Short communication

Acetylation of starch with vinyl acetate in imidazolium ionic liquids and characterization of acetate distribution

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Abstract

Starch was acetylated with vinyl acetate in different 1-butyl-3-methylimidazolium (BMIM) salts as solvent in effort to produce starches with different acetylation patterns. Overall degree of substitution was much higher for basic anions such as acetate and dicyanamide (dca) than for neutral anions such as chloride and nitrate. There was a strong preference for acetylation at the C2 position in BMIM dca while acetylation was similar for C2, C3 and C6 in BMIM OAc. Molecular weights were not changed significantly by the reaction conditions. These results suggest that ionic liquids can provide a convenient medium for the homogeneous modification of starches with some control over substitution patterns.

1. Introduction

Starch acetates have useful applications as water soluble thickeners in foods, coatings, plasma expanders, and adhesives (Jarowenko, 1986). Properties depend on overall degree of substitution (DS) as well as the relative DS of the three starch hydroxyls. Starch acetate substituted selectively at the C2 position was prepared by transesterification of starch with vinyl acetate in DMSO in the presence of certain salts (Dicke, 2004) and by reaction of starch with acetic acid imidazolide in DMSO (Liebert, Kulicke, & Heinze, 2008). Such 2-O-acetyl starches had enhanced viscosity suggesting an organized structure (Dicke, 2004) and enhanced stability toward ester hydrolysis (Liebert et al., 2008). A drawback of these procedures is that DMSO is rather difficult to extract from starch and difficult to recover from DMSO/alcohol mixtures.

Ionic liquids offer a convenient medium for starch reactions since some are good solvents for starch, they are generally inert to added reagents and have very low vapor pressures. Starch is solubilized by 1-butyl-3-methylimidazolium chloride (BMIM Cl) (Stevenson, Biswas, Jane, & Inglett, 2007) and 1-butyl-3-methylimidazolium dicyanamide (BMIM dca) (Biswas, Shogren, Stevenson, Willett, & Bhowmik, 2006) and reacts with acetic anhydride in BMIM dca/pyridine to give starch acetates (Biswas et al., 2006). Starch acetates made by reaction of starch with acetic anhydride in BMIM Cl/pyridine showed a slight preference for substitution at the C6 hydroxyl (Lehmann & Volkert, 2009). Thus, there is very little information available on the acetyl distribution of starch acetates prepared in ionic liquid solvents.

The purpose of this study was to determine the effect of anion type on acetate substitution of starch dissolved in BMIM type solvents and reacted with vinyl acetate. Substitution at the three hydroxyl groups of starch was determined by 13C NMR and molecular weights were assessed by GPC-MALLS.

2. Experimental

2.1. Materials

Starch was star-dri 1 corn maltodextrin from A. E. Staley (now Tate & Lyle, Decatur, IL). It was dried in a vacuum oven at 110 °C for 4 h prior to use. BMIM Cl (>95%) was a product of BASF and was purchased from Fluka. BMIM dca was prepared from BMIM Cl by addition of excess Na dca and precipitation with acetone (Liu, Janssen, van Rantwijk, & Sheldon, 2005). BMIM acetate and nitrate were prepared from BMIM Cl by anion exchange on a Dowex 1×8 column as described previously (Toral et al., 2007). Vinyl acetate (99 %) was from Aldrich.

2.2. Starch acetylation

Starch (0.324 g, 2 mmol) and ionic liquid (5 ml) were added to a 25 ml flask then heated in a vacuum oven at 90 °C for 0.5 h to dissolve the starch. Vinyl acetate (0.172–0.517 g, 2–6 mmol) was then added, ground glass stoppers were affixed and flasks were placed...
in an incubator/shaker for 70 h at 40 °C. Starch acetates were precipitated by addition of 50 ml cold ethanol followed by centrifugation. Residual ionic liquid was removed by three additional ethanol washes and the purified starch acetates were air dried then vacuum dried at 60 °C. Preparations were performed in duplicate.

2.3. NMR characterization

Starch acetates were dissolved in D₂O except for a high DS sample (experiment 4 in Table 1) which was dissolved in DMSO-d₆ at 60 °C. All spectra were obtained on a Bruker Avance 500 spectrometer (500 MHz ¹H) using a 5-mm BBO probe at 27 °C (60 °C for DMSO). Chemical shifts are reported as ppm from tetramethylsilane calculated from the lock signal. Inverse gated carbon-13 experiments were used to insure quantitative measurements. Recycle delay was 50 s and 1024 scans were acquired. Experiment time was about 14 h. Data was processed with Bruker Topspin version 1.3 software.

Total DS was determined either from the ¹H spectra as areas of acetyl CH₃ at 2.15 ppm divided by area of starch CH/7 at 3.5–5.5 ppm or from the ¹³C spectra as area of CH₂ at 20 ppm divided by area of starch C/6 at 60–103 ppm. Acetylation at C2 shifts the starch C1 resonance from 100 ppm to 96 ppm (see Fig. 1) so DS at C2 was determined as ratio of the peak at 96 ppm to the sum of the 100 and 96 ppm resonances. Acetylation shifts the C6 resonance from 60 ppm to 64 ppm so DS at C6 was calculated as the ratio of area of the 64 ppm resonance to the sum of the 60 and 64 ppm resonances. DS at C3 was then determined from total DS minus the sum of DS at C2 and C6.

2.4. Gel permeation chromatography

GPC-MALLS was carried out using a Waters 1525 HPLC system, a Waters 717 plus autosampler, a Waters 2414 refractive index detector and a Wyatt Technologies Dawn EOS light scattering detector. GPC analyses were performed using a Polymer Labs aquagel-OH 30 column (300 × 7.5 mm), an injection volume of 20 μL of 1–2% solutions in water and a temperature of 30 °C. The HPLC was set to an isocratic flow rate of 0.60 mL/min using 0.1 M NaCl, 0.01 M sodium phosphate, pH 7. A value of 0.145 ml/g was used for the refractive index increment (dn/dc) (Yoo & Jane, 2002). Weight average molecular weights were calculated using Wyatt Astra software.

3. Results and discussion

Overall degree of substitution (DS) and substitution at specific carbons for starch acetates are given in Table 1. Overall DS was rather high (0.75–1.8) for ionic liquids having basic anions such as acetate and dicyanamide (dca) while DS was low (<0.16) for neutral anions such as chloride and nitrate. Using 3 moles of vinyl acetate per mole starch, DS values were higher for BMIM acetate (1.8) than dca (1.1) probably due to the stronger basic character of the acetate anion. It is well known that the transesterification reactions of starch with vinyl acetate in water are catalyzed by alkaline catalysts such as sodium carbonate, amines, etc. (Jarowenko, 1986). Thus, it appears that BMIM acetate and dca serve this function in non-aqueous systems as well.

For BMIM dca, acetylation is strongly preferred at the C2 position. For example, DS at C2 was 0.64 versus DS of <0.1 for C3 and C6 using vinyl acetate/glucose of 1. In contrast, acetylations performed in BMIM acetate gave starch acetates with approximately equal DS at C2, C3 and C6. These starch acetates gave clear solutions in water at 10% concentration while those substituted primarily at C2 were slightly cloudy at 10%, suggesting some self-association due to regioselective substitution. This is consistent with increase in viscosity with increasing substitution at C2 seen by Dicke (2004).

The reason for preferred substitution at C2 is unknown but may be due to hydrogen bond formation both with solvent and intramolecularly within starch molecules. For example, regiospecific substitution at C2 was found for starch acetates made by reaction of starch with vinyl acetate in DMSO in the presence of neutral anions such as chloride (Dicke, 2004). The increased reactivity of the C2 hydroxyl in that system was probably due in part to increased acidity due to a hydrogen bond of the O2–H with O3 of a neighboring glucose residue as shown by solution NMR (St-Jacques, Sundararajan, Taylor, & Marchessault, 1976) and X-ray diffraction of amylose–DMSO V-type inclusion complexes (Winter & Sarko, 1974). Similar to our results, Dicke (2004) also found that basic anions such as acetate and carbonate gave more uniform substitution. In this case, hydrogen bonding differences between different hydroxyls are probably overcome by the rate acceleration of the more basic catalyst. In contrast, starch acetates with only a slight preference for C2 hydroxyl substitution result from reaction with vinyl acetate in water (Mormann & Al-Higari, 2004). These data suggest a need for a more detailed study of the molecular structure of starches in imidazolium solvents.

Table 1. Degree of substitution (DS) of starch acetates prepared in different ionic liquids.

<table>
<thead>
<tr>
<th>#</th>
<th>IL</th>
<th>VAc/starch (mol/mol)</th>
<th>DS tot.</th>
<th>DS C2</th>
<th>DS C3</th>
<th>DS C6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BMIM dca</td>
<td>1</td>
<td>0.84 ± 0.02</td>
<td>0.64 ± 0.03</td>
<td>0.10 ± 0.02</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1.10 ± 0.04</td>
<td>0.83 ± 0.01</td>
<td>0.12 ± 0.03</td>
<td>0.15 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>BMIM OAc</td>
<td>1</td>
<td>0.75 ± 0.03</td>
<td>0.27 ± 0.01</td>
<td>0.19 ± 0.02</td>
<td>0.28 ± 0.03</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>1.8 ± 0.1</td>
<td>0.56 ± 0.03</td>
<td>0.47 ± 0.05</td>
<td>0.77 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>BMIM NO₃</td>
<td>3</td>
<td>0.12</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>6</td>
<td>BMIM Cl</td>
<td>3</td>
<td>0.0008 ± 0.0001</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>
Affect measured values of $M_w$ of sample 2 compared to sample 1. Hydrolysis of acetate groups (sample 4, Table 2) eliminated the binding. Previous studies have indicated that dissolving native corn starches were preferentially absorbed and may account for the slightly higher $M_w$ of high amylose starch while significantly changed after acetylation. Thus, ionic liquids can provide a convenient, homogeneous reaction medium for preparation of starch acetates having defined substitution patterns and these may have new physical properties and applications.

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References


