Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Browarzik, Dieter(1997) 'Continuous Kinetics of Dextran Degradation', Journal of Macromolecular Science, Part A, 34: 3, 397 — 404
To link to this Article: DOI: 10.1080/10601329708014967
URL: http://dx.doi.org/10.1080/10601329708014967

J.M.S.—PURE APPL. CHEM., A34(3), pp. 397–404 (1997)

CONTINUOUS KINETICS OF DEXTRAN DEGRADATION

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ABSTRACT

Degradation of dextranes is studied in the framework of a first-order continuous kinetics. Here, the dextranes are approximately described by Schulz-Flory distributions, the parameters of which depend on the time. A new expression is introduced for the continuous rate function which is the continuous generalization of the rate constants of usual kinetics. One factor of this expression describes the scission probability in dependence on the molecular weight. The other factor describes the dependence on the location of the bond to be broken within the molecule. The rate function introduced is especially suitable if the bonds near the ends of a molecule are preferentially broken. The model is applied to four dextran samples degraded by acid hydrolysis. All experimental data may be described by a single set of three parameters.

INTRODUCTION

In continuous kinetics, degradation of polydisperse polymers is described by the continuous rate equation

$$\partial w(M,t)/\partial t = \int_M^\infty \kappa(M',M)\, w(M',t)\, dM' - \frac{1}{2}\, w(M,t) \int_0^M \kappa(M,M'')\, dM'' \qquad (1)$$

Equation (1) is based on a first-order formalism, and all species are assumed to be of the same type. In Eq. (1) $w(M,t)dM$ gives the amount of substance between

the values M and $M + dM$ of the molecular weight at time t. The rate function $\kappa(M',M)$ describes the breakage of a molecule of molecular weight M' into two molecules of molecular weights M and $M' - M$. The function $\kappa(M',M)$ may be interpreted as the continuous generalization of the rate constants of usual kinetics. The first integral in Eq. (1) describes the formation of molecules of molecular weight M by degradation of higher molecules. The other terms on the right-hand side of Eq. (1) describe the destruction of such molecules by splitting in smaller molecules. A detailed derivation of Eq. (1) from usual kinetics was given by Kehlen, Rätzsch, and Bergmann [1].

Analytical solutions of Eq. (1) were found for only some cases the simplest of which is the case of "random scission" [1–4], assuming all bonds break with equal probability. In the notation of this paper, that means $\kappa(M',M)$ = constant. In recent years an essential advantage in solving Eq. (1) has been reached by Ziff and McGrady [5–7]. For some special functions of $\kappa(M',M)$ they found explicit solutions of the continuous rate Eq. (1). For functions $\kappa(M',M)$ needed in practice, the exact solution of Eq. (1) is usually unknown. Recently, Williams [8] described a procedure to find general solutions of Eq. (1). At present, this very complicated method has not been demonstrated for a realistic case of $\kappa(M',M)$. Because in the most cases of some interest there are no analytical solutions of the continuous rate equation, numerical methods are applied to solve it [9].

Browarzik and Koch [10] proposed an approximation solution of Eq. (1) assuming a Schulz–Flory distribution with time-dependence parameters valid during the whole time of degradation. This method may be applied to a wide class of functions $\kappa(M',M)$ in more detail, but only the type

$$\kappa(M',M) = \alpha^*(M')^{\varepsilon^*}\left[1 - \beta^*\frac{M}{M'}\left(1 - \frac{M}{M'}\right)\right] \tag{2}$$

was considered. Despite its simplicity, Eq. (2) describes the scission probability in its dependence on the molecular weight of the polymer molecule and on the location of the bond to be broken within the molecule. If $\varepsilon^* > 0$ ($\varepsilon^* < 0$), a larger molecule is degraded more (less) rapid than a smaller one. If $\beta^* < 0$, the bonds near the center of a molecule break preferentially to those near the ends. If $\beta^* > 0$, the opposite case occurs. The parameter β^* is restricted by $\beta^* \leq 4$ because the rate function $\kappa(M',M)$ is defined as fulfilling the condition $\kappa(M',M) \geq 0$ for all M values between 0 and M'. (For example, for $M = M'/2$, the terms in brackets in Eq. 2 take the form $1 - \beta^*/4$ and, therefore, $\beta^* \leq 4$ results in $\kappa \geq 0$.)

There are a variety of mechanisms, including acid hydrolysis [11], enzymatic attack [12], ultrasonic irradiation [13], and shear action [14, 15], leading to dextran degradation. During the degradation of dextranes the distribution function and their moments strongly change. Thus, in the framework of continuous kinetics, dextranes are of some interest.

Browarzik and Koch [10] applied their approximation method to dextran degradation by acid hydrolysis, by enzymatic attack, and by ultrasonic irradiation through comparison of the calculated and the experimental [11–13] results. In all three cases highly positive values of β^* were found, corresponding to a favored scission of bonds near the ends of a molecule. On the whole, the experimental results were reasonably described by Eq. (2), but there are three disadvantages to applying Eq. (2). First, fitting the parameters to the restriction $\beta^* \leq 4$ results in

difficulties. In some cases, forbidden values of β^* ($\beta^* > 4$) describe the experimental data better than does any value $\beta^* \leq 4$. Second, in the treatment of Browarzik and Koch [10], all occurring integrals possess closed solutions only for $\varepsilon^* > -1$. Fortunately, this restriction does not matter for descriptions of dextran degradation. Third, considering the experimental values of the nonuniformity U as a function of the time t [11-13], some dextran samples show a maximum. In contrary to that, $U(t)$ calculated by Eq. (2) never shows a maximum. ($U = M_w/M_n - 1$, where M_n and M_w are the number- and the weight-average molecular weights.)

In this paper Eq. (2) is replaced by a more flexible expression in order to avoid the disadvantages mentioned above. In particular, this expression is able to describe $U(t)$ curves which possess a maximum. To appreciate the accuracy of Eqs. (2) and (3), dextran degradation by acid hydrolysis is considered in detail by comparing the calculated and the experimental [11] results.

BASIC TREATMENT

In this paper, instead of Eq. (2), the continuous rate function is assumed to be

$$\kappa(M',M) = \alpha e^{-\varepsilon M'}[e^{-\beta(M/M')} + e^{-\beta(1-M/M')}] \tag{3}$$

The background of Eq. (3) is similar to that of Eq. (2). The first factor of Eq. (3) describes the scission probability in its dependence on the molecular weight of the polymer molecule, and the factor in brackets gives the dependence on the location of the bond to be broken within the molecule. If $\varepsilon > 0$ ($\varepsilon < 0$), a larger molecule is degraded less (more) rapidly than a smaller one. If $\beta > 0$, the breakage of bonds near the ends of a molecule is favored. For the case $\beta < 0$, the bonds near the center of a molecule break preferentially to those near the ends. Because of the exponential form of the terms, in contrast to Eq. (2), there are no restrictions for the parameters. In particular, the parameter β may take very positive values which correspond to the strongly favored scission of bonds near the ends of a molecule.

To solve Eq. (1) based on Eq. (3), $w(M,t)$ is approximated by a Schulz-Flory distribution:

$$w(M,t) = n\frac{k^k}{\overline{M}_n\Gamma(k)}(M/\overline{M}_n)^{k-1}\exp(-kM/\overline{M}_n) \tag{4}$$

which is assumed to be valid during the whole time of degradation. In Eq. (4) the quantities n, $\overline{M}_n$, and k are functions of the time t. Here, n is the total amount of substance, and $\overline{M}_n$ is the number-average molecular weight. During the degradation process the number of molecules and, corresponding to that, n increase. Simultaneously, $\overline{M}_n$ decreases in such a way that the total mass of substance $n\overline{M}_n$ is a constant (law of conservation of mass). The quantity k is given by

$$k(t) = 1/U(t); \qquad U(t) = \overline{M}_w(t)/\overline{M}_n(t) - 1 \tag{5}$$

where U is the nonuniformity describing the breadth of the distribution and $\overline{M}_w$ is the weight-average molecular weight.

To prove the approximation introduced by Eq. (4), Browarzik and Koch [10] compared the results based on Eq. (4) and the exact results for the case of "random

scission," i.e., $\kappa(M',M)$ = constant. The Schulz–Flory distribution was verified to be in reasonable accordance with the exact function $w(M,t)$.

By introducing a general definition of moments of $w(M,t)$ by

$$\overline{M}^{(r)}(t) = \int_0^\infty M^r w(M,t)dM; \qquad r \geq 0 \tag{6}$$

the quantities $n(t)$, $\overline{M}_n(t)$, and $\overline{M}_w(t)$ may be expressed by

$$n(t) = \overline{M}^{(0)}(t); \qquad \overline{M}_n(t) = \frac{\overline{M}^{(1)}(t)}{\overline{M}^{(0)}(t)}; \qquad \overline{M}_w(t) = \frac{\overline{M}^{(2)}(t)}{\overline{M}^{(1)}(t)} \tag{7}$$

According to Eq. (4), the time dependence of the distribution function reduces to the time dependence of the total amount of substance n and of the parameters $\overline{M}_n$ and k.

With the aid of Eqs. (1), (3) (4), and (6), a relation for $d\overline{M}^{(r)}/dt$ may be obtained. Here, double integrals over M (the limits are 0 and ∞) and over M' (the limits are M and ∞) occur. The double integrals may be written as a product of a single integral over M' (the limits are 0 and ∞) and of a single integral over $y = M/M'$ (the limits are 0 and 1). Solving the first integral analytically, $d\overline{M}^{(r)}/dt$ obeys the relation

$$\frac{d\overline{M}^{(r)}}{dt} = n\alpha \frac{\Gamma(k + r + 1)}{\Gamma(k)} \frac{k^k}{(k + \varepsilon\overline{M}_n)^{k+r+1}} \times (\overline{M}_n)^{r+1}\left[I_r - \frac{1}{\beta}(1 - e^{-\beta})\right] \tag{8}$$

where I_r is given by

$$I_r = \int_0^1 y^r e^{-\beta y}dy + e^{-\beta}\int_0^1 y^r e^{\beta y}dy \tag{9}$$

Setting $r = 1$ because of the conservation of mass during the reaction, $d\overline{M}^{(1)}/dt = 0$ or $n(t)\overline{M}_n(t)$ = constant is obtained. If Eq. (8) is additionally applied to $r = 0$ and $r = 2$ with the aid of Eqs. (5) and (7), the temporal changes of the number-average molecular weight $\overline{M}_n$ and of the nonuniformity U obey the relations

$$\frac{d\overline{M}_n}{dt} = -\frac{\alpha}{\beta}(1 - e^{-\beta})\,(\overline{M}_n)^2(1 + \varepsilon\overline{M}_n U)^{-(1+1/U)} \tag{10}$$

$$\frac{dU}{dt} = \frac{\alpha}{\beta}\overline{M}_n(1 + U)(1 + \varepsilon\overline{M}_n U)^{-(1+1/U)}(1 - e^{-\beta}) \times \left(1 + \frac{2(1 + 2U)}{\beta(1 + \varepsilon\overline{M}_n U)^2}\left[\frac{2}{\beta} - \frac{1 + e^{-\beta}}{1 - e^{-\beta}}\right]\right) \tag{11}$$

Based on Eqs. (10) and (11), one can calculate $\overline{M}_n(t)$ and $U(t)$ from the initial values of $\overline{M}_n$ and U by increasing the time step by step (using sufficiently small time steps). By knowing $\overline{M}_n(t)$ and $U(t)$, with Eq. (4) the distribution function in its time dependence is known too.

An essential advantage of Eq. (11) is the ability to describe a maximum in $U(t)$ as is experimentally found in some cases [11–13]. This ability originates from the exponential form of the terms of Eq. (3).

The occurrence of a maximum in $U(t)$ requires that β be large enough to make the term in brackets of Eq. (11) negative. Nevertheless, at the beginning of degradation, $\overline{M}_n$ still takes high values, and if $\varepsilon > 0$, the fraction in front of the term in brackets is small, leading to $dU/dt > 0$. During degradation, $\overline{M}_n$ decreases rapidly and the fraction in front of the brackets increases. If this fraction is large enough, the derivative dU/dt becomes negative, corresponding to the occurrence of a maximum.

According to the fraction in front of the brackets of Eq. (11), high initial values of $\overline{M}_n$ and U favor the occurrence of a maximum in $U(t)$, presuming that $\varepsilon > 0$ and that β has a strong positive value. Thus, $U(t)$ may be expected to possess a maximum for degradation of high molecular samples of an initially broad distribution if the bonds near the ends of a molecular are preferentially broken ($\beta > 0$) and if smaller molecules are degraded more rapid than larger ones ($\varepsilon > 0$). Initially, nonuniformity U increases because of the formation of small fragments. In further degradation the larger molecular species disappear, which leads to a decrease of U.

MODELING OF DEXTRAN DEGRADATION

To test the model introduced by this paper, dextran degradation by acid hydrolysis is considered for two reasons. First, through the work of Basedow, Ebert, and Ederer [11] many experimental data of this type of degradation are available. Second, these authors investigated a sample which showed a strongly shaped maximum.

Basedow, Ebert, and Ederer [11] investigated degradation of four dextran samples at 80°C in 0.12 N sulfuric acid. The initial concentration of dextran was 1%. Samples *b*, *c*, and *d* have a narrow molecular weight distribution, and Sample *c* is of low molecular weight. Sample *a* has a high molecular weight and a broad molecular weight distribution. The initial values $\overline{M}_n(0)$ and $U(0)$ of the number-average molecular weight and of the nonuniformity are

Sample *a*:	$\overline{M}_n(0) = 738{,}000$ g/mol;	$U(0) = 4.83$
Sample *b*:	$\overline{M}_n(0) = 72{,}700$ g/mol;	$U(0) = 0.24$
Sample *c*:	$\overline{M}_n(0) = 4{,}380$ g/mol;	$U(0) = 0.45$
Sample *d*:	$\overline{M}_n(0) = 117{,}000$ g/mol;	$U(0) = 0.29$

The molecular weight distributions were measured by GPC in a time range of 110 minutes (Samples *a*, *b*, *c*) or of 450 minutes (Sample *d*). In the case of Sample *d*, experimental values of $\overline{M}_n$ and U are given. All other samples are characterized by $\overline{M}_n$ and by the "combined polydispersity ratio" CPR (instead of U). Here, CPR is defined by

$$\mathrm{CPR}(t) = \frac{(\overline{M}_w(t))^2}{\overline{M}_n(t)\overline{M}_z(t)} \tag{12}$$

where $\overline{M}_z$ is the z-average molecular weight ($\overline{M}_z = M^{(3)}/\overline{M}^{(2)}$). Presuming a Schulz-Flory distribution, $U(t)$ may be calculated from $\mathrm{CPR}(t)$ according to

$$U(t) = (\mathrm{CPR}(t) - 1)[1 + \sqrt{1 + (\mathrm{CPR}(t) - 1)^{-1}}] \tag{13}$$

Because the four dextran samples considered were degraded under the same conditions (by acid hydrolysis), the description of all measured values for $\overline{M}_n(t)$ and

$U(t)$ should be possible with the same set of parameters α, β, and ε. Therefore, a single parameter set for all four dextran samples is determined by simultaneous fitting of $\overline{M}_n$ and U to all available experimental data. Doing so, the parameters of Eq. (3) take the following values:

$$\alpha = 2.871 \times 10^{-6}\,\text{mol/(g min)}; \qquad \beta = 6.597; \qquad \varepsilon = 5.680 \times 10^{-7}\,\text{mol/g}$$

Considering the ε value, smaller molecules are preferentially broken. According to the β value, the bonds near the ends of a dextran molecule break easier than those near the middle, corresponding to the occurrence of many small fragments.

For the sake of comparison, the parameters of Eq. (2) were fitted to the experimental data in the same way as the parameters of Eq. (3), yielding

$$\alpha^* = 5.068 \times 10^{-5}(\text{mol/g})^{0.698}/\text{min}; \qquad \beta^* = 3.623; \qquad \varepsilon^* = -0.302$$

Because of the negative ε^* value, the scission of small molecules is favored. The highly positive values of β^* shows that the bonds near the ends of the molecules are preferentially broken. Thus, the adapted parameters of both Eqs. (2) and (3) result in the same conclusions concerning the breakage probabilities.

Figure 1 shows a comparison of the curves $\overline{M}_n(0)/\overline{M}_n(t)$ calculated by Eq. (3) and of the corresponding experimental points in the 110-minute time range. The mean deviation of the calculated $\overline{M}_n$ values from the experimental ones is 11.0%. On the whole, the description of $\overline{M}_n$ in its time dependence is satisfactory. In Fig. 1 the samples with narrow molecular weight distributions (Samples *b*, *c*, and *d*) have nearly linear curves. In the case of Sample *a*, there are considerable deviations from linearity in the time range up to 45 minutes. After a long degradation time, such deviations no longer exist. The curves $\overline{M}_n(0)/\overline{M}_n(t)$ calculated by the older Eq. (2) are not included in Fig. 1 because they are very similar to those calculated by the newer Eq. (3). Here, the mean deviation of the calculated $\overline{M}_n$ values from the

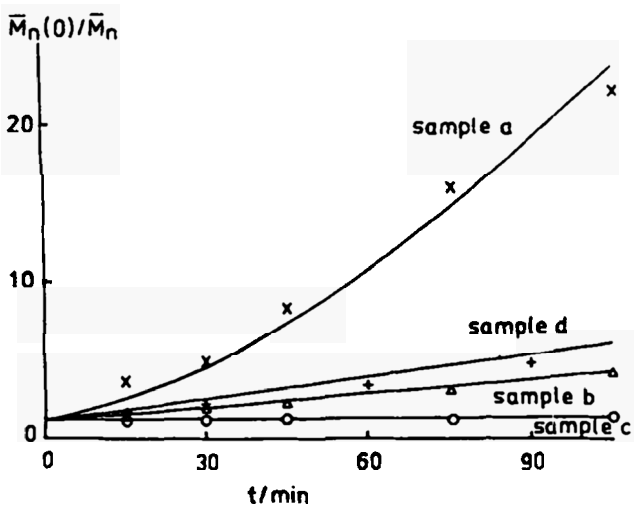

FIG. 1. Comparison of the curves calculated by Eq. (3) and of the experimental points for the time dependence of the number-average ratio $\overline{M}_n(0)/\overline{M}_n$ for the Samples *a*, *b*, *c*, and *d*: (×) Sample *a*, (△) Sample *b*, (○) Sample *c*, (+) Sample *d*.

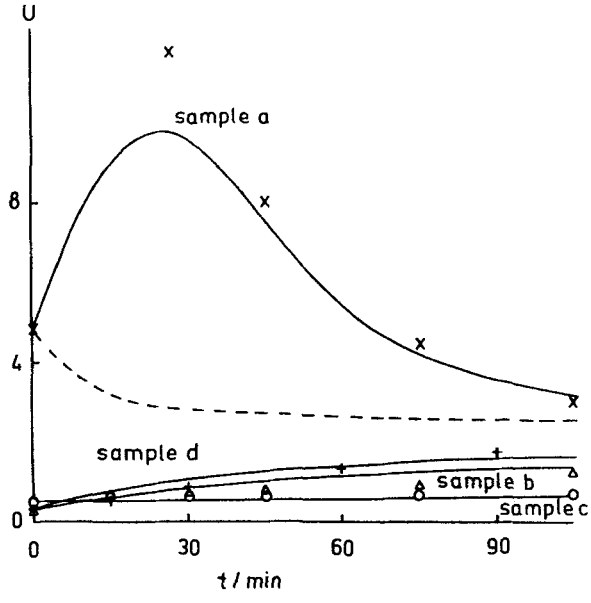

FIG. 2. Comparison of the calculated curves and of the experimental points for the time dependence of the nonuniformity U for the Samples a, b, c, and d: (—) calculated by Eq. (3), (- - -) Sample a calculated by Eq. (2), (×) Sample a, (△) Sample b, (○) Sample c, (+) Sample d.

experimental ones is 5.0%. Thus, for $\overline{M}_n$, Eq. (2) describes the experimentally found time dependence better than Eq. (3).

Figure 2 shows a comparison of the curves $U(t)$ calculated by Eq. (3) (full lines) and of the corresponding experimental points in the 110-minute time range. The mean deviation of the calculated U values from the experimental ones is 17.4%. Thus, the description of the time dependence of nonuniformity U is less reasonable than that of $\overline{M}_n$. However, one has to consider that the results of all four samples, which strongly differ in their initial values of $\overline{M}_n$ and U, are based on the same parameter values. Furthermore, in the case of Sample a, the maximum of $U(t)$ is described reasonable [except the extremely high experimental value $U(15\text{ min}) = 15.38$, which is not included in Fig. 2]. The curves calculated by the older Eq. (2) are very similar to those calculated by Eq. (3), except for Sample a. Therefore, only the curve $U(t)$ for Sample a as calculated by Eq. (2) (dashed line) is included in Fig. 2. The mean deviation of the U values calculated by Eq. (2) from the experimental ones is 23.9%. In the case of Sample a, Eq. (2) describes the experimental $U(t)$ data quite unsatisfactory. Instead of the experimentally found maximum, a continuous decrease of U with t is predicted by Eq. (2).

CONCLUSIONS

Continuous kinetics assuming first-order reactions is a comfortable way to treat dextran degradation. In particular, the mathematical treatment is simplified if the polydispersity of the dextrane is described by Schulz-Flory distributions, the

parameters of which are functions of the time t. The main problem is to find suitable expressions for the rate function $\kappa(M',M)$ which measures the scission probability in dependence on the molecular weight and on the location of the bond to be broken within the molecule. This expression has to be able to describe degradation of dextran samples strongly differing in the number-average $\overline{M}_n$ of the molecular weight and in the nonuniformity U (which measures the breadth of the distribution). In a previous paper the rate function defined by Eq. (2) was shown to be suitable for describing the degradation of some dextran samples. Unfortunately, this expression is not flexible enough to describe a maximum in $U(t)$. Furthermore, the parameters are restricted by $\varepsilon^* > -1$ and $\beta^* \leq 4$, which is uncomfortable for the parameter fit. Therefore, to avoid these disadvantages, in this paper a new expression Eq. (3) for the rate function $\kappa(M',M)$ is introduced.

To test both expressions for $\kappa(M',M)$, the parameters were adapted to experimental data [11] of dextran degradation by acid hydrolysis. Both Eqs. (2) and (3) result in the same conclusions:

1. Smaller dextran molecules are preferentially broken.
2. The bonds near the ends of a dextran molecule break easier than those near the middle.

The calculated time dependence of $\overline{M}_n$ is in reasonable accordance with the experimental data, particularly in the case of Eq. (2). The description of $U(t)$, especially if based on Eq. (2), is less accurate. Whereas in the case of Sample *a* the curve $U(t)$ calculated by Eq. (3) shows a maximum, as experimentally found, Eq. (2) predicts U will decrease continuously with time. Indeed, Eq. (2) partially gives better results than Eq. (3), but in contrast to Eq. (2), the newer Eq. (3) is able to describe $\overline{M}_n(t)$ and $U(t)$ qualitatively correct in all cases considered.

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Received January 28, 1996
Revision received July 8, 1996