

## Oligomer Formation in the Chemical Degradation of Dextran

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### SUMMARY

The production of oligomers - to a degree of polymerization 5 - during acid hydrolyzation of polymer dextrans was estimated quantitatively by a combined aqueous SEC and adsorption separation. It was found that the molar concentrations of the oligomers were higher for those with lower DP. This experimental result is in agreement with a degradation model, in which the molecular weight decreases with the power of  $2/3$  versus time, which has been proposed earlier.

### INTRODUCTION

Recently it was shown that acid degradation of dextran in aqueous solution follows a  $2/3$  order dependence on molecular weight (BASEDOW et al., 1978). In other words the degradation rate per polymer bond is greater for shorter chains.

There are in fact two possible reasons for this difference in reactivity. Firstly, the individual bonds along the polymer chain have different reactivity, with the terminal bonds being more active. Secondly, the presence of long or short chain branches would lead to a more rapid reduction in  $\bar{M}_n$  compared to linear chains of the same molecular weight (EBERT et al., 1979). This is true even for the case where all bonds have equal reactivity.

We have hypothesized a degradation mechanism and simulated the molecular weight development during chemical degradation for a number of model polymers having different branching frequencies and branch lengths (EDERER et al., 1981). These calculations suggest that measurement of molecular weight distribution during chemical degradation would permit the estimation of branch frequency and length.

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In order to determine the relative importance of the two effects on molecular weight development during degradation, we have been performing experiments on the acid degradation of dextran having different molecular weights and branching (branch frequencies and length). These investigations are continuing. Herein are presented certain positive results on the distribution of oligomers formed in the acid hydrolysis of well characterized dextrans and followed by aqueous SEC.

### EXPERIMENTAL

Solutions of dextran T20 (Pharmacia), 6% wt., were hydrolyzed with perchloric acid, pH 0.5, at 90°C. Samples have been taken after 15, 30, 60, 120, 240 and 360 min. The samples were analyzed by aqueous SEC on controlled pore glass (CPG 10, Electro Nucleonics) and a special column for oligomers (HPX-42, Bio Rad) involving combined SEC and adsorption separation. The molecular weight calibration curve and peak broadening parameters ( $\sigma$ ) were measured using 20 very narrow dextran standards in the molecular weight range  $180-9 \cdot 10^6$  made available by Basedow et al. (BASEDOW et al., 1980).

The molecular weight calibration curve and peak broadening parameters ( $\sigma$ ) for oligomers were measured using 13 oligomer standards including glucose, fructose and dextran oligomers with degrees of polymerization (DP 3, 4, 5, 6, 7, .....).

The elution curves were corrected for peak broadening using the analytical method of Hamielec et al. (HAMIELEC et al., 1981).

### RESULTS AND DISCUSSION

FIGURE 1 shows the elution curves corrected for peak broadening for different degradation times. In FIGURES 2 a - b are shown 'reduced integral' vs. time curves for oligomers with DP 1 - 5; the reduced integral is proportional to the number of moles of that species. As far as we know this is the first time that oligomer formation rates have been quantitatively measured during chemical degradation. To date published works have only been concerned with the change in concentration of higher molecular weight species. In this paper we will discuss the kinetic measurements qualitatively. Quantitative modelling is presently being done and the results will be published in the near future.

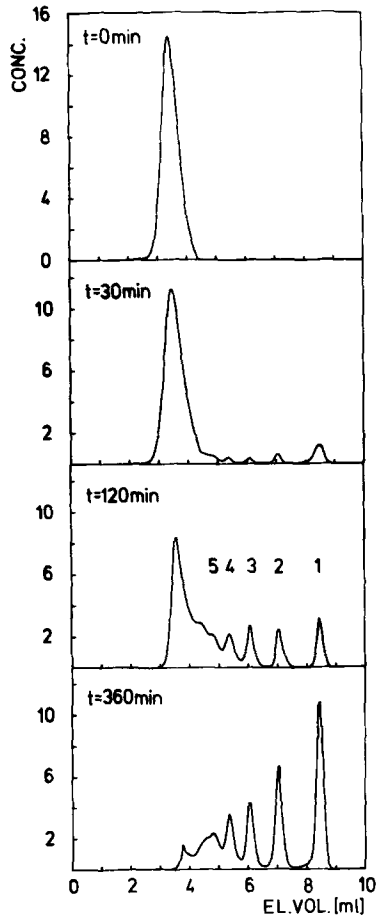


FIGURE 1: Elution curves of dextrans at different hydrolyzation stages (t: hydrolyzation time; the numbers at t = 120 min designate the degree of polymerization, DP, of the oligomers)

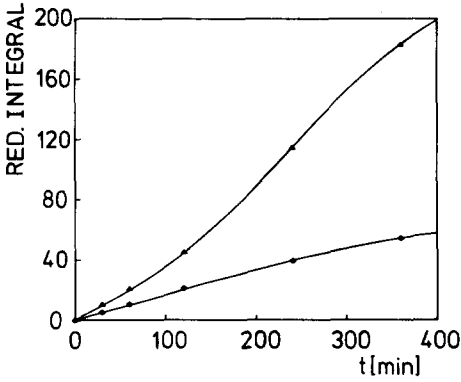


FIGURE 2a - b:

Oligomer formation with time during hydrolyzation of dextran (Reduced Integral is proportional to the molar concentration; ▲ = DP 1, ◆ = DP 2, + = DP 3, × = DP 4, \* = DP 5)

FIGURE 2a

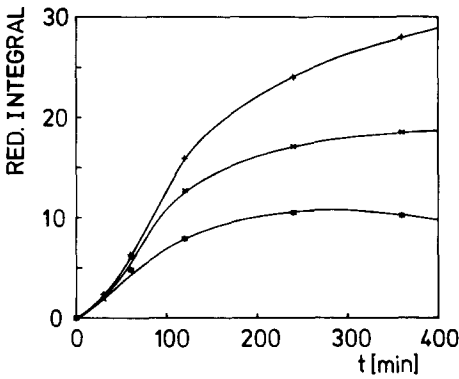


FIGURE 2b

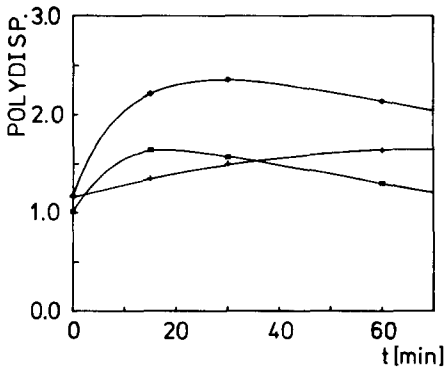


FIGURE 3:  
Polydispersity changes during hydrolyzation of dextran  
(◆ =  $\bar{M}_w/\bar{M}_n$ , + =  $\bar{M}_z/\bar{M}_w$ , \* =  $CPR^w$ )<sup>n</sup>

TABLE 1 shows the ratios of the initial formation rates of the oligomers. These results are consistent with the hypothesis that bonds at or near chain ends are more reactive than internal bonds, with activity at a maximum for the ultimate bonds. The curves for dimers, trimers, etc. are typical of intermediates whose concentrations initially rise and later fall being consumed by hydrolysis. In FIGURE 3 the polymer dispersity ratios  $\bar{M}_w/\bar{M}_n$ , and  $\bar{M}_z/\bar{M}_w$  and CPR ( $\bar{M}_w^2/\bar{M}_z \cdot \bar{M}_n$ ) versus time are shown to be consistent with an active chain end mechanism.

TABLE 1

Ratios of initial formation rates of oligomers

Glu	11.1
DP2	5.2
DP3	4.0
DP4	3.2
DP5	2.6

It might be of interest to speculate on the influence of short and long chain branches on the kinetics of hydrolysis. Short and long chain branching would give higher hydrolysis rates due to the higher concentration of active chain ends. The relative rates of formation of the oligomer species should however be independent of long chain branching; for short chain branching it is suspected that bonds near the polymer chain backbone would have lower reactivity than those near the end of a long chain. These questions will be considered in a quantitative investigation to be published in the near future.

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