Carbohydrate Polymers 81 (2010) 149–151

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

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

Randal L. Shogren *, Atanu Biswas

Plant Polymer Research Unit, National Center for Agricultural Utilization Research, USDA/ARS, 1815 N. University St., Peoria, IL 61604, USA

ARTICLE INFO

Article history:
Received 21 December 2009
Received in revised form 20 January 2010
Accepted 21 January 2010
Available online 29 January 2010

Keywords:
Starch
Ionic liquid
Starch acetate

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 dicyanimide (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.

Published by Elsevier Ltd.

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 dicyanimide (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 ^{13}C 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

---

☆ 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.

* Corresponding author. Tel.: +1 309 681 6354; fax: +1 309 681 6691.
E-mail address: Randy.Shogren@ars.usda.gov (R.L. Shogren).

0144-8617/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2010.01.045

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 D_2O except for a high DS sample (experiment 4 in Table 1) which was dissolved in DMSO-d_6 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 $CH_3/3$ at 2.15 ppm divided by area of starch CH/7 at 3.5–5.5 ppm or from the ^{13}C spectra as area of CH_3 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 dicyanimide (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.

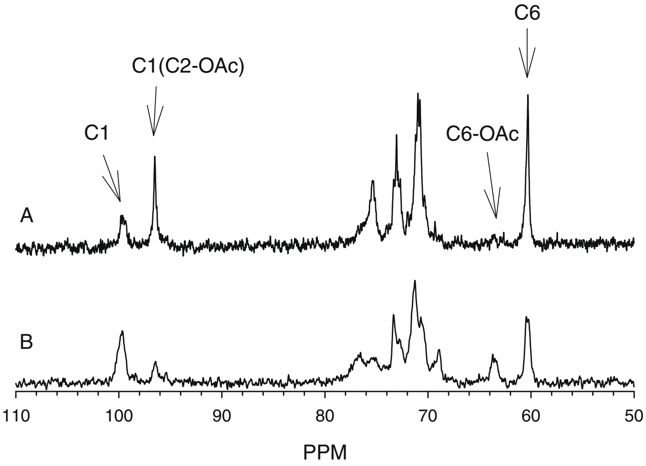

Fig. 1. ^{13}C NMR spectra of starch acetates, vinyl acetate/starch 1/1, prepared in BMIM dca (A) and BMIM acetate (B).

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.

Weight average molecular weights (M_w) for starch acetates are given in Table 2. M_w for the base starch (295,000) was rather low compared to native starches since it was prepared by acid hydroly-

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

#	IL	VAc/starch (mol/mol)	DS tot.	DS C2	DS C3	DS C6
1	BMIM dca	1	0.84 ± 0.02	0.64 ± 0.03	0.10 ± 0.02	0.09 ± 0.01
2	”	3	1.10 ± 0.04	0.83 ± 0.01	0.12 ± 0.03	0.15 ± 0.03
3	BMIM OAc	1	0.75 ± 0.03	0.27 ± 0.01	0.19 ± 0.02	0.28 ± 0.03
4	”	3	1.8 ± 0.1	0.56 ± 0.03	0.47 ± 0.05	0.77 ± 0.04
5	BMIM NO_3	3	0.12	nd	nd	nd
6	BMIM Cl	3	0.008 ± 0.001	nd	nd	nd

Table 2
Molecular weights of starch acetates prepared in different ionic liquids.

#	IL	VAc/starch (mol/mol)	M_w[a]	Recovery (%)[b]
0	None	–	295,000	100
1	BMIM dca	1	280,000	55
2	”	3	490,000	2
3	BMIM OAc	1	390,000	6
4	”	3	310,000[c]	100
5	BMIM NO_3	3	320,000	100
6	BMIM Cl	3	310,000	100

[a] Weight average molecular weight; standard deviation ± 10% for all samples.

[b] Mass recovery from column calculated from integration of refractive index peak.

[c] Sample #4 hydrolysed in 0.5 M NaOH for 3 days at 3 °C since it was not soluble in water.

sis. It was used here so that the viscosity of the reaction mixtures would be low enough to stir. In general, Mw of starch acetates were similar to or slightly higher than the starting starch (295,000). The presence of the acetate groups would be expected to increase molecular weight somewhat (to 370,000 for DS 1) based on the addition of one acetate group (M_w 43) to a glucose residue (M_w 162). It should be noted that recovery from the column was low for some samples such as #2 and #3, indicating portions of the starch acetates were binding to the column. This could affect measured values of M_w if species of different molecular weight were preferentially absorbed and may account for the slightly higher 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 in BMIM Cl lowered M_w considerably (Lehmann & Volkert, 2009; Stevenson et al., 2007). The lack of any significant decrease in M_w for the maltodextrin samples used by us may be due to the different structure of these starches. Lehmann and Volkert (2009), for example, found little change in M_w of high amylose starch while much larger changes were noted for waxy maize starch.

4. Conclusions

Starch (maltodextrin) was found to be solubilized in the ionic liquids BMIM acetate, nitrate, chloride and dicyanimide at 90 °C. After reaction with vinyl acetate, acetate substitution was higher for the more basic anions acetate and dicyanimide. Acetylation at C2 was highly preferred for BMIM dca while acetylation was more uniform for BMIM acetate. Molecular weights of starches were not 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.

Acknowledgements

Authors wish to thank Dr. Karl Vermillion for NMR experiments and Elizabeth Krietemeyer and Kelly Utt for technical assistance.

References

Biswas, A., Shogren, R. L., Stevenson, D. G., Willett, J. L., & Bhowmik, P. K. (2006). Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein. *Carbohydrate Polymers, 66*, 546–550.

Dicke, R. (2004). A straight way to regioselectively functionalized polysaccharide esters. *Cellulose, 11*, 255–263.

Jarowenko, W. (1986). Acetylated starch and miscellaneous organic esters. In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses* (pp. 55–77). Boca Raton: CRC Press.

Lehmann, A., & Volkert, B. (2009). Investigations of esterification reactions of starches in 1-*n*-butyl-3-methylimidazolium chloride and resulting substituent distribution. *Journal of Applied Polymer Science, 114*, 369–376.

Liebert, T., Kulicke, W.-M., & Heinze, T. (2008). Novel approach towards hydrolytically stable starch acetates for physiological applications. *Reactive & Functional Polymers, 68*, 1–11.

Liu, Q., Janssen, M., van Rantwijk, F., & Sheldon, R. A. (2005). Room-temperature ionic liquids that dissolve carbohydrates in high concentrations. *Green Chemistry, 7*, 39–42.

Mormann, W., & Al-Higari, M. (2004). Acylation of starch with vinyl acetate in water. *Starch/Stärke, 56*, 118–121.

Stevenson, D. G., Biswas, A., Jane, J.-L., & Inglett, G. E. (2007). Changes in structure and properties of starch of four botanical sources dispersed in the ionic liquid, 1-butyl-3-methylimidazolium chloride. *Carbohydrate Polymers, 67*, 21–31.

St-Jacques, M., Sundararajan, P. R., Taylor, K. J., & Marchessault, R. H. (1976). Nuclear magnetic resonance and conformational studies on amylose and model compounds in dimethyl sulfoxide solution. *Journal of the American Chemical Society, 98*, 4386–4391.

Toral, A. R., de los Rios, A. P., Hernandez, F. J., Janssen, M., Schoevaart, R., van Rantwijk, F., et al. (2007). Cross-linked *Candida antarctica* lipase B is active in denaturing ionic liquids. *Enzyme and Microbial Technology, 40*, 1095–1099.

Winter, W. T., & Sarko, A. (1974). Crystal and molecular structure of the amylose–DMSO complex. *Biopolymers, 13*, 1461–1482.

Yoo, S.-H., & Jane, J.-L. (2002). Molecular weights and gyration radii of amylopectins determined by high performance size-exclusion chromatography equipped with multi-angle laser light scattering and refractive index detectors. *Carbohydrate Polymers, 49*, 307–314.