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Group Interactions in Polyelectrolytes. I. Amination Kinetics of Chloromethylated Polystyrene

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Chloromethylated polystyrene is quantitatively aminated by *n*-butylamine or *n*-dibutylamine in dioxane, but the plot of the logarithmic term in the simple second-order rate equation against the time is not represented by a single straight line, but is divided into two lines which intersect nearly at the half-amination point. These results are interpreted in terms of the step-by-step amination resulting from the steric effect of the already-aminated neighbors which have bulky alkyl groups. By assuming two distinct reactivities of chloromethyl groups according to their neighboring environment, rate equations for two separate steps are derived; these equations give k_1, the rate constant in the first step, and k_2, that in the second step. In the presence of a large excess of amine, the over-all kinetics can be expressed by:

$$\mathrm{d}x/\mathrm{d}t = [ab/(2k_1 - k_2)][2k_1(k_1 - k_2)e^{-2k_1 a t} + k_1 k_2 e^{-k_2 a t}],$$

where x is the concentration of chloride ions at time t; a is the initial concentration of amine, and b, that of the chloromethyl group. The equation is found to be substantially valid for the values of k_1 and k_2 computed by the equations for the individual steps.

The kinetics of the reaction of chloromethylated polystyrene with triethylamine in dimethylformamide was studied by Noda and Kagawa,[1] who found that the rate conforms to the simple second-order equation. In dioxiane, however, they could measure only the rate at the initial stage, because the quaternized polymer precipitated in the solvent. Fouss *et al.*[2] observed that, in the quaternization of poly-4-vinylpyridine by *n*-butyl bromide in tetramethylene sulfone or in propylene carbonate, the rate becomes less than that corresponding to the simple second-order kinetics as the quaternization proceeds, rapidly beyond half-quaternization; they ascribed this to the charge being built up on the polymer.

The present authors have carried out the amination of chloromethylated polystyrene with *n*-butylamine or di-*n*-butylamine in dioxane and have found that the reaction proceeds quantitatively and that the apparent second-order rate constant decreases markedly beyond the half-amination point. Analysis of the experimental results suggests that the amination proceeds in two steps due to the steric effect of the already-aminated neighboring groups on the polymer, to which bulkyl alkyl groups are introduced by amination. The purpose

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[1] I. Noda and I. Kagawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 857 (1963).

[2] R. M. Fuoss, M. Watanabe and R. D. Coleman, *J. Polymer Sci.*, **48**, 5 (1960).

of the present study is to derive rate equations for the step-by-step reaction and to evaluate the kinetics data by means of those equations.

Experimental

Materials. The chloromethylated polystyrene was prepared as follows. Styrene, which had been distilled under a reduced pressure (69.5°C/60 mmHg), was polymerized by the suspension-polymerization procedure.[3] Styrene containing 1% benzoyl peroxide was stirred at 90°C for seven hours in a solution of polyvinyl alcohol. The process of polymerization was followed by occasional measurements of the specific gravity of the polymer beads; it reached a constant value of 1.05 after three hours. The chloromethylation of polystyrene was carried out by the procedure reported by Pepper *et al.*[4] Two samples of different degrees of chloromethylation were prepared; they are shown in Table 1. The anhydrous amines, benzyl chloride, and ethylene bromide were distilled before use. All the other chemicals were of a reagent grade, while de-ionized, de-carbonized water was used throughout.

TABLE 1. CHLOROMETHYLATION OF POLYSTYRENE

Code	Content of Cl	Degree of chloromethylation
SC-1	19.79%	0.85
SC-2	12.88%	0.55

Amination of Chloromethylated Polystyrene. Jones[5] found that the amination of chloromethylated polystyrene with ammonia or amines other than tertiary amines brought about cross-linking. Since this cross-linking is to be ascribed to a side-reaction of chloromethyl groups with amino groups formed on the polymer, it can be prevented by avoiding the contact of polymer molecules, by lowering the rate of the side-reaction, and by enhancing the principal reaction. This can be done under the following conditions: (i) a low concentration of the polymer, (ii) a large molar ratio of the amines to the chloromethyl group, and (iii) the use of an amine with a bulky alkyl group. Preliminary experiments carried out to examine these conditions showed that the precipitation of the polymer or the separation of the dissolved phase took place in amination with ammonia or monomethylamine. An experiment with a large excess of *n*-butyl amine proved that the amination proceeded to completion without any precipitation of the polymer or any separation of the dissolved phase. The polymer was also quantitatively aminated by di-*n*-butylamine without any separation of the polymer phase, though a few crystals of the amine hydrochloride precipitated.

Kinetic Measurements. One gram of chloromethylated polystyrene was dissolved in 50 m*l* of a dioxane and thoroughly mixed with 100 m*l* of a dioxane solution containing a large excess of an amine. The molar ratio of the amine to the chloromethyl group was about 20. The temperature of the reaction mixture was maintained within ±0.5°C by means of a thermostat. At appropriate intervals, portions of the solution, which were taken out by a pipet from the reaction vessel or which had previously been distributed in tubes dipped in the thermostat, were poured into aqueous solutions containing an amount of nitric acid sufficient to neutralize the amine. The precipitate of the polymer was then filtered off and washed with water, and the filtrate was potentiometrically titrated with 0.1 N silver nitrate by the use of Beckman's Model G pH meter to determine the chloride ions. The error caused by the titration was less than ±0.3%. The volume concentration of the amine and the chloromethyl group in a reaction mixture were calculated by considering the coefficient of the expansion of dioxane. The experimental conditions are listed in Table 2, where *a* denotes the initial concentration of the amine, and *b* the initial concentration of the chloromethyl group.

TABLE 2. AMINATION OF CHLOROMETHYLATED POLYSTYRENE

Code	Temp. °C	Polymer	*b* mol/*l*	Amine	*a* mol/*l*	*a*/*b*
A	30	SC-1	0.0367	*n*-Butyl	0.661	18
B	45	SC-1	0.0361	*n*-Butyl	0.657	18
C	60	SC-1	0.0356	*n*-Butyl	0.646	18
D	50	SC-1	0.0359	Di-*n*-butyl	0.723	20
E	60	SC-1	0.0356	Di-*n*-butyl	0.715	20
F	70	SC-1	0.0352	Di-*n*-butyl	0.708	20
G	60	SC-2	0.0232	*n*-Butyl	0.464	20

Amination Kinetics of Ethylene Dibromide and Benzyl Chloride. The amination of ethylene dibromide or benzyl chloride in dioxane was examined kinetically in the same way as the amination of chloromethylated polystyrene. The experimental conditions are shown in Table 3.

TABLE 3. AMINATION OF ETHYLENE BROMIDE AND BENZYL CHLORIDE

Code	Temp. °C	Halide	*b* mol/*l*	Amine	*a* mol/*l*	*a*/*b*
H	50	Ethylene bromide	0.0687	*n*-Butyl	1.374	20
I	60	Ethylene bromide	0.0680	Di-*n*-butyl	1.360	20
J	30	Benzyl chloride	0.0561	*n*-Butyl	1.123	20
K	40	Benzyl chloride	0.0514	*n*-Butyl	1.029	20
L	50	Benzyl chloride	0.0512	*n*-Butyl	1.395	27
M	60	Benzyl chloride	0.0522	*n*-Butyl	1.423	27

***N*-Methylation of Ethylenediamine.** In a vessel protected from light, there was placed a 300 m*l* portion of an aqueous solution of methyl iodide (0.1 mol/*l*), and then 5 m*l* of an aqueous solution of ethylenediamine

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[3] H. Kawabe and M. Yanagita, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **61**, 137 (1958); *J. Sci. Res. Inst.*, **51**, 182 (1957).

[4] K. W. Pepper, H. M. Raislay and M. A. Young, *J. Chem. Soc.*, **1953**, 4097.

[5] G. D. Jones, *Ind. Eng. Chem.*, **44**, 2686 (1952).

(1 mol/l) were added. The temperature of the system was maintained at 30±0.5°C during the course of the reaction. The initial concentrations of methyl iodide and ethylenediamine were 0.0984 mol/l and 0.0160 mol/l respectively. At time intervals aliquots were withdrawn; each was poured into diluted nitric acid and titrated potentiometrically with 0.1 N silver nitrate. An amount of iodide ions nearly equivalent to the quantitative methylation of both amino groups was produced within 48 hr; this amount remained substantially constant even after 100 hr. A blank test for the hydrolysis of methyl iodide in pure water showed that the error caused in amination by the hydrolysis would not exceed 0.8% after six hours, 1.4% after 24 hr, and 2.4% after 48 hr. The *N*-methylation of ethylenediamine was found to be fully inhibited by the presence of excess nitric acid; this was shown by the fact that no production of iodide ions was observed, even after six hours, when ethylenediamine had previously been neutralized with an excess of nitric acid.

Results

Since benzyl chloride is quantitatively aminated in dioxane by *n*-butylamine, its rate can be fully given by the simple second-order equation:

$$\mathrm{d}x/\mathrm{d}t = k(a-x)(b-x) \tag{1}$$

where x is the concentration of chloride ions at time t; a is the initial concentration of the amine, and b, that of benzyl chloride. Upon integration, Eq. (1) yields:

$$k = \frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(b-x)} = \frac{2.303}{(a-b)t}\log\frac{1-\alpha}{1-\beta} \tag{2}$$

where $\alpha(=x/a)$ is the fraction of converted amine, and $\beta(=x/b)$, that of benzyl chloride. As may be seen in Fig. 1, where the logarithmic term in Eq. (2) is plotted against the time, the linearity of the plots indicates that the amination proceeds normally; a single value of k is obtained from the slope for each temperature. Table 4 summarizes the values of k computed by Eq. (2); the activation energy, E, obtained from a plot of $\log k$ against $1/T$, and the frequency factor, A, computed by the relation $k=A\cdot\exp(-E/\boldsymbol{R}T)$. A value of k at any given temperature may be obtained by:

$$k = (7.88\times10^5)\cdot e^{-12500/\boldsymbol{R}T}\ l/\text{mol min}$$

TABLE 4. AMINATION OF BENZYL CHLORIDE BY *n*-BUTYLAMINE

Code	Temp. °C	$k\times10^3$ l/mol min	$A\times10^{-5}$ l/mol min	E kcal/mol
J	30	0.777	7.98	12.5±0.2
K	40	1.42	7.57	
L	50	2.73	7.76	
M	60	5.03	8.20	

The amination of a chloromethylated polystyrene, SC-1, in dioxane has been carried out in the presence of a large excess of *n*-butylamine or *n*-dibutylamine. The polymer, as well as benzyl chloride, is quantitatively aminated by the amines without separating polymer phase. This fact suggests that cross-linking can hardly take place. This effective inhibition of the cross-linking may be ascribed to the steric effect of bulky alkylamino groups, which hinder the access of halide groups.

The rate constant for the polymer computed by Eq. (2), in contrast to the case of benzyl chloride, decreases with β, markedly beyond $\beta=0.5$ Figures 2 and 3 show plots of the logarithmic term in Eq. (2) against the time. Each plot seems to consist of two straight lines which intersect near $\beta=0.5$; this implies that the amination proceeds in two steps. This results may be explained by postulating that the amination of chloromethyl groups proceeds normally at the initial stage, but that after the half-amination point it is obstructed by both nearest neighbors, which are already aminated.

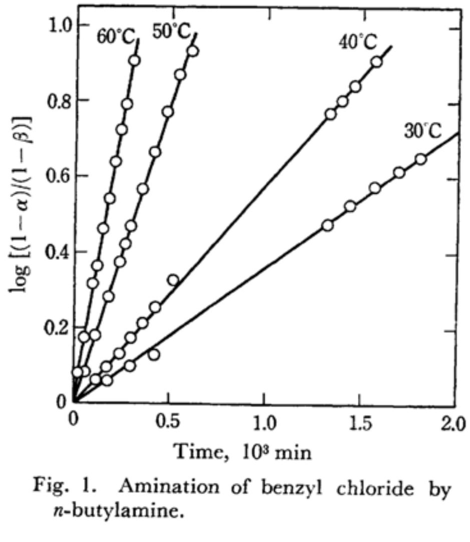


Fig. 1. Amination of benzyl chloride by *n*-butylamine.

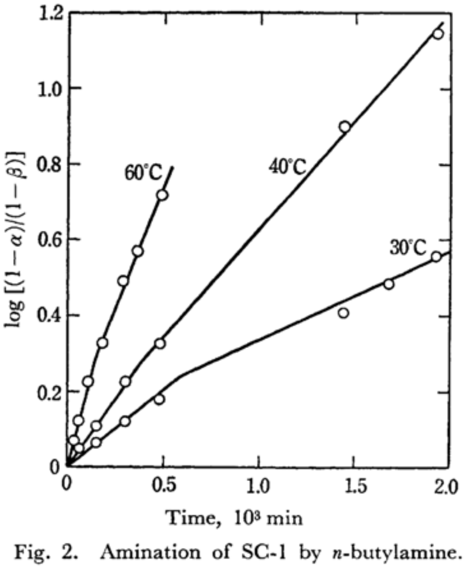


Fig. 2. Amination of SC-1 by *n*-butylamine.

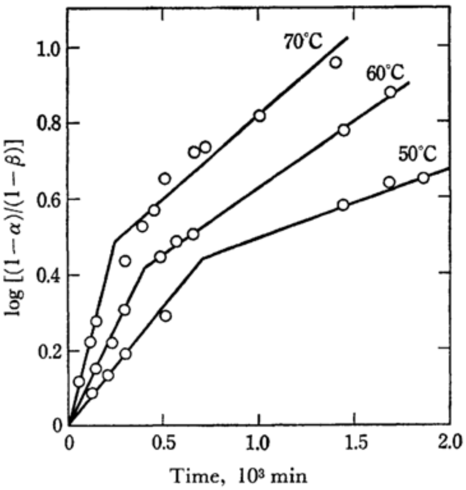


Fig. 3. Amination of SC-1 by di-*n*-butylamine.

The possible effect of this obstruction may be (i) electrostatic and/or (ii) steric. The electrostatic effect is less possible here, since amino groups formed on the polymer may not ionize because of a large excess of amine in the system and because of the rather non-polar property of dioxane as a solvent. The steric effect is more likely, since the amine molecules are presumably hindered from access to a reacting point by its nearest neighbors, which have bulky alkyl groups.

These assumptions have been examined by the aminations of a half-chloromethylated polystyrene, SC-2, and of ethylene dibromide, both of which are shown in Fig. 4. Since the plots are linear, the rates of these reactions are given fully by Eq. (1). The results support the second assumption (ii). If the effect of charged or polar groups is a dominant factor, the plots will not be linear, especially for ethylene dibromide. The linearity of the plot for SC-2 suggests, moreover, that the spacing of the groups can control the access of amine molecules. The value of k for SC-2, as computed by Eq. (2), is 4.61×10^{-3} l/mol min, which is comparable to that for benzyl chloride at the same temperature, 5.03×10^{-3} l/mol min.

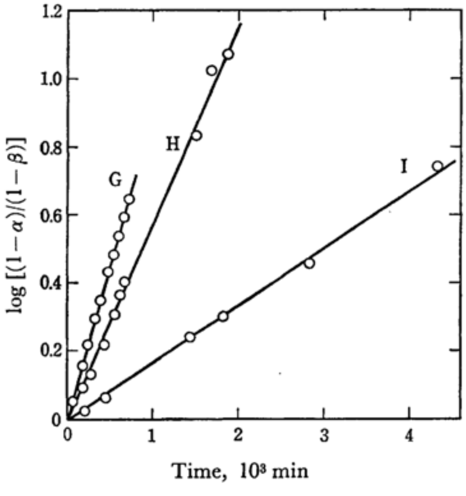


Fig. 4. Amination of half-chloromethylated polystyrene (SC-2) and ethylene bromide.

G: SC-2, *n*-butylamine, 60°C
H: Ethylene bromide, *n*-butylamine, 50°C
I : Ethylene bromide, di-*n*-butylamine, 60°C

Rate Equations

Derivation of the Rate Equations. In the reaction of chloromethylated polystyrene with the amines, two kinds of reactivity are assumed for chloromethyl groups, which are classified into the isolated ones which have a normal reactivity and the ones under the steric effect, both of whose nearest neighbors are already aminated. If each reaction is bimolecular and takes place separately, the rate constant for each reaction will be given by:

$$k = \frac{2.303}{(a-b)} \cdot \frac{\mathrm{d}\log[(1-\alpha)/(1-\beta)]}{\mathrm{d}t} \tag{3}$$

In the actual course of reaction, however, the two kinds of reaction may overlap. This situation is illustrated by Fig. 5, where the broken lines represent the assumed separated courses of reaction and the full line, the actual course of reaction. When the isolated chloromethyl groups are almost consumed at point P, only the groups under the steric effect remain and the actual curve lies essentially on the assumed one for the second step. Since the actual curve (full line) in the initial stage of reaction can be expressed approximately by the dotted line, the over-all course of the reaction may apparently be expressed by two straight lines intersecting at point Q. The experimental results summarized in Figs. 2 and 3 can be explained by this illustration based on the two-step-reaction concept.

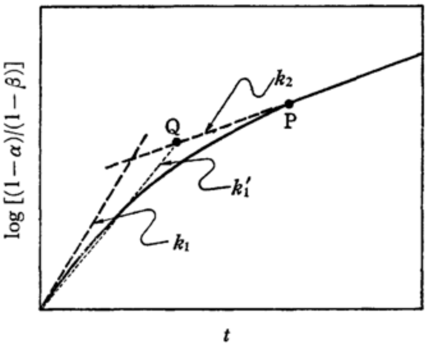
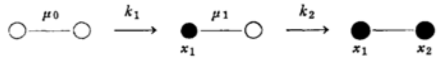


Fig. 5. Illustration of stepwise amination.

A polymer reaction of this kind may thus be reduced to a reaction between a low molecular compound with two reactive groups and a reagent, a reaction which is illustrated by the following figure:



where white circles represent unchanged groups and black circles, changed ones. The relationships among the concentrations are:

$$\mu_0 = M - x_1 = (b/2) - x_1 \tag{4}$$

$$\mu_1 = x_1 - x_2 = 2x_1 - x \tag{5}$$

where M is the initial concentration of the compound; μ_0 and μ_1 are the concentration of the unchanged and the partially-changed compound, respectively, at time t; b is the initial concentration of the reactive group; x is the change in the concentration of a reagent or the concentration of the changed group at time t, and x_1 and x_2 are concentrations of the first and second changed groups in the compound, respectively, at that time.

The over-all rate of the above reaction with the rate constants of k_1 and k_2 is given by :

$$\begin{aligned} dx/dt &= (a-x)(2k_1\mu_0 + k_2\mu_1) \\ &= (a-x)[k_1b - 2(k_1-k_2)x_1 - k_2x] \end{aligned} \tag{6}$$

where a is the initial concentration of a reagent.

On the assumption that $x \simeq x_1$ in the initial stage of reaction ($\beta < 0.5$) and $x_1 \simeq b/2$ in the final stage of reaction ($\beta > 0.5$), the integration of Eq. (6) yields:

$$k_1 = \frac{1}{[(2-k_2/k_1)a-b]t} \ln \frac{1-\alpha}{1-(2-k_2/k_1)\beta} \tag{7}$$

$$k_2 = \frac{1}{(a-b)(t-\tau)} \left(\ln \frac{1-\alpha}{1-\beta} - \ln \frac{1-\chi/a}{1-\chi/b} \right) \tag{8}$$

where τ is a time and χ is a value of x at a point, where $x_1 \simeq b/2$. An approximate value of k_1 may be obtained by Eq. (9), as is illustrated in Fig. 5:

$$k_1' = \frac{1}{(a-b)t} \ln \frac{1-\alpha}{1-\beta} \tag{9}$$

A value of k_1 can be determined from a value of k_2/k_1' by the use of Eq. (7).

When a large excess of a reagent is used, $(a-x)$ in Eq. (6) is replaced by a and x_1 is given by:

$$x_1 = (b/2)(1 - e^{-2k_1at}) \tag{10}$$

Thus, Eq. (6) integrates to:

$$x = b\left[1 - \frac{k_1-k_2}{2k_1-k_2} e^{-2k_1at} - \frac{k_1}{2k_1-k_2} e^{-k_2at}\right] \tag{11}$$

and the over-all rate is given by:

$$dx/dt = \frac{ab}{2k_1-k_2}[2k_1(k_1-k_2)e^{-2k_1at} + k_1k_2e^{-k_2at}] \tag{12}$$

Examination of the Equations by the *N*-Methylation of Ethylenediamine. The rate equation should first be tested on a low-molecular compound of two reactive groups as a model of the amination of chloromethylated polystyrene, where steric hindrance is a predominant factor. Since it was difficult to find such a compound, however, the equation have been examined by the *N*-methylation of ethylenediamine. Ethylenediamine is quantitatively *N*-methylated with an excess of methyl iodide in water, but the reaction is inhibited in the presence of excess acid. This fact means that the higher substitution of an amino group is inhibited, probably by the electrical charge formed on the methylated group. When one amino group of ethylenediamine is methylated, the charge of the group may also electrostatically hinder the methylation of another group on the same molecule. Thus, the reaction will proceed in two steps and the rate is given by Eq. (6), where a and b are the initial concentrations of methyl iodide and the amino group respectively. Figure 6, where α and β are fractional conversions of methyl iodide and the amino group respectively, shows that the reaction proceeds in two distinct steps. The value of k_2 is 1.30×10^{-2} l/mol min, a value which is obtained from the slope in the second step according to Eq. (8). An appropriate value for k_1', estimated according to Eq. (9), is 4.79×10^{-2} l/mol min. The values of k_1 obtained from repeated computations by Eq. (7) are 5.97×10^{-2} l/mol min for the first computation, 6.10×10^{-2} for the second, and 6.12×10^{-2} for the third.

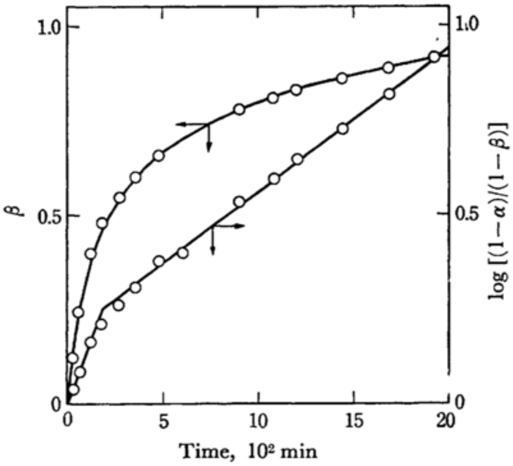


Fig. 6. *N*-Methylation of ethylenediamine in water at 30°C.

Discussion

The rate equations presented in the previous section were applied to the amination of chloromethylated polystyrene; the results of these calculations are summarized in Table 5.

Since a large excess of amine is used for the amination, the over-all course of reaction may be described by Eq. (11), using the values of k_1 and k_2 listed in Table 5. The values are compared in

TABLE 5. RATE CONSTANTS OF AMINATION OF SC-1

(a) *n*-Butylamine

Code	Temp. °C	Rate constants × 10³, *l*/mol min k_2 Eq. (8)	 k_1' Eq. (9)	 k_1 Eq. (7)	k_2/k_1
A	30	0.922	1.39	1.54	0.60
B	45	2.09	2.82	2.88	0.73
C	60	4.84	7.54	8.17	0.59

(b) Di-*n*-butylamine

Code	Temp. °C	Rate constants × 10³, *l*/mol min k_2 Eq. (8)	 k_1' Eq. (9)	 k_1 Eq. (7)	k_2/k_1
D	50	0.598	2.12	2.67	0.22
E	60	1.14	3.56	4.22	0.27
F	70	1.50	6.52	7.95	0.19

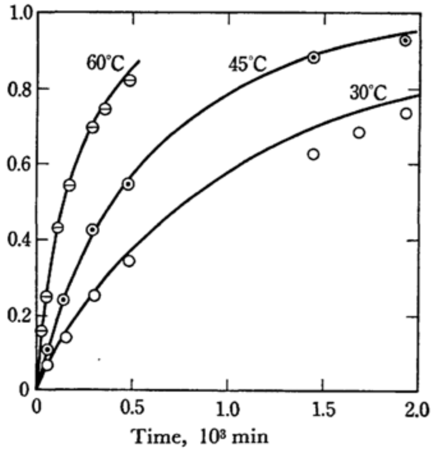


Fig. 7. Amination of SC-1 by *n*-butylamine.
○: 30°C ⊙: 45°C ⊖: 60°C

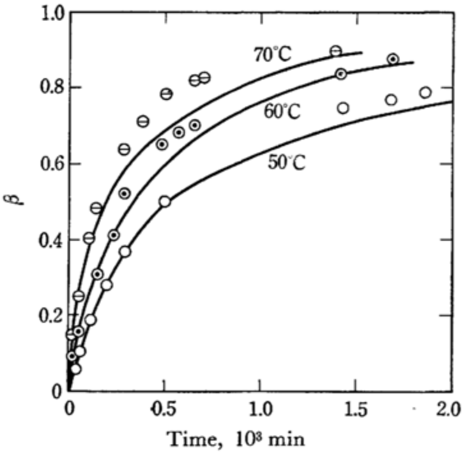


Fig. 8. Amination of SC-1 by di-*n*-butylamine.
○: 50°C ⊙: 60°C ⊖: 70°C

Figs. 7 and 8, where the full lines have been calculated by the use of Eq. (11) and where the circles represent the observed values. The reasonable agreement between the two values justifies the application of the rate equations to the polymer reaction. In Fig. 9, two runs, with *n*-butylamine and with di-*n*-butylamine, are compared; they have almost the same value of k_1. In the figure, β is divided into two components, *viz.* $\beta_1(=x_1/b)$ and $\beta_2(=x_2/b)$, by virtue of Eq. (10); the components apparently illustrate how overall rate is modified by the value of k_2, and also support the validity of the assumptions that $x \simeq x_1$ for the initial stage of reaction and that $x_1 \simeq b/2$ for the final stage.

The rate constants are plotted against $1/T$ in Fig. 10, while the values of E, the activation energy, as calculated by the least-squares method, are

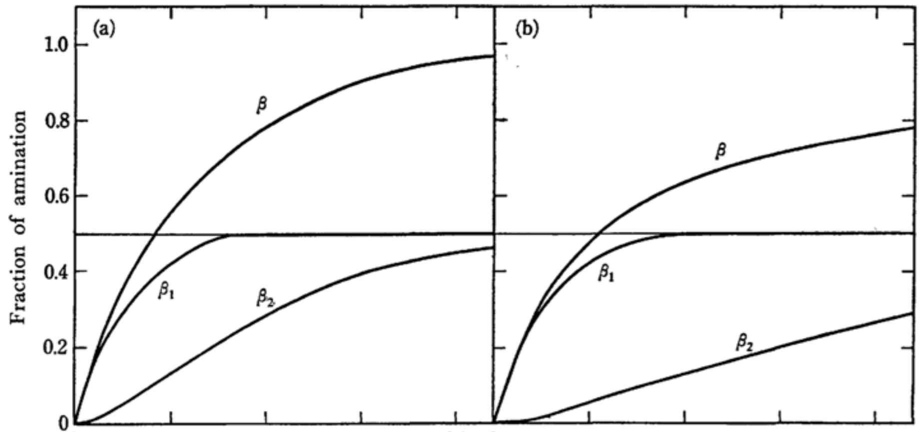


Fig. 9. Dependence of amination kinetics on the group interaction.
(a) Code B, *n*-butylamine, $k_1=2.88\ 10^{-3}$ *l*/mol min, $k_2=2.09\ 10^{-3}$ *l*/mol min
(b) Code D, di-*n*-butylamine, $k_1=2.67\ 10^{-3}$ *l*/mol min, $k_2=5.98\ 10^{-4}$ *l*/mol min

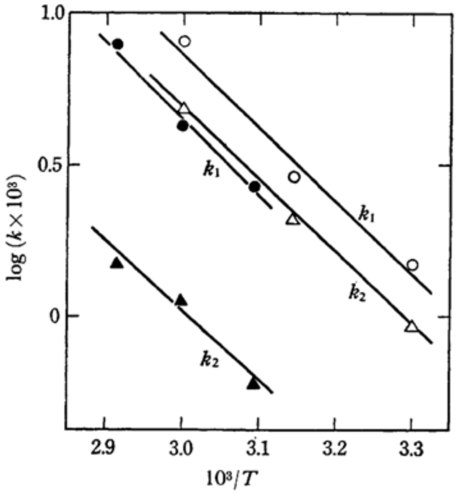


Fig. 10. Dependence of rate constants on temperature.

○, △: *n*-Butylamine
●, ▲: *n*-Dibutylamine

TABLE 6. ACTIVATION ENERGIES AND FREQUENCY FACTORS OF AMINATION OF SC-1

Amine		E kcal/mol	$A\times10^{-4}$ l/mol min
n-Butyl	k_1	11.1±1.3	14.5
	k_2	11.1±0.5	9.14
n-Dibutyl	k_1	12.0±0.9	8.69
	k_2	10.2±1.5	1.96

listed in Table 6, as are the mean values of A, the frequency factor, computed by means of:

$$k = A\cdot e^{-11100/RT}\ l/\text{mol min}$$

The values of E thus obtained are fairly constant, being comparable to that of the monomeric one. On the other hand, the A value for k_2 is lower than that for k_1, and the difference is significantly larger in *n*-dibutylamine than in *n*-butylamine. These facts also suggest that the abnormal decrease in the rate in the course of amination is due to the steric effect of the neighbors.

The authors wish to express their thanks to Mr. A. Oohata for his helpful assistance in preparing the polymers and in carrying out the measurements.