

Thermomechanochemical Depolymerization of Dextrans in Aqueous Phase

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Synopsis

This article centers on the depolymerization of dextrans under the action of thermomechanical forces induced by rapid passage of concentrated dextran solutions through capillaries and homogenizing valves. Viscosity measurements combined with theoretical equations related to the properties of the dextran solutions led us to characterize the flexibility of dextran chains in water. The influences of temperature and pressure gradient through the restrictions on the extent of depolymerization are described. The thermomechanical treatment is particularly effective in the presence of acid catalysts.

INTRODUCTION

Mechanochemical degradation of a polymer can be defined as a chemical scission which results in a decrease in molecular weight. The activation energy and the entropy for this type of reactions is supplied mechanically rather than thermally.¹

Degradation has been generally expressed in terms of macroscopic parameters such as the flow time of a solution through a capillary, the sedimentation coefficient, the viscosity, and the intrinsic viscosity.² Instrumental techniques have proven useful in determining molecular weights, via ultracentrifugation, light scattering, and size exclusion chromatography.³

Mechanical forces on the polymer can be induced by the following methods:

Ultrasonic irradiation.^{4,5} A possible physical interpretation of ultrasonic degradation of polymers is that cavitation bubbles are formed within the liquid. The high-velocity gradients may uncoil and stretch the polymer molecules.

High-speed stirring. Cavitation was thought to play a part in the degradation leading to the production of free radicals.⁶

Flow through capillaries, orifices, and homogenizing valves at high shear rates.¹

The factors influencing the mechanical degradation are the following:

Shear rate.⁷ High molecular weight molecules are more easily degraded at a given shear rate.

Temperature.^{8,9} A negative temperature coefficient is observed for mechanical degradation reactions because the efficiency of molecular entanglements decreases when the temperature increases.

Solvent.¹⁰ The "poor" solvents give solutions of low intrinsic viscosity in which the polymer coils are unexpanded and, thus, the polymer-polymer

interactions are quite strong. In this case, the number of available entanglements increases and then the degradation becomes more efficient.

Viscosity.¹¹ The viscosity of a solution depends on the following factors: solvent viscosity, polymer molecular size, polymer-polymer interactions, polymer-solvent interactions. For a given shear rate, a higher viscosity implies a higher shear stress.

Type of polymer.¹² The extent of degradation depends on the strength of polymer bonds and its flexibility. The onset of degradation has been theoretically defined in terms of a critical force at the wall:⁹

$$f_{cr} = (\mu - \mu_s) \cdot \Gamma_w \cdot M / (\mu \cdot c \cdot N_A \cdot z) \quad (1)$$

where

f_{cr} = minimum force required for a given molecular weight to be reached in the degradation process, N/molecule.

μ = viscosity of solution, kg/m · s

μ_s = viscosity of solvent, kg/m · s

Γ_w = shear stress at the wall, N/m²

M = polymer molecular weight, kg/mol

c = concentration, kg/m³

N_A = Avogadro number, molecule/mol

z = projected length of polymer chain, perpendicular to flow, m

A simple semiempirical rule has been put forward for predicting the onset of degradation.¹³ It is so-called Pohl's formula:

$$\mu \cdot \gamma_w \cdot M^2 > K \quad (2)$$

where

γ_w = shear rate at the wall, s⁻¹

K = constant for a given polymer-solvent system

A general equation for polymer degradation kinetics, which assumes that all scission reactions are first order, was mathematically developed by Ederer et al.:¹⁴

$$1/DP^a = 1/DP_0^a + a \cdot k \cdot t \quad (3)$$

where

DP = degree of polymerization at time t

DP_0 = initial degree of polymerization

k = kinetic constant, s⁻¹

t = time, s

a = parameter of the kinetic model

The global rate constant k depends on temperature, pH, and viscosity. The parameter a is dependent on the degradation process: ultrasonic ($a = 1$), acid hydrolysis ($a = 2/3$), shear ($1 < a < 2$), catalysis by enzymes ($a = 1$).

The energy required for polymer degradation is composed of at least two components: the energy required to cause viscoelastic flow and the energy required to break chemical bonds.¹⁵ In turn, the free energy, which can activate the bond rupture, is composed of two terms: entropy of deformation and potential energy, the latter being the only term contributing to bond scission.¹⁶

Three main mechanisms may occur depending on the nature of the chemical bonds as well as the solvent. These mechanisms are known as radical, ionic, and radical-ionic.¹⁷ Dextrans, which have C—O—C bonds, can undergo the three types of mechanochemical reactions.

At high temperature, the degradation of polymers can be due to a combination of thermal and mechanical reactions. It has been found that degradation can be induced with stress at temperatures where scission would not occur when induced by thermal effects only. Although the degradation is basically thermal, the activation stress is provided by mechanical energy.¹⁸

In this paper we will focus on the degradation of dextrans in relation to the flexibility of the polymer in aqueous solution. This flexibility can be quantified by the flexibility index, which is in turn a function of intrinsic viscosity, polymer molecular weight, monomer molecular weight, and mean molecular length of the monomer. The depolymerization of dextrans in aqueous solution is analyzed for different shear stresses (as obtained through a capillary or a homogenizing valve) and thermal severities. The role of acid catalysts in the depolymerization of dextrans is also considered.

EXPERIMENTAL

Dextrans were obtained from the Sigma Co., St. Louis, Missouri (produced by *Leuconostoc Mesenteroides*, Strain no. B-512). Structural studies by Sloan et al.¹⁹ have shown the dextran produced by B-512 to contain 95% of (1 → 6)-linked units of α -D-anhydroglucopyranose, and 5% of (1 → 3)-linked units.

Depolymerization experiments were carried out in two experimental systems:

1. A cascade reactor (Fig. 1), which consists of three interconnected vessels, the discharge being accomplished by actuated valves. The dextran solution (300–350 g solution, 25–30% wt/wt concentration) is charged in the top autoclave. It is then preheated (2–3 K/min) up to the desired temperature. Once this temperature is reached, the solution is kept at the top autoclave for five minutes. Then a rapid discharge of the solution into the second autoclave is made pneumatically using an inert gas. This discharge is achieved by forcing the solution through narrow capillaries: (a) $D = 2.1$ mm, $L = 12$ cm; (b) $D = 0.72$ mm, $L = 2.0$ cm, which are placed between the two top autoclaves. The reaction mixture is held in the second autoclave for a prescribed time (0 or 5 minutes) at a fixed temperature, which is the same as the preheating temperature, and then dropped into a quench receiver. Detailed procedures are described extensively elsewhere.²⁰

2. A continuous processing unit (Fig. 2), described by Koeberle et al.²¹ The dextran solution is pumped at 0.5–1.5 L/min and passes through a homogenizing valve at high pressure gradient ($\Delta P = 34$ –41 MPa). The mechanical

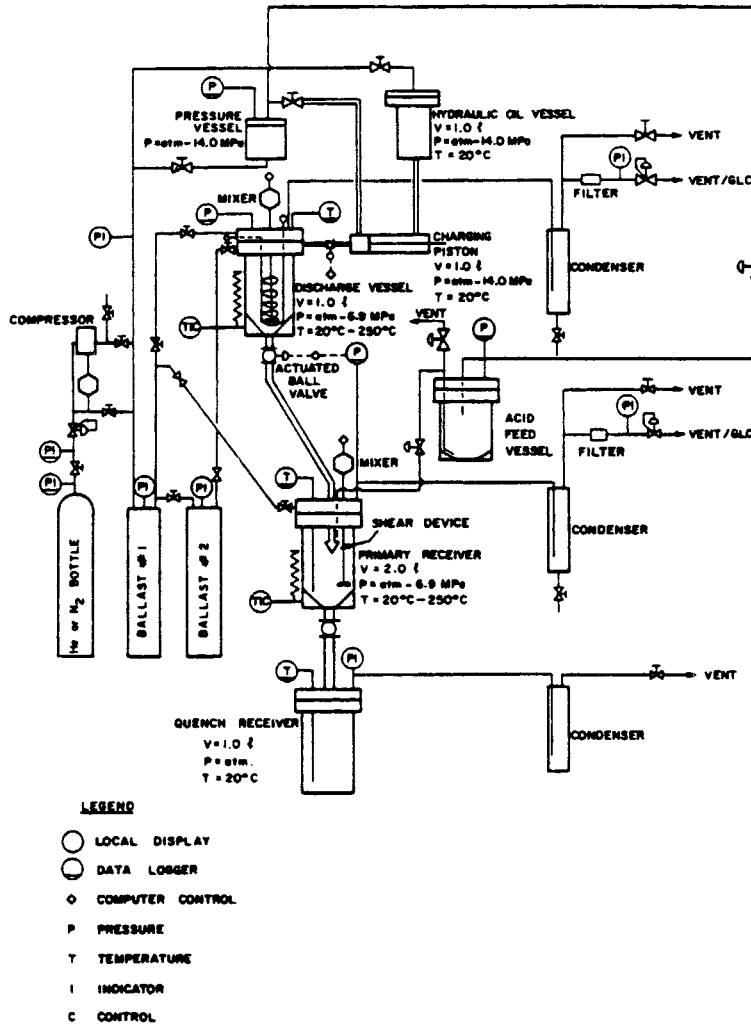


Fig. 1. Cascade reactor system for the studies on the depolymerization of dextrans.

work taking place during this homogenizing treatment heats the solution up to the normal boiling point. The solution was recirculated repeatedly through the valve. Under these conditions, the solution is treated as in a continuous tank reactor mode.

Products obtained from the treatment were characterized by size exclusion chromatography. The column was thermostated at 40°C and eluted with water containing NaN_3 (0.02%) at 0.4 mL/min.

We have developed a density-concentration correlation to determine the content of dextrans in solution:

$$d = A_0 + A_1 \cdot c + A_2 \cdot c^2 + A_3 \cdot c^3 \quad (4)$$

where

d = solution density, kg/m^3

c = dextran concentration, % wt solution

with: $A_0 = 990.3$, $A_1 = 1.83$, $A_2 = 0.18$, and $A_3 = -0.0034$.

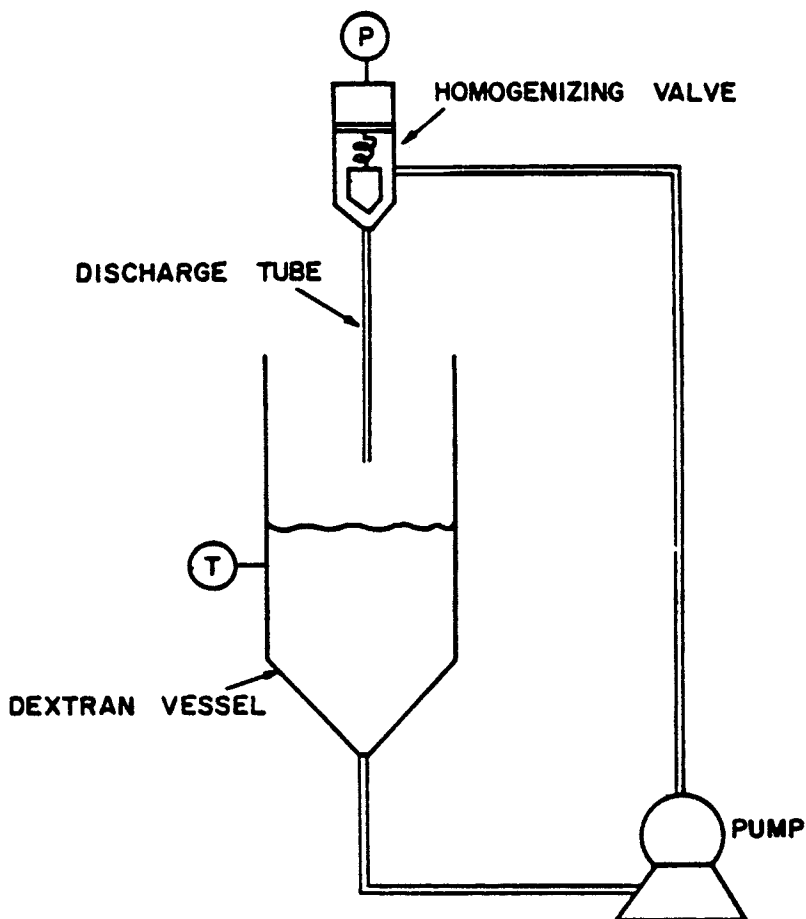


Fig. 2. Continuous processing system for the studies on the depolymerization of dextrans.

This equation is valid for a wide range of molecular weights ($M_w = 180-531,000$) and for concentrations up to 30% wt/wt.

Capillary viscosimeters of the Canon-Fenske type were employed in the viscosity measurements, leading to the intrinsic viscosities. Viscosimeters were submerged in a stirred thermostated bath ($\pm 0.02^\circ\text{C}$).

RESULTS AND DISCUSSION

Flexibility of Dextran Chains

Dextran is the general name of a biopolymer, which has mainly the following chemical formula (Fig. 3): $\alpha, 1 \rightarrow 6$ -anhydroglucopyranose. The flexibility of dextrans in aqueous solution was estimated by means of the flexibility index:²²

$$I = \langle r^2 \rangle \cdot M_m / (M \cdot l^2) \quad (5)$$

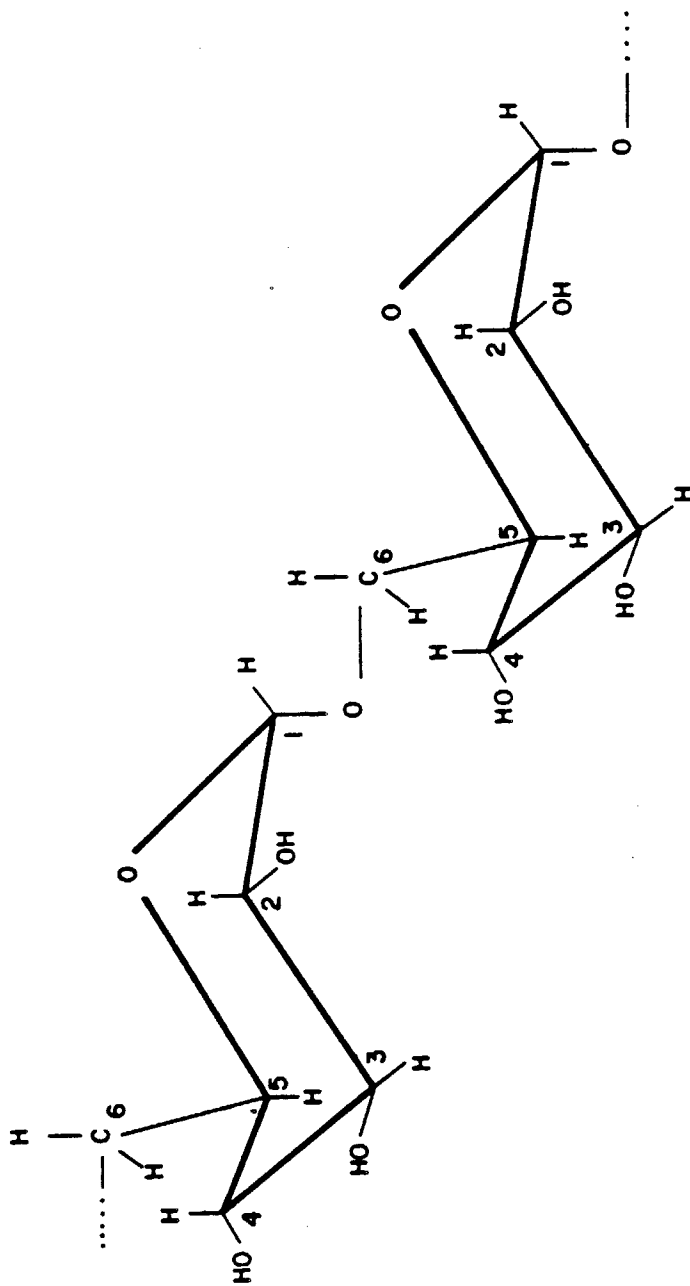


Fig. 3. Chemical formula of dextran ($\alpha, 1 \rightarrow 6$ -anhydro-D-glucopyranose).

where

$\langle r^2 \rangle$ = mean square end-to-end distance of dextran in aqueous solution at 25°C, m²

M = molecular weight of dextran, g/mol

M_m = molecular weight of monomer unit (162 g/mol)

l = molecular length of monomer unit ($5.7 \cdot 10^{-10}$ m, for linear dextrans)

I = flexibility index in a perturbed state (25°C)

Moreover, a well-known theoretical relationship between the intrinsic viscosity and the rms end-to-end distance is the Flory's equation:²³

$$[\mu] = \Phi \langle r^2 \rangle^{3/2} / M \quad (6)$$

where

$[\mu]$ = intrinsic viscosity, m³/kg

Φ = Flory constant ($2.1 \cdot 10^{26}$ mol⁻¹)

The intrinsic viscosity is generally related to the molecular weight by the well-known Kuhn-Mark-Houwink-Sakurada equation:²³

$$[\mu] = K_v \cdot M^\delta \quad (7)$$

where K_v and δ are constants depending only on the polymer-solvent system. Intrinsic viscosities at 25°C were obtained from the Huggings equation.²⁴ The values of K_v and α for aqueous solutions of dextrans ($M_w = 71,500$ – $531,000$) were evaluated by linear regression of Eq. (7) as: $K_v = 1.07 \cdot 10^{-4}$ m³/kg and $\delta = 0.47$.

By solving Eqs. (5), (6), and (7), a relationship between the flexibility index and the dextran molecular weight is obtained:

$$I = (K_v / \Phi)^{2/3} \cdot l^{-2} \cdot M^{(2\delta - 1)/3} \quad (8)$$

Since $(2\delta - 1) \rightarrow 0$, the flexibility index takes a value approximately constant ($I = 2.63$ – 2.54 for a wide molecular weight range 71,500–531,000). This flexibility index is similar to that of pullulan (α -glucan, $1 \rightarrow 6$), which is a flexible polymer.²⁵ We can conclude that dextrans behave as flexible polymers in aqueous solution, which is explained by the following: the α , $1 \rightarrow 6$ glycosidic bonds provide a macromolecular skeleton, which may easily rotate. This has a negative effect on the mechanical degradation of dextrans, since a fraction of the supplied energy will be lost in the macromolecular rotations.

Batch Experiments

For this set of experiments, the top autoclave, the second autoclave, and the capillary are at the same temperature.

No depolymerization of dextrans takes place when the temperature of treatment is lower than 100°C, even for the highest molecular weight and the maximum pressure gradient.

TABLE I
Operating Conditions for the Depolymerization of Dextrans via a
Thermomechanical Treatment in a Cascade Reactor System

Run	$t_p = t_r$, min	$T_p = T_r$, °C	c, % wt	ΔP , MPa	DP_0	DP	CO ₂ , % wt ^a
# 4	5	151	25	20.7	2913	1044	0
# 5	5	151	25	13.8	2913	1073	0
# 6	5	150	25	6.9	2913	1285	0
# 8	0	149	25	0.0	2913	2910	0
# 9	0	181	30	6.6	1537	76	0.61
#11	5	181	30	13.8	1537	11	1.70

^ag of CO₂/100 g of initial dextran. Capillary: D: 2.1 mm, L: 12.0 cm.

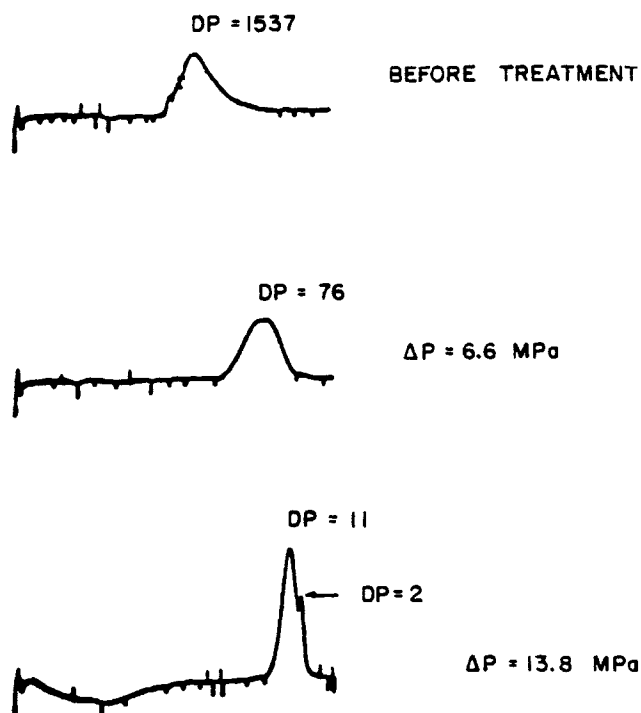
Table I contains the operating conditions for thermomechanical treatments (150–180°C), as well as the degree of polymerization of the products obtained. Experiment No. 8 corresponds to preheating–quenching sequence (no discharge nor reaction period). The size exclusion chromatogram of this experiment reveals no changes in the distribution molecular weight curve nor in the average molecular weight, in relation to the initial dextrans.

In the sequences preheating ($\approx 150^\circ\text{C}$)-discharge-postreaction-quenching, the degree of polymerization drops from 2900 to 1285 when the pressure gradient is as low as 6.9 MPa. It is important to note that at the temperatures used, the concentration in H₃O⁺ and OH⁻ increase due to H₂O dissociation, probably inducing hydrolytic effects. Moreover, mechanical effects begin to show since the degree of polymerization decreases slightly when the shear stress increases (i.e., pressure gradient through the capillary). At this temperature ($\approx 150^\circ\text{C}$), carbon dioxide is not detected. It indicates that there is no thermal decomposition under these conditions.

Table I also shows the results for depolymerization treatments at temperatures of about 180°C. The degree of polymerization of dextran is strongly decreased even for a low severity treatment (no postreaction and $\Delta P = 6.6$ MPa). When the treatment is more severe (Experiment No. 11), oligomers and a certain fraction of dimer are detected (Fig. 4). These features demonstrate that the depolymerization is greatly influenced by thermal effects. Moreover, the formation of carbon dioxide confirms the existence of an initial thermal decomposition during both preheating and reaction periods.

At 247°C, the pyrolytic effects produce an important charification of the dextran. The liquor obtained is composed of a low molecular weight polymer ($DP = 63$) and the dimer (65%). Even such a high thermal severity treatment in aqueous phase does not produce the monomer.

We have also analyzed the extent of the depolymerization process in relation to fluid dynamic parameters. Table II shows the operating conditions for concentrated dextran solutions, following through two different capillaries. The method leading to the evaluation of the mean velocity through the capillary as well as the determination of fluid dynamic variables are developed elsewhere.²⁰ The very concentrated solution flows slowly through the capillary due to the high viscosity. It is observed that even at high shear rates, the depolymerization is imperceptible when the treatment is carried out at 100°C. Otherwise, Pohl's modulus is quite similar for the three experiments (#19,



CONDITIONS :

COLUMN : TSK - PW - 4000 , 0,4 ml / min.

DETECTOR : DIFFERENTIAL REFRACTOMETER. ALTEX 156

ABCISSA TIME SCALE (1cm = 10 min.)

SAMPLE VOLUME : 1 μl

Fig. 4. Molecular weight distribution of dextrans at different pressure gradients ($T = 180^{\circ}\text{C}$).

TABLE II
Operating Conditions, Fluid Dynamic, and Viscosimetric Variables for the
Batch Thermomechanical Treatment of Aqueous Dextran Solutions

	Run #19	Run #20	Run #21
DP_0	3278	3278	1500
c , % wt of solution	31.9	36.4	29.0
$t_p = t_r$, min	5.0	5.0	5.0
$T_p = T_r$, $^{\circ}\text{C}$	150	101	101
ΔP , MPa	17.2	17.2	17.2
Capillary	D : 2.1 mm L : 12 cm	D : 2.1 mm L : 12 cm	D : 0.72 mm L : 2 cm
Depolymerization?	Yes	No	No
\bar{z} , m/s	49	22	128
ΔP_c , MPa	2.5	5.6	7.4
$10^{-6} \cdot \gamma_w$, s^{-1}	0.19	0.084	1.42
$10^3 \cdot \mu$, $\text{kg/m} \cdot \text{s}$	59	290	47
$10^{-18} \cdot \mu \cdot \gamma_w \cdot \text{M}^2$	3.2	6.9	3.9

#20, and #21). Thus, if the degradation was exclusively the consequence of mechanical effects, these three treatments should produce the same extent of depolymerization. Since this is not observed, we can conclude that thermal and/or hydrolytic effects are predominant under these conditions.

Continuous System Experiments

All the experiments carried out at 100°C, even at the highest pressure gradient ($\Delta P = 41.4$ MPa), were unsuccessful. We concluded that a catalyst was necessary to produce depolymerization at low thermal severities. Thus, we changed the strategy and the following operating conditions were employed:

Initial degree of polymerization of dextran: $DP_0 = 1500$
 Dextran concentration: $c = 26.8\%$ wt/wt
 Acidity of the aqueous solution: $\text{pH} = 1.37$
 Pressure gradient = 37.9 MPa
 Flow rate = 1.0 L/min
 Temperature = 98°C

SEC chromatograms show a gradual shift of the average molecular weight with processing time. The largest molecules are broken first to produce smaller molecules (the molecular distributions are skewed to the right).

Figure 5 shows the decrease of the degree of polymerization with reaction time for the acid thermomechanical treatment of dextran solutions. The experimental data (for $DP > 750$) are fitted assuming the Basedow model,¹⁴ by taking $\alpha = 2/3$. The hydrolytic rate constant is determined by the slope of the regression analysis: $k_h = 7.38 \cdot 10^{-6}$, $r = 0.9993$. Dextran hydrolysis has been studied by Szejtli,²⁶ who found that the rate constant was a function of pH and temperature:

$$k_h = 2.62 \cdot 10^{17} \cdot c_a^{1.21} \cdot \exp(-17790.8/T) \quad (9)$$

where

k_h = hydrolytic rate constant, s^{-1}
 c_a = hydronium concentration, mol/L

In our experimental conditions, this rate constant should take the value of: $k_h = 7.91 \cdot 10^{-6} \text{ s}^{-1}$, which is quite close to our rate constant.

Figure 5 also shows that beyond $DP \approx 750$ the mechanical effects impose an acceleration on the hydrolytic degradation. The latter should result in Szejtli's predicted depolymerization straight-line profile. However, at $DP \approx 750$ a faster degradation than the one predicted by Szejtli's model takes place, suggesting that a mechanohydrolytic mechanism is operational within a definite DP range, since at $DP < 80$ the pure hydrolytic mechanism seems to control the degradation as it can be concluded from an analysis of the slopes.

The sequence of mechanisms operating on the dextran polymers can be explained in terms of the chain flexibility of dextrans in solution as follows:

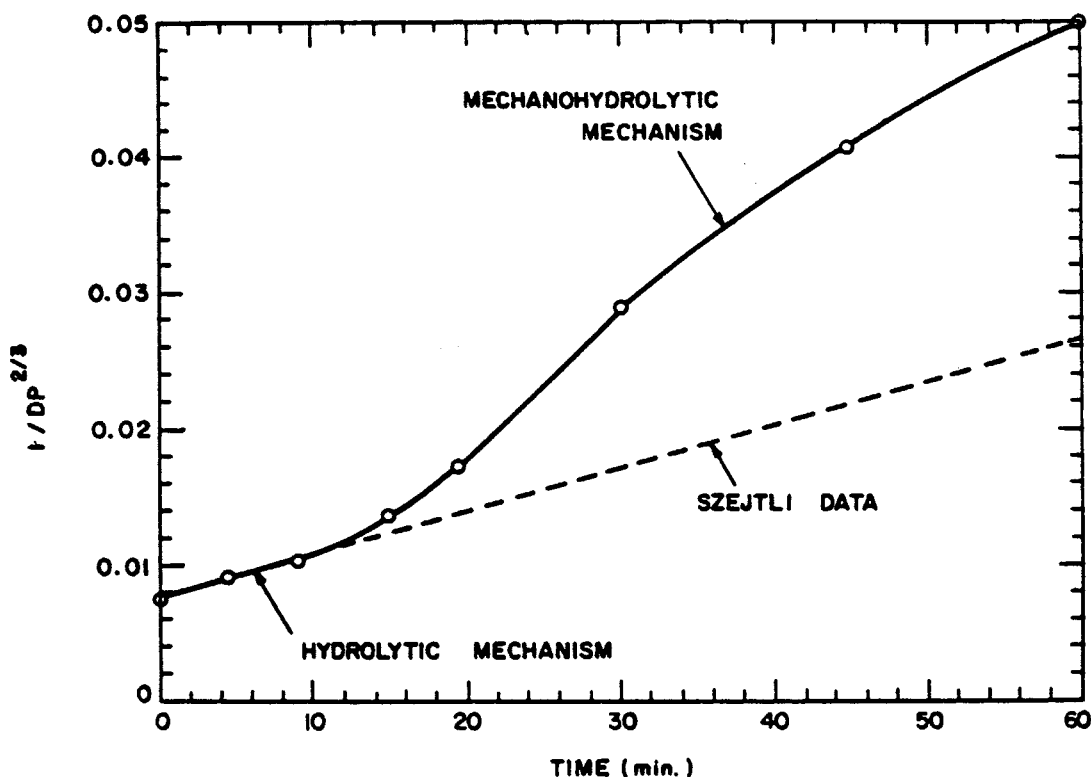


Fig. 5. Degree of polymerization profiles as a function of the processing time for two sequential mechanisms of reaction (following the Basedow kinetic model).

when the macromolecules are large ($DP > 750$), the number of entanglements is high and consequently the mechanical action is inefficient. The hydrolytic mechanism is predominant. At $DP < 750$, the number of entanglements decreases and thermomechanical action can then be more specific and localized, resulting in an enhancement of the degradation. A mechanohydrolytic mechanism is then operational. At low DP , the molecules are too small, the entanglements quasi-inexistent and the degradation is essentially hydrolytic.

CONCLUSIONS

The depolymerization of dextrans in aqueous phase and in the absence of catalyst is a process which is thermally activated. No depolymerization occurs at temperatures lower than 100°C . At higher temperatures, the rupture of glycosidic bonds becomes possible and the extent of the dextran depolymerization increases slightly when the pressure gradient increases. The preponderance of the thermal over the mechanical action is due to the flexibility of dextran chains, caused by easy rotation of the $\alpha, 1 \rightarrow 6$ glycosidic bonds.

The presence of acids causes a fast depolymerization of dextran macromolecules, the larger being broken first, as demonstrated by size exclusion chromatography. The shear induced by a rapid discharge through a capillary is responsible for an enhancement of the hydrolysis rates. Our kinetic model of polymer degradation suggests an initial hydrolytic mechanism, which is taken

over by a mechanohydrolytic contribution when the degree of polymerization reaches the 750 level. These mechanisms are explained in terms of the chain flexibility of dextrans in solution.

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NOMENCLATURE

a :	parameter of Basedow model of depolymerization.
δ :	exponent of Mark-Houwink equation.
A_0, A_1, A_2, A_3 :	coefficients of the density correlation for dextran solutions.
c :	concentration, kg/m^3 or % wt/wt.
c_a :	hydronium concentration, mol/L .
d :	density of the dextran solution, kg/m^3 .
D :	capillary diameter, m .
DP :	degree of polymerization after treatment.
DP_0 :	degree of polymerization before treatment.
f_{cr} :	minimum force required for a given molecular weight to be reached in the degradation process, $\text{N}/\text{molecule}$.
I :	flexibility index.
k :	kinetic constant, s^{-1} .
k_h :	hydrolytic rate constant, s^{-1} .
K :	constant of Pohl's equation.
K_0 :	coefficient of the Mark-Houwink equation.
l :	molecular length of monomer unit, m .
L :	capillary length, m .
M :	molecular weight, g/mol .
M_m :	molecular weight of monomer unit, g/mol .
N_A :	Avogadro number, $\text{molecule}/\text{mol}$.
ΔP :	pressure gradient between the two top autoclaves, MPa .
ΔP_c :	pressure loss through the capillary, MPa .
$\langle r^2 \rangle$:	mean square end-to-end distance, m^2 .
t :	time, s .
t_p :	residence time at T_p , s .
t_r :	residence time at T_r , s .
T :	temperature, K .
T_p :	maximum preheating temperature, K .
T_r :	postreaction temperature, K .
z :	projected length of polymer chain, perpendicular to flow, m .

Greek letters

Φ :	Flory constant, mol^{-1} .
γ_w :	shear rate at the wall, s^{-1} .
μ :	viscosity of solution, $\text{kg}/\text{m} \cdot \text{s}$.
μ_s :	viscosity of solvent, $\text{kg}/\text{m} \cdot \text{s}$.
$[\mu]$:	intrinsic viscosity, m^3/kg .
τ_w :	shear stress at the wall, N/m .

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