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Group Interactions in Polyelectrolytes. II. Kinetics of Alkaline Hydrolysis of Polymethyl Acrylate

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The second-order rate constant of the alkaline hydrolysis of polymethyl acrylate in an aqueous acetone solution decreases as the reaction proceeds. The plot of the logarithmic term of the second-order rate equation against the reaction time is divided into four lines; this suggests that the reaction proceeds in four steps. The rate equation of the reaction can be derived by assuming that the reactivity of ester groups is electrically affected mainly by a few neighboring hydrolyzed groups. The kinetic behavior is compared with the titration data of polyacrylic acid; the sets of data can be correlated through a simple equation containg two constants, k_0, the intrinsic rate constant, and pK_0, the intrinsic ionization constant.

Kawabe and Yanagita[1] studied the kinetics of the reaction of chloromethylated polystyrene with *n*-butylamine and di-*n*-butylamine in dioxane; they found that the apparent rate constant computed by the simple second-order rate equation decreased continuosly as the reaction proceeded, and that the plot of the logarithmic term in the equation against the reaction time was divided into two straight lines. The kinetics could be expressed by the rate equation of a two-step reaction derived by assuming two distinct reactivities of chloromethyl groups, depending on their environments.

In the present study, the above procedure of plotting the logarithmic term against the time has been applied to the published kinetic data of the alkaline hydrolysis of polymethyl acrylate;[2] it has been thus revealed that the reaction in a 29% (v/v) aqueous acetone solution proceeds in four steps. The rate equation for this reaction has been derived by assuming that the reactivity of the ester group on the macromolecule is electrostatically affected mainly by a few already-hydrolyzed groups situated within relatively short distance. The derived equation has first been examined in the alkaline hydrolysis of model compounds, such as dimethyl succinate and triethyl citrate. The results obtained by the application of the equation to polymethyl acrylate has then been discussed in relation to the titration data of polyacrylic acid.

Experimental

Materials. The polyacrylic acid used for the titration was prepared by the alkaline hydrolysis of polymethyl acrylate. One hundred grams of methyl acrylate containing 3 g of benzoyl peroxide were added, drop by drop, to boiling methyl ethyl ketone over the period of an hour, and then the solution was stirred for five hours. The solution was then poured into petroleum ether to precipitate polymethyl acrylate, which was dried in a vacuum oven, dissolved in acetone, and again precipitated in water. The purified polymer was hydrolyzed with sodium hydroxide in an aqueous acetone solution according to the procedure described in the literature.[2] The dry sodium salt of polyacrylic acid was dissolved in water and converted to polyacrylic acid by passing the solution through a column of Dowex-50 (X-8) in hydrogen form.

Titration of Polyacrylic Acid. An aqueous solution of polyacrylic acid (0.05 equiv/*l*) was titrated with a 0.1 N sodium hydroxide solution at 25°C; the pH of the solution was measured by means of a Beckman Model G pH meter.

Alkaline Hydrolysis of Dimethyl Succinate and Triethyl Citrate. Alkaline hydrolyses of dimethyl succinate and teiethyl citrate were carried out in water and in a 32% (v/v) aqueous ethanol solution respectively, both containing a slight excess of sodium hydroxide. During the course of this reaction, the temperature was kept constant to ±0.1°C. The rate of hydrolysis was followed, according to the usual method, by the removal of aliqots at appropriate intervals of time, pouring them into water containing an excess of hydrochloric acid, and titrating them with 0.1 N sodium hydroxide.

When a large excess of sodium hydroxide (about ten times as much as the moles of the ester group) was used as a hydrolyzing agent, it interfered with the precise determination of the percentage of hydrolysis in the usual method. Sodium ions in the solution, however, could be effectively removed by the use of Dowex-50. It was ascertained by preliminary tests that sodium ions in an aqueous solution containing succinic acid or citric acid, and also excess sodium hydroxide, could be removed practically at once and completely

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

[2] I. Sakurada, Y. Sakaguchi and S. Fukui, *Kobunshi Kagaku* (*Chem. High Polymers Japan*), **13**, 355, 361, 408 (1956).

within 45 sec by stirring the solution in the presence of Dowex-50 (X-8, 50—100 mesh) in hydrogen form, and also that the esters were not hydrolyzed, at least during the first 10 min. In the kinetic runs in which a large excess sodium hydroxide was used, portions of the reaction mixture were poured into water containing Dowex-50, which had previously been half neutralized, and the mixture was stirred for a few minutes. After the resin had then been removed, the solution was titrated with 0.1N sodium hydroxide. This method was tentatively applied to a run in which accurate determination by the usual method was possible; both methods produced the same results.

Rate Equations

The rate equation for a polymer reaction which proceeds in two steps has already been derived, in a previous paper,[1] by assuming two distinct reactivities of reactive groups, depending on their environments, and by rearranging the polymer reaction for a reaction between a low-molecular compound with two reactive groups and a reagent. If it is assumed, in a polymer reaction which proceeds in more than two steps, that any step of the reaction is controlled by two reactivities, the rate equation of the reaction can be similarly derived by considering the reaction of a low-molecular compound with a few reactive groups and a reagent, as is illustrated below:

$$\underset{(\mu_{n-1})}{\mathrm{X}_{n-1}\mathrm{Y}_{\sigma-(n-1)}} \xrightarrow{k_n} \underset{(\mu_n)}{\mathrm{X}_n\mathrm{Y}_{\sigma-n}} \xrightarrow{k_{n+1}} \underset{(\mu_{n+1})}{\mathrm{X}_{n+1}\mathrm{Y}_{\sigma-(n+1)}}$$

where X represents a changed group in a compound, and Y, an unchanged one; the suffix indicates the number of the group, in which σ is the total number of the group. The relationship among the concentrations are:

$$\mu_0 = M - x_1 = (b/\sigma) - x_1 \qquad (1)$$

$$\mu_n = x_n - x_{n+1} \qquad (2)$$

where M is the initial concentration of the compound; μ_0 and μ_n, the concentrations of the unchanged compound and the partially-changed one, n groups of which have been changed at time t; b, the initial concentration of the group, and x_1 and x_n, the concentrations of the first and nth changed groups respectively at time t.

By assuming the bimolecular mechanism for the individual reaction of each group, the over-all rate of the above reaction with σ rate constants is given by:

$$\mathrm{d}x/\mathrm{d}t = \sum_{n=1}^{\sigma}\mathrm{d}x_n/\mathrm{d}t = (a-x)\sum_{n=1}^{\sigma}(\sigma-n+1)k_n\mu_{n-1} \qquad (3)$$

where a is the initial concentration of a reagent and where x is the change in the concentration of a reagent or the concentration of the changed group at time t; k_n is the rate constant of the elementary reaction, *i.e.*, the reaction of the nth group. When it is assumed in any step of the reaction that its main part is practically composed of two elementary reactions at most, the rate can be formulated for the nth step by introducing $\mu_{n-2}\simeq 0$ and $\mu_{n+1}\simeq 0$ into Eq. (3) and by then combining Eq. (3) with Eq. (4):

$$x_{n-1} \simeq b/\sigma, \quad x_n \simeq x - b(n-1)/\sigma \qquad (4)$$

Thus, Eq. (3) becomes:

$$\mathrm{d}x/\mathrm{d}t = (a-x)[\{(\sigma-n+1)nk_n-(\sigma-n)(n-1)k_{n+1}\}b/\sigma - \{(\sigma-n+1)k_n-(\sigma-n)k_{n+1}\}x] \qquad (5)$$

Upon integration, Eq. (5) yields:

$$k_n = \frac{\ln[(1-\alpha)/(1-A\beta/B)] - \ln[(1-\chi_{n-1}/a)/(1-A\chi_{n-1}/Bb)]}{(Aa-Bb)(t-\tau_{n-1})} \qquad (6)$$

where τ_{n-1} is the time and χ_{n-1} is the value of x at a point where $x_{n-1}\simeq b/\sigma$; $\alpha(=x/\mathrm{a})$ is a fractional conversion of a reagent, and $\beta(=x/\mathrm{b})$ is that of the reactive group. A and B are:

$$\begin{cases} A = (\sigma-n+1) - (\sigma-n)k_{n+1}/k_n \\ B = [(\sigma-n+1)n - (\sigma-n)(n-1)k_{n+1}/k_n]/\sigma \end{cases}$$

When $\sigma=2$, k_1 and k_2 are given as follows:

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

$$k_2 = \frac{1}{(a-b)(t-\tau_1)}\left(\ln\frac{1-\alpha}{1-\beta} - \ln\frac{1-\chi_1/a}{1-\chi_1/b}\right) \qquad (8)$$

These equations are the same as those which have been derived directly for the two-step reaction in the previous paper,[1] in which the over-all course of the reaction with a large excess of reagent was also expressed by the equation:

$$\beta = 1 - \frac{k_1-k_2}{2k_1-k_2}e^{-2k_1at} - \frac{k_1}{2k_1-k_2}e^{-k_2at} \qquad (9)$$

When $\sigma=3$, Eq. (6) also yields three equations to determine k_1, k_2, and k_3. In the case with a large excess of reagent, the over-all kinetics can be expressed by a combination of two simple rate equations, each of which is derived on the assumption that the rate is cotrolled mainly by two rate constants in some range of β. If the reaction in the range of β, *i.e.*, 0—2/3, is assumed to be controlled by k_1 and k_2, Eq. (3) is simplified to:

$$\mathrm{d}x/\mathrm{d}t = a[k_1b - (3k_1-4k_2)x_1 - 2k_2x] \qquad (10)$$

and x_1 is given by:

$$x_1 = -(1-e^{-3k_1at})b/3 \qquad (11)$$

Upon integration, Eq. (10) becomes:

$$\beta = \frac{2}{3} - \frac{(3k_1-4k_2)}{3(3k_1-2k_2)}e^{-3ak_1t} - \frac{k_1}{3k_1-2k_2}e^{-2ak_2t} \qquad (12)$$

Similarly, in the 1/3—1 range of β, the following equations can be derived:

$$\mathrm{d}x/\mathrm{d}t = \mathrm{a}[(2k_2+k_3)b/3-2(k_2-k_3)x_2-k_3x] \qquad (13)$$

$$x_2 = (1-e^{-2k_2a(t-t_{1/3})})b/3 \qquad (14)$$

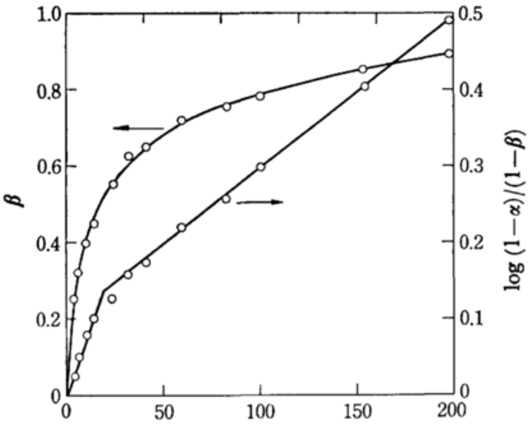

Fig. 1. Alkaline hydrolysis of dimethyl succinate in water at 10°C. (Run A)

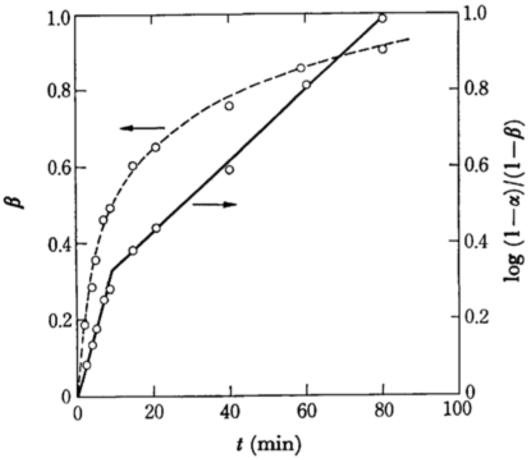

Fig. 2. Alkaline hydrolysis of dimethyl succinate in water containing a large excess of sodium hydroxide at 4.5°C. (Run B)

Upon integration, Eq. (13) then yields:

$$\beta = 1 - \frac{2(k_2-k_3)}{3(2k_2-k_3)}e^{-2k_2a(t-t_{1/3})} - \frac{2k_2}{3(2k_2-k_3)}e^{-k_3a(t-t_{1/3})} \tag{15}$$

where $t_{1/3}$ is the time, when β is 1/3.

Results and Discussion

Alkaline Hydrolysis of Dimethyl Succinate. The results obtained in the alkaline hydrolysis of dimethyl succinate in an aqueous solution are shown in Figs. 1 and 2. The apparent rate constant, $k_{\rm app}$, computed by Eq. (16) decreases as the reaction proceeds:

$$k_{\rm app} = \frac{1}{(a-b)t}\ln\frac{b(a-x)}{a(b-x)} = \frac{2.303}{(a-b)t}\log\frac{1-\alpha}{1-\beta} \tag{16}$$

where a and b are the initial concentrations of sodium hydroxide and the ester group, and where α and β are their fractional conversions, respectively. Plots of the logarithmic term of Eq. (16) against the time, which are shown in the figures, consist of two straight lines which intersect nearly at $\beta=0.5$, in accordance with the two-step reaction mechanism. The rate constants calculated by means of Eqs. (7) and (8) are shown in Table 1. Since a large excess of sodium hydroxide was used for the run B, the over-all course of reaction can be expressed by Eq. (9), using k_1 and k_2 values listed in Table 1. The calculated values are in good agreement with the observed values, as may be seen in Fig. 2, where the dotted line and the circles show the calculated and the observed values respectively.

TABLE 1. RATE CONSTANTS OF ALKALINE HYDROLYSIS OF DIMETHYL SUCCINATE

Run	Temp. °C	Concn. (10^{-2} mol/l) a	b	k_1 l/mol min	k_2 l/mol min	$\log(k_1/k_2)$
A	10	1.93	1.41	4.92	0.880	0.75
B	4.5	3.38	0.26	3.63	0.684	0.73

Since the numerical difference between k_1 and k_2 is based on the electrostatic effect of the first hydrolyzed group in the reaction of the second group, the electrostatic free energy of activation, $\varDelta F_{\rm el}^{\ddagger}$, is given by:

$$\varDelta F_{\rm el}^{\ddagger} = 2.303\boldsymbol{RT}\log(k_1/k_2) \tag{17}$$

where T is the temperature of the reaction. On the other hand, the electrostatic free energy of ionization, $\varDelta F_{\rm el}^{\rm i}$, of succinic acid is given by:

$$\varDelta F_{\rm el}^{\rm i} = 2.303\boldsymbol{R}T'({\rm p}K_2-{\rm p}K_1-\log 4) \tag{18}$$

$$\varDelta F_{\rm el}^{\rm i} = \boldsymbol{N}e^2/Dr \tag{19}$$

where T' is the temperature of the titration; pK_1 and pK_2 are negative logalithms of the ionization constants at the first and second ionization steps respectively; D is the effective dielectric constant, and r is the distance between the two ionizable groups. If the two electrostatic free energies are equal, a simple correlation between the titration and kinetic data may be established; the distance between the groups may also be estimated on the basis of the kinetic data by means of the above equations. On the basis of the dissociation constant data,[3] the pK_1 and pK_2 values of succinic acid at 10°C are found to be 4.246 and 5.649 respectively. By the use of Eqs. (17) and (18), log (k_1/k_2) is calculated to be 0.80; this is quite close to the kinetically-obtained values, which are given in Table 1. Furthermore, if D is assumed to

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[3] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London (1955), p. 521.

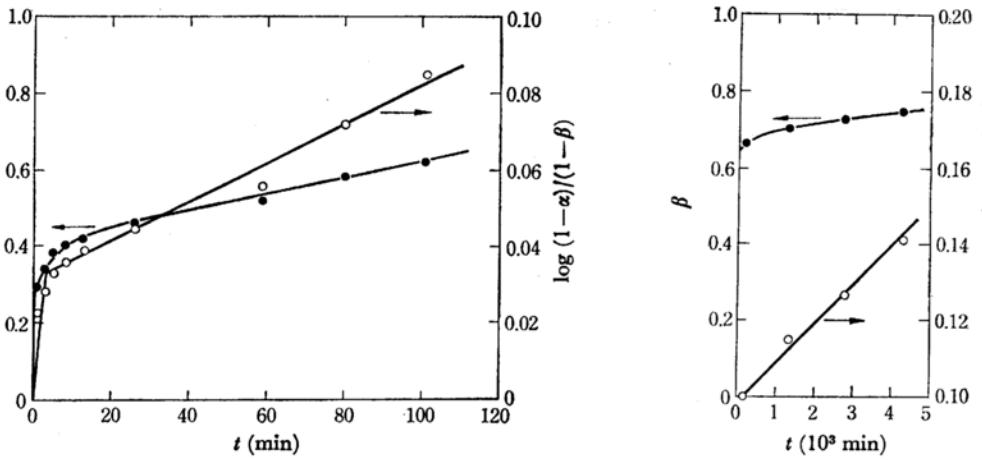

Fig. 3. Alkaline hydrolysis of triethyl citrate in 32% aqueous ethanol solution at 10°C. (Run D)

TABLE 2. RATE CONSTANTS OF ALKALINE HYDROLYSIS OF TRIETHYL CITRATE

Run		C	D	E	F
Concn., l/mol min	a	1.32×10^{-2}	2.97×10^{-2}	7.26×10^{-2}	2.95×10^{-1}
	b	1.34×10^{-2}	2.59×10^{-2}	6.70×10^{-2}	2.58×10^{-1}
k_n', l/mol min	k_1'	6.48	(5.46)		
	k_2'	(2.31×10^{-1})	3.10×10^{-1}	4.11×10^{-1}	
	k_3'		(5.90×10^{-3})	6.46×10^{-3}	6.47×10^{-3}
k_n, l/mol min	k_1	7.93			
	k_2		5.66×10^{-1}	6.43×10^{-1}	
	k_3			6.46×10^{-3}	6.47×10^{-3}

( ) shows less accurate measurement.

be 81, a reasonable value of 4.4 Å can be calculated for r by the use of Eqs. (17) and (19).

Alkaline Hydrolysis of Triethyl Citrate. The alkaline hydrolysis of triethyl citrate in a 32% aqueous ethanol solution was carried out at 10°C; an example of the kinetic runs is graphically shown in Fig. 3. The plot of the logarithmic term of Eq. (16) against the time is divided into three lines, which intersect nearly at $\beta=1/3$ and $\beta=2/3$; this indicates that the reaction proceeds in three steps. The experimental results are summarized in Table 2, where k_n' is the approximate value of the rate constant of the nth step, estimated by:

$$k_n' = [2.303/(a-b)]\times[\Delta\log\{(1-\alpha)/(1-\beta)\}/\Delta t] \quad (20)$$

The corrected value of the rate constant, k_n, has been calculated according to Eq. (6), assuming $\sigma=3$. An average value of k_2, 6.05×10^{-1} l/mol·min, is used for the calculation of k_1.

The reaction was also carried our by using a large excess of sodium hydroxide and the observed values were compared with those calculated by means of Eqs. (12) and (15). In Fig. 4 the circles represent the observed values, while the full and dotted lines are obtained by means of Eqs. (12) and

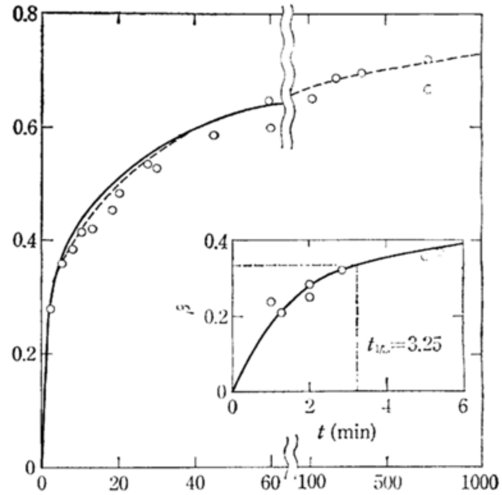

Fig. 4. Alkaline hydrolysis of triethyl citrate in 32% aqueous ethanol solution containing a large excess of sodium hydroxide at 10°C. ($a=3.38\times10^{-2}$, $b=3.04\times10^{-3}$ mol/l)

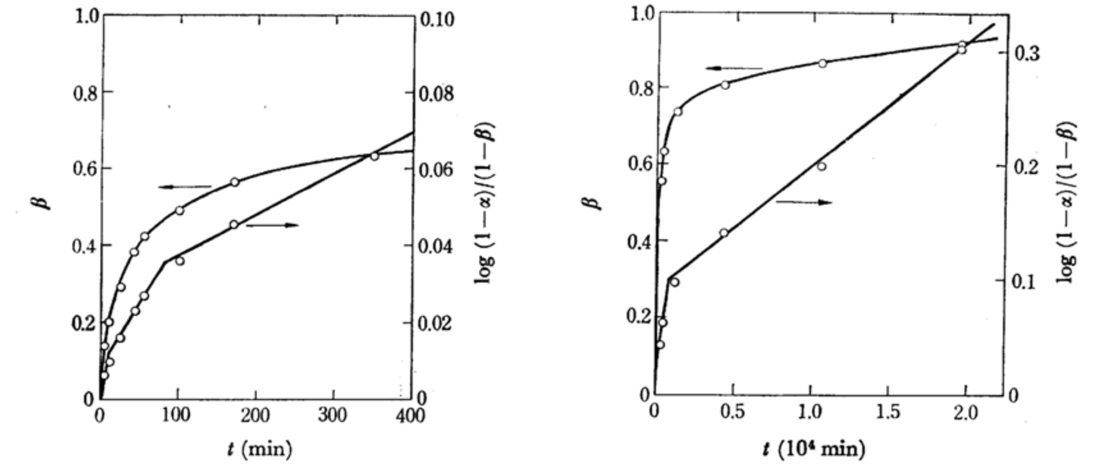

Fig. 5. Alkaline hydrolysis of polymethyl acrylate in 29% aqueous acetone solution at 55°C.[2)] (a=8.22×10^{-2}, b=7.41×10^{-2} mol/l)

(15) respectively, where the rate constants are: k_1=7.93, k_2=6.05×10^{-1}, and k_3=6.46×10^{-3} l/mol·min. The fairly good agreement between the two values in the figure may show the correctness of the application of the rate equations to a reaction which proceeds in more than two steps.

Application of the Rate Equations to the Alkaline Hydrolysis of Polymethyl Acrylate. When an ester of polymeric acid is hydrolyzed in an alkaline solution, the apparent rate constant computed by Eq. (16) decreases as the reaction proceeds[2,4)] as a result of the electrostatic effect of the hydrolyzed groups fixed on the macromolecule. If the reactivity of the ester group is mainly affected by a few hydrolyzed groups situated a relatively short distance apart, the k_n' given by Eq. (20) will remain almost constant over a relatively wide range, forming a step of the reaction, because it is expected that the environment of the reactive group will remain unchanged for some time and that the reaction will proceed discontinuously.

The value of log[$(1-\alpha)/(1-\beta)$], calculated on the basis of the kinetic data of the alkaline hydrolysis of polymethyl acrylate[2)] in a 29% aqueous acetone solution, are plotted aginst the reaction time in Fig. 5. The four straight lines in this figure, which intersect nearly at β=1/4, 2/4, and 3/4, suggest that the reaction proceeds in four steps. The corresponding four rate constants have been calculated by Eq. (6), assuming σ=4. The results are summarized in Table 3, where k_n' is the approximate value of the rate constant estimated by means of Eq. (20).

Table 3. Rate constnts of alkaline hydrolysis of polymethyl acrylate

n	k_n' l/mol min	k_n l/mol min	log(k_0/k_n)
1	3.99×10^{-1}	8.02×10^{-1}	0.405
2	1.40×10^{-1}	1.66×10^{-1}	1.09
3	3.07×10^{-2}	4.04×10^{-2}	1.70
4	3.31×10^{-3}	3.31×10^{-3}	2.79

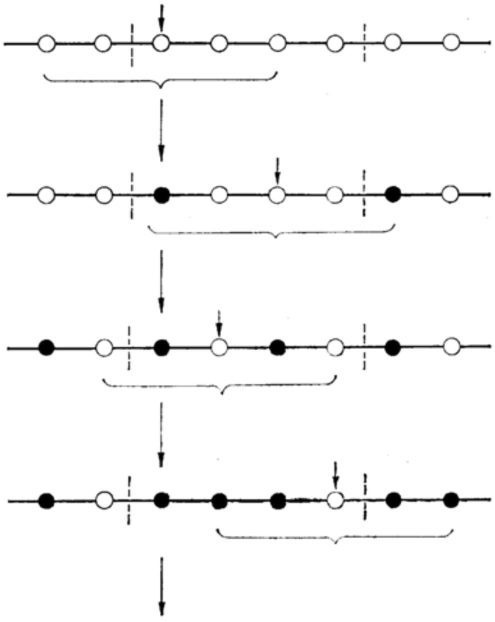

Fig. 6. Illustration of the four-step hydrolysis of polymethyl acrylate.

If it is assumed that the hydrolysis of the ester group is mainly affected by the electrical charge of the first and second neighboring groups, the electrical environment of the reactive group is considered to change in the four steps illustrated in Fig. 6, where the white and black circles represent ester and hydrolyzed groups respectively and where

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4) A. Katchalsky and J. Feitelson, *J. Polymer Sci.*, **13**, 385 (1954).

the arrows indicate reacting groups. The electrostatic free energy of the activation of the nth reaction is given by:

$$(\Delta F_{\mathrm{el}}^{\neq})_n = 2.303\boldsymbol{R}T\log(k_0/k_n) \tag{21}$$

where k_0 is the intrinsic rate constant. Since this energy is also given, on the basis of the above assumption, by summing up that shown in Eq. (19), the following relation is obtained:

$$\log(k_0/k_n) = (\boldsymbol{N}e^2/2.303\boldsymbol{R}TD)\sum_i(z_i/\bar{r}_i) \tag{22}$$

where z_i is the number of the electrical charge in the ith group apart from the reacting group ($z_i=$ 0, 1 or 2, $i=1$ and 2) and where $\bar{r}_i$ is the average distance between the reacting group and the ith group, which is defined by:

$$1/\bar{r}_i = \sum_j(X_{i,j}/r_{i,j}) \tag{23}$$

where j is related to the steric configuration of the ith group and where X is the mole fraction ($\sum_j X_{i,j}=$ 1). On the basis of the assumption illustrated in Fig. 6, three equations can be obtained:

$$\begin{cases} \log(k_0/k_2) = A(1/\bar{r}_2) \\ \log(k_0/k_3) = A(1/\bar{r}_1) \\ \log(k_0/k_4) = A(1/\bar{r}_1+1/\bar{r}_2) \end{cases}$$

where $A=2\boldsymbol{N}e^2/2.303\boldsymbol{R}TD=5.53$ ($T=328$, $D=$ 80). By using the value of the rate constant in Table 3, the equations are solved to give:

$$\bar{r}_1=3.23\,\text{Å},\quad r_2=5.07\,\text{Å},\quad k_0=2.04\ l/\text{mol min}$$

As the alkaline hydrolysis of polymethyl acrylate proceeds, the polymer chain stretches as a result of the charges formed on the polymer; the partly-hydrolyzed polymer may exhibit a planar zigzag structure, at least in the vicinity of reacting group. On the basis of the above assumption, two kinds of j (in Eq. (23)) may be defined; firstly, $j=1$, when both groups are situated sterically on the same side of the plane of zigzag, and secondly, $j=2$, on the opposite side. Then $X_{1,2}=1-X_{1,1}$. By introducing the two values $r_{1,1}=2.6$Å and $r_{1,2}=4.3$Å, which are estimated on the basis of the length and angles of the bonds, and the kinetically-determined value, $\bar{r}_1=3.25$Å, into Eq. (23), $X_{1,1}$ is found to be 0.5_0; this suggests that an atactic polymethyl acrylate exhibits a sterically random struture.

The relation given in Eq. (18) may be generalized in the formula given by Eq. (24) provided that a polybasic acid with σ carboxylic acid groups ionized in σ steps:

$$(\Delta F_{\mathrm{el}}^{\mathrm{i}})_n = 2.303\boldsymbol{R}T'[\mathrm{p}K'-\mathrm{p}K_0-\log(n/\sigma-n+1)] \tag{24}$$

where $(\Delta F_{\mathrm{el}}^{\mathrm{i}})n$ represents the electrostatic free energy at the nth step of ionization; K_0, the intrinsic dissociation constant of the acidic group, and K_n', the dissociation constant of the group at the nth step. If it is assumed, by analogy to the alkaline hydrolysis of polymethyl acrylate, that the ionization of polyacrylic acid is mainly affected by a few ionized groups on the polymer, $(\Delta F_{\mathrm{el}}^{\mathrm{i}})n$ is also given by $(\boldsymbol{N}e^2/D)\sum_i(z_i/\bar{r}_i)$. The comparison of Eq. (21) with Eq. (24) leads to the relation:

$$\log(k_0/k_n)=(T'/T)[\mathrm{p}K_n'-\mathrm{p}K_0-\log\{n/(\sigma-n+1)\}] \tag{25}$$

An aqueous solution of polyacrylic acid was titrated with a sodium hydroxide solution in the absence of added salt; the titrated data are represented in Fig. 7, in which the straight line represents the modified Henderson-Hasselbach relation,[5] $\mathrm{pH}=\mathrm{p}K_a-n'\log[(1-\alpha_i)/\alpha_i]$, where α_i is the degree of ionization. These data are in accordance with those given by Gregor and Frederic.[6] By assuming a four-step ionization for polyacrylic acid, $\mathrm{p}K_0$ may be estimated by using Eq. (25) in terms of the kinetic data. The results of the calculation are given in Table 4, where the pH values at $\alpha_i=3/8$, 5/8, and 7/8 are used as the $\mathrm{p}K_n'$ values, because $\mathrm{p}K_n'$ is, by definition, equal to pH at the half-ionization point in each ionization step.

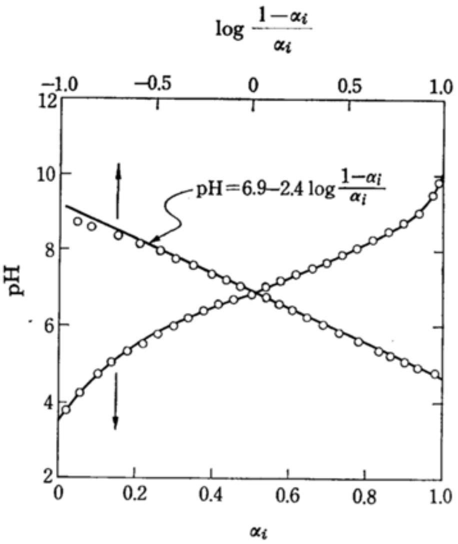

Fig. 7. Titration of polyacrylic acid with sodium hydroxide in the absence of salt.

TABLE 4. $\mathrm{p}K_0$ OF POLYACRYLIC ACID CALCULATED BY THE KINETIC DATA

n	$\mathrm{p}K_n'$	$\log[n/(5-n)]$	$(T/T')\log(k_0/k_n)$	$\mathrm{p}K_0$
2	6.40	−0.18	1.20	5.38
3	7.39	0.18	1.87	5.34
4	8.61	0.60	3.07	4.93

The fairly good constancy of the calculated value of $\mathrm{p}K_0$ suggests that both the alkaline hydrolysis of

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[5] A. Katchalsky and P. Spitnik, *J. Polymer Sci.*, **2**, 432 (1947).

[6] H. P. Gregor and M. Frederic, *ibid.*, **32**, 451 (1957).

polymethyl acrylate in an aqueous solution and the ionization of polyacrylic acid are controlled by the same electrostatic effect of the charged group on the polymer, and that the ionization of polyacrylic acid can be explained approximately in terms of the four-step ionization concept.

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