## CHARACTERISATION BY SEC AND HIGH FIELD NMR OF LIMIT-DEXTRINS FROM ENZYMATICALLY DEGRADED CATIONIC STARCHES

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Chemically modified Cationic Starches are widely-used derivatives in fields such as paper making, textile and cosmetic industries. The physicochemical macroscopic properties of these products are closely linked to their structural organisation at the molecular level. Starch is a complex of two macromolecular families : amylose, constituted of linear poly- $\alpha(1-4)$  <u>D</u> glucopyranose chains with few  $\alpha(1-6)$  branches and its highly-branched main component amylopectin. There is a wide range of possible modification patterns on macromolecules such as amylopectins. Different reaction processes may lead to a variety of structures.

In an earlier work we observed that highly acetylated starches of the same DS, but synthesised via two different acetylation processes, had different structures as seen from their NMR spectra [1]. Woortman and Steeneken [2] reported that granular starch was methylated in a more block-wise manner whereas when reacted in solution it was modified in a more random fashion. Based on the results of enzymatic degradation Kavitha and BeMiller [3] concluded that a commercial hydroxypropyl starch seemed to be more modified in areas near to the branching zones.

Commercial cationic starches can be synthesised in solution or more often by Dry Process, grafting hydroxypropyltrimethylammonium groups via ether bonds (fig 1)[4]. In a recent work we describe an alternative synthetic route to cationic starches using a glycerol plasticised molten medium to achieve the reaction [5]. The comparative enzymatic degradation using  $\alpha$ -,  $\beta$ -amylase, isoamylase and amyloglucosidase on those molten medium cationic starches and the Dry Process commercial products resulted in a very different degradation behaviour. The Dry Process samples showed a regular increasing resistance to the enzymatic action with increasing DS but surprisingly, an increase of DS did not seem to alter the action of both exo- and endo-enzymes on molten medium products, within a wide DS range, showing a much more specific regioselectivity of the reaction [6]. The products of the enzymatic degradation are separated by SEC and analysed by multidimensional



R= HPTMA or H

NMR spectroscopy. The results of the structural characterisation are presented.

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- [1] B. Laignel, C. Bliard, G. Massiot and J.M. Nuzillard, Carbohyd. Res., 298 (1997) 251-260.
- [2] P.A.M. Steeneken, A.J.JL Woortman, Carbohyd. Res 258 (1994) 207-221.
- [3] R. Kavitha, J.N. BeMiller, Carbohyd. Polym., 37 (1998) 115-121.
- [4] D.B. Solarek, O.D. Wurzburg ed. *Modified starches: properties and use*. CRC Press Boca Raton, FL, 1986.
- [5] A. Ayoub, C. Bliard, Starch/Stärke, (2003) (accepted).
- [6] A. Ayoub, C. Bliard, J. Biol Macromol., (2003)(submitted).