Kinetic Studies on the Acid Hydrolysis of Dextran

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ABSTRACT: A detailed kinetic analysis of the acid hydrolysis of well-defined dextran fractions is presented. The course of the reaction was measured by determining the molecular weight distributions with a sensitive permeation chromatography method. Results show that reaction rates are first order with respect to dextran concentration and rate constants are proportional to the molecular weight raised to the power of $^2/_3$. Further, the experimental molecular weight distributions were found to be much broader than would be expected, if the reaction rate constants were equal for all polymer bonds in the molecule. Calculations based on different reaction models were compared with experimental data. Good agreement was obtained with a model in which the individual rate of bond cleavage varies by a parabolic function along the polymer chain. This means that the reactivity of the bonds is higher near the ends of the polymer chain and decreases toward the center. With a model based on a diffusion controlled reaction an explanation can be given for the $^2/_3$ power dependence of the rate constants on the molecular weight.

Degradation reactions are of great interest in the study of the stability and applicability of polymers.[1] There are many different chemical reactions which lead to the degradation of polymers, depending on the nature of initiation (thermal, high energy, or UV radiation, etc.) and the reactive agents (oxygen, hydrogen ions, etc.). During degradation reactions different chemical bonds of the polymer chain can be attacked; in the present investigation depolymerization through scission of those chemical bonds which link two monomer units is considered exclusively.

In studying the kinetics of depolymerization reactions it is usually assumed that all polymer bonds have the same reactivity and therefore no dependence of the reaction rate on the molecular weight (MW) of the polymer is considered. This may be well founded by the fact that bond energies are essentially the same, whether the bonds are near the ends or at the center of a polymer molecule. Although Freudenberg et al.[2,3] and others[4,5] referred to the nonrandomness of the hydrolytic degradation of starch, cellulose, and other polysaccharides, earlier investigations of the hydrolysis of dextran based on MW averages (viscosity, light scattering) did not reveal a MW dependence of the rate constants or changes of bond reactivity along the polymer chain.[6,7] As an example, we have chosen the hydrolytic depolymerization of dextran, a bacteriologically produced polyglucose. Earlier, we have studied the mechanical degradation of this polymer by the action of ultrasound and found that chain scission takes place preferentially at the center of the molecule.[8]

Hydrolytic depolymerization of dextran at pH values around 1 is strictly of first order with respect to dextran concentration, since the hydrogen ion concentration does not change during the reaction. If the reactivity of all polymer bonds is constant, the reaction rate of depolymerization of a specific molecule should be proportional to its MW. Therefore, if the initial MWD of a polymer fraction is known, the course of the reaction can be simulated by applying elementary mathematical methods. The formulation of rate equations for the degradation of linear polymers was the subject of extensive work many years ago.[5,12] The most general approach to the kinetics was carried out by Simha[9] and Montroll,[10,11] who also considered polydisperse materials. Several authors adapted Simha's equations for specific problems, e.g., ultrasonic degradation.[13,14]

Since gel permeation chromatography has been developed to a rapid method for measuring MWD's and MW averages with great accuracy, it became possible to obtain full experimental information about the depolymerization process, which can be used to test different reaction models. The scope of this work is to investigate a depolymerization reaction by carrying out such an analysis.

Experimental Section

Materials. Original dextran samples were obtained from commercial products (prepared bacteriologically by leuconostoc mesenteroides, B 512F$^+$) by gel permeation chromatography (GPC) on Sephadex and Sepharose (Pharmacia Fine Chemicals, Uppsala, Sweden). Four dextran samples (a–d) with different molecular weights (MW) were produced for the study of the kinetics of acid hydrolysis. They were readily soluble in water. The characteristic data of these samples are listed in Table I.

Hydrolysis. The hydrolytic depolymerization reaction of dextran was carried out in closed, thermostated glass vessels of 100-mL capacity, at 80 ± 0.2 °C in 0.12 N sulfuric acid. The initial concentration of dextran was varied in the range of 0.25–2%. After definite time intervals samples of 10 mL were taken and poured immediately into 100 mL of cold (ca. −30 °C) methanol for precipitation of the dextran. The dextran was washed with methanol and dried under vacuum until constant weight. Oligosaccharides with degree of polymerization lower than 5 were not precipitated and therefore were disregarded.

Determination of Molecular Weights and Molecular Weight Distributions. MW averages and molecular weight distributions (MWD) of the dextran samples were determined by GPC on a mixture of equal parts of controlled pore glass CPG-10 (Electro Nucleonics, Fairfield, Conn.) (particle size 74–125 μm) with pore diameters of 8, 12, 24, 50, 140, and 300 nm. The columns (length 100 cm, diameter 1 cm) were installed in a chromatograph Model ALC/GPC 201 (Waters Associates, Milford, Conn.); the eluant was water containing 0.2% of potassium nitrate; the flow rate was 1 mL/min. Calibration of columns and peak broadening corrections were performed as described elsewhere.[15-17] The MW averages $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ were calculated from the MWD's by numerical integration of the MW distribution function. Reproducibility in the MWD's and MW averages is ±0.5%; deviations in the absolute values are ±2%.

Results

The kinetics of the acid hydrolysis of dextran was investigated by determining the MWD's and the MW averages after definite reaction times. The rate of the reaction, expressed as the number of chemical bonds broken per dextran molecule and per unit time, can be directly calculated from the change of the number average MW ($\overline{M}_n$).

In order to determine the concentration dependence of the reaction rate, four different initial dextran concentrations (0.25–2%) were used. In all cases the MWD's after the same reaction times were identical within experimental error, which means that the reaction rate is proportional to the initial concentration and the reaction order is unity. The $\overline{M}_n$ values for these experiments are compiled in Table II; the first order reaction rate constants k, calculated from the experimental data, show very good constancy in the concentration range investigated.

To investigate the dependence of the reaction rate of hydrolysis on the MW of dextran, experiments with samples with different MW's were performed. The results are compiled in

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Table I
Molecular Weights of Dextran Samples Used for the Study of Kinetics of Acid Hydrolysis

Sample	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
a	738 000	4 300 000	8 470 000
b	72 700	90 500	111 000
c	4 380	6 350	8 130
d	117 000	151 000	189 000

Tables III and IV. It was found that there exists no proportionality between the rate of the reaction and the MW.

A general rate equation can be formulated, in which the rate is set proportional to the number of bonds present in the polymer molecule raised to the power a:

$$\frac{dB}{dt} = -\frac{1}{\overline{M}_n}\frac{d\overline{M}_n}{dt} = k(\overline{M}_n/M_{\text{mon}})^a \tag{1}$$

in which dB is the number of chemical bonds broken per molecule with MW $\overline{M}_n$ in the time interval dt. The total number of bonds in a polymer molecule is

$$(S-1) = \frac{\overline{M}_n}{M_{\text{mon}}} - 1 \simeq \frac{\overline{M}_n}{M_{\text{mon}}} \tag{2}$$

where S is the degree of polymerization and M_{mon} is the MW of the monomer unit, which is 162 for dextran. For high degrees of polymerization the approximate form of eq 2 can be used. For a period of time t the number B of bonds broken per molecule with MW $\overline{M}_n(0)$ is

$$B = \frac{\overline{M}_n(0)}{\overline{M}_n(t)} - 1 \tag{3}$$

where $\overline{M}_n(0)$ is the initial number average MW and $\overline{M}_n(t)$ is the corresponding value after the time t.

The exponent a gives the dependence of the reactivity of the polymer molecules on the MW. From the experimental results a has been determined to be ⅔.

Integration of eq 1 for $a = ⅔$, between the limits $t = 0$ and t, gives

$$\frac{1}{\overline{M}_n(t)^{2/3}} = \frac{1}{\overline{M}_n(0)^{2/3}} + \frac{2}{3}\left(\frac{k}{162^{2/3}}\right)t \tag{4}$$

A plot of $1/\overline{M}_n^{2/3}$ versus reaction time should thus give a straight line with slope $2k/3(162^{2/3})$ and an axis intercept of $1/\overline{M_n(0)}^{2/3}$.

Figure 1 shows the data of Tables III and IV, according to eq 4. A set of four parallel lines is obtained; the constants k, calculated from the slopes, are added in Tables III and IV. The constancy of the k values is good; deviations are about 5%.

A more extensive analysis was performed with sample d (Table IV). In Figure 2 the variation of the average MW's is shown with reaction time. It can be seen that in the early stages of the reaction $\overline{M}_n$ decreases more rapidly than $\overline{M}_w$ and $\overline{M}_w$ decreases more rapidly than $\overline{M}_z$. Therefore, it can be concluded that at low conversions the amount of small fragments formed is relatively high. This can be quantitatively expressed by the polydispersity ratios $\overline{M}_w/\overline{M}_n$ and $\overline{M}_z/\overline{M}_w$, which are plotted against reaction time in Figure 3. It can be further seen that a "combined polydispersity ratio" (CPR) $[\overline{M}_w^2/\overline{M}_n\overline{M}_z]$ approaches a constant value of 1.8 already after a comparatively short period of time. The CPR value is unity for a log-normal MWD; enrichment in the low MW region leads to higher CPR's and vice versa.

The change in the MWD of sample d with reaction time is shown in Figures 4A and 4B. The original MWD can be approximated by a lognormal distribution function (CPR = 1) with good accuracy. In the early stages of hydrolysis a shoulder appears in the low MW branch of the distribution curve, which is evidence for the formation of relatively large amounts of small fragments. In the course of the reaction this shoulder is shifted toward lower MW's, developing into a very broad maximum for intermediate degradation times, and finally sharpens again at the very low MW's. At the time when the CPR has reached its limiting value of 1.8 the degraded dextran has a MWD which can be reasonably well approximated by a Schulz–Flory distribution function[18] (after ~150 min). Introducing the value of 1.8 for the CPR in this function, a coupling constant of ½ is obtained. The experimental values of the MW at the maximum of the MWD (M_{max}) are included

Table II
Determination of the Reaction Order of Acid Hydrolysis of Dextran ($\overline{M}_n$ = 72 700, $\overline{M}_w$ = 90 500, $\overline{M}_z$ = 111 000)

Reaction time, min	Concn 0.25%		Concn 0.5%		Concn 1%		Concn 2%	
	$\overline{M}_n$	$1000\overline{M}_n^{-2/3}$	$\overline{M}_n$	$1000\overline{M}_n^{-2/3}$	$\overline{M}_n$	$1000\overline{M}_n^{-2/3}$	$\overline{M}_n$	$1000\overline{M}_n^{-2/3}$
0	72 700	0.574	72 700	0.574	72 700	0.574	72 700	0.574
15	54 000	0.700	53 400	0.706	54 800	0.694	55 300	0.689
30	43 200	0.813	42 000	0.828	41 000	0.842	40 300	0.851
45	34 000	0.953	34 200	0.950	33 100	0.971	33 200	0.969
75	23 700	1.21	24 000	1.20	24 400	1.19	23 100	1.23
105	17 300	1.50	17 800	1.47	17 600	1.48	17 400	1.49
Rate constant k, s^{-1}	6.24×10^{-6}		6.29×10^{-6}		6.26×10^{-6}		6.35×10^{-6}	

Table III
Investigation of Dependence of Rate Constant of Degradation on Initial Molecular Weight of Dextran (concn 1%)

Reaction time, min	Sample a			Sample b			Sample c		
	$\overline{M}_n$	$1000\overline{M}_n^{-2/3}$	$\overline{M}_w^2/\overline{M}_n\overline{M}_z$	$\overline{M}_n$	$1000\overline{M}_n^{-2/3}$	$\overline{M}_w^2/\overline{M}_n\overline{M}_z$	$\overline{M}_n$	$1000\overline{M}_n^{-2/3}$	$\overline{M}_w^2/\overline{M}_n\overline{M}_z$
0	738 000	0.123	2.96	72 700	0.574	1.02	4380	3.74	1.13
15	213 000	0.281	8.45	54 800	0.694	1.15	4130	3.88	1.14
30	152 000	0.351	6.68	41 000	0.842	1.19	3920	4.02	1.16
45	88 900	0.502	4.79	33 100	0.971	1.23	3800	4.11	1.17
75	46 000	0.779	3.01	24 400	1.19	1.29	3450	4.38	1.17
105	33 500	0.963	2.29	17 600	1.48	1.43	3080	4.72	1.18
Rate constant k, s^{-1}	6.07×10^{-6}			6.26×10^{-6}			6.41×10^{-6}		

Table IV
Degradation Kinetics and MWD's of Degradation Products of Dextran (Sample d; concn 1%)

Reaction time, min	M_{max}	$\bar{M}_n$	$1000\bar{M}_n^{-2/3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}z/\bar{M}_w$	$\bar{M}_w^2/\bar{M}_n\bar{M}_z$	$\bar{M}_w^2/\bar{M}_n\bar{M}_z$ (model III)
0	106 000	117 000	0.418	1.29	1.25	1.03	1.03
15	90 100	76 000	0.558	1.54	1.31	1.18	1.22
30	81 800	55 100	0.691	1.83	1.38	1.33	1.36
60	59 700	34 800	0.939	2.33	1.48	1.57	1.59
90	39 000	24 400	1.19	2.70	1.60	1.69	1.74
150	12 200	14 200	1.71	3.21	1.77	1.81	1.81
210	8 200	9 870	2.19	3.38	1.88	1.80	1.78
330	4 750	5 650	3.15	3.55	1.96	1.81	1.72
450	3 150	3 650	4.22	3.56	1.98	1.80	1.67
Rate constant k, s^{-1}	6.30×10^{-6}						

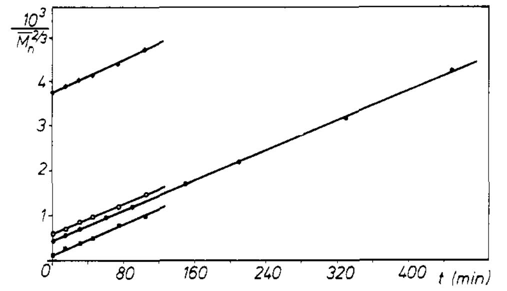

Figure 1. Linearized plot of the number average molecular weight ($\bar{M}_n$) vs. reaction time t: (■) sample a; (○) sample b; (◆) sample c; (●) sample d (Table I).

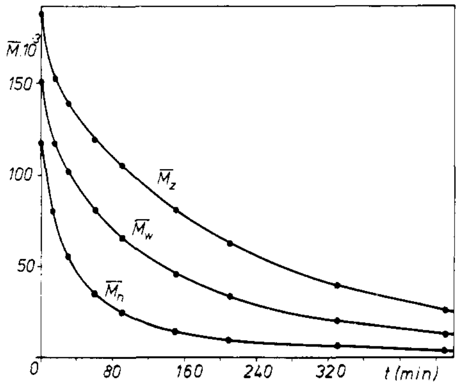

Figure 2. Variation of the molecular weight averages $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ with reaction time t. $\bar{M}$ represents average molecular weight (sample d, Table I).

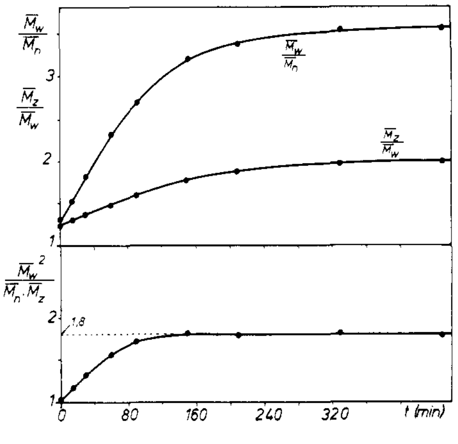

Figure 3. Variation of the polydispersity ratios $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ and the combined polydispersity ratio $\bar{M}_w^2/\bar{M}_n\bar{M}_z$ with reaction time t (sample d, Table I).

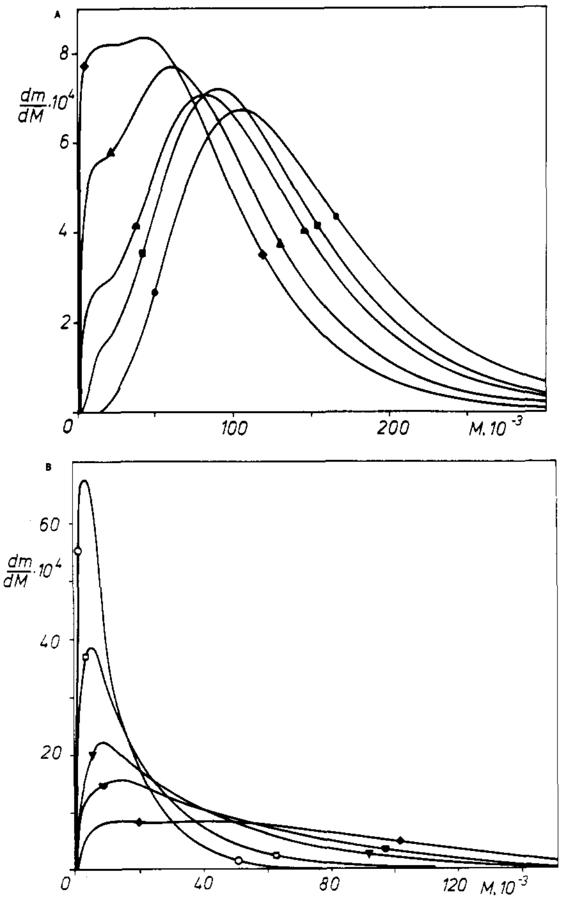

Figure 4. Variation of the molecular weight distribution (dm/dM) in the course of the reaction. M is molecular weight; dm is weight of polymer with molecular weight between M and $M + dM$. Reaction time: (●) 0 min; (■) 15 min; (▲) 30 min; (▲) 60 min; (◆) 90 min; (▼) 150 min; (▼) 210 min; (□) 330 min; (○) 450 min (sample d, Table I). Notice the different scales in Figure 4A and 4B.

in Table IV. In the case of a Schulz–Flory distribution, M_{max} is equal to $\bar{M}_n$. The experimental MWD's after long degradation times are in reasonable accordance with this requirement. The CPR values for the degradation of the narrow samples b and c show an increase with reaction time (Table III). For sample a, which has high MW and broad MWD, the CPR initially increases to 8.45, due to the formation of low MW fragments, but decreases in the further course of the reaction very rapidly.

Discussion

The experimental results show that the rate of the acid hydrolysis of dextran follows a first-order kinetics up to concentrations of 2%. An important fact to know is how the rate constants of degradation depend on the MW. If every chemical bond linking two monomer units in the polymer chain has the same probability of being broken, independent on the degree of polymerization, then one would expect a linear dependence on the MW and the value of a in eq 1 would be unity. In fact, from experimental results a has been determined to be $2/3$, which means that polymer molecules with higher MW's are more stable to acid hydrolysis than smaller ones.

The value of $2/3$ for a in connection with the fact that dextran molecules in aqueous solutions are slightly expanded coils may lead to the suggestion that the bonds on the surface of the coil are remarkably more reactive than those near the center, since the area of the coil increases with the MW raised to the power $2/3$, if the coil is approximated by a sphere. This assumption has to be rejected, since at concentrations of 1–2% dextran molecules in solution are already entangled, i.e., far away from being isolated coils, which is a requirement for such an explanation. Another possible explanation is to assume that the reactivity of the bonds changes due to the mobility of the chain segment as a function of the MW. This would mean that bonds near the end of the chain have a greater reactivity than those at the center.

The discussion of the reaction mechanism requires a detailed mathematical formulation of the kinetics of the degradation process and the comparison of the calculated results with experiments. To solve this problem three reaction models with increasing complexity were established and the kinetics computed numerically.

Mathematical Formulation of the Reaction Kinetics. It is assumed that each bond linking two monomer units (side chains are not considered) is broken according to a monomolecular decomposition process, since the concentration of the hydrogen ions remains constant during the reaction. For the general formulation it is assumed that each bond has an individual rate constant $K_{s,l}$ of degradation, which depends on the degree of polymerization S and on the location l of the bond in the polymer chain. The kinetic formulation of the reaction consists of a system of coupled linear differential equations (see Appendix, eq 17). Computational difficulties arise because the number of such equations is equal to the degree of polymerization and thus is exceptionally large. Computations are carried out in terms of the degree of polymerization; three models are presented, according to the simplifications and assumptions introduced.

Model I. This model resembles in many aspects those studied earlier by Montroll[11] and Simha.[9] So it is also assumed that each bond of the polymer chain has the same probability of scission, independent of its position in the chain and independent on the degree of polymerization, i.e.,

$$K_{s,l} = K \tag{5}$$

Then the system of differential equations (eq 19) can be analytically solved and the following equation is obtained (see Appendix):

$$n_s(t) = [A_s - 2A_{s+1}e^{-Kt} + A_{s+2}e^{-2Kt}]\exp[-(S-1)Kt] \tag{6}$$

where $n_s(t)$ is the number of molecules with degree of polymerization S at the time t. There is one equation of type of (6) for each S; the A_s terms are determined by the initial MWD and are defined in the Appendix (eq 23). Equation 6 is the general rate equation. Functional solutions of the problem formulated by eq 17 were given by Simha[9] for a uniform initial MW and by Montroll[11] for a normal MWD of the initial polymer. They can be considered special formulations of eq 6.

Table V
Comparison between Experimental Results and Calculations (Model I, sample d)

Reaction time, min	$\bar{M}_n$ Exptl	$\bar{M}_n$ Calcd
0	117 000	117 000
15	76 000	74 000
30	55 100	53 500
60	34 800	32 300
90	24 400	23 900
150	14 200	14 100
210	9 870	9 820
330	5 650	5 740
450	3 650	4 220

Numerical calculations according to eq 6, however, were not consistent with the experimental results. Therefore, in order to account for the fact that the reaction rate is proportional to $\bar{M}_n^{2/3}$, eq 1 was taken into consideration. An average rate constant $K(\bar{M}_n)$ is defined:

$$K(\bar{M}_n) \equiv \sum_{l=1}^{s-1} K_{s,l} = (S-1)K_{s,l} \tag{7}$$

$$K(\bar{M}_n) = \tilde{K}\frac{\bar{M}_n^{2/3}}{M_{\text{mon}}} \tag{8}$$

With $(S-1) \simeq S$ and $\tilde{K} = kM_{\text{mon}}^{1/3}$ (from eq 1 with $a = 2/3$) we obtain

$$K_{s,l} = k162^{1/3}/\bar{M}_n^{1/3} \tag{9}$$

where k is the experimental rate constant (Tables II, III, and IV).

Computations were carried out with eq 6 for small time intervals. The $\bar{M}_n(t)$ of the degradation products was then calculated and $K_{s,l}$ was evaluated by eq 9. The whole process was repeated until the desired reaction time was reached. Using the experimental value of $k = 6.30 \times 10^{-6}\ s^{-1}$ the degradation of the dextran sample d was simulated. A comparison of the experimental values of $\bar{M}_n$ and the results of the computations are given in Table V. The agreement of the results is very good, but the CPR ($\bar{M}_w^2/\bar{M}_n\bar{M}_z$) calculated from this model was in the range of 1.3–1.4 and therefore considerably lower than the experimental value of 1.8.

Model II. In this model eq 9 is replaced by

$$K_{s,l} = \tilde{K}M^{2/3}/M = \tilde{K}M^{-1/3} \tag{10}$$

which means that an individual rate constant is attributed to each MW and not $\bar{M}_n$ as in model I. The system in eq 19 becomes considerably more complex, but an analytical solution is still obtainable (Appendix, eq 26).

Computations of the degradation of dextran sample d show very good agreement with the experimental $\bar{M}_n$ values, as with model I, but the CPR obtained from the calculations reach 1.5 only, which is still inconsistent with experimental results.

Model III. In this model a dependence of the rate constant of depolymerization on the location of the bond in the polymer chain is introduced. The general system of differential equations (Appendix, eq 19) is solved, with the following restrictions of the rate constants $K_{s,l}$:

$$\sum_{l=1}^{s-1} K_{s,l} = \bar{K}_s(S-1) = K^*S^{-1/3}(S-1) \simeq K^*S^{2/3} \tag{11}$$

In this equation $\Sigma_{l=1}^{s-1}K_{s,l}$ is the average reaction rate constant for all bonds in the molecule with degree of polymerization S, $\bar{K}_s$ is the average rate constant for the degradation of one bond of the same molecule, and K^* is a rate constant independent of S. Since the experiments show that more low

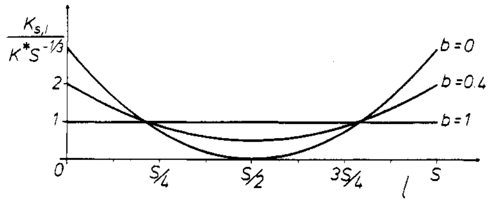

Figure 5. Variation of the rate constant of degradation $K_{s,l}/K^*S^{-1/3}$ (see eq 12) with the position l along the polymer chain. S is degree of polymerization. The parameter b defines the depth of the minimum of the parabola (eq 12).

Table VI
Variation of the Maximum Value of the Quotient $\overline{M}_w^2/\overline{M}_n\overline{M}_z$ with the Factor b (see Figure 5)

b	$\overline{M}_w^2/\overline{M}_n\overline{M}_z$	b	$\overline{M}_w^2/\overline{M}_n\overline{M}_z$
0	2.18	0.6	1.67
0.1	2.08	0.7	1.61
0.2	1.98	0.8	1.56
0.3	1.89	0.9	1.51
0.4	1.81	1.0	1.46
0.5	1.73		

MW fragments are produced than would be obtained by calculations according to models I and II, in which the constant $K_{s,l}$ is assumed to be independent on the location of the bond in the polymer chain, it was assumed in this model that $K_{s,l}$ changes along the polymer chain according to a parabolic function with the minimum at the midpoint of the chain (Figure 5). The reaction rate constants $K_{s,l}$ then have the form:

$$K_{s,l} = K^*S^{-1/3}\left[\frac{12(1-b)}{S(S-2)}\left(1-\frac{S}{2}\right)^2 + b\right] \tag{12}$$

$$S = 3, 4, 5, \ldots, r$$

where r is the maximum degree of polymerization and the parameter b defines the depth of the minimum of the parabola. If $b = 1$, the system reduces to model II.

As the analytical solution of this system seemed to be too difficult to obtain, numerical calculations were performed with the system of differential eq 19 for various values of b. Since computational time was excessively large if the calculations were performed for each degree of polymerization, a numerical simplification consisting of subdividing the polymer chain into segments of 15 monomer units was used. The accuracy of the results was not affected by this simplification.

The $\overline{M}_n$ values obtained with this model agreed very well with the experimental results and were independent of the value of b, according to eq 11. The CPR, however, showed a strong dependence on b. This is listed in Table VI, which contains the calculated maximum values of the CPR as a function of b. Best agreement with experimental results within the course of the reaction was obtained for $b = 0.4$. The corresponding CPR values are listed in Table IV. It could further be shown that the CPR calculated for a fixed value of b was independent of the initial MWD of the polymer used. The results thus indicate that during acid hydrolysis of dextran the bonds located at the ends of the polymer chain are more easily attacked than the central bonds.

Concluding Remarks

There are two rather unexpected results in our present work, first, the proportionality of the reaction rate constants on the MW raised to the power of ⅔, and second, the dependence of the rate constant of cleavage of the individual polymer bond on its location in the chain, which need some further comments.

Both results have been evaluated essentially from experimental work, particularly from the variation of the MWD in the course of the reaction. From this information it can be concluded that bonds near the ends of a polymer chain are more reactive than those at the center.

For further treatment of the problem, reaction models were set up and the reaction was simulated by mathematical methods to obtain numerical results. The models were based on the assumption that the polymer consists of unbranched chain molecules. In models I and II it was further assumed that the rate constants were the same for different locations within the molecule. To satisfy the experimental results the ⅔ dependency on MW had to be introduced as a basic premise, for which no physical explanation could be given. These models had to be tested on the variation of the MWD (in this work also characterized by the CPR) with reaction time, the results showing that both models fail. Therefore, an additional assumption was introduced, that there exists a parabolic dependency of the individual rate constants of the bonds along the polymer chain. The parabola was chosen for its relative computational simplicity. By an iterative method it was found that the parameter b, which defines the depth of the minimum of the parabola, was 0.4 for best fit with experimental CPR values. The premise that the reaction rate constants vary with the MW raised to the power of ⅔ also holds for this model. The individual rate constants therefore change in this model, due to the location of the broken bond within the molecule and also, naturally, with the MW.

No experimental data on the influence of different pH values and temperature on the characteristic variables are available now. Experimental work in this field is in progress.

Chain branching is not expected to have a remarkable effect on the value of the parameter b if the branches are smaller than the average length of the fragments split off at the ends of the molecules. Studies of Larm et al.[19] on the length of the side chains of dextran showed that 40% of them are only one glucose unit long, 45% are two glucose units, and maximally 15% are longer than two glucose units. Short side chains (degree of polymerization <5), however, do not affect appreciably the results of this study. Long-chain branching, on the other hand, may strongly affect b in direction to smaller values, as the number of chain ends may be considerably larger than two. In the course of hydrolysis the branching ratio decreases and therefore the value of b is expected to increase. It is not known with certainty to what extent long-chain branches are present in dextran. Very likely, it is about 1% for high MW's (>500 000) and becomes rapidly smaller as the MW decreases. The extremely small increase of the CPR during hydrolysis of the low MW fraction (sample c) gives evidence to this concept.

It cannot be expected that full explanations of the physical phenomena, which govern the process and its dependences, can be given. A very general concept would be to assume that the probability of initial cleavage of the polymer bonds is constant along the polymer chain and that the reaction rate constant is a function of the diffusion coefficient of the fragments. Then the individual rate constant $K_{s,l}$ for the reaction

$$M_s \rightarrow M_l + M_{s-l} \tag{13}$$

is proportional to the respective molecular diffusion coefficients D_l and D_{s-l}:

$$K_{s,t} \propto D_l + D_{s-l} \tag{14}$$

For spherical molecules the above equation can be written as

$$K_{s,l} \propto \left(\frac{1}{l^{1/3}} + \frac{1}{(S-l)^{1/3}}\right) \tag{15}$$

Since dextrans are slightly expanded coils in solution, this assumption seems reasonable as a first approximation. No precise values concerning the MW dependence of the diffusion constants of dextran are available,[20,21] so that this point needs further investigation. The rate constant for the decomposition of a certain molecule can be obtained by summing up all possible individual rate constants in the following way:

$$\begin{aligned} K(\overline{M}_{\mathrm{n}}) &= \sum_{l=1}^{s-1} K_{s,l} \propto \sum_{l=1}^{s-1} (D_l + D_{s-l}) = \sum_{l=1}^{s-1} 2D_l \\ &\propto \sum_{l=1}^{s-1} l^{-1/3} \simeq \int_0^s l^{-1/3}\,\mathrm{d}l = \tfrac{3}{2} S^{2/3} = A(M^{2/3}) \end{aligned} \tag{16}$$

where A is a proportionality constant.

From these considerations the dependence of the rate constants of the hydrolytic cleavage reaction on the MW of the polymer was derived without further assumptions, the same function being obtained as that evaluated from the experimental data. Furthermore, the function in eq 15 has a sagging shape, similar to the parabola assumed in Figure 5. This model thus also describes the variation of the rate constant along the polymer chain.

Appendix

General Formulation of the Depolymerization Kinetics. With the definitions r = maximum degree of polymerization, $K_{s,l}$ = monomolecular degradation constant of the lth bond of a polymer with degree of polymerization S, and n_s = number of polymer molecules with degree of polymerization S the following system of differential equations constitutes the general formulation of the degradation reaction (eq 17).

The $(S-1)$ negative terms indicate the $(S-1)$ different possibilities of depolymerization of a molecule with degree of polymerization S. Since such a molecule can be split off from a molecule with degree of polymerization i $(S < i \leq r)$ by the scission of either the Sth or the $(i-S)$th bond, there are two formation terms in the system (eq 13), consisting of the sums over the $(r-S)$ different molecules.

Introducing the vector **n**, defined as eq 18, system 17 can be written as in eq 19. Equation 19 represents the general formulation of the degradation process since no simplifications or approximations have been introduced.

Model I. It is assumed that all reaction rate constants for the polymer bonds within the molecule are constant, i.e.,

$$K_{s,l} = K \quad \text{for } S = 1, 2, 3, \ldots, r \text{ and } l = 1, 2, 3, \ldots, S - r \tag{5}$$

System 19 then simplifies to eq 20. The eigenvalues can be obtained directly from the diagonal and the eigenvectors ϵ_i were calculated as in eq 21.

$$\begin{aligned}
\frac{\mathrm{d}n_r}{\mathrm{d}t} &= -\sum_{i=1}^{r-1} K_{r,i} \cdot n_r = \left(-\sum_{i=1}^{r-1} K_{r,i}\right) \cdot n_r \\
\frac{\mathrm{d}n_{r-1}}{\mathrm{d}t} &= -\sum_{i=1}^{r-2} K_{r-1,i} \cdot n_{r-1} + K_{r,r-1} \cdot n_r + K_{r,1} \cdot n_r = \left(-\sum_{i=1}^{r-2} K_{r-1,i}\right) \cdot n_{r-1} + (K_{r,r-1} + K_{r,1}) \cdot n_r \\
\frac{dn_{r-2}}{\mathrm{d}t} &= -\sum_{i=1}^{r-3} K_{r-2,i} \cdot n_{r-2} + \sum_{i=(r-2)+1}^{r} K_{i,r-2} \cdot n_i + \sum_{i=(r-2)+1}^{r} K_{i,i-(r-2)} \cdot n_i = \left(-\sum_{i=1}^{r-3} K_{r-2,i}\right) \cdot n_{r-2} \\
&\qquad + (K_{r-1,r-2} + K_{r-1,i-(r-2)} \cdot n_{r-1} + (K_{r,r-2} + K_{r,2}) \cdot n_r \\
&\vdots \\
\frac{\mathrm{d}n_s}{\mathrm{d}t} &= -\sum_{i=1}^{s-1} K_{s,i} \cdot n_s + \sum_{i=s+1}^{r} K_{i,s} \cdot n_i + \sum_{i=s+1}^{r} K_{i,i-s} \cdot n_i = \left(-\sum_{i=1}^{s-1} K_{s,i}\right) \cdot n_s + \sum_{i=s+1}^{r} (K_{i,s} + K_{i,i-s}) \cdot n_i \\
\frac{\mathrm{d}n_r}{\mathrm{d}t} &= -\sum_{i=1}^{s-2} K_{s-1,i} \cdot n_{s-1} + \sum_{i=(s-1)+1}^{r} K_{i,s-1} \cdot n_i + \sum_{i=(s-1)+1}^{r} K_{i,i-(s-1)} \cdot n_i = \left(-\sum_{i=1}^{s-2} K_{s-1,i}\right) \cdot n_{s-1} \\
&\qquad + \sum_{i=s}^{r} (K_{i,s-1} + K_{i,i-(s-1)}) \cdot n_i \\
&\vdots \\
\frac{\mathrm{d}n_3}{\mathrm{d}t} &= -(K_{3,1} + K_{3,2}) \cdot n_3 + \sum_{i=4}^{r} K_{i,3} \cdot n_i + \sum_{i=4}^{r} K_{i,i-3} \cdot n_i = (-K_{3,1} - K_{3,2}) \cdot n_3 + \sum_{i=4}^{r} (K_{i,3} + K_{i,i-3}) \cdot n_i \\
\frac{\mathrm{d}n_2}{\mathrm{d}t} &= -(K_{2,1}) \cdot n_2 + \sum_{i=3}^{r} K_{i,2} \cdot n_i + \sum_{i=3}^{r} K_{i,i-2} \cdot n_i = (-K_{2,1}) \cdot n_2 + \sum_{i=3}^{r} (K_{i,2} + K_{i,i-2}) \cdot n_i \\
\frac{\mathrm{d}n_1}{\mathrm{d}t} &= -0 + \sum_{i=2}^{r} K_{i,1} \cdot n_i + \sum_{i=2}^{r} K_{i,i-1} \cdot n_i = +\sum_{i=2}^{r} (K_{i,1} + K_{i,i-1}) \cdot n_i
\end{aligned} \tag{17}$$

$$\left|\begin{array}{c} n_1 \\ n_2 \\ n_3 \\ \vdots \\ n_{s-1} \\ n_s \\ n_{s+1} \\ \vdots \\ n_{r-2} \\ n_{r-1} \\ n_r \end{array}\right| = \mathbf{n} \quad \text{and} \quad \left|\begin{array}{c} \frac{\mathrm{d}n_1}{\mathrm{d}t} \\ \frac{\mathrm{d}n_2}{\mathrm{d}t} \\ \frac{\mathrm{d}n_3}{\mathrm{d}t} \\ \vdots \\ \frac{\mathrm{d}n_{s-1}}{\mathrm{d}t} \\ \frac{\mathrm{d}n_s}{\mathrm{d}t} \\ \frac{\mathrm{d}n_{s+1}}{\mathrm{d}t} \\ \vdots \\ \frac{\mathrm{d}n_{r-2}}{\mathrm{d}t} \\ \frac{\mathrm{d}n_{r-1}}{\mathrm{d}t} \\ \frac{\mathrm{d}n_r}{\mathrm{d}t} \end{array}\right| = \frac{\mathrm{d}\mathbf{n}}{\mathrm{d}t} \qquad (18)$$

$$\frac{\mathrm{d}\mathbf{n}}{\mathrm{d}t} = \left|\begin{array}{cccccccc} 0 & (K_{2,1}+K_{2,1}) & (K_{3,1}+K_{3,2}) & (K_{4,1}+K_{4,3}) & (K_{5,1}+K_{5,4}) & \cdots & (K_{r-1,1}+K_{r-1,r-2}) & (K_{r,1}+K_{r,r-1}) \\ 0 & -K_{2,1} & (K_{3,2}+K_{3,1}) & (K_{4,2}+K_{4,2}) & (K_{5,2}+K_{5,3}) & \cdots & (K_{r-1,2}+K_{r-1,r-3}) & (K_{r,2}+K_{r,r-2}) \\ 0 & 0 & -\sum\limits_{i=1}^{2} K_{3,i} & (K_{4,3}+K_{4,1}) & (K_{5,3}+K_{5,2}) & \cdots & (K_{r-1,3}+K_{r-1,r-4}) & (K_{r,3}+K_{r,r-3}) \\ 0 & 0 & 0 & -\sum\limits_{i=1}^{3} K_{4,i} & (K_{5,4}+K_{5,1}) & \cdots & (K_{r-1,4}+K_{r-1,r-5}) & (K_{r,4}+K_{r,r-4}) \\ 0 & 0 & 0 & 0 & -\sum\limits_{i=1}^{4} K_{5,i} & \ddots & \cdots & \\ & & & & 0 & & & \vdots \\ & \Large 0 & & & \vdots & \Large 0 & \ddots & \\ & & & & 0 & \cdots & 0 & -\sum\limits_{i=1}^{r-1} K_{r,i} \end{array}\right| \cdot \mathbf{n} \qquad (19)$$

$$\frac{\mathrm{d}\mathbf{n}}{\mathrm{d}t} = K \left|\begin{array}{cccccccc} 0 & 2 & 2 & 2 & \cdots & 2 & \cdots & 2 \\ & -1 & 2 & 2 & \cdots & 2 & \cdots & 2 \\ & & -2 & 2 & \cdots & 2 & \cdots & 2 \\ & & & -3 & \cdots & 2 & \cdots & 2 \\ & & & & & \vdots & & \vdots \\ & & & & -(S-2) & 2 & \cdots & 2 \\ & \Large 0 & & & & -(S-1) & \cdots & 2 \\ & & & & & & & \vdots \\ & & & & & & & -(r-1) \end{array}\right| \mathbf{n} \qquad (20)$$

$$\epsilon_1 = \left|\begin{array}{c} 1 \\ 0 \\ \vdots \\ 0 \end{array}\right| \qquad \epsilon_2 = \left|\begin{array}{c} -2 \\ 1 \\ 0 \\ \vdots \\ 0 \end{array}\right| \qquad \epsilon_3 = \left|\begin{array}{c} 1 \\ -2 \\ 1 \\ 0 \\ \vdots \\ 0 \end{array}\right| \qquad (21a)$$

$$\epsilon_4 = \left|\begin{array}{c} 0 \\ 1 \\ -2 \\ 1 \\ 0 \\ \vdots \\ 0 \end{array}\right| \qquad \epsilon_s = \left|\begin{array}{c} 0 \\ \vdots \\ 0 \\ 1 \\ -2 \\ 1 \\ 0 \\ \vdots \\ 0 \end{array}\right| \qquad \epsilon_r = \left|\begin{array}{c} 0 \\ \vdots \\ 0 \\ 1 \\ -2 \\ 1 \end{array}\right| \qquad (21b)$$

With the original MWD of the polymer represented as

$$\mathbf{n}(0) = \left|\begin{array}{c} n_1(0) \\ n_2(0) \\ \vdots \\ n_r(0) \end{array}\right| \qquad (22)$$

the auxiliary quantities A_i (see eq 23), which were obtained iteratively, were introduced. From eq 23 the kinetics of degradation is obtained for each degree of polymerization S, as a function of time t, eq 6.

$$n_s(t) = [A_s - 2A_{s+1}e^{-Kt} + A_{s+2}e^{-2Kt}] \exp[-(S-1)Kt]$$

Model II. It is assumed that the reaction rate constant $K_{s,l}$ depends on the MW but is independent of the location of the bond in the polymer chain:

$$K_{s,l} = K_s = \tilde{K}M^{-1/3} = K'S^{-1/3} \qquad (10)$$

System 19 then reduces to eq 24. The solution of this system is derived by Laplace transformation and the subsequent

$$\begin{aligned} A_{r+2} &= 0 \\ A_{r+1} &= 0 \\ A_r &= n_r(0) \\ A_{r-1} &= n_{r-1}(0) + 2A_r \\ A_{r-2} &= n_{r-2}(0) + 2A_{r-1} - A_r \\ A_{r-3} &= n_{r-3}(0) + 2A_{r-2} - A_{r-1} \\ &\vdots \\ A_{s+1} &= n_{s+1}(0) + 2A_{s+2} - A_{s+3} \\ A_s &= n_s(0) + 2A_{s+1} - A_{s+2} \\ A_{s-1} &= n_{s-1}(0) + 2A_s - A_{s+1} \\ &\vdots \\ A_3 &= n_3(0) + 2A_4 - A_5 \\ A_2 &= n_2(0) + 2A_3 - A_4 \\ A_1 &= n_1(0) + 2A_2 - A_3 \end{aligned} \qquad (23)$$

$$\frac{\mathrm{d}\mathbf{n}}{\mathrm{d}t} = \left|\begin{array}{ccccccc}
0 & 2K_2 & 2K_3 & 2K_4 & 2K_5 \cdots\cdots & 2K_s \cdots\cdots\cdots & 2K_r \\
 & -K_2 & 2K_3 & 2K_4 & 2K_5 \cdots\cdots & 2K_s \cdots\cdots\cdots & 2K_r \\
 & & -2K_3 & 2K_4 & 2K_5 \cdots\cdots & 2K_s \cdots\cdots\cdots & 2K_r \\
 & & & -3K_4 & 2K_5 \cdots\cdots & 2K_s \cdots\cdots\cdots & 2K_r \\
 & & & & -4K_5 \cdots\cdots & 2K_s \cdots\cdots\cdots & 2K_r \\
 & & & & \ddots & \vdots & \vdots \\
 & \text{\huge 0} & & & & -(s-1)K_s \cdots\cdots & 2K_r \\
 & & & & & \ddots & \vdots \\
 & & & & & & -(r-1)K_r
\end{array}\right| \cdot \mathbf{n} \tag{24}$$

solution of the system of linear equations is obtained.[22] The inverse transformation is possible by means of a partial fraction expansion with the aid of the theorem of residues.[23] Using the following abbreviations:

$$\begin{aligned}
\hat{K}_j &= 2K'(r+1-j)^{-1/3} \\
\lambda_j &= -\frac{\hat{K}_j}{2}(r-j) \\
A_s(0) &= n_{r+1-s}(0) \\
A_s(t) &= n_{r+1-s}(t)
\end{aligned} \tag{25}$$

the solution is given by eq 26,

$$\begin{aligned}
A_s(t) = A_s(0)e^{\lambda_s\cdot t} &+ \sum_{j=1}^{s-1} \frac{A_j(0)\cdot\hat{K}_j}{(\lambda_j-\lambda_s)}\cdot(e^{\lambda_j\cdot t}-e^{\lambda_s\cdot t}) \\
&+ \sum_{i=1}^{s-2}\left\{(-1)^i \sum_{j=1}^{s-1-i} A_j(0)\cdot\hat{K}_j\right. \\
&\times \sum_{\substack{l_1,l_2,l_u,\ldots,l_i \\ s>l_u>j \\ l_u\in \mathrm{IN}}} \left(\prod_{u=1}^{i}\hat{K}_{l_u}\left[\frac{e^{\lambda_s\cdot t}}{(\lambda_j-\lambda_s)\cdot\prod_{u=1}^{l}(\lambda_{l_u}-\lambda_s)}\right.\right. \\
&+ \frac{e^{\lambda_j\cdot t}}{(\lambda_s-\lambda_j)\prod_{\substack{u=1\\u\neq v}}^{i}(\lambda_{l_u}-\lambda_j)} \\
&\left.\left.\left.+ \sum_{v=1}^{i}\frac{e^{\lambda_{l_v}\cdot t}}{(\lambda_s-\lambda_{l_v})(\lambda_j-\lambda_{l_v})\prod_{u=1}^{i}(\lambda_{l_u}-\lambda_{l_v})}\right]\right)\right\}
\end{aligned} \tag{26}$$

$$S=1,2,3,\ldots r$$

where the fourth summation comprises all ordered permutations of the indexes i between $(S-1)$ and $(j+1)$.

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