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Fast and highly efficient acetylation of xylans in ionic liquid systems

Agnes M. Stepan · Alistair W. T. King ·
Tia Kakko · Guillermo Toriz ·
Ilkka Kilpeläinen · Paul Gatenholm

Abstract In this study high molecular weight pure rye arabinoxylan and spruce arabinoglucuronoxylan were acetylated in ionic liquid (IL) systems. Two different ILs were used in our study. In both IL, using optimized procedures, it was possible to achieve acetylation within 5 min. The first system involved direct dissolution into 1-ethyl-3-methylimidazolium dimethylphosphate ([emim][Me$_2$PO$_4$]), followed by addition of acetyl chloride/pyridine (AcCl/Pyr) and additional chloroform (CHCl$_3$), as co-solvent. The other system involved direct dissolution into the novel protic IL 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]), followed by acetic anhydride/1,5-diazabicyclo[4.3.0]non-5-ene (Ac$_2$O/DBN) and no co-solvent added. The full acetyl substitution of the xylans was confirmed by FT IR and ^{1}H NMR. The acetylated xylans maintained a high molecular weight, which was confirmed by gel permeation chromatography. The products were soluble in CHCl$_3$ and dimethyl carbonate, which is considered as a 'green' reagent or solvent. This allowed for the casting of the materials into clear transparent films, opening opportunity for further processing and evaluation of these materials.

Keywords Spruce · Rye · Xylan · Ionic liquid · Acetylation

A. M. Stepan · G. Toriz · P. Gatenholm
WWSC, Wallenberg Wood Science Center, Chalmers
University of Technology, Kemivägen 10,
412 96 Göteborg, Sweden

A. M. Stepan · P. Gatenholm (✉)
Biopolymer Technology, Department of Chemical and
Biological Engineering, Chalmers University of
Technology, Kemivägen 10, 412 96 Göteborg, Sweden
e-mail: paul.gatenholm@chalmers.se

A. W. T. King · T. Kakko · I. Kilpeläinen
Department of Chemistry, University of Helsinki, PL 55,
00014 Helsinki, Finland

G. Toriz
Department of Wood, Cellulose and Paper Research,
University of Guadalajara, Guadalajara, Mexico

Introduction

There is an urgent need to change material production based on non-renewable resources to renewable resources, due to depletion of our fossil-based feedstocks. Lignocellulosics, such as wood, have received particular attention in recent decades, as an alternative feedstock sources (Ragauskas et al. 2006). Since then, researchers have been rapidly developing understanding about polysaccharides and their unique structure–property relationships, which can facilitate rational novel material design. Hemicelluloses are the second most abundant biopolymers on Earth, after cellulose, composing about 50 % of annual plants and 30 % of wood (Timell 1967). They are branched polysaccharides, formed from a number of different sugar

monomer units and their derivatives (Tombs and Harding 1997). Xylans in many annual crops, such as rye, are built from a β-(1–4) linked xylose backbone, with L-arabinofuranosyl side chain units. Xylans in softwood, such as spruce, have 4-O-methyl-glucuronoxylan side chains, in addition to the L-arabinofuranosyl units. These hemicelluloses have recently gained significant attention due to their excellent film-forming abilities and unique oxygen barrier properties (Escalante et al. 2012; Grondahl et al. 2004). As with cellulose, hemicelluloses have free hydroxyl groups that can be used for further functionalization. One of the important derivatization methods of cellulose and hemicelluloses are acylation reactions which potentially make these polysaccharides thermoplastic (Glasser et al. 1995; Jain et al. 2000). Furthermore, the acetylated arabinoxylans (AX) have improved water repellency compared to the native xylans and have other attractive mechanical properties, which open up new opportunities for applications in bio-based packaging (Stepan et al. 2012).

Full acetylation of hemicelluloses has until now been performed through chemical reactions, involving several non-recyclable organic solvents (Fang et al. 2000; Renard and Jarvis 1999; Sun et al. 1999; Sun et al. 2004; Timell 1967). Striving for environmentally more benign derivatization reactions and better solvation properties brings our attention to ionic liquids (ILs).

In the recent years there have been many novel approaches to derivatize polysaccharides in IL systems. A common definition for ILs is salts that are molten below 100 °C. Typically they have negligible vapor pressures at room temperature. For polymer processing it is preferable that they are thermally, and chemically stable, and have low viscosities (Pinkert et al. 2009; Welton 1999). They are also commonly promoted to be green-solvents, for the properties listed above, and for their recyclability (Barthel and Heinze 2006; Heinze et al. 2005).

There have been several recent papers and patents on IL systems for modification of cellulose. (Abbott et al. 2005; Barthel and Heinze 2006; Buchanan and Buchanan 2009; Gericke et al. 2011; Gericke et al. 2009; Heinze et al. 2005; Karatzos et al. 2012; Kosan et al.2010; Liu et al. 2009a, b Pinkert et al. 2009; Buchanan et al. 2010; Massonne et al. 2007). Literature on production of cellulose acetates gives a good basis to design hemicellulose modification reactions, under similar conditions.

Among others(Sun et al. 2004) have performed studies on different modification reactions of hemicelluloses in ILs, such as acetylation, maleylation and succinylation, reaching partial degree of substitution levels (Hansen and Plackett 2011; Peng et al. 2010, 2011; Ren et al. 2011, 2007a, b). However, achieving full substitution has remained a challenge. A few years ago the first reports were published on the full acetylation of woods in IL's (Qu et al. 2012; Qu et al. 2011; Xie et al. 2007; Kilpelaeinen et al. 2007). These reports use mechanical treatment to prepare the raw material. Extended milling was shown to be necessary for the dissolution of wood in ILs (King et al. 2009b). Ball milling as pretreatment was confirmed to decrease the degree of polymerization (DP) of cellulose with about 400–500 times (Lu and Ralph 2003). Hemicelluloses are lower molecular weight compared to cellulose, and are less resistant to extreme treatments. Modified hemicelluloses obtained from these heavy pulverization procedures will surely yield low DP hemicelluloses. Up to now, there are no reports on successful full acetylation of hemicelluloses in IL's with DPs close to the native polymer or holocellulose.

In this paper we target for the full acetylation of hemicelluloses under well-defined conditions, for pure rye and spruce xylans. The hemicellulose samples were extracted using mild procedures to yield the highest molecular weights possible. We aim to overcome the challenges of achieving high degrees of substitution (DS) and long reaction times. In this study we have been investigating two new IL systems to reach full acetylation on xylans. One is a commonly used 1-ethylmethylimidazolium ([emim]) based system, using a co-solvent during the acetylation step. The other system is a novel 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN)-based IL also reaching full acetylation, without the addition of co-solvents.

Experimental

Spruce arabinoglucuronoxylan (AGX) was isolated according to the method described elsewhere (Escalante et al. 2012). The ratio of A:GlcA:X sugars was 1:2:11 respectively, as determined by NMR and supported by ion chromatography, and the structure of the spruce xylan was elucidated through NMR, Fig. 1a (Escalante et al. 2012). Rye arabinoxylan (AX) was purchased from Megazyme (∼95 % purity, LOT 20601a). The

arabinose to xylose ratio was 0.52 as determined by ion chromatography. The structure is described in Fig. 1b, also based on literature (Hoije et al. 2008).

1-Ethyl-3-methylimidazolium dimethylphosphate ([emim][Me$_2$PO$_4$]) and 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]) was synthesized to high purity, as published by (King et al. 2012) and as described below, respectively. 1-allyl-3-methylimidazolium chloride ([amim]Cl) was prepared according to a previous publication (Leskinen et al. 2011). Acetic acid was purchased from Acros Organics. DBN was purchased from Fluorochem (UK). Acetyl chloride (AcCl), dimethyl carbonate (DMC), chloroform (CHCl$_3$) and d1-chloroform (CDCl$_3$) were purchased from Sigma-Aldrich. Acetic anhydride (Ac$_2$O) was purchased from both Fluka and Sigma-Aldrich. Pyridine and the dimethyl sulfoxide (DMSO) were purchased from both Riedel–de Haen and Sigma-Aldrich. Ethanol (95 %) was purchased from Solveco. All chemicals were used without further purification except for DBN, which was vacuum distilled prior to use.

Dissolution and acetylation of rye and spruce xylans in [emim][Me$_2$PO$_4$]

Acetylation of both the rye AX and the spruce AGX was carried out the same way in [emim][Me$_2$PO$_4$]: 50 mg of xylan was mixed with a needle into 950 mg of the IL in an 8 ml vial, resulting in a 5 % solution. The vial was rinsed with argon, and sealed. The system was heated and stirred at 90 °C for 2 h, for total dissolution of the AX. 350 µl of pyridine was added to the warm solution and vortexed to give a homogenous mixture. After letting the solution cool to room temperature, 250 µl of acetyl chloride (4,5 eq per hydroxyl functionality in xylans) was added drop-wise and mixed with a needle, until a homogenous paste was obtained. CHCl$_3$ was added stepwise to the reaction mixture, with vortexing between each addition (2*250 µl, 2*500 µl, 3* 1 ml). The reaction was heated to 50 °C for 5 min and then transferred into a 50 ml centrifuge tube. 10 ml of water was then added and vortexed followed by 10 ml of ethanol, with vortexing. The CHCl$_3$ was evaporated under a nitrogen stream until a total volume of 17.5 ml was reached. The solution was made up to a total volume of 30 ml by adding water, followed by vortexing and the solid was recovered by centrifugation at 2,500 rpm for 5 min, This was then washed with water 3 more times. The white precipitate was dried in a vacuum oven for over 18 h.

Dissolution and acetylation of rye and spruce xylans in [DBNH][OAc]

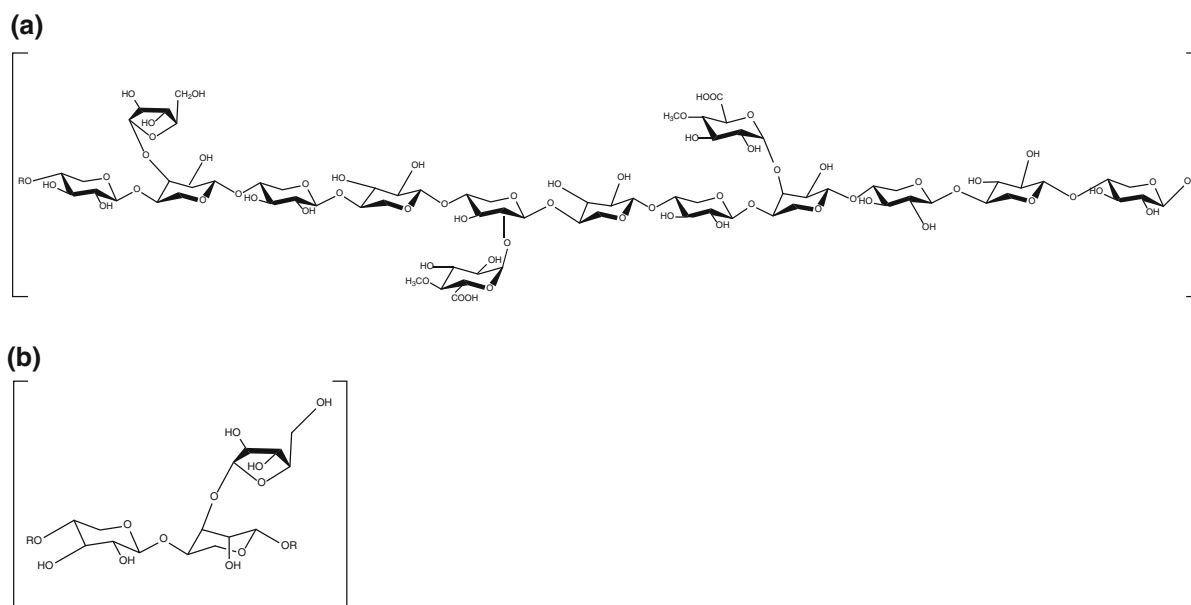Acetylation of both the rye AX and the spruce AGX was carried out the same way in [DBNH[OAc]: The IL

Fig. 1 Schematic structure of **a** rye AX and **b** spruce AGX

[DBNH][OAc] was synthesized by mixing 1 g of DBN and 0.6 g of acetic acid (1:1 molar ratios). After the IL was prepared, 80 mg of xylan was added (5 %). The rye AX solution was heated at 80 °C and the spruce AGX at 90 °C for 2 h, for total dissolution. 0.25 g of DBN was then added and thoroughly mixed before 0.42 g of Ac_2O was added (2,5 eq per hydroxyl functionality in xylans). The reaction was heated for 5 min at 50 °C. The product was recovered by precipitation in 4.5 ml of 95 % ethanol. The precipitate was centrifuged at 2,800 rpm for 5 min then washed with 95 % ethanol and deionized (DI) water 2 more times. The product was dried at 40 °C in a vacuum oven for 18 h.

Rheology of solutions

The rheological properties of the solutions were characterized with a Bohlin Rheometer CS 30 (Malvern Instruments Ltd, UK). The measurements were conducted using a cone-and-plate geometry with a diameter of 25 mm and a cone angle of 5.4° at 80 °C. Steady state shear viscosity was measured at shear stresses in the range 0.25–367 Pa, as set by the viscosity of the solutions. Complex viscosity was measured by performing dynamic oscillatory shear tests from the angular frequency 0.0628 to 188.496 rad/s.

Fourier transform infrared (FT-IR)

Infrared spectra were recorded on a Bruker Alpha attenuated total reflection (ATR) IR spectrometer. Twenty scans were taken for each sample.

Nuclear magnetic resonance (NMR)

Sample solutions for NMR analysis were prepared in $CDCl_3$ by dissolving 3–4 mg of acetylated xylan in 1 ml of $CDCl_3$. NMR spectra were recorded using either a Varian Mercury 300 (300 MHz), Varian Unity Inova 500 (500 MHz) or Varian Unity Inova 600 (600 MHz) spectrometer.

Molecular weight distribution determination

The molecular weight of the unmodified, native xylans was determined using a HPSEC.MALS.RI.UV aqueous system consisting of a Waters 2,690 (Waters Corporation). The system had an online degasser, auto sampler,

column oven and three serial-connected columns (Shodex OHpak SB-803, 804 and 806 M HQ), controlled at 50 °C. The detectors were a multi-angle laser light scattering (MALS; DSP equipped with a He–Ne laser at 632.8 nm, Wyatt Technology Corp.) detector, refractive index (RI) detector and a UV–vis detector. The eluent used was sodium nitrate (0.1 M $NaNO_3$) containing 0.02 % of sodium azide (NaN_3). The flow rate was 0.4 ml/min. All samples were dissolved in 0.1 M $NaNO_3$ solution, at a concentration of 2 % (w/w) and pre-filtered (GHP syringe filter, 0.45 μm, PALL). The weight-average molecular weight (M_w) was determined using ASTRA3 software.

The molecular weights of the acetylated rye AX and spruce AGX were measured on a PL-GPC 50 Plus, Integrated GPC System, by Polymer Laboratories (A Varian Inc. Company), with both RI and UV detection. The system was equipped with two PolarGel-M (300 × 7.5 mm) columns and a PolarGel-M Guard column (50 × 7.5 mm). The mobile phase was DMSO with the addition of 10 mM LiBr and the samples were injected using a PL-AS RT GPC Autosampler. The samples were dissolved in DMSO to a 2.5 mg/ml concentration and were filtered through a 0.45 μm filter, from Nylon or GHP. The flow rate was (0.5 ml/min). The samples were evaluated with the software Cirrus GPC, version 3.2. Ten different molecular weights of pullulan (708, 375, 200, 107, 47.1, 21.1, 11.1, 5.9, 0.667, and 0.180 kDa) were used for calibration.

Film casting of the acetylated xylan films

Acetylated rye and spruce xylans were dissolved in $CHCl_3$ or DMC, then casted on glass petri dishes and left to dry, until all solvent evaporated and clear transparent films were formed.

Results and discussion

Table 1 summarizes the experimental setups used, attempting to achieve fully acetylated xylans using ILs. The aim was to produce a non-colored and fully acetylated xylan that is soluble in solvents such as $CHCl_3$ or DMC, which is important for future processability of the product. Initial experiments were performed with 2 % rye AX in the starting IL solution. Successful experiments were repeated for acetylation of the spruce xylan. These were also successful.

Table 1 Summary of reaction systems in attempts to acetylate rye AX

Ionic liquid[b]	Reagent	Reaction temp. (°C)	Time	IR[c]	Product color	Solubility in CHCl$_3$[d]
–	Ac$_2$O[a]	50	20 h	Partial	Yellowish	–
[emim] [OAc]	Ac$_2$O[e]	50	16 h	High	Dark sand	–
	AcCl[e]	50	2 h	n.a.	Dark	–
	AcCl[f]	50	5 min	Full	Dark brown	–
[amim] Cl	Ac$_2$O[d]	50	16 h	Full	Brick red	–
	Ac$_2$O	50	4 h	Partial	White	–
	AcCl[f]	50	5 min	Full	Orange	–
[emim] [Me$_2$PO$_4$]	Ac$_2$O[d]	50	16 h	High	Brown/red	–
	AcCl[f]	50	5 min	Full	White	+
	Ac$_2$O[f]	50	5 min	Partial	White	–
[DBNH] [OAc]	Ac$_2$O[f, g]	50	5 min	Full	White	+
	Ac$_2$O[h]	50	5 min	Partial	White	–

[a] Ionic liquid-free acetylation: 1.5 % AX suspended in pyridine, then Ac2O added (Molar ratio of pyridine to Ac2O was 4:3); [b] 2 % rye AX was dissolved in IL on 80 °C; [c] acetylation degree based on IR spectra; [d] + soluble;–not soluble; [e] additional pyridine (1:1 molar ratio compared to reagent); [f] the methods are described in detail in methods section; [g] also performed with 5 % rye AX in the IL; [h] DBN:Ac2O molar ratio was 5:4

Discussion of the successful acetylations

The products

Both the rye AX and the spruce AGX were successfully acetylated in two different IL systems, to give good quality products. One in [emim][Me$_2$PO$_4$] using pyridine as proton-scavenger and CHCl$_3$ as co-solvent, which was introduced during the progress of the reaction. The other method used [DBNH][OAc], without additional co-solvent.

The reaction mixtures were heated in the [emim][Me$_2$PO$_4$] system after the addition of CHCl$_3$ for a further 5 min at 50 °C, to make sure acetylation was complete. The products were recovered through precipitation in water and ethanol and a white fluffy precipitate was obtained. The acetylated rye arabinoxylan (AcAX) also maintained its nice white appearance after drying, while the acetylated spruce arabinoglucuronoxylan (AcAGX) formed a white, but more dense product. The rye AcAX was soluble in CHCl$_3$ and dimethyl carbonate (DMC), while the spruce AcAGX was not. The spruce AcAGX was soluble only in DMSO with heating at 50 °C. The products from the [DBNH][OAc] reaction were recovered by pouring the reaction solution into ethanol. The white fluffy precipitate of the rye AX

was easy to wash a few times and stayed white and fluffy after drying. The spruce had similar precipitate, but after drying it formed a denser structured and light colored product. Both acetylated xylan products from the [DBNH][OAc] reaction system were soluble in CHCl$_3$ and DMC.

These products were subjected to NMR, IR and GPC analysis.

Viscosity of the xylan solutions

During the dissolution, the xylans were stirred at elevated temperatures (80 °C for the rye AX and 90 °C for the spruce AGX) for 2 h total dissolution time. Before adding the reagents the viscosities of all solutions were measured at 80 °C, to give an indication and comparison between the reaction systems. The solutions were measured at 80 °C, because cooling them back to room temperature caused them to solidify. Figure 2 shows that the higher molecular weight rye AX has two order of magnitudes higher viscosity than the lower molecular weight spruce AGX. For the [DBNH][OAc] solutions, the visually apparent lower viscosity is also clearly visible on Fig. 2. This allows for more rapid homogenization upon addition of reagents and easier processing of the solutions, in general.

Fourier transform infrared spectroscopy (FT-IR)

The high degrees of acetylation were first confirmed by IR. Figure 3 shows the infrared spectra of hemicelluloses before and after acetylation in [DBNH][OAc]. Figure 3a shows the spectra of rye AX before and after acetylation in [emim][Me₂PO₄]. The broad and strong signal from the hydroxyl (OH) groups in the blank sample can be found at 3,000–3,500 cm⁻¹. This signal disappears completely after the acetylation reaction, indicating that possibly no, or very low amount of free OH groups can be found in the material and essentially high degree of replacement of the OH groups has occurred. Moreover, three distinct new signals appear on the spectrum. A characteristic signal at 1,740 cm⁻¹ indicates the carbonyl group (C=O) in ester bonds; a signal around 1,380 cm⁻¹ is the stretch for the methyl group (CH₃) in the acetyl group; and a strong signal around 1,215–1,250 cm⁻¹ results from the acetate stretch (CC(= O)−O). The spectra for the rye AX acetylated in [emim][Me₂PO₄] (Fig. 3a) can be interpreted the same way as Fig. 3b. The same changes can be observed from Fig. 3d, which demonstrates the full acetylation of spruce AGX in [DBNH][OAc]. The spectrum of the acetylated spruce AGX in [emim][-Me₂PO₄] shows that it was also highly acetylated (Fig. 3c).

Nuclear magnetic resonance (NMR)

The acetylated products were fully soluble in conventional NMR solvent such as CDCl₃. This also indicates a high degree of acetylation, since lower DS still

Fig. 2 Viscosities of xylan-IL solutions (5 wt%) at 80 °C

enhances water solubility by acting as spacer between the polymer molecules. At higher DS the lack of OH groups will result in the product losing water solubility and will also result in an increase in solubility in aprotic and non-polar solvents, such as CHCl₃.

The appearance of acetylated sugar backbone and substituent resonances in the proton spectra are similar to previous products assigned in the literature. The acetylated arabinose and xylose peaks were assigned based on (Escalante et al. 2012; Stepan et al. 2012) which is based on 2D COSY, TOCSY and ¹H-¹³C HSQC experiments.

There are in average 6 protons in a sugar monomer unit, and a sugar monomer unit has in average 2 acetyl groups in the case of full substitution, which also mean 6 protons from the two acetyl groups, making the ratio of acetyl protons to sugar protons in case of full acetylation 6:6 (1:1). The integral of the total sugar protons was calibrated at 1.00. The integrals of the acetyl signals were estimated to be 0.98, 1.03 and 0.96 for the AX acetylated in [emim][Me₂PO₄], [DBNH][OAc] and AGX acetylated in [DBNH][OAc], respectively (Fig. 4). The degree of acetylation was determined based on the ratio of the integrals of the total acetyl protons and the total sugar protons. In the case of a full acetylation of the rye AX samples, the ratio of these two areas is 1:1 as discussed above. In the case of full acetylation of the spruce AGX samples this ratio is 1.02:1.00 based on similar calculations. For the spruce sample the DS was calculated by dividing the measured ratio by the theoretical maximum ratio in case of full acetylation.

The DS of acetylation was calculated by comparing the relative intensities of the signals of the acetyl groups (at 2 ppm) and those of all carbohydrate signals (3.0–5.6 ppm) (Grondahl and Gatenholm 2005; Grondahl et al. 2003; Stepan et al. 2012). Following equation (1) DS can be calculated for acetylated AX and following equation (2) for acetylated AGX:

1. DS = (integral of acetyl group protons/3)/(integral of carbohydrate ring protons/6)
2. DS = (integral of acetyl group protons/3)/(integral of carbohydrate ring protons/6.3)

Where 3 in both equations stands for the 3 protons of the acetyl group per substitution, and 6 stands for the average number of protons in a sugar monomer ring in the AX, and 6.3 stands for the average number
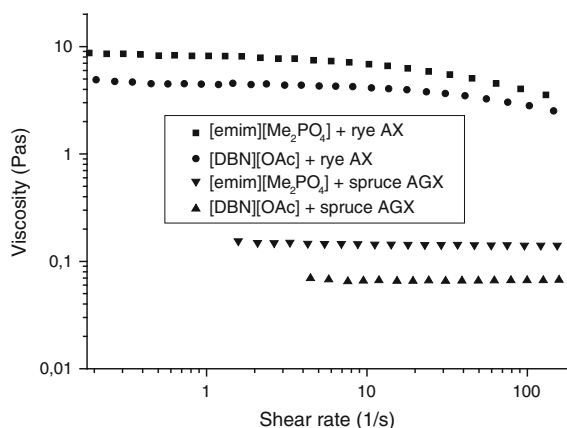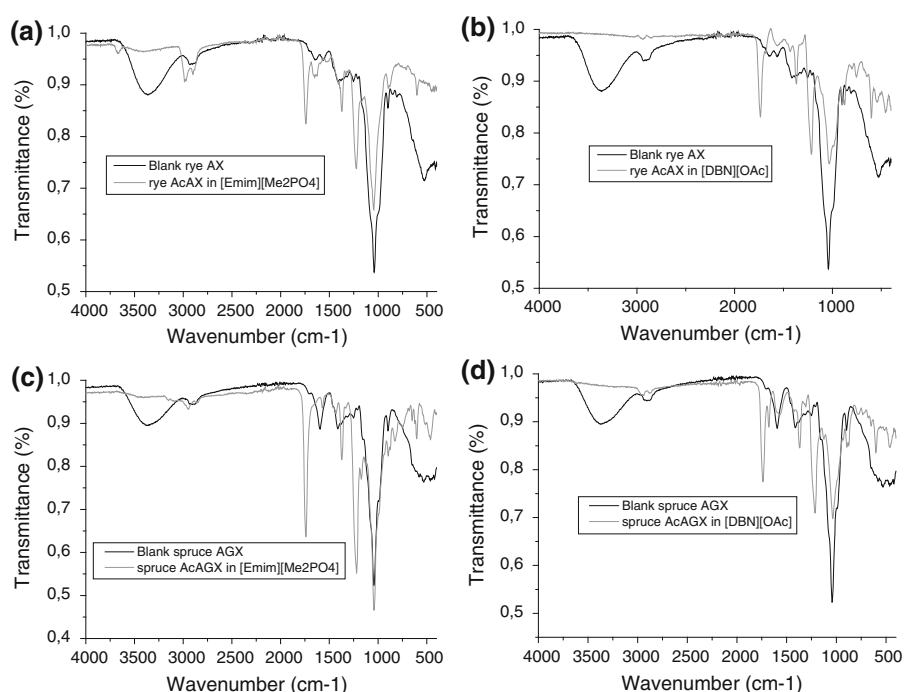
Fig. 3 FT-IR spectra of **a** blank and acetylate rye AX acetylated in [emim][Me$_2$PO$_4$]; **b** blank and acetylated rye AX in [DBNH][OAc]; **c** blank and acetylated spruce AGX in [emim][Me$_2$PO$_4$]; **d** blank and acetylated spruce AGX in [DBNH][OAc]

of protons in the AGX polymer. The number 6.3 comes from averaging 14 sugar monomers (representative of a "repeating unit" where 1 is an arabinose 2 are glucuronic acids and 11 are xyloses) not exchangeable protons.

The maximum DS can be determined for both xylans by calculating the maximum possible acetyl groups per repeating unit divided by the number of sugar monomers in the repeating unit. A repeating unit of on AX is 3 sugar monomers which can have in total 6 acetyl groups. On AGX the repeating unit is 14 sugar monomers which can have theoretically a maximum of 26 acetyl groups in total. This means a maximum DS of 2 for AX and 1.9 for AGX.

The DS can be determined in percentage based on the integral ratios, where for rye AX acetylated in [emim][Me$_2$PO$_4$] was 98 % and acetylated in [DBNH][OAc] it was full. For spruce AGX acetylated in [DBNH][OAc] the DS was full. These percents correspond to DS values of 1.96, 2 and 2 respectively.

The spruce AGX acetylated in [emim][Me$_2$PO$_4$] was only soluble in DMSO with heating and stirring at 50 °C. Therefore the NMR was run in d-DMSO (instead of CDCl$_3$ as for the other samples). Unfortunately the spectra had an inevitable water peak. This water peak disturbs the integration to predict degree of

acetylation. According to the IR there were very little free hydroxyl groups left, indicating high degree of acetylation. However, the insolubility of the sample in CHCl$_3$ can suggest two things. On one hand, the high glucuronic acid content or lower DS of acetyl groups can prevent solubilization of the material in apolar solvents. The ATR-IR shows a high degree of acetylation, but compared to KBr method, only measures the surface material, so the sample might not be homogeneously highly acetylated. On the other hand, some other side reactions might have taken place, such as cross-linking of carboxyl groups. This has been proposed to occur previously by (Zoia et al. 2011) where wood biopolymers containing both acid and alcohol functionalities may have cross-link during a benzoylation treatment from [amim]Cl. GPC data is not available for this sample, therefore cross-linking cannot be confirmed. The predominant mechanism for insolubility is not obvious to predict.

Discussion of the [emim][Me$_2$PO$_4$] reaction system

Complete acetylation of rye AX in [emim][Me$_2$PO$_4$] was carried out after the dissolution of the hemicellulose in the IL. Pyridine was added as a acid scavenger
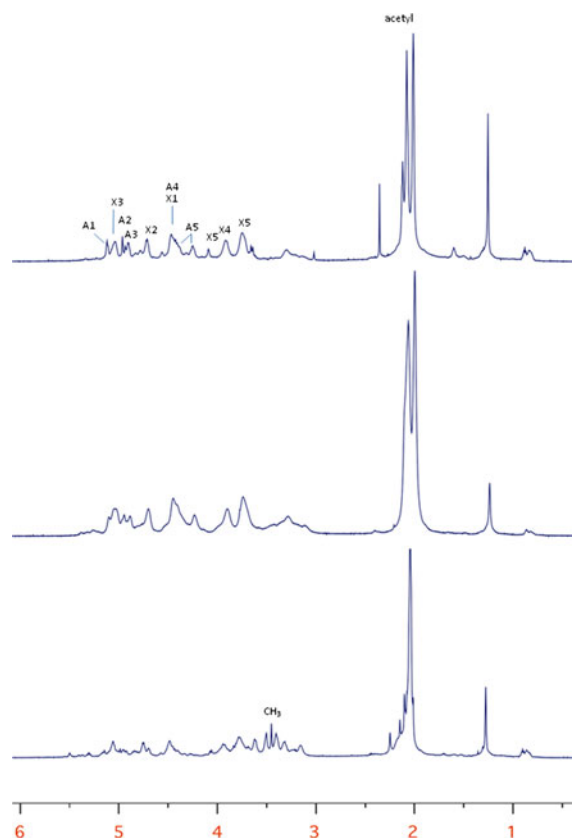
Fig. 4 ^{1}H NMR Spectra in CDCl$_3$ of acetylated rye AX in [emim][Me$_2$PO$_4$], [DBNH][OAc] and acetylated spruce AGX (from *top* to *bottom*)

(Xie et al. 2007). After the drop-wise addition of AcCl the mixture was a whitish paste and the temperature rose approximately to 60 °C for 1–2 min. The solution became transparent after the addition of the CHCl$_3$. Previous publications on the acetylation of hemicelluloses, using [emim]-based systems have previously used pyridine and/or iodine and/or LiCl (Ren et al. 2007b), as catalysts/acid scavengers. These reaction conditions have not led to full acetylation. One of the reasons for incomplete acetylation is that, as the acetylation proceeds the partially acetylated product starts to precipitate or form a gel in the IL, giving a heterogeneous system. The addition of CHCl$_3$ is hypothesized to resolubilize the partially acetylated xylans, allowing for full acetylation. This effect has been illustrated previously in a publication by (King et al. 2009a) where hydrophobic cellulose phosphite esters precipitate and need to be homogenized, prior to NMR analysis showing complete reaction.

It has also been shown that in certain reaction systems, if cellulose is functionalized with hydrophobic functionalities, the product typically precipitates at a certain DS value and variation of dosage of reagents typically does not change the DS (Xie et al. 2007). Precipitation in the solvent depends on the solubility of the polymer at a specific DS. If a co-solvent is added to those mixtures during the reactions, it is typical that one can drive the DS values to nearly 100 % (Gericke et al. 2011).

Addition of co-solvent not only decreases the viscosity of the IL-polysaccharide reaction system, but also re-solubilizes the partially modified material, thus providing a homogeneous reaction system.

The phenomena can also be described also with the help of solvatochromic parameters. However, one must be careful, because precise quantitative statements are difficult to make due to the different measurement techniques, different probe molecules and IL purity deviations. Taking cellulose as a model compound in IL systems one can make careful assumptions regarding the behavior of our IL/hemicellulose systems. It is clear that only strong hydrogen bond acceptor ($\beta > 0.8$) ILs are able to dissolve cellulose. Table 2 presents the solvatocromic parameters of the ILs used in our study or ILs similar to them.

In order to decrease the viscosity of the reaction media, the addition of co-solvent is also supported by solvatochromatic parameters. For example compounds, with high normalized empirical polarity (E_T^N) > 0.3 are miscible with cellulose-IL solutions. As a guide, co-solvents with low hydrogen-bond donor acidity ($\alpha < 0.5$) and high basicity ($\beta > 0.4$) can be added without causing precipitation (Gericke et al. 2012). Pyridine satisfies these criteria, assuming a suitable co-solvent in the IL-hemicellulose system used Table 2. For the CHCl$_3$ the normalized empirical polarity (E_T^N) is close to the suggested value and the hydrogen-bond donor acidity (α) value is in the suitable region.

Discussion of the [DBNH][OAc] reaction system

Full acetylation of both rye AX and spruce AGX in [DBNH][OAc] was also achieved in this solvent. At 5 weight % concentrations of xylan, the addition of a co-solvent was not necessary. The reagent Ac$_2$O was added in fourfold excess, compared to the monomer anhydro units. The reaction system uses the additional

Table 2 Solvatochromic parameters of ILs and of co-solvents used in IL systems

Ionic liquid		Solvatochromic parameters[a] Reference				
Cation	Anion	E_T^N	α	β	π*	
[emim]$^+$	[Me$_2$PO$_4$]$^-$	n.a.	0.51	1.0	1.06	(Fukaya et al. 2008)
[DBNH]$^+$	[CO$_2$Et]$^-$	–	0.64	1.11	1.04	(Parviainen et al. 2013)
Molecular Solvents						
Pyridine		0.302	0.0	0.64	0.87	(Marcus 1993)
CHCl$_3$		0.259	0.2	0.10	0.58	(Marcus 1993)

[a] E_T^N: normalized empirical polarity; α: hydrogen bond donor ability; β: hydrogen bond acceptors ability; π*: dipolarity/polarizability

DBN as a proton scavenger of the acetic acid, which is formed as a by-product. This forms new IL during the reaction. When the DBN was in excess compared to the Ac$_2$O (5:4 molar ratio), the reaction did not go to completion. Therefore the excess of Ac$_2$O compared to additional DBN was essential (see Table 1).

The biggest advantage of using the [DBNH][OAc] as the reaction media is that this system can be distilled (according to methods described (King et al. 2013)) in milder and consequently less expensive conditions. This is in comparison to the other ILs most commonly used for esterification of polysaccharides, such as [emim[OAc] (King et al. 2012).

Molecular weights (SEC and GPC)

The molecular weight of the acetylated rye AX and spruce AGX was measured to ensure no significant molecular weight degradation occurred during the esterification reaction. The Mn values from the measurements are in good agreement, showing some increase in the acetylated samples due to the added acetyl groups, which can result up to a molecular weight increase of 1.6 times the original in case of no molecular weight degradation. The polydispersity index of the acetylated xylans increased only slightly, which indicates that acetylated chains were proportional in length to the original samples. The calculated degree of polymerization (DP) for each sample are shown in Table 3, and are based on the number-average molecular weights measured on the respective SEC and GPC devices. The calculations are based on the average weight of an anhydro sugar unit for the native xylans, and the average weight of a fully acetylated anydro sugar unit in case of the acetylated samples. It is safe to conclude that no significant

molecular weight degradation took place during the acetylation reactions in the case of the rye samples. The spruce samples suffered a minor depolymerization resulting in a DP decrease of 25 %. Most importantly the acetylated spruce AGX still has a high DP and is still a polymer after the reaction. The mild DP loss during the acetylation of the spruce xylan indicates it to be more sensitive. This could be due to the more complex structure and originally a magnitude lower molecular weight of these hemicelluloses compared to the rye AX.

Important note is that, one must be careful when comparing these numbers, since the measurements were ran on two different instruments in two different solvents before and after the acetylation. The hydrodynamic volume of a sample is dependent on the type of solvent used, and the measured values of molecular weights are relative numbers compared to the standards in the specific solvent used for the measurements. Therefore quantitative comparison of the molecular weight cannot be made between two relative values from two different solvent systems. Thus the presented numbers are only indicative.

Film formation

It has been shown that CHCl$_3$ was a good solvent for fully acetylated AXs. To decrease the environmental impact of this step, dimethyl carbonate (DMC) was introduced for dissolution and film-casting of the products. After casting from DMC, the films had the similar desired appearance to those cast from CHCl$_3$, by being transparent and colorless (Fig. 5). As discussed above, the spruce AcAGX acetylated in [emim][Me$_2$PO$_4$] was not soluble in CHCl$_3$ or DMC.

Table 3 The degree of polymerization calculated based on the number-average molecular weights (DP_n) of the native and acetylated xylans

Type of xylan	Native DP_n[a]	IL system used	DP_n after acetylation[b]
Rye AX	1140	[emim][Me2PO4]	n.a.
		[DBNH][OAc]	1199
Spruce AGX	186	[emim][Me2PO4]	139
		[DBNH][OAc]	121

[a] Values measured on water based HPSEC.MALS.RI.UV

[b] Values were measured on a DMSO based PL-GPC 50 PLUS

Fig. 5 Picture of successfully cast films
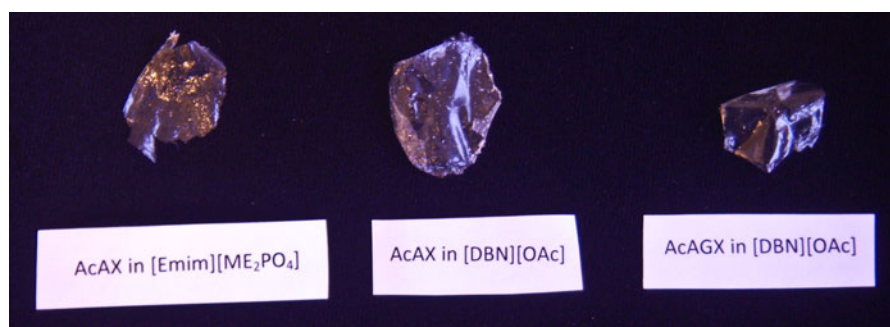
Conclusion

Full acetylation of rye and spruce xylans was achieved under well-defined conditions, in ionic liquids. This has previously not been reported in literature. The present work demonstrates reaction systems leading to complete acetylation in only a few minutes. Two new IL systems were used to modify xylans. One of them was [emim][Me2PO4] with CHCl3 as co-solvent, and the other one was [DBNH][OAc], with no co-solvent added.

Secondly, due to the diverse composition and structure of the spruce arabinoglucuronoxylan (AGX) so far such high degree of acetylation resulting in a soluble material was not achieved. This is the first report on the preparation of relatively high molecular weight and well-defined acetylated spruce xylan. This opens great potential in utilizing paper industrial side streams, such as black liquor, as a source of hemicellulose, as a raw material for novel value added bio-based plastics.

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