Iodine-catalyzed esterification of polysaccharides

ABSTRACT

Esters of cellulose and starch are well-known commercial materials. Cellulose acetate, for example, is a major product with annual global production of over 1.5 billion pounds. The conventional acetylation processes involve solvents such as methylene chloride or high temperature with sulfuric or perchloric acid as a catalyst. A review is provided here of the recent reports concerning rapid, alternative preparation of cellulose and starch esters. The process entails reaction of the cellulose or starch with acetic anhydride in the presence of a catalytic level of iodine, and in the absence of additional solvents. The reactant stoichiometry, reaction temperature, and reaction time all have effects on the degree of substitution of the ester and the reaction yield. Included in the review are the proposed modes of action for iodine, the mechanism, and assessment of the utility of this approach.

KEYWORDS: cellulose acetate, starch acetate, iodine, acetylation, polysaccharides

INTRODUCTION

Acetylation of polysaccharides has been known for many decades (1-8). For example, acetylation of cellulose (3) and starch (4) in the presence of acetic acid and acetic anhydride (5) is well known. In the case of cellulose acetate, it is customary to produce cellulose triacetate (CTA) first, and then hydrolyze it to produce cellulose acetate (CA) with the desired degree of substitution (1, 2). Conventional acetylation processes typically involve solvents such as methylene chloride or high temperatures (3) with sulfuric or perchloric acid as a catalyst. There has been some recent studies in polysaccharide esterification (6), particularly the use of ionic liquids to dissolve (7) cellulose and prepare cellulose acetates (8). Other paths for esterification include dialkylcarbodiimide, N,N-carbonyldiimidazole, iminium chlorides, transesterification, and ring-opening esterification (6). An alternative approach reported is to use iodine as a catalyst for the esterification of cellulose and starch in the presence of acetic anhydride (9-11). The reactions are generally conducted at 100°C without the use of additional solvents (9). Starch acetates are produced using both conventional or microwave heating (10). In this article, we aim to review this development, summarize the major results, and evaluate its usefulness.

REACTION PROCEDURE

The iodine-catalyzed acetylation of starch and cellulose appears straightforward (9). In a typical reaction, 1.7 g of starch (corresponding to 10 mmoles of anhydroglucose unit or AGU), 1.7 g (16.6 mmoles) of acetic anhydride, and 120 mg (0.47 mmoles) of iodine are heated at 100°C for 10 minutes (Table 1). The reaction mixture is then cooled to room temperature and treated with a saturated solution of sodium thiosulfate (2 ml) while stirring. The mixture colour changes from dark brown to colourless, indicating the transformation of iodine to iodide. The mixture is poured into 50 ml of ethanol and stirred for 15-30 minutes. The product is isolated by filtration, washed with water, and dried in a vacuum oven at 60°C. As examples, the data on reactions of cellulose and starch with acetic anhydride in the presence of...
iodine are reproduced in Table 1 (9). The yield percent shown in the table corresponds to the weight yield of the product relative to the yield if all of the cellulose or starch is converted. After 10 minutes of heating at 100°C, yields of 57-95 percent are obtained. At concentrations of ca. 4.7 percent or more, iodine promotes reactive dissolution of cellulose in acetic anhydride at 100°C. Below 5 mole% iodine, the reaction mixture remains heterogeneous. The yield of cellulose acetate increases as a function of iodine concentration, presumably as a result of enhanced catalysis of acylation and increased solubility. Note that the starch/iodine reaction mixtures appear mostly heterogeneous; the acetylation reaction proceeds, but the yield is relatively lower.

Table 1. Acetylation of polysaccharides at 100°C for 10 minutes.

<table>
<thead>
<tr>
<th>Polysaccharide</th>
<th>Ac₂O (eq)</th>
<th>I₂ (eq)</th>
<th>DS</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>5.03</td>
<td>0.047</td>
<td>3.1</td>
<td>94.8</td>
</tr>
<tr>
<td>Cellulose</td>
<td>6.63</td>
<td>0.031</td>
<td>2.8</td>
<td>70.0</td>
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<td>6.63</td>
<td>0.016</td>
<td>2.8</td>
<td>57.5</td>
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<tr>
<td>Starch</td>
<td>1.66</td>
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<td>1.6</td>
<td>64.3</td>
</tr>
<tr>
<td>Starch</td>
<td>5.03</td>
<td>0.047</td>
<td>1.3</td>
<td>58.0</td>
</tr>
</tbody>
</table>

**REACTION MECHANISM**

What is the role of iodine? First of all, it is known that iodine can form a complex with amylose and other glucose polymers (12). The complexation may help the solubility of cellulose or starch in the acetic anhydride. As shown in ref. 9, the cellulose-Ac₂O-I₂-iodine reaction mixture appears to be heterogeneous at 100°C below 5 mole% iodine but becomes homogeneous as iodine approaches 5 mole%. Secondly, iodine may serve as a catalyst. For example, Borah et al. (13) and Phukan (14) both suggested that iodine may act as an acetyl transfer catalyst for anhydrides. A proposed mechanism by Borah et al. (13) is given below:

Bowman (15) provides a similar view for the iodine-catalyzed acetylation of thiophene. In that case, he envisions a simple Lewis acid-base complex formation.

Finally, iodine is also known to absorb microwave energy. Thus, this reaction is particularly suited for the use of microwave as a source of heat.

**EFFECTS OF REACTION PARAMETERS**

**Reactant stoichiometry**

A more detailed study of the acetylation of starch was reported in ref. 10, particularly the effects of the stoichiometry of Ac₂O and I₂. Using microwave as the source of heat, it was shown that reaction could be completed in 2 minutes, compared to conventional heat that required 10 minutes. In a control experiment (without I₂) the acetylation reaction barely proceeded, and starch acetate was obtained with a DS of 0.03. With iodine, the results are summarized in Figure 2.

It is clear that the DS increases with increasing iodine and increasing acetic anhydride levels. However, as the iodine level increases the yield also decreases. Thus, there are optimal levels of iodine and acetic anhydride, depending on the DS desired. Commercial starch esters typically have low DS values; thus, for starch esters, lower acetic anhydride and iodine levels are needed.

It may be cautioned that excessive levels of acetic anhydride and iodine can cause acid hydrolysis. Because of acid hydrolysis, the observed DS can be higher than 3.0, as shown in some data points in Figure 2. These high DS materials are peracetylated oligomers, and they give similar NMR spectra as reported in the literature (16).

**Reaction temperature and time**

The effects of reaction temperature and time were reported for iodine-catalyzed acetylation of cellulose (11). Two sets of reactions were reported, one at room temperature, and one at 100°C. The room-temperature reactions were slow and could be followed as a function of time. At a given time, the reaction was quenched with ethanol. The solid product that was isolated was a mixture of unreacted

Table 2. Data on CTA produced by iodine-catalyzed acetylation of cellulose at room temperature.
cellulose, partly acetylated cellulose and CTA. The sample was fractionated using chloroform which dissolved only CTA. Table 2 shows that the yield of CTA increased with reaction time until it levelled off near 90 percent after 12 hours. After 12 hours, all of sample became soluble in chloroform indicating that the conversion of cellulose to CTA was complete. In contrast, the reaction was found to be fast at 100°C (11). The reaction time was set for 10 minutes, and different iodine levels were used (Table 3). It is clear that the yield of CTA increased with increasing iodine. At 4.3 mole% I₂, the CTA yield increased to 94 percent. However, the molecular weight decreased with increasing iodine, just as in the case of starch. Here again, peracetylated oligomers were obtained, due to acid hydrolysis.

**Use of different anhydrides**

In addition to acetic anhydride, other aliphatic anhydrides were also studied (11). In the case of propionic anhydride, iodine-catalyzed esterification of cellulose at 100°C gave cellulose trimpropionate (DS = 3.08) in 45 percent yield. GPC indicated that the product had a lower molecular weight (Mₙ = 20 K) relative to the cellulose triacetates. In the case of butyric and other longer chain anhydrides, no acylated products were isolated.

**ASSESSMENT AND POTENTIAL APPLICATIONS**

From prior publications (9-11), the reaction of cellulose or starch with acetic anhydride in the presence of a catalytic amount of iodine can result in the formation of cellulose or starch acetate in good yield. At a reaction temperature of 100°C using 4.3 mol% I₂, only 10 min was required to obtain a 94 percent yield of CTA. At ambient temperature, a higher catalyst loading (9 mole percent) and longer reaction times (12 h) were required to achieve comparable yields of CTA. For starch acetate, the amount of iodine and acetic anhydride can be adjusted to produce the DS of interest. The fact that the method for esterification of cellulose and starch described in this review is fast, easy, and requires no extra solvent is a potential benefit. This reaction should be readily applicable to other polysaccharides. In addition, other anhydrides can be used. For example, succinic anhydride and maleic anhydride may be amenable to this reaction, producing maleated or succinylated polysaccharides. Furthermore, with a diacylhydride, this reaction may be used to crosslink polysaccharides, thereby increasing the molecular weight. However, it should be noted that this reaction needs to be conducted with care. Thus, the amount of iodine catalyst and acetic anhydride used can influence the molecular weight of the product. In addition, the formation of peracetylated oligomer may plasticize the cellulose or starch acetate products and modulate the physical properties of the final product. Indeed in Tables 2 and 3, the T_g of the starch and cellulose acetate made with iodine catalysis was found to be lower, partly due to the presence of peracetylated oligomers and partly due to decreased molecular weight of the product.

**REFERENCES AND NOTES**


<table>
<thead>
<tr>
<th>I₂ (mole%)</th>
<th>Yield (%)</th>
<th>DS</th>
<th>DP (Mn)</th>
<th>Mₙ</th>
<th>Mₚ/Mₙ</th>
<th>T_g (°C)</th>
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</table>

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