Group Interactions in Polyelectrolytes. VII.[1]   Amination Kinetics of Chloromethylated Polystyrene with Butylamine Isomers

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The amination of chloromethylated polystyrene (CMPS) and benzyl chloride with butylamine isomers and diethylamine was investigated kinetically in dioxane, methyl ethyl ketone (MEK), and N,N-dimethylformamide (DMF). Although the amination of i- and s-butylamine conformed to the ordinary second-order kinetics in all the solvents, deceleration was observed during the course of the amination of CMPS with n-butylamine in MEK as well as in dioxane, with t-butylamine in DMF, and with diethylamine in both dioxane and DMF. The intrinsic rate constants of the amination of CMPS were generally almost the same as those of benzyl chloride. The magnitudes of the rate constants in each solvent were in this order; n-butyl>i-butyl>s-butyl>t-butyl; it was in the order of DMF≫MEK≈dioxane with all the amines investigated. These results were interpreted in terms of both the structures of the amines and the interaction between the amine and the solvent molecules.

The kinetics of the amination of chloromethylated polystyrene (CMPS) with several primary and secondary amines was investigated by Kawabe and Yanagita.[1-3] They found that the apparent second-order rate constant of the amination with n-butylamine in dioxane decreased as the amination proceeded and that the rate constant of the amination with 2-aminobutanol increased in dioxane, though both the aminations obeyed the ordinary second-order kinetics in N,N-dimethylformamide (DMF). On the other hand, the rate constant of the amination with di-n-butylamine decreased in both dioxane and DMF. The amination of benzyl chloride with all the above amines obeyed the ordinary second-order kinetics. If the decrease in the rate constant during the amination of CMPS is caused by the steric effect of the already-aminated neighbors with bulky amine, this decrease must be related to the bulkiness of the amine. In the present study, the kinetics of the aminations of CMPS and benzyl chloride with butylamine isomers and diethylamine have been investigated in dioxane, methyl ethyl ketone (MEK), and DMF. The authors have found that the rate constant decreases slightly in the amination of CMPS with t-butylamine and appreciably in the amination of CMPS with diethylamine. It has also been found that the magnitudes of the rate constants in the aminations of both CMPS and benzyl chloride are greatly affected by the species of amine and solvent.

Experimental

Materials.   Chloromethylated polystyrene (CMPS) was prepared and purified by the procedures described in the previous papers.[1-3] The chlorine contents and the molecular weights of the CMPS used in the present study are tabulated in Table 1. The amines 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 deionized, decarbonized water was used.

Kinetic Measurements.   The procedures of the kinetic measurements in the amination of CMPS and benzyl chloride were almost the same as those described in a previous paper.[1]

TABLE 1.   CHLOROMETHYLATED POLYSTYRENE

Code	Content of Cl %	Degree of chloro-methylation	Molecular weight
SC-3	22.87	0.98	—
SC-5	21.15	0.87	10.2×10^4
SC-7	22.04	0.93	7.3×10^4
SC-8	22.11	0.93	9.2×10^4
SC-9	21.83	0.91	9.6×10^4
SC-10	21.07	0.87	11.6×10^4

The experimental conditions in the amination of CMPS are listed in Table 2. The temperature of a reaction mixture was kept constant by means of a thermostat (within±0.1°). In the amination of benzyl chloride, the initial concentrations were almost the same as those in the amination of CMPS. All the reactions except Run 9 were homogeneous and reached completion. In Run 9, since hydrochloric acid salt of diethylamine was deposited during the amination, the reaction mixture was previously distributed in test tubes dipped in a thermostat to avoid uneven sampling.

Viscometric Measurements.   In the amination of CMPS, the change in the viscosity of the reaction mixture was also checked for Runs 1—8 by the procedures described in the previous paper.[1]

Results

The aminations of chloromethylated polystyrene (CMPS) and benzyl chloride with butylamine isomers and diethylamine were investigated kinetically in dioxane, MEK, and DMF.[4] The kinetic measurements could not be carried out in dimethyl sulfoxide, because all the aminations of CMPS with these amines in the solvent were accompanied by the precipitation of the polymer in an earlier stage of the reaction.

The amination of benzyl chloride could be expressed by the ordinary second-order equation:

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

1) Part VI. H. Kawabe, and M. Yanagita This Bulletin, **46**, 38 (1973).

2) H. Kawabe and M. Yanagita, *ibid.*, **41**, 1518 (1968).

3) H. Kawabe and M. Yanagita, *ibid.*, **44**, 896 (1971).

4) Several aminations of CMPS were carried out by using different CMPS samples (Suns 4 and 24, Runs 7 and 19, and Runs 8 and 16 for butylamine isomers; and also Runs 9 and 10 for diethylamine), and almost the same value of rate constant was obtained in each case. It was also shown in these cases that difference in concentration of amine revealed no difference in the rate constant.

Table 2. Amination of chloromethylated polystyrene

Run	Amine[a]	Solvent	Temp. °C	CMPS	a[b] mol/l	b[c] mol/l	a/b
1	A	MEK	50	SC-7	0.7863	0.0376	20.9
2	B	Dioxane	50	SC-5	0.9351	0.0411	22.8
3	B	MEK	50	SC-5	0.8491	0.0410	20.7
4	B	DMF	50	SC-5	0.8216	0.0402	20.4
5	C	Dioxane	50	SC-5	0.8739	0.0410	21.3
6	C	MEK	50	SC-5	0.8380	0.0406	20.6
7	C	DMF	50	SC-5	0.8137	0.0427	19.1
8	D	DMF	50	SC-5	0.8485	0.0410	20.7
9	E	Dioxane	30	SC-3	0.8811	0.0459	19.2
10	E	DMF	30	SC-3	0.8818	0.0437	20.2
11	E	DMF	30	SC-8	0.8319	0.0416	20.0
12	D	DMF	30	SC-8	0.8323	0.0416	20.0
13	D	DMF	35	SC-8	0.8321	0.0416	20.0
14	D	DMF	40	SC-8	0.8325	0.0416	20.0
15	D	DMF	45	SC-8	0.8317	0.0416	20.0
16	D	DMF	50	SC-8	0.8323	0.0416	20.0
17	C	DMF	30	SC-9	0.4107	0.0411	10.0
18	C	DMF	40	SC-9	0.4120	0.0412	10.0
19	C	DMF	50	SC-9	0.4106	0.0411	10.0
20	C	DMF	60	SC-9	0.4099	0.0422	9.7
21	B	DMF	20	SC-10	0.4001	0.0400	10.0
22	B	DMF	30	SC-10	0.4000	0.0400	10.0
23	B	DMF	40	SC-10	0.4000	0.0400	10.0
24	B	DMF	50	SC-10	0.4000	0.0423	9.5

a) A: n-butylamine, B: i-butylamine, C: s-butylamine, D: t-butylamine, E: diethylamine. b) a: Initial concentration of amine. c) b: Initial concentration of the polymer expressed in moles of chloromethyl group per liter.

where a and b are the initial concentrations of an amine and the chloromethyl group respectively, while x is the concentration of the chloride ions after time t.

Although most of the aminations of CMPS conformed to Eq. (1), deceleration during the amination was observed in the following cases: n-butylamine in dioxane and MEK, t-butylamine in DMF, and diethylamine in dioxane and DMF. In these cases, the plot of $\overline{kt}$ against t was expressed substantially by straight lines which intersected nearly at half-amination, and the over-all kinetics in the presence of a large excess of amine $(a \gg b)$ could be expressed by Eq. (2):[2]

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

$$k_1 = \frac{1}{[(2 - k_2/k_1)a - b]} \ln \frac{1 - \beta}{1 - (2 - k_2/k_1)\alpha} \qquad (3)$$

$$k_2 = \frac{1}{(a - b)(t - \tau)} \left(\ln \frac{1 - \alpha}{1 - \beta} \ln \frac{1 - \chi/a}{1 - \chi/b} \right) \qquad (4)$$

where 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. In Eq. (4), $\alpha = x/a$, 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 was aminated independently of its neighbors. By combining Eqs. (1) and (4), we get Eq. (5):

$$\overline{kt} = k_2 t + C \qquad (5)$$

where C is a constant in a given system: $C = \ln[(1 - \chi/a)/(1 - \chi/b)] - k_2(a - b) \tau$. The value of k_2 can be determined, therefore, directly as the slope of the $\overline{kt}$ vs. t plot: $k_2 = \Delta \overline{kt}/\Delta t$. With regard to k_1, on the other hand, the slope of the plot gives merely an approximate value of k_1. The real value of k_1 can be determined only by repeated computations by means of Eq. (3).[2]

Amination with Butylamine Isomers. The rate constants of the amination of CMPS and benzyl chloride with butylamine isomers at 50°C are tabulated in Table 3.[4] It is clearly shown in the table that the rate constant, k or k_1, in any solvent is in this order: n-butyl > i-butyl > s-butyl > t-butyl. It is also shown for any amine that the numerical value of the rate constant in MEK is almost the same as that in dioxane, while the value in DMF is much higher than those in dioxane and MEK.

Table 3 shows three cases in which the deceleration was observed; the values of k_2/k_1 are cited in parentheses. The course of the amination of CMPS with n-butylamine in MEK at 50 °C is shown in Fig. 1, where the solid line was calculated on the basis of Eq. (2) by using these rate constants:

$$k_1 = 2.85 \times 10^{-3}, \quad k_2 = 1.77 \times 10^{-3} \quad \text{l/mol·min}$$

which were obtained on the basis of Eqs. (3) and (4) (or Eq. (5)) respectively. The white circles in Fig. 1, which represent the observed values, are substantially on the calculated curve. The value of k_2/k_1 in MEK, 0.62, is comparable to that in dioxane, 0.65 (the aver-

TABLE 3. RATE CONSTANTS OF AMINATION OF BENZYL CHLORIDE AND CHLOROMETHYLATED
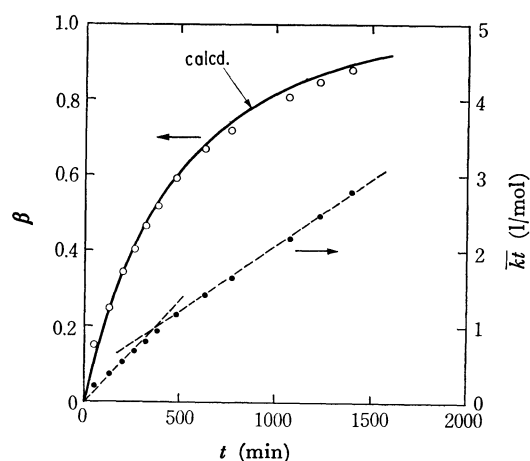POLYSTYRENE WITH BUTYLAMINE ISOMERS AT 50 °C[a]

Chloride	Amine	$k \times 10^3$, 1/mol min		
		Dioxane	MEK	DMF
Benzyl chloride	n-Butyl	2.73[b]	1.49	102[c]
	i-Butyl	1.80	1.12	99.7
	s-Butyl	0.726	0.972	37.9
	t-Butyl			17.1
CMPS	n-Butyl	6.59[d]	2.85[d]	88.9[c]
		(0.58)[e]	(0.62)	
	i-Butyl	1.84	1.30	72.2
	s-Butyl	0.870	0.982	32.7
	t-Butyl			11.3[d]
				(0.87)[f]

a) In the table, the values of k or k_1 are shown, and in parentheses are shown the values of k_2/k_1.
b) Data in Ref. 2.   c) Data in Ref. 1.   d) The value of k_1.   e) The average value at various temp. is 0.65.
f) The average value at various temp. is 0.79.

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

Temp. °C	Rate constants $\times 10^3$, 1/mol·min				E_a kcal/mol	$\log A$[c]
	k_1[a]	k_2[a]	k_B[b]			
30	3.28	2.57	4.76	(k_1)	12.0±0.03	6.17±0.02
35	4.53	3.68	6.70			
40	6.24	4.67	9.16	(k_2)	12.2±0.4	6.19±0.28
45	8.42	7.07	12.4			
50	11.3	8.86	17.1	(k_B)	12.4±0.1	6.60±0.06

a) k_1 and k_2: Rate constants of CMPS.   b) k_B: Rate constants of benzyl chloride.   c) A is expressed by 1/mol·min.

Fig. 1. Amination of chloromethylated polystyrene with n-butylamine in MEK at 50 °C (Run 3).
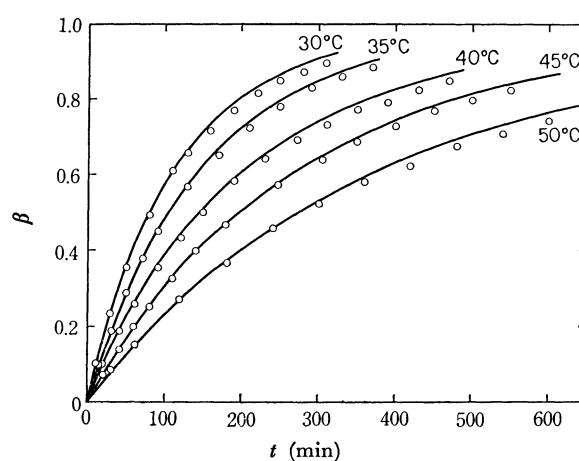
Fig. 2. Amination of chloromethylated polystyrene with t-butylamine in DMF.

——: calculated values,   O: observed values

age value at various temperatures).

Deceleration was also observed in the amination of CMPS with t-butylamine in DMF. The results of kinetic measurements at various temperatures are shown in Fig. 2, where open circles represent the observed values and where the solid lines show the values calculated on the basis of Eq. (2) by the use of the values of k_1 and k_2 tabulated in Table 4. The rate constants of the amination of benzyl chloride, k_B, and the activation energies, E_a, and the frequency factors, A, which were computed by the least-squares method, are also listed

in Table 4. The average value of k_2/k_1 is 0.79, higher than those of n-butylamine in dioxane and MEK. The amination of CMPS with s- and i-butylamine conformed to Eq. (1) in all the solvents. The results of the amination of CMPS and benzyl chloride with these amines are summarized in Tables 5 and 6.

Amination with Diethylamine.   In the amination of CMPS with diethylamine, the deceleration during the amination was observed in both dioxane and DMF. The results at 30 °C are shown in Figs. 3 and 4, where

TABLE 5. AMINATION OF CHLOROMETHYLATED POLYSTYRENE AND BENZYL CHLORIDE WITH s-BUTYLAMINE IN DMF

Temp. °C	Rate constants× 10², 1/mol·min		E_a kcal/mol	$\log A^{c)}$ 1/mol·min
	$k_P{}^{a)}$	$k_B{}^{b)}$		
30	0.932	1.08		
40	1.84	2.00	(k_P) 12.1±0.1	6.69±0.09
50	3.27	3.79		
60	5.72	6.67	(k_B) 12.2±0.1	6.85±0.07

a) k_P: Rate constant of CMPS. b) k_B: Rate constant of benzyl chloride. c) A is expressed by 1/mol·min.

TABLE 6. AMINATION OF CHLOROMETHYLATED POLYSTYRENE AND BENZYL CHLORIDE WITH i-BUTYLAMINE IN DMF

Temp. °C	Rate constants× 10², 1/mol·min		E_a kcal/mol	$\log A^{c)}$
	$k_P{}^{a)}$	$k_B{}^{b)}$		
20	1.24	1.52		
30	2.46	3.04	(k_P) 11.6±0.2	6.72±0.15
40	4.64	5.61		
50	7.72	9.97	(h_B) 11.8±0.1	6.97±0.05

a) k_P: Rate constants of CMPS. b) k_B: Rate constants of benzyl chloride. c) A is expressed by 1/mol·min.

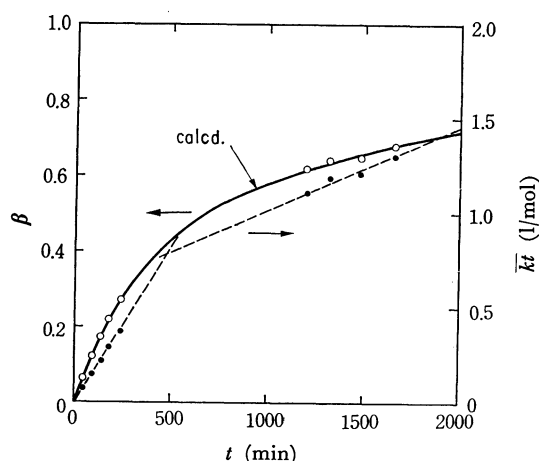Fig. 3. Amination of chloromethylated polystyrene with diethylamine in dioxane at 30 °C   (Run 9).

Fig. 4. Amination of chloromethylated polystyrene with diethylamine in DMF at 30 °C   (Run 11).

the observed values, represented by the white circles, are substantially on the curves calculated on the basis of Eq. (2) by the use of the following values of k_1 and k_2:

(in dioxane) $k_1 = 1.71 \times 10^{-3}$ 1/mol·min, $k_2 = 3.96 \times 10^{-4}$ 1/mol·min; $k_2/k_1 = 0.43$

(in DMF) $k_1 = 3.48 \times 10^{-2}$ 1/mol·min, $k_2 = 1.81 \times 10^{-2}$ 1/mol·min; $k_2/k_1 = 0.52$

In DMF, the rate constant of benzyl chloride was also measured at 30 °C as:

(in DMF) $k_B = 2.82 \times 10^{-2}$ 1/mol·min

Viscosity Change in the Reaction Mixture During the Amination of CMPS with Butylamine Isomers.   The change in the viscosity in the amination of CMPS was measured in various solvents; the results in DMF are shown in Fig. 5, where H, the viscosity ratio defined in the previous paper,[1] is plotted against β. The values of H are in this order: t-butyl>s-butyl> i-butyl>n-butyl. In the other solvents, the order was
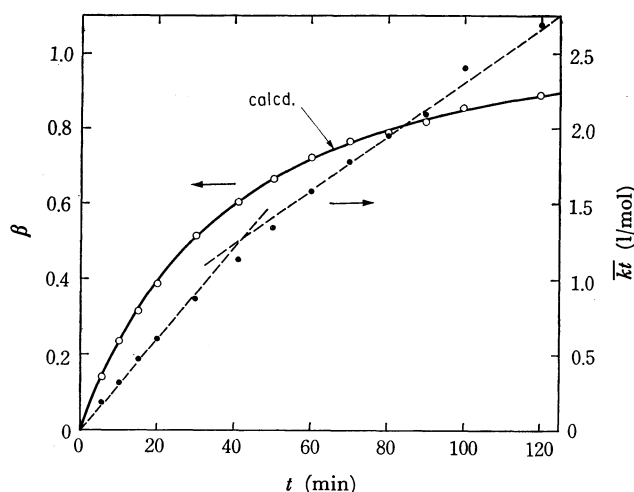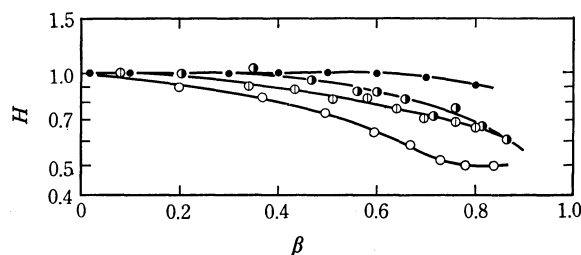

Fig. 5. Viscosity change of reaction mixture in the amination of chloromethylated polystyrene in DMF.

○: n-Butylamine (Ref. 1),   ◑: i-Butylamine (Run 4),
◐: s-Butylamine (Run 7),   ●: t-Butylamine (Run 8).

the same; however, the viscosity changes do not seem to be related to the kinetic behavior of the aminations.

Discussion

Deceleration During the Amination of CMPS.   In the amination of CMPS with butylamine isomers,

the amination with i- and s-butylamine conformed to the ordinary second-order kinetics in dioxane, MEK, and DMF; however, deceleration during the reaction was observed with n-butylamine in dioxane and MEK, and not in DMF, though a slight deceleration was observed with t-butylamine in DMF. On the other hand, a stronger deceleration was observed in the amination with diethylamine in both dioxane and DMF. Since all the aminations of benzyl chloride proceeded normally, and since the formation of charged groups on the polymer is not likely to take place during the reaction,[5] this deceleration seems to be caused by the steric effect of the already-aminated neighboring groups; this kinetic behavior can be fully expressed by Eq. (2). The kinetic behavior of the amination of CMPS is dependent on the species of amine and the solvent. The experimental results may be explained in terms of the geometry of amines, which is itself determined by the structural factors of the amines, such as the branching and the flexibility through the rotation around the bond axes, and also by the interactions between amine and solvent molecules and by the conformational change in the amine molecules (or groups) at the transition state of the reaction. The steric effect must be mainly determined by the conformational free energy, that is, the difference in the free energy of amine molecules (or groups) at the transition state under the influence of the neighboring groups from that at the initial state; it consists of the difference in the potential energies of the molecules between the two states and the difference between the conformational entropies.

In the case of diethylamine, an appreciable deceleration was observed in both dioxane ($k_2/k_1=0.43$) and DMF ($k_2/k_1=0.52$), though it was not so marked as the cases of di-n-butylamine, a higher homologue of the former, in dioxane ($k_2/k_1=0.23$)[2] and in DMF ($k_2/k_1=0.27$).[1] These results may be related to the bulky structure of secondary amines, in which two alkyl groups occupy the apices of the trigonal pyramid, and in which, therefore, the steric obstruction is pronounced with secondary amines, irrespective of the species of solvent. A weaker deceleration was observed in some cases of butylamine isomers. The slight deceleration with t-butylamine in DMF ($k_2/k_1=0.79$) may be ascribed to its rigid and bulky structure. The difference in kinetic behavior between n-butylamine and i- and s-butylamine may be supposed to be mainly due to the difference in their conformational entropies.

In the case of n-butylamine, the deceleration was observed in dioxane ($k_2/k_1=0.65$) and MEK ($k_2/k_1=0.62$), but it was not observed in DMF. Since the value of the solubility parameters, δ,[6] of n-butylamine

($\delta=9.15$) is almost the same as those of dioxane ($\delta=9.95$) and MEK ($\delta=9.16$), the amine molecules in these solvents may be considered to be statistically elongated and their conformational change at the transition state will require an increase in energy and a loss of entropy. On the other hand, the n-butylamine molecule in DMF ($\delta=12.11$) is considered to be contracted as a result of the intramolecular interaction among the segments; therefore, its conformational change at the transition state will require less energy and less entropy loss than those in dioxane and MEK. The normal kinetic behavior with i- and s-butylamine in both dioxane and DMF is properly to be ascribed to the branching structure of these molecules, the conformational entropies of which are much smaller than that of n-butylamine.

Comparison Between the Rates of CMPS and Benzyl Chloride. The values of k_1 or k of CMPS are generally almost the same as the corresponding values of benzyl chloride. The effects of the species of amine and solvent are, therefore, essentially the same for both CMPS and benzyl chloride. The ratios of the intrinsic rate constants of CMPS (denoted as k_P) to the corresponding rate constants of benzyl chloride (k_B) are somewhat higher than unity in dioxane and MEK. In DMF, the relative rates are slightly less than unity except in case of diethyl amine. Table 7 shows the numerical values of thermodynamic quantities, $\Delta H^{\ne}$; the enthalpy of activation, $\Delta S^{\ne}$; the entropy of activation, and $\Delta G^{\ne}$, the free energy of activation, all of which have been calculated at 25 °C by means of the equations described in the previous paper.[1] As is shown in Table 7, all the reactions in DMF have a tendency to be accompanied by a decrease in $\Delta S^{\ne}$ as well as the increase in $\Delta H^{\ne}$ from benzyl chloride to CMPS. This is also the case with the amination with 2-aminobutanol in DMF ($k_P/k_B=0.81$) or in DMSO ($k_P/k_B=0.76$).[1] On the other hand, in dioxane, the change in $\Delta S^{\ne}$ is not significant in the amination with n-butylamine or 2-aminobutanol.[1] Thus, this tendency of $\Delta S^{\ne}$ to decrease from benzyl chloride to CMPS seems to be characteristic of dipolar aprotic solvents, in which the solvation of the transition state plays an important role in the determination of the amination rate.

Effect of Amine on the Amination Rate. The intrinsic rate constants of CMPS as well as of benzyl chloride are dependent on the species of amine—$e.g.$, in butylamine isomers, in the following order: n-butyl$>i$-butyl$>s$-butyl$>t$-butyl. The values of the relative rate with respect to an amine are approximately the same, irrespective of the species of solvent and chloride (CMPS or benzyl chloride). This order among butylamine isomers is not likely to be dependent on their basicities, because the pK values of the conjugated acids are almost the same: 10.64; (n), 10.42 (i), 10.56 (s), and 10.45 (t). It seems rather dependent on the branching structures of the alkyl groups of the amines; this dependence produces the difference in the steric hindrance of the benzene ring to the alkyl group of amine in the transition state. This is supported, especially in the case of t-butylamine, by the fact, shown in Table 7, that the increase in $\Delta G^{\ne}$ from

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5) In fact, a completely aminated CMPS sample, which was obtained simply by pouring the reaction mixture into a poor solvent, was proved to contain no chlorine by its elementary analysis for halogen. This may be ascribed to that the aminated group on the polymer is the N-benzyl substituent of an alkylamine used as a reagent and it is a weaker base than the alkylamine which is used in a large excess in the present study.

6) The δ values were calculated at 25 °C on the basis of the data shown in the book: J. A. Riddick and W. B. Bunger, "Organic Solvents," third edition, Wiley Interscience, New York, N. Y. (1970).

TABLE 7. THERMODYNAMIC QUANTITIES AT 25 °C IN THE AMINATION OF CHLOROMETHYLATED POLYSTYRENE
AND BENZYL CHLORIDE

Solvent	Amine	Chloride	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ e.u.	$\Delta G^{\neq}$ kcal/mol
Dioxane	n-Butyl[a]	CMPS, k_1	11.5±0.1	−41.2±0.3	23.8
		k_2	11.5±0.9	−42.2±2.6	24.1
		Benzyl	12.0±0.2	−41.5±0.6	24.3
DMF	n-Butyl[a]	CMPS	10.8±0.1	−38.1±0.4	22.2
		Benzyl	11.0±0.2	−37.2±0.7	22.1
	i-Butyl	CMPS	11.0±0.2	−37.9±0.7	22.3
		Benzyl	11.2±0.1	−36.8±0.2	22.2
	s-Butyl	CMPS	11.5±0.1	−38.1±0.4	22.8
		Benzyl	11.7±0.1	−37.3±0.3	22.8
	t-Butyl	CMPS, k_1	11.4±0.0$_3$	−40.4±0.1	23.5
		k_2	11.6±0.4	−40.3±1.3	23.6
		Benzyl	11.8±0.1	−38.5±0.3	23.3
	2-Amino-butanol[a]	CMPS,	12.5±0.2	−35.8±0.7	23.1
		Benzyl	12.7±0.1	−34.5±0.2	23.0

a) Data in Ref. 1.

n-butyl to t-butylamine is based on the decrease in $\Delta S^{\neq}$ as well as by the increase in $\Delta H^{\neq}$. It is also shown in Table 7 that the $\Delta H^{\neq}$ of 2-aminobutanol is considerably higher than that of s-butylamine (2-aminobutane); this is probably related to an inductive effect of the hydroxyl group.

Effect of Solvent on the Amination Rate. The intrinsic rate constant of CMPS as well as the rate constants of benzyl chloride are also dependent on the species of solvent. In dioxane and MEK, the rates are approximately the same, but that in DMF is very high. Since the dielectric constants (D) are 2.21 (dioxane), 18.51 (MEK), and 36.71; (DMF), no relation between k and D can be established in this case.

The high rate constants in DMF are considered to be due to the solvation of the transition state in this dipolar aprotic solvent, as has been discussed in the previous paper.[1] Since the δ value of MEK is almost the same as that of dioxane, the contributions of both solvents to $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are expected to be almost the same.