Amination of Chloromethylated Polystyrene with Amino Alcohols[1]

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The amination of chloromethylated polystyrene (CMPS) and benzyl chloride (BC) with amino alcohols was investigated kinetically in dioxane, N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). The amination rate was related mainly to the branching structure and partly to the pK of amino alcohols; ΔG^* and ΔH^* increased in the following order: 2-aminobutanol$<$1-amino-2-propanol$<$2-amino-1-butanol$<$2-amino-2-methyl-1-propanol$<$tris(hydroxymethyl)methanamine$<$triethanolamine. The rate was also related to the polarity of the solvent; ΔG^* and ΔH^* decreased in the following order: dioxane$>$DMF$>$DMSO. The difference in the amination rate between CMPS and BC is also discussed in terms of the activation parameters. The amination rate of the polymer partly containing quaternary ammonium groups (QCMPS) in DMSO was found to be greater than that of CMPS probably owing to the ion-dipole interaction.

The amination kinetics of chloromethylated polystyrene conforms to a second-order rate equation in many cases. However, there are cases where the rate constant increases or decreases during the course of the amination. The reaction of CMPS with 2-amino-1-butanol (AB), for example, followed second-order kinetics in N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).[2] However, it exhibited self-acceleration in dioxane.[3] The reactions of CMPS with various amino alcohols containing a primary amino group in the above-mentioned solvents have been investigated in the present study and the same kinetic behavior as that in the reaction with AB is found. Dragan et al.[4] found a self-accelerating effect in the amination of CMPS with such N-(hydroxyalkyl) tertiary amines as 1-dimethylamino-3-propanol and 3-dimethylamino-1-propanol in dioxane and N,N-dimethylacetamide. The same kind of acceleration was also observed by Luca et al.[5] in the amination of CMPS with N,N-dimethyl-2-hydroxyethylamine and N,N-bis-(2-hydroxyethyl)methylamine in DMF. Kawabe[1] noted an example of self-deceleration in the reaction of CMPS with triethylamine (TEA) in DMSO, although the usual second-order kinetics was observed in the reaction in DMF. The reaction of CMPS with triethanolamine (TEOA) in the present study, however, has been shown to exhibit a different kinetic behavior from that with TEA; it follows the second-order kinetics in DMSO and exhibits the self-acceleration in DMF. The amination of benzyl chloride (BC), a low molecular weight species having a chloromethyl group, follows second-order kinetics in all cases. The author has determined the activation parameters of the aminations of CMPS and BC with a view to discussing the dependence of the reaction rate on the species of the amino alcohols, the solvents, and the chlorides (CMPS or BC). The acid-base equilibria of the polyelectrolytes produced by the reactions of CMPS with the amino alcohols have also been investigated.

Experimental

Materials. The chloromethylated polystyrene (CMPS) was prepared and purified as previously reported;[3,6] chlorine contents of the samples: 22.38—22.89%, degrees of chloromethylation: 0.979—0.984, and mol wts.: 9.65—11.43 × 10⁴.

The (R)-2-amino-1-butanol was prepared and purified as previously reported.[3] The triethanolamine used was of analtical grade. The other amino alcohols, triethylamine (TEA), and benzyl chloride (BC) were of reagent grade. Except for tris(hydroxymethyl)methanamine (TRIS), the amino alcohols, TEA, BC, and the solvents were distilled before use and proved to be pure by their refractive indices.

Kinetic Measurements. In the reactions of CMPS and BC with the amino alcohols in dioxane, the initial concentration of chloromethyl groups (b) was 0.040 mol dm⁻³, while that of the amino alcohol (a) was 0.8000 mol dm⁻³. It was not possible to examine the reactions with TRIS in dioxane and DMF because of its insolubility. The author also examined the reactions in DMSO of QCMPS, the chloromethylated polystyrene with half of its chloromethyl groups being converted to quaternary ammonium groups. In practice, CMPS ($b=0.040$ mol dm⁻³) was first treated with TEA ($a=0.020$ mol dm⁻³) in DMSO at 318 K until 48% of chloromethyl group was converted to quaternary ammonium groups, and QCMPS thus obtained was then aminated with the amino alcohols in DMSO at 318 K on the conditions that the initial concentrations of the remaining chloromethyl groups and amino alcohol were 0.017 and 0.170 mol dm⁻³ respectively. In all the kinetic measurements, temperature was kept constant within ±0.1 K and aliquots of a reaction mixture were removed at appropriate intervals, poured into dilute nitric acid, and titrated potentiometrically with a standard silver nitrated solution (1/10 mol dm⁻³) to determine the concentration of chloride ions produced by the reaction.

Purification of the Polyelectrolytes Produced by the Reactions of CMPS and the Amino Alcohols. The reaction of CMPS (degree of chloromethylation: 0.979) with amino alcohols was carried out in DMSO until the conversion rose to 99%, and each reaction mixture was dialysed in dilute hydrochloric acid (pH 2.0) and lypophilized. Deionized water was used throughout. The polyelectrolytes produced by the reactions of QCMPS with the amino alcohols were also purified by the same procedure.

Acid-Base Titrations of the Amino Alcohols and the Polyelectrolytes. An aqueous solution containing 0.2—0.5 mmol of an amino alcohol was titrated with a standard hydrochloric acid (0.1006 mol dm⁻³) to determine the pK_a value of the amino alcohol on the basis of the pH value at the midpoint of the titration curve. The acid-base titrations of the polyelectrolytes were carried out with and without the addition of salt. A 50 ml acidic solution of each purified polyelectrolyte, containing about 0.15 mmol of amino alcohol residues and about 0.30 mmol of hydrogen chloride, was titrated with a standard sodium hydroxide solution (0.1007 mol dm⁻³). To aother

solution containing the same amount of polyelectrolyte and hydrogen chloride (50 ml) 0.1 mol of sodium chloride and 20 ml of DMSO were added; the mixture was diluted with water to 100 ml and was also titrated with the standard sodium hydroxide solution. The addition of DMSO was intended to avoid the deposition of the polymer in a higher pH range. In the foregoing process, deionized and decarbonized water was used, and nitrogen gas was bubbled through the solution during the titration.

Results and Discussion

The reactions of chloromethylated polystyrene (CMPS) and benzyl chloride (BC) with amino alcohols such as 2-aminoethanol (AE), 1-amino-2-propanol (AP), 2-amino-2-methyl-1-propanol (AMP), tris(hydroxymethyl)methanamine (TRIS), and triethanolamine (TEOA) were investigated in dioxane, N,N-dimethylformamide (DMF), and dimethyl sufoxide (DMSO).

Reactions in Dioxane.   The reactions of BC with AE and AP in dioxane stopped at low fractional conversions. Since the maximum fractional conversion in the reaction with AE was only 0.1, it was difficult to determine the reaction rate exactly. It was proved, however, that the reaction rates of BC with AP and AMP in dioxane conformed to the following second-order rate equation:

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

where a and b are initial concentrations of an amine and the chloromethyl group respectively, while x is the concentration of the chloride ions produced at time t, and $\alpha=x/a$ and $\beta=x/b$. On the other hand, the reactions of CMPS with AE, AP, and AMP, which proceeded nearly to completion, were found to conform to Eq. 2:

$$k = k_0(1+m\beta), \qquad (1)$$

where k is the apparent rate constant obtained by Eq. 1, and where k_0 and m are constants. Kawabe and Yanagita[3] found similar self-acceleration with respect to the reaction of CMPS with 2-amino-1-butanol (AB) in dioxane, and the author attributed such acceleration to the intramolecular hydrogen bonding between the hydroxyl group of the already-aminated neighbor and the chlorine of the chloromethyl group in the transition state.[1] The observed value of m were 2.0 for AE, 1.9 for AP and 0.9 for AMP, whereas the m value for AB was 1.2. The m value decreases in the following order;

$AE>AP>AB>AMP$, and this order conforms to the branching structures of the amino alcohols. Since the m value is a measure of the acceleration, the foregoing suggests that the more complex the branching structure, the more the formation of the hydrogen bond is sterically obstructed.

The k values of BC and the k_0 values of CMPS are listed in Table 1. No further kinetical analysis was performed for the reactions of CMPS with AE and AP because of the deposition of the polymer beyond $\beta=0.5$. The process of the reaction of CMPS with AMP which proceeded in a homogeneous system was found to be represented by Eq. 3:

$$\beta = 1 - A'\exp(-3k_1at) - B'\exp(-k_2at), \qquad (3)$$

where $A'=(k_1-k_2)/(3k_1-k_2)$ and $B'=2k_1/(3k_1-k_2)$. The author[1] found the reaction of CTPS with AB in dioxane to follow closely the same equation. The exact values of k_1 and k_2 are determined by correcting the approximate values of k_1 and k_2 obtained as slopes of the plot of kt against t, which is represented approximately by two lines intersecting at the point corresponding to $\beta=1/3$; the correction of the k_1 and k_2 values was made by means of the repeated computation of the equations:[1]

$$k_2t = -\ln X'/a \equiv \overline{k_2t}$$
$$X' \equiv [(1-\beta)-A'\exp(-3k_1at)]/B' \qquad (4)$$
$$k_1t = -\ln Y'/3a \equiv \overline{k_1t}$$
$$Y' \equiv [(1-\beta)-B'\exp(-k_2at)]/A'. \qquad (5)$$

The observed β values of the reaction of CMPS with AMP fall exactly on the line computed on the basis of Eq. 3 as shown in Fig. 1. This suggests that the self-acceleration in the reaction of CMPS with AMP can be explained by the same mechanism as in the case of the reaction with AB. Table 1 indicates that the k_1 value agrees with the k_0 value (for AMP) with the k_0 values being equal to the k values of BC (for AP and AMP). In Table 1 are also listed the activation energies (E_a) and the frequency factors (A) which are computed by means of the least-squares method on the basis of the equation:

$$\ln k = \ln A - E_a/RT. \qquad (6)$$

The k_0 value decreases and the E_a value increases in the following order: AE, AP, (AB),[1] AMP. Arrhenius plots for the amination of CMPS are shown in Fig. 2, where dotted lines are calculated in accordance with Eq. 6.

TABLE 1. AMINATION IN DIOXANE

| Amine | Chloride | $k\times10^5/dm^3\;mol^{-1}\;s^{-1}$ | | | $\dfrac{E_a}{kJ\;mol^{-1}}$ | $\log A^{a)}$ |
		318.2 K	333.2 K	348.2 K		
AE	CMPS, k_0	5.08	12.1	28.2	52.6±0.7	4.336±0.107
AP	BC	3.27	9.17	20.3	56.2±2.0	4.752±0.275
	CMPS, k_0	3.70	8.42	22.2	54.9±2.6	4.558±0.409
AMP	BC	0.408[b)]	1.35	4.38	61.0±3.0	4.760±0.474
	CMPS, k_0	0.612	1.60	4.23	59.3±1.2	4.522±0.181
	k_1	0.605	1.54	4.27	59.9±2.0	4.602±0.307
	k_2	1.65	3.60	9.92	55.0±3.6	4.225±0.560

a) A is expressed by $dm^3\;mol^{-1}\;s^{-1}$.   b) The k value at 313.2 K.
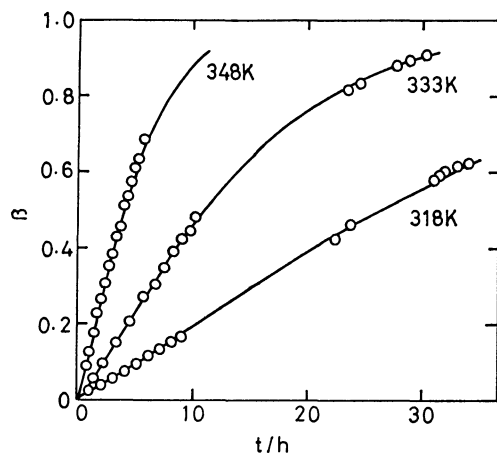
Fig. 1. Amination of CMPS with 2-amino-2-methyl-1-propanol in dioxane.
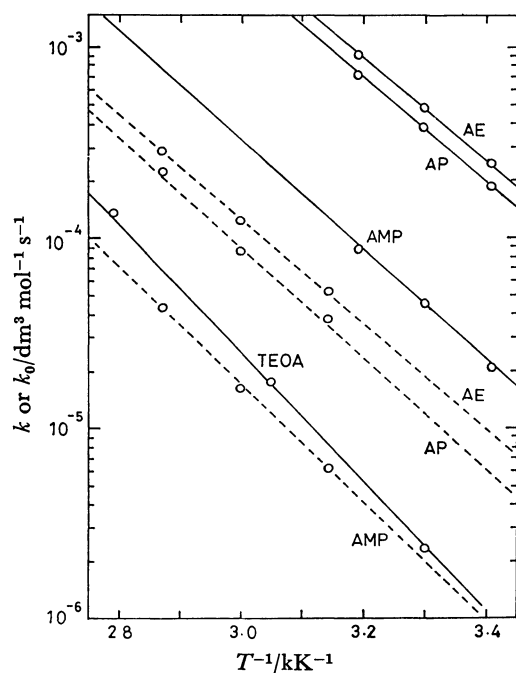——: Calculated values, ○: observed values.

Fig. 2. Arrhenius plots for the aminations of CMPS in dioxane and DMF.
○: Observed values, ----: calculated values in dioxane, ——: calculated values in DMF.

Reactions in DMF and DMSO. The reactions of CMPS, with AE, AP, AMP, and TRIS in DMF and DMSO all comformed to the second-order rate equation, Eq. 1, as in the case of BC. The values of the rate constant (k), E_a and A are tabulated in Tables 2 and 3. Arrhenius plots for the amination of CMPS are shown in Figs. 2 and 3, where solid lines are calculated in accordance with Eq. 6.
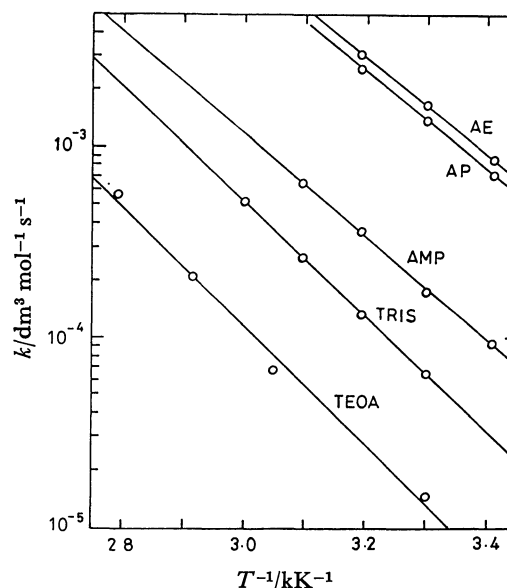

Fig. 3. Arrhenius plots for the amination of CMPS in DMSO.
○: Observed values, ——: calculated values.

The reactions of BC with TEOA in DMF and DMSO and that of CMPS with TEOA in DMSO, all of which proceeded in a homogeneous system, conformed to Eq. 1. The reaction of CMPS with TEOA in DMF exhibited the self-acceleration represented in the form of Eq. 2 up to $\beta=0.5$ with the m value of 0.8. In the process, deposition of the polymer was observed with the progress of the reaction due to cross-linking as reported by Luca *et al.*[7] and Drǎgan *et al.*[8] The values of k or k_0, E_a, and A are listed in Table 4. Arrhenius plots for the amination of CMPS are shown in Figs. 2 and 3.

The reaction of CMPS with triethylamine (TEA) was found by the author to follow second-order kinetics in DMF and self-decelerate in DMSO.[1] The difference

TABLE 2. AMINATION IN DMF

Amine	Chloride	$k \times 10^4/\mathrm{dm^3\ mol^{-1}\ s^{-1}}$				$\dfrac{E_a}{\mathrm{kJ\ mol^{-1}}}$	$\log A^{a)}$
		293.2 K	303.2 K	313.2 K	323.2 K		
AE	BC	2.53	4.87	9.77		51.5±1.3	5.567±0.217
	CMPS	2.42	4.80	9.05		50.4±0.1	5.363±0.021
AP	BC		4.33	8.43	16.1	54.3±0.5	5.842±0.088
	CMPS	1.82	3.78	7.12		52.1±0.8	5.552±0.139
AMP	BC	0.300	0.635	1.33		56.7±0.5	5.573±0.085
	CMPS	0.205	0.445	0.867		55.0±0.9	5.124±0.150

a) A is expressed by $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

TABLE 3. AMINATION IN DMSO

Amine	Chloride	$k \times 10^4/dm^3$ mol^{-1}s^{-1}					$\dfrac{E_a}{kJ\ mol^{-1}}$	log $A^{a)}$
		293.2 K	303.2 K	313.2 K	323.2 K	333.2 K		
AE	BC	10.9	21.5	40.2			49.7±0.1	5.898±0.024
	CMPS	8.63	16.6	30.8			48.6±0.1	5.592±0.008
AP	BC	9.85	19.7	37.2			50.7±0.2	6.025±0.027
	CMPS	7.07	13.7	25.7			49.2±0.1	5.619±0.020
AMP	BC	1.42	2.98	5.68			53.0±0.8	5.606±0.134
	CMPS	0.943	1.75	3.62	6.50		51.3±1.0	5.106±0.170
TRIS	BC	0.718	1.51	2.12	5.82		54.6±0.5	5.587±0.084
	CMPS		0.645	1.32	2.63	5.20	58.4±0.5	5.865±0.079

a) A is expressed by dm^3 mol^{-1} s^{-1}.

TABLE 4. AMINATION WITH TEOA IN DMF AND DMSO

Solvent	Chloride	$k \times 10^5/dm^3$ mol^{-1}s^{-1}						$\dfrac{E_a}{kJ\ mol^{-1}}$	log $A^{a)}$
		303.2 K	328.2 K	343.2 K	358.2 K	373.2 K	388.2 K		
DMF	BC	0.208	1.24		9.35		54.8	64.3±0.9	5.361±0.145
	CMPS, k_0	0.230	1.77		13.6	35.2	59.8	65.3±1.1	5.625±0.172
DMSO	BC	1.40	7.47	19.5	45.0			57.2±1.0	4.984±0.161
	CMPS	1.48	6.62	21.2	57.3			60.0±2.6	5.454±0.414

a) A is expressed by dm^3 mol^{-1} s^{-1}.

in kinetic behavior between TEOA and TEA, which are both tertiary amines, may be due to the presence of hydroxyl groups in TEOA. The self-acceleration in the reactions of CMPS with amino alcohols in dioxane may be attributed to the formation of the intramolecular hydrogen bond between the hydroxyl group of the already aminated neighbor and the chlorine of the chloromethyl group at the transition state. The formation of the bond does not take place in DMF and DMSO which are much more polar solvents than dioxane. This does not preclude the possibility of the bond formation in DMF in the case of TEOA with three hydroxyl groups. The author suggested that the deceleration during the reaction of CMPS with TEA in DMSO can be ascribed to the electrostatic effect of the quaternary ammonium groups formed in the polymer.[1] In the case of TEOA, pK_a of the quaternary ammonium groups is made to decrease by the hydroxyl groups as described later, so that their electrostatic effect must be insufficient to cause the deceleration.

Reactions of QCMPS in DMSO. The treatment of CMPS with a limited amount of TEOA (equivalent to half the chloromethyl groups) in DMSO yielded the polymer composed of 48 mol% quaternary ammonium groups and 52 mol% chloromethyl groups (QCMPS). QCMPS thus obtained was made to react with the amino alcohols in DMSO at 318 K. The reaction proceeded to completion (β=0.99) in conformity with Eq. 1. The reaction rate constants of QCMPS are compared with those of CMPS in Table 5, which indicates that k of QCMPS (k_{QCMPS}) is two or three times as large as k of CMPS (k_{CMPS}). This may be because the positive charges of the quaternary ammonium groups in QCMPS attract amino alcohol molecules by an ion-dipole interaction thereby increasing the local concentration of amino alcohol and hence increasing

TABLE 5. COMPARISON OF AMINATION RATE CONSTANTS, k, IN DMSO AT 318.2 K BETWEEN QCMPS AND CMPS

Amine	$k \times 10^4/dm^3$ mol^{-1}s^{-1}		$\dfrac{k_{QCMPS}}{k_{CMPS}}$
	QCMPS	CMPS$^{a)}$	
AE	74.0	41.3	1.8
AP	66.8	34.5	1.9
AB	18.7	9.25$^{b)}$	2.0
AMP	9.20	4.93	1.9
TRIS	5.53	1.87	3.0

a) The k values at 318.2 K computed on the basis of the equation $k=A\exp(-E_a/RT)$, by the use of the E_a and A values given in Table 3. b) E_a=51.08 kJ mol^{-1} and log A=5.350.[2]

the reaction rate.

Activation Parameters. The activation parameters, ΔH^*, ΔS^*, and ΔG^*, of the reactions of CMPS and BC with the amino alcohols are summarized in Tables 6—8. The difference in ΔG^* between CMPS and BC is generally small. In each solvent, the magnitude of ΔG^* of CMPS or BC depends on the species of amino alcohols, increasing in the following order:

AE < AP < AB < AMP < TRIS < TEOA.

This order of ΔG^* in each solvent corresponds to the order of ΔH^*; the difference in ΔG^* among the amino alcohols is mainly ascribed to the difference in ΔH^*, since the difference in ΔS^* is slight. It seems that the difference in ΔG^* or ΔH^* is largely due to the structural differences of the amino alcohols in question. Since the pK_a of the amino alcohols composed of monohydric alcohol (AE, PA, AB, and AMP) are similar to each other (refer to the pK_a values in Table 10), the difference in ΔG^* among the amino alcohols is ascribed to the difference in their structures. That is to say, the differ-

Table. 6 Activation parameters of the amination in dioxane at 298.2 K

Amine	Chloride	ΔH^{*} kJ mol^{-1}	ΔS^{*} J K^{-1}mol^{-1}	ΔG^{*} kJ mol^{-1}
AE	CMPS, k_0	50.1±0.7	−170±2	100.9
AP	BC	53.7±2.0	−162±5	102.1
	CMPS, k_0	52.4±2.6	−166±8	101.9
AB[a]	BC	53.5±0.4	−169±1	103.9
	CMPS, k_0	54.4±0.3	−168±1	104.5
AMP	BC	58.5±3.0	−162±9	106.8
	CMPS, k_0	56.9±1.2	−167±3	106.6
	k_1	57.4±2.0	−165±6	106.7
	k_2	52.5±3.6	−172±11	103.9

a) The values calculated on the basis of the data in Ref. 3.

Table 7. Activation parameters of the amination in DMF at 298.2 K

Amine	Chloride	ΔH^{*} kJ mol^{-1}	ΔS^{*} J K^{-1}mol^{-1}	ΔG^{*} kJ mol^{-1}
AE	BC	49.0±1.3	−147±4	92.7
	CMPS	47.9±0.1	−151±0	92.8
AP	BC	51.0±0.5	−141±2	93.1
	CMPS	49.7±0.8	−147±3	93.5
AB[a]	BC	53.4±0.2	−144±1	96.4
	CMuS	52.2±1.0	−150±3	96.8
AMP	BC	54.2±0.5	−147±2	97.9
	CMPS	52.6±0.9	−155±3	98.8
TEOA	BC	61.8±0.9	−151±3	106.7
	CMPS, k_0	62.8±1.1	−146±3	106.3

a) The values calculated on the basis of the data in Ref. 2.

Table 8. Activation parameters of the amination in DMSO at 298.2 K

Amine	Chloride	ΔH^{*} kJ mol^{-1}	ΔS^{*} J K^{-1}mol^{-1}	ΔG^{*} kJ mol^{-1}
AE	BC	47.3±0.1	−140±1	89.1
	CMPS	46.1±0.0	−146±0	89.7
AP	BC	48.2±0.2	−138±1	89.3
	CMPS	46.8±0.1	−146±0	90.2
AB[a]	BC	50.0±0.6	−144±2	92.9
	CMPS	48.6±0.7	−151±2	93.6
AMP	BC	50.6±0.8	−146±3	94.1
	CMPS	48.9±1.0	−156±3	95.2
TRIS	BC	52.2±0.5	−146±2	95.8
	CMPS	55.9±0.5	−141±2	98.0
TEOA	BC	54.7±1.0	−158±3	101.8
	CMPS	57.5±2.6	−149±8	101.9

a) The values calculated on the basis of the data in Ref. 2.

ence in the branching structure of the hydroxyalkyl group may produce the difference in the steric hindrance of the benzene ring to the group in the transition state. Kawabe and Yanagita[9] reported on this kind of structural effect on ΔG^{*} in regard to the reactions of CMPS and BC with butylamine isomers in DMF; ΔG^{*} increases in the following order: butylamine< isobutylamine<s-butylamine<t-butylamine. The higher ΔG^{*} values for TRIS and TEOA may be ascribed

not only to their increased steric hindrance but also to their decreased basicity, as indicated by the lower pK_a values (refer to the pK_a values in Table 10). Both ΔH^{*} and ΔS^{*} values of CMPS are lower than those of BC for the amino alcohols composed of a monohydric alcohol, while the ΔH^{*} and ΔS^{*} values of CMPS are higher than those of BC for the amino alcohols with three hydroxyl groups, TRIS and TEQA.

Review of Tables 6—8 with respect to the solvent effect on the activation parameters reveals that for each amino alcohols examined, ΔG^{*} is higher in dioxane than in DMF due to higher ΔH^{*} and lower ΔS^{*} in the former. The fact that ΔG^{*} is higher in DMF than in DMSO is mainly due to the higher ΔH^{*} in the former. The author reported a similar solvent effect for primary alkylamines such as butylamines[9,10] and for amino alcohols such as AB[2] and diethanolamine.[11]

It is to be noted that ΔG^{*} is a linear function of the electrostatic factor of the solvent, EF, for the amination of CMPS and BC with AE, AP, AB, and AMP, and the slopes of the lines range (−0.52)—(−0.61); EF is the product of dielectric constant, ε, and dipole moment, μ. It takes on values of 1 for dioxane, 140 for DMF, and 209 for DMSO.[12] The plots of ΔG^{*} against the Hildebrand solubility parameter, δ, or against δ^2, are also approximately linear; the δ values were calculated on the basis of the equation, $\delta=[(\Delta H^{v}-RT)\rho/M]^{1/2}$, where ΔH^{v} is the heat of vaporization of a solvent with molecular weight M and density ρ, taken to be 40.3 for dioxane, 49.3 for DMF and 54.4 kJ$^{1/2}$ dm$^{-3/2}$ for DMSO at T=298.2 K.[13] However, the plot of ΔG^{*} against $1/\varepsilon$ or $(\varepsilon-1)/(2\varepsilon+1)$ is not linear. These results, in addition to the dependence of the change in ΔG^{*} on the change in ΔH^{*} and ΔS^{*} mentioned above, suggest that the solute-solvent interactions, notably the solvation of the activated complex, are controlling factor of the rate of the amination of CMPS or BC.

Comparison of the activation parameters of CMPS with those of BC in Tables 6—8 shows the polymer effects described below, where the difference in the activation parameters (ΔX^{*}: ΔH^{*}, ΔS^{*}, ΔG^{*}) between CMPS and BC is represented by $\delta\Delta X^{*}(= \Delta X_{CMPS}-\Delta X_{BC})$:

(1) $\delta\Delta H^{*}$ are negative for the reactions with the amino alcohols composed of a monohydric alcohol (AE, AP, AB, and AMP) in dioxane, DMF and DMSO ($-\delta\Delta H^{*}=1$—2 kJ). This is also the case with the reactions with primary, secondary, and tertiary alkylamines such as butylamines,[9,10] diethylamine,[11] and TEA.[1] Negative $\delta\Delta H^{*}$ values may due to some energetic interactions between the polymer skeleton and the alkyl or hydroxyalkyl group of the amine or amino alcohol molecule at the transition state.

(2) The reactions with the amino alcohols and alkylamines described in paragraph (1) above all exhibit negative values of $\delta\Delta S^{*}$ in DMF and DMSO ($-T\delta\Delta S^{*}=1$—3 kJ). In DMF and DMSO, the solvation of the activated complex is an important factor in determining the amination rate of CMPS or BC, and this solvation works to decrease ΔG^{*} in DMF and DMSO. The negative value of $\delta\Delta S^{*}$ in DMF and

DMSO appears to have resulted from the steric hindrance to the solvation in the polymer. This is evident from the results of the author's study[10,14] on the reactions with AB and the butylamines, isobutylamine and s-butylamine, in DMF-dioxane binary system, which showed that $T\Delta S^{*solv}$ (ΔS^{*solv}: the entropy of the solvation of the activated complex) of CMPS was lower some 2 kJ than that of BC. The $\delta\Delta G^*$ values of all these reactions in DMF and DMSO are slightly positive, since the $T\delta\Delta S^*$ values are lower than the $\delta\Delta H^*$ values. On the other hand, the $\delta\Delta G^*$ are zero or otherwise slightly on the negative side in dioxane, since its solvation effect is much smaller than that of DMF or DMSO.

(3) The reactions with TEOA and TRIS in DMSO and the one with TEOA in DMF are characterized by the positive values of both $\delta\Delta H^*$ and $\delta\Delta S^*$; the magnitudes of $\delta\Delta H^*$ and $\delta\Delta S^*$ in DMSO are greater than those in DMF. Both amino alcohols contain three hydroxyl groups and it is expected that they are strongly solvated in DMF and DMSO. Considering that both ΔH^* and ΔS^* of CMPS are higher than the respective values of BC, it is quite reasonable to assume that the desolvation is required for the activated complex to form in the polymer.

Elementary Analysis of the Polyelectrolytes. The polymers obtained by the reaction of CMPS with the amino alcohols (AMPS) were dialysed in diluted hydrochloric acid and lypophylized. The composition of AMPS is represented by:

$$-(CH-CH_2)_x-(CH-CH_2)_y-(CH-CH_2)_z-$$

CH₂   CH₂

NHR·HCl   Cl
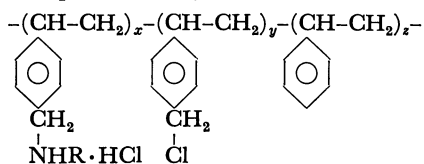
where –NHR represents the amino alcohol residue composed of secondary amino group and the residue is assumed to form monohydrochloride. The reaction of CMPS with TEOA produces the quaternary ammonium chloride residue ($-NR_3Cl$). The mole fractions, x, y, and z, were determined by the following equations:

$$
\begin{aligned}
x &= r_c r_a \\
y &= r_c(1-r_a) \\
z &= 1 - r_c
\end{aligned}
\Biggr\} \tag{7}
$$

where r_c is a fractional conversion in the chloromethylation of polystyrene and r_a that in the amination of CMPS. The mole fractions were $x=0.97, y=0.01$, and $z=0.02$ for all the AMPS polymers shown in Table 9, in which the data of elementary analysis are listed.

The best agreement of the found and calculated values in Table 9 is shown for the reaction product from TEOA. The agreement is fairly good for the other AMPS polymers, though the found nitrogen content is a little lower than the calculated one for the AMPS polymers from EA and PA. The result suggests that the reaction of CMPS with the amino alcohols scarcely induce such a side reaction as an intramolecular reaction of the chloromethyl groups with the neighboring amino alcohol residues in the polymer.

Acid-Base Equilibria of the Polyelectrolytes. A 50 ml acidic solution of AMPS containing about 0.15 mmol

TABLE. 9 ELEMENTARY ANALYSIS OF THE POLYELECTROLYTES PRODUCED BY THE AMINATION OF CMPS[a,b]

Amine		C(%)	H(%)	N(%)	Cl(%)	O(%)
AE	Found	61.88	6.95	5.40	19.61	6.16
	Calcd	62.21	7.54	6.43	16.47	7.35
AP	Found	64.71	7.43	5.04	17.05	5.76
	Calcd	63.62	7.96	6.05	15.47	6.91
AB	Found	67.91	7.95	5.43	12.50	6.21
	Calcd	64.89	8.31	5.69	14.60	6.50
AMP	Found	66.05	7.22	5.63	14.68	6.43
	Calcd	64.88	8.33	5.74	14.58	6.52
TRIS	Found	61.81	7.06	4.52	11.15	15.47
	Calcd	57.32	7.37	5.08	12.85	17.39
TEOA	Found	60.87	7.60	4.43	11.91	15.18
	Calcd	60.02	8.00	4.57	11.74	15.67

a) The found values are the ones corrected for water contents. b) The calculated values are the ones calculated on the basis of the fractional conversions by means of Eq. 7.

amino alcohol residues was titrated with a standard sodium hydroxide solution ($1/10$ mol dm^{-3}). The titration curves of the AMPS polymers containing AB, AMP, TRIS, and TEOA residues are shown in Fig. 4. The titration curve of the AMPS polymer containing AB residues in the absence of salt gives an inflection point at a higher pH range, and another inflection point is observed in a lower pH range in the presence of salt (Fig. 4A). The acid-base equilibria of the AB residues are represented by the titration curves in a region between the two inflection points. Similar titration curves were obtained for the AMPS polymers
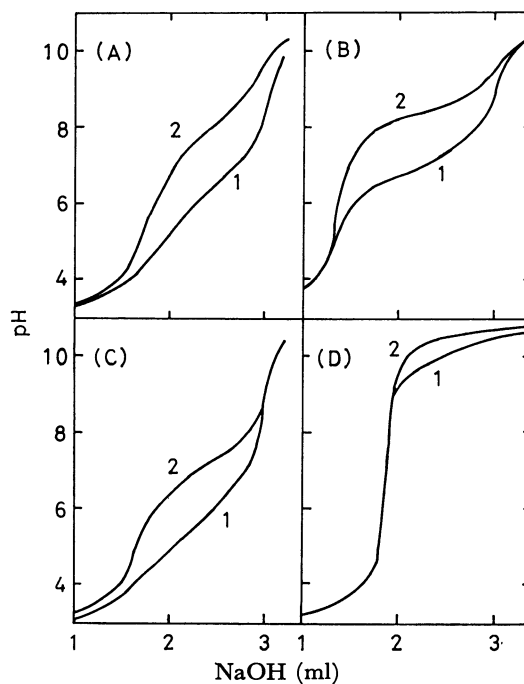

Fig. 4. Titration curves of the polyelectrolytes (AMPS) produced by the amination of CMPS with (A) AB, (B) AMP, (C) TRIS, and (D) TEOA.
Curve 1: In the absence of salt, Curve 2: in the presence of NaCl (1 mol dm^{-3}).

prepared from AE and AP. Since the pK_a of AMP residue is higher than that of AB residue, the titration curve in the absence of salt in Fig. 4B has two inflection points. In contrast, the curve in the presence of salt in Fig. 4C has two inflection points due to the fact that the pK_a of TRIS residue is lower than that of the AB residue. On the other hand, the inflection point does not appear in Fig. 4D in a higher pH range, as expected from the fact that TEOA produces a strong basic quaternary ammonium residue.

The acid-base equilibria of these AMPS polymers, except for the one from TEOA, can be described by the modified Henderson-Hasselbach equation:

$$pH = pK_m - n'(1-\alpha_i)/\alpha_i, \qquad (8)$$

where α_i is the degree of dissociation of the conjugated acid of the amino alcohol residue, n' is a constant, and pK_m is the pK_a value at $\alpha_i=0.5$. The results are summarized in Table 10, where the pK_a values of the

TABLE 10. THE pK VALUES OF THE AMINO
ALCOHOLS AND THE POLYELECTROLYTES

Aminoalcohol		AMPS		QAMPS
Species	pK_a	(No salt)[a] pK_m	(Salt)[b] pK_m	(Salt)[b] pK_m
AE	9.49	6.63	7.77	7.43
AP	9.43	6.31	7.62	7.20
AB	9.23	6.10	7.73	7.69
AMP	9.69	7.00	8.37	8.21
TRIS	8.15	5.53	6.94	—
TEOA	7.86	>10	>10	—

a) The values in the absence of added salt. b) The values in the presence of 1 mol dm^{-3} sodium chloride.

amino alcohols are also listed. The values of n' were 1.8—2.0 in the absence of salt and 1.5—1.7 in the presence of salt, except for the polymer from AMP (n' was close to unity). The addition of sodium chloride (1 mol dm^{-3} concentration) weakens the electrostatic field effect and pK_m becomes higher ($\Delta pK_m=1.1$—1.6). The difference between the pK_a value of an amino alcohol and the pK_m value of the corresponding AMPS in the presence of the salt becomes smaller in the following order: AE>AP>AB>AMP>TRIS ($\Delta pK=$ $pK_a-pK_m=1.7$—1.2). Since this order is related to the branching structure of the amino alcohol residue, it may be that the branching structure has the shielding effect on the electrostatic interaction or that it lowers the local dielectric constant around the amino group thereby decreasing the effective charge of the the charged group. The reason that the pK_m value of AMPS does not agree with the pK_a value of the corresponding

amino alcohol is to certain extent explained by the amino alcohol residue being combined with the benzyl group. pK_a are found in certain cases to decrease by about unity due to the effect of the benzyl group.[15] The pK_m of the TEOA residue is greater than the pK_a value of TEOA, because TEOA combines with the benzyl group to form the strong basic quaternary ammonium group. Neverthless, the pK_a of the TEOA quaternary ammonium residue is lower than that of the TEA quaternary ammonium residue (pK_m>11) because of the inductive effect of the hydroxyl groups in the former residue. Table 10 also lists the pK_m values of QAMPS or the amino alcohol residues of the reaction products of QCMPS and the amino alcohols in the presence of salt. They are found to be practically identical with those of AMPS.

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15) For instance, the difference of pK_a between methylamine and N-methylbenzylamine is nearly unity.