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Scandium triflate catalyzed acetylation of starch at low to moderate temperatures ☆

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Abstract

Scandium (III) trifluoromethane sulfonate ($Sc(OTf)_3$) was investigated as a catalyst for the acetylation of starch in order to determine the potential for preparing new types of starch esters under mild (low to moderate temperature) conditions. At room temperature, dry granular corn starch reacts with acetic anhydride in the presence of $Sc(OTf)_3$ to form starches highly acetylated on the granular surface only. At higher temperatures (80 °C), starch acetates of degree of substitution (DS) 1.2 and 0.40 were obtained by reaction of granular starch with acetic anhydride or acetic acid, respectively. When starch was gelatinized in acetic acid prior to reaction, acetylation with acetic anhydride was much more rapid with DS reaching 3 after 1 h at 80 °C. Acetylation was rapid at levels of $Sc(OTf)_3$ down to 0.1 mol%. These data suggest that powerful Lewis acid catalysts such as $Sc(OTf)_3$ may be useful in preparing novel starch esters using either carboxylic acids or anhydrides.
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Keywords: Starch; Scandium triflate; Acetylation

1. Introduction

There is increasing interest in discovering new biobased materials to replace petroleum-based polymers (Gross & Kalra, 2002). Starches, in particular, have attracted considerable interest in diverse applications such as biodegradable plastics, coatings, adhesives, foams, flocculants, dispersing agents, sequestering agents (Belard, Dole, & Averous, 2005; Davis & Song, 2006; Knill & Kennedy, 2005; Roper, 2002; Zobel & Stephen, 2006). To improve functionality and economics, new methods of chemically modifying starch are needed to control substitution patterns and to reduce energy inputs and byproducts (BeMiller, 1997).

Currently, most starch esters produced commercially are low DS products made by aqueous suspension reaction of starch, anhydrides and NaOH to maintain pH 7–9 (Jarowenko, 1986; Rutenberg & Solarek, 1984). Some starch acetates of moderate to high DS are also made by this process (Tessler & Billmers, 1996; Xu, Miladinov, & Hanna, 2004). Large amounts of wastewater and sodium acetate byproduct are produced, resulting in high cost. There is no control of substitution pattern.

There have been many studies of preparation of starch esters in non-aqueous systems including heating in acetic acid (Shogren & Biswas, 2006), formic acid (Aburto, Alric, & Borredon, 1999), pyridine, DMSO, and dimethylacetamide (Rutenberg & Solarek, 1984). Catalysts used have included minerals acids and bases (Jarowenko, 1986), Lewis acids such as I_2 (Biswas, Shogren, & Willett, 2005), and enzymes such as lipases and proteases (Bruno et al., 1995; Qiao, Gu, & Cheng, 2006; Rajan & Abraham, 2006). Starch esters specifically substituted at the 2 (Dicke, 2004; Klohr, Koch, Klemm, & Dicke, 2005) and 6 (Chakraborty, Sahoo, Teraoka, Miller, & Gross, 2005) positions

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☆ Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by the USDA implies no approval of the product to the exclusion of others that may also be suitable.

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have been prepared. The drawbacks of enzyme catalysis are that the starch must be dissolved in polar solvents such as DMSO which usually severely decrease the activity of the enzyme. Alternatively, lipase catalyzed acylation of a suspension of starch nanoparticles in toluene is facile (Chakraborty et al., 2005) but this requires a major alteration in starch structure to first form nanoparticles.

Strong Lewis acid catalysts such as scandium (III) triflate ($Sc(OTf)_3$) have been shown to rapidly catalyze ester formation between alcohols and anhydrides (Ishihara, Kubota, Kurihara, & Yamamoto, 1996) as well as between diols and diacids to form polyesters (Takasu, Oishi, Iio, Inai, & Hirabayashi, 2003). Catalysis occurs at ambient or slightly elevated temperatures and specificity for primary versus secondary alcohols has been shown under certain conditions (Procopiou, Baugh, Flack, & Inglis, 1998). Although $Sc(OTf)_3$ is expensive, it is active at low levels (~0.1 mol%) and can be easily recovered and reused making it a potential "green" catalyst.

The purpose of this study was to determine the potential of $Sc(OTf)_3$ as a catalyst for the preparation of starch acetates under mild conditions. The effects of temperature, time, reactant (acetic anhydride versus acetic acid), reactant concentration, catalyst concentration and starch gelatinization on DS were studied. Bulk versus surface DS were measured using NMR and XPS, respectively.

2. Materials and methods

2.1. Materials

Normal corn starch (pure food grade) was purchased from A.E. Staley (now Tate & Lyle, Decatur, IL) and had a moisture content of 9.6%. The starch was dried in a vacuum oven at 110 °C for 3 h before use. Glacial acetic acid, acetic anhydride (99+%) and scandium (III) trifluromethanesulfonate (99%) were purchased from Aldrich (Milwaukee, WI).

2.2. Acetylation of starch

Reactions were performed in 10 ml glass Reacti-Vials (Pierce, Rockford, IL) with teflon screw caps. Starch (1 g), acetic anhydride (0.63–1.89 g, 1–3 mol/mol glucose), acetic acid (0–1.89 g, 0–5.1 mol/mol glucose), and $Sc(OTf)_3$ (0–0.03 g, 0–0.01 mol/mol glucose) were added. Vials were stirred magnetically and heated to the desired temperature in a block heater (Pierce, Rockford, IL). After reaction, the contents of the vial were added to 40 ml ethanol, centrifuged, rewashed with ethanol three more times, air dried and then dried in vacuum at 50 °C. In some experiments, dry starch was first gelatinized (melted) in glacial acetic acid (starch/acid 1/1 w/w) by heating 20–150 °C over 3.5 min. then 150–160 over 2.5 min. in a microwave reactor (Milestone Microwave Labstation 1600 (Milestone, Inc., Shelton, CT) (Shogren & Biswas, 2006).

2.3. Analytical methods

Bulk degree of substitution (DS) values were estimated using ^1H NMR as described previously (Shogren, 2003). Briefly, samples (2%) were dissolved and hydrolysed in 0.5 M NaOD and areas of acetyl CH_3 and starch CH resonances were measured. Reaction efficiencies were based on the amount of acetic anhydride added and were calculated as $RE = DS/(w_{aa}/102)/(w_{cs}/162)$, where w_{aa} and w_{cs} are the weights of acetic anhydride and starch, respectively. Standard deviations in DS and RE were determined from results from three different reactions. ^{13}C NMR spectra were obtained at 25 °C on a Bruker Ultrashield 500 at 125.76 MHz.

Surface DS values were estimated using X-ray photoelectron spectroscopy (XPS). Spectra were collected with a PHI model 5400 X-ray photoelectron spectrometer (Physical Electronics, Eden Prairie, MN) equipped with small area electron extraction optics, a spherical capacitor electrostatic energy analyzer and a dual channel plate position sensitive detector. Starch powder samples were mounted with double stick Cu tape (a thin copper foil with adhesive on both sides) onto the sample holder. Samples were excited using characteristic MgKα X-rays, 1253.6 eV (15 kV, 300 W). Spectra were collected from a 1 mm^2 area of the surface at a 45° emission angle. Carbon spectra were collected using a pass energy of 35.75 eV, 0.1 eV/step. The binding energy scale was calibrated using $Au4f_{7/2} = 84.0$ eV; the scale was shifted by ~2 eV to make C (CH_2) = 285.0 eV to correct for charging effects. Chemical state assignments were made based on tabulated energies. Quantitative analyses were carried out by dividing elemental peak areas by the appropriate relative sensitivity factors as reported by the instrument manufacturer. Peaks were fit to mixed Gaussian (G)/Lorentzian (L) lineshapes (80–100% G) using AugerScan 3 software. DS values were calculated from the area of the acetyl C═O peak at 289.2 eV divided by the sum of the areas of starch C–O peaks at 286.7 and 288.0 eV (6×).

3. Results and discussion

Compositions of starch acetates prepared by reaction of granular (native) corn starch with acetic anhydride (3 mol/mol glucose) and $Sc(OTf)_3$ (1 mol% based on starch) at room temperature are shown in Table 1. DS values as determined by ^1H NMR were very small (<0.02), indicating very little total acetylation. After reaction, however, the starch granules were difficult to disperse in water, suggesting some surface reaction. This was confirmed by XPS spectra of corn starch before and after reaction (Fig. 1). For native corn starch, the XPS spectrum shows peaks corresponding to C_{2-6}–O at 286.7 eV, O–C_1–O at 288.0 eV and extraneous hydrocarbon at 285 eV. The XPS spectrum of the acetylated starch (Fig. 1b) shows a new peak at 289.2 eV due to the carbonyl carbon of the acetate groups and added intensity at 285 eV due to the acetyl CH_3 group.

Table 1
Surface versus bulk acetylation of granular corn starch in acetic anhydride with $Sc(OTf)_3$ at 20 °C

Dry starch (g)	Acetic anhydride (g)	$Sc(OTf)_3$ (g)	Time (h)	DS (bulk)[a]	DS (surface)[b]
1	1.89	0.03	1	0.001	1.77
1	1.89	0.03	5	0.002	1.91
1	1.89	0.03	24	0.016	2.55
1	1.89	0	1	0.002	
1	1.89	0	5	0.005	0.14
1	1.89	0	24	0.008	

[a] Determined by ^1H NMR.
[b] Determined by XPS.

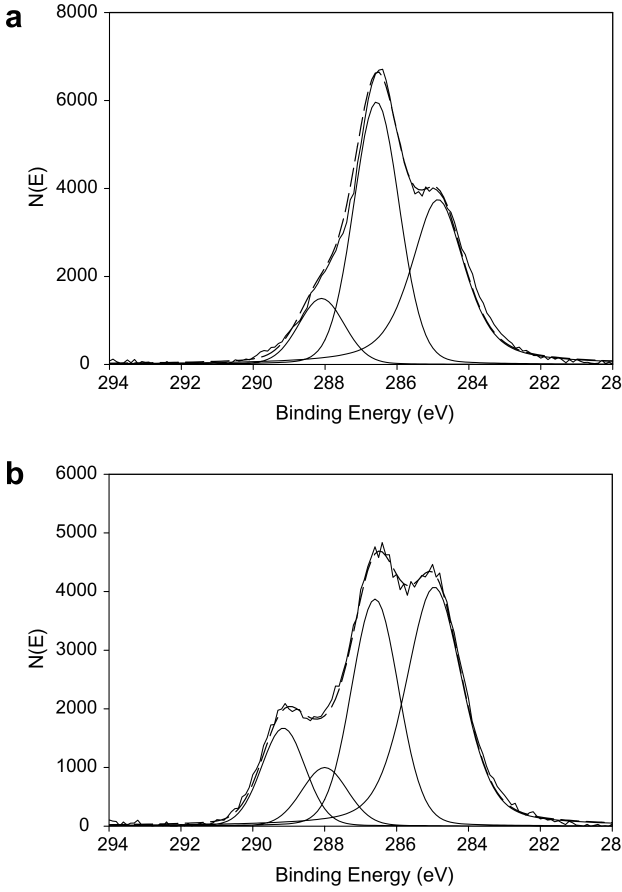

Fig. 1. XPS of native corn starch (a) and surface acetylated corn starch (b, reaction 2 from Table 1).

Compositions calculated from the XPS experiments revealed rather high surface DS values ranging from 1.8 to 2.6 for reaction times of 1–24 h (Table 1). The combination of high surface DS and low bulk DS suggests that acetylation occurred only in a thin surface layer of the starch granule. This is consistent with studies of corn starch which show little permeability of starch granules to hydrophobic solvents except for small channels and perhaps interior cavities (Huber & BeMiller, 1997). Without water present to swell the hydrogen bonded starch network, little anhydride would be expected to penetrate the starch granule.

Although other surface modified starch esters have been prepared previously (Bengtsson, Koch, & Gatenholm, 2003; Hauber, BeMiller, & Fannon, 1992; Thielemans, Belgacem, & Dufresne, 2006; Whistler, Madson, Zhao, & Daniel, 1998), this is the first report of a surface modified starch acetate. In addition, these other studies used expensive acyl chlorides rather than cheaper anhydrides. Such starch granules having a thin layer of hydrophobic starch ester on the surface might exhibit some interesting frictional, permeability and swelling properties. Potential applications as lubricants, controlled release, and hollow microspheres could be contemplated.

Compositions of starch acetates prepared by reaction of granular (native) corn starch with acetic anhydride (3 mol/mol glucose) or acetic acid (5.1 mol/mol glucose) and $Sc(OTf)_3$ (1 mol% based on starch) at 80 °C are shown in Fig. 2. After 1 h, DS for the reaction with acetic anhydride was 1.2 compared to a DS of 0.40 for acetic acid. This suggests that the higher temperature allows the starch granules to swell during reaction, giving much higher DS. A light brown color was noted for the 1 h acetic anhydride reaction, suggesting some degradative reactions were occurring. Browning was not seen with acetic acid. It is quite significant that acetylation occurred with acetic acid, even without water of esterification being removed. This is the first report of starch esters being prepared from starch and an organic acid under rapid, mild conditions using a non-enzymatic catalyst. It suggests that new types of starch esters which were impossible to synthesize before (because there was no reactive form of the acid available) could now be prepared using $Sc(OTf)_3$. These results are consistent with previous work showing that $Sc(OTf)_3$ catalyzes the

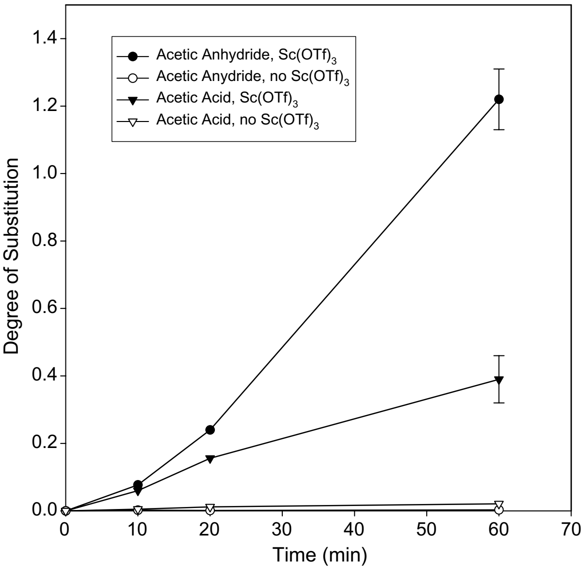

Fig. 2. Acetylation of native corn starch with acetic anhydride or acetic acid catalyzed by 3% scandium triflate at 80 °C. Dry starch (1 g) was heated with acetic anhydride (1.89 g) or acetic acid (1.89 g) and 0.03 g $Sc(OTf)_3$ in sealed, stirred vials.

esterfication of diols and diacids under mild conditions (Takasu et al., 2003).

The effect of starch pregelatinization on reaction with acetic anhydride (3 mol/mol glucose) and $Sc(OTf)_3$ (1 mol% based on starch) is shown in Fig. 3. Aceylation is complete (DS = 3) after 1 h at 80 °C when starch is pregelatinized. This is much more rapid than the reaction with granular starch from Fig. 2, indicating that highly swollen starch reacts much more rapidly. Even at room temperature, a DS of 1.2 is obtained after 20 h, compared with a DS of 0.016 for granular starch from Table 1. Results for reaction of pregelatinized starch with acetic anhydride (0, 1, 2 mol anhydride/mol glucose) at 80 °C are shown in Fig. 4. Reactions are complete, i.e. DS > 1 for 1 mol anhydride/mol glucose and DS > 2 for 2 mol anhydride/mol glucose. Less $Sc(OTf)_3$ can be used and still obtain good extent of reaction. Fig. 5 shows that as little as 0.1 mol% $Sc(OTf)_3$ can be used while still reaching a DS of 1 and 60% reaction efficiency after 1 h at 80 °C. Reaction efficiency exceeds 100% at higher levels of $Sc(OTf)_3$ since reaction efficiency is calculated based on amount of acetic anhydride only and some esterification with acetic acid also occurs. ^{13}C NMR indicated a preference for substitution at the C6 position but C2 and C3 were also substituted (data not shown) as found previously for high temperature acetylation of starch in acetic acid/acetic anhydride (Shogren and Biswas, 2006).

In summary, $Sc(OTf)_3$ catalyzed the reaction of corn starch with acetic anhydride to form highly surface acetylated starches at room temperature and bulk acetylated starches at 80 °C. Surface modification of starches, starch nanoparticles and lignocellulosics is becoming desirable as a way to improve their adhesion to matrix polymers in composites. Significant acetylation occurred using acetic acid at 80 °C, even without removal of water of esterification. This finding opens the possibility of preparing novel starch esters by reaction of starch with a variety of carboxylic acids under mild conditions, particularly non-volatile ones that would tolerate partial vacuum. Since $Sc(OTf)_3$ is soluble in water or ethanol, $Sc(OTf)_3$ could be recovered from the supernatant by evaporation after precipitation of modified starches in either of these solvents after reaction. $Sc(OTf)_3$ is also active in the presence of water so anhydrous conditions are not essential.

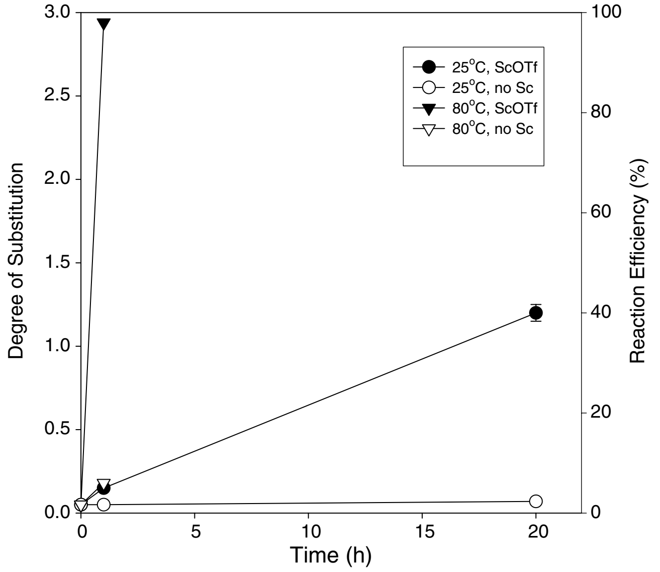

Fig. 3. Acetylation of gelatinized starch with acetic anhydride catalyzed by 3% scandium triflate. Starch/acetic acid (1 g/1 g) were gelatinized by microwave heating then 1.89 g acetic anhydride and 0.03 g $Sc(OTf)_3$ were added.

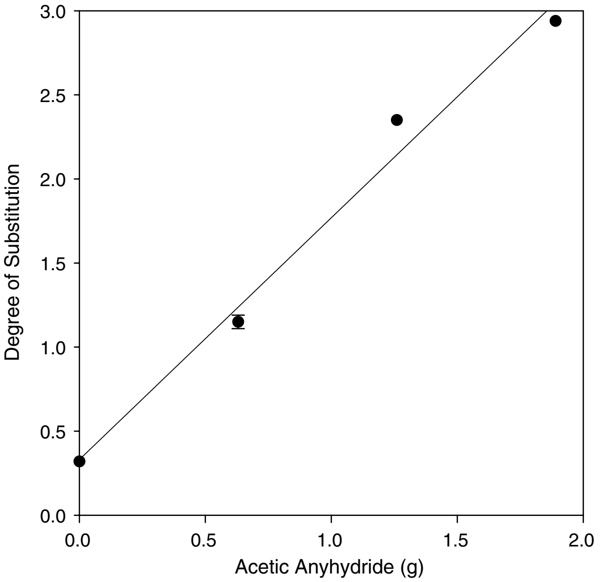

Fig. 4. Effect of acetic anhydride concentration on acetylation of gelatinized starch for 1 h at 80 °C. Starch/acetic acid (1 g/1 g) were gelatinized by microwave heating, then acetic anhydride and 0.03 g $Sc(OTf)_3$ were added.

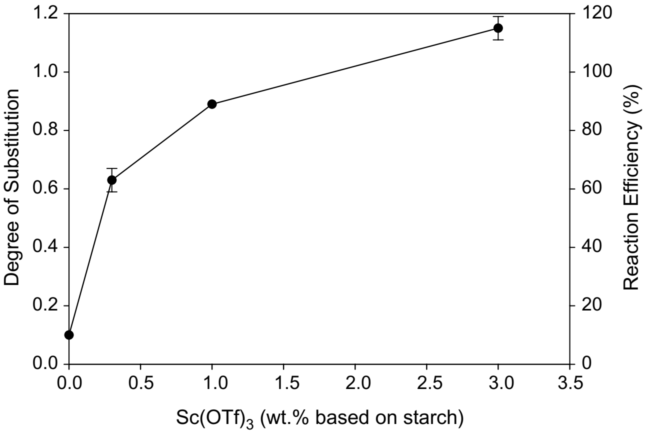

Fig. 5. Effect of scandium triflate concentration on acetylation of gelatinized starch with acetic anhydride for 1 h at 80 °C. Starch/acetic acid (1 g/1 g) gelatinized by microwave heating, then 0.65 g acetic anhydride and $Sc(OTf)_3$ added.

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