

## CALCULATION OF THE DIFFERENTIAL RATE CONSTANTS OF QUATERNIZATION REACTIONS OF POLYMER AMINES

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A method is described for the calculation of differential rate constants using an empirical description of the time dependence of the product of integral rate constant and time or of conversion. The method has been verified for quaternization reactions of poly(2-dimethylaminoethyl methacrylate), poly(4-dimethylaminomethylstyrene), poly[N-(3-dimethylaminopropyl)acrylamide], poly(4-vinylpyridine), poly(iminoethylene), and poly[4-bis(2-hydroxyethyl)aminomethylstyrene] as a function of conversion of the reaction. The calculations were carried out using reported data on the dependence of conversion on time.

Our preceding paper<sup>1</sup> was dealing with the kinetics of quaternization of poly(2-dimethylaminoethyl methacrylate) (PDAEM) with methyl iodide in water-ethanolic solutions. The reaction course was described by means of the dependence of the integral rate constant on conversion. This course was found to be dependent on the water content in the solvent. However, the kinetic description by means of the integral rate constant has a drawback in that it does not show the instantaneous reactivity of the macromolecule. This reactivity is e.g. described by the difference rate constant:

$$k_d = \frac{1}{a-b} \left[ \ln \frac{b(a-x_i)}{a(b-x_i)} - \ln \frac{b(a-x_{i-1})}{a(b-x_{i-1})} \right] / (t_i - t_{i-1}), \quad (1)$$

where  $a$ ,  $b$  are the initial concentrations of structural units of PDAEM and methyl iodide,  $x_i$  or  $(x_{i-1})$  is the concentration of iodide ions at a time  $t_i$  or  $t_{i-1}$ , respectively, and  $k_d$  is the difference rate constant at a time  $(t_i + t_{i-1})/2$ , which has the meaning of the mean differential rate constant within the time interval  $(t_{i-1}, t_i)$ . It should be pointed out, however, that the calculated difference rate constant considerably depends on the accuracy of kinetic data (i.e. on the accuracy of determination of  $x_i$  and  $t_i$ ), which gives rise to serious problems in polymer-analogous reactions.

The description most frequently used for the kinetics of reactions of polymers is based on the calculation of individual rate constants  $k_0$ ,  $k_1$ , and  $k_2$  (rate constants of the functional group with none, one, and two reacted adjacent groups, respectively).

The method of calculation has been reported in e.g. refs<sup>2-4</sup>. In our previous paper<sup>5</sup> we reported that such description is not suitable for the system under investigation (quaternization of PDAEM with methyl iodide in water-ethanolic solutions), because the constants  $k_0$ ,  $k_1$ , and  $k_2$  probably vary during the reaction, or the effect of more distant reacted groups becomes operative.

In this paper we describe a method for the calculation of differential rate constants which give the instantaneous reactivity of the macromolecule as a function of the conversion of reaction. Suitability of the method has been checked using the following quaternization reactions reported in the literature: quaternization of atactic PDAEM with methyl iodide<sup>1</sup>, quaternization of PDAEM with benzyl chloride<sup>6</sup>, quaternization of poly(4-vinylpyridine) with isobutyl bromide<sup>7</sup>, quaternization of poly(4-dimethylaminomethylstyrene) with methyl iodide<sup>8</sup>, quaternization of poly[4-bis(2-hydroxyethyl)aminomethylstyrene] with methyl iodide<sup>9</sup>, quaternization of poly[N-(3-dimethylaminopropyl)acrylamide] with benzyl chloride<sup>6</sup>, quaternization of poly(iminoethylene) with methyl iodide<sup>2</sup>.

## RESULTS AND DISCUSSION

It has been pointed out in the introduction that the treatment of the kinetics of polymer-analogous reactions using the difference rate constants meets with experimental difficulties. Fig. 1 shows these constants for the reaction of PDAEM with benzyl chloride taken from data reported earlier<sup>6</sup>. In many reactions the scatter

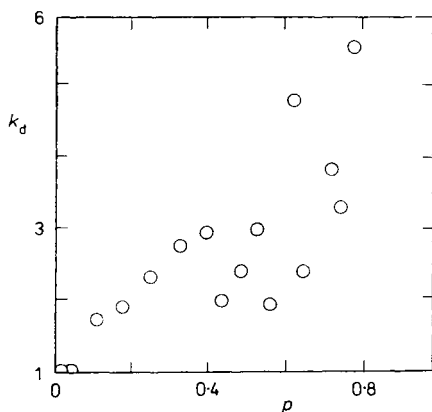


FIG. 1

Difference rate constants ( $k_d$ ,  $\text{dm}^3 \text{mol}^{-1} \cdot \text{h}^{-1}$ ) for reaction B. For reaction conditions see Table I

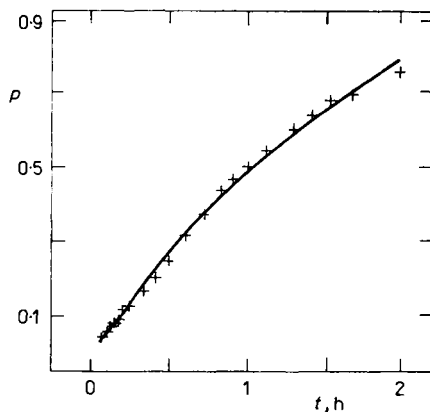


FIG. 2

Logarithmic regression of the dependence of conversion fraction ( $p$ ) on time for reaction B

of the constants is even larger, so that no approximation of the dependence of the difference rate constant on conversion of the reaction using some empirical function is possible. This dependence was obtained by means of the second-order differential rate constant, given by the relation

$$k = \frac{1}{(1-p)(b-pa)} \frac{dp}{dt}, \quad (2)$$

in which  $p$  is the conversion fraction of the reaction related to structural polymer units ( $p = x/a$ ) at a time  $t$ . In second-order reactions of low-molecular weight compounds  $k$  is constant, and Eq. (2) can be easily integrated. In reactions of polymers, however, this assumption is usually not satisfied, and Eq. (2) cannot be integrated directly. To calculate the differential rate constants, we must know  $dp/dt$ , i.e. the function  $p = p(t)$ . This function may be empirically replaced by another chosen function, the parameters of which can be determined from experimental data using linear or nonlinear regression by the least squares method. We tested polynomial functions

$$p = \sum_{i=0}^n c_i \cdot t^i \quad (3)$$

and a logarithmic function

$$p = e \cdot \ln(f + g \cdot t), \quad (4)$$

in which  $c_i$ ,  $e$ ,  $f$ ,  $g$  are parameters of the respective functions and  $n$  is the degree of the polynomial. As follows from Fig. 2, the use of the logarithmic function is not suitable (systematic deviations of balanced and experimental values, low correlation coefficient\*,  $r = 0.91$ ). On the contrary, the use of a polynomial function of the 4th degree (Fig. 3) very adequately satisfies experimental data (correlation coefficient 0.99). In the other experiments, the parameters and correlation coefficients of which are summarized in Table I, the best regression was also reached for a polynomial function of the 4th degree. Theoretically, the coefficients  $c_0$  ought to be zero. Their

$$\begin{aligned} * \quad r &= s_{xy} / (s_x \cdot s_y), \quad s_{xy} = \left[ \sum_{i=1}^N x_i \cdot y_i - \left( \sum_{i=1}^N x_i \cdot \sum_{i=1}^N y_i \right) / N \right] / (N-1) \\ s_x &= \left\{ \left[ \sum_{i=1}^N x_i^2 - \left( \sum_{i=1}^N x_i \right)^2 / N \right] / (N-1) \right\}^{1/2}, \\ s_y &= \left\{ \left[ \sum_{i=1}^N y_i^2 - \left( \sum_{i=1}^N y_i \right)^2 / N \right] / (N-1) \right\}^{1/2}, \end{aligned}$$

$N$  is the number of measurements,  $y_i$  is the measured value at the point  $x_i$ .

TABLE I

Parameters of polynomial functions according to Eq. (3) and correlation coefficients ( $r$ ) for quaternization reactions A–G. Initial concentration of structural units is  $a$  ( $\text{mol dm}^{-3}$ ), initial concentration of alkylating agent is  $b$  ( $\text{mol dm}^{-3}$ )

Reaction <sup>a</sup>	Solvent <sup>b</sup>	$T, ^\circ\text{C}$	$a$	$b$	$c_0$	$c_1$	$c_2$	$c_3$	$c_4$	$r$
A	EtOH–H <sub>2</sub> O(4)	11	0.01737	0.1257	0.02803	0.08694	1.043	-0.4693	-0.01284	0.994
A	EtOH–H <sub>2</sub> O(21)	11	0.01077	0.1058	0.1511	0.4179	0.2695	-0.2535	0.05417	0.990
A	EtOH–H <sub>2</sub> O(43)	11	0.009745	0.09982	0.006598	1.112	-0.5753	0.1506	-0.01621	0.972
A	EtOH–H <sub>2</sub> O(58)	11	0.009417	0.07586	0.01176	1.845	-1.823	0.9772	-0.2230	0.955
A	EtOH–H <sub>2</sub> O(64)	11	0.005011	0.01118	0.01696	0.3507	-0.07572	0.008443	$3.613 \cdot 10^{-4}$	0.920
A	EtOH–H <sub>2</sub> O(70)	11	0.01575	0.07132	0.03511	2.322	-2.749	1.596	-0.3516	0.903
A	EtOH–H <sub>2</sub> O(76)	11	0.004961	0.02846	0.03374	1.211	-0.7410	0.2248	-0.02653	0.908
B	DMF	50	0.04341	0.08728	-0.01792	0.1312	0.007766	-0.003086	$2.027 \cdot 10^{-4}$	0.990
C	sulfolane	52	0.1060	0.4060	0.02124	0.5806	-0.2014	0.03507	-0.002296	0.906
D	DMF	0	0.1360	0.2720	-0.1477	0.2138	-0.02521	0.001001	$1.280 \cdot 10^{-5}$	0.991
E	DMF–H <sub>2</sub> O(50)	30	0.03620	0.3797	0.04960	1.6810	-1.255	0.3527	-0.0154	0.917
F	DMF	50	0.03971	0.07935	0.04007	0.5015	-0.1089	0.01160	$5.355 \cdot 10^{-4}$	0.963
G	H <sub>2</sub> O	30	0.01710	0.9840	0.09530	0.09667	0.006973	$1.983 \cdot 10^{-4}$	$1.840 \cdot 10^{-6}$	0.785

<sup>a</sup> A PDAEM – methyl iodide<sup>1</sup>, B PDAEM – benzyl chloride<sup>6</sup>, C poly(4-vinylpyridine) – isobutyl bromide<sup>7</sup>, D poly(4-dimethylaminomethylstyrene) – methyl iodide<sup>8</sup>, E poly[4-bis(2-hydroxyethyl)aminomethylstyrene] – methyl iodide<sup>9</sup>, F poly[N-(3-dimethylaminopropyl)acrylamide] – benzyl chloride<sup>6</sup>, G poly(iminoethylene) – methyl iodide<sup>2</sup>. <sup>b</sup> For the ethanol–water and dimethylformamide–water mixtures the numerical value in brackets means wt. % water.

calculated nonzero values are due to experimental errors and to the lack of data at very low conversions. Table I shows that for some reactions the regressions are not very successful (a value above 0.99 is regarded as a satisfactory correlation coefficient). In these cases the differential rate constants were calculated by using a different method.

Eq. (2) may be rearranged to

$$1/(a-b) \cdot \ln \frac{b(1-p)}{b-ap} = \int k dt. \quad (5)$$

In second-order reactions of low-molecular weight compounds the left-hand side of Eq. (5) is proportional to the time which has passed from the onset of the reaction; the proportionality constant is the rate constant of the reaction. In polymer reactions the proportionality usually no more holds, but the time dependence of the left-hand side of Eq. (5) can be expressed by using some empirical function, the parameters of which can be determined by the least squares method. In this case too the best results have been obtained with a polynomial function of the 4th degree:

$$1/(a-b) \cdot \ln \frac{b(1-p)}{b-ap} = \sum_{i=0}^4 d_i t^i, \quad (6)$$

where  $d_i$  are parameters of the polynomial function. By rearranging Eq. (6), we obtain

$$p = \frac{b \exp \left[ (a-b) \sum_{i=0}^4 d_i t^i \right] - b}{a \exp \left[ (a-b) \sum_{i=0}^4 d_i t^i \right] - b}. \quad (7)$$

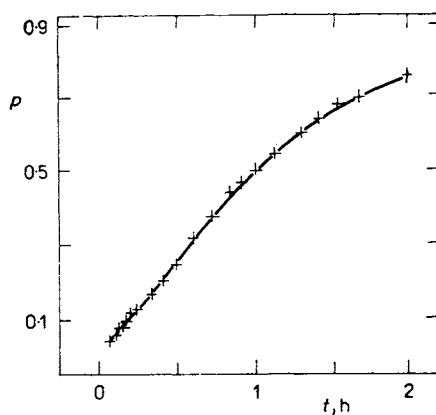


FIG. 3

Polynomial regression of 4-th order of the same data as in Fig. 2

By differentiating this function with respect to time and using Eq. (2), the differential rate constants of the reaction can be determined as functions of conversion. Table II summarizes the coefficients  $d_i$  and correlation coefficients for the individual experiments. The nonzero values of the coefficients  $d_0$  are due to experimental errors and to the lack of data at very low conversions. It can be seen from the correlation coefficients in Table II that such calculation procedure is more successful for most of the reactions under investigation. Fig. 4 shows the differential rate constants calculated by employing the procedures described above depending on the conversion fraction of the reaction. The procedure giving a higher correlation coefficient was selected in each case. The character of the curves representing the quaternization of PDAEM is the same as for the dependence of integral rate constant on conversion described earlier<sup>1</sup>, i.e. in reaction media rich in water (above 43 wt. %) the constant decreases with conversion, while at a low water content the dependence increases. The absolute values of the constants are different, however, in agreement with theoretical assumptions. For instance, in the reaction medium of azeotropic ethanol the dependence of the differential rate constant on conversion is much steeper, compared with that for the integral rate constant. At the conversion fraction 0.5 the differential rate constant is  $14.8 \text{ dm}^3 \text{ mol}^{-1} \text{ h}^{-1}$ , while the integral constant is  $7.9 \text{ dm}^3 \text{ mol}^{-1} \cdot \text{h}^{-1}$  (ref.<sup>1</sup>).

TABLE II

Parameters of polynomial functions according to Eq. (6) and correlation coefficients ( $r$ ) for quaternization reactions. Solvents, symbols denoting reactions, temperatures, and initial concentrations  $a$ ,  $b$  are the same as in Table I

Reaction	$d_0$	$d_1$	$d_2$	$d_3$	$d_4$	$r$
<i>A</i>	0.5332	-3.366	19.56	-9.176	1.762	0.978
<i>A</i>	0.1893	3.485	5.026	-2.196	0.2980	0.991
<i>A</i>	0.03333	11.55	0.2855	0.1615	-0.2447	0.992
<i>A</i>	0.1660	24.81	-0.1420	-3.195	0.2000	0.993
<i>A</i>	1.486	33.50	-0.5990	-0.1577	0.01056	0.991
<i>A</i>	0.3665	37.30	-3.934	-3.934	1.246	0.990
<i>A</i>	0.7100	48.56	-2.306	-1.516	0.1885	0.990
<i>B</i>	-0.1332	1.188	0.4756	-0.0735	0.005080	0.993
<i>C</i>	0.0324	1.669	-0.2281	0.01993	$-2.199 \cdot 10^{-4}$	0.991
<i>D</i>	-0.7073	0.8549	-0.04391	-0.003501	$4.064 \cdot 10^{-4}$	0.993
<i>E</i>	0.1171	4.744	1.806	-2.715	0.6639	0.991
<i>F</i>	-0.3393	10.00	-2.283	1.413	-0.1907	0.996
<i>G</i>	0.7263	1.494	-0.1039	0.002925	$-2.703 \cdot 10^{-5}$	0.962

A comparison between Table I and II shows that for some types of reactions regressions are successful, if both procedures described above are used. In such cases the differential rate constants are virtually the same, if regressions are performed by using relations (3) or (6). This is illustrated by Fig. 5.

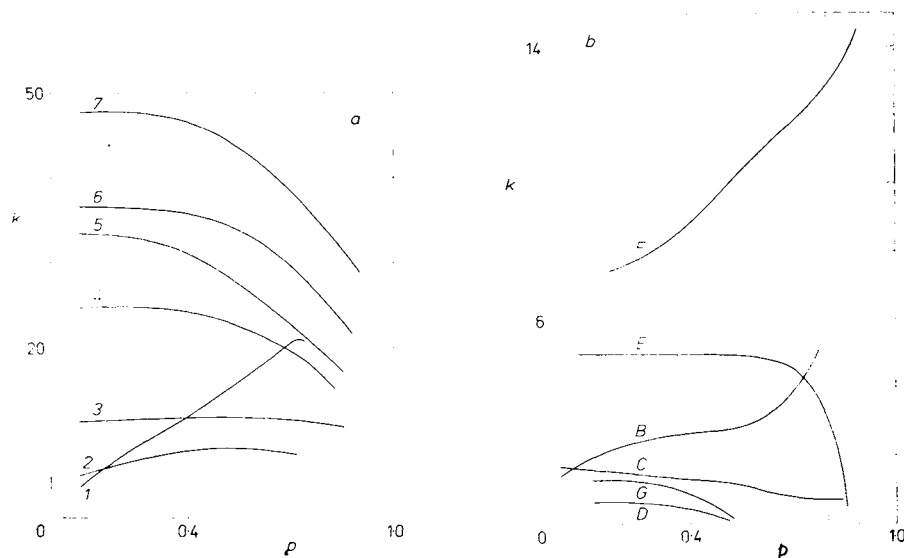


FIG. 4

Dependence of the differential rate constant ( $k$ ,  $\text{dm}^3 \text{mol}^{-1} \text{h}^{-1}$ ) on conversion fraction ( $p$ ) for quaternization reactions. *a* Reaction A in water-ethanolic solutions with water content (wt. %): 1 4, 2 21, 3 43, 4 58, 5 64, 6 70, 7 76. *b* Reactions B–G (reactions A–G explained in Table I)

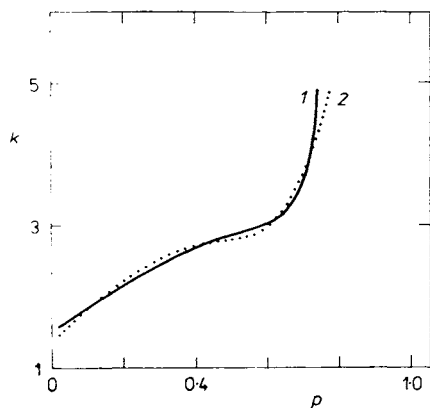


FIG. 5

Dependence of the differential rate constant ( $k$ ,  $\text{dm}^3 \text{mol}^{-1} \text{h}^{-1}$ ) calculated using Eq. (3) (curve 1) and Eq. (6) (curve 2) from the same data as in Fig. 2

The method described in this study may be employed as an alternative to the description of polymer transformations using three individual rate constants.

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