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Tosylation and acylation of cellulose in 1-allyl-3-methylimidazolium chloride

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Abstract Tosylation and acylation of cellulose were performed under mild reaction conditions using imidazolium based ionic liquids (ILs) as solvents. The non-degradative nature, lower viscosity, as well as higher solubility of cellulose in [amim]Cl encouraged us to carry out the reactions in this media. The reactions described here were optimised for this particular solvent in order to obtain different cellulose derivatives with high yields, homogeneity and degree of substitution (DS). Two reagents employed for the in situ activation of carboxylic acids were *N,N′*-carbonyldiimidazole (CDI) and 1-ethyl-3-(3′-dimethylaminopropyl)carbodiimide hydrochloride (EDCI). Final products were characterised by solution and solid-state NMR techniques.

Keywords 1-Allyl-3-methylimidazolium chloride · Cellulose · Cellulose modification · Ionic liquid · Synthesis of cellulose derivatives

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Introduction

The poor solubility of cellulose in common solvents is due to the strong inter- and intramolecular hydrogen-bonding network (Fig. 1) (Kondo 1997). It has been difficult to achieve a homogeneous solution of cellulose without using harsh conditions, which in turn often lowers the degree of polymerisation (DP). On the other hand, the hydrogen-bonding pattern also affects the reactivity of cellulose, and often the DS values achieved from heterogeneous modifications reactions have ranged from poor to moderate.

Recent publications on the dissolution and chemical modification of cellulose in binary solvent systems, such as dimethylsulfoxide/tetrabutylammonium fluoride (DMSO/TBAF) or dimethylacetamide/lithium chloride (DMA/LiCl) (Heinze et al. 2000, 2003; Liu and Baumann 2002; Rahn et al. 1996; Krouit et al. 2006), have opened new possibilities for

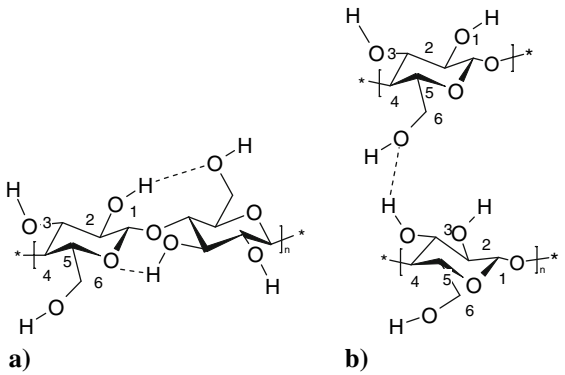
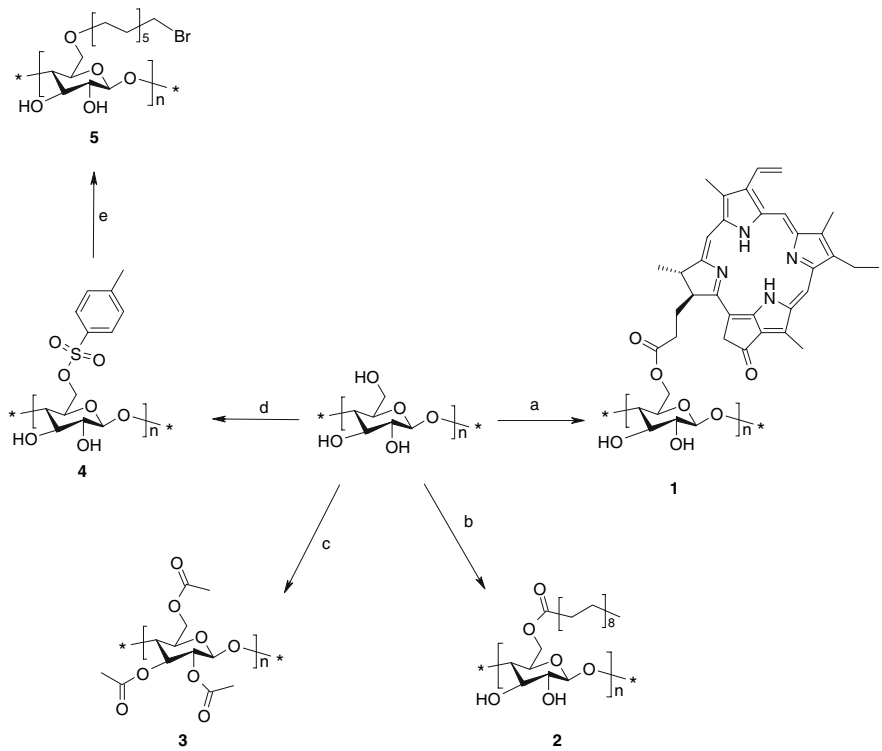


Fig. 1 Cellulose structure showing (**a**) the intramolecular hydrogen bonding between C2-OH and C6-OH and C3-OH with endocyclic oxygen, and (**b**) the intermolecular bonding between C3-OH and C6-OH (Krässig 1993)

the cellulose modification. Also, N-methylmorpholine N-oxide (NMMO) has also been shown to be an efficient solvent for cellulose (Eastman Kodak 1969). It is commercially utilised in the lyocell process to produce fibres (Heinze and Liebert 2001a).

Gentle and simple dissolution process provided by ionic liquids (ILs), as well as their inert nature provides efficient means for the synthesis of cellulose derivatives. Both 1-butyl-3-methylimidazolium chloride [bmim]Cl and 1-allyl-3-methylimidazolium chloride [amim]Cl have shown to be good solvents for the cellulose (Swatloski et al. 2002; Zhu et al. 2006).

Recent reports on the dissolution of cellulose in ILs (Heinze et al. 2005; Myllymäki and Aksela 2005; Wu et al. 2004) inspired us to screen and optimise the synthesis of some useful cellulose derivatives with [amim]Cl as a reaction media (Scheme 1). The non-degradative nature, lower viscosity, as well as the higher solubility of cellulose in [amim]Cl, prompted us to carry out the synthesis in this media. The majority of publications regarding the chemistry of cellulose have quoted the use of microcrystalline cellulose (Avicel® PH-101), which is relatively soluble into traditional cellulose solvents, such as DMSO/TBAF (Heinze et al. 2000, 2003; Liu and Baumann 2002; El Seoud et al. 2000; Regiani et al. 1999; Hussain et al. 2004). In the present study, we have used microcrystalline cellulose as a starting material and optimised tosylation in a way that the DS close to 1 could be achieved in [amim]Cl, and thus avoid the use of protection group chemistry in subsequent nucleophilic displacement reactions. This simplifies synthesis



Scheme 1 General synthetic route to cellulose derivatives: (a) [amim]Cl, *pyro*-pheophorbide *a*, CDI (b) [amim]Cl, EDCI, Stearic acid, Et_3N (c) [amim]Cl , pyridine, acetic acid anhydride (d) [amim]Cl, tosyl chloride, pyridine (e) DMF, Et_3N, 11-bromoundecanol

pathways considerably. Also acylation reactions using in situ activation were carried out in [amim]Cl using either *N,N′*-carbonyldiimidazole (CDI) or 1-ethyl-3-(3′-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) as activating agents. In these reactions, DS values can be controlled, as before (Rahn et al. 1996), by adjusting the molar ratio between the reagent to AGU. Furthermore, possible aspects affecting DS values in in situ activation methods are also discussed. The reactions presented here can be easily adopted to produce a range of cellulose derivatives.

Experimental

Materials

Microcrystalline cellulose (Aldrich) was dried in vacuum oven at 60 °C for 24 h prior the use. All reactions were carried out under argon atmosphere. Tosyl chloride, stearic acid, pyridine, triethylamine and acetic acid anhydride were purchased from Aldrich, Fluka and J. T. Baker and used without further purification.

[amim]Cl was synthesised according to Zhang et al. (2005) with slight modification to their procedure; both allyl chloride (Aldrich) and 3-methylimidazole (Aldrich) were distilled prior to use. [amim]Cl was further purified, to remove trace colour, by dissolving the crude [amim]Cl mixture in water and refluxing with activated charcoal (18 h). The solution was filtered through celite plug and the water was removed by distillation and dried for 2 days in vacuo to yield [amim]Cl as a pale yellow crystalline solid with a melting point of 52 °C.

The chlorophyll was extracted from green leaves and modified according to reference (Kavakka et al. 2007; Iriyama et al. 1979).

NMR spectra (^{1}H, ^{13}C, ^{1}H–^{13}C HSQC, ^{1}H–^{13}C HMBC, ^{1}H–^{1}H COSY and ^{1}H–^{1}H TOCSY) were measured with Varian Inova 500 MHz NMR spectrometer in DMSO-d_6 or $CDCl_3$. CP–MAS–NMR spectra were measured on Varian Inova 300 MHz NMR spectrometer. IR spectra were recorded with PE Spectrum One (ATR) FT-IR spectrometer. UV–VIS spectra were recorded on a UV–Vis–NIR Varian Cary 5E spectrophotometer. Rheological measurements were carried out by TA instruments AR2000 stress controlled rheometer using steel plate geometry with diameter of 20 mm. In order to remove thermal and loading history, the cellulose samples were first heated at 150 °C and presheared at 10 1/s shear rate for 10 min.

Typical cellulose dissolution process in [amim]Cl

Cellulose was dissolved in [amim]Cl by stirring at 60 °C for 2 h under an argon atmosphere. All the further reactions were carried out under inert atmosphere.

Typical workup procedure for the derivatives

Cellulose derivatives were regenerated either from ice cold water, methanol or ethanol (depending on the solubility of the final product). The precipitate was filtered off, washed with excess of water, methanol or ethanol. Further purification was done by continuous extraction with the methanol or water and dried in vacuo.

Esterification of cellulose with *pyro*-pheophorbide a with CDI (**1**)

Pyro-pheophorbide *a* (0.02 g, 3.75×10^{-5} mol) was dissolved in [amim]Cl (1.0 g), under an argon atmosphere. CDI (0.04 g, 2.47×10^{-4} mol) was added in one portion. The mixture was heated with stirring, at 60 °C for 24 h. Cellulose (0.02 g, 1.23×10^{-4} mol) was dissolved in [amim]Cl (1.0 g). The cellulose solution in [amim]Cl was added into the imidazolide solution in one portion and the reaction mixture was stirred at 60 °C for further 24 h, followed by the workup procedure. Yield: 0.02 g (83%) DS = 0.07 (determined by ^{1}H NMR).

^{1}H NMR (300 MHz, 27 °C, $CDCl_3$): δ = 1.4 (H-8^2), 1.8 (H-18^1), 2.8/2.9 (H-17^1), 3.3 (H-7^1), 3.4 (H-5′), 3.7 (H-12^1), 3.9 (H-8^1), 4.1 (H-6), 4.2 (H-6^1), 4.5 (H-1), 4.6 (H-2), 5.3 (H-13^2), 5.4 (H-3), 6.2 (H-3^2), 8.0 (H-3^1), 8.6 (H-20), 9.4 (H-5), 9.6 (H-10).

IR (cm^{-1}): 3422 (OH), 3110 (aromatic), 1690 (C=O), 1466 (C–O), 650 (aromatic).

UV–VIS (λ_{max}, nm): 416, 669.

Esterification of cellulose with stearic acid using EDCI (**2**)

Stearic acid (2.67 g, 9.4 mmol) was dissolved in [amim]Cl (2.0 g) under an argon atmosphere. EDCI (1.8 g, 9.4 mmol) and Et_3N (catalytic amount) were added. The solution was heated and stirred at 60 °C for 24 h to obtain the activated carboxylate. Cellulose (0.3 g, 1.85 mmol) was dissolved in [amim]Cl (5.0 g) and added to the activated stearic acid solution in one portion. The reaction mixture was stirred at 60 °C for a further 24 h, followed by the workup procedure. Yield: 0.35 g (89%) DS = 0.16 (determined by elemental analysis).

^{13}C NMR (75 MHz, 27 °C, $CDCl_3$): δ = 14.1 (C-15), 20.7 (C-12, C-10), 22.9 (C-14), 24.4 (C-9), 29.8 (C-13), 32.1 (C-9), 35.5 (C-8), 62.1 (C-6), 72.1 (C-2, C-3, C-5), 77.5 (C-4), 101.2 (C-1), 173.1 (C-7).

IR (cm^{-1}): 3338 (OH), 3010 (CH_2), 2905 (CH_2), 1710 (C=O), 1646 (C–O).

Synthesis of triacetylcellulose (**3**)

Cellulose (1.0 g, 6.2 mmol) was dissolved in [amim]Cl (10.0 g). Acetic anhydride (5.0 mL, 0.05 mol) and pyridine (5.0 mL, 0.06 mol) were added in one portion. The solution was stirred at RT for 2 days, followed by the workup procedure. Yield: 2.0 g (96%) DS = 2.99 (determined by elemental analysis).

^{1}H NMR (300 MHz, 27 °C, DMSO-d_6): δ = 1.88 (H-8 at C-3), 1.9 (H-8 at C-2), 2.1 (H-10), 3.68 (H-5), 3.85 (H-4), 4.02 (H-6′), 4.22 (H-6), 4.52 (H-2), 4.68 (H-1), 5.08 (H-3).

IR (cm^{-1}): 1752 (C=O).

Structure was confirmed by 2D experiments: HSQC, COSY and TOCSY.

Synthesis of tosylcellulose (**4**)

Cellulose (1.0 g, 6.2 mmol) was dissolved in [amim]Cl (10.0 g). The solution was cooled to 10 °C and tosyl chloride (3.8 g, 20 mmol) in pyridine (2.8 mL, 36 mmol) was added dropwise. The reaction mixture was stirred for 2 days followed by the workup procedure. Yield: 1.72 g (95%) DS = 0.84 (determined by elemental analysis).

^{1}H NMR (300 MHz, 27 °C, DMSO-d_6): δ = 2.35 (H-11), 3.5 (H-5), 3.8 (H-4), 4.1 (H-6), 4.3 (H-1), 4.6 (H-2), 5.5 (H-3), 7.4 (H-9), 7.7 (H-8).

CP–MAS–NMR (75 MHz): δ = 22.1 (C-11), 62.1 (C-6), 73.4 (C-2, C-3, C-5), 82.2 (C-4), 103.4 (C-1), 138.8 (C-9, C-10), 145.6 (C-7, C-8).

IR (cm^{-1}): 3475 (OH), 3057 (aromatic), 1607 (C–O), 1410 (OSO_2), 1390 (OSO_2), 802 (aromatic).

Structure was confirmed by 2D NMR experiments: HSQC, COSY and TOCSY.

Etherification of tosylcellulose with 11-bromoundecanol (**5**)

A mixture of tosylcellulose (1.0 g, 1.6 mmol), Et_3N (0.8 g, 8.0 mmol) and 11-bromoundecanol (2.0 g, 8.0 mmol), in DMF (20.0 mL), was stirred at 50 °C for 3 days, followed by the workup procedure. Yield: 1.61 g (95%) DS_{Tos} = 0.11 DS_{alkyl} = 0.73 (determined by elemental analysis).

^{13}C NMR (75 MHz, 27 °C, DMSO-d_6): δ = 20.2 (C-13), 29.5 (C-8), 33.3 (C-8), 35.3 (C-9), 60.1 (C-6), 72.3 (C-2, C-3, C-5, C-7), 78.3 (C-4), 101.2 (C-1), 127.5 (C-12), 131.2 (C-11).

CP–MAS–NMR (75 MHz): δ = 20.1 (C-13), 34.5 (C-8, C-9), 61.2 (C-6), 72.2 (C-2, C-3, C-5, C-7), 82.3 (C-4), 102.3 (C-1), 131.3 (C-11, C-12).

IR (cm^{-1}): 3422 (OH), 2920 (CH_2), 2850 (CH_2), 1466 (C–O), 725 (CH_2).

Results and discussion

Dissolution of cellulose in [amim]Cl

In a previous study by Swatloski et al. (2003) microwave irradiation was used to speed up the dissolution process of cellulose into ILs. However, in our hands, the microwave assisted dissolution process was difficult to handle in small scale, often resulting in pyrolysis or partial degradation. Especially, this proved to be a problem when >5% cellulose solutions in ILs were prepared using microwave irradiation. Therefore, we adopted a more practical approach, which was simply to use a mechanical stirrer at constant temperature (max. 70 °C) under argon atmosphere using [amim]Cl. At these temperatures, it was also possible to carry out the dissolution using

a magnetic stirring bar. With mechanical stirring, high molecular weight microcrystalline cellulose was dissolved in [amim]Cl at concentrations of 5% (w/w) in about 2 h. However, the complete dissolution of samples with high concentrations (up to 40% (w/w)) takes place in two weeks. The complete dissolution was confirmed by optical microscopy and viscosity measurements.

With macromolecules, the efficiency and reproducibility of modification reactions are usually highly dependent on the viscosity of the solution. To access this, the flow properties of the cellulose solutions in [amim]Cl with concentrations of 10, 15, 22, 35 and 40% (w/w) were measured. At 100 °C, the solutions with cellulose content above 15% (w/w) are shear thinning, which means that the viscosity is decreased as the applied shearing stress increases (pseudoplastic behaviour) (Fig. 2). The solutions of 10 or 15% (w/w) show Newtonian behaviour (Fig. 2) as the viscosities are not affected by the shear rate. In all, this behaviour is typical to that of high molecular weight macromolecules. Due to the viscosity behaviour of the solutions, it is important to take the effect of the cellulose concentration under consideration when carrying out modification reactions on cellulose. It can be concluded that cellulose modification reactions in [amim]Cl should be carried out with relatively low (<10% w/w) concentrations in order to enable the free movement of cellulose chains in the solution.

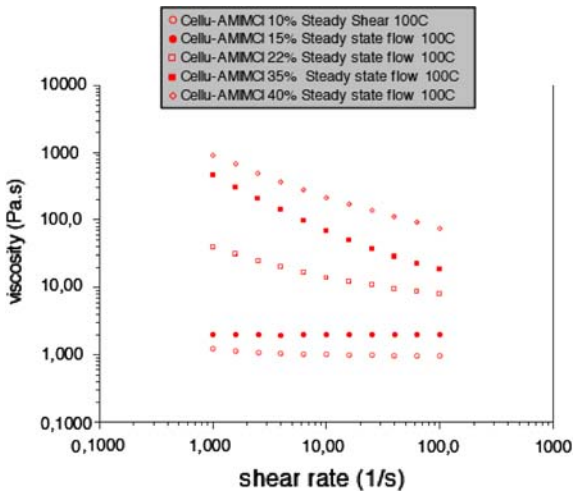


Fig. 2 Flow curves of the cellulose solutions in [amim]Cl with concentrations of 10, 15, 22, 35 and 40% (w/w)

Tosylation

The *p*-toluenesulfonyl (tosyl) group is commonly used as a leaving group in nucleophilic substitution (S_N) reactions making it a practical intermediate for subsequent cellulose modification reactions (Heinze et al. 1996; Einfeldt et al. 2002; Heinze et al. 2001b; Mais et al. 2000; Koschella and Heinze 2003). In this work, the goal was to optimise the reaction in [amim]Cl in a way that the DS of close to 1 (i.e. in C6-OH) could be achieved, and thus avoid the use of the protecting group chemistry. This simplifies synthesis pathways considerably.

Homogeneous reaction yielding tosylated cellulose was carried out by allowing cellulose to react with tosyl chloride in [amim]Cl in the presence of either triethylamine or pyridine as a base. Previously, tosyl cellulose has been prepared under homogeneous reaction conditions in DMA/LiCl giving similar results as our reaction carried out in [amim]Cl. This intermediate has been used as a starting material in reactions with a wide variety of nucleophiles such as chloride, bromide, iodide (McCormick and Callais 1987) and different mono-, di-, tri- as well as chiral amines (Koschella and Heinze 2001; Heinze et al. 2001b; Kern et al. 2000).

Subsequent S_N reactions on tosylated cellulose have some limitations if reactions are carried out on tosyl cellulose with DS value of greater than 1. Due to steric reasons, nucleophiles tend to be fairly selective towards to the C-6 and hence, leaving the remaining tosyl groups intact at the positions C-2 and C-3. These remaining tosyl groups may enhance the solubility of the final product, or they could be removed by hydrolysis or by additional reduction step (Liu and Baumann 2002). In principle, it was possible to carry tosylation of cellulose at least up to DS of 1.4 in [amim]Cl solutions. However, if the degree of tosylation was higher than $\sim$0.84, also position C2-OH was partially substituted. Consequently, the subsequent reactions were carried out with tosylated cellulose with DS = 0.84.

In [amim]Cl the degree of tosylation can be varied by changing the molar ratio of the tosyl chloride to AGU. This has also been the case when the reaction has been conducted in DMA/LiCl solvent system (Heinze and Rahn 1997). It is also known that primary alcohols react most rapidly, and it is often possible to sulphonate selectively a primary OH

group in a molecule that also contains secondary or tertiary OH groups.

Crucial aspects in the tosylation of cellulose in [amim]Cl were the reaction temperature and the base. When the reaction was done at room temperature, the obtained yield was extremely poor compared to that of the reaction prepared at 10 °C, which improved the yields notably. It has already been reported for DMA/LiCl, that by carrying out the reaction either at RT or at elevated temperatures, an undesirable side-reaction (chlorination) can take place (Liu and Baumann 2002). From commonly used bases, pyridine turned out to work efficiently, and the optimal molar ratio between the AGU and pyridine was 1:6. In [amim]Cl solutions of cellulose, the tosylation reaction did not proceed at all when triethylamine was used as a base, possibly because at higher concentrations triethylamine was not fully miscible with [amim]Cl. The addition of DMA as a co-solvent did not improve the situation.

According to the ^{1}H–^{13}C HSQC spectrum, the C6-OH groups were tosylated as there was no signal at ^{13}C δ of 59.4 ppm, but the corresponding signal has shifted to 69 ppm. This is in good agreement with obtained DS value of 0.84. Also from 2D NMR spectrum it was obvious that the chlorination side reaction has not taken place at C-6 as there was no correlation at ^{13}C shift of 59 ppm. Evidence of the selective tosylation at C-6 position can also been confirmed by looking at the C-1 shift. Only one signal for the C-1 carbon can be seen at 102 ppm without any other signals in the same region. Also, the value of the chemical shift is typical to that of the C-1 shift of unsubstituted cellulose. If the DS value is greater than 1, two separate signals for C-1 can be seen having chemical shift values of 100 ppm (C-1) and 98 ppm (C-1′). The 98 ppm shift is caused by the substituent also at C-2 position.

After tosylation, the product with DS of close to 1 was soluble in organic solvents, such as DMF, which is known to enhance nucleophilic substitution reactions. To explore the efficiency of the subsequent nucleophilic substitution reaction, a further modification of freshly tosylated cellulose with 11-bromoundecanol was carried out. The reason for choosing the 11-bromoundecanol as a nucleophile in the subsequent reaction was the possibility to continue further with additional reactions once attached at C-6 of cellulose backbone. These further modification reactions are currently under investigation. Another advantage is that the bromine atom also enables accurate results from the elemental analysis for the DS determination. By carrying out the reaction with fairly unreactive long chain alkyl alcohol, one can really see the efficiency of the displacement reaction done on tosyl cellulose. However, despite of excessive attempts, it was not possible to fully substitute the tosyl groups even with extended reaction times. Therefore, both DS_1 and DS_2 for the alkylated cellulose were determined. $DS_1 = 0.11$ is the value for the tosyl substituent, whereas $DS_2 = 0.73$ stands for the alkyl substituent. This was a good indication of the importance of the reactivity of the nucleophile, and hence when structurally more demanding groups were used, it was decided to carry out the modification reactions by using the in situ activation approach.

Acylation

It has been previously reported that acylation of cellulose can be efficiently carried out by acid anhydrides or acid halides, and that some ionic liquids themselves can function as reaction media and catalysts for these reactions, in place of a base (Zhu et al. 2006; Barthel and Heinze 2006). However, in our hands, only moderate DS could be achieved when carrying out the reaction in the absence of base. In addition, without a scavenger for the released acid, acetylation led into partial degradation of the cellulose chain. In the presence of pyridine, the acylation reaction of cellulose with acid anhydrides in [amim]Cl proceeded with high yield producing completely acetylated cellulose with DS of 2.99. The acetylation reaction also proceeded efficiently with other cellulose derivatives (e.g. tosylated cellulose). In all cases, all the remaining hydroxyl functionalities could be acetylated completely. In fact, this proved to be an efficient way to determine the DS by NMR, as well as reaction patterns of other modification reactions. After acetylation, samples were, in most of the cases, soluble in chloroform, and yielded high-resolution ^{1}H NMR spectra, which could easily be integrated providing direct measures for substitution patterns and DS. The efficiency of the acetylation reaction can also be conveniently verified from IR data. However, the use of anhydrides for acylation reaction is usually limited to small symmetrical anhydrides, such as acetic anhydride (i.e. acetylation).

An interesting pathway for cellulose ester preparation is homogeneous acylation after in situ activation of carboxylic acids with tosyl chloride (Heinze et al. 2003; Srokova et al. 2004), *N,N′*-carbonyldiimidazole (CDI) (Hussain et al. 2004) or *N,N*-dicyclohexylcarbodiimide (DCC) (Samaranayake and Glasser 1993). In the activation method, the acylation is carried out by an activated ester which is generated in situ from the corresponding carboxylic acid with an activating agent. We explored the use of acid-free activation provided by CDI and a new activator for the cellulose modification, 1-ethyl-3-(3′-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) in [amim]Cl. The efficiency of this approach in [amim]Cl either with CDI or EDCI was demonstrated with large substituents such as stearic acid and with a bulky *pyro*-pheophorbide *a*. In both cases, these reactions proceeded with relatively high DS subject to the size of the substituent (maximum DS values were 0.16 and 0.07, respectively). It should also be noted that cellulose is extremely poor nucleophile and that the reactions were carried out without the use of auxiliary nucleophiles. Under these reaction conditions, degradation of cellulose was not observed. According to ^{13}C NMR spectra, in both cases the substitution reactions took place mainly at C-6 position, which is not surprising considering the reactivity differences between the hydroxy groups as well as steric factors.

In spite of successive trials with different in situ activation methods, and increasing the molar ratio between the substituents to AGU, we were not able to get higher DS values in [amim]Cl with the tested large substituents. Even when large excess of stearic acid (5 eq.) was used, the maximum DS of 0.16 was obtained. It should also be noted here that small scale synthesis with ILs is relatively cumbersome due to the difficulties in sample handling and in the extraction step.

In the reaction with *pyro*-pheophorbide *a*, CDI was used as an activating agent whereas with stearic acid EDCI was employed. In both cases, the molar ratio between CDI or EDCI to corresponding carboxylic acid was kept equal. To see if our conclusion about the possible hydrolysis of the non-reacted activating agent in [amim]Cl was accurate and hence affecting the DS, the amount of either CDI or EDCI was increased from 1 equivalent to 2, but the result was no different.

In the carboxylic acid activation by EDCI, triethylamine is needed to enhance the nucleophilicity of the free carboxylic acid. In this reaction, the immiscibility of triethylamine with [amim]Cl was not an issue, as triethylamine was used only in catalytic amounts. Generally, when the carboxylic acid reacts with C=N double bond of EDCI, *O*-acyl isoureas are obtained which are then further reacted with nucleophiles to obtain esters (Bruckner 2002). However, when the reaction is carried out with poor nucleophiles such as with cellulose, side reaction takes place. Cellulose reacts with *O*-stearyl isourea so slowly that the latter starts to decompose. This unwanted intramolecular side reaction yields to *N*-stearyl urea product which is no longer acylating agent. We assume that this is the main cause for the observed relatively low DS values. In the literature, acylation of cellulose with long chain fatty acids, such as lauroyl chloride in ILs yielded in various DS values starting from 0.34 up to 1.54 depending on the acyl chloride/AGU molar ratios (Schlufter et al. 2006). Even though, fully substituted (e.g. DS = 3) derivatives were not obtained (Schlufter et al. 2006), the DS values were considerably higher than ones obtained by us employing the activation method.

Conclusions

In the present work, we have carried out tosylation and acylation reactions for microcrystalline cellulose in [amim]Cl. Tosylation reaction yielded DS of ≈ 1, which is practical when considering subsequent selective nucleophilic displacement reaction at position C-6 from the tosylated intermediate. Acylation reactions were carried out either using activated esterification through selected peptide coupling reagents (CDI or EDCI), or by acetylating with acetic acid anhydride. Furthermore, it has been demonstrated that structurally demanding or functionalised substituents can be introduced to cellulose. We have shown that it is possible to synthesise high molecular weight cellulose covalently bonded to a chlorophyll derivative, in one chemical step. This novel material could be seen as a key intermediate for a fully bio-organic light harvesting antenna.

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