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Molecular Weight-Viscosity Relationship for Amylopectin, a Highly Branched Polymer

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Summary

Rate of acid hydrolysis of amylopectin is discussed from molecular weight variation ; a two step mechanism is found. The highly branched amylopectin fractions obtained by partial acid hydrolysis allow experimental determination of Mark-Houwink's law exponents. Theoretical and experimental "a" values are compared.

Introduction

Amylopectin is one of the main components of starch ; it is the only one in waxy maize starch used as reference. It is formed by (1 → 4)-α-D-glucose units chains with side chains branched on C-6 position (1). Average distance between two branches is 21 units along the linear chain as determined by the methylation technique (2). The aim of this work is to establish the Mark-Houwink relationship $[\eta] = KM^a$ using partially hydrolyzed samples on which the molecular weight distribution is determined by gel permeation chromatography. Till now, no relation was proposed to relate the intrinsic viscosity to the molecular weight.

Experimental

The amylopectin is a commercial sample of waxy maïze starch produced by Société Française du Maïs. It is defatted by DMSO/MeOH extraction. Homogeneous aqueous solution of amylopectin is prepared and HCl is added to 1 M. The hydrolysis is performed at 50° C ; the polymer samples are recovered by methanol precipitation after neutralization for different times of hydrolysis.

The viscosity is determined using an automatic viscosimeter from FICA (France) equipped with an Ubbelohde capillary (inner diameter 0.58 mm) thermostated at 25° C, and a system avoiding water absorption by the solvent (DMSO). The gel permeation chromatography is performed on a set of four columns of diol silica porous gel from MERCK (granulometry 10 µm, porosity Å : 2 x 1 000, 1 x 500, 1 x 100, ref : 250-4-RT) thermostated at 60° C.

Using a light scattering detector (Chromatix CMX 100) and a differential refractometer (IOTA JOBIN YVON S.A.) both on line, molecular weight determination is made as previously described (3).

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Results and discussion

a) Kinetics of acid hydrolysis

The hydrolysis was investigated on amylopectin solubilized first in water ; the solution was clear then the reaction is performed in homogeneous phase. The samples recovered after partial hydrolysis were characterized by their intrinsic viscosities $[\eta]$, their molecular weight distribution obtained by G.P.C. (figure 1) and their weight average molecular weight $(\overline{Mw})$ obtained from light scattering in the effluent of G.P.C. Acid hydrolysis is generally assumed to split randomly the polysaccharide ; then one plots the dependance of $(\overline{Mn})^{-1}$ as a function of hydrolysis time.
The results are given on figure 2 ; the linear dependance confirms this mechanism but the curve presents two hydrolysis rate constants. After 30 minutes of hydrolysis, the rate increases by a factor around 2. This behaviour must be related to the structure of the molecules tested (degree of branching, density of branching points, cooperative interaction between the starch molecules).

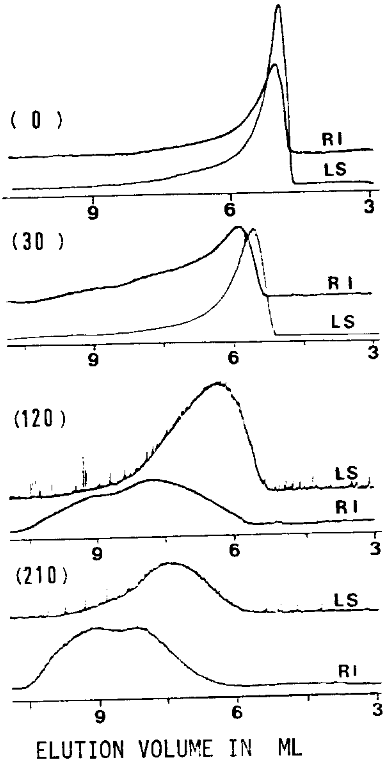

Figure 1 : Chromatograms showing molecular weight distribution as a function of acid hydrolysis time. (indicated by number between parenthesis).
L.S. light scattering trace
R.I. differential refractometer trace.

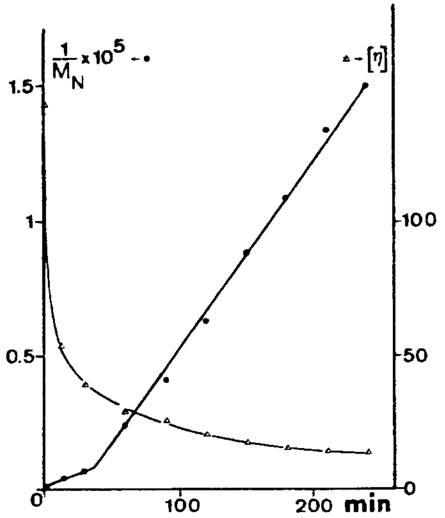

Figure 2 : Variations of $(\overline{M}_n)^{-1}$ and $[\eta]$ with hydrolysis time.

b) Molecular weight-viscosity relationship

Recently Daoud et al. (4) discussed the exponent of the relation between Mw and [η] for polydisperse randomly branched polymers obtained by polycondensation. In dilute solution, the prediction is $[\eta] \alpha Mw^{0.37}$. On figure 3, we give the dependance of log [η] as a function of log $\bar{M}w$ for the samples with different degrees of hydrolysis. Two domains are clearly shown : the initial and 15 min of hydrolysis samples give an exponent a ≅ 0.67 then the experimental slope becomes 0.36. This last value is in quite good agreement with the value predicted by Daoud et al. The relations found for the two parts of the curve are : $[\eta]_1 = 2.16 \times 10^{-3}\ Mw^{0.67}$; $[\eta]_2 = 1.84 \times 10^{-1}\ Mw^{0.36}$. In the first part of the hydrolysis the larger exponent seems to indicate a more expanded chain ; the first step of the hydrolysis should be a split of part of linear chain between more dense domains. In the same time, the iodine binding (0.5 %) does not show any significant variation.

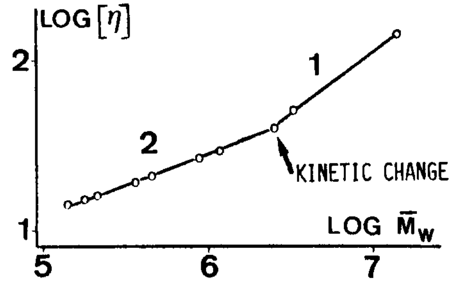

Figure 3 : Plot of log [η] versus log Mw.

It will be interesting to follow the hydrolysis of different amylopectins but also to compare acid and enzymic hydrolysis. It seems that the type of analysis proposed in this work may inform on structural feature of the molecule.

Conclusion

This work was performed to investigate the rate of hydrolysis of amylopectin from the molecular weight decrease. One concludes on a two step kinetic process. The hydrolysis seems to be a random split of the molecules ; the first step proceeds with a lower rate as long as large inital molecules exist. From G.P.C. measurements, we demonstrate the production of two well defined types of molecules ($\bar{M}w$ ≃ 300 000 and 60 000 respectively). The behaviour of these molecules from viscosity measurements is in agreement with that of a polydisperse randomly branched polymer.

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