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# Interactions of Ionic Liquids with Polysaccharides – 2: Cellulose

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**Summary:** Some general comments about ionic liquids (ILs) and carbohydrates are given. The main scope of the review is to discuss the present state of the art of chemical modification of cellulose applying IL as reaction media considering own research results. ILs, namely 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-ethyl-3-methylimidazolium chloride (EMIMCl), 1-butyl-2,3-dimethylimidazolium chloride (BDMIMCl), 1-allyl-2,3-dimethylimidazolium bromide (ADMIMBr) and 1-ethyl-3-methylimidazolium acetate (EMIMAc) are solvents for cellulose (even for high molecular bacterial synthesized cellulose) and can easily be applied as reaction media for cellulose modification. We investigated the homogeneous acylation, carbanilation and silylation of the biopolymer cellulose. Under mild conditions and within short reaction time at low temperature (65 °C to 80 °C) and low excess of reagent, various cellulose esters and carbanilates, dendronized cellulose and trimethylsilyl cellulose were obtained. The DS of the cellulose derivatives can be controlled by varying the reaction time, reaction temperature and the IL used as reaction medium.

**Keywords:** carbohydrate; cellulose; cellulose esters; cellulose ethers; dendronized cellulose; ionic liquid

## Introduction

Ionic liquids are low-melting salts, thus forming liquids that consist only of cations and anions. Today, a salt melting below the boiling point of water is known as an ionic liquid (IL). Several synonyms including ionic fluid, molten salt, fused salt, or neoteric solvent are used to describe this type of solvents. Interest in developing and investigating the properties and applications of ILs in many fields of science and technology has been intensified as a result of introduction of the principles of green chemistry. Briefly, this approach sets guidelines designed to secure sustainable development, while increasing process biocompatibility and economy; with emphasis on an increase in, and/or upgrading of: [1–3]

- Process economy, by preventing waste generation. This represents a much superior approach to waste treatment;
- Atom economy, by incorporating all reagents employed in the final product. This also contributes to reduction and/or elimination of waste;
- Process safety, e.g., by using non-toxic, non-inflammable solvents and reagents;
- Process efficiency, e.g., by material recycling into the process; use of catalytic pathways; use of catalysts that can be regenerated and/or recycled; rational

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use of energy, and reduction of the number of intermediate steps;

- Environmental compatibility, by employing chemicals from renewable sources, and producing biodegradable end products.

These principles call for thorough understanding the roles of all components of the chemical reaction/process including solvent or solvent mixture employed. In this context the use of the renewable resource cellulose and IL exactly meets the requirements of "green chemistry". For readers more interested in the field of IL, there are several review articles on the synthesis, properties and applications of ionic liquids, including in carbohydrate chemistry.[4–13] The aim of this contribution is to discuss the present state of the art of chemical modification of cellulose applying ILs considering in particular own research results.

## Types, Synthesis and Properties of IL

Figure 1 shows the structure of cations and anions of ILs most extensively employed. Most ILs are quaternized nitrogen compounds; their synthesis includes two distinct steps: The first one (Mentschutkin reaction) is an $S_N$ reaction, yielding a halide, i.e., an IL-precursor. The second step (Finkelstein reaction) consists, in most cases, of metathesis of the halide counter-ion; leading to "second generation" ILs with bulky anions including $BF_4^-$, $PF_6^-$, $(H_3CSO_2)_2N^-$, and $(F_3CSO_2)_2N^-$.[4,9,14,15]

A nice example is a carbohydrate-based IL, which is synthesized according to reaction scheme shown in Figure 2. The products are liquids, and are similar to their imidazolium-based counterparts regarding physical properties like viscosities and miscibilities with water and classical solvents, and in performance as solvents in the Heck reaction between methyl acrylate and iodobenzene.[16]

Depending on the method of synthesis, impurities of the IL are tertiary amine, alkyl halide or alkyl sulfate or their side-reaction products, and, after metathesis, residual halide or sulfate. Methods of purification include extraction of the IL with polar solvents, e.g., ethyl acetate, extraction of the aqueous solution of IL with an immiscible organic solvent, e.g., dichloromethane; flash column chromatography of a solution of IL in an organic solvent, or

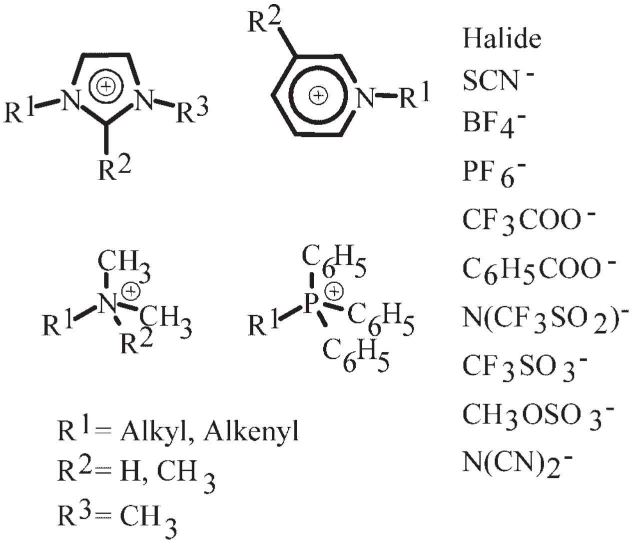


***Figure 1.***
Structures of typical ionic liquids.

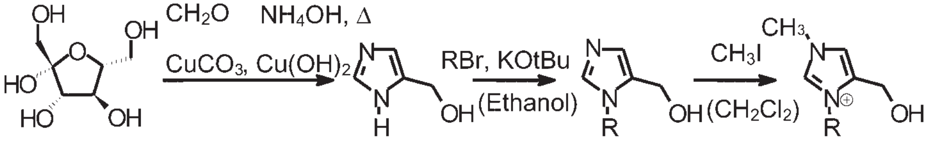


**Figure 2.**
Reaction scheme for the preparation of carbohydrate-based ionic liquid (R = n-butyl).

treatment of the latter solution with activated charcoal.[16] At present, an increasing number of purified IL become commercially available that is an important prerequisite to understand reactivity of the dissolved compound as carbohydrates.

Moreover, increased IL viscosity hinders carbohydrate swelling and hence subsequent dissolution. Residual water in the IL may lead to several undesired side reactions. The presence of adventitious water in IL may even render the carbohydrate like cellulose insoluble. Whereas 3–10 wt% cellulose solutions in 1-butyl-3-methylimidazolium chloride (BMIMCl) may is easily obtained, the biopolymer was not soluble in the same IL in the presence of 1% water (corresponding to 0.5 mol fraction water).[18] Since water affects the aggregation state of dissolved cellulose, it also affects its reactivity.[19–22] Additionally it consumes reagent employed, acyl halide, carboxylic acid anhydride and sulfonyl chloride. The acid liberated, especially HCl, may decrease the degree of polymerization (DP) of the polymer or may decrease the degree of substitution (DS) of the product due to acid-catalyzed ester hydrolysis. Some anions, in particular $[PF_6^-]$

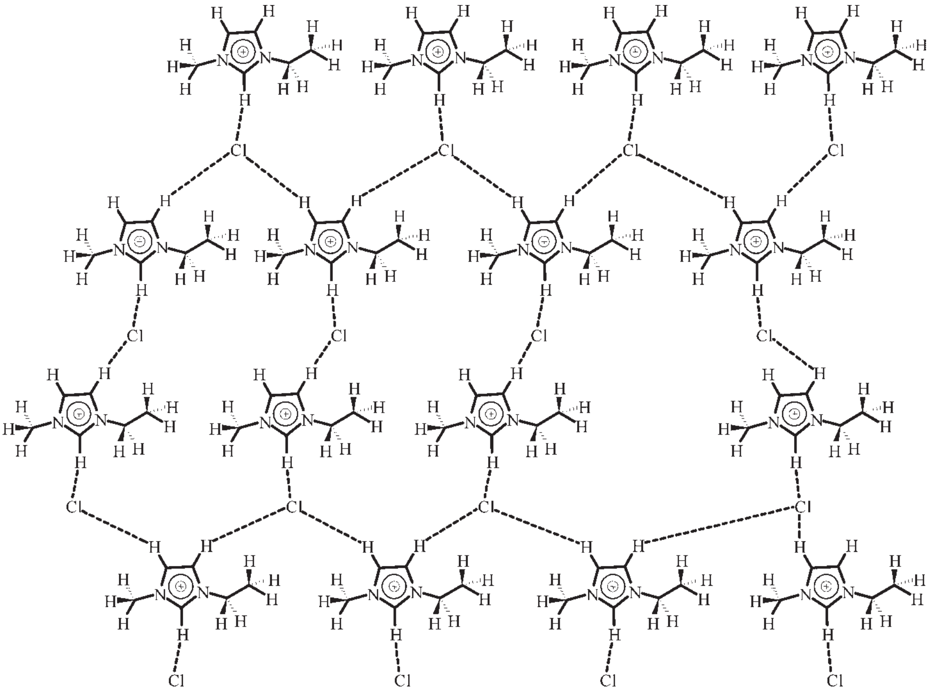


**Figure 3.**
Schematic representation of hydrogen-bonding in a typical EMIMCl (redrawn from Dong et al.[27]).

and [$BF_4^-$] hydrolyze (by residual water) at the relatively high temperatures employed for carbohydrate dissolution/functionalization and *vice versa*, liberating HF; this may affect both DP and DS adversely. Hydrolysis of these anions at room temperature, e.g., during extraction of the aqueous IL solution with an immiscible organic solvent has been referred to.[23] In summary, the purity of the IL employed for carbohydrate dissolution/functionalization should not be overlooked.

A limitation of the use dimethyl sulfoxide (DMSO) in combination with tetrabutylammonium fluoride, a novel efficient solvent for cellulose [24,25] is Hofmann degradation of the electrolyte upon heating.[26] To our knowledge, there are no reports on a similar degradation of, e.g., BMIMCl, probably because the chloride ion, acting as a base, is not "naked", but is efficiently "solvated" via hydrogen-bonding to H2 and H4 of the imidazolium cation, as shown in Figure 3.[27]

## Unexpected Reactions in ILs

It must be pointed out that 1-ethyl-3-methylimidazolium acetate (EMIMAc) may not exclusively act as a solvent during the modification of cellulose but also as a reagent. Thus, the reaction of cellulose with esterifying- and etherifying agents including 2-furoyl chloride, *p*-toluenesulfonyl chloride, and triphenylmethyl (trityl) chloride with EMIMAc results in the formation of mixed anhydrides and trityl acetate, which does not react with the biopolymer to the expected cellulose derivative, but to cellulose acetate (Figure 4). The results indicate that the formation of the mixed anhydride applying 2-furoyl chloride proceeds faster than the formation of the intermediates from *p*-toluenesulfonyl chloride and trityl chloride, which should be studied by kinetic experiments applying NMR spectroscopy. Moreover, the IL will partly transferred to the chloride.[28]

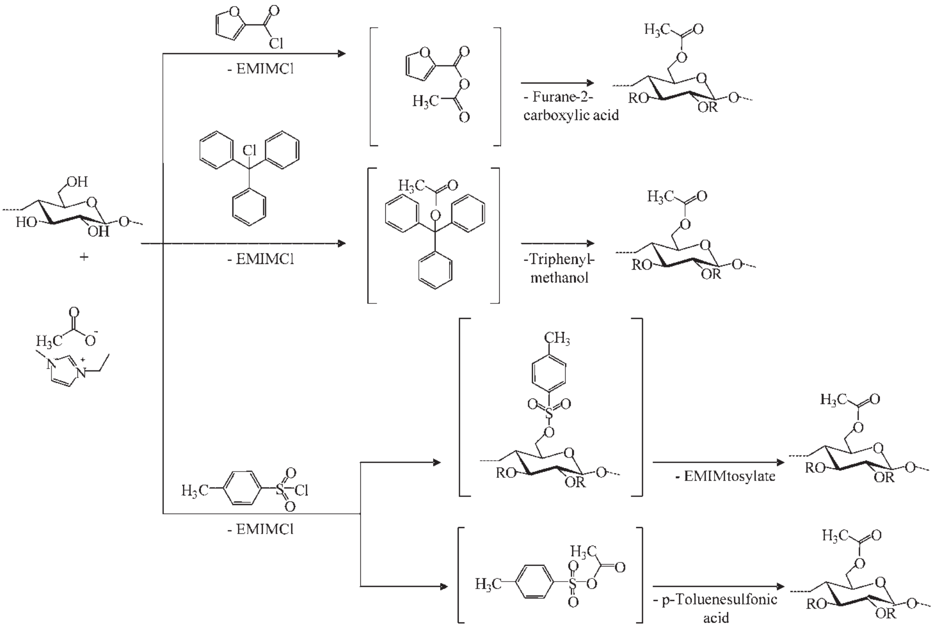


**Figure 4.**
Typical synthesis path leading to cellulose acetates in EMIMAc/cellulose (R = acetyl group or H depending on the degree of substitution) as a result of the conversion of the biopolymer with 2-furoyl chloride, triphenylmethyl chloride, and p-toluenesulfonyl chloride.

For example, a treatment of cellulose dissolved in EMIMAc with trityl chloride yields cellulose acetate with a DS of 0.75. The reactive intermediate was synthesized and studied by means of $^{13}$C NMR spectroscopy (Figure 5). New peaks for a carbonyl moiety at 168.7 ppm (C-2), for C atoms of the phenyl ring at 148.3 ppm (C-4) and 130.0-127.0 ppm (C-5-7), for the triphenyl substituted methyl moiety at 89.0 ppm (C-3), and for the methyl function of the converted acetyl group at 22.5 (C-1) ppm were observed. These chemical shifts and the splitting pattern correspond to the formation of reactive trityl acetate during the reaction of trityl chloride with EMIMAc. Obviously, the reactive ester of the voluminous trityl carbinol is well suited for transesterification reactions towards the cellulose acetate.

It should be mentioned that the conversion of cellulose dissolved in BMIMCl with trityl chloride using pyridine as base yields the expected cellulose ether.[29] The influences of reaction time and the ratio of trityl chloride to cellulose control the DS. However, the reaction is not as efficient as the preparation of trityl cellulose applying the solvent DMA/LiCl.

## Esterification of Cellulose Applying IL as Reaction Medium

In the course of our studies about cellulose solvents various IL are included. It was found that not only 1-butyl-3-methylimidazolium chloride (BMIMCl) but also 1-ethyl-3-methylimidazolium chloride (EMIMCl), 1-butyl-2,3-dimethylimidazolium chloride (BDMIMCl) and 1-allyl-2,3-dimethylimidazolium bromide (ADMIMBr) are promising reaction media (Figure 6).

To investigate the reactivity of the cellulose dissolved in IL, the acylation with several acid chlorides and acid anhydrides was studied. Highly substituted cellulose derivatives were obtained by applying acetyl chloride, pentanoyl chloride, hexanoyl chloride and benzoyl chloride (Figure 7).

Within 2 h at 80 °C in BMIMCl, cellulose derivatives with different DS in the range of 0.8 to 3.0 were obtained. Next to acetyl chloride, pentanoyl chloride and benzoyl chloride were the most efficient agents studied. Hexanoyl chloride is less reactive in BMIMCl, but an increase of the amount of hexanoyl chloride leads to highly substituted products. This type of reaction

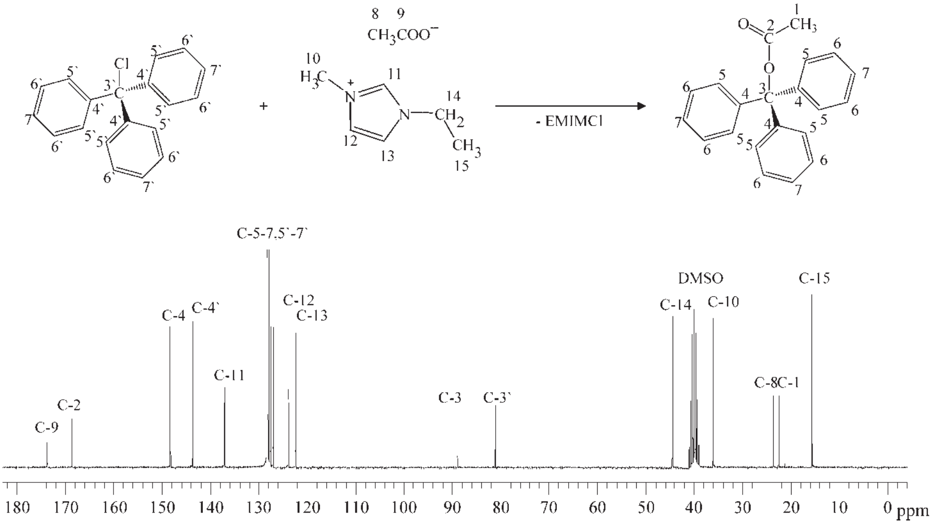
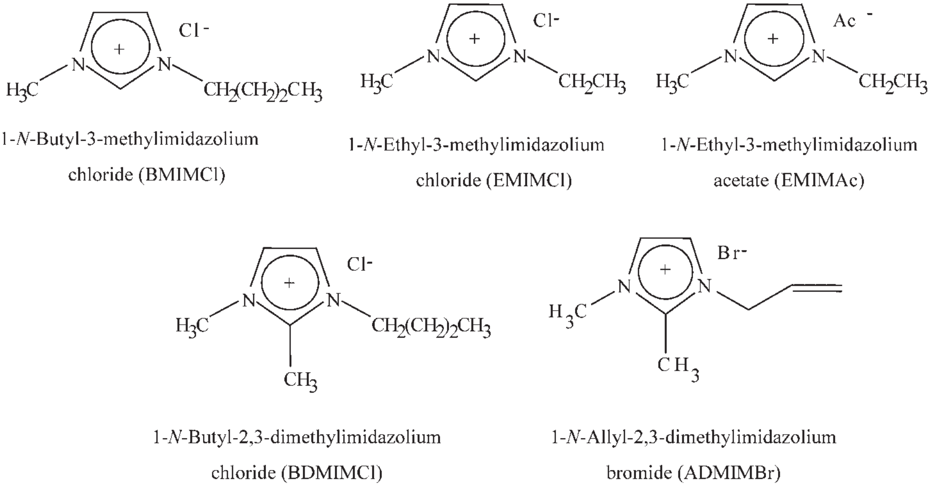


**Figure 5.**
$^{13}$C NMR spectrum of the mixture of EMIMAc/trityl chloride in DMSO-$d_6$ showing the trityl carbinol–acetate.



1-*N*-Butyl-3-methylimidazolium chloride (BMIMCl)

1-*N*-Ethyl-3-methylimidazolium chloride (EMIMCl)

1-*N*-Ethyl-3-methylimidazolium acetate (EMIMAc)

1-*N*-Butyl-2,3-dimethylimidazolium chloride (BDMIMCl)

1-*N*-Allyl-2,3-dimethylimidazolium bromide (ADMIMBr)

***Figure 6.***
Structures of ionic liquids used as reaction medium for cellulose functionalization.

requires the addition of 2.5 mol pyridine. On one hand, pyridine activates the acid chloride to form the reactive acylium ion and, on the other, pyridine neutralizes the liberated HCl. In case of the acylation with acetyl chloride, it is possible to synthesize cellulose acetate without any additional base.[30]

Obviously, an excess of reagent of 5 mol per mol anhydroglucose unit (AGU) leads to completely substituted cellulose derivatives like cellulose pentanoates, cellulose hexanoates, and cellulose benzoates, which are soluble in DMSO, acetone and chloroform.

Comparing the acylating agents, it was found that the acid chlorides are more efficient than the acid anhydrides at comparable molar ratio in BMIMCl. However, there are significant differences in the

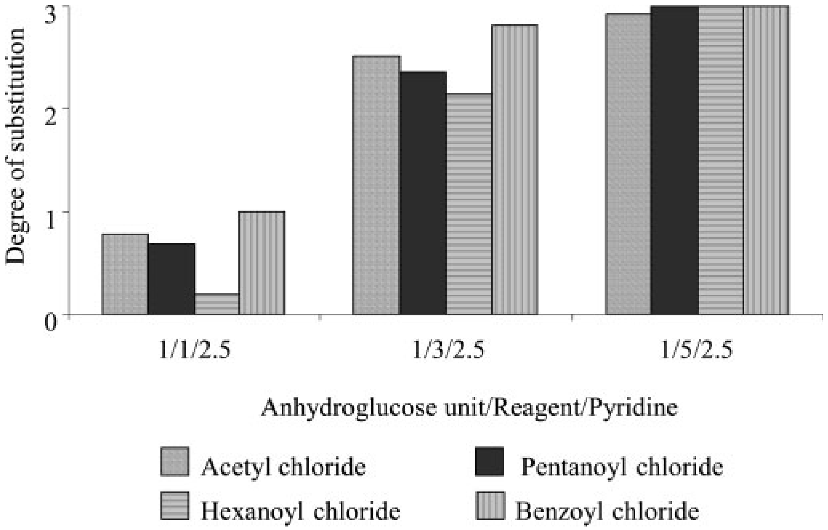


***Figure 7.***
Typical values of degree of substitution of acylated cellulose (cellulose acetate, cellulose pentanoate, cellulose hexanoate, and cellulose benzoate) synthesized in BMIMCl within 2 h at 80 °C.

reagent used. For example, propionic anhydride and butyric anhydride leads to very low substituted cellulose derivatives ($DS_{propionate} = 0.9$; $DS_{butyrate} = 0.4$) compared to the cellulose pentanoates (DS 2.4) and cellulose hexanoates (DS 2.7) obtained at comparable molar ratio of 1/3 (AGU/reagent, Figure 8).

Apart from the conversion of butyric anhydride, the DS of the cellulose samples can be increased by increasing the molar ratio in the range from 0.5 to 3.0. In the case of butyric anhydride, a maximal DS of 0.4 can be achieved in BMIMCl. The variation of the reaction time, reaction temperature and IL showed no effect on the DS obtained. Nevertheless, the cellulose derivatives with DS above 0.9 are soluble in DMSO and at DS of 2.3 in DMSO, acetone and chloroform. The cellulose acetates formed from microcrystalline cellulose show the following substitution pattern: O-6 > O-2 > O-3.[31] The cellulose acetates prepared by Wu et al.[32] with acetic anhydride in 1-allyl-3-methylimidazolium chloride (AMIMCl) possess lower DS values than cellulose derivatives prepared in BMIMCl, EMIMCl, BDMIMCl, and ADMIMBr, even by using a lower molar ratio. An acetylation of cellulose in AMIMCl leads to DS values of 1.61 (after 1 h), 1.86 (after 2 h) and reaches 2.49 after 8 h of reaction times. For homogeneous acetylation BMIMCl, EMIMCl, BDMIMCl, and ADMIMBr are more effective reaction media, because within 2 h at comparable or lower molar ratio, cellulose acetates with DS values in the range of 1.8 to 3.0 can be achieved.[31]

The application of ILs leads to very highly substituted products without any impurities, which can easily be obtained by precipitation in ethanol (Figure 9). The IR spectrum of a cellulose hexanoate, synthesized in BMIMCl with a molar ratio of 1/5 (AGU/hexanoic anhydride) shows the typical signals for the acylated cellulose sample (DS 3.0) at 2999, 2933, 2868 $cm^{-1}$ ($\nu CH_2$), 1751 $cm^{-1}$ ($\nu CO$) and no OH signal.

A comparison of the DS values of the cellulose derivatives, obtained by applying microcrystalline cellulose with a DP of 350 and a molar ratio of 3 mol acid anhydride per mol AGU in BMIMCl, is interesting (Figure 10). Obviously, there is a relation

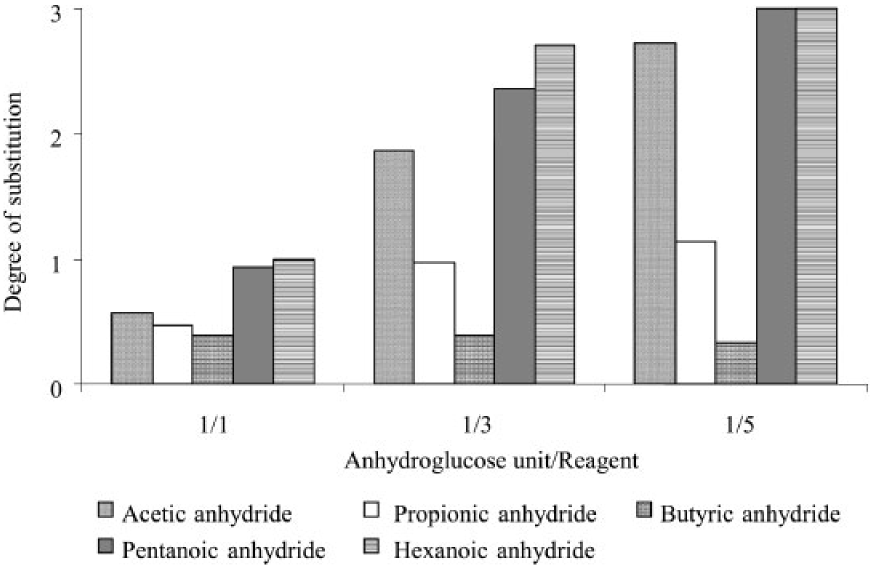


**Figure 8.**
Degree of substitution of cellulose derivatives obtained with different reagents and different molar ratio anhydroglucose unit to reagent applying BMIMCl as reaction medium at 80 °C for 2 h.

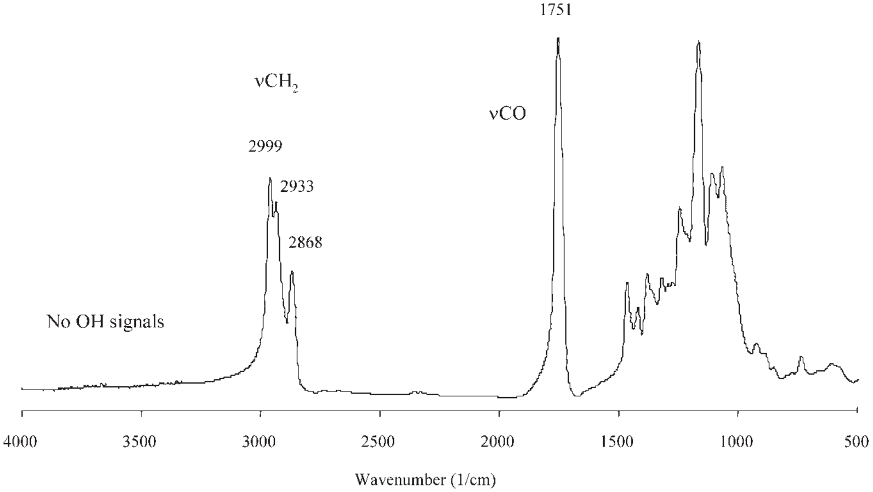


***Figure 9.***
IR spectrum of a completely substituted cellulose hexanoate synthesized in BMIMCl with a molar ratio of 1/5 (anhydroglucose unit/hexanoic anhydride), 2 h at 80 °C.

between the length of the alkyl chain of the acid anhydride and the length of the alkyl chain of the imidazolium based cation of the IL. The observation that similar length of the alkyl chain of the reagent and the alkyl chain of the cation used, leads to low substituted cellulose samples must be further investigated by studies of different ILs as reaction media and of the state of dissolution of the cellulose in the IL.

BMIMCl was approved to be a reaction medium for the synthesis of soluble cellulose furoates. Within 3 h at 65 °C, it is possible to prepare cellulose furoates with a DS in the range from 0.5 to 3.0 independent of the DP of the cellulose (microcrystalline cellulose, DP = 330 and cotton linters, DP = 1800 were studied). The cellulose furoates obtained are soluble in DMSO and at DS > 2.4 additionally soluble in DMA (Table 1).

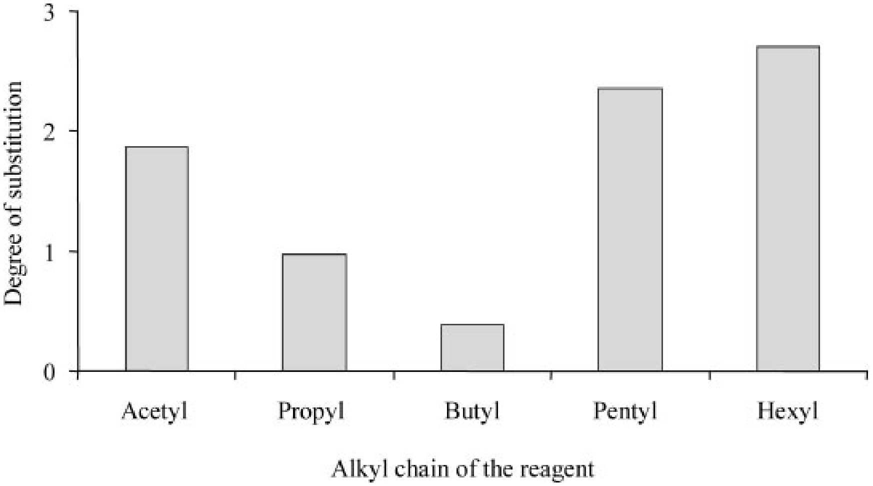


***Figure 10.***
Comparison of the degree of substitution of different cellulose esters synthesized in BMIMCl (2 h, 80 °C) at a molar ratio of 3 mol reagent per mol anhydroglucose unit.

**Table 1.**
DS and solubility of the cellulose furoates prepared in BMIMCl with 2-furoyl chloride (FC) for 3 h at 65 °C.

| Cellulose | Molar ratio | Cellulose furoate | | | | | |
|---|---|---|---|---|---|---|---|
| Type[a)] | AGU/FC/Py[b)] | $DS_{overall}$ | $DS_{O\text{-}6}$ | $DS_{O\text{-}2,3}$ | Solubility | | DP |
| | | | | | DMSO | DMA | |
| MC | 1/1/0 | 0.46 | 0.38 | 0.08 | + | + | – |
| MC | 1/1/1 | 0.62 | 0.47 | 0.15 | + | − | – |
| MC | 1/3/3 | 2.43 | – | – | + | + | 228 |
| CL | 1/3/3 | 0.67 | 0.48 | 0.19 | − | − | – |
| MC | 1/5/5 | 3.00 | 1.00 | 2.00 | + | + | 273 |

[a] MC - microcrystalline cellulose, DP = 330; CL-cotton linters, DP = 1800.
[b] Anhydroglucose unit/furoyl chloride/pyridine.

The conversion of 1 mol 2-furoyl chloride per mol AGU in BMIMCl leads to a cellulose furoate with a DS of 0.46. The equimolar addition of pyridine results in an increase of the DS value to 0.62. Next to the activation of the 2-furoyl chloride (formation of the reactive acylium ion), pyridine acts as base binding the liberated hydrogen chloride. The increase of the molar ratio and, therefore, the increase of the amount of pyridine added, lead to an increase of the DS of the cellulose furoate (1/3/3 → DS 2.43; 1/5/5 → DS 3.0).

The reactivity of the 2-furoyl chloride with cellulose depends on the DP of the starting biopolymer. A cellulose of high DP of 1800 leads to products with DS of 0.67 at a molar ratio of 1/3/3 (AGU/FC/pyridine), while with the microcrystalline cellulose with a DP of 330 cellulose furoates with DS of 2.43 (comparable molar ratio) could be generated. Independent of the type of cellulose used, the position 6 is more reactive than positions 2 and 3.[33] The change of the reaction medium from BMIMCl to EMIMCl leads to less substituted cellulose

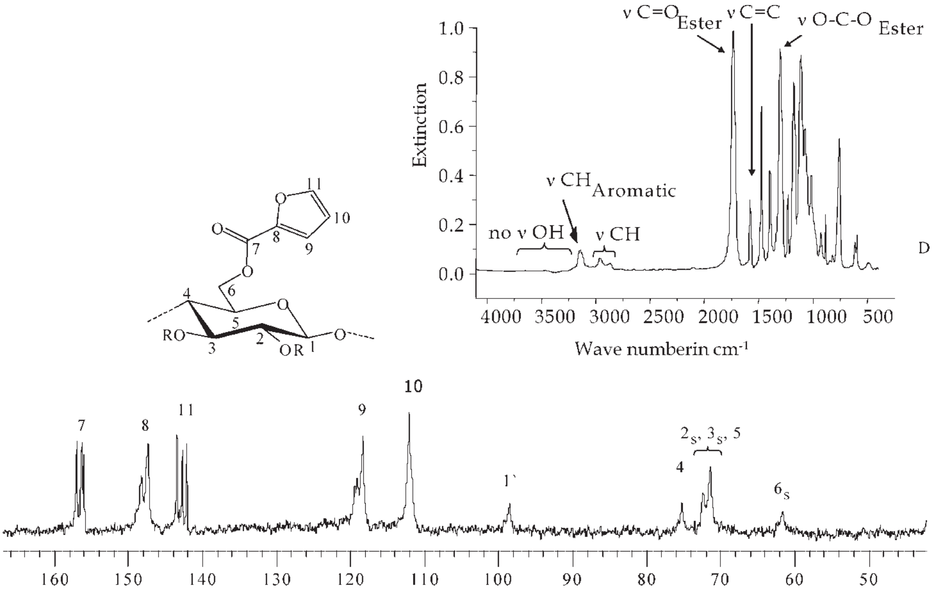


**Figure 11.**
IR- and $^{13}C$ NMR spectra (NMR in DMSO-$d_6$) of a completely substituted cellulose furoate obtained by conversions of cellulose in BMIMCl (3 h at 65 °C).

derivatives. The acylation with 2-furoyl chloride in EMIMAc was not possible. The reaction leads not to cellulose furoates as expected, but cellulose acetates occur as discussed above.[28] The cellulose furoates prepared in BMIMCl can easily be precipitated by ethanol and are obtained as soluble products without any impurities (Figure 11). The IR spectrum of the cellulose furoate with DS 3.0 shows the typical signals $\nu(CH_{Aromatic})$ at 3200 cm$^{-1}$, $\nu(CH_2)$ at around 3000 cm$^{-1}$, $\nu(CO_{Ester})$ at 1750 cm$^{-1}$ and $\nu(C{=}C)$ at 1550 cm$^{-1}$ and no OH signal. The $^{13}$C NMR spectrum shows all typical peaks for a completely substituted cellulose furoate. In the range from 60 to 100 ppm, the typical peaks of the AGU carbon can be found. In the range from 110 to 150 ppm, the peaks of the carbons of the furoyl moiety and at 159 ppm the carbonyl carbon can be assigned.

A comparison of the DS values of cellulose furoates synthesized in the cellulose solvent N,N-dimethylacetamide (DMA)/LiCl proved the high efficiency of BMIMCl as reaction medium. Hon and Yan[34] prepared a cellulose furoate in DMA/LiCl with a DS of 2.81 applying an excess of 7.5 mol 2-furoyl chloride and 15 mol pyridine per mol AGU. A completely substituted cellulose furoate can be synthesized after 22 h reaction time. In addition, DMA/LiCl cannot be easily recycled compared to BMIMCl.

## Dissolution and Chemical Modification of Bacterial Cellulose

BMIMCl does not only dissolve microcrystalline cellulose and cotton linters but also bacterial cellulose (BC) with very high DP of 6500. Applying BMIMCl, within 20 min a clear solution of BC can be achieved (Figure 12). In BMIMCl 10 to 12% of BC can be dissolved. In general, the chemical modification of BC is quite difficult, for this purpose, the acetylation with acetic anhydride and the carbanilation with phenyl isocyanate of BC in BMIMCl was studies. The reactions proceed very fast (2 h, 80 °C), under mild condition and without an additional base. With increasing the molar ratio from 1/1 to 1/10 (AGU/reagent) different DS values can be generated (Figure 13). Already with an excess of 3 mol acetic anhydride per mol AGU, a cellulose acetate with DS 2.5 was obtained. An increase of the molar ratio to 10 mol per mol AGU leads to completely substituted cellulose acetates. In contrast to the cellulose acetates based on microcrystalline cellulose, the BC cellulose acetates possess a substitution pattern in the order O-6 > O-3 > O-2. The cellulose acetates based on BC are soluble in DMSO at a DS higher than 0.7, but they are not soluble in acetone.

The carbanilation of BC was also possible. An increase of the molar ration from 1/1 to 1/10 (AGU/phenyl isocyanate)

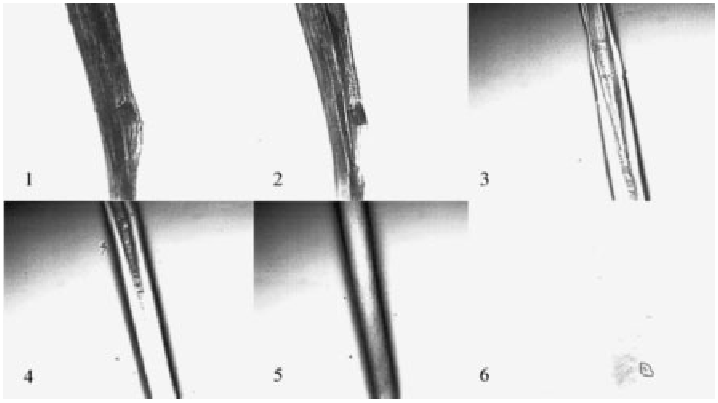


*Figure 12.*
Microscopic images of bacterial cellulose (BC); Native BC (1), after contact with the solvent BMIMCl (2), after 5 min (3), after 10 min (4), and after 15 min (5) and 20 min (6).

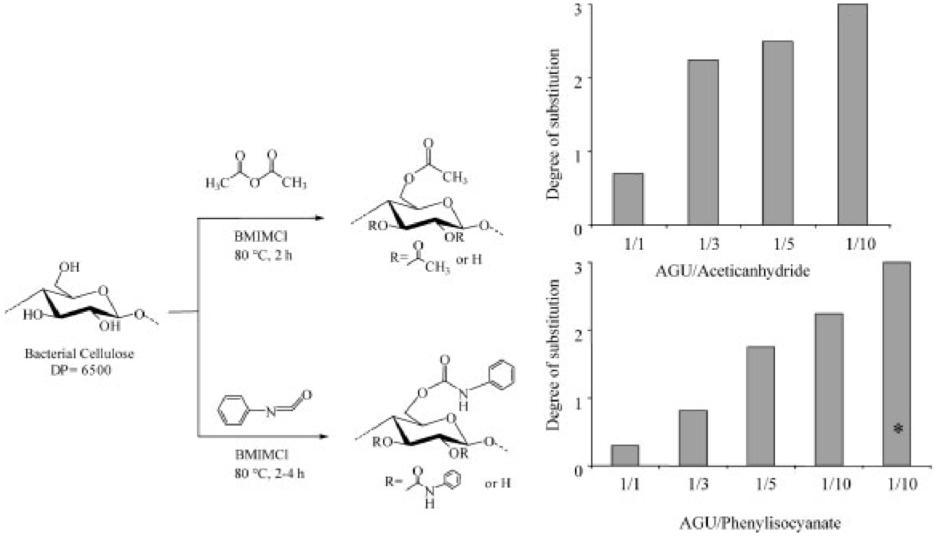


***Figure 13.***
Reaction scheme of the conversion of bacterial cellulose with acetic anhydride and phenyl isocyanate and values of degree of substitution of the products, reaction temperature 80 °C, reaction time 2 h, * 4 h.

generates cellulose carbanilates with a DS in the range from 0.4 to 3.0. A completely substituted cellulose carbanilate was obtained with an excess of reagent of 10 mol per mol AGU and a reaction time of 4 h. A DS higher than 0.8 caused solubility in DMSO. At higher DS (starting at 2.2), the BC carbanilates are soluble in DMSO, DMF and THF. The molar mass of the cellulose carbanilates was studied by the means of GPC and shows that during the reaction in BMIMCl no degradation of polymer chain occurred.[35]

## Unconventional Cellulose Derivatives Obtained in IL

An unconventional type of cellulose products[36], dendronized cellulose, could be synthesized homogeneously applying IL as well. Starting with 6-deoxy-6-azido cellulose and applying EMIMAc as reaction medium, it is possible to obtain dendronized cellulose with DS of 0.6 with first generation PAMAM and second generation PAMAM within 48 h at 25 °C (Figure 14).

The synthesis and the detailed characterization of structure and properties of dendronized cellulose is a recent research project showing already that these polymers possess promising properties.

## Etherification of Cellulose in IL

Beside acylation and carbanilation of different cellulose types in BMIMCl, EMIMCl, BDMIMCl and ADMIMBr we investigated etherification of cellulose, especially silylation of cellulose in EMIMCl and EMIMAc. The silylation in IL proceeds very fast (1 h) and the DS could be controlled by the variation of the IL used (Figure 15). Applying hexamethyldisilazane (HMDS) as reagent, silyl ether with a DS in the range from 1.6 to 2.9 can be achieved depending on the molar ratio used. The trimethylsilyl cellulose (TMSC) samples are soluble in DMA and at a DS of 2.3 in addition in THF.

EMIMAc is more efficient for this type of reaction than EMIMCl. During the reaction two problems appear; next to the insolubility of the HMDS in the IL, the precipitation of the TMSC appears. The reaction starts homogeneously and ends heterogeneously. To guarantee a completely homogeneous synthesis pathway, the

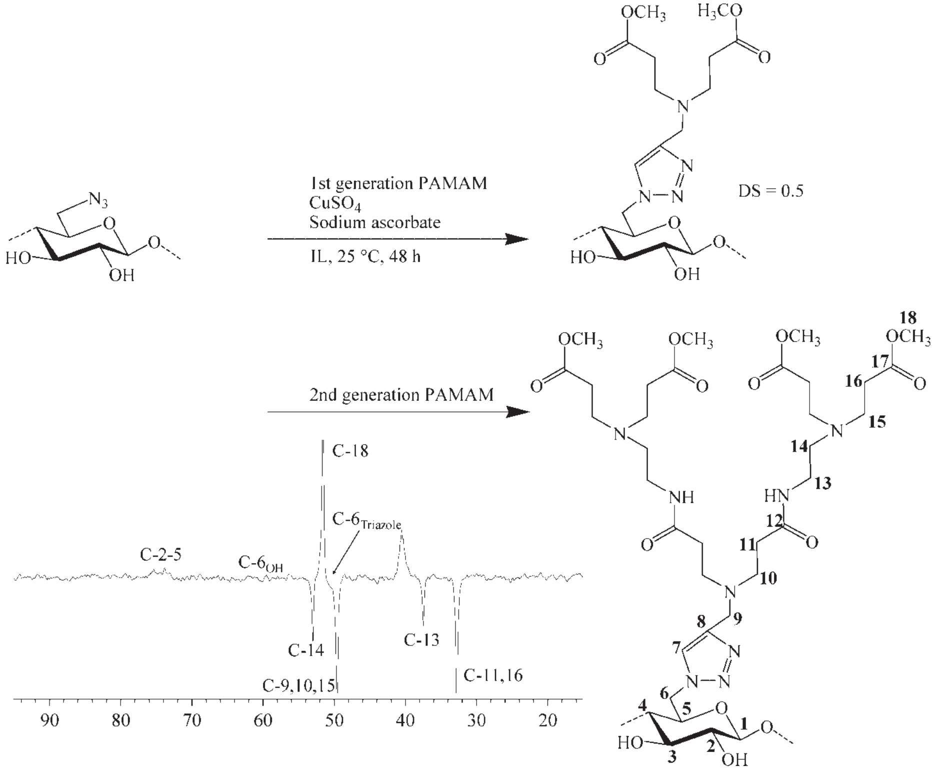


**Figure 14.**
Reaction scheme and DEPT 135 NMR spectrum of the first and second generation PAMAM-triazolo-cellulose (degree of substitution = 0.6, $2^{nd}$ generation).

addition of co-solvents like DMSO or DMA is necessary.

The TMSC samples, an amphiphilic polymer, were included in our studies about the formation of polysaccharide nanoparticles applying a dialysis process. The TMSC samples form particles by dialysis of the polymer dissolved THF against water. The size of the particles is in the range from 200 to 3000 nm (measured by light scattering, Figure 16).

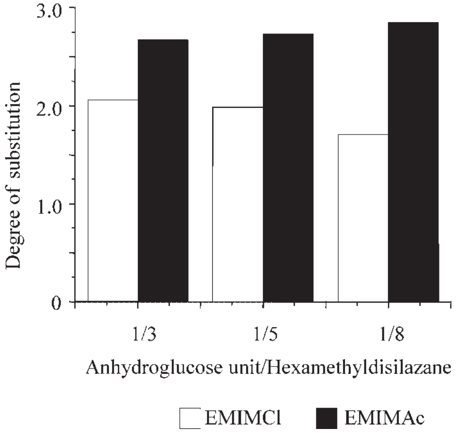


**Figure 15.**
Values of degree of substitution of trimethylsilyl cellulose prepared in EMIMCl or EMIMAc, 1 h at 80 °C.

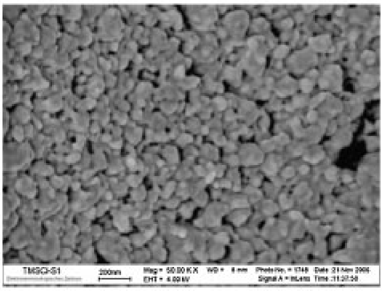
Interestingly, the silyl ether of the TMSC is cleaved off during the dialysis process as clearly indicated by the corresponding IR spectra (Figure 17). The typical signals of TMSC decrease and the characteristic signals for cellulose increase. Cellulose particles with almost no TMS groups were obtained.

## Interactions of Cellooligomers with IL

The interaction of cellooligomers (DP 6-10) with ILs (BMIMCl, EMIMAc, EMIMCl)

| Sample | Solvent | Particle | | |
|---|---|---|---|---|
| DS | | | Size$^a$ (nm) | PDI |
| 0.88 | DMA | - | - | - |
| 1.85 | DMA | + | 176 | 0.11 |
| 1.93 | THF | - | - | - |
| 1.93 | DMA | + | 265 | 0.28 |
| 2.26 | THF | + | 1150 | 0.76 |
| 2.28 | THF | - | - | - |
| 2.85 | THF | + | 3165 | 0.46 |

$^a$ Dynamic light scattering



DS 1.85

***Figure 16.***
Size of cellulose particles and particle distribution index (PDI) obtained from trimethylsilyl cellulose (TMSC) depending on degree of substitution (DS) of the starting polymer. SEM image of particles formed via TMSC with a DS of 1.85.

were investigated by NMR spectroscopy. $^{13}$C NMR spectra recorded in BMIMCl show a very bad resolution of the AGU region in contrast to the signals for the IL leading to the assumption that there is an aggregation and hence a high viscosity. Nevertheless, all signals for carbon atoms of the AGU were determined. In particular the C-1 signal could be clearly observed in the spectrum. Surprisingly, these peaks are not present if the cellooligomers are dissolved in EMIMAc although a good resolution of the spectrum appeared that indicates a good solubilization of the chains in this solvent. An explanation is the formation of a covalent bond between the IL and the aldehyde function as depicted in Figure 18.

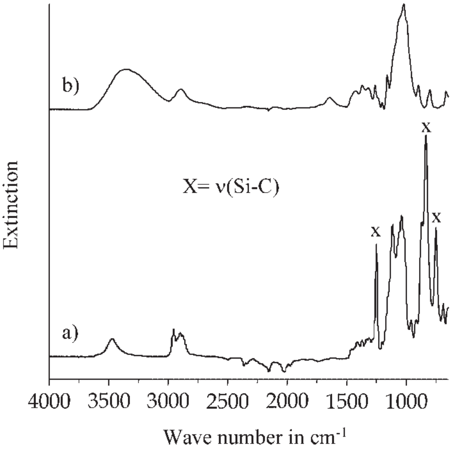


***Figure 17.***
IR spectrum of trimethylsilyl cellulose, DS 1.94 (a) versus the IR spectrum of the cellulose particles (b) formed after the dialysis of tetrahydrofuran against water.

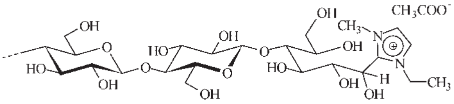


***Figure 18.***
Structure proposed for a covalent binding of EMIMAc to cellooligomer (DP 6–10).

It is known that an aldehyde moiety can react with ILs at the reactive proton in position 2[37] according to the formula shown in Figure 18. This reaction is particularly pronounced during the interaction with EMIMAc. In case of EMIMCl the C-1 peaks of the reducing end groups can still be found. This suggests that chloride containing ILs do not bind so efficiently to the reducing end of the carbohydrate.[38]

## Conclusion

In the course of our studies BMIMCl, EMIMCl, BDMIMCl, ADMIMBr and EMIMAc were studied as reaction media for homogeneous functionalization of cellulose. It could be shown that cellulose esters and even unconventional cellulose derivatives like dendronized cellulose as well as trimethylsilyl cellulose with different DS could be prepared efficiently by varying the molar ratio and the reaction time. In the case of trimethylsilyl cellulose, the reaction takes place in EMIMCl and EMIMAc and starts homogeneously leading to a heterogeneous system during the reaction. BMIMCl could be applied as solvent and reaction medium for the homogeneous modification for high molecular cellulose like bacterial cellulose (BC, DP 6500). The acetylation and carbanilation of BC with low excess of reagent and without an additional catalyst was possible. Preparing further cellulose derivatives including cellulose esters and ethers and detailed studies about the interaction cellulose/solvent are under investigation. It may be concluded that the importance of ILs in the field of polysaccharides will increase not only for chemical modification but also for shaping of cellulose to fibers, particles, and films as well as to design cellulose blends with other polymers.

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