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Group Interactions in Polyelectrolytes. V. The Kinetics of the Amination of Chloromethylated Polystyrene with 2-Aminobutanol

Hiroshi KAWABE and Masaya YANAGITA

The Institute of Physical and Chemical Research, Wako-shi, Saitama

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The amination of chloromethylated polystyrene with 2-aminobutanol in dioxane was studied. The apparent rate constatns, k_{app}, as computed by the simple second-order equation, were found to increase linearly with the degree of amination; this was in contrast with the amination with *n*-butylamine, in which the k_{app} decreased as the amination proceeded. By assuming that the reactivity of the chloromethyl group is enhanced when it is situated next to the already-aminated group as a result of the "hydrophilic effect" of the hydroxyl group, rate equations which give the elementary rate constants were derived. In the presence of a large excess of amine, the over-all kinetics can be expressed by:

$$dx/dt = [ab/(3k_1-k_2)][3k_1(k_1-k_2)e^{-3k_1at} + 2k_1k_2e^{-k_2at}]$$

where x is the concentration of chloride ions at time t; where a is the initial concentration of amine, and b, that of the chloromethyl group, and where k_1 and k_2 are the rate constants of the elementary reactions which are independent of the neighboring group and under the influence of it respectively. The values of k_{app} calculated on the basis of k_1 and k_2 were also found to agree with the observed values.

Amination kinetics of chloromethylated polystyrene with *n*-butylamine or di-*n*-butylamine in dioxane was reported previously.[1] The apparent rate constant, as calculated by the simple second-order rate equation, k_{app}, decreased as the amination proceeded. The results were interpreted in terms of the two-step amination resulting from the steric effect of already-aminated neighboring groups, and the over-all kinetics in the presence of a large excess of amine could be expressed by an equation containing two rate constants.

In the present study, the amination of chloromethylated polystyrene with 2-aminobutanol has been carried out in dioxane, and k_{app} has been found to increase linearly with the degree of amination. The difference between the kinetic behavior in the amination of chloromethylated polystyrene with *n*-butylamine and with 2-aminobutanol is considered to arise from the different position of the amino group in the amines and the presence of the hydroxyl group in 2-aminobutanol. Analysis of the experimental data reveals that the amination proceeds in two steps. Rate equations for this reaction are derived on the basis of the kinetic data.

Experimental

Materials. Polystyrene and chloromethylated polystyrene were prepared by the procedure described in the previous paper;[1] their molecular weights were determined, by means of osmometry in toluene, to be 5.44×10^4 and 7.33×10^4 respectively. These results indicate that neither cross-linking nor degradation of the polymer occurred in the chloromethylation process. The chlorine content of the chloromethylated polystyrene, which was purified by reprecipitation with dioxane and methanol, was 22.87%, corresponding to the degree of chloromethylation of 97.8%. (−)-2-aminobutanol was prepared from its tartaric acid salt by the use of an ion-exchange resin column (Dowex-50, X-8, 20—50 mesh) according to the procedure reported by Tsuboyama *et al.*[2] It had a bp of 86—87°C/15 mmHg; n^{20} 1.4532; $[\alpha]^{20}_{D}$ −10.23. All the other chemicals were of a reagent grade, and de-ionized, de-carbonized water was used throughout the experiments.

Kinetic Measurement of the Amination. Fifty milliliters of a dioxane solution containing one gram of chloromethylated polystyrene, benzyl chloride, or ethylene bromide was throughly mixed with 100 m*l* of a dioxane solution containing a large excess of 2-aminobutanol (about twenty times as many moles as the chloromethyl group). The solution thus obtained was stirred during the reaction, and its temperature was maintained within ±0.1°C by means of a thermostat. Throughout the reaction, the system was kept homogeneous. At appropriate intervals, aliquots were taken out; each of them was poured into dilute nitric acid and titrated potentiometrically with 0.1 N silver nitrate. The experimental conditions are listed in Table 1.

TABLE 1. EXPERIMENTAL CONDITIONS OF AMINATION

Run	Temp. °C	Halide	$b^{b)}$ mol/l	$a^{b)}$ mol/l	a/b
A	40	Benzyl Chloride	0.0541	1.0561	19.5
B	50.5	Benzyl Chloride	0.0525	1.0538	20.1
C	60	Benzyl Chloride	0.0528	1.0550	20.0
D	70	Benzyl Chloride	0.0528	1.0542	20.0
E	70	Ethylene Bromide	0.0725	1.4212	19.6
F	40	CMPS[a)]	0.0430	0.8549	19.9
G	50	CMPS[a)]	0.0431	0.8590	19.9
H	60	CMPS[a)]	0.0441	0.8589	19.5
I	70	CMPS[a)]	0.0439	0.8641	19.7

a) Chloromethylated polystyrene (Cl: 22.87%)

b) a : initial concentration of 2-aminobutanol

b : initial concentration of halide expressed by mol of halogen per l

Results

Benzyl chloride was quantitatively aminated with 2-aminobutanol in dioxane, and its rate constant was

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

[2] K. Tsuboyama, S. Tsuboyama, and M. Yanagita, *Reports I.P.C.R.* (in Japanese), **41**, 194 (1965).

given by the second-order equation:

$$k=\frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(b-x)} \qquad (1)$$

where a is the initial concentration of the amine and b, that of benzyl chloride, while x is the concentration of chloride ions at time t. Although chloromethylated polystyrene was also quantitatively aminated with 2-aminobutanol in dioxane without any separation of the polymer, the rate constant computed by Eq. (1) increased as the reaction proceeded. The experimental results are summarized in Figs. 1 and 2, where t is the time and $\overline{kt}$ is the term defined as follows:

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

In the case of benzyl chloride (Fig. 1), the plot of $\overline{kt}$ against t is represented by a single line, while in the case of chloromethylated polystyrene (Fig. 2), the plot is divided into two lines which intersect at one-third of the amination. These results may be explained by assuming that the chloromethyl group of the polymer is aminated at a normal rate unless its neighboring group is changed, while the amination is accelerated when one of the nearest-neighbors is aminated. This assumption is partly supported by the amination of ethylene bromide shown in Fig. 3, where $\beta(=x/b)$ denotes the degree of amination. Acceleration, as expected, is observed in this reaction, though it is not very remarkable and the $\overline{kt}$ *vs.* t plot intersects nearly at half-amination. These results are in contrast with those of the amination of ethylene bromide with *n*-butylamine and di-*n*-butylamine, which is controlled by a single rate constant.[1]

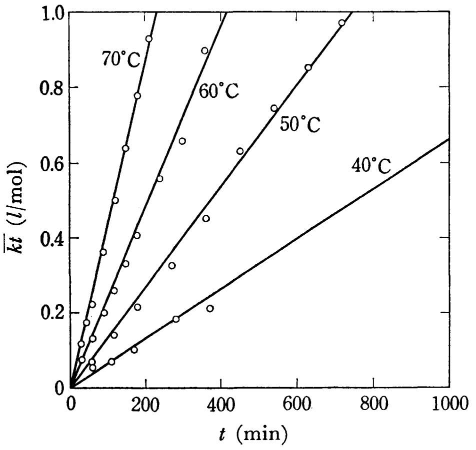

Fig. 1. Amination of benzyl chloride.

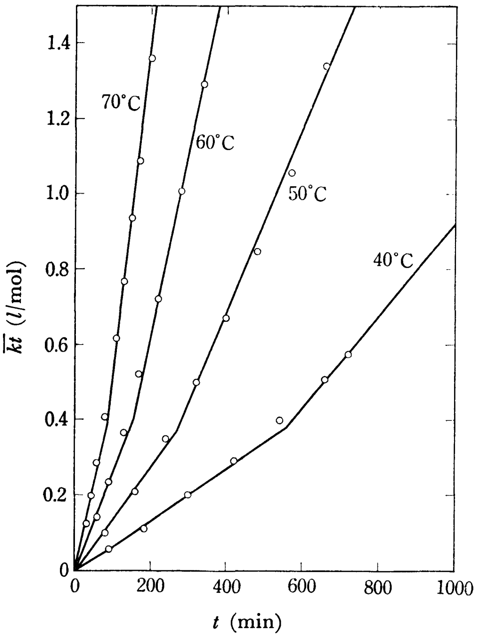

Fig. 2. Amination of chloromethylated polystyrene.

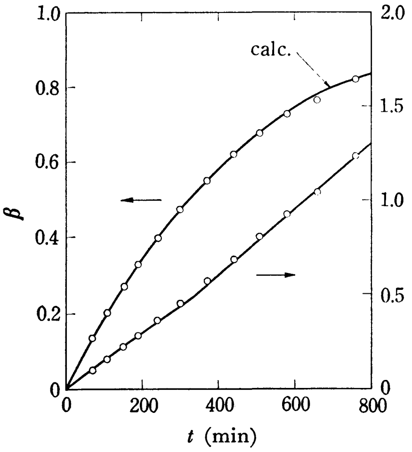

Fig. 3. Amination of ethylene bromide.

Sakurada[3] reported that the rate of the alkaline hydrolysis of polyvinyl acetate in an aqueous acetone solution increased as indicated in the following relation:

$$\mathrm{d}x/\mathrm{d}t=k_0(1+m\beta)(a-x)(b-x) \qquad (3)$$

where k_0 and m are constants and where $\beta=x/b$. On the other hand, we may express the rate of bimolecular polymer reaction by:

$$\mathrm{d}x/\mathrm{d}t=k_{\mathrm{app}}(a-x)(b-x) \qquad (4)$$

where k_{app} is the apparent rate constant. On the basis of Eqs. (3) and (4), we obtain the relation:

$$k_{\mathrm{app}}=k_0(1+m\beta) \qquad (5)$$

which means that k_{app} is a linear function of β.

The above relation has also been found in the present study to be applicable to the amination of chloromethylated polystyrene, as is shown in Fig. 4. The values of k_0 and m thus determined are listed in Table 2. Although k_0 increases with an increase in the tem-

TABLE 2. k_0 AND m IN THE AMINATION OF CHLOROMETHYLATED POLYSTYRENE

Run	Temp. °C	$k_0\times10^3$ l/mol min	m
F	40	0.56	1.14
G	50	1.12	1.20
H	60	2.10	1.24
I	70	3.78	1.16

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3) I. Sakurada, *Kobunshi*, **17**, 21 (1968). I. Sakurada and Y. Sakaguchi, *Kobunshi Kagaku*, **13**, 441 (1956).

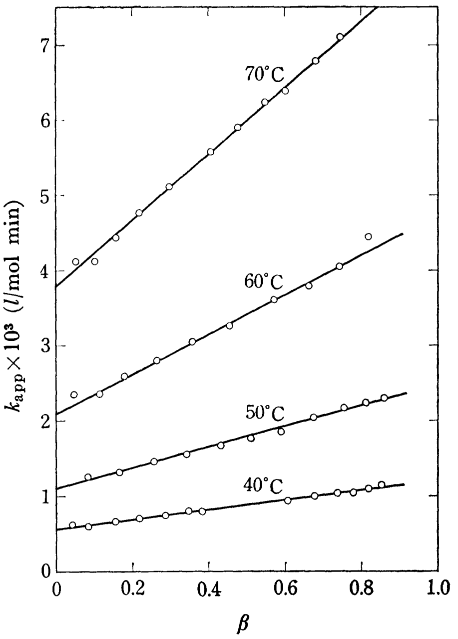


Fig. 4. Dependence of apparent rate constant on fractional conversion in the amination of chloromethylated polystyrene.

perature, m has an almost constant value irrespective of the temperature. It is interesting that these different kinds of reaction can be expressed by such a simple linear relation. It should be noted that k_{app} in the amination with n-butylamine or di-n-butylamine is not a linear function of β, but decreases markedly beyond half-amination.

Sakurada[3] ascribed the acceleration of the alkaline hydrolysis of polyvinyl acetate to the adsorption of alkali by the hydroxyl group formed in the polymer. He suggested the designation of "hydrophilic effect" for this phenomenon. It also seems possible that aminated groups in chloromethylated polystyrene adsorb 2-aminobutanol in dioxane because of the hydroxyl groups.

Rate Equations

The amination of chloromethylated polystyrene, as described in the preceding section, is a two-step reaction composed of two elementary reactions, one of which is independent of the neighbors and the other of which is accelerated by the neighboring aminated group. The rate equations for this reaction are derived on the model of low-molecular compounds to be described below.

Bifunctional Compound Model (Model I). The rate equation for a bifunctional compound, whose reactivity alters when one of the groups is changed, has previously been described.[1] It is given by:

$$\mathrm{d}x/\mathrm{d}t = (a-x)[k_1b - 2(k_2 - k_1)x_1 - k_2x] \tag{6}$$

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

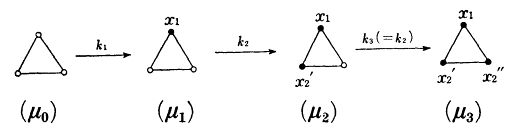
$$k_2 = \frac{1}{(a-b)(t-\tau)}\left(\ln\frac{1-\alpha}{1-\beta} - \ln\frac{1-\chi/a}{1-\chi/b}\right) \tag{8}$$

where x_1 is the concentration of the first changed group; τ and χ are the values of t and x when $x_1 \simeq b/2$; $\alpha = x/a$ and $\beta = x/b$. When a large excess of a reagent is used ($a \gg b$), the over-all kinetics is expressed by this equation:

$$\beta = 1 - \frac{k_1 - k_2}{2k_1 - k_2}\mathrm{e}^{-2k_1at} - \frac{k_1}{2k_1 - k_2}\mathrm{e}^{-k_2at} \tag{9}$$

The amination of ethylene bromide can properly be expressed by this equation. These rate equations were found to be useful in describing the amination kinetics of chloromethylated polystyrene with n-butylamine or di-n-butylamine, in which the amination of a chloromethyl group placed between two already-aminated neighbors is sterically hindered and the $\overline{kt}$ *vs.* t plot is divided into two lines intersecting nearly at $\beta = 0.5$.[1]

Trifunctional Cyclic Compound Model (Model II). In the reaction of chloromethylated polystyrene with 2-aminobutanol, in which the intersection lies nearly at $\beta = 1/3$, the amination of a chloromethyl group is assumed to be accelerated when one of its neighbors is aminated. Accordingly, the chloromethyl groups may be classified into three groups depending upon their environment; one is situated between unchanged neighbors, another is situated next to an aminated neighbor, while a third is situated between two aminated neighbors. In this case, the trifunctional cyclic compound model, shown below, is considered to be more suitable than Model I:



In the above figure illustrating the reaction of a trifunctional compound and a reagent, the white circles represent unchanged groups, and the black circles, changed groups. The relationships among the concentrations are:

$$\mu_0 = M - x_1 = (b/3) - x_1 \tag{10}$$

$$\mu_1 = x_1 - x_2,\ \mu_2 = x'_2 - x_2'' \tag{11}$$

$$x = x_1 + x_2,\ x_2 = x_2' + x_2'' \tag{12}$$

where M is the initial concentration of the compound and b, that of the reactive group of the compound; μ_n(n=0, 1, 2, and 3) is the concentration of the compound, n groups of which are changed at time t; x_1, x_2', and x_2'' are the concentrations of the first, secondary and last changed group respectively at time t. Since only two steps are observed in the amination of chloromethylated polystyrene with 2-aminobutanol, k_3 is simply assumed to be equal to k_2 in this case.

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

$$\begin{aligned}\mathrm{d}x/\mathrm{d}t &= (a - x)[3k_1\mu_0 + k_2(2\mu_1 + \mu_2)]\\ &= (a - x)[k_1b - 3(k_1 - k_2)x_1 - k_2x]\end{aligned} \tag{13}$$

where a is the initial concentration of a reagent. On the assumption that $x \simeq x_1$ in the initial stage of reaction ($\beta < 1/3$) and that $x_1 \simeq b/3$ in the final stage ($\beta > 1/3$), the integration of Eq. (13) yields:

$$k_1 = \frac{1}{[(3 - 2k_2/k_1)a - b]t}\ln\frac{1-\alpha}{1-(3-2k_2/k_1)\beta} \tag{14}$$

$$k_2 = \frac{1}{(a-b)(t-\tau')}\left[\ln\frac{1-\alpha}{1-\beta} - \ln\frac{1-\chi'/a}{1-\chi'/b}\right] \qquad (15)$$

where τ' is a time when $x_1 \simeq b/3$ and χ' is a value of x at this time. When a large excess of reagent is used ($a \gg b$), the term ($a-x$) in Eq. (13) can be replaced by a, and x_1 is given by:

$$x_1 = b(1 - e^{-3k_1at})/3 \qquad (16)$$

Hence, by integrating Eq. (13), we obtain;

$$x = b\left[1 - \frac{k_1 - k_2}{3k_1 - k_2}e^{-3k_1at} - \frac{2k_1}{3k_1 - k_2}e^{-k_2at}\right] \qquad (17)$$

and the over-all rate is given by:

$$dx/dt = \frac{ab}{2k_1 - k_2}[2k_1(k_1 - k_2)e^{-2k_1at} + k_1k_2\,e^{-k_2at}] \qquad (18)$$

Equations (14) and (15) can also be derived by considering the polymer reaction itself. The relative position of changed groups on a polymer molecule may be illustrated as follows:

---●—○—○—○—●-----●—●-----●—○—●---

x_1 x_1 x_1 x_2 x_1 x_1

[I] [II] [III]

Two groups may be situated independently (I), side by side (II), or with an unchanged group between them (III). In the initial stage of the reaction, the situation [III] can be neglected; the rate is then given by:

$$\begin{aligned} dx/dt &= dx_1/dt + dx_2/dt \\ &= (a-x)[k_1\{(b-x) - 2x_1\} + 2k_2x_1] \qquad (19)\end{aligned}$$

On the assumption that $x \simeq x_1$ in the initial stage, we obtain;

$$dx/dt = (a-x)[k_1b - (3k_1 - 2k_2)x] \qquad (20)$$

In the final stage of the reaction, only reactive groups next to the changed group are left and the rate is given by:

$$dx/dt = k_2(a-x)(b-x) \qquad (21)$$

By integrating Eqs. (20) and (21), we obtain Eqs. (14) and (15) respectively.

Discussion

The rate constants of the amination of ethylene bromide at 70°C were calculated on the basis of Eqs. (7) and (8) for Model I (bifunctional compound model) to give $k_1 = 1.39 \times 10^{-3}$ ($k_1' = 1.45 \times 10^{-3}$) and $k_2 = 1.91 \times 10^{-3}$ l/mol min respectively; k_1' is an approximate value of k_1 which is obtained from the slope of the $\overline{kt}$ *vs.* t plot according to:

$$k_1' = \Delta\overline{kt}/\Delta t \qquad (22)$$

The values of β calculated on the basis of Eq. (9) by using the above values of k_1 and k_2 are plotted against t in Fig. 3, in which a solid line show this calculated plot. The experimental values, which are represented by white circles, fall excellently on this plot.

In the case of chloromethylated polystyrene, the rate constants were calculated on the basis of Eqs. (7) and (8), on the one side, and on the basis of Eqs. (14) and (15) for Model II (the trifunctional compound model), on the other side. The results are summarized in Table 3, where the rate constants of benzyl chloride are also listed. The over-all kinetics expressed by Eq. (9) for Model I and by Eq. (17) for Model II were evaluated by using the respective values of k_1 and k_2. In Fig. 5, the broken and solid lines are the calculated plots for Model I and II respectively, and the white circles represent observed values. The agreement of the calculated and observed values are not so excellent as in the case of ethylene bromide, though Model II expresses the experimental results more closely than does Model I.

Table 3. Rate constants of the amination with 2-aminobutanol

Temp.	Rate constants $\times 10^3$, l/mol min				
	Chloromethylated polystyrene				Benzyl chlorride
	k_1'	k_1		k_2	k
°C		Model I	Model II	Eq. (8)	
	Eq. (22)	Eq. (7)	Eq. (14)	or (15)	Eq. (1)
40	0.709	0.596	0.529	1.32	0.678
50	1.41	1.19	1.05	2.77	1.35
60	2.78	2.25	2.07	4.81	2.46
70	4.49	4.04	3.51	9.30	4.48

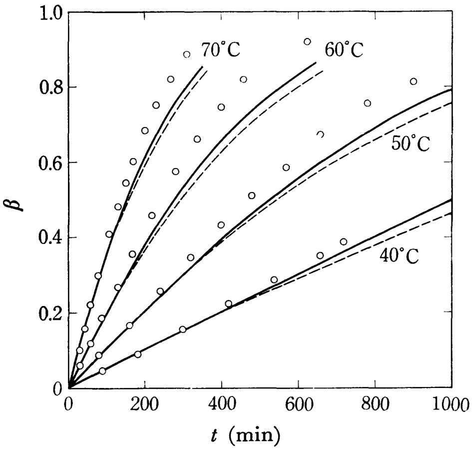


Fig. 5. Amination of chloromethylated polystyrene.
---- calculated for Model I
—— calculated for Model II
○ observed values

Equation (6) for Model I can be expressed in the form of Eq. (3) as follows:

$$dx/dt = k_1\left[1 + (k_2/k_1 - 1)\left(\frac{2\beta_1/\beta - 1}{1-\beta}\right)\beta\right](a-x)(b-x)) \qquad (23)$$

where β_1 is given by the following equation when $a \gg b$:

$$\beta_1 = x_1/b = (1 - e^{-2k_1at})/2 \qquad (24)$$

By comparing Eqs. (23) with (4), we obtain:

$$k_{app}/k_1 = 1 + (k_2/k_1 - 1)(2\beta_1 - \beta)/(1 - \beta) \qquad (25)$$

Equation (13) for Model II can also be transformed to:

$$dx/dt = k_1\left[1 + (k_2/k_1 - 1)\left(\frac{3\beta_1/\beta - 1}{1-\beta}\right)\beta\right] \qquad (26)$$

and:

$$k_{app}/k_1 = 1 + (k_2/k_1 - 1)(3\beta_1 - \beta)/(1 - \beta) \tag{27}$$

where β_1 is given by Eq. (16) when $a \gg b$.

The value of k_{app} at a given time can be calculated as a function of k_1, k_2, and t on the basis of Eqs. (25) and (27) respectively; the calculated values are compared with the observed values in Fig. 6. The agreement of the two sets of values is better in Model II than in Model I.

On the other hand, k_{app}/k_1 in Eqs. (25) and (27) has the same meaning as k_{app}/k_0 in Eq. (5), since the values of k_0 and k_1 are almost the same, as is shown in Tables 2 and 3. The plots of k_{app}/k_0 against β for Model I, Model II, and the original data are shown in Fig. 7. The plot for Model II is closer to the observed one than is that for Model I.

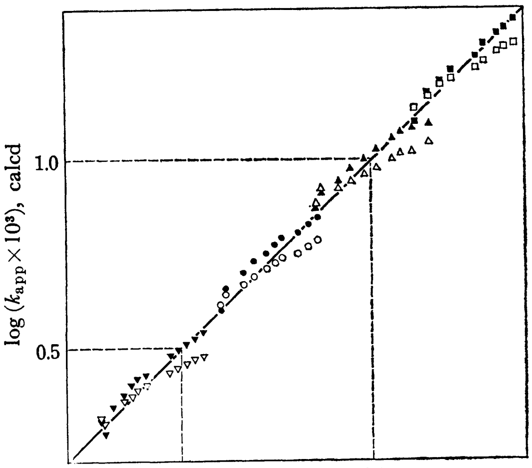


Fig. 6. Comparison between calculated and observed values of apparent rate constant in the amination of chloromethylated polystyrene.
Model I ▽ : 40°C, ○ : 50°C, △ : 60°C, □ : 70°C
Model II ▼ : 40°C, ● : 50°C, ▲ : 60°C, ■ : 70°C

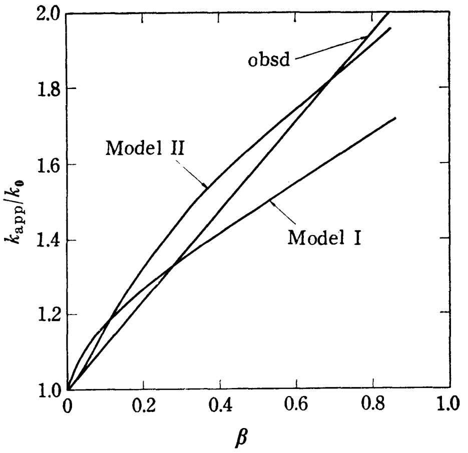


Fig. 7. Plots of k_{app}/k_0 *vs.* β in the amination of chloromethylated polystyrene.

It may be concluded, on the basis of the facts to be summarized below, that Model II is better for such a self-accelerated reaction as that shown in the present study: (i) the intersection in the $\overline{kt}$ *vs.* t plot lies near $\beta = 1/3$; (ii) the amination of ethylene bromide is also self-accelerated; (iii) the rate equations for Model II which give k_1 and k_2 can be derived in terms of the polymer reaction; (iv) the calculated plot of β *vs.* t for Model II is closer to the observed one than is that for Model I, and (v) the k_{app} values calculated for Model II are almost the same as the observed values.

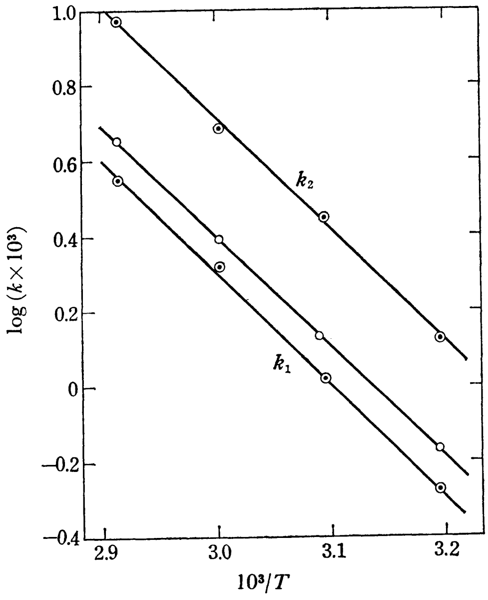


Fig. 8. Dependence of rate constants on temperature in the amination with 2-aminobutanol.
○ : Benzyl chloride
⊙ : Chloromethylated polystyrene

The Arrhenius plots of the rate constants listed in Table 3 are shown in Fig. 8, where the plot for k_1 is the one calculated on the basis of Model II. The values of E_a, the activation energy, which were calculated by the least-squares method, are listed in Table 4, where the mean values of A, the frequency factor, have been computed by means of:

$$k = A \exp(-E_a/\boldsymbol{R}T) \ l/\text{mol min}$$

In the table are also listed the mean value of $\Delta S_0^{\ddagger}$, the entropy of activation, which was calculated by:

$$A/60 = e(\boldsymbol{k}T/\boldsymbol{h}) \exp(\Delta S_0^{\ddagger}/\boldsymbol{R})$$

Table 4. Activation energies, frequency factors, and activation entropies of amination

Halide	Amine		E_a kcal/mol	A l/mol min	$\Delta S_0^{\ddagger}$ cal/deg mol
Chloromethylated polystyrene	2-Aminobutanol	k_1	13.6±0.2	1.57×10⁶	−40.5
		k_2	13.6±0.1	4.50×10⁶	−38.4
Benzyl chloride	2-Aminobutanol		13.4±0.1	1.60×10⁶	−40.5
Benzyl chloride	*n*-Butylamine		12.5±0.2	7.88×10⁵	−41.8

where e=2.713, $\boldsymbol{k}$ is the Boltzmann constant, and $\boldsymbol{h}$, the Planck constant; the standard state refers to a unit concentration of one mole per liter.

The same value of E_a is obtained for k_1 and k_2; this value is comparable to that of the monomeric one, benzyl chloride. The value of A or $\Delta S_0^{\ne}$ for k_2 is slightly higher than that for k_1, whereas the latter is consistent with the values for benzyl chloride. This suggests that the amination of chloromethylated polystyrene proceeds normally in the initial stage.

The above-described facts also support the assumption that the self-acceleration in the amination is due to the adsorption of 2-aminobutanol by the hydroxyl group in the nearest-neighbor. In addition, the stronger self-acceleration has been observed in the amination with diethanolamine in dioxane.[4] On the other hand, such a steric hindrance of the neighboring groups as is observed in the amination with *n*-butylamine has not been found in the amination with 2-aminobutane in dioxane.[4] The "hydrophilic effect" of the hydroxyl group can, therefore, be considered to be the predominant factor in the amination of chloromethylated polystyrene with 2-aminobutanol in dioxane.

The authors wish to express their thanks to Mr. M. Takahashi for his technical assistance in preparing the polymer and in carrying out the measurement.

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[4] The present authors' unpublished data.