Polymer Bulletin 1, 299–306 (1979)

Polymer Bulletin

Effects of Mechanical Stress on the Reactivity of Polymers: Activation of Acid Hydrolysis of Dextran by Ultrasound

Arno Max Basedow and Klaus Heinrich Ebert

Institut für Angewandte Physikalische Chemie, Universität Heidelberg,
6900 Heidelberg, Federal Republic of Germany

SUMMARY

The influence of ultrasonic irradiation on the kinetics and mechanism of acid hydrolysis of dextran is studied. The increase in the rate constants of the combined hydrolytic and ultrasonic degradation was investigated as a function of the molecular weight of dextran. For molecular weights higher than the limiting value for ultrasonic degradation the rate constants are proportional to the molecular weight raised to the power of 4/3; for molecular weights below the limiting value the rate constants are proportional to the molecular weight raised to the power of 5/6. The effects are discussed in connection with stretching forces which act on the polymer molecules as a result of ultrasonic cavitation.

INTRODUCTION

It has been shown recently that mechanically strained dextran molecules are more easily degraded by chemical agents than molecules not subjected to mechanical stress (BASEDOW et al.1979). Mechanical energy can be supplied to the polymer solution by means of flow fields or by ultrasonic irradiation. Mechanical degradation of polymers has been reviewed recently (CASALE and PORTER 1978).

The hydrolytic depolymerization of dextran has been extensively studied several years ago (SENTI et al. 1955, ANTONINI et al. 1964, SZEJTLI 1976), but it was found only recently that the rate constants of degradation are proportional to the molecular weight (MW) raised to the power of 2/3 (BASEDOW et al. 1978). For the degradation of dextran in solution by the action of ultrasound it was found that the rate constants are proportional to the MW and that chain scission takes place preferentially at the center of the molecule (BASEDOW and EBERT 1975, 1977).

In the present study the influence of ultrasonic irradiation on the kinetics of acid hydrolysis of dextran is investigated. Two dextran fractions with MW's

0170-0839/79/0001/0299/$01.60

higher and lower than the limiting MW (M_ℓ) for ultrasonic degradation (which was found to be 7000) were used for the experiments.

EXPERIMENTAL

Two dextran fractions with narrow molecular weight distributions (MWD) were used for the degradation experiments. The number average MW's were $\overline{M}_n$=72600 ($\overline{M}_w/\overline{M}_n$=1.14, $\overline{M}_z/\overline{M}_w$=1.14) for sample A and $\overline{M}_n$=5880 ($\overline{M}_w/\overline{M}_n$=1.03, $\overline{M}_z/\overline{M}_w$=1.04) for sample B. They were prepared from commercially available products(Pharmacia Fine Chemicals, Uppsala, Sweden) by preparative GPC on Sephadex. In the present study dextran is considered to be a linear polymer, since there are only relatively few and mostly short side chains (LARM et al. 1971).

Experiments were carried out with samples of 10 ml in closed thermostated glass cells (BASEDOW and EBERT 1977) at 82±0.1°C in water and in 0.60 molar phosphoric acid. Ultrasonic energy was applied by a generator (Branson Model B-12, Danbury, USA) operating at a frequency of 20 kHz and an intensity of 10 W/cm^2. The polymer concentration was 0.5 mg/ml in all experiments. After definite times of degradation the polymer was precipitated by cold (~-30°C) methanol and dried under vacuum. Oligosaccharides with a degree of polymerization smaller than 5 were not precipitated and were disregarded.

The MW averages and the MWD's of the dextran samples were obtained by GPC on controlled pore glass CPG-10 (Electro Nucleonics, Fairfield, USA) as described in detail previously (BASEDOW et al. 1976, BASEDOW 1977). Reproducibility in the MWD's and MW averages is ±0.5%; deviations in the absolute values are ±2%.

RESULTS and DISCUSSION

The experimental results are summarized in TABLE 1. The kinetics of degradation of dextran were determined for acid hydrolysis (I) and for ultrasonic degradation (II) in separate experiments and the results compared with the combined hydrolytic and ultrasonic degradation (III). It can be easily seen that the degradation is stronger in experiment III, compared to the summation of the hydrolytic and ultrasonic degradation (I and II). In TABLE 1 the column B' represents the relative increase in the additional number of bonds broken (BASEDOW et al. 1978) due to the cooperation of hydrolysis with ultrasonic irradiation (experiment III). It can be seen from FIG. 1

TABLE 1

Kinetic analysis of the degradation of dextran

Time t (min)	$\overline{M}_n$ I	II	III	B'	CPR	$\overline{M}_n$ IV	V
0	72600	72600	72600		1.00	5880	5880
10	53900	63500	35500	1.120	1.31	5420	4800
20	39900	55900	24600	0.740	1.39	5200	4000
30	32500	50400	19000	0.684	1.42	4870	3570
40	27000	45200	16000	0.538	1.40	4550	3020
50	22500	41400	13900	0.419	1.37	4360	2750
60	18800	38300	12200	0.328	1.32	4040	2450
Rate constant k (s^{-1})	1.0×10^{-5}	5.5×10^{-7}	5.9×10^{-7}			1.0×10^{-5}	1.8×10^{-5}

I: Hydrolysis, sample A
II: Ultrasonic degradation, sample A
III: Combined hydrolytic and ultrasonic degradation, sample A
IV: Hydrolysis, sample B
V: Hydrolysis activated by ultrasound, sample B

CPR = $\overline{M}_w^2/\overline{M}_n\overline{M}_z$, column III, sample A

$$B' = \frac{B_{III} - (B_I + B_{II})}{B_I + B_{II}}$$

B_I, B_{II}, B_{III} calculated from the $\overline{M}_n$-values of columns I, II, and III, respectively that B' is proportional to the MW (column III in TABLE 1). The cooperative effect thus increases the higher the MW of the polymer is. In TABLE 1 a combined polydispersity ratio (CPR), defined as $\overline{M}_w^2/\overline{M}_n\overline{M}_z$ (BASEDOW et al. 1978), which constitutes an adequate parameter to characterize the degradation products, is included for experiment III. Dextran sample B was treated in the same way. From the results of TABLE 1 (IV, V) it is evident that ultrasound has also in this case an enhancing effect on the hydrolytic degradation.

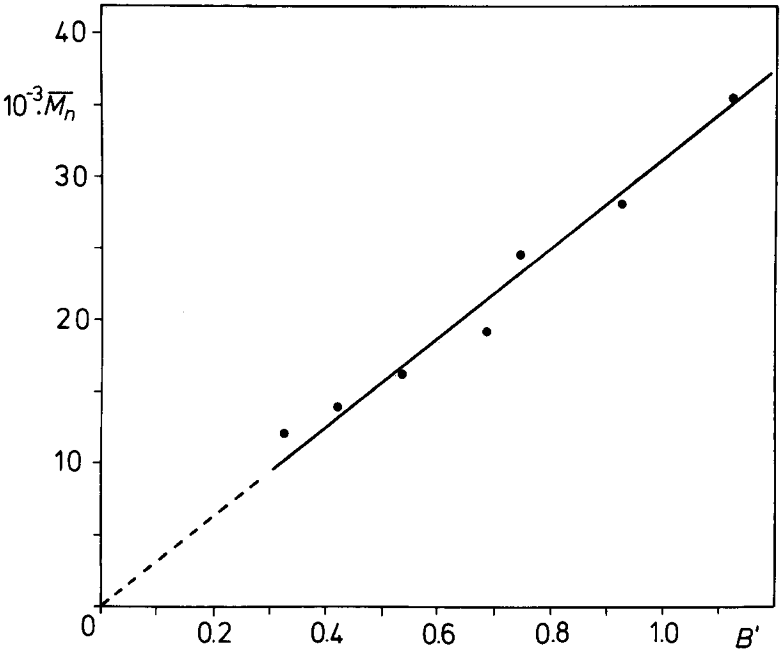

FIGURE 1: Plot of the relative increase B' in the number of bonds broken per molecule due to the cooperative effect of hydrolytic and ultrasonic degradation vs. $\overline{M}_n$.

For further discussions of the cooperative effect in the combined experiments, the dependence of the degradation rate constants on the MW was determined. As shown recently (BASEDOW et al. 1978), this can be expressed by the following equation:

$$\frac{1}{\overline{M}_n(t)^{a}} = \frac{1}{\overline{M}_n(o)^{a}} + a\left(\frac{k}{162^{a}}\right)t \qquad (1)$$

in which $\overline{M}_n(o)$ and $\overline{M}_n(t)$ are the MW's at the beginning of the reaction and after the reaction time t, k is the first order rate constant, 162 is the MW of the monomer unit and a is a constant which represents the dependence of the rate constant of degradation of a definite molecule on its MW. The exponent a was evaluated for each experiment by applying equation (1) and performing a computer regression analysis. The results obtained are summarized in TABLE 2.

TABLE 2

Values of the exponent a for different types of degradation reactions.

Reaction	a	CPR
Hydrolysis	2/3	1.80
Ultrasonic degradation	1	1.15
Combined hydrolytic and ultrasonic degradation	4/3	1.42
Hydrolysis activated by ultrasound	5/6	

In TABLE 2 the maximum CPR-values found for the different types of reaction are included. The low value of a for acid hydrolysis is readily understood because smaller molecules are more easily degraded than larger ones (BASEDOW et al. 1978). Ultrasonic degradation rate constants are proportional to the MW, resulting in $a=1$. Furthermore, whereas the probability of chain scission for acid hydrolysis is higher near the ends of the polymer chain, ultrasonic degradation takes place predominantly at the midpoint of the chain. This effect can be represented by the maximum CPR-values obtained for each reaction, which is 1.80 for hydrolysis and approximately 1.15 for ultrasonic degradation. Therefore, the exponent a and CPR can be used to characterize the mechanism of the degradation reaction. The linearized plot of $\overline{M}_n$ vs. reaction time t, according to equation (1), is shown in FIG. 2 using the values of a obtained for the different types of reaction (TABLE 2). The rate constants k listed in

TABLE 1 were calculated from the slopes of the straight lines in FIGURE 2.

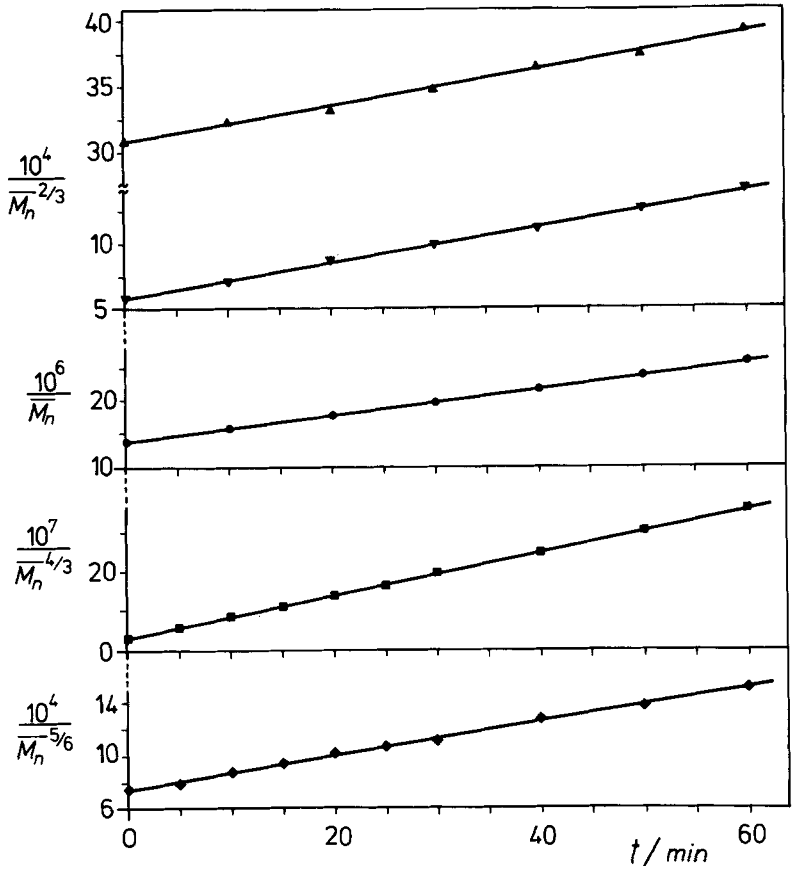

FIGURE 2: Linearized plots of $\overline{M}_n$ vs. reaction time t: ▲ hydrolysis (sample B), ▼ hydrolysis (sample A), ● ultrasonic degradation (sample A), ■ combined hydrolytic and ultrasonic degradation (sample A), ◆ hydrolysis under action of ultrasound (sample B).

An explanation for the cooperative effect of hydrolytic and ultrasonic degradation is given by the fact that the stretching forces acting on the polymer molecules due to ultrasound accelerate acid degradation in MW ranges in which ultrasonic degradation is not effective by itself. This is clearly shown in experiment V (TABLE 1). The CPR-value of 1.42 obtained for experiment III points to the same effect. For a semi-quantitative evaluation it is assumed that in the combined experiment the degradation rate constant K(M) of a molecule with MW M is equal to the geometric mean of the rate constants of ultrasonically activated hydrolysis $K_h(M)$ and the rate constant of ultrasonic degradation $K_{us}(M)$:

$$K(M) = \left[K_h(M) \cdot K_{us}(M)\right]^{1/2} \qquad (2)$$

For the ultrasonically activated hydrolysis, $K_h(M)$ then consists of two terms: M for the activation by ultrasound and $M^{2/3}$ for acid hydrolysis:

$$K_h(M) \propto M \cdot M^{2/3} \qquad (3)$$

Since $K_{us}(M) \propto M$ for $M > M_\ell$, K(M) is given by:

$$K(M) \propto \left[M \cdot M^{2/3} \cdot M\right]^{1/2} = M^{4/3} \qquad (4)$$

For $M < M_\ell$ the MW dependence of the rate constant K(M) should consequently be:

$$K(M) \propto \left[M \cdot M^{2/3}\right]^{1/2} = M^{5/6} \qquad (5)$$

An inspection of FIG.2 shows that the experimental results are in full agreement with these rather crude considerations, which imply that both effects, acid hydrolysis and ultrasonic degradation occur independently. Further analyses which take the MWD's into consideration are necessary to differentiate more clearly between both effects. Such investigations in connection with more general evaluations of degradation reactions are in progress.

ACKNOWLEDGEMENT

Financial support of the Deutsche Forschungsgemeinschaft is greatfully acknowledged.

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Received December 22, 1978

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