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Preparing esters from high-amylose starch using ionic liquids as catalysts

André Lehmann, Bert Volkert*

Fraunhofer Institute for Applied Polymer Research, Department Polysaccharide Chemistry, Geiselbergstr. 69, 14476 Golm, Germany

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ABSTRACT

The use of different ionic liquids (IL), mainly 1-*N*-alkyl-3-methylimidazolium chlorides as possible catalysts for esterification of starch is reported. A high amylose maize starch is used and the esterification is performed with the aid of different carboxylic anhydrides. These are used both as a reactant and a solvent for all reactions using a maximum of 1.2 molar equivalents (moleq) of IL per anhydro glucose unit (AGU). Highly substituted starch esters can be achieved within a 4–24 h reaction time depending on the molar ratios of ionic liquid and esterifying agent. The ionic liquids used for these reactions can easily be recovered and reused. The influence of the structure and amount of ionic liquid used in the preparation of starch acetate and starch propionate as model substances are analyzed in terms of their degree of substitution (titration), reaction rate, solubility and average molecular weight (SEC-MALLS). A study of the effects of different bases on degradation of the starch was investigated, too. We conclude that imidazolium-based ionic liquids with halogenides as counter ions can be used as catalysts for the esterification of starch and thus fulfill the definition of a recyclable catalyst that lowers activation energy.

1. Introduction

Polysaccharide esters have been extensively studied over the last two decades and many methods have been developed in order to meet certain requirements. Starch acetates based on a sustainable native polymer, for example, can be used as a thermoplastic material**.** Esterification reactions of starch are very well documented. The first starch acetates were already described in literature in 1865 (Schuetzenberger, 1865). The reaction of starch with acetic anhydride as esterifying agent for 15 h at 140 °C only results in a starch acetate with low substitution and a degree of substitution of 0.4 (Seiberlich, 1941). An activator is essential for achieving highly-substituted starch. The base pyridine is often used as an activator. A lot of work in this field was carried out by various groups in the US around the middle of the last century (Mullen & Pascu, 1942; Rutenberg & Solarek, 1984; Whistler & Hilbert, 1944). An important step and also a common synthesis of starch acetates were mentioned by Mark and Mehltretter (1972). They described the use of acetic anhydride as a reactive solvent and induced the acetylation of untreated starch using an aqueous sodium hydroxide solution. The reaction time could thus be decreased to 5 h. This means that over the years the reaction time could steadily be decreased. Biswas et al. (2008) describe the acetylation of starch in 2 min in a microwave using iodine as a catalyst. The examples mentioned so far always use acetic anhydride as both a reactant and a solvent. Another possibility is to first dissolve starch in order to increase the accessibility and reactivity of the hydroxyl groups. Possible solvents are dimethyl sulfoxide (DMSO) or alkaline aqueous media (Aburto, Alric, & Borredon, 2005; Narayan, Bloembergen, & Lathia, 1995).

In addition to these traditional starch solvents, there has been a major focus on ionic liquids in polysaccharide chemistry over the last few years. A widely used ionic liquid is 1-*N*-butyl-3-methylimidazolium chloride ($[C_4mim]^+Cl^-$) as a solvent and reaction media for starch to carry out homogeneous derivatization (Biswas, Shogren, Stevenson, Willett, and Bhowmik, 2006). In addition to $[C_4mim]^+Cl^-$, other ILs, mostly imidazole-based ones with chloride as a counterion, such as 1-*N*-allyl-3-methylimidazolium chloride and 1-*N*-ethyl-3-methylimidazolium chloride, have become more and more prevalent in the derivatization of polysaccharides (Cao et al., 2007). Special 1-*N*-ethyl-3-methylimidazolium acetate ($[C_2mim]^+AcO^-$) exhibits very interesting properties as a solvent for polysaccharides as opposed to $[C_4mim]^+Cl^-$. Compared to the latter, $[C_2mim]^+AcO^-$ is not corrosive or toxic, can dissolve higher amounts of polysaccharide and has a ten times lower viscosity (Uerdingen, 2006). Papers or patents that describe the use of ILs in starch derivatization are limited (Myllymaeki & Aksela, 2007). This is due to the fact that it is easier to produce a homogenous reaction of starch as opposed to cellulose. Nevertheless quite interesting properties are the result of, for example, starch acetate synthesized in $[C_4mim]^+Cl^-$ in terms

* Corresponding author. Tel.: +49 331 568 1516.
E-mail address: bert.volkert@iap.fraunhofer.de (B. Volkert).

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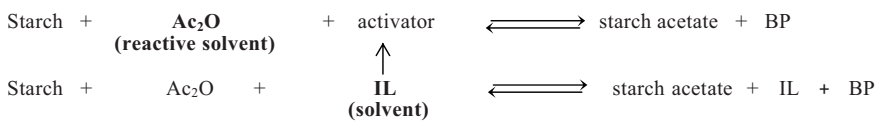

Scheme 1. Comparison between the synthesis of starch acetate in acetic anhydride as a reaction media and ionic liquid as a solvent; BP = by-product.

of the substituent distribution when compared to cellulose acetate (Lehmann & Volkert, 2009).

Chemical modification of polysaccharides, e.g. esterification reactions of mostly 1–8 wt. % polysaccharide dissolved in IL, are achieved using five or more molar equivalents of carboxylic acid anhydride or carboxylic acid chlorides per anhydro glucose unit (AGU) resulting in highly-substituted polysaccharide esters (Liu, Sun, Zhang, & Ren, 2007; Heinze et al., 2008). The papers mentioned show that an activator is not necessary to produce esterification in an ionic liquid. The use of imidazole (Liebert, Kulicke, & Heinze, 2008; Neumann, Wiege, & Warwel, 2002) as well as imidazolium derivatives such as 1-acetyl-3-methyl imidazolium chloride (Tessler, 1972; Tessler & Billmers, 1996) for esterification of starch is widely described in literature. But always these imidazole compounds esterify the starch in form of carboxylic acid imidazolides and so changes their chemical structure during the reaction.

This paper will investigate the method of esterifying starch (Scheme 1) with carboxylic acid anhydrides, the possibility of using an ionic liquid as a catalyst therefore in just small amounts and not as a solvent, and the resulting chemical properties of starch esters.

2. Materials and methods

2.1. Materials

Acetic acid, acetic anhydride, propionic anhydride (Riedel de Haën), diethylamine, triethylamine (Fluka), pyridine (Acros), 1-methylimidazol, DABCO (ABCR), and piperidine were used with an analytical grade of ≥96%.

High amylose maize starch (HAMS, amylose content of 51%; M_w: 6.2×10^6 g/mol; Cargill), was dried (at 105 °C, >12 h) before being used as a polysaccharide.

1-*N*-methylimidazolium chloride ([Hmim]$^+$Cl$^-$; purity ≥95%; water ≤0.5%; Fluka), 1-*N*-ethyl-3-methylimidazolium chloride ([C_2mim]$^+$Cl$^-$, purity ≥95%; water ≤ 0.5%; Fluka), 1-*N*-ethyl-3-methylimidazolium acetate ([C_2mim]$^+$AcO$^-$, purity ≥96.5%; water ≤ 0.1%; Aldrich), 1-*N*-ethyl-3-methylimidazolium bromide ([C_2mim]$^+$Br$^-$, purity ≥99%; water ≤ 0.5%; ABCR), 1-*N*-ethyl-3-methylimidazolium tetrafluoroborate ([C_2mim]$^+$$BF_4^-$, purity ≥99%; water ≤ 0.5%; ABCR), 1-*N*-ethyl-3-methylimidazolium methylphosphonate ([C_2mim]$^+$(MeO)(H)PO_2^-, purity ≥99%; water ≤ 0.5%; solvionic), 1-*N*-butyl-3-methylimidazolium chloride ([C_4mim]$^+$Cl$^-$, purity ≥99%; water ≤ 0.5%; solvent innovation) and 1-*N*-hexyl-3-methylimidazolium chloride [C_6mim]$^+$Cl$^-$ 99.5%; water ≤ 0.5%; ABCR) were used as ionic liquids.

2.2. Methods

2.2.1. Determining the degree of substitution by titration

The acetyl content of the starch acetates and propionates, was determined using the method of Klemm, Philipp, Heinze, Heinze, and Wagenknecht (1998). Esterified starch (150 mg dry sample) was allowed to swell by placing it in 10 ml of an acetone–water mixture (1:1 by volume) for 24 h at room temperature. 5 ml of a 1 M ethanolic potassium hydroxide solution were added to the suspension to start the complete deacetylation for 24 h at ambient temperature. The same procedure was performed for 2 blank values without starch ester. Excess potassium hydroxide was titrated with 0.5 M aqueous hydrochloric acid back to a pH of 7.0. The consumption of hydrochloric acid was ascertained and the DS was calculated as follows:

$$\%\mathrm{Sub} = \frac{(\mathrm{BV} - V_{\mathrm{HCl}}) \times M_{\mathrm{Sub}} \times c_{\mathrm{HCl}} \times 100\%}{E}$$

$$\mathrm{DS} = \frac{162 \times \%\mathrm{Sub}}{M_{\mathrm{Sub}} \times 100 - (M_{\mathrm{Sub}} - 1) \times \%\mathrm{Sub}}$$

BV, blank value [ml] (consumption of HCl for blank values, average value); V_{HCl}, volume of hydrochloric acid [ml]; E, weight of esterified starch [mg]; c_{HCl}, molarity of hydrochloric acid [mol/l]; M_{Sub}, molar mass of substituent [g/mol] (acetate: 43 g/mol, propionate: 57 g/mol)

2.2.2. Determining molecular weight distribution

2.2.2.1. SEC conditions. Molecular weight averages were determined using SEC-MALLS. The SEC-MALLS system consisted of a Waters 515 pump module, degasser, 717 autosampler, column heater (Jet Stream), MALLS and a Waters 2414 DRI detector. The MALLS detector was a Dawn-HELEOS (Wyatt Technology, Santa Barbara, USA) fitted with a K5 flow cell and an He–Ne laser operating at λ_0 = 658 nm and equipped with 16 detectors at angles ranging from 15.6° to 162.3°. Three columns in a row were used: SUPREMA S30000, S1000 and S100 (PSS, Mainz, Germany). The samples were eluted with DMSO containing 0.09 M $NaNO_3$ at a flow rate of 0.5 mL min^{-1} and temperature of 70 °C. During the sample run on the SEC-MALLS system, the data from the MALLS and DRI detectors were collected and processed using ASTRA software 5.3.0.18 to calculate the concentration of the injected solution and molar mass M_i at each retention volume. The basis for the absolute characterization of macromolecules by SEC light scattering experiments was described by Wyatt (1993).

2.2.2.2. Sample preparation. The esterified samples were saponified under mild conditions and no degradation of the polymer was observed. For this purpose, the starch esters were dispersed in water and saponified by adding 1 M NaOH. The mixture was stirred for 24 h at room temperature before it was neutralized with 1 M HCl. The deacetylated starch was 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 for molecular weight analysis.

2.2.3. Determination of the nephelometric turbidity unit (NTU)

A 1.7 wt.% solution of starch acetates or starch propionates in acetone or ethyl acetate were prepared. 30 ml of these solutions were put into a glass tube and measured using a Hach 2100AN Laboratory Turbidimeter. Three values were determined and the average was calculated.

2.2.4. Representative preparation of starch acetate

Dried starch (3 g; 18.6 mmol), acetic anhydride (8.6 g; 83.7 mmol; 4.5 moleq/AGU) and 1-*N*-butyl-3-methylimidazolium chloride (1.1 g; 6.2 mmol; 0.33 moleq/AGU) were placed into a 150 ml 3 neck flask with condenser and mechanical stirrer in an oil-bath. The temperature was kept at 130 °C for 4 h. The cooled reaction mixture was cast in an excess of ethanol under strong

Table 1
Degree of substitution and solubility of starch acetates and propionates as well as molar mass averages of saponified starch esters in dependency on the molar ratios; reaction temperature was 130 °C for all samples.

Sample	moleq $[C_4mim]^+Cl^-$ per AGU	Esterification agent	moleq anhydride per AGU	Time [h]	DS_{Ester}	M_w [$\times 10^6$ g/mol]	Solubility [NTU][a]	
							Acetone	Ethyl acetate
I	0.33	$(CH_3CO)_2O$	4.5	4	2.81	0.52	92.0	181.0
II	0.20	$(CH_3CO)_2O$	4.5	4	2.73	0.36	105.6	131.4
III	0.15	$(CH_3CO)_2O$	4.5	4	1.62	0.33	–	–
IV	0.075	$(CH_3CO)_2O$	4.5	4	1.53	0.34	–	–
V	0.075	$(CH_3CO)_2O$	4.5	24	2.96	0.33	51.7	39.7
VI	0.0375	$(CH_3CO)_2O$	4.5	24	2.61	0.14	205	518
VII	0.0188	$(CH_3CO)_2O$	4.5	24	0.61	0.16	–	–
VIII	/	$(CH_3CO)_2O$	4.5	4	0.05	n.d.	–	–
XI	0.33	$(CH_3CO)_2O$	3.25	4	2.83	0.26	37.4	36.9
X	0.20	$(CH_3CO)_2O$	2.5	4	2.54	0.22	14.7	31.1
XI	0.20	$(CH_3CO)_2O$	1.5	4	1.68	0.16	–	–
XII	1.2	$(CH_3CH_2CO)_2O$	4.5	4	2.86	1.48	33.6	34.9
XIII	0.5	$(CH_3CH_2CO)_2O$	4.5	4	2.76	0.75	251.0	232.0
XIV	0.33	$(CH_3CH_2CO)_2O$	4.5	4	2.22	1.19	–	–
XV	0.15	$(CH_3CH_2CO)_2O$	4.5	4	1.47	0.47	–	–
XVI	0.075	$(CH_3CH_2CO)_2O$	4.5	4	0.77	0.32	–	–
XVII[b]	0.33	$(CH_3CO)_2O$	4.5	4	2.06	0.82	–	–

[a] Measured as 1.7 wt.% solution, – insoluble.
[b] Air dried starch was used (content of water 11 wt.%).

agitation for precipitation. Ethanol was also used to wash the sample free of remaining ionic liquid and by-products. The product was dried at 60 °C and 40 mbar.

If a base was used, it was added before heating the reaction mixture.

Yield: 4.48 g.
$DS_{Acetate}$ = 2.81.

2.3. Representative preparation of starch propionate

The synthesis of starch propionate was accomplished like that of starch acetate using propionic anhydride instead of acetic anhydride. Dried starch (3 g; 18.6 mmol), propionic anhydride (10.9 g; 83.7 mmol; 4.5 moleq/AGU) and 1-*N*-butyl-3-methylimidazolium chloride (1.1 g; 6.2 mmol; 0.33 moleq/AGU) were used for this synthesis.

Yield: 4.51 g.
$DS_{Propionate}$ = 2.22.

3. Results and discussion

3.1. Preparation of starch esters using $[C_4mim]^+Cl^-$ as a catalyst

First we investigated the influence of different ratios of starch to esterification agent as well as reaction time and amount of IL. $[C_4mim]^+Cl^-$ was chosen as IL to catalyze the esterification of starch for these investigations. Table 1 demonstrates the catalytic effect of $[C_4mim]^+Cl^-$ for the esterification of starch.

Using 1.2 moleq–0.20 moleq of $[C_4mim]^+Cl^-$ per AGU under the reaction conditions stated results in highly-substituted starch acetates or propionates. When applying less $[C_4mim]^+Cl^-$, the reaction time must be increased in order to achieve starch esters with a high degree of substitution (**V**, **VI**). It was interesting to find a higher DS value for **X** and **XI** which does not correspond to the molar ratio of the amount of acetic anhydride used. A maximum DS of 1.5 was assumed based on the reaction mechanism. Multiple repetitions of these samples show the same result. To investigate this fact, two reactions of starch with 2.5 moleq of acetic acid per AGU were performed for 24 h at 130 °C. 0.2 moleq of $[C_4mim]^+Cl^-$ per AGU were also added to the one slurry of starch in acetic acid. While no substitution could be observed for the reaction mixture without the IL, a starch acetate with a $DS_{Acetate}$ = 0.51 could be isolated from the experiment with the IL. This demonstrates the effect $[C_4mim]^+Cl^-$ has on carboxylic acids during esterification when used as activating agent and explains why the DS values mentioned are higher than the molar ratio of added acetic anhydride. Acetic acid as a by-product can also esterify the hydroxyl groups of starch. This assumption is underlined by the work of Biswas, Shogren, and Willett (2009) in which the esterification of maltodextrin with stearic acid using 1-*N*-butyl-3-methylimidazolium dicyanoamide as solvent without any other reactants is described.

A starch diacetate can be isolated (**XVII**) if air-dried starch (water content ~11 wt.% means 1.2 moleq per AGU) is used as a starting material whereas the degree of substitution is lower than that of the starch acetate produced from dried starch **I**. Water from starch decreases the concentration of non-hydrated chloride ions in the reaction system and therefore the effectiveness of breaking the starch's H-bonds. Furthermore, the water can react with acetic anhydride to create acetic acid. This decreases the amount of acetic anhydride which can esterify the starch.

The esterification of starch with propionic anhydride results in lower degrees of substitution than for acetylation under the same reaction conditions (compare **I** and **XIV**). One reason for this is the lower activity of the carbonyl carbon for the propionyl group.

Investigation into the solubility and resulting turbidity of the prepared starch esters (Table 1) show, that only starch acetates and propionates with a DS > 2.5 are soluble in acetone or ethyl acetate.

3.2. Influence of the reaction temperature

To determine to what extent the reaction temperature and time have on the acetylation rate, we applied the reaction conditions for the synthesis of starch acetate **II,** but instead of using 130 °C, temperatures of 110 °C and 150 °C were used. A starch acetate (DS 2.5) can already be achieved after 3 h at a temperature of 130 °C. A temperature of 150 °C results in completely acetylated starch. Thus the rate of acetylation is faster at 150 °C than at 130 °C as was assumed and starch acetate (DS 2.5) can be achieved after only 2 h at this temperature. The curves prove that a reaction temperature of at least 110 °C only leads to low-substituted starch acetate within after 4 h.

It can also be seen in Fig. 1 that the degradation of the starch backbone increases with increasing reaction temperature.

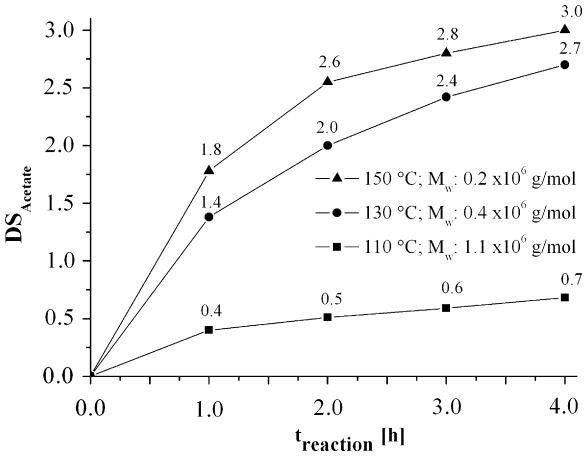

Fig. 1. Acetylation rate and values for the molecular weight averages of starch with 4.5 moleq of Ac_2O per AGU when 0.2 moleq of $[C_4mim]^+Cl^-$ per AGU is used as a catalyst at different reaction temperatures.

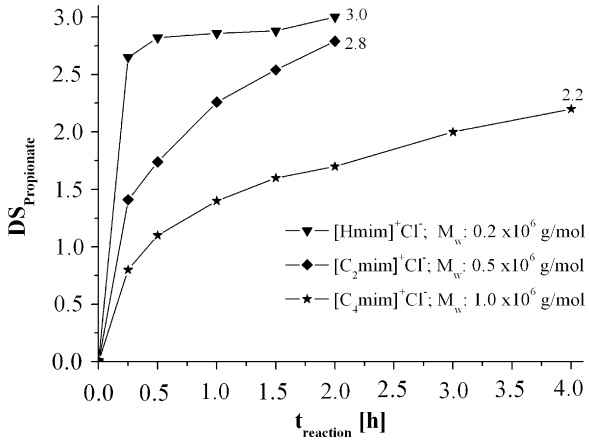

Fig. 2. Esterification rate of and values for the molecular weight averages starch with 4.5 moleq of propionic acid anhydride per AGU when 0.33 moleq of ionic liquid per AGU is used as a catalyst, $T_{reaction}$ = 130 °C.

3.3. Using different IL's for the acetylation of starch

We investigated the influence of different ionic liquids on the acetylation of starch and molecular degradation. The applied ionic liquids differed in the length of the alkyl side chain as well as in the type of the counterion (Table 2).

The DS value decreases slightly when the chain length of the imidazolium-based ionic liquids with chloride as counterion increases, and it decreases considerably when $[C_6mim]^+Cl^-$ is used. Swatlowski, Spear, Holbrey, and Rogers (2002) described how the solution power of 1-*N*-alkyl-3-methylimidazolium chlorides for biopolymers decreases with increasing chain length caused by the reduction in effective chloride concentration. The partial solubilization or swelling of starch might be the lowest for $[C_6mim]^+Cl^-$ and less for $[C_4mim]^+Cl^-$ than for $[C_2mim]^+Cl^-$ and $[Hmim]^+Cl^-$. Halogenides as counterions for the positively charged imidazolium ring lead to highly-substituted starch acetates. With acetate and methylphosphonate as counterions, two ionic liquids with high solubility properties for cellulose (due to their higher β-values > 1 hydrogen bond alkalinity) with Kamlet–Taft parameters (compare $[C_2mim]^+Cl^-$ ($\beta < 1$)) were applied (Fukaya, Hayashi, Wada, & Ohno, 2008; Kamlet & Taft, 1976). However this resulted in a much lower degree of substitution.

Furthermore, the question of how the different ionic liquids influence the speed of the esterification of starch was investigated by preparing starch propionate with $[Hmim]^+Cl^-$, $[C_2mim]^+Cl^-$ and $[C_4mim]^+Cl^-$ respectively and comparing these (Fig. 2).

Using $[C_4mim]^+Cl^-$ as a catalyst for the esterification of starch along with propionic anhydride, a $DS_{Propionate}$ of 2.2 is reached after 4 h. Using $[Hmim]^+Cl^-$ instead of $[C_4mim]^+Cl^-$ results in a degree of substitution of 2.6 after 0.25 h and after 2 h the hydroxyl groups of starch are completely esterified. Furthermore, a nearly fully substituted starch propionate can be isolated after 2 h when $[C_2mim]^+Cl^-$ is used. The much faster reaction time for $[Hmim]^+Cl^-$ compared to the other two ionic liquids may be due to the additional acidic character of $[Hmim]^+Cl^-$, which can also be seen in the values of the molar mass averages.

3.4. Investigating molecular degradation

The initial investigation of molecular degradation for starch dissolved in $[C_4mim]^+Cl^-$ was carried out by Stevenson, Biswas, Jane, and Inlett (2007). It revealed that $[C_4mim]^+Cl^-$ causes high degradation of starch chains. For example the molecular weight average for a wheat starch decreased from 10.1 [$\times 10^8$ g/mol] to 0.24 [$\times 10^8$ g/mol] when wheat starch was dissolved in $[C_4mim]^+Cl^-$ and was held 1 h at 100 °C. A high degradation of starch chains can also be found in all experiments on starch esters mentioned in this paper. This may be an indication of the acidic nature of the ionic liquids used as catalysts for esterification reactions or may hint at the acidic impurities of the ionic liquids used. Bases with different alkalinity were also used (Table 3) to investigate this in detail and analyze their possible influence on degradation.

Compared with the result of starch acetate **II** in terms of the molecular weight average, only the addition of 1-methylimidazole as a base reduce the degradation. All other bases do not result in the least degradation regardless their concentration. Taking into consideration a 10% statistical variation for the SEC-MALLS measurement, the degradation seems to be a bit higher when compared with starch acetate **II**.

Further on the results indicate a relation between the steric effects of the applied base and the degree of acetylation. The alkalinity of triethylamine (**XIX**) and diethylamine (**XXII**) is nearly the same but the degree of acetylation is different. A lower degree of substitution can also be seen when using DABCO (triethylendiamine, **XXIV**) as a sterically inhibited base. Klemm et al. (1998) describe the effect of deacetylation while acetylation reaction when reagents containing amino groups are added to acetylation reactions. This behavior can be found here too.

Table 2
Degree of substitution averages of starch acetates prepared at 130 °C for 4 h with 4.5 moleq Ac_2O and 0.2 moleq of IL per AGU as well as molar mass averages of saponified starch acetates.

Significance of alkyl chain			Significance of $[C_2mim]^+X^-$ counterion		
Ionic liquid	$DS_{Acetate}$	M_w [$\times 10^6$ g/mol]	Counterion	$DS_{Acetate}$	M_w [$\times 10^6$ g/mol]
$[Hmim]^+Cl^-$	2.93	0.24	Cl^-	2.81	0.48
$[C_2mim]^+Cl^-$	2.81	0.48	Br^-	2.98	0.28
$[C_4mim]^+Cl^-$	2.73	0.36	AcO^-	0.62	0.79
$[C_6mim]^+Cl^-$	1.34	0.83	$(MeO)(H)PO_2^-$	0.14	0.96

Table 3
Degree of substitution and molar mass averages of starch acetates prepared at 130 °C for 4 h with 4.5 moleq of Ac_2O and 0.2 moleq of IL per AGU and appropriate amount of base.

Sample	Base	pK_b value of used base	moleq per AGU	$DS_{Acetate}$	M_w [$\times 10^6$ g/mol]
XVIII	1-Methylimidazole	6.6	0.1	2.79	0.81
XIX	Triethylamine	3.3	0.1	1.27	0.60
XX	Piperidine	2.8	0.1	2.48	0.25
XXI	Piperidine	2.8	0.3	2.45	0.29
XXII	Diethylamine	2.9	0.1	2.46	0.23
XXIII	Diethylamine	2.9	0.3	2.56	0.24
XXIV	DABCO	11.0	0.1	1.39	0.36
XXV	Pyridine	8.8	0.1	2.66	0.28
XXVI	Pyridine	8.8	0.2	2.21	0.32
XXVII	Pyridine	8.8	0.3	2.76	0.29
XXVIII	Pyridine	8.8	1.0	2.83	0.56
XXIX	Pyridine	8.8	4.5	2.89	1.68

Piperidine, 1-methylimidazole and pyridine possess planar structures and differ greatly in their alkalinity. They are not sterically inhibited bases, however this does not have much impact on the degree of acetylation.

Increasing the amount of pyridine in terms of the ionic liquid in a large excess influences the degradation most (**XXIX**). Degradation can be lowered if pyridine is used as a base in equimolar amounts with acetic anhydride. This indicates that the molecular degradation of the starch backbone is a result of the acetic acid as a by-product, as well as a result of the reaction time and temperature.

4. Conclusion

For the first time it could be shown that ionic liquid in low amounts can catalyze esterification reactions of starch to produce starch acetate and propionate. Therefore the requirements that the catalyst be recyclable, decrease activating energy and be used in small amounts are fulfilled. Products from esterification with a degree of substitution ~2.5 exhibit a low average molecular weight and good solubility in acetone or ethyl acetate. A relationship between the type of ionic liquid used as a catalyst for esterification and properties like degree of substitution and average molar mass of starch esters could be shown. The degradation can be reduced by the addition of pyridine. The molar mass averages can be adjusted based on the amount of pyridine used.

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