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Short communication

Rapid and environmentally friendly preparation of starch esters ☆

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Abstract

The effects of microwave heating and reactant composition on the iodine-catalyzed acetylation of starch by acetic anhydride were investigated. After only 2 min at 100 °C, significant amounts of acetylation occurred using small amounts of iodine (0.16–2.5 mol%). Values of degree of substitution (DS) increased as iodine/starch and acetic anhydride/starch ratios increased. Starch acetates having DS of up to 3 were prepared using 2.5 mol% iodine. Molecular weights decreased as iodine levels increased. This method of starch acetylation is attractive since no solvent is needed, reaction is rapid, energy inputs are relatively small, and the catalyst has low toxicity.
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1. Introduction

Most starch esters used commercially such as starch acetates, alkenylsuccinates and adipates have low (<0.1) degree of substitution (DS) (Shogren, 2003). They are commonly used in the form of aqueous solutions/suspensions for food applications (Billmers & Tessler, 1994). They are prepared by reacting aqueous starch/water with an anhydride for several hours. Starch esters of moderate to high DS (0.5–2.5) can have very different properties such as hydrophobicity, melt processibility, and solubility in organic solvents. These higher DS polymers have been used for non-food applications such as tablet binders, hot melt adhesives, coatings, cigarette filters, biodegradable plastics and metal ion absorbants (Tessler & Billmers, 1996). Market penetration has been low, however, due to relatively high costs of the solvents needed, catalysts, and wastewater handling.

In a previous account, Biswas et al. reported that cellulose could be converted to cellulose triacetate by heating with acetic anhydride at 100 °C for 10 min. in the presence of a catalytic amount of I_2 (Fig. 1) (Biswas, Selling, Appell, Woods, Willett, & Buchanan, 2007; Biswas, Sharma, Willet, Vermillion, Erhan, & Cheng, 2007; Biswas, Shogren, & Willett, 2005). Starch acetates of DS up to 1.6 were prepared by the same method. Only a few reactant and catalyst concentrations were studied in this initial communication and heating was conducted using a conventional block heater. The potential of microwave-assisted reactions has been demonstrated recently using bio-related materials such as starch (Biswas, Shogren, Kim, & Willett, 2006) or soybean oil (Biswas, Sharma et al., 2007).

The goals of this study were to explore the effects of microwave heating, catalyst loading and anhydride/starch ratio on starch acetate DS and molecular weight. The ultimate objectives are to develop new processes to prepare starch acetates in a more economical and environmentally friendly way by minimizing energy consumption, minimizing solvent, minimizing toxicity and amount of catalyst

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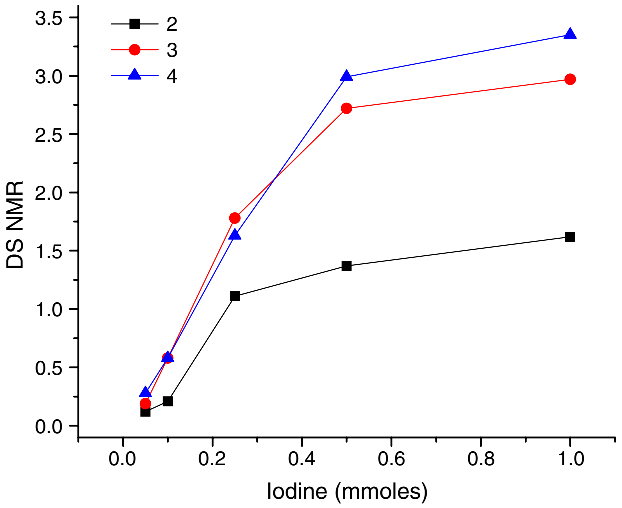

Fig. 1. Effect of iodine amount on DS. “2,3,4” indicate the mmole ratio of acetic anhydride to glucose unit.

needed, increasing reaction efficiency, and minimizing byproducts. Such less expensive starch acetates would then have better potential to replace petroleum-based polymers currently used.

2. Experimental

2.1. Chemicals

Native corn starch (11% moisture) from Sigma and used as is without drying. All other chemicals were obtained from Aldrich. All water used was deionized. Deuterium oxide was obtained in ampoules from Cambridge Isotope Laboratories. All chemicals were used without further purification.

2.2. Instrumentation

Microwave reactions were carried out using an Ethos MicroSYNTH 1600 microwave labstation from Milestone. Reactions were performed in a 50 mL quartz pressure vessel, QRS1550 from Milestone. Pierce Reacti-Vial™ glass vials, 10 ml, equipped with magnetic stirrer were used as reactors. A Pierce Reacti-Therm™ heating block was used as the conventional heat source. IR spectra were obtained on a Nicolet Avatar 370 midrange Fourier Transform Infrared spectrometer using a SenIR Duroscope diamond ATR. NMR samples were prepared from 10 mg of product and 0.7 mL of D_2O and heated at 80 °C with stirring for 5 h. NMR spectra were obtained by using a Bruker DRX 400 spectrometer.

2.3. Preparation of starch acetate

A mixture of 6.125 g acetic anhydride (60 mmol) and three different concentrations of starch 4.86 g (30 mmol), 3.24 g (20 mmol) or 2.43 g (15 mmol) were placed in a 50 mL quartz reactor vessel with a stir bar. For each ratio of acetic anhydride to starch, six different concentrations of iodine were added (e.g. 0.05, 0.1, 0.25, 0.5, 0.75, and 1.0 mmol) to the reactor vessel. When the mixture was uniformly mixed, the vessel was placed into the Milestone Ethos® microwave equipped with the Easywave® operating program and a fiber optic temperature probe. The mixture was heated to 100 °C, held there for 2 min, removed from the microwave oven, and cooled to room temperature. A saturated sodium thiosulfate solution (1–2 mL) was added and mixed. The mixture was transferred to a beaker containing 50 ml of ethanol, stirred for 30 min, and filtered. The residue was washed with water and again with ethanol, filtering after each wash. Samples were dried in 60 °C vacuum oven overnight. All experiments were performed in triplicate. The percent yield was calculated based on the amount of starch used, starch acetate recovered and the degree of substitution (DS).

2.4. Molecular weight by GPC

Samples (0.5 g) were ground in a mortar and pestle, added to 10 ml 1.0 M NaOH and stored at 3 °C with occasional shaking for 3 days. Deacetylated samples were then titrated to pH 7 with 1 M HCl; 10 ml 0.1 M phosphate buffer, pH 7 was added and the total volume was made up to 100 ml with distilled water. GPC was carried out using a Waters 1525 HPLC system with a Waters 717 plus autosampler and Waters 2414 refractive index detector. GPC analyses were performed using a Polymer Labs Aquagel-OH 30 column (300 × 7.5 mm), an injection volume of 50 mL and a temperature of 30 °C. The HPLC was set to an isocratic flow rate of 0.75 mL/min of a pH 7, 0.01 M phosphate, 0.1 M NaCl aqueous buffer solution. Molecular weights were calculated using dextran standards (American Polymer Standards Corp, Mentor, OH) and Waters GPC software.

2.5. Determination of DS

The DS values of the starch acetates were determined using NMR spectroscopy. The DS was further confirmed by titration with aqueous sodium hydroxide solution. The DS values were also verified by infrared spectrometry.

3. Results and discussions

In general, microwave heating of a polar solvent differs little in comparison to conventional heating. The reaction is accelerated under microwave conditions mainly due to the speed with which a mixture can be heated and the high temperatures easily obtainable in pressurized vessels. However, as iodine is a good absorber of microwave radiation, we assumed that any reaction containing iodine would be greatly accelerated by microwave heating.

The various variables of the reaction were each studied independently. The important parameters were found to

Table 1
Microwave assisted iodine-catalyzed acetylation of starch at 100 °C for 2 min by microwave heating: reaction conditions, yield, degree of substitution

Sample ID	Ac_2O (eq/glu)	Iodine (meq/gl)	Ac_2O (meq I_2/eq)	DS (^1H, D_2O)	Starch acetate % Yield
34-1	2	1.7	0.83	0.12	87.4
34-2	3	2.5	0.83	0.19	89.9
34-3	4	3.3	0.83	0.28	87.5
24-1	2	3.3	1.7	0.21	87.2
24-2	3	5.0	1.7	0.58	88.0
24-3	4	6.7	1.7	0.58	87.4
35-1	2	8.3	4.2	1.11	64.9
35-2	3	12.5	4.2	1.78	87.8
35-3	4	16.7	4.2	1.63	82.0
23-1	2	17	8.3	1.37	58.3
23-2	3	25	8.3	2.72	72.5
23-3	4	33	8.3	2.99	71.8
25-1	2	33.3	16.7	1.62	49.0
25-2	3	50.0	16.7	2.97	48.3
25-3	4	66.7	16.7	3.35[a]	61.9

[a] Chloroform-soluble fraction only.

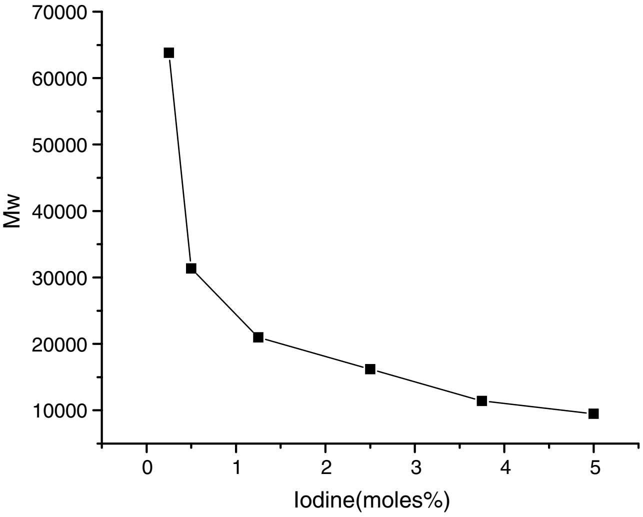

Fig. 2. Effect of iodine amount on starch acetate M_W.

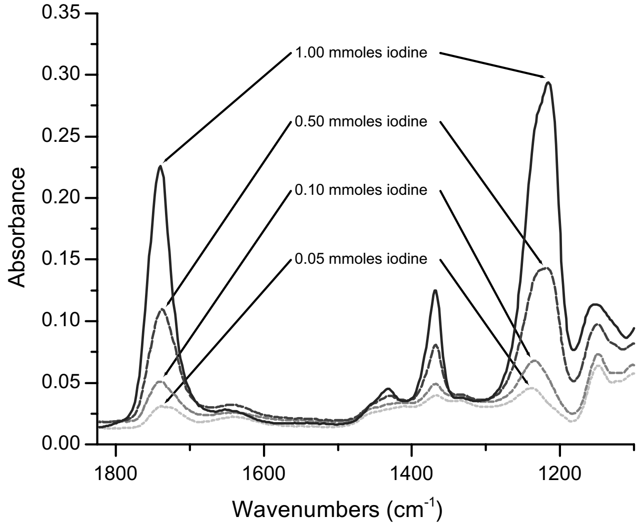

Fig. 3. IR spectra (1200–1850 cm^{-1}) showing higher acetyl content with increasing iodine amount.

be reaction time, temperature, ratio of starch to acetic anhydride, and the amount of iodine. The reaction was over in less than 2 min at 100 °C. The ratio of acetic anhydride to starch was found to be important, but the proportion of iodine was the most important factor. Without iodine, the acetylation reaction hardly proceeded and starch acetate with a DS of 0.03 was obtained. However, even very small amounts of iodine (0.16 mol%) yielded starch acetates with a DS of 0.2–0.57. These are the very levels of DS starch acetates that are sought for many applications.

Table 1 summarizes the results. As seen in Fig. 1 the DS increases with increasing amounts of iodine. Starch-to-acetic anhydride ratios of 1:2, 1:3 and 1:4 were employed. For each 30 mmol of starch, the amounts of iodine used were 0.05 mmol (0.16 mol%), 0.1 mmol (0.33 mol%), 0.5 mmol (1.66 mol%), 0.75 mmol (2.5 mol%) and 1 mmol (3.33 mol%).

As the proportion of iodine increased, the DS increased and the molecular weight decreased. Fig. 2 shows the effect of iodine concentration on the M_w of starch acetate. Since iodine is also an oxidizing agent, it is not surprising that higher iodine concentrations result in lower molecular weight of starch. Other oxidants like hypochlorite (bleach) and oxygen are also known to cleave starch chains.

The higher acetyl content with increasing iodine amount is demonstrated in the IR spectra detailed in Fig. 3. With increasing iodine, absorption increased proportionately in the regions associated with C=O ester stretching (1730 cm^{-1}) and in the regions associated with the methyl of the acetyl group (1220 cm^{-1}) A corresponding decrease was seen in the OH stretch regions and the CO stretch regions at 1155 and 1080 cm^{-1}.

The ^1H NMR spectrum of sample 25-2 (Table 1) is shown in Fig. 4a. The DS is calculated to be 2.97. Note that under the most extreme conditions of reaction (sample 25-3, Table 1) the reaction product has a DS around 3.35–3.5 via all three determinations of DS (NMR, titration, and FTIR). This is probably due to the hydrolysis of starch and acetylation of the chain ends of hydrolyzed starch. The ^1H NMR spectrum (Fig. 4b) is similar to that of the acetylated hydrolyzed starch reported in the literature (Elomaa 2004). Both the DS and the chain end peaks in the NMR spectrum suggest that the degree of polymerization of the starch acetate is around 4–5.

It is of interest to note that whereas the microwave reaction of acetyl anhydride is facile, the reaction of propionic anhydride with starch was more difficult, even with iodine catalysis.

This new microwave reaction has the advantages of being more energy efficient and also environmentally friendly because of the absence of solvent (or reduced solvent usage). It can also lend itself readily to on-line produc-

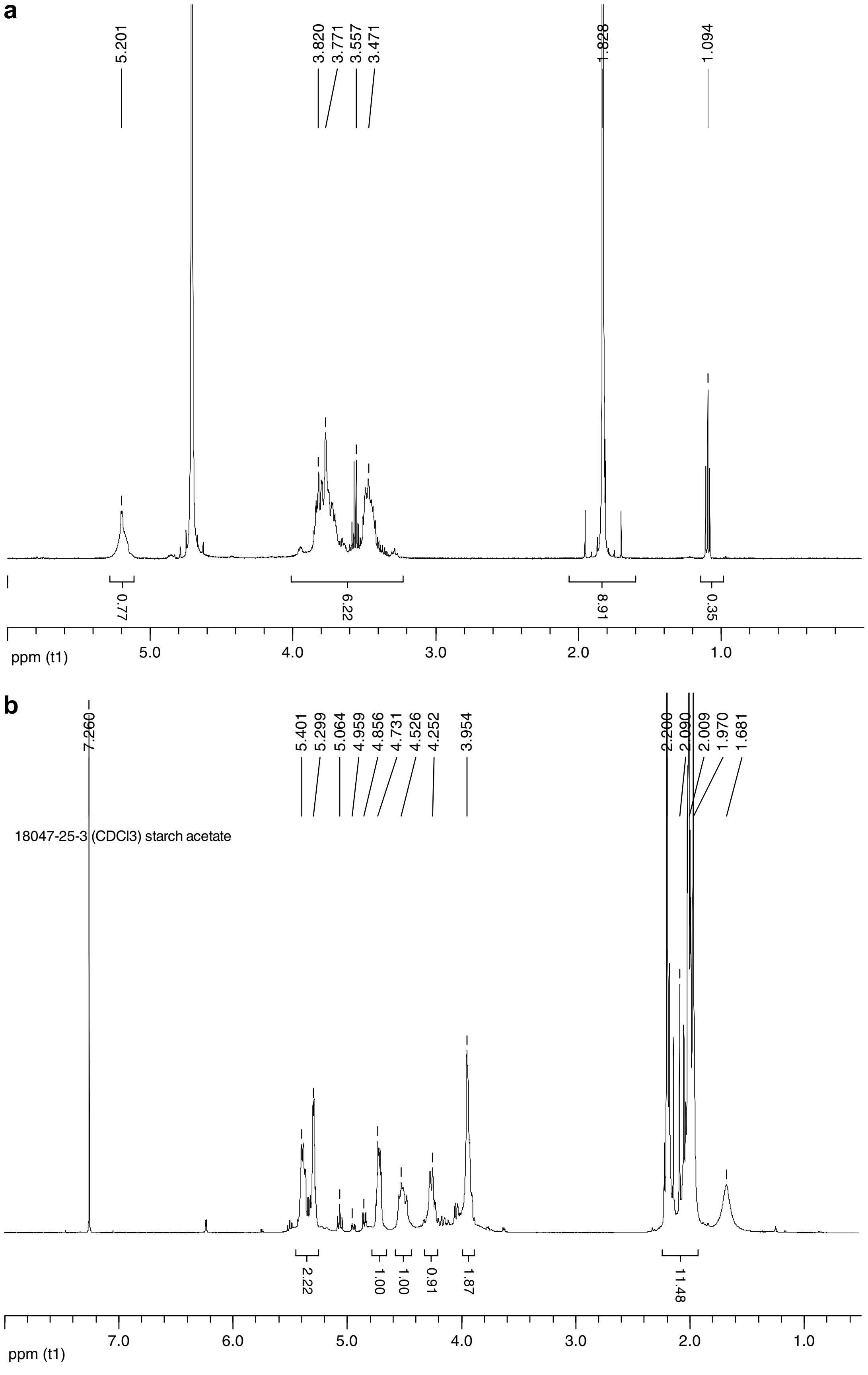

Fig. 4. (a) NMR spectrum of sample 25-2 in D_2O. (b) NMR spectrum of chloroform soluble fraction of sample 25-3.

tion of starch films in an industrial setting. Another possibility is to produce starch acetate in a tubular reactor where the heating zone can be kept hot by using microwave energy. This reaction can also be useful for small lab preparations of starch acetate, e.g., for specialties and for diagnostic uses.

4. Conclusions

A microwave-assisted method to prepare starch acetates with DS up to 3 was developed. A reaction time of 2 min at 100 °C in a microwave reactor using 0.16–2.5 mol% I_2 was sufficient to obtain starch acetates with a DS range of 0.13–3.0. The amount of iodine catalyst also influenced the DS of the starch acetates as well as the molecular weight of the product. This simple microwave-assisted synthetic methodology provides a rapid, efficient, and environmentally friendly method of preparing starch acetates by minimizing energy consumption, minimizing solvent, minimizing toxicity and amount of catalyst needed, increasing reaction efficiency, and minimizing byproducts.

References

Billmers, R. L., & Tessler, M. M. (1994). Method of preparing intermediate DS starch esters in aqueous solution. *US Patent Office,* Pat. No. 5,321,132.

Biswas, A., Selling, G., Appell, M., Woods, K. K., Willett, J. L., & Buchanan, C. M. (2007). Iodine catalyzed esterification of cellulose using reduced levels of solvent. *Carbohydrate Polymers, 68*, 555–560.

Biswas, A., Sharma, B. K., Willet, J. L., Vermillion, K., Erhan, S. Z., & Cheng, H. N. (2007). Novel modified soybean oil containing hydrazino-ester: Synthesis and characterization. *Green Chemistry, 9*, 85–89.

Biswas, A., Shogren, R. L., Kim, S., & Willett, J. L. (2006). Rapid preparation of starch maleate half-esters. *Carbohydrate Polymers, 64*, 484–487.

Biswas, A., Shogren, R. L., & Willett, J. L. (2005). A sovent-less method to prepare cellulose or starch acetate. *Biomacromolecules, 6*, 1843–1845.

Elomaa, M. (2004). Determination of the degree of substitution of acetylated starch by hydrolysis,[1] H NMR and TGA/IR. *Carbohydrate Polymers, 57*, 261–267.

Shogren, R. L. (2003). Rapid preparation of starch esters by high temperature/pressure reaction. *Carbohydrate Polymers, 52*, 319–326.

Tessler, M. M., & Billmers, R. L. (1996). *Journal of Environmental Polymer Degradation, 4*(2), 85.