

# Investigations on Esterification Reactions of Starches in 1-*N*-Butyl-3-methylimidazolium Chloride and Resulting Substituent Distribution

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**ABSTRACT:** The ionic liquid (IL) 1-*N*-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}]^+\text{Cl}^-$ ) was used as solvent for different esterification reactions of the biopolymer starch. Therefore, maize starches with varying content of amylose were used. Different carboxylic acid anhydrides were applied to esterify starch with a degree of substitution (DS) in the range of 0.7–3.0. For example, starch acetates with the mentioned DS are accessible within 30 min at a 105°C-reaction temperature. The DS distribution of starch acetates synthesized in IL was compared with the common starch acetate synthesis of Mark and Mehlretter. Also, a

consideration of starch acetates and cellulose acetates synthesized in  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  is given. The starch esters were characterized by means of Raman spectroscopy for qualitative- and nuclear magnetic resonance spectroscopy for quantitative determination of the functionalization pattern. Moreover, the molecular mass distribution was determined after saponification by means of GPC-MALLS. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 369–376, 2009

**Key words:**  $^{13}\text{C}$ -NMR; ester; ionic liquid; polysaccharides; substituent distribution

## INTRODUCTION

In recent years ionic liquids (ILs) have become more and more important as replacements for organic solvents for polymeric reactions. ILs have been used mostly in polysaccharide chemistry as nonderivatizing solvent for cellulose.<sup>1,2</sup> ILs have melting points around and less than 100°C and own other properties like biodegradability,<sup>3</sup> low hydrophobicity, electrochemical stability, and low or negligible vapor pressure.<sup>4</sup> These properties rate ILs as green solvents. The potential of ILs to be used and recycled, while eliminating the emission of commonly used volatile organic compounds, underlines this claim. But some authors in the past<sup>5,6</sup> have shown 1-*N*-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}]^+\text{Cl}^-$ ) to be toxic and environmentally hazardous. Although an exposure to air is not really given, an exposure to water can not be barred. Toxic consequences for freshwater algae were shown via the growth rates.<sup>7</sup>

The most published articles for polysaccharide chemistry have focused on the use of ILs as solvent for cellulose. Only the authors of a few articles have described the use of IL as solvent for starch. In general dissolution of a polysaccharide for chemical deriviti-

zation increases the reactivity enormously. Also, the properties of some polysaccharide derivatives can be different depending whether they were synthesized under homogeneous or heterogeneous reaction conditions. The easier way to dissolve starch (heating an aqueous solution, using alkaline aqueous media) compared with cellulose might be a reason for the limited number of research articles. Nevertheless using IL as solvent for starch derivitization has to be analyzed regarding to resulting properties like it is known from cellulose chemistry.

For esterification of starch in  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  by method of Biswas and Shogren,<sup>8</sup> an unequal substituent distribution within the anhydro glucose unit (AGU) can be observed by liquid  $^{13}\text{C}$ -NMR. Investigations for that purpose as well as influence on molecular weight average and of reaction temperature were made by synthesizing different starch esters (Fig. 1).

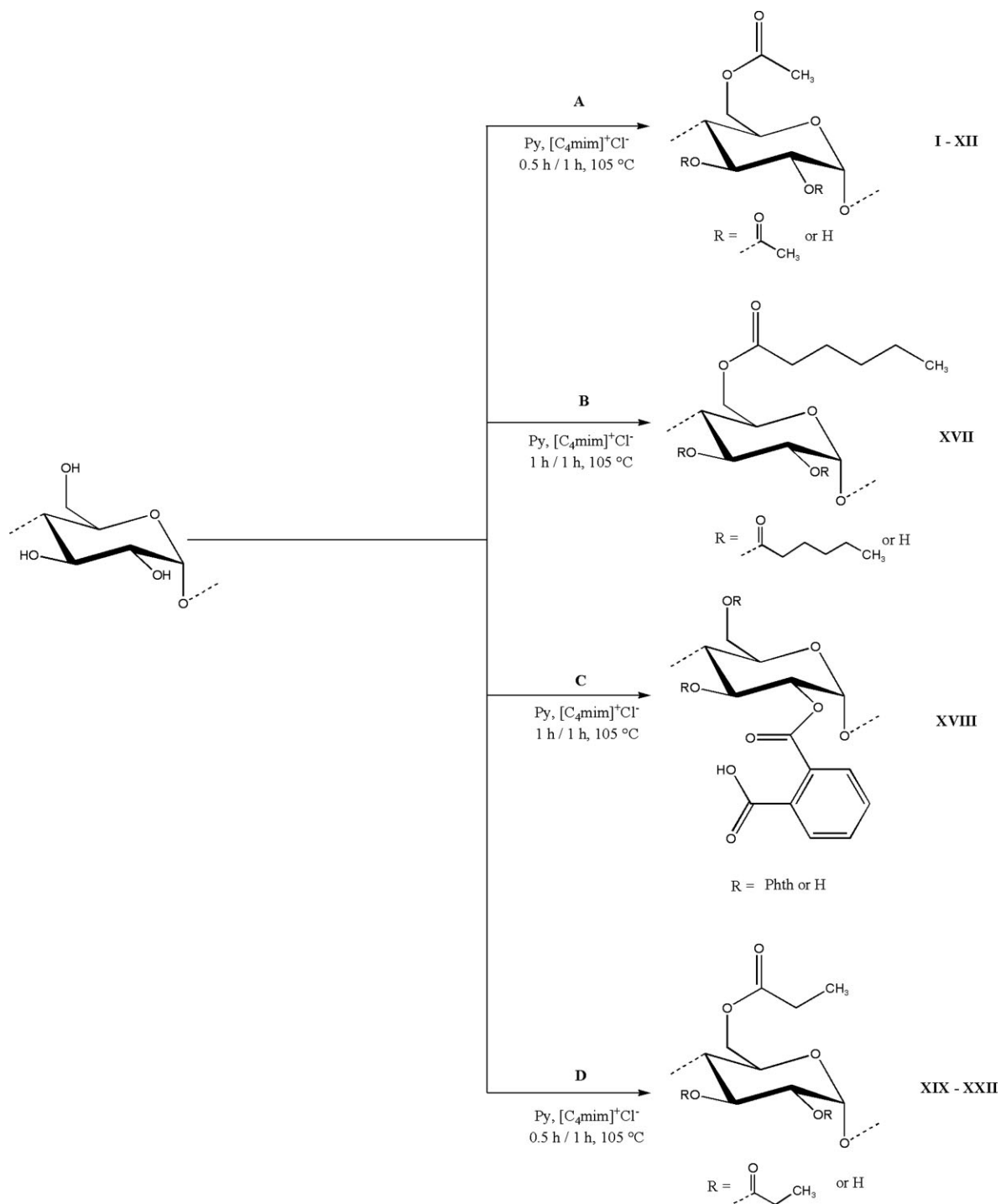
## EXPERIMENTAL

### Materials

The IL  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  was used as received by Sigma Aldrich, Germany (BASF-quality  $\geq 95\%$ ; water  $< 0.5\%$ ). Acetic anhydride, propionic anhydride, phthalic anhydride (Riedel de Haen), hexanoic anhydride (AlfaAesar), and pyridine (Acros) were used as obtained with an analytical grade of  $\geq 96\%$ .

High amylose maize starch (HAMS, content of amylose: 51%;  $M_w$ :  $6.2 \times 10^6$  g/mol), maize starch

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**Figure 1** Reaction scheme; Py = pyridine, A = acetic anhydride, B = hexanoic anhydride, C = phthalic anhydride, D = propionic anhydride.

(MS, content of amylose: 19%;  $M_w$ :  $31.1 \times 10^6$  g/mol) and waxy maize starch (WMS, content of amylose: <5%;  $M_w$ :  $46.1 \times 10^6$  g/mol) were received by Cargill (Minneapolis, MN).

### Measurements

$^{13}C$ -NMR spectra were measured with the Varian Unity Inova 500 spectrometer. The esterified polysac-

charides were measured after dissolution in dimethyl sulfoxide ( $d_6$ -DMSO) (125 MHz; 80 °C). The chemical shift was related to the signal of  $d_6$ -DMSO [ $\delta$  = 39.5 ppm relative to tetramethylsilane  $\delta$  = 0 ppm]. The distribution of the substituent moiety among the three OH groups of the AGU of starch acetate and starch propionate was calculated by integrating the  $^{13}C$ -NMR spectrum. All signals in the region from  $\delta$  = 102–94 ppm are caused by  $C1_{AGU}$

carbons and were therefore normalized to 1. The total DS was then obtained from the integrals of the methyl group signals ( $\delta \sim 20$  ppm) for the acetates and of the methylene group signals ( $\delta \sim 26$  ppm) for the propionates. The partial DS for  $C2_{AGU}$  and  $C6_{AGU}$  were determined using the splitting of the  $C1_{AGU}$  and  $C6_{AGU}$  signals into two parts resulting from the substitution at  $C2_{AGU}$  and  $C6_{AGU}$ , respectively. The value of the integral of the upfield shifted signal of  $C1_{AGU}$  ( $\delta \sim 96$  ppm) corresponds to the degree of substitution in  $C2_{AGU}$  position, whereas the signal at 100 ppm represents the relative amount of unsubstituted  $C2_{AGU}$ . The same procedure was used for position  $C6_{AGU}$  ( $\delta = 65\text{--}60$  ppm). Here the downfield shifted signal at  $\delta \sim 62$  ppm corresponds to the degree of substitution in this position. With the total DS and the partial degrees of substitution of  $C2_{AGU}$  and  $C6_{AGU}$  the DS in position  $C3_{AGU}$  can be calculated.

Molecular weight averages were determined using GPC-MALLS. The GPC-MALLS system consisted of a 515 pump, DRI detector (2414 der Fa. Waters), MALLS detector (Dawn HELEOS, Wyatt Technologies Inc.), and columns from SUPREMA. Esterified samples were saponified under mild conditions so that no degradation of the polymer was observed. Starch esters were dispersed in water and saponified by addition of 1N NaOH. The mixture was allowed to stir for 24 h at room temperature before it was neutralized with 1N hydrochloric acid (HCl). The deacetylated starch was then precipitated with 60 wt % aqueous methanol. After centrifugation the starch was washed several times with 60 wt % aqueous methanol and dried under reduced pressure. 0.5 wt % of this starch was dissolved in DMSO to analyze the molecular weight average via GPC-MALLS. The Raman spectrum was recorded on a BRUKER RFS 100/S from the pure product with 64 scans by a laser power of 300 mW in the range by wavelength from  $3500\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$ .

### Representative esterification of starch

The esterification reactions of different starches were performed as described by Biswas and Shogren. For example a typical procedure was to mix 10.5 g (60 mmol) of  $[C_4mim]^+Cl^-$  with 1 g (6 mmol) of dried starch ( $105^\circ\text{C}$ ,  $\geq 15$  h) in a 150-mL three-necked flask. This flask was then placed in an oil-bath and equipped with a condenser. A mixture of 3.8 g (37 mmol, 6 equiv/AGU)  $Ac_2O$  and 2.9 g (37 mmol, 6 equiv/AGU) pyridine were added to the flask at room temperature and the reaction mixture was stirred. The reaction temperature was heated up to  $105^\circ\text{C}$  and reaction time was 0.5 h up to 1 h. The reaction mixture was precipitated in ethanol and washed

furthermore twice with ethanol. The acetylated starch (IV) was then dried at  $60^\circ\text{C}$  in vacuum.

The results are as follows: DS, 2.89; yield, 83%; Raman, 2940 ( $-C-H$ ), 2721 ( $-C-H_{Acetate}$ ), 1740 ( $C=O$ ), 1438 ( $C-H$ ), 1261 (COC twist),  $1135\text{ cm}^{-1}$  (CC stretch); and  $^{13}\text{C-NMR}(d_6\text{-DMSO}; 80^\circ\text{C})$ :  $\delta = 169.9\text{--}168.8$  ( $C=O_{Ester}$ ); 95.0 ( $C-1_{AGU}$ ); 73.7–68.6 ( $C2,3,4,5_{AGU}$ ); 62.5 ( $C-6_{AGU}$ ); 19.9 ( $C_{methyl}$ ) ppm.

Similarly, spruce cellulose was used as starting material and esterified under the same procedure to give cellulose acetate.

For comparison starch acetates were synthesized by a method described by Mark and Mehlretter.<sup>9</sup> By this acetic anhydride were used as reactive solvent. For example, 1.3 g (7.5 mmol; water content 11%) of HAMS was put in a flask followed by 4.6 g (45 mmol; 6 equiv/AGU) of acetic anhydride. Then, 2.6 g of 50% aqueous sodium hydroxide (NaOH) solution (33 mmol; 0.4 equiv/AGU) was added dropwise. The reaction was heated to  $115^\circ\text{C}$  for 5 h before the product was precipitated and washed several times with distilled water. The esterified starch was then dried as mentioned previously.

DS, 2.70; yield, 77%; Raman, 2942 ( $-C-H$ ), 2721 ( $-C-H_{Acetate}$ ), 1746 ( $C=O$ ), 1440 ( $C-H$ ), 1261 (COC twist),  $1138\text{ cm}^{-1}$  (CC stretch).  $^{13}\text{C-NMR}(d_6\text{-DMSO}; 80^\circ\text{C})$ :  $\delta = 169.5\text{--}168.2$  ( $C=O_{Ester}$ ); 95.1 ( $C-1_{AGU}$ ); 73.7–68.6 ( $C2,3,4,5_{AGU}$ ); 62.6 ( $C-6_{AGU}$ ); 19.9 ( $C_{methyl}$ ) ppm.

## RESULTS AND DISCUSSION

The described esterification reaction of starch by Biswas and Shogren resulted in starch acetates with different degrees of substitution by varying the molar equivalents of acetic anhydride and pyridine per AGU. The dissolution process of starch in the IL was very fast. After 5 min of stirring at  $105^\circ\text{C}$  the reaction mixture already was viscous and, after further 5 min, the starch was clear dissolved. The most reaction mixtures became very viscous.

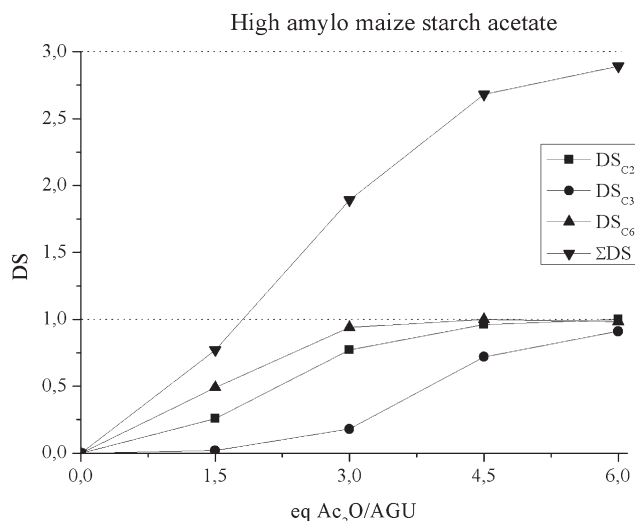
Furthermore, there is an interesting substituent distribution, which Biswas and Shogren did not mention, caused by the fact that one-dimensional  $^1\text{H-NMR}$  and IR spectroscopy were used to determine the total DS. In comparison with different esterification reactions of cellulose in IL, where the substituent distribution within the AGU is  $C6 > C3 > C2$ ,<sup>10,11</sup> we found a reactivity order for reactions of different starches in IL of  $C6 > C2 > C3$  up to DS values of 2.7. This effect cannot be explained satisfactorily. Interactions between the IL as solvent and the polymeric hydroxyl groups may be the reason for the described substituent distribution. Therefore, the partial substitution of differently esterified starches as well as starches with different

substituents were analyzed with  $^{13}\text{C}$ -NMR. Also, analyses for reaction temperature and the influence of  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  on polymeric degradation were made.

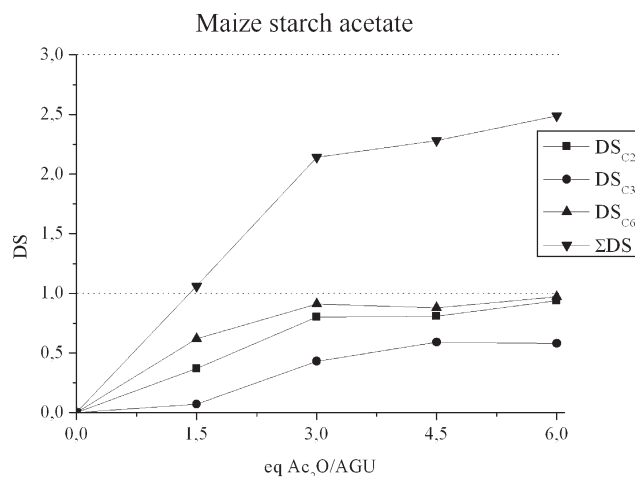
With 6 equiv acetic anhydride per AGU, starch-2.5-acetate is almost always possible to achieve, sometimes nearly starch-3-acetate (IV). The reaction rate of the acetylation in  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  was very high; therefore, starch-3-acetate could already be isolated after 30 min. Compared with the well-known acetylation reaction,<sup>12</sup> not many of these esterification reactions of starch<sup>13</sup> are so fast or even faster like the described reaction. Most of the time, faster acetylation reactions are conducted under greater reaction temperatures.

Considering the partial DS values of acetylated starch, we could mention that the reactivity of the hydroxyl groups of starch in  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  differs. Of course the primary hydroxyl group at C6 showed the greatest reactivity, followed by C2 and then C3, which is the expected reactivity order, but the reactivity of C3 seems to be lower for esterification reaction with acetic anhydride in  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  than normal. Therefore, it could be seen for all starch species that position C3 is less substituted and for a total DS < 1, nearly no substitution at C3 takes place.

Figures 2–4 demonstrate the DS distribution curves of acetate groups from each starch species. In general, the use of high amylose maize starch as starting material gave the highest total DS by using 6 equiv acetic anhydride per AGU (IV), whereas maize starch as starting material led to a total DS of 2.5 (VIII) under these reaction conditions and therewith the lowest DS. Waxy maize starch as starting material showed the highest DS with 2.7 (XII) and so between the acetate of high amylose maize starch and maize starch.



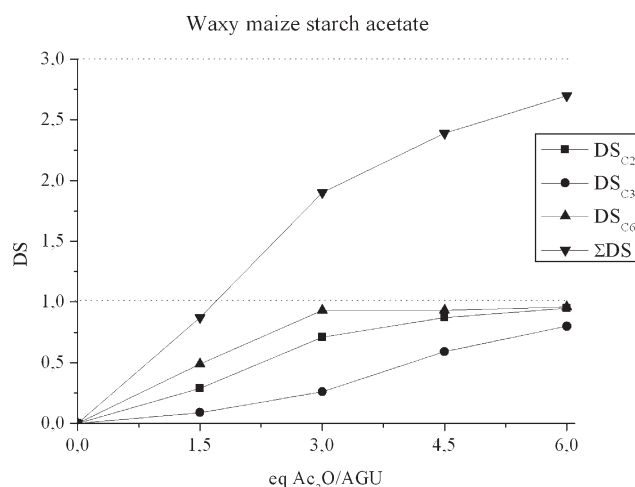
**Figure 2** DS distribution curves of high amylose maize starch acetate (determined by  $^{13}\text{C}$ -NMR spectroscopy).



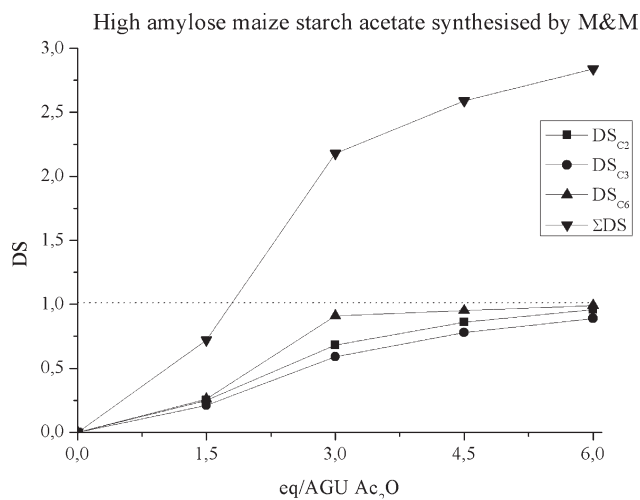
**Figure 3** DS distribution curves of maize starch acetate (determined by  $^{13}\text{C}$ -NMR spectroscopy).

As mentioned previously, the primary hydroxyl group at C6 had the greatest reactivity; this could be seen in all three figures, where this position is nearly complete substituted at a total DS of  $\sim 2.0$ . The reactivity of the secondary hydroxyl group at C2 is slightly lower than the one at C6. This also could be found for all three starch species. The substitution of the secondary hydroxyl group in position C3 was remarkable. The partial DS curve of C3 was much lower than the one of C2. The curves of partial substitution in position C3 and C2 converged each other at a total DS  $\sim 2.5$ . By DS  $\leq 2$ , the hydroxyl group of C3 is barely substituted. For a DS around 2.5, the substitution in C3 is always minimum 50% less substituted than in C2.

In Figure 5 the DS distribution curves of HAMS acetate that was synthesized by method of Mark and Mehlretter is shown. The partial substitution at C3



**Figure 4** DS distribution curves of waxy maize starch acetate (determined by  $^{13}\text{C}$ -NMR spectroscopy).



**Figure 5** DS distribution curve of high amylose maize starch acetate by method of Mark and Mehltretter (determined by  $^{13}C$ -NMR).

was unlike the one from acetylation in  $[C_4mim]^+Cl^-$ . Although the reactivity order of the hydroxyl groups for acetylation with acetic anhydride as derivatizing solvent is  $C6 > C2 \sim C3$ , the reactivity order by reaction in  $[C_4mim]^+Cl^-$  is  $C6 > C2 > C3$ . A detailed consideration of partial DS values at a total  $DS < 1$  is presented in Table I (compare I and XVIII). The total DS value of the shown starch acetates were nearly the same. For synthesized starch acetates by method of Mark and Mehltretter the three hydroxyl groups were substituted nearly equal (comp. Fig. 5). In contrast to that for sample I the hydroxyl group at C6 is higher substituted and the one of C3 is not really substituted. In C2-position we found in both cases practically the same DS values.

The results discussed so far show that, in general, the DS distribution of the acetate substituent was independent from the starch source by using  $[C_4mim]-Cl^-$  as non derivatizing solvent for acetylation reaction. A minor reactivity of hydroxyl group at C3 was found for all three starches.

#### Comparison between starch acetate and cellulose acetate

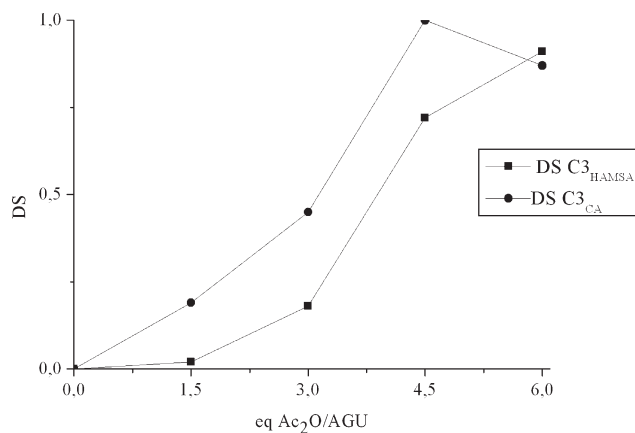
As a comparison with cellulose acetates, spruce cellulose was used as starting material and the esterification reactions were performed under the same reaction conditions in  $[C_4mim]^+Cl^-$ . Surprisingly, the reactivity order of the hydroxyl groups in this case from cellulose ( $DP_{Cuen}$ : 1218) was  $C6 > C2 > C3$  (see Table I), which does not confirm with the most published articles<sup>14</sup> concerning synthesis of cellulose acetates in IL. A reason might be the different reaction procedures. Although in most articles cellulose was dissolved in IL before adding the reactants, by method of Biswas and Shogren all reactants and  $[C_4mim]^+Cl^-$  are already in the starting mixture. This difference might influence the accessibility of the OH groups from cellulose. Detailed consideration of the partial substitution in C3 for cellulose acetates and high amylose maize starch acetates (see Fig. 6) showed the higher reactivity in C3 from cellulose compared with C3 from starch.

#### Analysis of molecular weight average

Earlier publications<sup>15</sup> described that  $[C_4mim]^+Cl^-$  degraded different native starches by dispersing them in this IL. Analyzed starches lose up to 96% of

**TABLE I**  
Substituent Distribution of Different Starch Acetates Synthesized from Different Starches in  $[C_4mim]^+Cl^-$  (9.5% Starch w/w)

Polysaccharide	Sample No.	Eq $Ac_2O$ and Py per AGU	$\Sigma DS$	DS C2	DS C3	DS C6
High amylose maize starch	I	1.5	0.77	0.26	0.02	0.49
	II	3.0	1.89	0.77	0.18	0.94
	III	4.5	2.68	0.96	0.72	1.00
	IV	6.0	2.89	1.0	0.91	0.98
Maize starch	V	1.5	1.06	0.37	0.07	0.62
	VI	3.0	2.14	0.80	0.43	0.91
	VII	4.5	2.28	0.81	0.59	0.88
	VIII	6.0	2.49	0.94	0.58	0.97
Waxy maize starch	IX	1.5	0.87	0.29	0.09	0.49
	X	3.0	1.90	0.71	0.26	0.93
	XI	4.5	2.39	0.87	0.59	0.93
	XII	6.0	2.70	0.95	0.80	0.96
Spruce cellulose ( $DP_{Cuen}$ : 1218)	XIII	1.5	1.11	0.31	0.19	0.61
	XIV	3.0	2.14	0.77	0.45	0.92
	XV	4.5	2.81	0.88	1.00	0.90
	XVI	6.0	2.73	0.91	0.87	0.95
High amylose maize starch (M&M)	XVIII	1.5 (50% <sub>aq</sub> NaOH instead of pyridine)	0.72	0.21	0.25	0.26



**Figure 6** Partial DS curves of C3 from spruce cellulose acetate (CA) and high amylose maize starch acetate (HAMSA).

their molecular weight average when they are dissolved for 1 h at 100°C in ionic liquid.

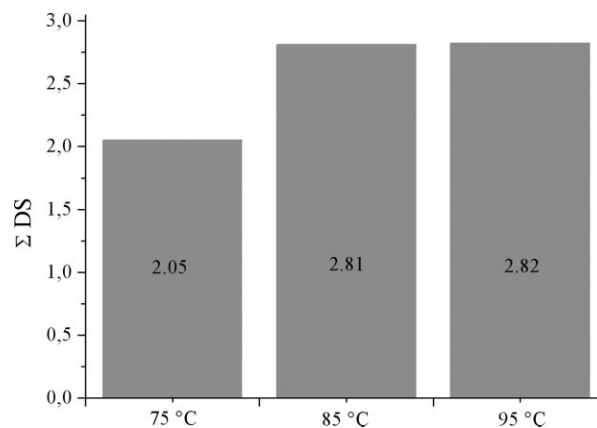
To analyze how the molecular weight average of the different maize starches changed after acetylation in  $[C_4mim]^+Cl^-$  starch acetates were analyzed via GPC-MALLS and also the starting materials were analyzed after dissolution for 30 min by 105°C in  $[C_4mim]^+Cl^-$ . To check the influence of pyridine as possible scavenger for acidic impurities in the IL, experiments regarding to that were performed. The results for high amylose maize starch and waxy maize starch are shown in Table II.

Although for dissolution and esterification reactions of cellulose in  $[C_4mim]^+Cl^-$  no molecular degradation appears,<sup>16</sup> by dissolving the starches without any reagents in  $[C_4mim]^+Cl^-$ , the degradation was up to 86%. The experiments for using pyridine and  $[C_4mim]^+Cl^-$  as solvent for starches indicate the assumption that pyridine acts as a scavenger for acidic impurities in the ionic liquid. Therefore, the molecular degradation of waxy maize starch is greater than the one of high amylose maize

**TABLE II**  
Molecular Weight Average for HAMS and WMS as Starting Materials

Starch	$M_w \times 10^6$ (g/mol)	Starch	$M_w \times 10^6$ (g/mol)
HAMS	6.2	WMS	46.1
No reagents	1.1	No reagents	6.4
4.5 equiv/AGU	4.2	4.5 equiv/AGU	14.0
pyridine		pyridine	
I	4.0	IX	12.5
II	4.5	X	19.7
III	6.6	XI	16.1
IV	5.3	XII	17.1

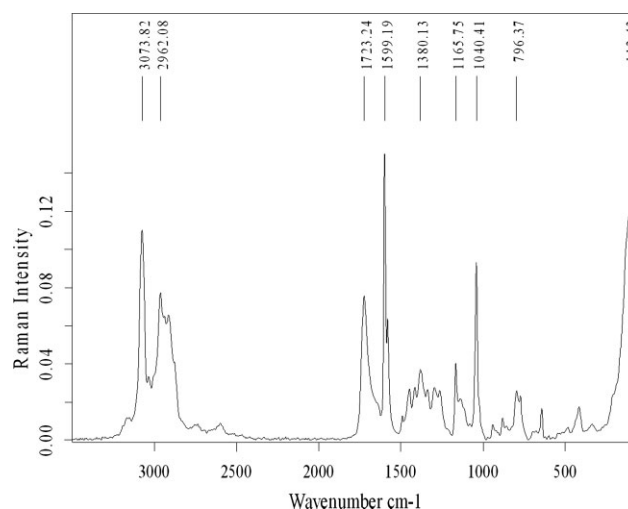
All samples were measured in DMSO, and starch acetates were deacetylated by treatment with 1N NaOH without degradation.



**Figure 7** DS values of high amylose maize starch acetates synthesized by different temperatures.

starch. Products from esterification with acetic anhydride had greater molar mass averages than the starches without any reagent. The esterification and usage of pyridine seem to protect the starch from molecular degradation. For acetylated waxy maize starch, the molecular weight is up to three times greater than the starting material dissolved in  $[C_4mim]^+Cl^-$ .

More interesting were the molecular weight averages for high amylose maize starches after esterification. Samples I and II showed greater molecular degradation than III and IV, where nearly no degradation seems to be (considering a 10% statistical variation for GPC-MALLS measurement). The results demonstrate, that there seems to be a relation for molecular degradation firstly with the content of amylose in the different starches and secondly with the degree of substitution. For samples with a higher DS and higher amylose content the molecular degradation is not high compared with waxy maize starch.



**Figure 8** RAMAN spectrum of high amylose maize starch phthalate.

**TABLE III**  
**Partial DS Values of High Amylose Maize Starch**  
**Propionates Synthesized in  $[C_4mim]^+Cl^-$**

Sample No.	equiv/AGU	$\Sigma DS$	DS C2	DS C3	DS C6
XIX	1.5	/	/	/	/
XX	3.0	2.08	0.80	0.32	0.96
XXI	4.5	2.40	0.96	0.49	0.95
XXII	6.0	3.00	1.00	1.00	1.00

For 1.5 equiv/AGU propionic anhydride, no product could be isolated and no appropriate precipitation media could be found.

### Influence of the reaction temperature on degree of substitution

For this analysis, we increased the reaction time up to 1 h and esterified the starch (HAMS, 9.5 wt %) in  $[C_4mim]^+Cl^-$  with 6 equiv acetic anhydride and pyridine per AGU. In Figure 7 can be seen that a reaction temperature of just some degrees Celsius above the melting point of  $[C_4mim]^+Cl^-$  led already to starch-2-acetate. Increasing the temperature to 85°C resulted in nearly full substituted starch. Higher temperatures do not increased the degree of substitution further.

### Beyond esterification of starch in $[C_4mim]^+Cl^-$

Further, HAMS was esterified with 6 equiv/AGU pyridine and carboxylic acid anhydrides shown in Figure 1, respectively, to produce starch hexanoate ( $\Sigma DS = 1.92$ ;  $DS_{C2} = 0.66$ ,  $DS_{C6} = 0.85$ ,  $DS_{C3} = 0.41$ ) and starch phthalate ( $\Sigma DS = 2.12^*$ , see Fig. 8). The reaction conditions for these reaction were the same like described before, only the reaction time was increased to 1 h.

High amylose maize starch was esterified with different eq/AGU propionic anhydride and pyridine to analyze the DS distribution in greater detail. For the synthesis of starch propionates in  $[C_4mim]^+Cl^-$  the same substituent distribution (Table III) as for starch acetates was found. Also, here the reactivity of the hydroxyl group from C3 in  $[C_4mim]^+Cl^-$  as solvent was lower than the one of C2 and C6.

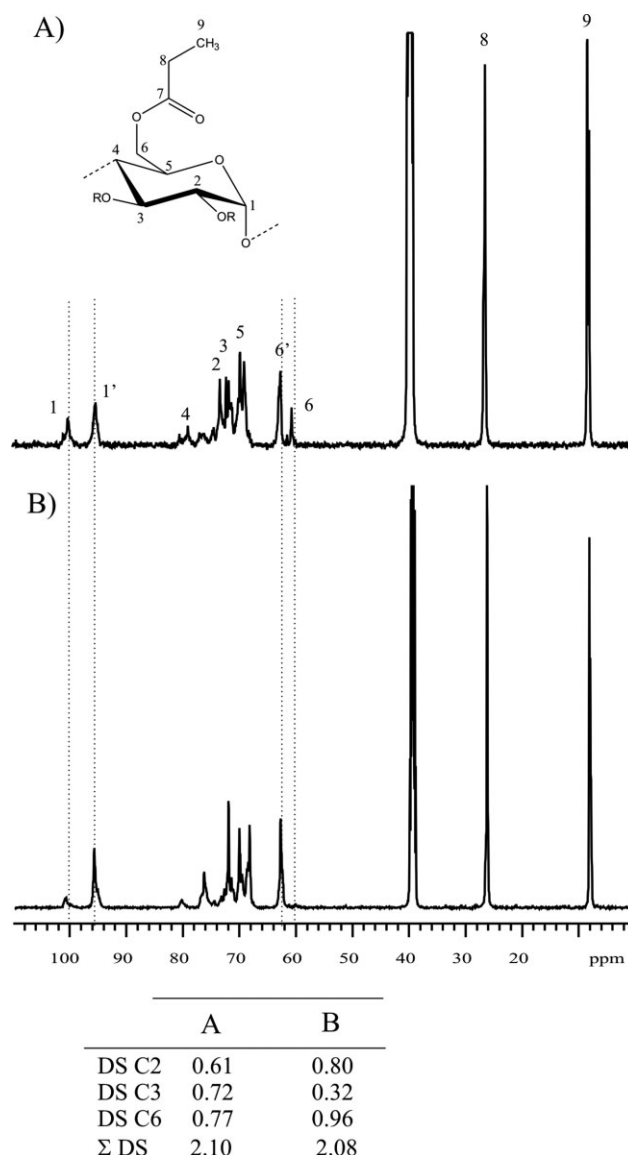
The  $^{13}C$ -NMR spectra of two starch propionates with similar degree of substitution are shown in Figure 9. While starch propionate of spectra (A) was synthesized by the method of Mark and Mehlretter,<sup>9</sup> (B) was synthesized in  $[C_4mim]^+Cl^-$ .

There was a difference in the signals of C6 unsubstituted (6;  $\delta = 60.35$  ppm) and C6 substituted (6';  $\delta = 62.55$  ppm) in both spectra. In spectra (B), only the signal of C6 substituted could be found, what means that the hydroxyl group in C6 is fully substituted along the AGU chain, whereas in spectra (A) a

signal from C6 unsubstituted also could be found. In addition, the integrals of C2 substituted (1';  $\delta = 95.22$  ppm) and C2 unsubstituted (1;  $\delta = 100.1$  ppm) also differ in both spectra. The integrals from 1' and 6' were subtracted from the integral of the methylene carbon signal (8;  $\delta = 27.34$  ppm) to give DS C3.

## CONCLUSIONS

We have found that the IL  $[C_4mim]^+Cl^-$  also influences the substituent distribution by esterification reactions of starch as it has been known from cellulose. Thereby is the reactivity order of the different hydroxyl groups  $C6 > C2 > C3$ , independent from amylose content of the used starch. Comparison with cellulose acetate synthesized by the same reaction procedure



**Figure 9**  $^{13}C$  NMR spectra of starch propionate (both  $\Sigma DS \sim 2.1$ ) in  $DMSO-d_6$  ( $\delta = 39.5$  ppm) (A) synthesized by Mark and Mehlretter (B) synthesized in  $[C_4mim]^+Cl^-$  (XX).

\*DS was determined by solid-state  $^{13}C$ -NMR.

showed surprisingly the same reactivity order of hydroxyl groups from cellulose. Investigations regarding to the reaction temperature indicates that a reaction temperature already  $\sim 10^\circ\text{C}$  above the melting point of  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  leads to a maximum degree of substitution for starch acetates. Experiments to analyze the molecular degradation of starch while esterification also were performed. Thereby, greater molar mass averages of starch could be observed compared with the dissolution of starch in  $[\text{C}_4\text{mim}]^+\text{Cl}^-$  without any reagents.

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### References

1. Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y.; Wu, G. *Green Chem* 2006, 8, 325.
2. Seoud, O.; Koschella, A.; Fidale, L. C.; Dorn, S.; Heinze, T. *Biomacromolecules* 2007, 8, 2629.
3. Gathergood, N.; Garcia, M. T. *Green Chem* 2004, 6, 166.
4. Welton, T. *Chem Rev* 1999, 99, 2071.
5. Landry, T. D.; Brooks, K.; Poche, D.; Woolhiser, M. *Bull Environ Contam Toxicol* 2005, 74, 559.
6. Bailey, M.; Townsend, M.; Jernigang, P.; Sturdivant, J. *Green Chem* 2008, 10, 1213.
7. Kulacki, K. J.; Lamberti, G. A. *Green Chem* 2008, 10, 104.
8. Biswas, A.; Shogren, R. L. *Carbohydr Polym* 2006, 66, 546.
9. Mark, A. M.; Mehlretter, C. L. *Starch/Stärke* 1972, 24, 73.
10. Wu, J.; Zhang, J. *Biomacromolecules* 2004, 5, 266.
11. Heinze, T.; Schluffer, K. *Macromol Rapid Commun* 2006, 27, 1670.
12. Kakuschke, R.; Rappthel, I. (to Buna Sow Leuna Olefinverbund GmbH). WO/2000/036,007 (2000).
13. Reinisch, G.; Radics, U. *Angew Makromol Chem* 1995, 233, 113.
14. Cao, Y.; Wu, J. *Carbohydr Polym* 2007, 69, 665.
15. Stevenson, D. G.; Biswas, A.; Jane, J.; Inlett, G. E. *Carbohydr Polym* 2007, 67, 21.
16. Heinze, T.; Barthel, S. *Green Chem* 2006, 8, 301.