INTERACTION OF IONIC LIQUIDS WITH POLYSACCHARIDES 5. SOLVENTS AND REACTION MEDIA FOR THE MODIFICATION OF CELLULOSE

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The use of ionic liquids (ILs) in the field of cellulose chemistry opens up a broad variety of new opportunities. Besides the regeneration of the biopolymer to fibers, films, and beads, this new class of cellulose solvents is particularly useful for the homogeneous chemical modification of the polysaccharide. In this review, the potential of ILs as a reaction medium for the homogeneous cellulose functionalization is discussed. It is shown that numerous conversions proceed very efficiently and the ILs may be recycled. But it is also demonstrated that some side reactions have to be considered.

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INTRODUCTION

Molten organic salts with low melting points, now referred to as ionic liquids (ILs), attracted remarkable interest in the early 1960s at the U.S. Air Force Academy as salt electrolytes for thermal batteries (Wasserscheid et al. 2003). The compounds used in the beginning had alkylpyridinium cations (Gale et al. 1978). Problems of these salts arose from their tendency to be reduced easily. Thus, salts of the more stable 1-alkyl-3-methylimidazolium type had been developed (Wilkes et al. 1982). Most of these substances melt below 100°C. Some of them are liquid at room temperature. These water-free systems consist completely of ions, making ILs the solvents of choice for a variety of syntheses. Because of their low vapor pressure and the possible recycling, they are considered as green solvents.

In 2002, the use of ILs as cellulose solvent, in particular for the regeneration of the polysaccharide, was published (Swatloski et al. 2002). Although that publication started a new development in the field of cellulose research, there were earlier attempts to use comparable compounds for the dissolution and modification of cellulose. The first report on salt-like cellulose solvents was published in 1934 (Graenacher 1934). Here N-alkylpyridinium salts were applied. Almost parallel to the research at the U.S. Air Force Academy, Husemann and co-workers in Freiburg/Germany used *N*-ethylpyridinium chloride (EPyCl) as medium for the homogeneous conversion of cellulose (Husemann et al. 1969). In the 1990s, Fischer et al. published some interesting papers concerning the use of molten inorganic salt hydrates as solvents and reaction media for cellulose (Fischer et al. 1999).

Nevertheless, the most promising ILs for the modification of cellulose are 1-alkyl-3-methylimidazolium salts. An increasing number of papers appear annually concerning this issue. The results support the assumption that ILs can open up new paths for the shaping of the most abundant, renewable organic compound on earth. Additionally, they could also lead to a first commercially relevant route towards homogeneous cellulose chemistry, which would significantly broaden the number of tailored cellulose derivatives. Although ILs, in particular the imidazolium salts, are described as chemically inert during a large variety of syntheses, they still exhibit a potential reactivity. Basically three paths for side reactions have to be taken into account, the fairly high reactivity of the anion as a nucleophile, the abstraction of the proton at position 2 of the 1,3-alkyl substituted imidazolium moiety, and ring opening reactions. One of the limitations, not discussed in this review, is the toxicity some of the ILs may exhibit (Stepnowski et al. 2004). It was found that an increasing length of the alkyl chain in 1-alkyl-3-methylimidazolium salts increases the toxicity and can even lead to substances more toxic than methanol (Couling et al. 2006; Ranke et al. 2004; Stock et al. 2004). Consequently, one of the issues in the development of ILs as green solvents is the synthesis of less toxic compounds. A second drawback that should be mentioned but also exceeds the frame of this work is surely the biodegradability (Gathergood et al. 2006).

Thus, the goal of this paper is a critical view of new developments concerning the interaction cellulose-ILs but also on the limitations determined, to give a realistic picture on the opportunities ILs offer. The focus of this paper is to discuss the potential of ILs as medium for the homogeneous chemical modification of cellulose.

Purity of Ionic Liquids

The purity of the ILs available today is a serious problem. One of the major impurities one has to consider is water. Most of the ILs are hygroscopic and contain water, if not prepared or stored properly. This water content has a significant influence on the dissolution process of the polysaccharide and on the modification opportunities as well. Thus, BMIMCl is able to dissolve cellulose, even bacterial cellulose with a huge molecular weight of about 6500 g/mol, very efficiently to an extent of up to 10% if it is anhydrous (Schlufter et al. 2006). If the water content exceeds 1%, cellulose is no longer soluble (Swatloski et al. 2002). 0.1 to 1% water in the IL still influences the aggregation of the polymer chains (El Seoud et al. 2005). Aggregation decreases the accessibility of the polymer and thereby the reactivity. In addition, the aggregation may lower the viscosity of the solutions. Furthermore, the water in the solvent can easily hydrolyze reagents used for the polymer modification, e.g. acyl chlorides. This hydrolysis does not only lead to a lower yield but may in turn cause side reactions, especially chain degradation initiated by the HCl formed. The formation of the HCl can be partially prevented by using a base, even in the presence of water. Some ILs may be degraded by water at higher temperatures as applied for modification reactions. It is known that tetrafluoroborates and hexafluorophosphates may liberate HF under such conditions (Visser et al. 2000). Thus, the water content has to be controlled by Karl-Fischer-Titration (Gallo et al. 2002) or via NIR spectroscopy (Tran et al. 2003). Interestingly, ILs considered as hydrophobic, such as octanyl-group containing imidazolium derivatives, are hygroscopic as well and can adsorb 1 wt% water within 3 h (Holbrey et al. 2001;

Seddon et al. 2000). Besides water the most common impurities result from the synthesis process of the ILs. These impurities, e.g. tertiary amines, alkyl halides, methylimidazole, and metal cations may give side products during synthesis in ILs but can also act as catalysts as shown for the silylation (Köhler et al. 2008) and have to be analyzed or removed to guarantee reproducibility. In addition, it should be mentioned that the number of commercial ILs with high purity is increasing.

Cellulose Dissolution

A huge variety of ILs is known today and the number of low melting organic salts is growing rapidly. Nevertheless, according to the literature (El Seoud et al. 2007; Zhu et al. 2006) and our own experiences ILs with ammonium cations, pyridinium cations**,** and imidazolium cations are able to dissolve cellulose (Fig. 1). Only organic salts with asymmetric cations give melts, which can properly interact with the cellullose backbone. Phosphonium and sulfonium salts are not suitable as cellulose solvents up to now. Dissolution of cellulose in pyridinium salts is combined with degradation if no protective gas is applied (see Table 1). If nitrogen is used, degradation can be diminished. Thus, the acetylation of higher molecular mass wood cellulose in the system EPyCl/pyridine was discussed as polymeranalogous reactions (Husemann et al. 1969).

Table 1. Solubility and DP of Cellulose Samples in BMIMCl, BMPyCl, BDTACl

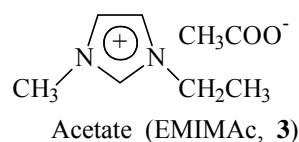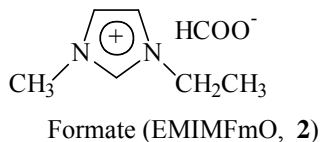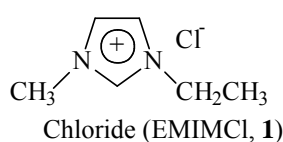| Cellulose		Solvent					
Type	DP	BMIMCl		BMPyCl		BDTACl	
		%	DP[a]	%	DP[a]	%	DP[a]
Avicel	286	18	307	39	172	5	327
Spruce sulfite pulp	593	13	544	37	412	2	527
Cotton linters	1198	10	812	12	368	1	966

a) After regeneration

There is no clear theory concerning the interaction between the ILs and the polymer. They are considered as non-derivatizing solvents, i.e. there are no covalent interactions involved, as demonstrated by ^{13}C NMR studies (Heinze et al. 2005, see Fig. 2). It was concluded from NMR spectroscopy, in particular from ^{13}C and [35/37]Cl-NMR experiments (Moulthrop et al. 2005; Remsing et al. 2006) on solutions of cellulose oligomers and cellulose in BMIMCl, that the chloride anion is much more involved in the disruption of the hydrogen bond system and the solubilization of the chains than the cation. The postulated interaction Cl-OH-cellulose is comparable to the structure discussed for cellulose/DMAc/LiCl but should be more efficient because the anion is freer due to a loser binding to the large asymmetric cation (El Seoud et al. 2007). Still, this finding cannot explain the fact that only ILs with nitrogen-containing cations are able to dissolve cellulose. No measurements are known for ILs with acetate as counter-ion, which dissolve cellulose even better than the chloride. Recently formate-, methyl-phosphate- (Fukaya et al. 2006, 2008), and dicyanoamide-containing solvents (Liu et al. 2005), were described as cellulose solvents. Thus, the dissolution mechanism is still a matter of ongoing research.

Interestingly, the solubility of cellulose in 1-alkyl-3-methylimidazolium type ILs is directly related to the length of the alkyl chain. But the solubility does not regularly
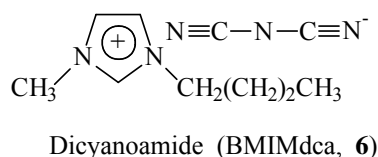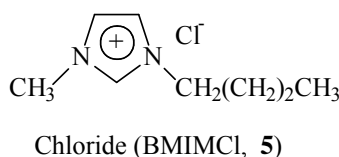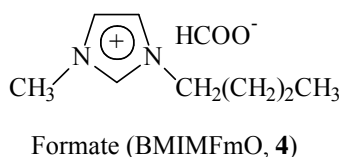
decrease with increasing length of the alkyl chain. An odd-even effect was determined for short alkyl chains (Erdmenger et al. 2007). The polymer dissolves more efficiently in ILs with even-numbered alkyl chains compared to odd-numbered alkyl chains (Fig. 1).
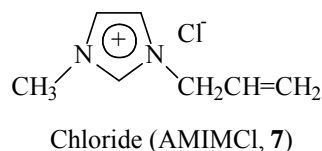
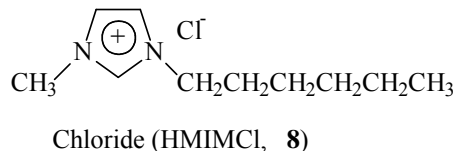### Imidazolium salts

1-Ethyl-3-methylimidazolium salts

Chloride (EMIMCl, **1**)   Formate (EMIMFmO, **2**)   Acetate (EMIMAc, **3**)

1-Butyl-3-methylimidazolium salt

Formate (BMIMFmO, **4**)   Chloride (BMIMCl, **5**)   Dicyanoamide (BMIMdca, **6**)
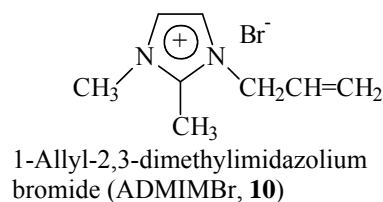
1-Allyl-3-methylimidazolium salt   *1-Hexyl-3-methylimidazolium salts*

Chloride (AMIMCl, **7**)   Chloride (HMIMCl, **8**)

Imidazolium salts with substitution at position 2

1-Butyl-2,3-dimethylimidazolium
chloride (BDMIMCl, **9**)

1-Allyl-2,3-dimethylimidazolium
bromide (ADMIMBr, **10**)
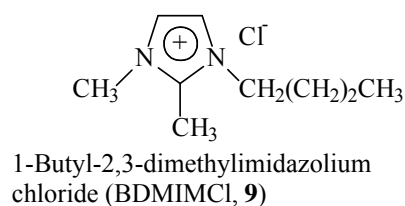
Pyridinium salts   ### Ammonium salts

1-Butyl-3-methylpyridinium-
chloride (BMPyCl, **11**)

N-Ethlylpyridinium-
chloride (EPyCl, **12**)

Benzyldimethyl(tetradecyl)-
ammoniumchlorid (BDTACl, **13**)
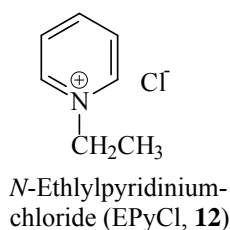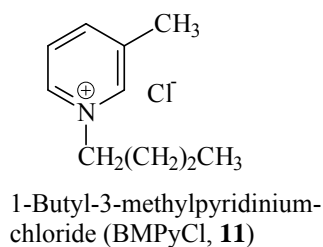
Fig. 1. Examples of ILs suitable for the dissolution of cellulose

Table 2. DP Values for Cellulose (DP 4300) Regenerated from Solutions in EPyCl/pyridine With and Without Protective Gas (nitrogen)

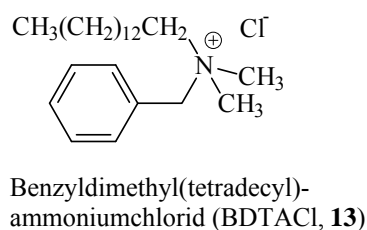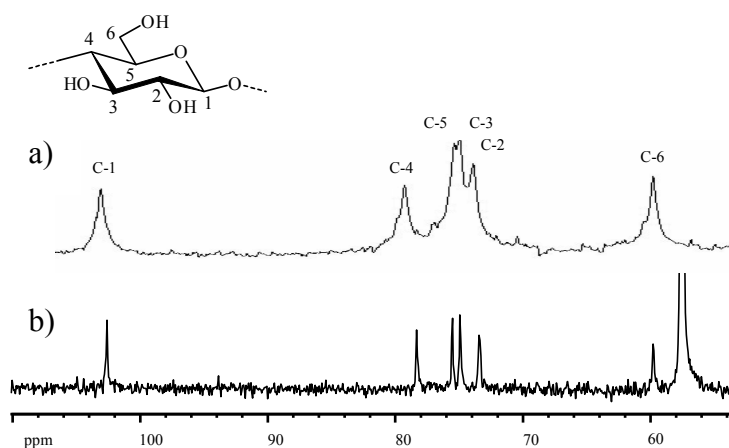| Time of Treatment at 85°C (min)	Air		Nitrogen	
	DP	Degradation %	DP	Degradation %
10	4100	5	4200	2
45	3900	9	4100	5
90	3900	9	4100	5
960	3000	30	4000	7

Fig. 2. ^{13}C NMR spectra of cellulose dissolved in BMIMCl (a) and DMSO/TBAF (b)

As expected, BMIMCl gave the best results of ILs with even-numbered alkyl chains (20 wt.-% of cellulose). In case of the odd-numbered ILs 1-heptyl-3-methylimidazolium chloride (HpMIMCl) was the most efficient, dissolving 5 wt.-% of cellulose. For the 1-alkyl-3-methylimidazolium type ILs, clear solutions were obtained after 15 min at 100°C, without activation of the cellulose. In case of other ILs a heat treatment in combination with sonication or microwave irradiation might be necessary (Swatloski et al. 2002). During microwave irradiation local heating must be avoided and the completeness of the dissolution can be a problem (Egorov et al. 2007). The addition of DMSO decreased the viscosity of the solution without precipitating the dissolved cellulose (Heinze et al. 2005; Erdmenger et al. 2007). The high efficiency of BMIMCl as cellulose solvents is confirmed by the fact that it even dissolves high molecular mass bacterial celluloses (DP about 6500) completely within 20 min at 80°C without degradation (Fig. 4, Schlufter et al. 2006).

Five ILs of the selection shown in Fig. 1 are more or less established now in cellulose chemistry (Kosan et al. 2008), i.e. BMIMCl (**5**), EMIMCl (**1**), AMIMCl (**7**), EMIMAc (**3**) and BDMIMCl (**9**). New ILs with EMIM, AMIM or BMIM cations may be easily prepared by a simple treatment of the corresponding hydrogencarbonates with carboxylic acids (Figs. 5, 6). Via this path various formates, trifluoroacetates, mono-, di-, and trichloroacetates are accessible (Liebert 2008). Formates are suitable solvents for

cellulose. A fairly good dissolution was found for halogenated acetates such as BMIMtrichloroacetate, but these salts had melting points above 100°C and therefore are by definition not considered as ILs.
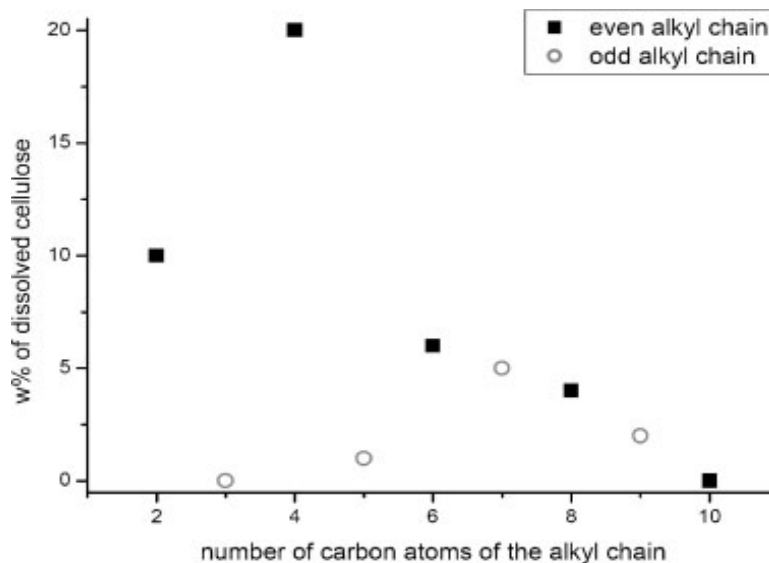

Fig. 3. Solubility of cellulose in 1-alkyl-3-methylimidazolium type ILs with different alkyl chain length
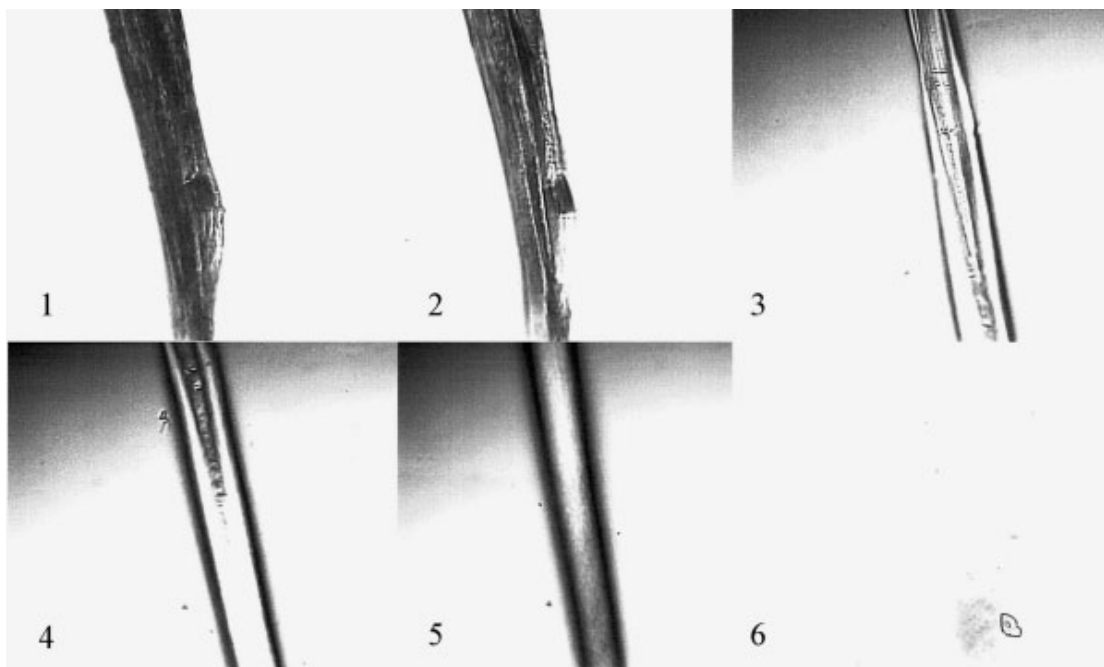

Fig. 4. Microscopic images of bacterial cellulose (BC); native BC (1), after contact with the solvent BMIMCl (2), after 5 min (3), after 10 min (4), and after 15 min (5) dissolving time, and completely dissolved after 20 min (6)

Cellulose can be regenerated from solutions in IL by precipitation into water, alcohols**,** or acetone (Swatloski et al. 2002; Michels et al. 2005; Kosan et al. 2008). A huge amount of work is spent currently to explore this path as an alternative route to the traditional cellulose shaping processes and the NMNO method (Michels et al. 2005, Kosan et al. 2008; Swatloski et al. 2003). First results show that the membrane preparation and fiber spinning yield high quality products making a commercial application reasonable. One advantage here is the possible regeneration of the cellulose in different media leading to a broad variety of topographic and morphologic features (Fig. 7).
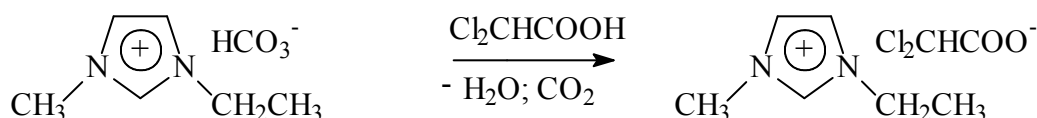
Fig. 5. Preparation of 1-ethyl-3-methylimidazolium dichloroacetate (EMIMdiclac) via 1-ethyl-3-methylimidazolium hydrogencarbonate
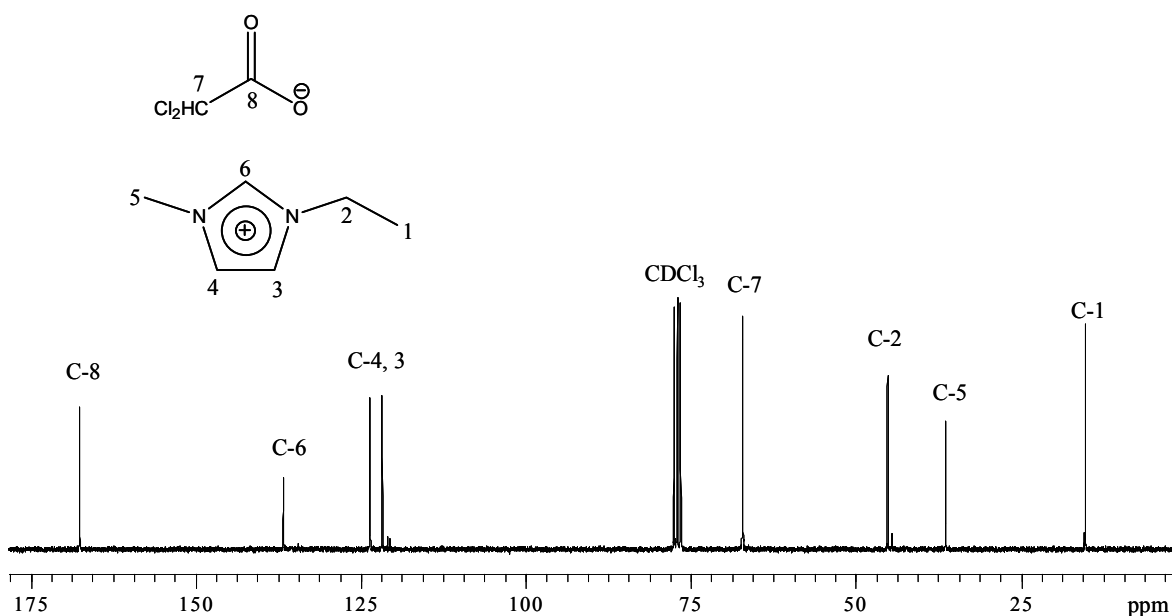
Fig. 6. ^{13}C-NMR spectrum of 1-ethyl-3-methylimidazolium dichloroacetate (EMIMdiclac)

Of growing interest for the modification reactions of cellulose are solvents that are liquid at room temperature and show low viscosities. These solvents can yield reaction media with high cellulose contents, which still can be handled. Furthermore, they are suitable for gentle reaction conditions, making unstable derivatives accessible. Among the room temperature ILs (RTILs) suitable for cellulose dissolution are EMIMAc (Kosan et al. 2008) and the formates of allylimidazolium based ILs (Fukaya et al. 2006). AMIMCl, which was claimed to be liquid at room temperature (Zhang et al. 2005), has a melting point of 55°C if it crystallizes after proper purification. Remarkable are the extraordinarily low viscosities found for the formates of the IL with the AMIM- and 1-

allyl-3-ethylimidazolium cation. Values of 66 and 67 cPas were determined (Fukaya et al. 2006).

Nevertheless, for chemical conversions the EMIMAc was favored, because it does not have a reactive side group such as the unsaturated function of the AMIM ion. Moreover, EMIMAc is considered to be non-toxic, non-corrosive, and even biodegradable. Some of the side reactions, which may be caused by the acetate ion, will be discussed later. To gain insight into the state of dissolution of EMIMAc in comparison to EMIMCl and BMIMCl the solubilization of cellodextrin (average DP 7) obtained by degradation of cellulose was studied with NMR spectroscopy. A series of these NMR spectra is shown in Fig. 8 (Liebert 2008). A rather bad spectral resolution is found for the BMIMCl solution (Fig. 8d) indicating some aggregation.
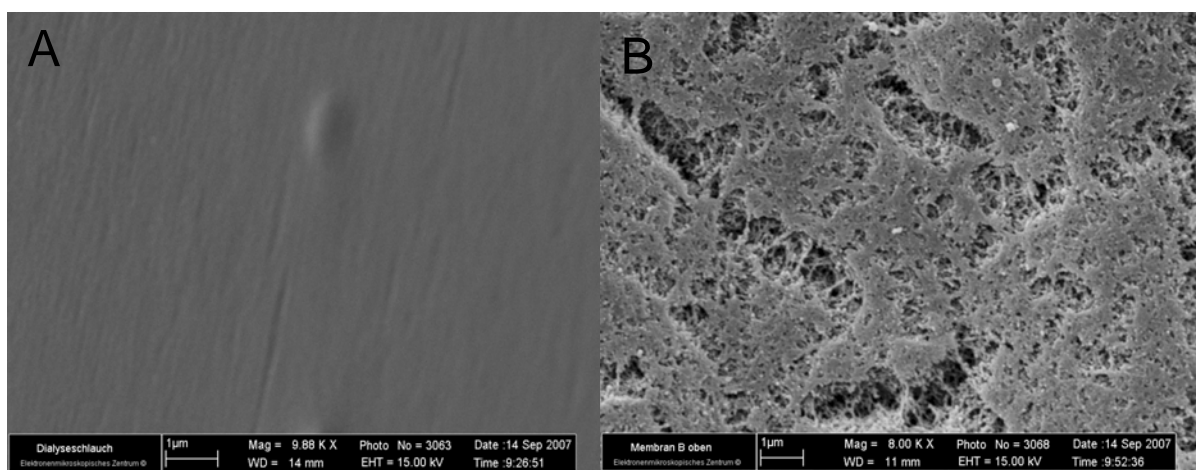

Fig. 7. SEM images of cellulose membranes prepared via the Viscose process (A) and by dissolution of cellulose in EMIMAc and precipitation in ethanol (B)

The surprising finding was that in case of the EMIMAc the signals for the reducing end groups of the cellodextrin were not determined (Fig. 8b). It was shown that simple aldehydes can be converted with ILs at the reactive proton in position 2 according to the formula depicted in Fig. 9, giving a semiacetal-type structure (Handy et al. 2005). This reaction is most pronounced for EMIMAc. EMIMCl and BMIMCl bind to a much smaller extent onto the reducing end. Up to now it is not known if this conversion of the end group leads to side reactions during the chemical modification of oligomeric and polymeric cellulose as well as on other polysaccharides. The process seems to be reversible. Further investigation is needed to elucidate if this fairly complete carbonyl reaction can be used for the activation of the aldehyde or if it even serves as a protective group.

The dissolution of other polysaccharides in ILs is not in the focus of this review, but it should be mentioned that starch (Biswas et al. 2006; Stevenson et al. 2007), chitin, and chitosan (Lu et al. 2006; Xie et al. 2006) can be dissolved in BMIMCl. Xylan and inulin give solutions in AMIMfmO (Fukaya et al. 2006), and more complex polysaccharides such as heparin dissolve in, e.g. BMIM tetrafluoroborate (Murugesan et al. 2006). In case of starch a rather drastic degradation is observed in particular of the

amylose (Stevenson et al. 2007). Chitosan and chitin are not fully soluble and still show some crystallinity in the solutions (Xie et al. 2006). The solubilization of cyclodextrins is combined with penetration of the ILs into the cavity (Gao et al. 2005). Interestingly, heparin and cellulose could be dissolved together in one IL (EMIMBzO) and were subjected to electrospinning. The heparin incorporated into the cellulose was still bioactive (Viswanathan et al. 2006).
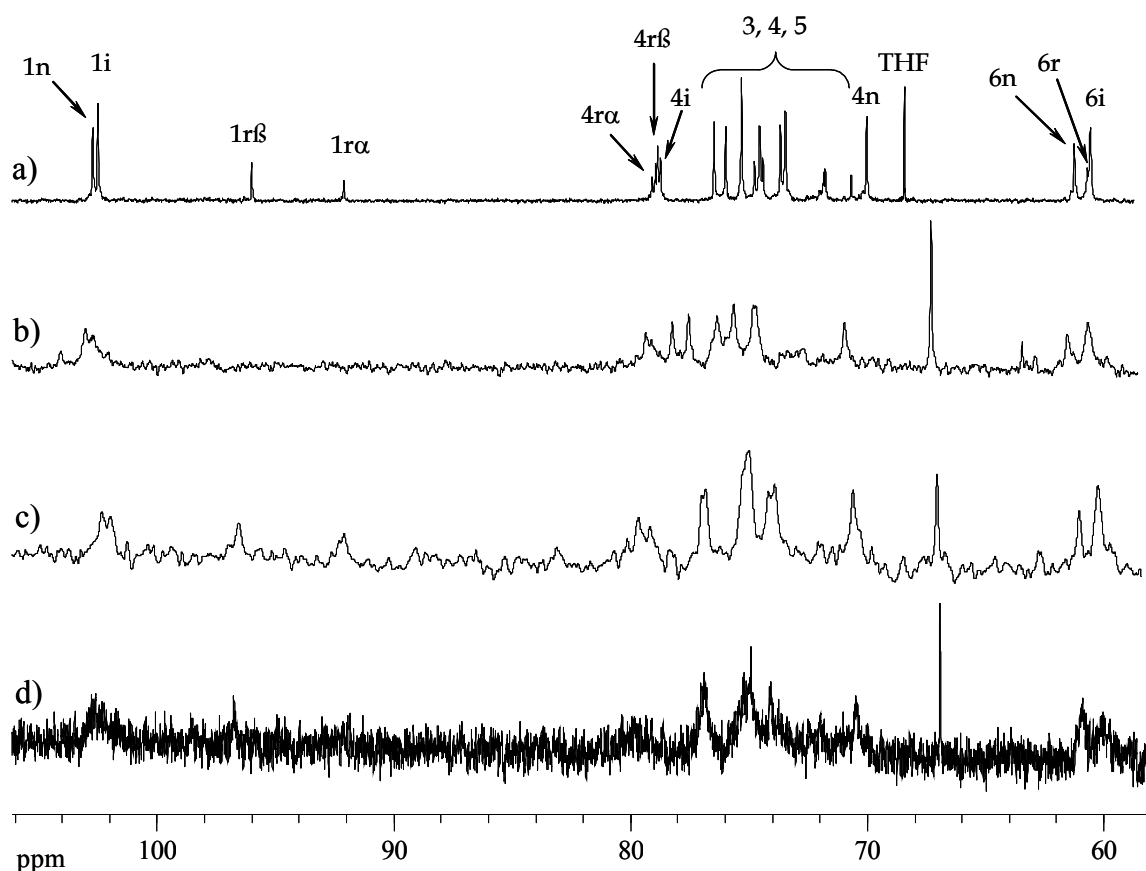

Fig. 8. ^{13}C NMR spectra of cellodextrin (average DP 7) in a) D_2O, b) EMIMAc, c) EMIMCl, and d) BMIMCl
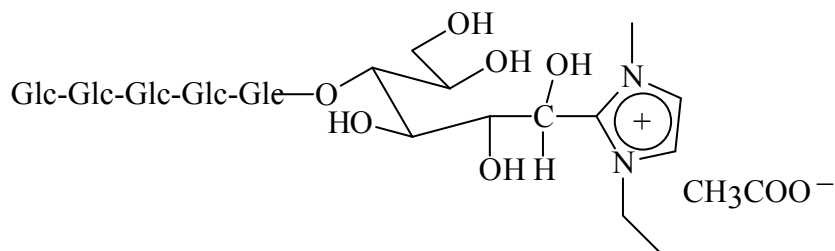

Fig. 9. Structure proposed for the conversion of the reducing end group of cellodextrins with EMIMAc

Esterification Reactions in ILs

The first ILs with significance for the esterification of cellulose were *N*-alkylpyridinium halides, especially EPyCl and *N*-benzylpyridinium chloride (Graenacher 1934; Husemann et al. 1969). The advantage of an easy work-up procedure after modification of polysaccharides in these solvents is ruled out by the fact that they are solid at room temperature and have to be diluted with common organic liquids to give appropriate reaction media. Among the additives were DMF, DMSO, sulfolane, pyridine, and *N*-methyl pyrrolidone, leading to a decreased melting point of 75°C (Philipp 1990).

The homogeneous acylation of cellulose in mixtures of *N*-benzylpyridinium chloride or EPyCl with pyridine was simply achieved with carboxylic acid anhydrides or chlorides (Graenacher 1934; Husemann et al.1969). These systems were exploited for the synthesis of acetates (**E1**), butyrates (**E2**), benzoates (**E3**), phthalates (**E4**) and anthranilic acid esters (**E5**) of cellulose (Fig. 10). Unfortunately, no data concerning the degree of substituent (DS) were given.
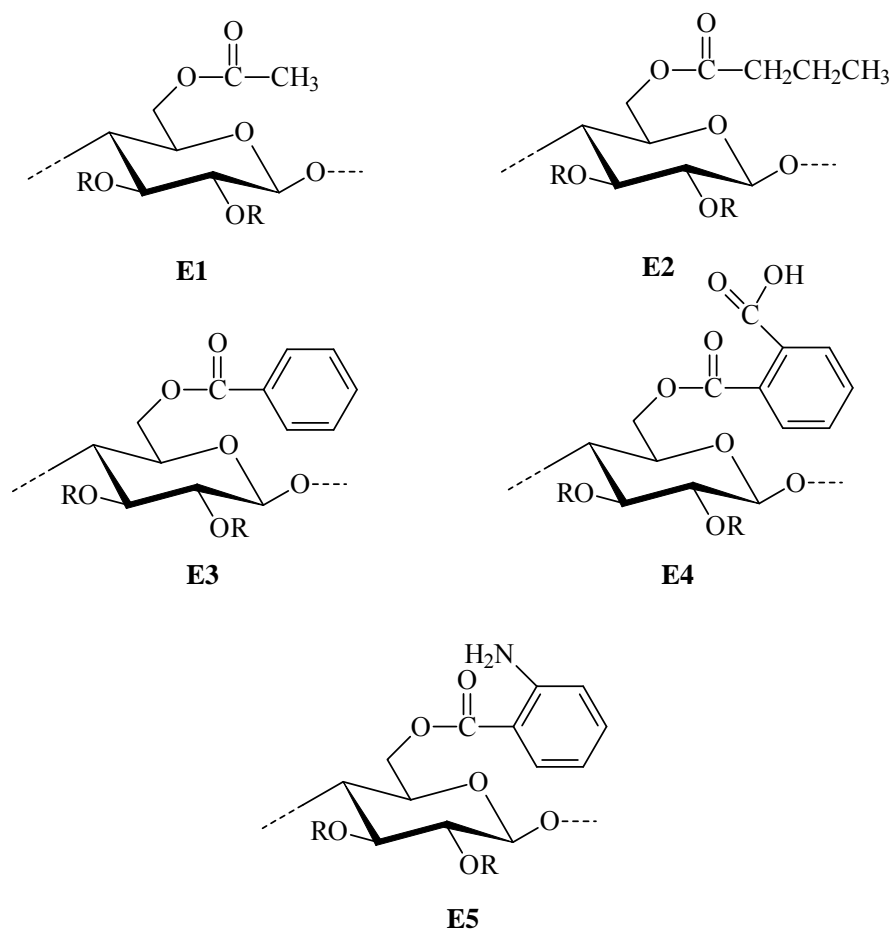

Fig. 10. Cellulose esters prepared in the solvent *N*-benzylpyridinium chloride/pyridine

Aliphatic acid esters of cellulose

Acetylation in *N*-ethylpyridinium chloride/pyridine is rather fast (DS 2.65 within 44 min) and can be controlled via the reaction time. Preparation of cellulose triacetate, which is completed within one hour, has to be carried out at 85°C (Husemann et al.

1969). It was claimed that the acetylation proceeds for cellulose with DP values below 1000 without degradation, i.e., strictly polymeranalogous. Cellulose acetate samples with a defined solubility, e.g. in water, acetone, or chloroform, respectively (Table 3), were accessible in one step in contrast to the heterogeneous conversion. A correlation between solubility and distribution of substituents was attempted by means of ^{1}H-NMR spectroscopy via this acetylation procedure (Deus et al. 1991). Comparable results can be obtained for solvents containing substituted imidazolium ions. It was stated that the conversion of cellulose with acetic anhydride (Ac_2O) in ILs, e.g. AMIMCl, succeeds without an additional catalyst (Wu et al. 2004; Zhang et al. 2005; Cao et al. 2007). It is necessary to mention that the results discussed in this work were obtained with an IL not completely purified after the preparation. No elemental analysis or spectroscopic data are available. The melting point was determined to be 17°C, which is almost 40°C below the value for the pure compound.

Table 3. Reaction Conditions for the Preparation of Cellulose Acetate in *N*-ethyl-Pyridinium Chloride

Reaction conditions				Acetyl Content %	Solubility
Molar ratios per mol AGU		T [°C]	t [min]		
Pyridine	Acetic anhydride				
16.2	5.4	40	60	12.1	H_2O/pyridine 3/1
16.2	5.4	40	295	27.1	CCl_4/MeOH 4/1
32.5	32.5	50	120	37.7	CCl_4/MeOH 4/1
32	32.0	85	55	41.3	$CHCl_3$
32.5	32.5	50	285	42.2	Acetone; $CHCl_3$

Therefore, methyl imidazole or imidazole has to be considered as impurities. They may act as catalysts for the esterification. Nevertheless, the cellulose acetates obtained started to dissolve in acetone at DS 1.86. The control of the DS by prolongation of the reaction time is nicely displayed in Table 4. For a cellulose solution with lower concentrations (2.9 wt%) in the same solvent, a maximum DS of 2.30 is reached. The order of reactivity of the hydroxyl functions was C6-OH > C3-OH > C2-OH similar to that observed for the acteylation in LiCl/DMAc (El Seoud et al. 2000). The reactions in recycled ILs, which were obtained by removal of volatiles under reduced pressure, gave products of similar DS.

Table 4. Results of the Acetylation of Cellulose (DP 650) with Acetic Anhydride in AMIMCl (4 wt% cellulose, molar ratio 1:5, temperature 80°C, adopted from Wu et al. 2004)

Time	DS	Solubility[a]	
[h]		Acetone	Chloroform
0.25	0.94	-	-
1.0	1.61	-	-
3.0	1.86	+	-
8.0	2.49	+	+
23.0	2.74	+	+

[a] All cellulose acetates were soluble in DMSO, +soluble, -insoluble

Still the most promising solvent regarding commercial use is BMIMCl, although it is corrosive and shows some toxicity. Thus, it was employed for the acetylation of cellulose (Heinze et al. 2005; Barthel et al. 2006). Starting materials were micro-crystalline cellulose, spruce sulfite pulp, and cotton linters, with DP values of 307, 544 and 814, respectively. Dissolution of the polymer was carried out at 10°C above the melting point of the IL. Esterification with acetyl chloride or acetic acid anhydride (Ac$_2$O)/pyridine at 80°C for 2 h yielded pure soluble products of controlled DS (Table 5).

Table 5. DS and Solubility of the Cellulose Acetates Homogeneously Prepared in BMIMCl (reaction temperature 80°C, reaction time 120 min)

Cellulose type	Reagent		DS[b]	Solubility[c]	
	Type	Mol per AGU		(CH$_3$)$_2$SO	CHCl$_3$
Avicel	Acetic Anhydride	3.0	1.87	+	-
Avicel	Acetic Anhydride	5.0	2.72	+	-
Avicel	Acetic Anhydride	3.0[a]	2.56	+	-
Avicel	Acetic Anhydride	10.0[a]	3.0	+	+
Avicel	Acetyl chloride	3.0	2.81	+	-
Avicel	Acetyl chloride	5.0	3.0	+	+
Spruce sulfite pulp	Acetyl chloride	3.0	3.0	+	+
Spruce sulfite pulp	Acetyl chloride	5.0	3.0	+	+
Cotton linters	Acetyl chloride	3.0	2.85	+	+
Cotton linters	Acetyl chloride	5.0	3.0	+	+

[a]with 2.5 mol Pyridine per AGU, [b]determined by NMR spectroscopy, [c]+soluble, -insoluble

Complete functionalization could be achieved with acetyl chloride if a molar ratio reagent/AGU of 1/3 was applied, suggesting that complete conversion of the acetylating reagent occurred. For acetylation with acetic anhydride a higher excess was necessary, and pyridine should be used as catalyst (see entries 3 and 4 in Table 5). In addition, the ILs EMIMCl, BDMIMCl, and AMIMBr were exploited for the acetylation (Barthel et al. 2006). Under the same experimental conditions, the following dependence of DS, hence reactivity, on the IL was observed: EMIMCl > BDMIMCl > AMIMBr > BMIMCl (see Table 6). Although BMIMCl showed the lowest reactivity, it seems to be the solvent of choice for the synthesis of cellulose acetates soluble in chloroform. Even the acetylation of high molecular mass cellulose such as bacterial cellulose with a DP of about 6500 was possible in BMIMCl (Schlufter et al. 2006). The cellulose acetates were found to be soluble in DMSO; the order of reactivity of the OH groups is C6-OH > C3-OH > C2-OH. For comparable reactions with lauroyl chloride a maximum DS of 1.54 was achieved in BMIMCl for a molar ratio acyl chloride/AGU of 3/1. Fully functionalized samples, DS=3, were unattainable, probably because the system turns heterogeneous. The efficiency of the reaction in dependence on the IL decreased in the order BMIMCl > EMIMCl > BDMIMCl > AMIMBr. Attempts for the acetylation of cellulose in BMPyCl and BDTACl were not successful up to now (Barthel et al. 2006).

Alternative ILs used for the acetylation of cellulose are choline chloride (ChCl) based compounds, in particular ChCl with ZnCl$_2$ (Abbott et al. 2005). It represents a cheap and readily available alternative to the more commonly employed alkyl imidazolium-aluminium chloride mixtures (Abbott et al. 2004). In an analogous manner to the chloroaluminate systems, it was shown that these zinc based liquids form complex anions such as [ZnCl$_3$]$^-$ and [Zn$_2$Cl$_5$]$^-$. In contrast to the aluminium counterparts, ChCl–

$ZnCl_2$ is water-insensitive and zinc is supposed to be environmentally more benign. Although it was claimed that the reactivity during an acetylation with acetic acid anhydride in this IL is comparable to that in AMIMCl, the majority (90 wt%) of the cellulosic material was insoluble in acetone. IR analysis of this insoluble fraction indicated that a significant proportion was acetylated. This uneven acetylation could be due to per-acetylation of low molecular weight cellulose, which was concluded from SEC experiments.

Table 6. DS and Solubility of the Cellulose Acetates Homogeneously Prepared in Different ILs with Acetic Anhydride (3.0 mol per mol AGU, reaction temperature 80°C, reaction time 120 min)

| IL	DS	Solubility[a]	
		$(CH_3)_2SO$	$CHCl_3$
BMIMCl	1.87	+	-
AMIMBr	2.67	-	-
BDMIMCl	2.92	+	-
EMIMCl	3.0	+	-

[a] +soluble, -insoluble

Esters of dicarboxylic acids and unsaturated acids

It was attempted to react cellulose from sugarcane bagasse with succinic anhydride. Experiments were carried out in AMIMCl (Liu et al. 2007) or in a mixture of BMIMCl/DMSO (Liu et al. 2006) at different temperatures, up to 110°C, reaction times, up to 160 minutes, and molar ratios of succinic anhydride/AGU of 1/1 to 14/1, respectively. The DS values obtained were in the range from 0.07 to 0.22 for the conversions in AMIMCl and 0.04 to 0.53 for the BMIMCl/DMSO system. The reason for this inefficient esterification, even under favorable reaction conditions, is unclear. In a comparable manner phthalate functions were introduced, yielding products with DS values up to 0.73 (Liu et al. 2007). In addition to the esterification with aliphatic carboxylic acid chlorides, the introduction of unsaturated ester functions was possible via this synthesis path (Fig. 11A). It was shown that the reactivity of a 2-furoyl chloride in BMIMCl is comparable to that of acetyl chloride, i.e. with a molar ratio AGU/reagent of 1/5 complete functionalization can be obtained (Köhler and Heinze 2007).

Attempts were made to apply the room temperature liquid EMIMAc (FLUKA, 90% purity, no $Ag(CH_3COO)_2$ detectable) for homogeneous acetylation of cellulose. Thus, 2-furoyl chloride was converted with cellulose in EMIMAc in the presence of pyridine to obtain membrane-forming photo-cross-linkable materials (Fig. 11B). Surprisingly the organosoluble cellulose derivative obtained was not the furoate but a pure cellulose acetate, as could be confirmed by ^{13}C NMR spectroscopy (Köhler et al. 2007, Fig. 12). A reasonable explanation for this phenomenon would be the assumption that intermediately the mixed furan carboxylic - acetic acid anhydride is formed (Fig. 13). Thus, the first stage of the reaction was studied with NMR spectroscopy. Both ^{1}H and ^{13}C NMR spectra confirmed the formation of this highly reactive intermediate. A comparable experiment with acetyl chloride showed the formation of the more stable and easily detectable symmetric acetic acid anhydride.

A)
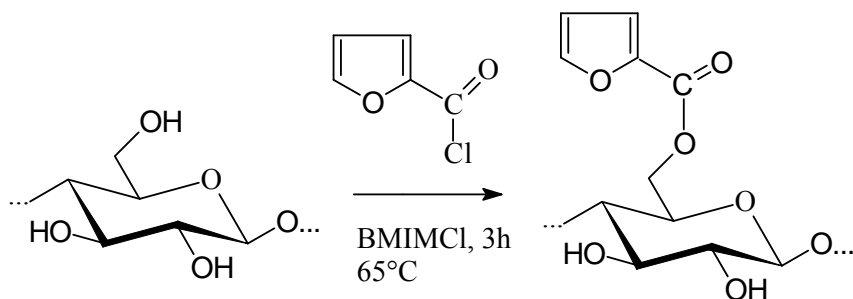
B)

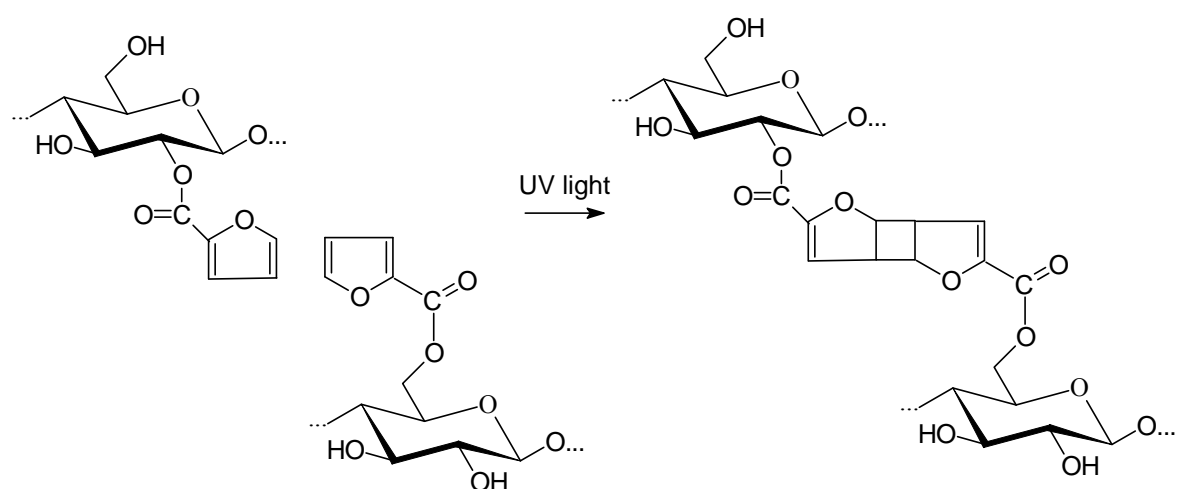**Fig. 11.** Schematic plot of the reaction of cellulose with 2-furoyl chloride (A) yielding photo-crosslinkable material (B)
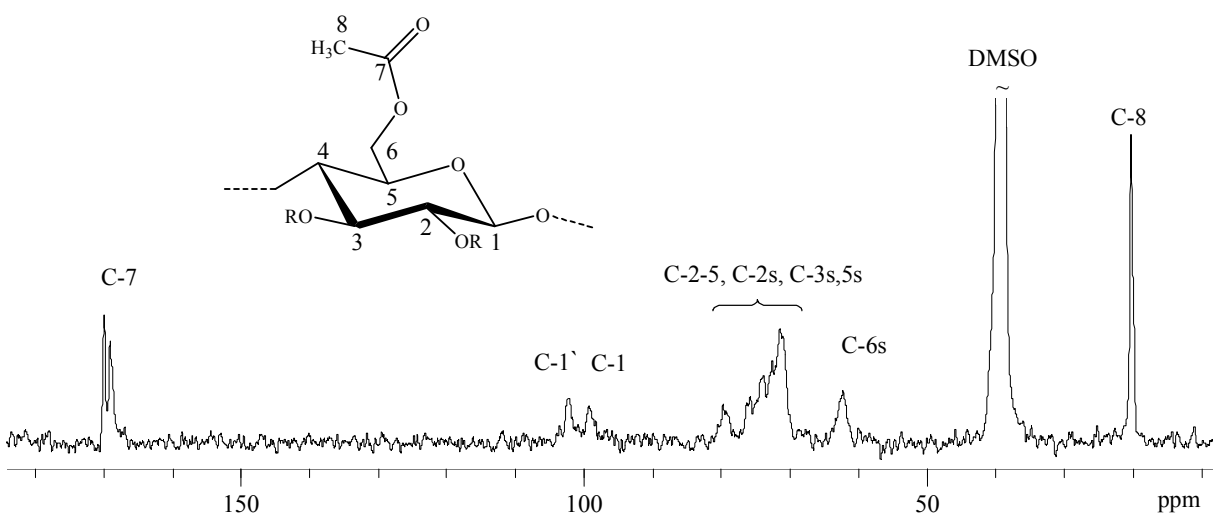

Fig. 12. ^{13}C NMR spectrum of a cellulose acetate obtained by conversion of cellulose with furoyl chloride in EMIMAc
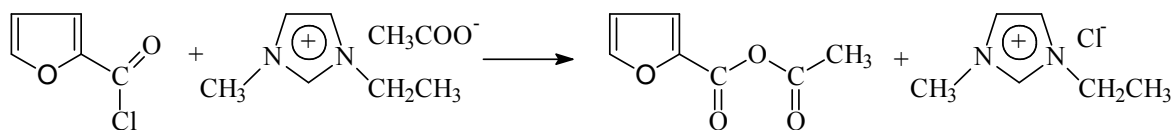
Fig. 13. Schematic plot for the formation of the intermediately formed furan carboxylic - acetic acid anhydride

Besides the fact that such side reactions have to be considered during the chemical modification of cellulose in ILs with carboxylate as anion, it could also be a tool for the highly efficient synthesis of cellulose derivatives because the IL can act both as reagent and solvent, as discussed.

Etherification Reactions
Tritylation

The first experiments towards etherification in organic salt melts were again published by Graenacher (1934). A mixture of alkylated pyridinium salts with pyridine was used as reaction medium for the homogeneous conversion of cellulose with triphenylmethyl chloride. The product obtained was soluble in pyridine. Recently, comparable experiments for the tritylation of cellulose in imidazolium salts were published. The usefulness of this conversion for the preparation of trityl cellulose with DS values of about 1 is shown in Table 7 (Erdmenger et al. 2007).

Table 7. Tritylation of Cellulose in BMIMCl for 14 h at 100°C.

Molar ratio per AGU		DS	
Trityl chloride	Pyridine	EA	NMR
3	5.0	0.71	0.88
4	6.7	1.14	0.96
5	8.3	0.98	1.17
6	10.0	1.22	1.30

[a)]determined by elemental analysis; [b)]determined by ^{1}H NMR spectroscopy.

During the etherification the addition of a base was necessary. Otherwise complete degradation of the cellulose occured. Pyridine could be used to capture the hydrogen chloride formed. A reaction time of only 3 h was sufficient to obtain trityl cellulose with a DS value of about 1.0, using a six-fold excess of trityl chloride. Recycling of the IL was not achieved for this reaction procedure, since pyridinium hydro-chloride and BMIMCl seem to be similar, which prevented separation by extraction. Alternatively triethylamine could be used as base, leading to a more efficient recylcling of the IL. Trityl cellulose with a DS of 0.98 after 1.5 h was synthesized. No results concerning the selectivity of the process in comparison with other tritylation procedures were given.

Surprisingly, the treatment of cellulose in EMIMAc with trityl chloride yielded cellulose acetate with a DS of 0.75 if a molar ration AGU/trityl chloride of 1/3 was applied (Köhler et al. 2007). This side reaction seems comparable to the acetylation

observed for conversion of cellulose in EMIMAc with acyl chlorides (see esterification). In case of the trityl chloride the formation of a reactive trityl acetic acid ester as intermediate was concluded from ^{13}C NMR spectroscopy. Cellulose acetate is generated via a transesterification reaction (Fig. 14).
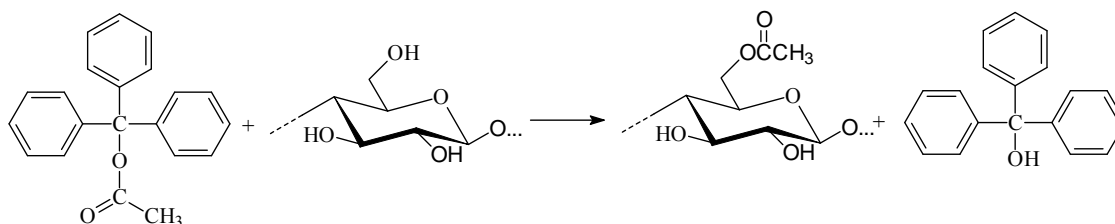

Fig. 14. Schematic plot for the transesterification step of the trityl acetic acid ester during the conversion of cellulose in EMIMAc with trityl chloride

Hydroxyalkylation and carboxyalkylation reactions

　　　The commercially important hydroxyalkylation and carboxyalkylation reactions of cellulose in ILs are scarcely studied. A patent by Myllymäki and Aksela (2005) claims etherification of this type in a large variety of ILs, but only the carboxymethylation of cellulose in BMIMCl in the presence of inorganic base, e.g. sodium hydroxide is given as an example. The only structural evidence is FTIR spectroscopy. No DS values, substitution pattern or properties such as viscosity are described. Basically the same is true for a Korean patent (Park and Park 2006) claiming hydroxyalkylation in ILs.

　　　According to our experiences the carboxymethylation under these conditions is possible but badly reproducible. For carboxymethylation, BMIMCl solutions of cellulose were diluted with DMSO to achieve a suitable medium viscosity (Heinze et al. 2005). Solid NaOH and sodium monochloroacetate dissolved in DMSO were added to the solution resulting in a gel-like mixture. After a typical work-up procedure, carboxy-methyl cellulose (CMC) with DS of 0.49 applying the molar ratio of 1 mol AGU per 1 mol reagent was obtained. An increase of the molar ratio to 1/3 did not increase the DS of the CMC. The carboxymethylation cannot be conducted as a homogeneous process because the base necessary is insoluble in the IL. If an excess is used and the system is heavily agitated, the cellulose partially or completely precipitates. The conversion of cellulose under alkaline conditions in 1-alkyl-3-methylimidazolium salts is combined with numerous side reactions caused by the proton at position 2. This leads to an unspecific hydrolysis of the etherification reagent, e.g. the monochloroacetic acid used for carboxymethylation. The IL could not be recovered due to the ion exchange. Thus, it was not possible to recycle the IL. Moreover, the destructive influence of the alkali on the ILs has to be considered. In case of imidazolium salts preferably ring opening occurs. An alternative path would be the use of cellulose solvents with an addtional alkyl function at position 2, e.g. ADMIMBr (**10**, Barthel and Heinze 2006) and BDMIMCl (**9**, Kosan et al. 2008).

　　　In addition to carboxymethylation reactions, the carboxyethylation and carboxy-propylation of cellulose were investigated (Mikkola et al. 2007). A selection of results obtained is summarized in Table 8. Rather low DS values, particularly in the case of carboxypropylation, were observed. As can be seen, the most acceptable results were

obtained if sodium hydroxide was added to the reaction mixture. Unfortunately, this results in destruction of the IL, as discussed for the carboxymethylation.

Table 8. DS Values for the Carboxyalkylation of Cellulose in the ILs AMIMCl and BMIMCl. (Carboxyethylation was carried out with sodium monochloroprorionate and carboxypropylation with sodium monochlorobutyrate.)

IL	Type of alkylation	Molar ratio per AGU		t in [h]	T in [°C]	DS
		Reagent	NaOH			
AMIMCl	Carboxypropylation	1	-	1	60	0.01
AMIMCl	Carboxypropylation	8	-	1	60	0.13
BMIMCl	Carboxypropylation	1	-	2	80	0.02
BMIMCl	Carboxypropylation	8	-	2	80	0.15
AMIMCl	Carboxyethylation	1	-	1	60	0.01
AMIMCl	Carboxyethylation	8	-	1	60	0.27
AMIMCl	Carboxyethylation	4	8	2	80	0.36
AMIMCl	Carboxyethylation	8	8	2	80	1.53

An interesting etherification reaction leading to a cationic functionalization of cellulose (see Fig. 15), is the conversion with choline chloride (Abbott et al. 2006). The IL employed to dissolve cellulose was a eutectic mixture of choline chloride and urea, with a molar ratio of 1/2.
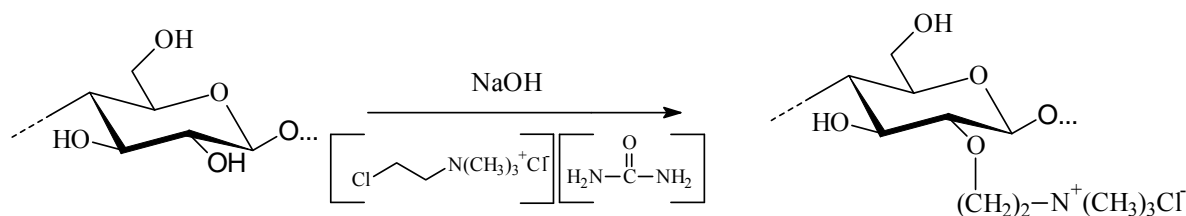

Fig. 15. Cationic derivatization of cellulose in choline-urea eutectic mixture

The reaction was carried out by treating cellulose with NaOH in this medium; the latter is acting both as solvent and reactant. The best conditions involved the reaction of the biopolymer for 15 h at 90°C. One half of the nitrogen present in the product was chemically bound, as a quaternary ammonium group. The product formed was found to be efficient in removing a typical water-soluble dye, orange II.

Miscellaneous Reactions of Cellulose in ILs

Among the first results concerning the completely homogeneous cellulose functionalization were carbanilation reactions. The carbanilation with phenyl isocyanate occurred smoothly in BMIMCl, without an additional base (Barthel and Heinze 2006). Products with DS values ranging from 0.3 to 3.0 were obtained, for phenyl isocyanate/AGU ratios of 1/1 to 10/1, respectively (Table 9). For higher molecular weight pulp celluloses prolongation of the reaction times to 240 min yielded fully functionalized derivatives. Most samples were soluble in DMSO, DMF, and THF. The presence of water in the carbanilation reaction mixture caused the formation of aniline (detected by ^{13}C NMR spectroscopy), which was removable from the product by washing. The IL could be reused. The success in dissolving bacterial cellulose of very high DP of about

6500 in BMIMCl prompted work on its carbanilation by phenyl isocyanate. The reactions were carried out for 2h (after cellulose dissolution), at 80°C. Even these high molecular weight cellulose carbanilates were found to be soluble in DMSO, DMF, and THF (Schlufter et al. 2006).

Table 9. DS and Solubility of the Cellulose Phenyl Carbanilates Homogeneously Prepared in BMIMCl with Phenyl Isocyanate at 80°C, for 120 min, Starting with Cellulose Spruce Sulfite pulp

Molar ratio	DS	Solubility[a]	
AGU/reagent		$(CH_3)_2SO$	THF
1	0.26	-	-
3	1.46	+	-
5	2.39	+	+
10	2.55	+	+

[a]+soluble, -insoluble

Tosylation of cellulose in EMIMAc with *p*-toluenesulfonic acid chloride (tosyl chloride) was studied, but surprisingly pure cellulose acetates were isolated (Schöbitz, 2007, Köhler et al. 2007). In contrast, the above-mentioned side reaction during the conversion with 2-furoyl chloride acetylation may succeed via two different reaction pathways here. One possibility may be the formation of the cellulose tosylate and subsequent nucleophilic displacement reaction with the acetate anion of the IL. This assumption was confirmed with a model reaction of cellulose tosylate (DS 1.33), dissolved in EMIMAc at 70°C. A decrease in DS of tosyl moieties down to 0.14 after 4 h was observed, and the nucleophilic displacement with acetyl moieties was determined by FTIR spectroscopy (see Fig. 16). Alternatively, the reaction may run through a mixed *p*-toluenesulfonic acid-acetic acid anhydride formed from tosyl chloride and EMIMAc. ^{13}C NMR spectra showed the appearance of new signals for a carbonyl moiety and for a methyl moiety of the acetyl group. Consequently, the acetylation caused by the conversion with tosyl chloride could be a combination of both mechanisms, i.e. acetylation by nucleophilic displacement and reaction with the mixed anhydride formed *in situ*.

Silylation of cellulose in ILs was investigated. Trimethylsilyl celluloses (TMSC) with a wide range of DS values were synthesized with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) in the ILs EMIMAc, EMIMCl and BMIMCl (Köhler et al. 2008). The silylation of cellulose can be controlled by the IL used, reaction time, reaction temperature, molar ratio AGU/HMDS and addition of co-solvents. TMSC with DS up to 2.85 were prepared. The limited solubility of HMDS in the applied ILs resulted in a two-phase system. Therefore, co-solvents, e.g. chloroform, were used to guarantee a better mixing of HMDS with the cellulose solution. During the synthesis of highly functionalized derivatives precipitation of the TMSC occurred. The products were isolated easily by filtration, which simplifies the recycling of the IL.
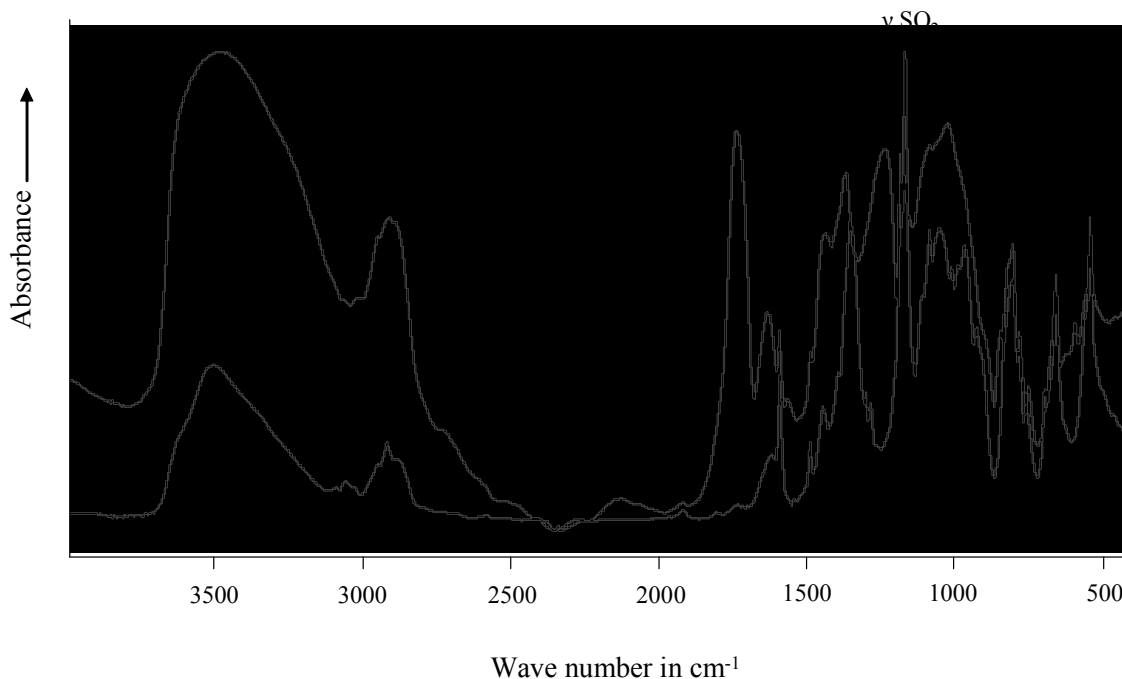
Fig. 16. IR spectra of a) cellulose tosylate (DS 1.33), and b) cellulose acetate obtained by dissolution of cellulose tosylate in EMIMAc for 4 h at 70°C

A fairly new development is the preparation of inorganic esters of cellulose in ILs. Cellulose sulfates may be synthesized by treatment of cellulose in BMIMCl with pyridine/SO_3 or DMF/SO_3 complexes. Water-soluble low-substituted derivatives (DS about 0.4) are accessible in this way, which are promising materials for symplex membranes and microspheres in biomedical applications (Gericke et al. 2007). Mixed cellulose sulfate esters with hydrophobic functions were prepared in a comparable manner to obtain detergents (Scheibel 2007).

Moreover, synthesis of an interesting cellulose-polymerized ionic liquid composite was demonstrated by an *in situ* polymerization method using two kinds of ionic liquids, which dissolved cellulose as a solvent and had a polymerizable acrylate group (Murakami et al. 2007). Cellulose was dissolved in BMIMCl in the presence of the IL 1-(4-acryloyloxybutyl)-3-methylimidazolium bromide and the radical polymerization of the polymerizable ionic liquid was carried out by 2,2'-azobis (isobutyroniitrile) in the solution. The results of the IR spectrum and elemental analysis indicated that the isolated product was the desired composite.

OUTLOOK

This review reveals the potential of ILs for cellulose regeneration and homogeneous chemical modification, although some shortcomings clearly appear that must be considered in further work concerning the interesting and promising system cellulose/IL. One of the opportunities not discussed yet is the fact that ILs can be tailored

according to the needs of a specific dissolution or functionalization step because of the huge structural versatility. A defined structural adjustment for the dissolution is only scarcely done, because a basic understanding of the interaction between ILs and cellulose does not exist yet. Investigations are under progress to reveal the mechanisms behind the dissolution process. From this knowledge a more specific structure property relation is expected and the synthesis of optimal ILs would be possible.

Nevertheless, tailored ILs will open up new routes for blending processes, because one can adjust the solvent properties for the components or the stability of a colloidal system. Interesting new approaches were already published for biologically active materials accessible by incorporating enzymes in a cellulose matrix (Turner et al. 2004, 2005) or blending cellulose with heparin (Viswanathan et al. 2006) to obtain fibers or membranes with increased anticlotting behavior. Moreover, the loading of cellulose dissolved in BMIMCl with magnetite yielded "magnetic cellulose" (Swatloski et al. 2006). A comparable process was used for the preparation of sensor materials containing dendrimers (Bagheri et al. 2008) or dyes suitable, e.g. for detection of heavy metal ions (Poplin et al. 2007).

In case of the modification reactions the requirements for tailored ILs are more obvious. ILs suitable for homogeneous cellulose modification should have low melting points and low viscosities. Moreover, they need to be inert during the conversion. An example for an adjustment of the ILs is the use of imidazolium ILs with an alkyl function at position 2 for the etherification of cellulose, decreasing side reactions. Room temperature ILs (RTIL) could open up new paths for the cellulose modification even by enzymatic transformations such as transesterification. The possible use of RTILs for this type of conversion was already shown. Attempts for the enzymatic esterification of carbohydrates in ILs, able to dissolve cellulose as well, are known (Liu et al. 2005).

The side reactions revealed for EMIMAc, the cationic functionalization of cellulose with choline chloride, and the reaction of cellulose with polymerized ionic liquid showed another potential of the ILs, i.e. the combination of the solvent with the features of a reagent. Especially the nucleophilic properties of the easily exchangeable anions are of interest.

A challenging question is still the dissolution of wood in ILs. Attempts were undertaken to dissolve pine and oak wood saw dust in BMIMCl in combination with DMSO. Heating for several hours can dissolve the wood (Fort et al. 2007). These solutions are usable for the analysis and fractionation of wood. In addition, these solutions can be applied for a direct chemical modification of wood in this medium to obtain cellulose derivatives after proper work up or to obtain blends of cellulose derivatives with hemicelluloses and lignin as recently shown for the acetylation of wood (Kilpelainen et al. 2007, Xie et al. 2007).

It could be shown that the IL EMIMAc, which dissolves 6-azido-6-deoxy cellulose with a degree of substitution of 0.75, is a suitable reaction medium for the homogeneous conversion of 6-azido-6-deoxy cellulose with propargyl-PAMAM dendrons via copper-catalysed Huisgen reaction ("click" reaction). First to third generation PAMAM-triazolo dendrons derivatives could be prepared. It could be shown that there are no impurities or remaining ionic liquid in the products (Heinze et al. 2008).

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ABBREVIATIONS AND ACRONYMS

AcO: Acetate.
Ac_2O: Acetic anhydride.
ADMIMBr: 1-Allyl-2,3-dimethylimidazolium bromide.
AGU: Anhydroglucose unit.
AMIMCl: 1-Allyl-3-methylimidazolium chloride.
BDMIMCl: 1-Butyl-2,3-dimethylimidazolium chloride.

BDTACl: Benzyldimethyl(tetradecyl)ammonium chloride.
BMIMCl: 1-Butyl-3-methylimidazolium chloride.
BMIMFmO: 1-Butyl-3-methylimidazolium formate.
BMIMDCA: 1-Butyl-3-methylimidazolium dicyanoamide.
BMPyCl: 1-Butyl-3-methylpyridinium chloride.
BzO: Benzoate
ChCl: Choline chloride.
CMC: Carboxymethyl cellulose.
DMAc: *N,N*-Dimethylacetamide.
DMF: *N,N*-Dimethylformamide.
DMSO: Dimethylsulfoxide.
DP: Degree of polymerization of the native biopolymer.
DS: Degree of substitution of the fuctionalized biopolymer.
EMIMAc: 1-Ethyl-3-methylimidazolium acetate.
EMIMCl: 1-Ethyl-3-methylimidazolium chloride.
EMIMFmO: 1-Ethyl-3-methylimidazolium formate.
HMIMCl: 1-Hexyl-3-methylimidazolium chloride.
FmO: Formate
HMDS: 1,1,1,3,3,3-Hexamethyldisilazane.
IL: Ionic liquid. compounds with m.p. below 100°C.
Me: Methyl.
M_r: Relative molecular mass of a simple compound, or average molecular mass
for a biopolymer.
m.p. : Melting point.
$N(CN)_2$: Dicyanamide anion (dca).
NIR: Near-infrared spectroscopy.
NMR: Nuclear magnetic resonance
Py: Pyridinium.
SEC: Size exclusion chromatography.
SEM: Scanning electron microscopy.
RTIL: Room temperature ionic liquids.
TBAF Tetra-n-butylammonium fluoride.
TEM: Transmission electron microscopy.
THF: Tetrahydrofuran.
TMSC: Trimethylsilyl cellulose
TosCl: Tosyl chloride.
Trityl: Triphenylmethyl