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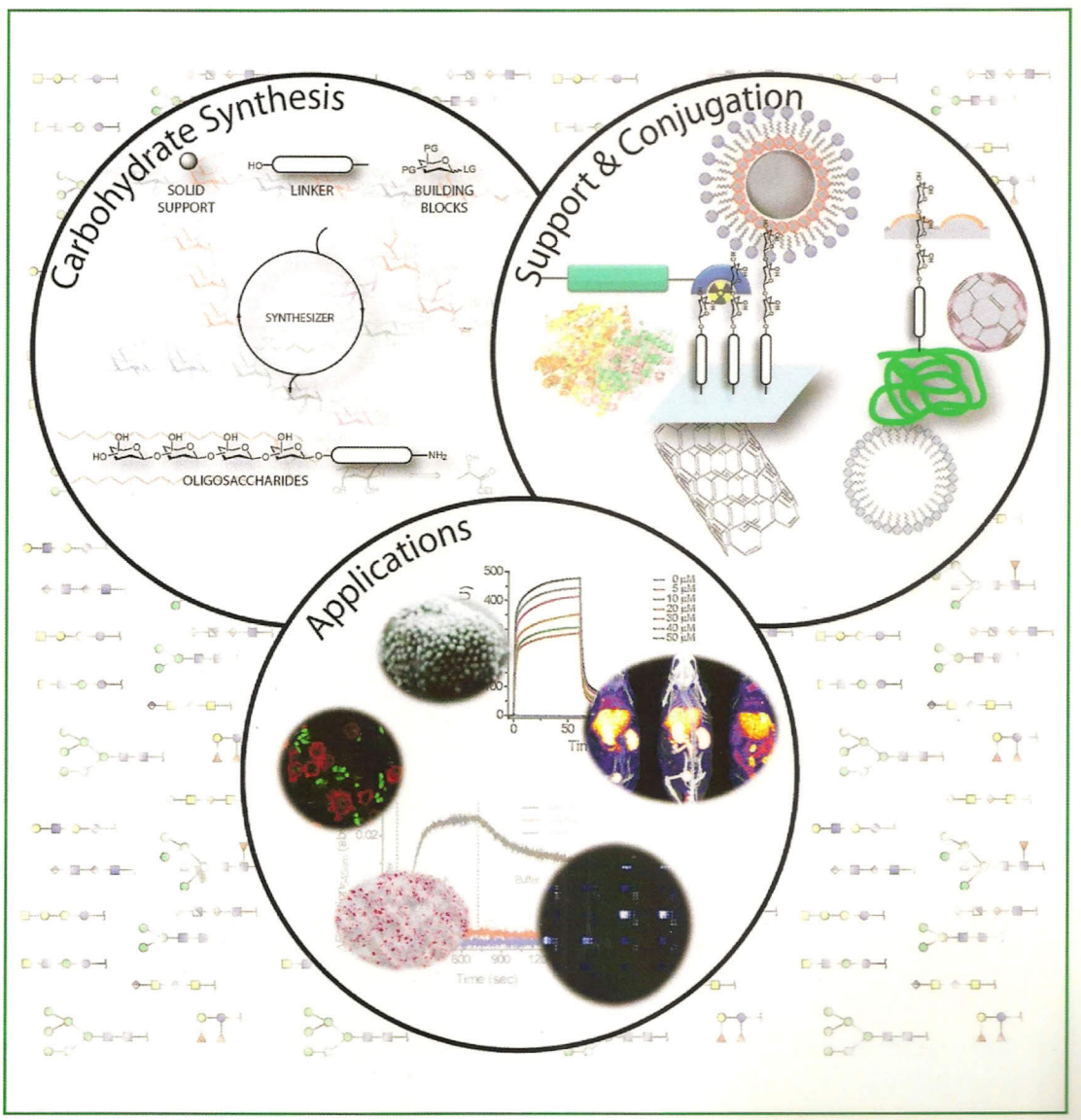

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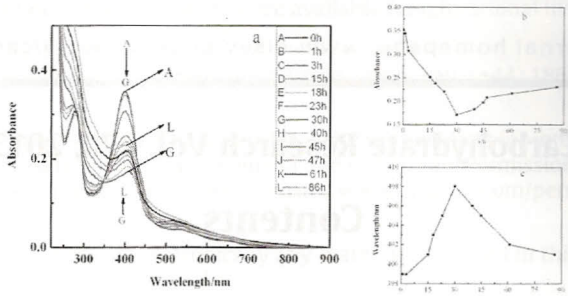

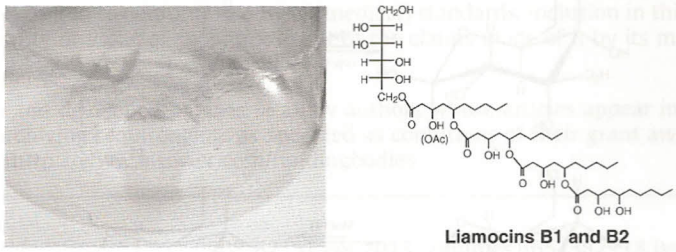

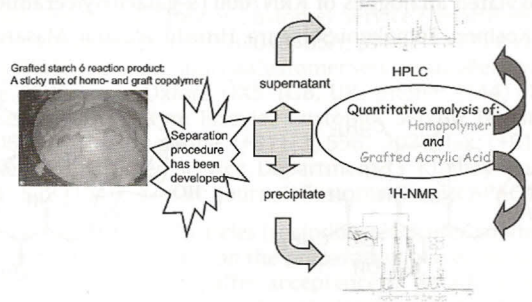

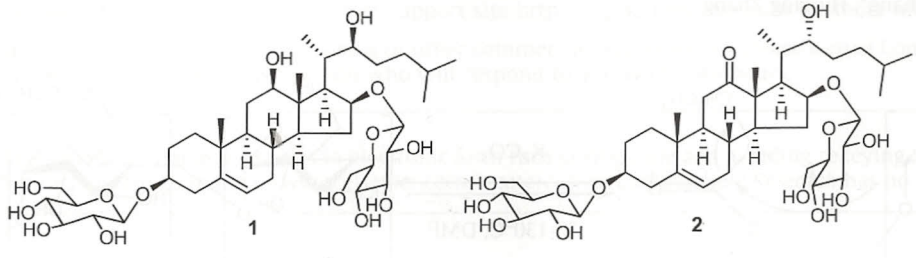

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Improved homopolymer separation to enable the application of ^{1}H NMR and HPLC for the determination of the reaction parameters of the graft copolymerization of acrylic acid onto starch

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ABSTRACT

Graft copolymers of starch with acrylic acid are a promising green, bio based material with many potential applications. The grafting of acrylic acid onto cassava starch in an aqueous medium initiated by Fenton's reagent has been studied. Common grafting result parameters are add-on (yield) and graft efficiency (selectivity). However, the analysis of the reaction products and an accurate determination of these parameters stand or fall with a complete separation of the entangled but ungrafted homopolymer from the grafted product. Therefore, this separation is the core of the newly developed analytical procedure. An appropriate solvent has been selected with dedicated testing from the range methanol, ethanol, acetone, dioxane, 2-propanol, and 1-propanol. Acetone showed the best performance in many respects. It has a high dissolving power for the homopolymer, as well as the highest yield of precipitation for the starch derivatives and it is the most economical in use. After the successful separation, the precipitated graft copolymers could be analyzed quantitatively by nuclear magnetic resonance. The liquid with homopolymer and unreacted monomer was analyzed by high pressure liquid chromatography. Proof of grafting has been found by FTIR and TGA analyses. The mass balance calculation shows a systematic error which appears fairly consistent: 18.0 ± 2.5 wt %. This was used as a correction factor in the calculation of the grafting parameters but more importantly, it means that the method we developed has a high level of repeatability, in the order of 97%.

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1. Introduction

Cassava starch is becoming increasingly important as a renewable base material for performance polymers. An important method of synthesis is the graft copolymerization of acrylic monomers onto the biopolymer starch.[1–3]

These sources also report about many potential applications of grafted starches, for example, superabsorbent, co-builder and flocculation, thickening agents, and purification of industrial effluents. It is generally recognized that the important parameters to monitor the result of the grafting reaction are add-on (yield) and grafting efficiency (selectivity). Regarding the literature data, it appears however that the challenge of the quantitative analysis of these parameters and the products of the grafting process have not yet been solved to full satisfaction. At least, there is not a clear and satisfactory procedure available for the characterization of the reaction product which is a mixture of starch with grafted polymer, homopolymer, initiator residue, and perhaps also some unreacted monomer. Many early characterizations of grafted starch products were based on gravimetric and titration analyses.[4] Usually, starch graft copolymer and the homopolymer as an undesired by-product were separated by extraction with an excess of a certain solvent. The commonly used solvents are water,[5–7] methanol,[8–11] ethanol,[12,13] acetone,[14] or mixtures of those. The remaining material containing starch with grafted synthetic polymer was then analyzed through several methods. One of the first analytical techniques in the literature is the determination of the carboxyl content by titration, as introduced by Daul et al.[15] The complete separation of the homopolymer from the grafted product is a bottleneck in these methods. Another method to determine the amount of grafted PAA is to disconnect it from the starch again by Soxhlet's extraction[8,12,14] using an organic solvent, for example,

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