_B = 1.06$ (DMF)). Table 9 shows the activation parameters in the amination of CMPS and benzyl chloride with diethylamine and diethanolamine; $\Delta H^{\neq}$, the enthalpy of activation, $\Delta S^{\neq}$, the entropy of activation, and $\Delta G^{\neq}$, the free energy of activation, all of which have been calculated for 25 °C by means of

TABLE 9. THERMODYNAMIC QUANTITIES AT 25 °C IN THE AMINATION OF CMPS AND BENZYL CHLORIDE

Amine	Solvent	Chloride	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e. u.	$\Delta G^{\neq}$ kcal/mol
Diethyl	DMF	CMPS, k_1	11.2±0.2	−36.9±0.7	22.1
		k_2	11.6±0.2	−36.4±0.6	22.5
		Benzyl	11.5±0.1	−35.8±0.3	22.2
Diethanol	DMF	CMPS, k_1	12.2±0.3	−35.1±0.8	22.7
		k_2	12.2±0.1	−35.9±0.6	22.9
		Benzyl	12.2±0.1	−34.9±0.2	22.6
Diethanol	DMSO	CMPS, k_1	11.2±0.1	−35.4±0.4	21.7
		k_2	11.4±0.1	−35.0±0.4	21.8
		Benzyl	11.2±0.1	−35.0±0.4	21.6

the equations described in a previous paper.[4)]

Although k_p is generally almost the same as k_B, and although there are not many differences in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ between CMPS and benzyl chloride, some features in regard to these parameters may be deduced from the data obtained thus far. It was previously shown, in the amination with butylamine isomers and 2-aminobutanol in a dipolar aprotic solvent, that $k_p<k_B$; this was attributed to the $\Delta S^{\neq}$ value of CMPS being lower than that of benzyl chloride.[1)] In addition, it was shown that, in most cases, the $\Delta H^{\neq}$ value of CMPS was lower than that of benzyl chloride.[1,4,10)] In a dipolar aprotic solvent, the solvation of the transition state plays an important role in the determination of the amination rate, and it may be sterically obstructed by the neighboring groups of the polymer, resulting in the $\Delta S^{\neq}$ value for CMPS being lower than that for benzyl chloride. On the other hand, if such an energetic interaction as that due to the London dispersion force is operative between alkyl groups of the amine molecule and non-polar polymer segments at the transition state, it will lower the $\Delta H^{\neq}$ value for CMPS as compared with that for benzyl chloride.

In the amination with diethylamine, the fact shown in Table 9 that the $\Delta G^{\neq}$ of CMPS is a little lower than that of benzyl chloride ($k_p>k_B$) may be explained by the fact that the lower $\Delta H^{\neq}$ value surpasses the lower value of $\Delta S^{\neq}$. In the amination with diethanolamine with two hydroxyl groups, however, since the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are almost the same for CMPS and benzyl chloride, it is difficult to explain value of the $\Delta G^{\neq}$ of CMPS being little higher than that of benzylchloride ($k_p<k_B$) in terms of the differences in the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values.

Effect of Amine on the Amination Rate. The $\Delta G^{\neq}$ values in the amination with diethylamine are comparable to those with *n*-butylamine or isobutylamine,[1)] and there is little difference in the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values. These results may be explained by the face that the steric hindrance by the benzene ring to the alkyl group of the secondary amine in the transition state is not so large as the hindrance to that of *n*-butylamine or isobutylamine, and also by the fact that the basicity of the secondary amine is higher than that of the primary amines. On the other hand, the higher $\Delta G^{\neq}$ value with diethanolamine than that with diethylamine is due to the higher $\Delta H^{\neq}$ value; this may be ascribed to the inductive effect of the hydroxyl groups, as in the case of 2-aminobutanol.[1)]

Effect of the Solvent on the Amination Rate. The $\Delta G^{\neq}$ values in the amination with diethanolamine in DMSO are about 1 kcal/mol lower than the corresponding values in DMF. This is due merely to the difference in $\Delta H^{\neq}$, as was the case of the amination with 2-aminobutanol.[4)] Since both DMF and DMSO are dipolar aprotic solvents, the lower $\Delta H^{\neq}$ in DMSO is considered to be caused by the stronger solvation of the transition state in DMSO resulting from its stronger polarity.

Quaternization of AMPS. Charged groups are not formed on polymer molecules in the amination of DMPS with primary and secondary amines, because the hydrochloric acid produced by the reaction is transformed to amine, which is present in a large excess. The deceleration observed in the amination of CMPS is due to the steric hindrance of the neighboring groups. In the reaction of AMPS with methyl iodide and bromoacetic acid in 50% aq. DMF, however, the observed deceleration may be ascribed to the electrostatic interactions, because charged groups (quaternary ammonium groups) are formed on the polymer in these reactions. The assumption of the electrostatic effect is supported, by the acid-base titration data of AMPS, and also by the facts shown in Table 8, which indicates that the k_2/k_1 ratio is almost the same for two reactions with different quaternizing reagents. The facts that the deceleration is marked beyond $\beta \approx 1/2$ and that the over-all kinetics can be followed by Eq. (3) suggest that k_1 represents the intrinsic rate constant and k_2, the rate constant under the influence of two nearest-neighboring charged groups.

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