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Group Interactions in Polyelectrolytes. IV. Kinetics of the Alkaline Hydrolysis of Polymethyl Acrylate (Part II)

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Rate equations which express the over-all kinetics of the alkaline hydrolysis of polymethyl acrylate in the presence of a large excess of alkali were derived. The over-all course of this reaction was calculated by using the rate constants given in the previous paper, which were derived from the kinetic data obtained by the reaction in a 29% (*v*/*v*) aqueous acetone solution with a slight excess of sodium hydroxide at 55°C. The partially-hydrolyzed polymethyl acrylate (30.6% hydrolyzed) was hydrolyzed by the addition of about sixteen times as much sodium hydroxide as the amount of the ester group; the kinetic data thus obtained were found to be in good agreement with the calculated values.

In the previous study,[1] the rate equations of a polymer reaction which proceeds in more than two steps were derived and applied to the alkaline hydrolysis of polymethyl acrylate. Upon the examination of the published kinetic data,[2] the reaction in a 29% (*v*/*v*) aqueous acetone solution with a slight excess of sodium hydroxide was found to proceed in four steps, and the corresponding four rate constants were determined.

In the present study, rate equations which express the over-all kinetics have been derived in a simple case; that is, the over-all rate of a reaction with a large excess of alkali has been calculated by using the rate constants at 55°C given previously. It is the purpose of the present study to confirm the validity of the assumptions, adopted in the derivation of these rate equations, by comparing the calculated values with the experimental values. For this reason, the alkaline hydrolysis of polymethyl acrylate in the presence of a large excess of sodium hydroxide has been carried out in a 29% aqueous acetone solution at 55°C.

Experimental

Materials. Polymethyl acrylate was prepared and purified as previously.[1] It was dissolved in acetone and partially hydrolyzed by carefully adding a limited amount of an aqueous sodium hydroxide solution over a long period so as to keep the solution homogeneous. The volume ratio of acetone to water in the solution was finally adjusted to 2/5. The solution was kept at 40°C until the alkalinity of the solution almost disappeared; this solution was then used for the kinetic measuremtns. The degree of hydrolysis was deter-

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[1] H. Kawabe and M. Yanagita, This Bulletin, **42**, 3109 (1969).

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

mined by the usual titration method; it was found to be 30.6%.

Determination of the Degree of Hydrolysis. Partial and complete hydrolyses of polymethyl acrylate were carried out in aqueous acetone solutions containing the necessary amount and a slight excess of sodium hydroxide respectively. The degree of hydrolysis was determined by pouring an aliquot of the solutions into water containing an excess of hydrochloric acid and by then titrating the mixture with 0.1 N sodium hydroxide. In kinetic runs, since a large excess of sodium hydroxide (about sixteen times as much as the moles of the ester group) was used, it was necessary before titration to remove sodium ions in the solution by Dowex-50. This method has already been described with respect to low-molecular esters;[1] also in the present study it was found to be effective for polymethyl acrylate. Five grams of Dowex-50 (X-8, 50—100 mesh), which had previously been half-neutralized and which had an effective capacity of 0.668 meq/g-wet, were added to a 50-m*l* aqueous solution containing 0.104 meq of polyacrylic acid and 1.074 meq of sodium hydroxide. The mixture was stirred, and its pH was measured by the use of Beckman's model G pH meter. The results are shown in Table 1. After removing the resin, the solution was titrated with 0.1 N sodium hydroxide in the presence of sodium chloride in order to determine the original amount of polyacrylic acid.

TABLE 1. REMOVAL OF SODIUM IONS FROM AN AQUEOUS SOLUTION CONTAINING POLYACRYLIC ACID AND SODIUM HYDROXIDE BY DOWEX 50

Time, sec	0	30	45	60	600
pH	12.39	4.91	3.95	3.92	3.99

Kinetic Measurement. The alkaline hydrolysis of the 30.6% hydrolyzed polymethyl acrylate was carried out in an aqueous acetone solution (acetone/water=2/5) containing a large excess of sodium hydroxide. During the course of this reaction, the temperature was kept at 55±0.1°C. The total concentration of sodium hydroxide in the solution, including that used for preliminary partial hydrolysis, was 0.0905 mol/*l*, and the concentration of the total carboxylate groups was 0.0055 mol/*l*. At appropriate intervals, aliquots of the solution were taken out and poured into water containing Dowex-50, after which the mixture was stirred for a few minutes in order to remove sodium ions. After removing the resin, the carboxylic acid content was determined by titration.

Rate Equations

In the previous paper,[1] the rate equations for a polymer reaction which proceeds in σ steps was derived on the model of the reaction of a low-molecular compounds containing σ groups whose reactivity altered when one of the groups was changed.

$$X_{n-1}Y_{\sigma-(n-1)} \xrightarrow{k_n} X_nY_{\sigma-n} \xrightarrow{k_{n+1}} X_{n+1}Y_{\sigma-(n+1)}$$

where X represents a changed group in a compound; Y, an unchanged one; n, the number of the changed group, and σ, the total number of groups. The over-all kinetics in the presence of a large excess of reagent was also expressed by a pair of rate equations in the case when $\sigma=3$. The derivation of the equations was based on the assumption that the reaction at nth and $(n+1)$th steps was controlled by the two rate constants, k_n and k_{n+1}.

When $\sigma=4$, the corresponding equations can similarly be derived on the same assumption. When $n=1$, the rate is thus controlled by k_1 and k_2 in the range of fractional conversion (β) from 0 to 1/2 and can be expressed by the following equation:

$$dx/dt = a[k_1b - (4k_1 - 6k_2)x_1 - 3k_2x] \qquad (1)$$

where a and b are the initial concentration of a reagent and that of the group in the compound respectively, and where x_1 and x are the concentration of the first changed group and that of the total changed groups in the compound, again respectively, at the time t. Moreover, x_1 is given by:

$$x_1 = (1 - e^{-4k_1at})b/4 \qquad (2)$$

Upon integration, Eq. (1) becomes:

$$\beta = \frac{1}{2} - \frac{2k_1 - 3k_2}{2(4k_1 - 3k_2)}e^{-4k_1at} - \frac{k_1}{4k_1 - 3k_2}e^{-3k_2at} \qquad (3)$$

where $\beta=x/b$. When $n=2$, the rate, which is controlled by k_2 and k_3 in the 1/4—3/4 range of β, is given by:

$$dx/dt = a[(3k_2 + 2k_3)b/4 - (3k_2 - 4k_3)x_2 - 2k_3x] \qquad (4)$$

where x_2 is the concentration of the secondly-changed group in the compound and is given by:

$$x_2 = (1 - e^{-3k_2a(t-t_{1/4})})b/4 \qquad (5)$$

Upon integration, Eq. (4) yields:

$$\beta = \frac{3}{4} - \frac{3k_2 - 4k_3}{4(3k_2 - 2k_3)}e^{-3k_2(t-t_{1/4})} - \frac{3k_2}{4(3k_2 - 2k_3)}e^{-2k_3a(t-t_{1/4})} \qquad (6)$$

where $t_{1/4}$ is the time where β is 1/4. Similarly, when $n=3$, the following equations can be derived in the β range from 1/2 to 1:

$$dx/dt = a[(k_3 + k_4)b/2 - 2(k_3 - k_4)x_3 - k_4x] \qquad (7)$$

$$x_3 = (1 - e^{-2k_3a(t-t_{1/2})})b/4 \qquad (8)$$

where x_3 is the concentration of the thirdly-changed group in the compound and where $t_{1/2}$ is the time when β is 1/2. Upon integration, Eq. (7) becomes:

$$\beta = 1 - \frac{k_3 - k_4}{2(2k_3 - k_4)}e^{-2k_3a(t-t_{1/2})} - \frac{k_3}{2(2k_3 - k_4)}e^{-k_4a(t-t_{1/2})} \qquad (9)$$

Results and Discussion

The alkaline hydrolysis of the partially-hydrolyzed polymethyl acrylate (30.6% hydrolyzed) was carried out in a 29% aqueous acetone solution at 55°C. Since a large excess of sodium hydroxide was used in this experiment (a=0.0905 mol/*l*, b=0.0055 mol/*l*, and a/b=16.5), the over-all course of the reaction is given by Eqs. (3), (6), and (9). In the previous paper,[1] the rate constants were given on the basis of Sakurada's data[2] for the reaction in a 29% aqueous acetone solution containing a slight excess of sodium hydroxide at 55°C. They were $k_1=8.02\times10^{-1}$, $k_2=1.66\times10^{-1}$, $k_3=4.04\times10^{-2}$, and $k_4=3.31\times10^{-3}$ *l*/mol min. The values of β were first computed on the basis of Eq. (3) and plotted against t as is shown by the full line in Fig. 1 (Curve I), from which $t_{1/4}$ was determined to be 6.5 min. The plots obtained by means of Eq. (6)

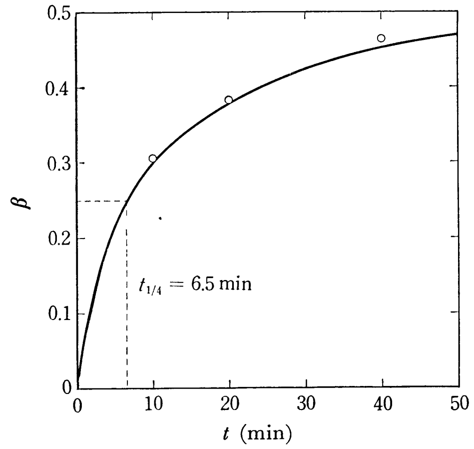

Fig. 1. Alkaline hydrolysis of polymethyl acrylate. Calculated curve I.

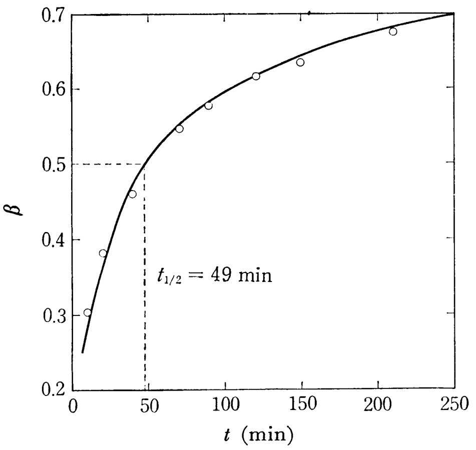

Fig. 2. Alkaline hydrolysis of polymethyl acrylate. Calculated curve II.

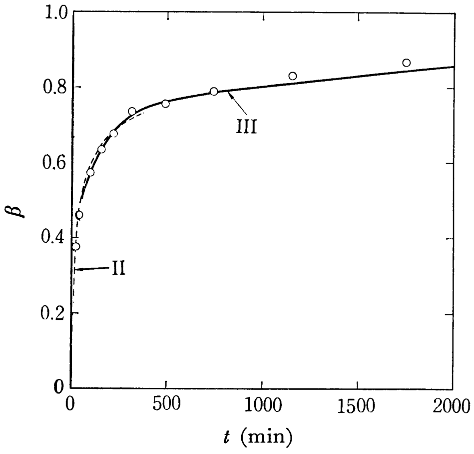

Fig. 3. Alkaline hydrolysis of polymethyl acrylate. Calculated curves II and III.

are shown in Fig. 2 (Curve II); $t_{1/2}$ was determined to be 49 min. Finally, the plots fitting Eq. (9) are shown in Fig. 3 (Curve III).

In Figs. 1, 2, and 3, the white circles indicate the values observed in the present experiment. Since polymethyl acrylate used in this experiment was preliminarily 30.6% hydrolyzed, and since this value of β corresponds to the reaction time of 10 min, as may be seen in Figs. 1 and 2, the observed values of β are plotted against the corrected time, namely, the actual reaction time plus 10 min. A fairly good agreement is shown between the calculated and observed values. Although the conditions in this experiment and those in Sakuradas' are different except for the temperature and the composition of the medium, the agreement is remarkable; this justifies deriving the rate equations on the basis of the assumption adopted in the previous paper, the assumption that the reactivity of ester groups in a polymethyl acrylate molecule is electrostatically affected mainly by the first and second neighboring groups when the reaction is carried out in a water-rich system.

In the previous paper, it was also shown that the plot of the logarithmic term of the simple second-order rate equation (Eq. (10)) against the time could be divided into four lines:

$$k_{\text{app}} = \frac{1}{(a-b)t} \ln \frac{b(a-x)}{a(b-x)} \tag{10}$$

where k_{app} is the apparent rate constant. This is also true of the present experiment, as is shown in Fig. 4,

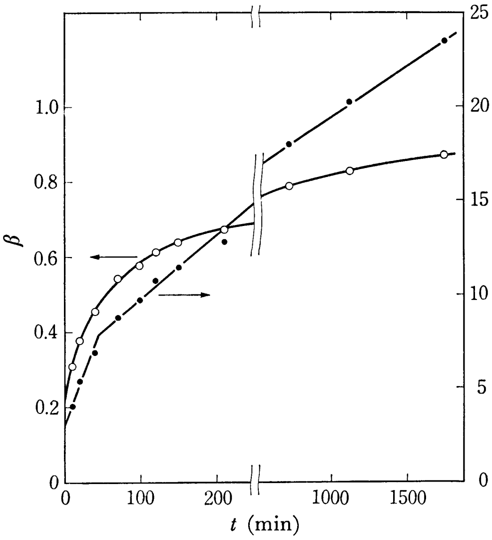

Fig. 4. Plot of $\overline{kt}$ *viz.* t in the alkaline hydrolysis of polymethyl acrylate.

where $\overline{kt} \equiv [1/(a-b)]\ln[b(a-x)/a(b-x)]$, and where the white and black circles represent the observed values of β and $\overline{kt}$ respectively. The approximate value of the rate constant, k_n', as estimated in terms of the slope, can be expressed thus:

$$k_n' = \Delta\overline{kt}/\Delta t \tag{11}$$

The values are shown in Table 2, in which those values obtained from Sakurada's data in the previous paper are also given for comparison.

Table 2. Approximate values of the rate constants

n	k_n' (l/mol min) present experiment	k_n' (l/mol min) Sakurada's data
1		3.99×10^{-1}
2	1.10×10^{-1}	1.40×10^{-1}
3	2.75×10^{-2}	3.07×10^{-2}
4	5.40×10^{-3}	3.31×10^{-3}

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