

THE THERMAL DEGRADATION KINETICS OF DEXTRAN AND PULLULAN

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The effect of molar mass and, in the case of dextran, of the degree of branching on the thermal degradation kinetics of dextran and pullulan was studied in the presence and absence of oxygen. Although the initial mass loss of the dextran samples occurred at higher temperatures than that of the pullulan samples, the overall thermal degradation activation energies were lower for dextran than for pullulan. In the case of dextran the thermal stability was found to decrease with molar mass and degree of branching. The molar mass of pullulan, in the range of 10^4 to 10^5 g/mol, appeared to have no significant influence on the thermal characteristics of the samples.

Keywords: dextran, kinetics, pullulan, thermal degradation

Introduction

Dextran is a polysaccharide composed of α -glucose units linked by α -1,6 glucosidic bonds with the possibility of the occurrence of branch points at α -1,4 and α -1,3 positions (Fig. 1). Pullulan also consists of α -glucose units but is a linear polysaccharide. The regularly repeating structural unit is maltotriose, an α -1,4 triglucoside linked by α -1,6-glucosidic bonds (Fig. 1).

The data available in the literature on the thermal properties of these materials are scarce. Differential thermal analysis (DTA) of a series of dextran samples was performed by Morita [1]. Gekko studied the properties of low molar mass dextrans by thermogravimetric analysis (TG) and DTA [2]. The purpose of this

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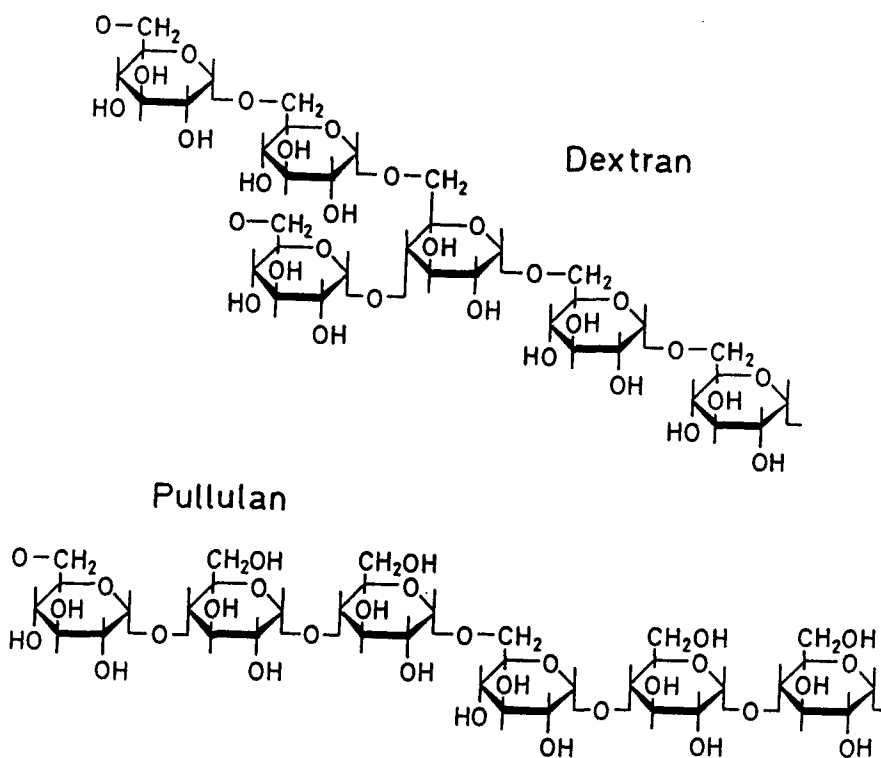


Fig. 1 Structures of dextran and pullulan

Table 1 Weight-average molar masses, \bar{M}_w of the investigated polymers

Polymer sample	Designation	$\bar{M}_w/\text{g}\cdot\text{mol}^{-1}$
predominantly linear dextrans	T - 10	1.0×10^4
	T - 40	4.0×10^4
	T - 60	6.4×10^4
	T - 500	4.9×10^5
	T - 2000	2.0×10^6
branched dextrans	Dx - 1	1.1×10^5
	Dx - 2	1.0×10^6
native dextran	NDx	2.2×10^7
pullulan	P - 1	1.2×10^4
	P - 2	1.1×10^5

paper was to study the influence of molar mass, molar mass distribution and degree of branching on the thermal stability of dextran and to compare it to that of the structurally similar pullulan.

Experimental

Five commercial, predominantly linear dextran samples of varying molar mass (T-10, T-40, T-60, T-500 and T-2000) were obtained from Pharmacia, Uppsala (Sweden). Two samples of dextran (Dx-1 and Dx-2) and one of native dextran (NDx), as well as two samples of pullulan (P-1 and P-2) were obtained from Zdravlje Pharmaceutical Works, Leskovac (Yugoslavia). The Dx-1 and Dx-2 samples were obtained by depolymerisation of the NDx sample. On the basis of viscosity measurements of NDx, Dx-1 and Dx-2, the exponent a of the Mark-Kuhn-Houwink equation was found to be around 0.3 [3], which was an indication that these samples were branched.

The weight average molar masses of the samples were determined by light scattering measurements. A Chromatix KMX-6 low angle laser photometer operating at 633 nm was used. The specific refractive index increments of the polymers in water were measured by a Chromatix KMX-16 differential refractometer at 633 nm.

Non-isothermal TG experiments were performed at heating rates of 2.5, 10, 20 and 40 deg·min⁻¹ in nitrogen or air using a Perkin Elmer TGS-2 instrument. The average sample mass was about 3 mg and the gas flow rate 25 cm³/min. The overall thermal degradation energies were calculated by the Flynn-Wall method [4].

Results and discussion

A set of typical non-oxidative non-isothermal TG curves is shown in Fig. 2a. Generally, the samples contained 3 to 5% adsorbed moisture. The average amount of carbonaceous residue at 650°C was about 10%. The amount of char formed was dependent on the heating rate. More residue was detected at lower heating rates.

The onset of the thermal degradation, expressed as the temperature of 10% mass loss at a heating rate of 2.5 deg·min⁻¹, was found to be dependent on the degree of branching of the samples and independent of the sample molar mass upon exceeding a critical, minimal value (Fig. 3). The values of $T_{10\%}$ of predominantly linear samples were higher than those of branched samples regardless of the nature of the surrounding atmosphere.

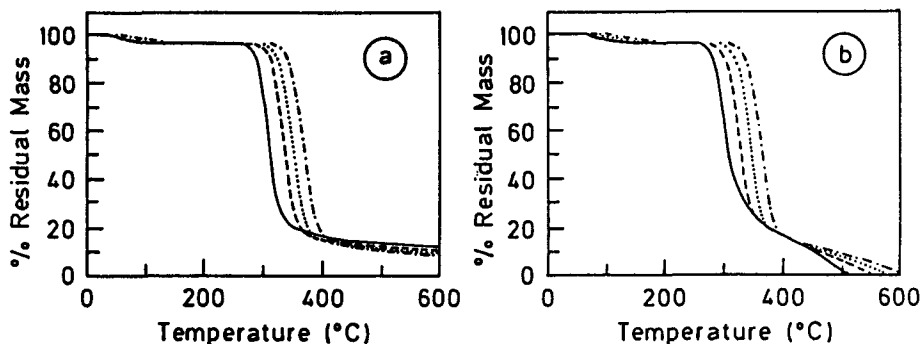


Fig. 2 Characteristic non-isothermal TG curves of dextran, (T-70), in a) nitrogen and b) air, heating rates 2.5 (—), 10 (---), 20 (.....) and 40 deg·min⁻¹ (-.-), gas flow rate 25 cm³/min

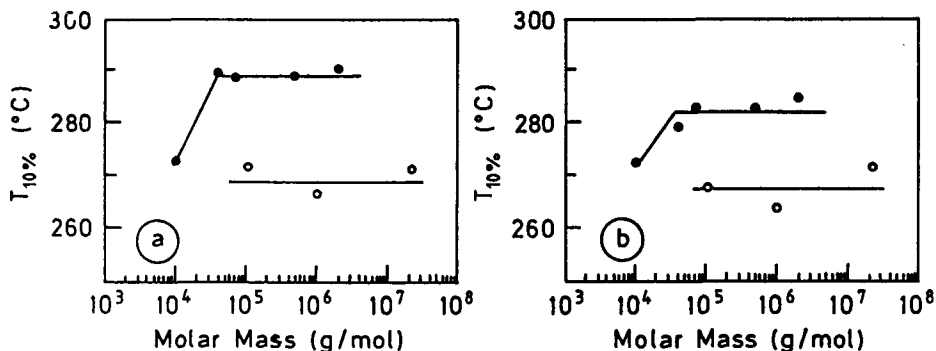


Fig. 3 Dependence of $T_{10\%}$ obtained at 2.5 deg·min⁻¹, on dextran molar mass in a) nitrogen and b) air, (•) predominantly linear and (o) branched samples

The $T_{10\%}$ value of the predominantly linear dextran sample of the lowest molar mass, $T - 10 \bar{M}_w = 1.0 \times 10^4$ g/mol, was lower than the values for other linear dextran samples. These results led us to believe that the parameter $T_{10\%}$ depends on the sample molar mass when oligomers are involved. This confirms previous results [5], where it was found that disaccharides degrade at lower temperatures than oligosaccharides which in turn show mass loss at lower temperatures than polysaccharides. The critical value at which $T_{10\%}$ becomes independent of \bar{M}_w for dextran lies between 1.0×10^4 and 4.0×10^4 g/mol.

As expected, sample mass loss was detected at lower temperatures in air than in nitrogen atmosphere.

Typical oxidative non-isothermal TG curves of dextran are shown in Fig. 2b. Two stages of thermal decomposition are registered, the second one leading to 100% mass loss.

The dependence of the overall activation energy of thermal degradation, E_a , of dextran on sample molar mass and branching is presented in Fig. 4. The non-oxidative E_a values of predominantly linear samples, determined for the mass loss range of 10 to 60%, are somewhat lower than those of the branched ones. The deviation of the non-oxidative E_a values from the mean is larger for branched samples (about ± 10 kJ/mol) than for predominantly linear ones (about ± 5 kJ/mol). The average value of E_a in both the absence and presence of oxygen is about 120 ± 10 kJ/mol.

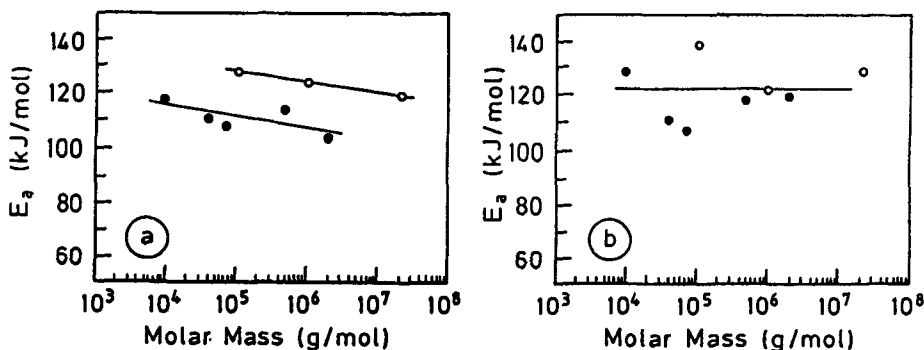


Fig. 4 Dependence of E_a on dextran molar mass in a) nitrogen and b) air, (•)predominantly linear and (o) branched samples

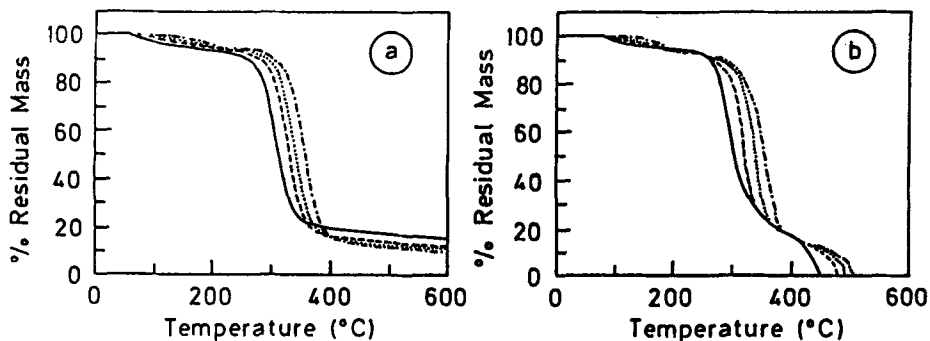


Fig. 5 Characteristic non-isothermal TG curves of pullulan, P-2, in a) nitrogen and b) air, heating rates 2.5 (—), 10 (---), 20 (· · · ·) and 40 $\text{deg}\cdot\text{min}^{-1}$ (— · —), gas flow rate $25 \text{ cm}^3\cdot\text{min}^{-1}$

Characteristic non-isothermal TG curves of pullulan in nitrogen and air are given in Fig. 5. In nitrogen, at 650°C about 20% carbonaceous residue is detected, which is more than in the case of dextran. The formation of char is also heating rate dependent with more residue being produced at lower heating rates.

The characteristic mass loss temperatures, $T_{10\%}$, of pullulan were found to be lower than those of dextran, while the E_a values were higher (Table 2).

Table 2 Characteristic thermal degradation parameters of pullulan

Sample	P - 1	P - 2
Molar mass (\bar{M}_w) / g·mol ⁻¹	1.2 x 10 ⁴	1.1 x 10 ⁵
$T_{10\%}$ (N ₂)	257	262
$T_{10\%}$ (air)	260	260
E_a (N ₂) / kJ·mol ⁻¹	137 ± 22	138 ± 9
E_a (air) / (kJ·mol ⁻¹)	156 ± 37	126 ± 19

The DTG curves of dextran and pullulan, obtained at a heating rate of 2.5 deg·min⁻¹, are shown in Fig. 6. The position of the single non-oxidative peak of dextran almost coincides with that of pullulan (at 310°C), whereas the oxidative maxima were registered at about 300°C. Both oxidative DTG curves have second maxima, the peak maximum of pullulan being at 445°C and of dextran at 487°C.

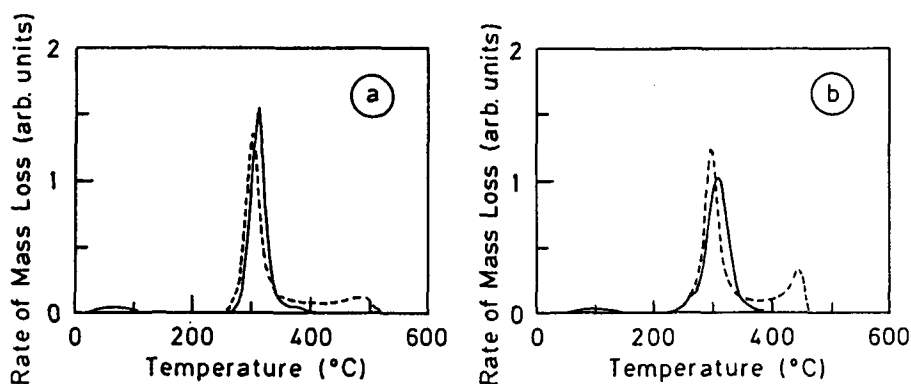


Fig. 6 DTG curves of a) dextran and b) pullulan in nitrogen (—) and air (---), heating rate 2.5 deg·min⁻¹, gas flow rate 25 cm³/min

In the case of pullulan a small shoulder was registered at about 270°C in both the non-oxidative and oxidative case. This mass loss can probably be ascribed to the decomposition of lower molar mass fractions of the sample.

M. C. Ramos-Sanchez *et al.* [5] in a thermoanalytical study of a series of sugars established that α -1,4-glycosidic bonds are thermally more stable than α -1,6 bonds. Therefore, pullulan should be thermally more stable than dextran as it

has more α -1,4 bonds. This assumption is corroborated by the slightly higher average E_a values of pullulan, as well as the difference in the average non-oxidative E_a s of predominantly linear and branched dextran samples. The branched dextran samples have more α -1,4-bonds than predominantly linear ones and, consequently, slightly higher non-oxidative E_a s. However, comparison of the $T_{10\%}$ values for dextran and pullulan do not support this hypothesis (Table 2 and Fig. 3).

The thermal stability of a series of predominantly linear dextrans of varying molar mass showed that the mass loss of oligomeric dextran commences at lower temperatures than that of samples of higher molar mass. Therefore, it can be expected that dextran samples of very wide molar mass distributions will have lower thermal decomposition thresholds than samples of the same average molar mass but with a narrow distribution.

Conclusions

Generally, it may be concluded that the thermal stabilities of dextran and pullulan are similar and that differences among them probably arise due to variations in molar mass, molar mass distribution and degree of branching. As shown by the differences between dextran and pullulan, and between branched and linear dextran, the nature of the bonds linking the glucose moieties also has an influence on the overall thermal degradation activation energy.

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Zusammenfassung — In und ohne Gegenwart von Sauerstoff wurde der Einfluß der Molekülmasse, im Falle von Dextran auch der Einfluß des Verzweigungsgrades auf die thermische Zersetzungskinetik von Dextran und Pullulan untersucht. Obwohl der anfängliche Masseverlust der Dextranproben bei höheren Temperaturen eintrat als bei den Pullulanproben, ist die Gesamtaktivierungsenergie der thermischen Zersetzung für Dextran niedriger als für Pullulan. Im Falle von Dextran sinkt die thermische Stabilität mit der Molekülmasse und dem Verzweigungsgrad. Die Molekülmasse von Pullulan scheint im Bereich 10^4 bis 10^5 g/mol keinen signifikanten Einfluß auf die thermischen Merkmale der Proben zu haben.