STRUCTURAL DETERMINATION OF FRACTIONATED HYDROXYETHYL STARCH

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Starch, a common constituent of higher plants is a major form in which carbohydrate are stored (1). Most starches are mixtures of two macromolecular entities : amylose which is a linear polymer of rather low molecular weight (10^3 to 10^4 a -1-4-D-glucopyranosyl residues) and amylopectin composed of same residues and branched, of very high molecular weight. The amount of pure amylopectin in the starch granules depends mainly on the origin and growth of the plants from which starch is extracted (the soil enrichment and the sun exposure). Starch and amylopectin are now currently used in industrial application particularly as thickening agents and food gelifiers of by paper manufacturers. Nevertheless amylopectin whose a schematic model is given in Fig.1, is badly water soluble because the helices of the branches from crystalline domains are not entirely destroyed by hydratation at least by current solubilization process.

It is the reason why they are often used in a modified form (2-4). For instance a serie of products prepared by Roquette SA and called HES are hydrophobically modified amylopectin (see reaction in Fig.2) which are more soluble. The various medical uses of hydroxyethylamylopectin as plasma volume expanders have caused considerable interest in its molecular characterization.

We are interested in the understanding of the relations between the molecular weight, branching and local structure (ordered helix or disordered structure) and the thickening properties of such polymers.

We have already performed a systematical study by elastic or quasielastic light scattering, viscosimetry, GPC + Low angle laser light scattering on different unfractionnated HES and two series of fractions of polydipersity IP : $1.2 < IP < 1.4$ and molecular weight M_w : $4.10^4 < M_w < 10^6$. The following scaling laws were found for the molecular weight dependences of the static and dynamic radius of giration and viscosity :

$$R_g = 0.044\ M^{0.48}\ nm \qquad I$$

$$R_H = 0.091\ M^{0.37}\ nm \qquad II$$

$$[n] = 2.32\ 10^{-1}\ M^{0.33}\ cm^3\ .g^{-1} \qquad III$$

The exponents of relations II and III are very low in agreement with previous works (5), and indicate either a very compact structure or a variation of the branching through the fractions.

In this range of explored molecular weight, the radius of giration is ranging between 5 to 20 nm so we undergo SAXS (Synchrotronics Small angles X-Ray Scattering) measurements to determine also radius of giration and the structure of the graft parameters for the lowest molecular weight. The determinations of these parameters are usefull for all the applications.

The relation between the scaling laws of the dependences of [n], Rg and RH with the molecular weight M was the object of much debate. From the Kirkwood theory in the free draining region, Flory and Fox have proposed the well known relation : $[n] = \Phi_0\ 6^{3/2}\ R_G^3 / M$

Such an expression was improved by Yamakawa (7) and more recently by Weill *et al.* (8) who proposed to substitute $R_H * R_G^2$ for R_G^3 in the Fox Flory relation. This improvement give a very good agreement between the three experimental laws.

The branching parameters : according to Zimm and Stockmayer (9), the branching parameter g_m is defined as the ratio of the average square radius of giration of branched (R_{gb}^2) and linear (R_{gL}^2) polymer of same molecular weight :

$$g_m = R_{gb}^2 / R_{gL}^2$$

If we assume that the chemical modifications do not change the local chain conformation of amylopectin we can use as a linear homologous the Amylose and the radius of giration law obtained by Burchard (10). So we were able to deduce the branching law :

$$g_m = 502\ M^{-0.266}$$

This means that the branching effects disappear for the low molecular weight through the fractionation process. A more complete study of such effects is in progress by exploring the Small angles Xrays scattering enveloppes of these polymers.

Figure 1 : schematic model of amylopectine molecule from A-type starch granule

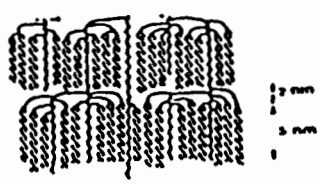
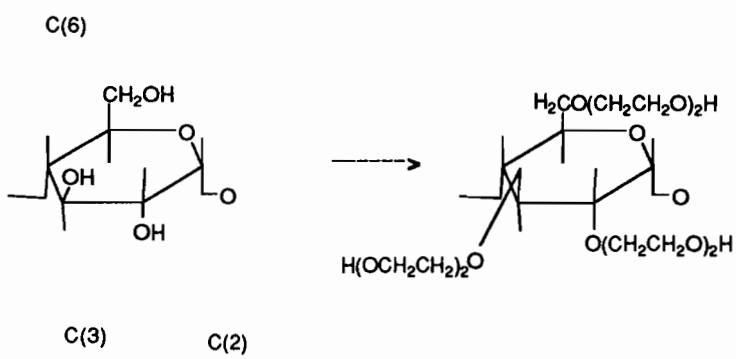


Figure 2



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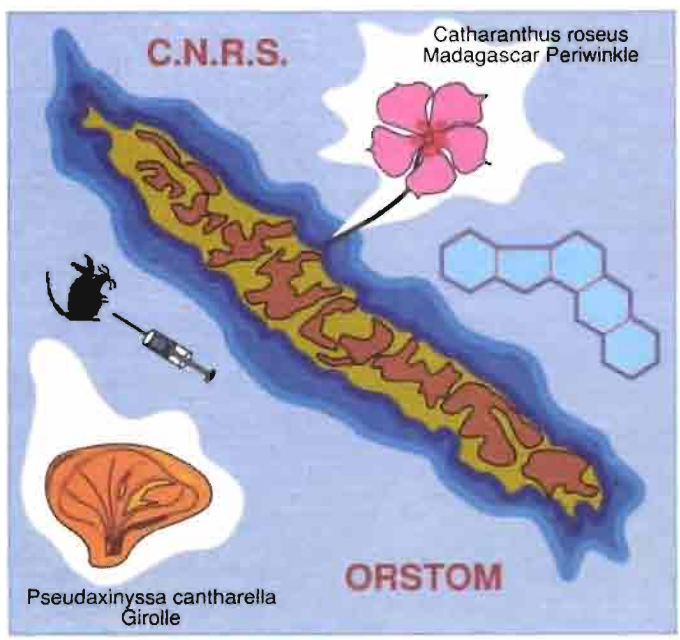
Troisième Symposium sur les substances naturelles d'intérêt biologique de la région Pacifique-Asie

Nouméa, Nouvelle-Calédonie, 26-30 Août 1991

ACTES



Editeurs : Cécile DEBITUS, Philippe AMADE,
Dominique LAURENT, Jean-Pierre COSSON