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Short communication

Synthesis and biodegradation studies of new copolymers based on sucrose derivatives and styrene

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ABSTRACT

Novel unsaturated esters of sucrose were synthesised directly and in good yields from sucrose using a simple, mild, and selective Mitsunobu procedure. These regioisomerically pure vinyl sugars have been copolymerised with styrene by a free radical process, yielding unbranched linear polymer materials with pendant sucrose moieties. Their physical properties indicate that these polymers have potential technological relevance as amphiphilic and biodegradable materials. Biodegradation tests on the copolymer samples by a fungal (*Aspergillus niger*) culture method showed a fungal growth $\geqslant$60%, indicating good biodegradability and that the copolymers were partially bio-assimilated during microbial attack.

1. Introduction

The demand for biodegradable plastics has increased over the past few decades, not only due to increasing environmental concerns, but also for biomedical applications [1]. Sucrose is a low molecular weight renewable carbohydrate feedstock from which it is possible to elaborate new materials [2], such as water-soluble and/or amphiphilic, biocompatible polymers [3] and other new compounds due to its low price. The synthesis and applications of different sucrose esters has been reported [4–10]. Since sucrose has eight chemically active hydroxyl groups, regioselective derivatisation is important for the selective synthesis of sucrose-containing linear polymers [11,12]. Protection–deprotection strategies have been discussed by Jarosz et al. [13].

Using sugar functionalised petrochemical polymers such as polystyrene for use as biodegradable polymers is a recently discovered application of a sugar linked synthetic polymer [14]. The class of sugar based polymers, generally known as poly(vinylsaccharide)s, have also been investigated for a variety of applications, particularly in the biomedical field [15,16]. The most widely used method for the synthesis of poly (vinylsaccharide)s has been based on free radical polymerisations of vinyl sugars [17]. For an extensive review on the preparation and applications of this type of polymers, see [18] and references therein.

Our approach was to introduce polymerisable carbohydrate containing moieties into polyvinyl chain polymers [7,8,19]. There has been a worldwide realisation that nature derived monosaccharides, disaccharides, oligosaccharides and polysaccharides can provide the raw materials needed for the production of numerous industrial consumer goods [1,20]. The present investigation was also intended to study the extent of biodegradability of poly(vinyl saccharide ester)s under culture incubation.

Mitsunobu esterification conditions [21] are known to provide good selectivity, even in the case of a complex polyol like sucrose, thus allowing a rapid and efficient synthesis of sucrose esters. Although the atom economy of the procedure was poor, it gave excellent results on a small scale and allowed us to avoid the use of protecting group chemistry and multi-step procedures. The regioselectivity of the Mitsunobu reaction towards 6-*O*-monoesters and

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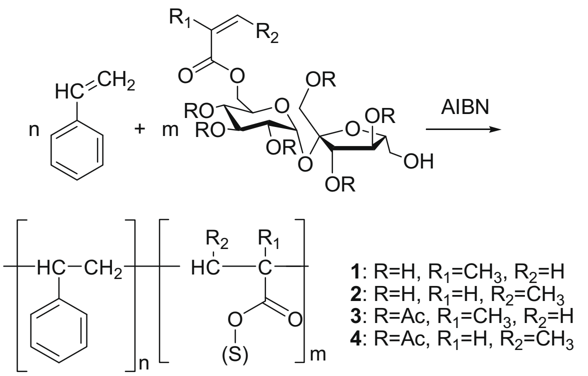
6,6′-*O*-di-esters of sucrose has been documented earlier [22,23], and we explored its application for obtaining unsaturated monomers capable of polymerizing. Herein, the synthesis of novel unsaturated sucrose esters by reacting sucrose with unsaturated carboxylic acids under Mitsunobu conditions is presented (Scheme 1), as well as their successful free radical copolymerisation with styrene (Scheme 2). Some physical properties of the resulting polymeric materials are also reported.

2. Synthesis of unsaturated sucrose esters

The procedure adopted was based on the Mitsunobu reaction [21] as a convenient method for selective esterification to afford mono- and di- esterified products (Scheme 1). To a solution of sucrose in dry DMF, triphenylphosphine and the corresponding acid were added, and cooled to 0 °C. Diisopropyl azodicarboxylate (DIAD) was added slowly, and the mixture was stirred at room temperature for 24 h (see SI). In order to obtain the sucrose monoesters the reaction was monitored by TLC, and it was stopped when the di-esters were detected. Thus, it was possible to optimise the yields of regioisomerically pure unsaturated monoesters of sucrose.

The differentiation between the regioisomeric esters of sucrose can be verified by several methods [25,26]. However, the assignment was normally made by HMBC NMR experiments [27]. Thus, a crosspeak between the C of the carbonyl group and H-6 was observed, confirming the position of the substituent at C-6, as well as the longer range couplings between C-4 and H-6, between C-6 and H-4, and C-5 and H-6, which were consistent with structures **1–4**. The sucrose 6,6′-*O*-di-esters were isolated in smaller amounts and it was not possible to avoid their formation. The presence of other possible side products such as anhydro derivatives was not observed [22].

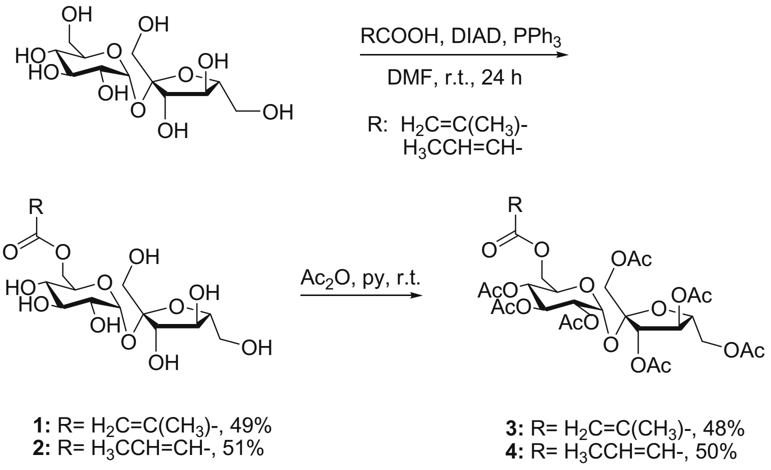
The Mitsunobu reaction applied to sucrose and acrylic acids is selective for the 6-position, unlike the corresponding silylation reaction with bulky silyl reagents such as TBDPSCl, which is regioselective for the 6′-position [28]. The reason for this differentiation is probably determined during the reaction of the pentavalent phosphorus complex, formed between triphenyl phosphine and DIAD, with the primary hydroxyls of the sucrose molecule [29,30].



Scheme 2. General scheme for the free radical copolymerisation of monomers **1–4** with styrene.

Subsequent conventional acetylation afforded the corresponding acetylated products in quantitative yields. The monomers obtained were not stable and tended to polymerise spontaneously upon concentration. This difficulty was overcome by adding hydroquinone to the mixture for storage and which was removed by flash column chromatography prior to the copolymerisation experiments [24].

Two useful measures of the potential environmental acceptability of chemical processes are the *E* factor, defined as the mass ratio of waste to desired product, and the atom utilization, calculated by dividing the molecular weight of the desired product by the sum of the molecular weights of all substances produced in the stoichiometric equation [31]. For mono-esterification of sucrose by Mitsunobu procedure these values are as follows: *E* factor = 2.35; Atom utilization = 46%. In this calculation the solvent DMF was



Scheme 1. Sucrose esterification under Mitsunobu conditions, and subsequent peracetylation of the products.