

*Chapter 1*

# CHALLENGES AND PERSPECTIVES OF IONIC LIQUIDS VS. TRADITIONAL SOLVENTS FOR CELLULOSE PROCESSING

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## ABSTRACT

It is commonly accepted that world-wide production of oil, coal and natural gas will eventually come to a halt, although we still heavily depend on these non-renewable feed stocks and their associated chemical derivatives. Therefore, new, sustainable resources for the production of industrially important chemicals are required. Biomaterials offer much promise in this regard, since they generally contain a lot of cellulose which can be transformed and potentially provide a great source of industrially important chemicals. Presently, only a small part of the annual biomass growth in the world is utilized by industry, while the rest is decaying along natural pathways. In order to effectively process cellulose, it needs to be dissolved in some liquid medium. Present state-of-the-art commercial technologies employ very toxic and hazardous processing with volatile organic solvents like CS<sub>2</sub>. However, this need not be the case. Ionic liquids (ILs) have shown great potential for the dissolution of cellulose. Some ILs also have attractive physical properties such as: low vapor pressure, high thermal stability and reusability. Thus, they are potentially viable and more environmentally friendly alternatives. Hereby, we present and discuss some of the challenges and perspectives for ILs in terms of their potential for cellulose processing. We briefly review the historical processes and current methods for cellulose processing, and look at alternative processes taking advantage of ILs.

## INTRODUCTION

### Historical Prologue – ‘The Chemical Dangers’

During the past few centuries, the industrial revolution completely reformed the socioeconomic and cultural conditions of the world. There were major changes affecting farming, fisheries, food industry, manufacturing/production/transportation of goods, mining, chemical industry and so forth. More importantly, it had a positive impact on the average income of people, with an unprecedented 10-fold increase within a few generations. The revolution was found to be short sighted with respect to ecological health of our planet. The rapid positive growth came hand in hand with slow but long-term negative effects that became serious issues later on. Only in the 20<sup>th</sup> century, numerous examples of accidents caused by chemical plants killed thousands of people and resulted in environmental disasters ruining the local flora and fauna and sometimes risking the ecology on global scales. Just to mention a few of the most serious accidents during the past 100 years that happened in various chemical plants: an explosion of ammonium sulfate and ammonium nitrate fertilizer mixture in Oppau, Germany (1921) [1]; release of methyl-mercury in the industrial wastewater in Minamata, Japan (1932-1968) [2]; release of dioxins into the atmosphere in Seveso, Italy (1976) [3]; toxic gas leak at a pesticide plant in Bhopal, India (1984) [4]; an explosion at a fertilizer factory in Toulouse, France (2001) [5] and a flood of red-sludge from injured storage pools in a bauxite process plant in Devecser, Hungary (2010) [6]. These incidents stirred the entire global community and scientific world; and have inevitably contributed to the emergence of the concept of ‘Green Chemistry’. In order to realize the principles of Green Chemistry, Paul Anastas and John Warner devised a guideline of 12 principles for chemists [7]. One of the important principles is the use of renewable feedstocks. Nature works on the principle of conservation of mass and it recycles everything. We can look upon Mother Nature for providing solutions to our present problems viz. a shortage of fossil fuels, growing energy demand, concerns over security of fuel supply, environmental changes and shortage of suitable, natural fibers for textile industry (e.g. cotton).

Throughout most of the human history, biomass has always been a popular starting material for the production of a variety of goods. Wood has been widely used as a raw material for buildings, ships, fuel, and various products for centuries. However, in the light of the development of bioengineering and catalytic chemistry, it has later been utilized for the production of biofuels, various multi-value-added chemicals and biomaterials. Wood is known to be the richest source of low carbon lignocellulosic material [8]. Lignocellulose mostly contains 35-50% of cellulose, 20-35% hemicellulose, and 5-30% lignin as well as extractives. Cellulose represents the most significant fraction of biomass on our planet [9]. It has garnered immense importance as a low cost biorenewable and biodegradable raw material. It not only can regenerate quicker than fossil fuels but also it can be obtained from the sources other than the human food source [10]. Once isolated, cellulose can act as an useful feedstock for a variety of industrially important materials. In fact, cellulose, its derivatives and related compounds have found enormous applications in our day-to-day life (fibers, tissues, paper, membranes, polymers, paints etc.) [11] and more recently for the production of biofuels obtained by various processes e.g. fermentation of sugar monomer units after hydrolyzing cellulose [12-14]. Furthermore, cellulose and its composites have also



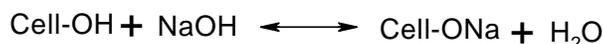
The positions of inter- and intra-molecular hydrogen bonding in strands define the different crystalline structures of cellulose.

Cellulose I, which is also called natural cellulose, exists with structures I $\alpha$  and I $\beta$ . Bacteria and algae produce cellulose with high contents of I $\alpha$  cellulose while higher plants contains mainly I $\beta$  cellulose. However, when cellulose is regenerated as cellulosic fibers, it turns into cellulose II which is more amorphous. The conversion of cellulose I to cellulose II is irreversible indicating that the amorphous phase is stable, whereas cellulose I is only metastable [20]. The degree of polymerization in cellulose varies with the source strongly affecting many properties [21]. Cellulose obtained from wood pulp has a low degree of polymerization ranging from a few hundred to a few thousand units; whereas the bacterial celluloses, cotton and other plant fibers have the higher degree of polymerization [23].

## CLASSICAL CELLULOSE DISSOLUTION PROCESSES

Due to molecular and supra molecular rigid structure of cellulose, it is extremely difficult to dissolve in water and most of the conventional organic solvents. Moreover, the decomposition temperature of cellulose is lower than its melting point. Therefore, in order to explore the potentials of cellulose fully, there is the need of an efficient solvent system. In order to dissolve cellulose, it is commonly believed that it is extremely necessary to disrupt the hydrogen bonding system of cellulose to initiate solvation of the cellulose chains [29]. In 1983, Turbak classified solvents for cellulose dissolution into four main categories based on the possible cellulose-solvent interactions [24]. The cellulose polymer basically acts as an amphoteric compound as it acts as a base when solvent is an acid while it acts as an acid when solvent is a base, e.g. viscose process. It also acts as a ligand with certain types of complexing solvents, such as nickel ammonium hydroxide (Nioxam) and cadmiumethylenediamine (Cadoxen). It can also be transformed into soluble chemical derivatives or intermediates, e.g. acetate, formate. Philipp *et al.* and Heinze *et al.* further distinguished solvents for cellulose dissolution into aqueous, non-aqueous, derivatizing or non-derivatizing mediums [25, 26].

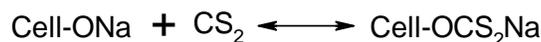
Almost 150 years ago, the first efforts of dissolution of cellulose or derivatives of cellulose were reported [27]. They were then followed by the development of vastly diversified solvents for cellulose dissolution. The most extensively used cellulose dissolution process is the “viscose process” [28-30]. It is the oldest process and is still currently used to manufacture cellulose fibers (cellulose is transformed to cellulose xanthate using carbon disulphide then dissolved in sodium hydroxide. Even today, cellulosic fibers are produced about 95% annually by this process [31]. Initial treatment with approximately 20% w/w NaOH solution converts cellulose to a slurry of alkali cellulose (Scheme 1).



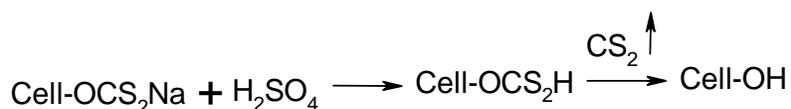
Scheme 1. The formation of alkali cellulose.

The residual low molecular weight cellulose and hemicellulose dissolves partially in alkaline solution and is removed when slurry is filter pressed. The resultant material is called white crumb which is then allowed to ripen for controlled depolymerization to give

manageable viscosities in a spinning solution, but still keeps long enough chain lengths to impart good physical properties to the final fiber product. The properly aged white crumb is then treated with carbon disulfide ( $\text{CS}_2$ ) where soda-cellulose is converted into cellulose xanthate along with colored inorganic impurities to produce the material which is referred to as 'yellow crumb' (Scheme 2). The yellow crumb is mainly a block co-polymer of cellulose and cellulose xanthate [28, 32].



Scheme 2. Formation of the 'yellow crumb'.



Scheme 3. Cellulose restructuring and carbon disulfide recovery.

Furthermore, this yellow crumb is dissolved in an aqueous alkali solution. However, because of the blocks of non-xanthated cellulose, the yellow crumb is not completely soluble and gives a highly viscous solution which is termed as "viscose". The viscose is then allowed to ripen. During ripening, the loss of few xanthate groups followed by its relocation on other hydroxyl groups gradually turn the crystalline cellulose into amorphous cellulose leading to its complete dissolution in the solution. The filtered viscose is then forced through a spinneret. The viscose exits the spinneret and comes in contact with a solution of dilute sulphuric acid, sodium sulphate and  $\text{Zn}^{2+}$  ions. As soon as viscose enters into the acidic spin bath, the sodium xanthates convert into unstable xanthic acid groups. The spontaneous loss of  $\text{CS}_2$  leads to regeneration of cellulose in fine filament of cellulose fiber or rayon fibers (Scheme 3) [32].

The viscose solution contains about 8–12 wt.% cellulose [31]. There are a lot of environmental issues related to the viscose process. Particularly, the consumption of raw materials (solvents and auxiliaries such as carbon disulphide, sodium hydroxide, sulfuric acid) is more than twice the amount of cellulose fibers produced. [31]. Moreover, less than perfect recyclability of carbon disulphide as well as waste water and exhaust air treatment issues are also complicated due to rigid environmental requirements.

In an attempt to dissolve cellulose, a few other processes were developed which explore the use of intermediate derivatization to produce hydrolytically unstable carboxylic acid esters of the cellulose [29]. There are few other processes developed which exploit the strategy of using intermediate derivatization to produce hydrolytically unstable carboxylic acid esters of the cellulose for the dissolution of cellulose [29]. Among those, cellulose acetate (CA) [33, 34], cellulose formate (CF) [35-41] and cellulose trifluoroacetate (CTFA) [42-54] have been extensively studied. The homogeneous solution of cellulose is obtained during the acetylation of cellulose with acetic anhydride in the solutions containing co-solvents such as methylene chloride or DMF. Moreover, the isolated CA can be functionalized on remaining hydroxyl groups in other solvents. Fibers with improved orientation can be drawn by dry spinning a solution of cellulose acetate in acetone.

Subsequently, saponification in caustic soda or sodium acetate results in a highly oriented cellulose yarn [55, 56]. The process is called the Fortisan process.

Cellulose formates can be readily obtained by a catalyst-free treatment of cellulose with an excess of formic acid over periods of 4–15 days, leading to major formylation at C-6 position [35, 36]. The rate of the dissolution process can be markedly increased by using sulphuric acid as catalyst. A mixture of formic acid and phosphoric acid was able to dissolve cellulose via in situ formation of cellulose formate [28, 57]. The solution of cellulose formate in the acid mixture is liquid crystalline in nature. The spinning of the solution into an acetone bath using an air gap spinning process results into the filaments which are further saponified using an alkali solution. This process is called the Michelin process [28, 58] and it produces high modulus and high tenacity yarns.

In the case of cellulose trifluoroacetate, NMR spectroscopy showed that the primary OH-groups are almost completely functionalized during trifluoroacetylation [41, 42]. Partial derivatization occurs in mixtures containing TFA/CH<sub>2</sub>Cl<sub>2</sub> with slow degradation of the polysaccharide [44]. It is noteworthy to mention that the mesophasic solution obtained from 4% (w/w) cellulose concentrations can be used to regenerate strong fibers. However, all of these methods involving hydrolytically unstable cellulose esters suffer from the high cost and corrosive nature of the reagents [29].

In the mid 19<sup>th</sup> century, the cuprammonium fiber process was discovered, which involved the dissolution of cotton in Schweizer reagent (alkaline solution of ammonia and copper salt) followed by its regeneration in a coagulation bath [59-60]. Later, the fiber process was extended for the production of artificial silk [61-62]. Furthermore, Hermann Staudinger used the Schweizer reagent for elucidating macromolecular structure of cellulose for which he was awarded the Nobel prize in the year 1953 [63]. Though the relatively high cost of cotton and copper salts hampered the process to turn out into a large manufacturing process, it is still used for the preparation of hollow fibers for dialysis. Today, many variants of this process are in use, containing mainly a transition metal and an amine or an ammonium component. One could mention [64] e.g. Cuoxen ([Cu(NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>2</sub>][OH]<sub>2</sub>), Nioxam ([Ni(NH<sub>3</sub>)<sub>6</sub>][OH]<sub>2</sub>), Zinkoxen, ([Zn(NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>][OH]<sub>2</sub>), Cadoxen ([Cd(NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)<sub>3</sub>][OH]<sub>2</sub>), Nitren ([Ni(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N][OH]<sub>2</sub>) and Pden ([Pd(NH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>)][OH]<sub>2</sub>). The dissolution of cellulose was mainly accomplished by deprotonation and coordinative binding of the hydroxyl groups in the C2 and C3 position of the glucose monomer unit with a metal complex [65].

The well-known and immensely explored technical process of cellulose activation (also known as mercerization) involves the treatment of cellulose with alkaline solution [29]. There are various methods reported for the dissolution of cellulose in solvent systems like cellulose-NaOH-water. These ternary systems are particularly attractive since the only added chemical is a cheap and abundant inorganic one. The cellulose dissolves in the narrow dissolution zone below -5 °C in the 7–10 wt.% aqueous NaOH solution, however the molecular weight and the degree of crystallinity also influences the process [66-70]. An aqueous solution of 1.0 wt.% poly(ethylene glycol) (PEG) and 9.0 wt.% of NaOH dissolves 13 wt.% of cellulose, with DP around 800 [71]. Recently, a number of reports are published on the dissolution and derivatization of cellulose in an alkaline solution of urea and thiourea [72-75]. Zhang *et al.* have shown that cellulose can be quickly dissolved in a precooled (-12 °C) aqueous solution of 7 wt.% NaOH and 12 wt.% urea [76]. The dissolution is due to the formation of urea hydrates by self-assembly at the surface of the NaOH hydrogen-bonded cellulose. The

solution is also found to be thermodynamically unstable over a longer time period [77-78]. Few interesting modifications of the concept are represented by the use of LiOH/urea [79-80] and NaOH/thiourea solution [81]. Aqueous solutions of trimethylbenzylammonium (Triton B), dimethyl dibenzylammonium (Triton F) or guanidinium hydroxide have also been used either for the dissolution or mercerization of cellulose [28, 82].

Various aqueous inorganic salts and molten salts hydrates have also been attempted in the dissolution of cellulose [83]. Calcium thiocyanate monohydrate, lithium thiocyanate monohydrate and eutectic NaSCN/KSCN, with different additives such as calcium thiocyanate trihydrate or dimethyl sulphoxide are able to dissolve cellulose. [82-89]. Few other molten lithium hydrate salts such as lithium iodide, lithium nitrate, lithium acetate and lithium perchlorate were also able to dissolve cellulose with a chain length as high as 1,500 [89-92]. The combination of a lithium salt with a non-aqueous solvent was found to be an important tool in the dissolution of cellulose. In 1979, McCormick *et al.* reported the first *N,N*-dimethylacetamide (DMAc)/LiCl system for the dissolution of cellulose with negligible degradation [93-105]. It was followed by diverse combination of solvent compositions in which DMAc was substituted in the solvent mixture with a series of organic amide-based solvents such as *N*-methyl-2-pyrrolidone (NMP) [104], *N,N*-dimethylformamide (DMF) [105], DMSO [106], 1,3-dimethyl-2-imidazolidinone (DMI), *N,N'*-dimethylethylene urea (DMEU) [107,108], *N,N'*-dimethylpropylene urea (DMPU) [106] and hexamethylphosphoric triamide (HMPT) [109]. Among those, NMP and DMI were able to dissolve cellulose without any major chain degradation and have a higher thermal stability [28]. However, partial recycling of the expensive solvent systems halted their utilization in large scale applications.

The DMAc/LiCl solvent system is a very important solvent system for the functionalization of polysaccharide owing to its inactive and thermally stable nature [29]. DMAc/LiCl was employed for the esterification of cellulose using carboxylic acid anhydrides and chlorides under totally homogeneous conditions [86,103,104]. Acetates, propionates, butyrates, mixed acetates/propionates, a broad variety of halogenated, alicyclic, aromatic and unsaturated esters with a stoichiometric control of the acetyl content can be also obtained with various acyl chlorides in a homogeneous phase [29, 112-116].

In 1939, a new non-derivatizing method on the dissolution of cellulose in amine oxides was introduced [117]. Later, *N*-methylmorpholine-*N*-oxide (NMMO) was found as a direct solvent for cellulose [28, 118-126].

The NMMO process is currently the only one that provides an industrial alternative to viscose process for fiber production. After overcoming many obstacles, such as investment costs and recovery of the expensive solvent, the process is now applied in large scale production of textile fibers under different brand names: Lyocell (Lenzing), Tencel (Courtaulds), Alceru (TITK Rudolstadt) and Newcell (Akzo Nobel). In the NMMO process, the 3-phase diagram of the components NMMO, cellulose and water is of crucial importance. In a typical dissolution range of approximately 14% cellulose, 10% water and 76% NMMO and at the temperature of over 100 °C, homogeneous solution for spinning is obtained. The process starts with a suspension of approximately 14% cellulose, 22% water and 68% NMMO. Cellulose is not soluble in this solution. Then water is evaporated and cellulose starts dissolving in the narrow range of water concentrations. It is a well-known fact that explosive mixtures may be formed and particularly the presence of metal ions leads to more unstable systems. Therefore, the solution is usually stabilized by the addition of propyl gallate [127-128]. In a subsequent step, the mixture is removed from the dissolution area by forcing a

degassed and clear solution through the spinneret which enters in a water bath and fibers are drawn. Finally, the finishing steps, i.e. washing, finishing and drying, complete the process [28]. The aqueous NMMO solution is reused for the process by maintaining concentration of suspension described earlier. The possible decomposition of NMMO at high temperatures causes many safety concerns about the NMMO process. Moreover, few side reactions result in the loss of solvent and irreversible changes in the final fiber product [129-130].

## IONIC LIQUIDS

The question of what an ionic liquid (IL) actually is, has been debated for a long time. Perhaps the answer is as simple as ‘a liquid salt consisting of ions and ion pairs’ [131]. However, today when ILs are mentioned they are often looked upon as organic salts that are liquid at a temperature of 100 °C or below, also known as room temperature ionic liquids (RTILs). It is often stated that ILs possess certain highly desired properties like a low vapor pressure, high thermal stability [132], non-flammability and low toxicity [133]. Often these properties have been realized, although numerous ionic liquid formulations can be found that do not fulfill each and every criteria mentioned above. However, an ionic liquid consists of at least two components, an anion and a cation, but also multi-ionic substances like deep eutectic solvents [134,135], dual charged ions [136,137] and zwitterions [138] are many. Moreover, many formulations are frequently consisting of a mixture of ions and molecular species, resulting in a vast amount of different potential ILs. In fact, estimations have been made that up to  $10^{18}$  different ion combinations are possible and, in this case, finding properties common to all ILs will be difficult. This statement should instead be looked at as a generalization of the field as a whole, and should not be taken as an overall rule or law. As an example, it can be mentioned that e.g. 3-methyl-1-*H*-imidazolium nitrate and 3-butyl-1-*H*-imidazolium nitrate are easily ignited upon contact with an open flame and will explode at elevated temperatures, 255 °C and 225 °C, respectively, even in the absence of O<sub>2</sub> [139]. Still, 3-butyl-1-methyl-imidazolium dicyanamide and 3-butyl-1-methyl -pyrrolidinium dicyanamide are known to be used as hypergolic fuels [140]. Several studies have also shown that ionic liquids subjected to elevated temperatures for a prolonged time decompose at a much lower temperature than previously assumed [141]. A number of studies demonstrate that certain ionic liquids are distillable at elevated temperature and reduced pressure [142-146]. While the toxicity of ionic is not thoroughly investigated, some studies have shown that many ionic liquids commonly used today are toxic in nature and their toxicity might vary significantly between trophic levels and organisms in an aquatic ecosystem [147-150]. The fact that even ‘hydrophobic’ ILs are frequently (at least marginally) soluble in water renders contamination of water effluents something that needs to be considered. Another claim often assigned to ILs is that they are ‘green chemicals’. However, today’s ILs are often made from non-renewable petroleum-based feed-stocks and frequently require alkyl halide precursors. Even though some ILs are generally reported as being non-toxic, the synthetic procedures required to prepare them often contain multi-step reactions, resulting in poor atom economy and the accumulation of hazardous wastes. These practices are not in line with the 12 principles of green chemistry [7] and procedures resulting in ILs cannot be considered as truly ‘green’ if such synthesis practices are employed. This is something that needs to be addressed

and is usually 'forgotten' when declaring ionic liquids as 'green' chemicals. However, it is wrong to claim that none of the ILs can be considered environmentally beneficial since many ILs demonstrate properties desirable from both environmental and technical points of view. Also, in recent years, interest in more eco-friendly ways of synthesizing ILs have emerged with several methods that use renewable resources as ion precursors [148]. Considering this in combination with their reusability and (frequent) non-volatility makes them valid green alternatives to many of the solvents and chemicals used today.

Volatile organic compounds (VOCs) have been used as solvents and extraction media for a long time. Setting aside the problem of the ever diminishing supply of oil and other fossil resources, the use of VOCs is becoming more and more restricted due to rising environmental and safety concerns. Most of these hydrocarbon chemicals are known for their toxicity, both in terms of the environment and to the process operators exposed to them. They are often highly flammable resulting in a potential risk for explosions upon use and storage that can be especially dangerous on an industrial scale [151]. Many of the drawbacks of VOCs are in no small part due to their highly volatile nature. Many ILs possess no such drawbacks and, instead, they can be characterized by properties like a wide liquid range, negligible vapor pressure and extremely complex solvation properties. Even though the toxicity of ILs has not yet been fully investigated, their low saturation vapor pressures minimize atmospheric emissions and some ILs have even been shown to be biodegradable [149,150]. Nevertheless, it should be pointed out that industrial applications for ILs are still at a pioneering state and much more development is needed before ILs can be commonly applied on an industrial scale - though some exceptions exist [152,154].

The versatility of ILs, as associated with their physico-chemical properties makes them a very interesting group of solvents for industrial applications. Even though most IL applications are still at an infant state, they have been exploited in many areas of technology [153-155] ranging from chemistry and biochemistry to energy and materials technology. Many potential applications have already emerged, such as in the field of tribochemistry in the form of lubricants or lubricant additives [156], supported catalytic media [157], fuel for rocket engines [140], capturing of greenhouse gases [158] or as solvents for well-known organic chemical reactions such as Diels-Alders [159] or Friedel-Craft [160]. The literature is full of applications and potential applications taking advantage of ILs. In recent years, the number of papers in this area has increased massively although to tackle each and every application area falls out of the scope of this work.

## CELLULOSE DISSOLUTION IN IONIC LIQUIDS

As previously mentioned, the possibility to dissolve cellulose is of vital importance for the utilization and processing of it. The processing of cellulose is currently performed by means of different methods (see earlier sections) many of which include the use of toxic chemicals and the accumulation of toxic waste. Ionic liquids, however, have many desirable properties in line with the concepts of green chemistry and some ionic liquids are capable of dissolving cellulose in large quantities. In some cases, loadings as high as 25 wt-% have been claimed [161], often without the need of any pre-treatments [162]. Cellulose dissolution in ILs is a direct dissolution process contrary to the currently dominating viscose process. In

fact, it is more similar to the less common NMMO process which manages to dissolve cellulose without derivatization by using a mixture of N-methylmorpholine oxide and water (see earlier). The precipitation of cellulose is then performed by increasing the ratio of water in the solution. Cellulose is directly solvated by ILs and can be precipitated via addition of an anti-solvent, usually water, but in some cases, other solvents like primary alcohols such as methanol are used [163, 164]. By altering the regeneration process, various cellulose structures can be obtained, such as powders, beads, tubes, fibers and films [165]. While the morphology of the cellulose structure is often drastically different, the degree of polymerization and poly-dispersity has been observed to remain more or less intact [165]. Large scale industrial applications of ILs for cellulose processing have not yet emerged but some criterion for ILs intended for cellulose processing have already been established [166] and criteria for ILs that are considered for the dissolution of cellulose are listed below (list adopted from [166]).

- Low melting point (<20 °C) and high decomposition point (>200 °C)
- No cellulose decomposition
- Stable and storable spinning dopes
- Easy processing (low viscosity)
- Easy cellulose regeneration
- Uncomplicated recovery of the ionic liquid
- No toxicity and no odors
- More cost effective process than the NMMO or Viscose process
- Fiber quality equal or surpassing those of the MNNO or Viscose process

Today, traditional cellulose processing methods are facing many challenges due to environmental and energy related problems and concerns [165, 167]. Unlike solvents used in classical methods, ILs can often be completely recovered and reused [161, 168, 169]. Also, ILs have the ability to dissolve cellulose at room temperature or at only slightly elevated temperatures [162,169,170]. Therefore, the use of them requires less energy and provokes a lower degree of decomposition in the final product [141]. Moreover, microwave and ultrasound techniques have also been studied in order to increase dissolved mass fractions, without the need for increased operating temperatures. Imidazolium-based ILs have been reported to dissolve up to 10% wt cellulose using conventional heating but can dissolve up to 25 wt-% upon exposure to microwave heating [161]. The reasons are not obvious but the nature of microwave dielectric heating is different than conventional conductive and convective heating. In microwave heating, the heat comes from the absorption of microwaves by the molecules, an internal heating process, contrary to the conventional methods that conducts heat from an external heat source [171]. The absorption of microwaves is closely related to the polarity of the solvent where the higher the polarity is, the higher the absorption is, resulting in a more rapid and intense heating. Also, ionic compounds interact particularly well with microwave irradiation. Thus, ILs are excellent solvents for microwave heating due to their exceptional ability to absorb microwave irradiation [172]. In fact, decomposition of dissolved cellulose in ionic liquids can occur during prolonged heating [173]. Instead, shorter bursts of radiation followed by vigorous stirring is recommended [161,174] thereby avoiding localized hot-spots of intense heat that easily occurs during microwave heating.

**Table 1. Common ionic liquids capable of dissolving cellulose**

nr	Ionic liquid	cellulose	wt % dissolved	Dissolution temperature	Dissolution time	Viscosity (P) 25	Kamlet-Taft values			ref
							$\alpha$	$\beta$	$\pi$	
1	[BMIM][Cl] (1-butyl-3-methyl imidazolium chloride)	Avicel 398	20%	100° C	<60 min	n.n.	0.46	0.85	1.10	186, 285
2	[AMIM][Cl] (1-allyl-3-methyl imidazolium chloride)	Avicel 398	15%	100° C	<60 min	1.16	0.46	0.83	1.17	186, 284
3	[BDMIM][Cl] (1-N-butyl-2,3-dimethyl imidazolium chloride)	Avicel 286	9%	80° C	<12 h	n.n.	n.n.	n.n.	n.n.	169
4	[ADMIM][Br] (1-N-allyl-2,3-dimethyl imidazolium bromide)	Avicel 286	12%	80° C	<12 h	n.n.	n.n.	n.n.	n.n.	169
5	[EMIM][OAc] (1-ethyl-3-methyl imidazolium acetate)	Avicel 398	8%	100° C	<60 min	n.n.	n.n.	n.n.	n.n.	186
6	[BMIM][OAc] (1-butyl-3-methyl imidazolium acetate)	Avicel 398	12%	100° C	<60 min	0.44	0.36	0.85	0.74	186, 199, 195
7	[AMIM][OFo] (1-allyl-3-methyl imidazolium formate)	Micro cry 250	22%	85° C	NA	0.66	0.48	0.99	1.08	188
8	[EMIM][Pho] (N-ethyl-N-methyl imidazolium methylphosphonate)	MCC	10%	45° C	30 min	n.n.	0.52	1.00	1.06	162
9	[BDTAC] (benzylidimethyl(tetradecyl) ammonium chloride)	Avicel 286	5%	62° C	<12 h	n.n.	n.n.	n.n.	n.n.	194
10	[BmPy][Cl] (3-methyl N-butyl pyridinium chloride)	Avicel 286	18%	105° C	<12 h	n.n.	n.n.	n.n.	n.n.	194
11	[TMGH] <sup>+</sup> carboxylates	Microcrystalline cellulose	5%	100 <sup>0</sup> C	10 min	n.n.	n.n.	n.n.	n.n.	146

A lot of studies have been devoted to the utilization of ultrasound for dissolution [175] and synthesis [175-179] purposes. Surprisingly, little has been done in the field of ultrasonic-assisted cellulose dissolution in ILs. A study has shown that ultrasound irradiation, either continuously or in short bursts, can be used to enhance the dissolution process of different types of cellulose in imidazolium-based ILs [157]. The work demonstrated that some ILs seemed to be able to dissolve as much as 27 wt-% of microcrystalline cellulose, contrary to earlier reported 14.5 wt-% upon conventional heating. Moreover, the dissolution time was drastically decreased, in some cases down to 2 minutes upon using ultrasound instead of 1 hour when using conventional heating. No significant degradation of the cellulose or ILs occurred during the use of an ultrasonic-aided dissolution process. Other studies involving the dissolution of wood in ILs have shown that by pre-treating a wood-IL mixture with ultrasound irradiation, the dissolution time could be reduced by half [180]. Yet another study involving enzymatic saccharification of cellulose in ILs demonstrated that the conversion of microcrystalline cellulose increased by 53 % after ultrasonic pre-treatment [181]. It should be noted that the dissolution of cellulose is also greatly dependent on the type of cellulose used [157, 169, 182].

## CELLULOSE AND MOLTEN SALTS

One of the earliest attempts to dissolve cellulose using molten salts was done by C. Graenacher in 1934 [183]. He managed to dissolve cellulose using different alkyl-pyridinium chloride salts together with nitrogen bases. The importance of this discovery was not recognized right away because no practical applications were realized due to the high melting point of the salts employed. Like in many other cases regarding the applications of ionic liquids, it took several decades until the use of ILs for the dissolution of cellulose were re-evaluated. In 2002, Swatloski *et al.* demonstrated that low melting imidazolium-based ILs could be used as non-derivatizing solvents for the dissolution of cellulose [161]. The study revealed that 3-butyl-1-methylimidazolium chloride [BMIM][Cl] could dissolve up to 10 wt-% cellulose under conventional heating, 100 °C, and 25 wt-% cellulose when microwave heating was applied. Later on, other reports emerged that uncovered the fact that 3-allyl-1-methylimidazolium chloride [AMIM][Cl] could be used to dissolve up to 14.5 wt-% of dissolved pulp cellulose in less than one hour of heating at 80 °C [167, 168]. The studies also concluded that even though the morphology of the cellulose changed - actually meaning that the crystallinity was lower for the regenerated cellulose compared to the original cellulose - the regenerated cellulose still demonstrated good mechanical strength. In fact, if degradation of the cellulose polymer and consequent further processing of the monomeric units is desired, a decrease in cellulose crystallinity is highly desired. The mechanical strength of cellulose is closely related to its degree of polymerization (DP). Consequently, it should be mentioned that even though the temperature had very minor effects on the resulting cellulose DP, the time the cellulose spent dissolved had a clear negative effect on the DP for cotton cellulose [168]. Other halogen containing ILs that are known to dissolve high to moderate amounts of cellulose are 1-butyl-2,3-dimethylimidazolium chloride [BDMIM][Cl] (9 wt-% of Avicel 286 cellulose at 80 °C) and 1-allyl-2,3-dimethylimidazolium bromide [ADMIM][Br] (12 wt-% of Avicel 286 cellulose at 80 °C) [169]. Moreover, compounds like certain tetramethyl

guanidine derivatives have more recently shown promise as distillable cellulose dissolving solvents [146].

For a long time it was believed that in order for an IL to dissolve cellulose, a halogen anion had to be used. However, lately, many studies have concluded that the ability for an IL to dissolve cellulose is closely linked to the hydrogen bond basicity ( $\beta$ -value) of the IL [162,184,185]. This opens up the field for other types of anions, of which multiple with higher hydrogen bond basicity ( $\beta$ -value) than halogens. In recent years, many ILs with different types of anions have emerged. It has been shown that 1-ethyl-3-methylimidazolium acetate [EMIM][OAc] and 1-butyl-3-methylimidazolium acetate [BMIM][OAc] were able to dissolve 8 wt-% and 12 wt-% of Avicel 398, respectively, in one hour at 100 °C during direct dissolution and conventional heating [186]. Interesting enough, by using a different dissolution method, [EMIM][OAc] and [BMIM][OAc] were able to dissolve 13.5 wt-% and 13.2 wt-% of eucalyptus pulp Eu-569, respectively [187]. This was performed by creating a suspension of cellulose in an IL-water mixture followed by the removal of water at 90-130 °C under vacuum. This study also demonstrated that when using the same type of cellulose, the viscosity was substantially higher for ILs consisting of chloride instead of acetate as an anion. For this reason, a higher cellulose concentration was possible in ILs consisting of the acetate anion compared to chloride anions, thus making them more efficient for cellulose dissolution and the cellulose shaping processes. However, the acetate anion is not entirely stable and will partially react with the cellulose backbone to cause a partial acetylation. Consequently, 1-allyl-3-methylimidazolium formate [AMIM][OFo] that had a significantly lower viscosity than 1-allyl-3-methylimidazolium chloride [AMIM][Cl] was able to dissolve a higher amount of cellulose at lower temperatures [188]. 1-allyl-3-methylimidazolium formate [AMIM][OFo] was able to dissolve 22 wt-% microcrystalline cellulose, at 85 °C. Unfortunately, the dissolution time was never reported. Other imidazolium carboxylate based ILs known to dissolve cellulose have also been reported [170,189]. Nevertheless, it should be pointed out that halogens and carboxylates are not the only anions that are known to dissolve cellulose. Phosphonate anions combined with an imidazolium-based cation constitute yet another group of ILs that show high  $\beta$ -value and low viscosity - both interesting properties for an IL designed to dissolve cellulose [162,190]. It was shown that several ILs in this group have the ability to dissolve cellulose under mild conditions, the most promising being 3-ethyl-1-methylimidazolium methyl phosphonate [EMIM][(CH<sub>3</sub>O)HPO<sub>2</sub>] that managed to dissolve 10 wt-% of microcrystalline cellulose in 30 min, at 45 °C [162]. Thus, imidazolium phosphonate ILs show great potential for dissolving cellulose although further studies into the degradation of cellulose dissolved in these ILs are needed.

It was recently reported that in some cases a neat IL solvent might not always be the most efficient way to dissolve cellulose but instead a different kind of mixed solvent system can be used. One such mixed solvent system reported constitutes of various [BMIM][OAc]-lithium salt systems [170]. This report presented a study where 1 wt-% lithium salt (LiAc, LiCl, LiBr, LiClO<sub>4</sub>, LiNO<sub>3</sub>) was dissolved in [BMIM][OAc] and then used to dissolve microcrystalline cellulose. The conclusions were that the [BMIM][OAc]-Lithium salt systems demonstrated an increased cellulose solubility compared to neat [BMIM][OAc], especially around 50-60 °C. [BMIM][OAc]-LiAc manages to dissolve 16 wt-% microcrystalline cellulose at 50 °C compared to neat [BMIM][OAc] that dissolved only 12.5 wt-%. This observation supports the hypothesis that lithium salt hydrates can dissolve cellulose due to fact that Li<sup>+</sup> interacts with the cellulose hydroxyl groups [170,191]. Thus, it is speculated that Li<sup>+</sup> disrupts the intra-

molecular hydrogen bonds in cellulose leading to an increase in solubility. Another case of a mixed solvent system was demonstrated by the electrolyte solution of DMI-IL [192]. 1,3-dimethyl-2-imidazolidinone (DMI) is a molecular solvent used together with LiCl as a conventional solvent for dissolving cellulose but that solvent system can only dissolve 2 wt-% cellulose under harsh conditions, 150 °C, dissolution time 30 min [193]. As ILs [BMIM]Cl and [EMIM][OAc] were used, the dissolution capacity was now 10 wt-% [161] and 19.6 wt-% cellulose, respectively. The dissolution of cellulose was performed by first suspending the cellulose in DMI at 100 °C and thereafter adding a certain amount of IL ( $\chi_{IL} = 0-0.4$  molar ratio of IL) in the mixture. A significant reduction in dissolution time was achieved and it can be mentioned that a mixture of 0.40 DMI and 0.60 [BMIM][Cl] managed to dissolve 10 wt-% microcrystalline cellulose after only 3 min, at 100 °C. This is to be compared to neat [BMIM][Cl] that can dissolve 5 wt-% of the same cellulose in 120 h, at 90 °C [184]. Further studies including other molecular solvents showed a clear correlation between the  $\beta$ -value of the electrolyte solution and the solubility of cellulose. An electrolyte solution containing a molecular solvent with a high  $\beta$ -value and low hydrogen bond acidity ( $\alpha$ -value) demanded less IL to reach the same  $\beta$ -value as the neat IL while the electrolyte solution had a significantly lower  $\alpha$ -value than the neat IL. Unfortunately, no tests determining the viscosity of the electrolyte solution were carried out but a preliminary test showed promising results towards lowering the viscosity of the solution compared to neat ILs.

Until now, we have presented mostly examples involving imidazolium based ILs but there are also other ILs capable of dissolving cellulose. Other examples constitute e.g. benzyl dimethyl (tetradecyl) ammonium chloride (BDTAC) that only managed to dissolve a very low amount of cellulose and 3-methyl-1-butylpyridinium chloride [BmPy][Cl] [194]. However, [BmPy][Cl] was able to dissolve up to 37 wt-% of cellulose pulp 593, at 105 °C. Unfortunately, this IL has a high melting point of 95 °C and also significantly contributed to the degradation of cellulose during the dissolution process [194]. There are many other ILs, both imidazolium and non-imidazolium ones, known to dissolve cellulose. Several of these have been thoroughly documented in previous reports [182,189]. So far, the research efforts on the field of IL enabled cellulose processing has mostly focused on imidazolium based ILs [186,189] that frequently exhibit desired properties in terms of low melting point and low viscosity - both important factors for cellulose processing.

## CELLULOSE RECONSTRUCTION

Perhaps one of the most common reasons for cellulose dissolution is the desire to reconstruct it into the shapes and for the application needed. A report demonstrating the feasibility of using ILs for wet- and air-gap spinning showed that 3-butyl-1-methylimidazolium chloride had interesting potential [161] and a spinning dope containing up to 16.5 wt-% could be produced. However, technical drawbacks like a high melting point (70 °C), severe cellulose decomposition and a corrosive nature of the solvent system were observed [166]. The interest shifted, instead, towards 3-ethyl-1-methylimidazolium acetate that exhibits no corrosive nature, dissolves cellulose in the amount as high as 20 wt-% without severe decomposition and has a melting point below room temperature (below -20 °C) [166]. Existing wet-spinning techniques have already been developed and adapted for the

use of 3-ethyl-1-methylimidazolium acetate by TITK [164, 166] and the fibers produced demonstrated similar properties when looking at tenacity and elasticity as the ones produced from the viscose or NMMO process [166].

Another form of cellulose reconstruction is exemplified with the creation of nano-porous cellulose foam for isolation, packaging, filters or catalytic applications [195]. It was shown that nano-porous cellulose foam could be made in a three-step process: first, the cellulose was dissolved in [BMIM][Cl], followed by a precipitation as a thin layer on a glass surface and washed until all IL was gone. The foam was now quickly frozen in liquid nitrogen and freeze dried to remove all water while keeping the pore size to a minimum. This procedure left us a material with a porosity of 99 % and a contact surface of 186 m<sup>2</sup>/g when 4 wt-% of cellulose was dissolved. At this point it is worth mentioning that the cellulose concentration also had an impact on the morphology of the reconstructed cellulose [195,196]. Another method to create nano-porous cellulose materials using supercritical CO<sub>2</sub> has also been published [197]. Still, reconstructed cellulose has also been used in ultra-filtration filters as barrier layers [198].

The ability to dissolve cellulose also opens up the possibility to create mixtures with other materials which then can be precipitated out in different shapes and thereby introducing different materials evenly inside a cellulose structure (composite materials). This concept has been demonstrated; e.g. as biodegradable and inexpensive sensor platforms for various suitable sensor probe molecules. First, a dope consisting mainly of a cellulose dissolving IL, a suitable sensor probe molecule and cellulose was created. Subsequently, the dope was then shaped in desirable forms using molds. Finally, the cellulose was precipitated by using an anti-solvent, usually water, thereby forming a homogeneous layer of cellulose and the sensor probe molecule. These types of sensor platforms were used for detecting NO<sub>x</sub> using calixarenes as the probe molecule and [BMIM][Cl] as the cellulose solvent [199]. It was claimed that the novel optical sensors that rely on color changes that occur when a chemical reaction between calixarenes and NO<sub>x</sub> takes place, was more selective than current NO<sub>x</sub> sensors relying on electrochemical phenomena. This is due to the fact that vapors like (H<sub>2</sub>O, O<sub>2</sub>, HCl, HBr, SO<sub>x</sub> and NH<sub>3</sub>) can influence the detection selectivity and sensitivity of electrochemical sensors. Another benefit is that the coloration of calixarenes embedded cellulose films could be reversed using either water or alcohol, making the sensor platform reusable. Similar sensor platforms were also prepared for the detection of Hg (II) in water solutions using 1-(2-pyridylazo)-2-naphthol as the sensor probe molecule and [BMIM][Cl] as the cellulose dissolving IL [200]. Ionic liquids are not only known for their dissolution properties; they are also often capable of suspending solid particles as well. By adding solid particles to a mixture of dissolved cellulose and IL, different kinds of nanoparticles like gold [201] and TiO<sub>2</sub> [196] can be incorporated onto cellulose support via cellulose reconstruction. Moreover, reconstructed cellulose can also be used to create composite materials with other polymers [202]. Some ILs are able to dissolve not only cellulose but other hard-to-dissolve polymers as well. Upon varying the ratio between cellulose and a hydrocarbon polymer, new materials with improved properties could be prepared. For instance, cellulose and different types of primary amine containing polymers were co-dissolved in [BMIM][Cl] and then precipitated as cellulose-polyamine films or beards. These structures were then, consequently, used as a solid support for Laccase, although other enzymes capable of anchoring to the primary amine group can also be considered [203]. Bio-degradable structures like this can be used as a solid support for enzyme-catalyzed reactions in continuous flow reactors or as solid support in chromatography.

Yet another study introduced a way to prepare micro- and nano-sized particles with anti-coagulant activity by combining cellulose and heparin [174]. The composite material was made by means of electro-spinning after mixing two different ILs loaded with cellulose and heparin, respectively. Initially, cellulose was dissolved in [BMIM][Cl] and heparin in 1-ethyl-3-methylimidazol benzoate [EMIM][Ba]. The same technique was later used to coat active charcoal to minimize the pore size effect, thus decreasing protein absorption while maintaining the charcoal's ability to absorb smaller drug molecules [204]. The bio- and blood- compatibility of this composite material also renders it as a potential agent for direct hemoperfusion for the removal of small size toxins from the bloodstream. Further *in vivo* testing is needed before any medical applications can be considered. Also, recently, a new biodegradable composite material stemming from cellulose, starch and lignin was prepared via dissolution in [AMIM][Cl] [205]. These polymers all stem from renewable resources and show promising properties towards fresh food packaging, rivaling the petroleum-based polymers currently dominating the market. Furthermore, in some cases, the IL itself can be used as a polymer in the composite material by polymerizing it in-situ [202].

## MODIFICATION AND FUNCTIONALIZATION OF CELLULOSE IN IONIC LIQUID MEDIA

As previously discussed, the ability to dissolve cellulose and later reconstruct it in a suitable form for different applications is of vital importance since cellulose cannot be melted but will instead decompose upon extensive heating. Nevertheless, reconstruction is not the only way of utilizing cellulose. In some cases, the modification of cellulose will give access to a variety of new interesting compounds and in this, ILs can play an important role. During the last decade, homogeneous functionalization of cellulose has attracted considerable attention [26]. Homogeneous functionalization involves the introduction of a functional group onto a cellulose backbone in a dissolved state and it is preferable to heterogeneous methods where the cellulose is merely dispersed in a solvent rather than dissolved. Homogeneous methods are beneficial in many ways - one of the most important benefits being the even distribution of functional groups along the cellulose chain [26] but also the ability to introduce exotic and bulkier functional groups than what is otherwise possible. Moreover, by controlling the reaction time, temperature and the ratio between the reagent and the anhydroglucose units, the degree of substitution (DS) can be controlled [26,206]. The problem, however, has always been to find appropriate cellulose dissolving solvents. Even though such solvent systems exist and have been used for functionalization of cellulose [26, 207-210], problems like toxicity, solvent recovery or harsh conditions still persists. As previously stated, ILs could be a suitable replacement for these type of solvent systems and we have already seen many examples. [AMIM][Cl] is an IL that has been frequently used for this purpose resulting in cellulose acetylation [167] or esterification by the incorporation of functional groups from reagents like benzoyl chloride [206] and phthalic anhydride [212] under homogenous conditions. The same IL was also used in making of cellulose furoates [213], cellulose acetate [214] and cellulose carbonates [214] under mild conditions. Other ionic liquids, like [EMIM][Cl], [BDMIM][Cl] or [ADMIM][Br] have also been applied in

homogeneous functionalization of cellulose [169] but the line does not stop there: many other ILs have been evaluated as well [215].

## CELLULOSE DEPOLYMERIZATION IN IONIC LIQUID MEDIA

Cellulose and hemicellulose by far constitute the most abundant form of renewable biomass on the planet that can potentially help in fulfilling our needs for energy in the future. The first prerequisite for efficient processing is, however, that the polymeric structures need to be efficiently broken down to smaller, more energy dense chemicals like sugars. The various sugars can then, in turn, be converted to fuels and other platform chemicals [216-220], potentially with the help of ILs [215]. We will here, nevertheless, discuss IL-assisted de-polymerization of cellulose only. The de-polymerization of cellulose is often carried out via hydrolyses, commonly either acidic or enzymatic catalysis. Acid catalyzed hydrolysis is often carried out under harsh conditions, resulting in substantial sugar degradation. The process uses nasty and toxic chemicals demanding corrosion-resistant reactors and causes waste disposal problems. Although the conditions are milder in the case of enzymatic catalysis, the process often suffers from low conversion rates of cellulose-to-sugar and of high price of the enzymes. For a hydrolysis reaction to be efficient, the cellulose should preferably be at least partly dissolved - something that ILs can be helpful in.

In a study carried out by Zhao *et al.*, they demonstrated that hydrolysis carried out in [BMIM][Cl], combined with different mineral acids, had a substantial acceleration effect on the conversion rate. For example, total reducing sugar (TRS) yield of 73% was reached after 25 min, at 100 °C, using a mixture of 8% Avicel (DP 220) cellulose dissolved in [BMIM][Cl] and 3% H<sub>2</sub>SO<sub>4</sub> [221]. It was also speculated that when cellulose was dissolved in [BMIM][Cl], the homogenic solution made the  $\beta$ -glucosidic bonds more accessible for H<sup>+</sup>, thus accounting for the higher conversion rate of cellulose to sugar compared to other solvents. Furthermore, it has also been demonstrated that a solid (heterogenic) acid catalyst can be used for the depolymerization of cellulose dissolved in ILs under mild (100 °C) conditions [222]. The study also concluded that resins with larger pores, such as Amberlyst 15DRY and Amberlyst 35, are particularly well-suited for the depolymerization of cellulose dissolved in an ionic liquid. In some cases, ILs alone without the use of any additional catalysts have been used for the depolymerization of cellulose. The authors speculated that the high  $K_w$ -value in some IL-water mixtures is enough to promote the depolymerization of cellulose [223]. The study reported a total reducing sugar (TRS) yield reaching 97%, at 140 °C in 3 h, for the conversion of cellulose to sugar in a water-[EMIM][Cl] (4:1) mixture. The cellulose could also be directly converted to HMF in the presence of CrCl<sub>2</sub>. Another study showed that Brønsted acidic ILs like 1-(1-propylsulfonic)-3-methylimidazolium chloride, were able to de-polymerize cellulose to sugar with a TRS yield of 62%, at 70 °C, in 1.5 h but only after a small amount of water (2 cellulose equivalents) was added [224]. However, it should be mentioned that some ILs ability to dissolve carbohydrates in large amounts [225] can pose a potential problem considering separation of sugar monomers from the IL.

Cellulases, enzymes with the ability to hydrolyse cellulose, have shown many potential industrial applications, there among the process comprising fermentation of bio-ethanol from wood [226,227]. Unfortunately, the process is often slow due to the water insoluble nature of

the crystalline cellulose. The crystalline, tight packing of cellulose effectively excludes the enzyme and results in a limiting amount of absorption sites [226,228]. Thus, to open up the crystalline cellulose structure is of vital importance for improved enzymatic hydrolysis. So far, the studies performed indicate that bacterial cellulases are generally not compatible with higher concentrations of ILs [229, 230] and IL concentrations less than 30 wt% was the upper limit to see any significant activity for certain cellulases [229]. The main reason for the inactivity was the denaturation of cellulases by the ILs [230], although it was admitted that further focus on cellulases from a broader spectrum of microbes are needed. Interestingly, in the case of lipases, ILs with the ability to dissolve cellulose without considerably inactivating the enzyme could be designed [231]. While hydrogen bonding forming anion, oxygen-containing cation and a less bulky cation promoted cellulose dissolution, a low anion concentration was beneficial to the stability of the enzyme. Unfortunately, the same strong hydrogen bonding affinity that is needed for the dissolution of cellulose by ILs [232] will also make them more prone to the denaturation of enzymes [230, 233, 234]. Instead, a pretreatment of cellulose with ILs could be considered. Studies into the possibility of pretreating the cellulose prior to hydrolysis have been reported: first, dissolving the cellulose in either ILs [163, 235, 236] or non-IL solvents [235, 237], followed by precipitation using an anti-solvent were conducted. Results demonstrated overall increases in the enzymatic reaction rate; in some cases, a 50-fold increase in the reaction rate compared to the untreated cellulose was observed [163]. It was speculated that the reason for this is the less crystalline and more amorphous nature of the pretreated cellulose [163, 235, 236, 238], consequently resulting in an easier access to the  $\beta$ -(1-4) glycosidic linkages for the enzymes.

## RECOVERY OF IONIC LIQUIDS AND CELLULOSE

Cellulose recovery is a crucial step and the recovery procedure might vary depending on the intended use of the reconstructed cellulose. Common to all recovery processes is the use of an anti-solvent - a solvent that when added to the solution will initiate the precipitation process of solid cellulose. The most common anti-solvent is water but other solvents like, ethanol, methanol, acetone, dichloromethane and acetonitrile have also been reported [163, 164]. Not all solvents, however, can be used as anti-solvents: in fact, some solvents will enhance the dissolving properties of certain ILs [192]. Therefore, a solvent-like water and short-chain alcohols with the affinity for hydrogen bonding should be used. These solvents will interact with the IL through hydrogen bonding, dipolar, and Coulombic forces [239] and form shields of solvent molecules around the IL that will effectively cut off any hydrogen bond between the IL and the cellulose. Consequently, the cellulose will reform its intra- and inter-molecular bonds thus forming larger cellulose structures that precipitate as an amorphous state [236, 240, 241]. The shape of the reconstructed cellulose can, to a large extent, be controlled by using different precipitation techniques. Rapid mixing of the IL while adding a steady stream of water will result in a powdery flock [161]. On the contrary, if the dope was poured into an aqueous face, solid structures like films, beads, monoliths and fibers could be made [161,166,168].

Always, some sort of feasible IL recovery process is needed if any industrial application is to be considered. Regardless, every so often when reading papers on the area, one comes

across a phrase like: ‘IL was recovered by simple evaporation of the anti-solvent’. The problem here is that there is no such thing as ‘simple evaporation’ when it comes to industrial applications. Around 60-80% of the cost for an average chemical process is associated with separation steps [242]. Therefore, the IL recovery phase needs to be taken into consideration: of the various possible anti-solvents, water seems to be the most frequently used. Although otherwise green, cheap and abundant, water is notoriously energy demanding to heat up (boiling) and has a higher heat capacity and enthalpy of vaporization than e.g. both ethanol and methanol [243]. Evaporation in itself is often a very energy intense separation process and two of the larger commercialized IL processes, BASIL<sup>TM</sup> and Difasol<sup>TM</sup>, refrain from using evaporation at all as a separation method; instead, both rely on simple decantation. Decantation is the most desirable form of liquid-liquid separation but it demands a phase separation between the two liquids. This can be achieved by tuning the hydrophobicity and hydrophilicity of the IL-solvent system but other properties like pH [244] and temperature [245] can also be used to induce phase separation. Some studies have also illustrated that an addition of salts like tri-potassium phosphate [246] or potassium chloride [248] to an IL-water mixture, will result in a ‘salting-out’ effect, leading to a biphasic system with an IL-rich phase and a potassium-rich phase. Other separation methods for IL extraction have been reported elsewhere [153] but will not be discussed further here.

## DISSOLUTION OR DISPERSION?

When discussing if something is dissolved or not, the first thing that needs to be established is what we mean with dissolution? The question about cellulose structure in solution has been the focus of much research and debate over the past decade [248, 249]. Arguments can be made that cellulose and cellulose derivatives, in a highly diluted state, might be considered dissolved. However, when concentrated, different dissolution states with inter-molecular interactions might occur [248]. A study involving cellulose dissolved in *N*-methyl morpholine-*N*-oxide-monohydrate also illustrated the existence of cellulose aggregates of different sizes present in the solution, some including several hundreds of cellulose chains, most likely due to partial dissolution of the cellulose [250].

Common methods used for measuring whether or not cellulose is dissolved are optical absorption and light scattering techniques [184, 251-253]. Even though light scattering intensity and angle are normally suited for the determination of size, distribution and shape of a large variety of particles in various media; in the case of cellulose-IL dispersions/solutions, some special attention should be always paid. Light scattering occurs only at the interface of materials having different optical densities, i.e. refractive indices. Since cellulose has a refractive index of 1.477 at 20 °C and 589 nm [254], in fact very close to that of several ILs (e.g. 1.480 for [EMIM][EtSO<sub>4</sub>] [255], 1.4935 for [EMIM][MeOHPO<sub>2</sub>] [256] and 1.4766 for [EMIM][OcSO<sub>4</sub>] [256]), the scattered light intensities will be very small as soon as the cellulose fibers are wetted - *however not necessarily dissolved* - by the solvent. Accordingly, any result (especially those measured indirectly by optical absorption) should be handled with special care, and one may consider additional analyses such as viscosity, surface probe or electron microscopy measurements to make sure the fibers are properly dispersed [257-260].

The average unprocessed cellulose has a certain degree of crystallinity. However, if cellulose is dissolved and then precipitated under vigorous stirring, the cellulose will lose its crystalline structure and transform into an amorphous state [236, 240]. This decrease in crystallinity can be measured by X-ray crystallography technique and can be used as an indirect measurement to determine the degree of cellulose dissolution [198, 236, 240]. Visual methods for determining the dissolution of cellulose in IL is perhaps one of the easiest ways when attempting to prove that dissolution really takes place and also frequently used by many authors [161, 184, 251].

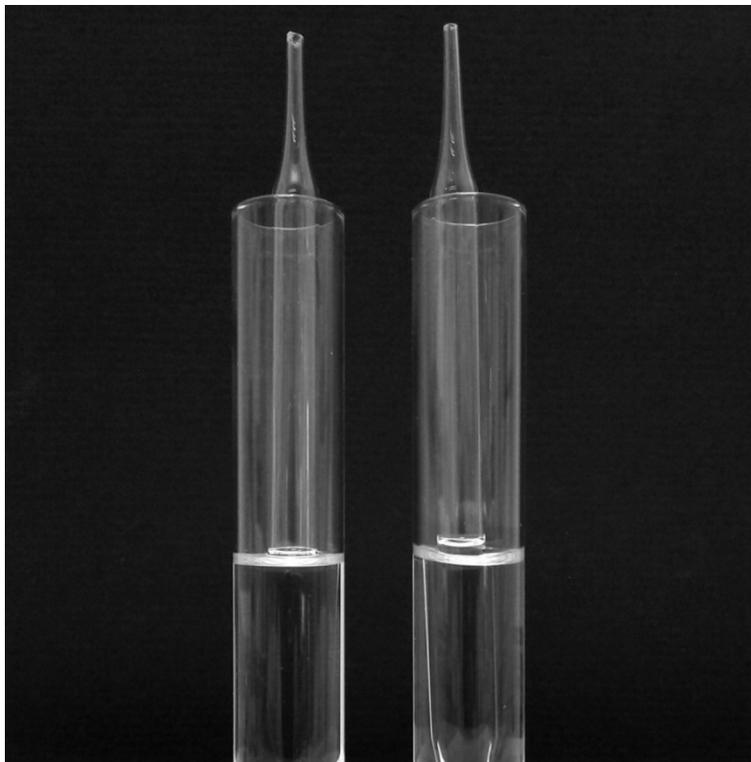


Figure 3. A glass tube submerged in benzene (left) and in water (right). The tube submerged in benzene is ‘invisible’ since both glass and benzene have coinciding refractive indexes.

Whenever visual methods are used, regardless of magnification, the refractive index of the IL is important to take into account. To illustrate the challenges, let us look at a glass in clean benzene in Figure 3: glass and benzene both have the same refractive index and thus, the glass tube swimming in benzene cannot be detected by a visual inspection despite the fact that it obviously is not dissolved [148]. If a microscope is used, consideration must also be taken in to the magnification capacity of the equipment and the desired degree of dissolution of cellulose.

Viscosity is perhaps one of the most challenging problems to overcome when adapting cellulose dissolving techniques to industry processing and are, therefore, often reported in the literature [166, 252, 253]. The rheological and viscosity properties of IL/cellulose dope are important factors for different types of cellulose processing like the wet-spinning process [166] but factors like concentration and temperature [253] can be used to improve these

properties. NMR-spectroscopy has also been used to determine the solubility of cellulose in specific ILs. NMR studies have indicated that the chemical shifts of glycosidic bond carbons correlate to the conformational behavior of said glycosidic linkage [261, 262]. High-resolution NMR studies of the  $\beta$ - (1 $\rightarrow$ 4) glycosidic linkage of cellulose have indicated that the cellulose is disordered in [BMIM][Cl] [263]. Furthermore,  $^{13}\text{C}$  and  $^{35/37}\text{Cl}$  NMR studies of cellulose dissolved in [BMIM][Cl] confirmed hydrogen bonding between the cellulose hydrogen and the chloride of the IL [232]. This is in line with previous theories that for cellulose to dissolve, the intra- and inter-molecular hydrogen bonds need to be broken [168, 264].

## DISSOLUTION MECHANISM

Cellulose is notoriously hard to dissolve due to an extensive network of intra- and inter-molecular hydrogen bonds and van der Waals interactions between cellulose molecules. Also, the large size and stiffness of the cellulose molecule also complicate any dissolution process [265]. Nevertheless, different solvents or solvent systems have been used to accomplish just this [266-269]. The question is, why do different solvents or solvent systems manage to dissolve cellulose and some do not? To dissolve cellulose, the carbohydrate-carbohydrate hydrogen bonds in the structure need to be broken [168, 264]. Anyhow, a solvent capable of hydrogen bonding alone is not enough. When considering water, we can see that is the case. Instead, arguments have been made that other factors like van der Waals and hydrophobic interaction need to be taken as well [265]. In fact, a few studies have shown that cellulose has both hydrophobic and hydrophilic parts [270, 271] and can actually be considered amphiphilic by nature. Thus, co-solvents that have a tendency to weaken the hydrophobic interaction in aquatic solution or amphiphilic solvents, like ILs, could be used to increase the solubility of cellulose [265].

As previously stated, a solvent's ability to dissolve cellulose is, in large part, related to its ability to break the intra- and inter-molecular bonds. NMR [232] as well as simulation [272] studies have indicated that chloride anions in different ILs form hydrogen bonds while the hydroxyl groups of cellulose associate with the cation thus disrupting the hydrogen bonding between the cellulose molecules. For a long time it was believed that a halogen atom was needed as an IL anion, whereas more recent studies have shown that other anions like acetate also interact with cellulose [273]. This confirms the fact that the cellulose dissolution tendency of an anion is linked to the basicity [162, 185, 188, 190, 192] of the anion and not to a specific type of anion used. This is further supported by data collected by screening [170, 186] and computer modeling [241] of different types of anions in the pursuit of ILs capable of dissolving cellulose. However, anions are not the only ones that are capable of hydrogen bonding. Simulation [241, 272] and NMR [273] studies of [MMIM][Cl] and [EMIM][OAc], respectively, have shown some hydrogen bonding between the imidazolium-based cations and the hydroxyl groups of cellulose. Especially the acidic C2 proton of imidazolium likes to interact with hydroxyl groups that have less steric hindrance (bulky cation). Even though hydrogen bonding between the IL and cellulose is believed to be the major contributing factor to cellulose dissolution [273], it has been shown that the ILs can interact with cellulose in other ways as well. Previous studies of the interactions between aromatic compounds and

carbohydrates have shown that given the right opportunity, persistent intra-molecular interactions involving extended hydrophobic contact and significant electron overlapping can occur [274]. In a computer simulation study involving the interaction between [EMIM][OAc] and cellulose, arguments were made that the hydrophobic interactions between imidazolium and D-glucose play an important role in terms of dissolving cellulose[241].

## SYNTHESIS ASPECTS OF IONIC LIQUIDS FOR CELLULOSE DISSOLUTION

Throughout this paper we have discussed different ILs and their ability to dissolve cellulose and we can see that the application of ILs is still at an early stage. Companies like BASF have already began to market ILs that dissolve cellulose, currently 5 wt-% cellulose dissolved in [EMIM][OAc] can be bought under the name CELLIONIC™ produced by BASF. However, when designing new ILs for cellulose dissolution, there are a few things that need to be considered. A lot of work has been done looking at different anions like halogens [161, 167, 168] and Lewis bases [162, 170, 186-188, 190]. The common agreement seems to be that a high  $\beta$ -value, a high affinity for donating an electron pair, is the key property for anions when it comes to the ability of dissolve cellulose [162, 185, 188, 190, 192]. Furthermore, the anion should not be bulky or hydrophobic [275] since that might diminish the ILs dissolving capability. A previous work in this subject states that, in general, using the same cation, the solubility of cellulose decreases, depending on the anion used, in the following order:  $[(\text{CH}_3\text{CH}_2\text{O})_2\text{PO}_2]^- \approx [\text{OAc}]^- > [\text{SHCH}_2\text{COO}]^- > [\text{HCOO}]^- > \text{Cl}^- > \text{Br}^- \approx [\text{SCN}]^-$  [182].

Cations contribution to the dissolving of cellulose have not yet been fully understood but they seem to have some influence nevertheless. There has been some speculation in the literature about the odd-even effect of short-chained (pentyl or shorter) imidazolium chloride-based ILs [186, 276] meaning that side chains with an even number of carbons tends to dissolve cellulose, while those with an odd number do not or only to a small extent dissolve cellulose. This effect was not noted for Bromide-based ILs [186] although that might be contributed to the overall low solubility of cellulose in these ILs. Alkyl chains longer than 6 carbons appear to be less effective in dissolving cellulose [161] and show a diminishing solvent capacity with longer chain length (between 6-10 carbons) [276]. Interestingly, the unsaturated 3 carbon chain, allyl, in [AMIM][Cl] demonstrates a great dissolving potential [157, 168]. It has also been speculated that aromatic heterocyclic rings with a  $\text{sp}^2$  nitrogen, dipolar ring character, and the ability to participate in hydrogen bonding and delocalize the positive charge, are suitable precursors for cations [275].

However, one should point out that there are many possible combinations of solvent systems that can be used besides the straight-forward one anion/one cation combination. As previously mentioned, additives like solvents [192] and salts [170] have been successfully used to enhance the solubility of cellulose in ILs. In addition, different ILs like deep eutectic solvents [134, 135], dual charged ions [136, 137] and zwitterions [138] exist and we can see that the potential for designing target specific ILs for cellulose dissolution are seemingly endless and even harder to comprehensively grasp and predict. Thus, computer modeling with predictive capability [277, 278] can play a vital role in screening for potential ILs. Let us

instead have a look at different attributes that are desirable in ILs that have the ability to dissolve cellulose: overall, we need to take into account the ever diminishing supply of oil and look towards renewable recourses for our starting materials, Also, the overall atom efficiency of the production of such ILs also needs to be considered. Still, toxicity also needs to be taken into account. Even though the negligible vapor pressure of ILs results for a minimum of atmospheric emission, potential water contamination is still a real problem that needs to be addressed [147] - most of the ILs commonly used today are toxic in nature to a certain degree [147-150]. Anyhow, some studies have demonstrated that introducing functional polar groups to the side chains of the cation reduces the toxicity and increases the biodegradation to some extent [147]. Furthermore, it was stated that pyridinium is more environmentally friendly than imidazolium and perfluorinated anions have been proven hazardous in contact with water. Instead, non-toxic pharmaceutically acceptable anions like  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$  and  $\text{HCOO}^-$  can be used [279].

The viscosity of ILs has always been a point of concern for industrial applications. Good viscosity properties results in more manageable dope and higher dissolving capacity of the IL [166,187]. The viscosity of the dope is also heavily dependent on the cellulose concentration. A 4 wt-% cellulose solution in [AMIM][Cl] show a viscosity of 110 Pa s, at 80 °C while a 8%wt-% solution, using the same cellulose, demonstrated a viscosity value of 1480 Pa s [168]. Also, the [EMIM] cation results into a lower viscosity than the [BMIM] cation when using the same anion and cellulose concentration [187]. The study also concluded that the anion [OAc] was more suitable for industrial wet spinning than Cl. The reasons listed were such as lower viscosity, higher load of cellulose and lower melting point. The melting point of an IL is usually decreasing with a cation with low symmetry, weak intermolecular interaction and a delocalized charge [280]. The same study also concluded that the size increase of the anion with the same charge led to a decrease in the melting point of the IL.

Reusability of an IL is also important from an environmental as well as economical point of view. This involves a simple and cheap recovery method of the IL as well as little to no degradation of the IL. A decomposition temperature significantly higher than the process and IL recovery temperature used is needed to avoid direct decomposing of the IL. Although decomposition is not the only problem, ILs are not totally inert since competing side reactions inside the dope have been observed: the acidic C2 carbon of [BMIM] will react and create a carbon-carbon bond with the reducing end of cellulose and the reaction rate speeds up under basic catalysis [281]. This side reaction can, however, be minimized by ensuring the removal of any base and can even be completely avoided by using C2 alkyl substituted imidazolium ions [169, 282]. It have also been indicated that [EMIM][OAc] and [EMIM][Cl] might not be suitable in certain types of cellulose modification reactions due to the risk of nucleophilic displacement reactions [283].

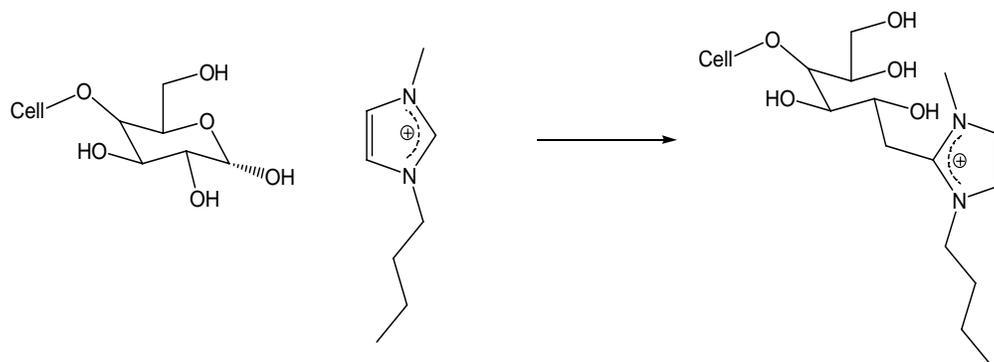


Figure 4. Carbon-carbon bond formation between the acidic C2 carbon of [BMIM]<sup>+</sup> and the reducing end of cellulose in line with the reasoning described in [281].

## CONCLUSIONS

Molecular cellulose solvent systems have a long history of industrial use. However, more or less all of them suffer from questionable environmental effects and poor toxicity profile. Also, the high cost of any current process encourages us to look at alternatives.

When considering dissolving cellulose and ILs, we can draw the conclusion that extensive research and effort have been put into the development and screening of different anions. However, considering the development of suitable cations, we see that most of the ILs used today contain some imidazolium derivative as a cation precursor. Imidazole species are perhaps not the optimal precursors for ILs designed for large scale industrial applications. One obvious reason is that imidazole, as being made today, stems from non-renewable resources and is relatively expensive when considering large scale use. Instead, we need new and cheaper precursors, preferable obtained from renewable resources and, therefore, should also look outside ammonium based chemicals in our quest for suitable precursors.

The scientific and industrial community is ever more interested in any industrial applications of ILs in cellulose processing. So far, we have seen many interesting applications of IL-assisted cellulose processing but not that many with industrial potential. Considering large scale cellulose processing, we are forced to realize that ILs are still in a development phase and problems like, but not exclusively, easy and low-cost cellulose separation, recyclability, stability, high cost and high viscosity of any ionic liquids need to be overcome before any industrial applications are rendered feasible. Recent studies indicate that ILs are not as inert solvents as previously presumed and, in fact, different side-reactions between the IL and cellulose can occur inside the dope, deteriorating both the IL and the cellulose. Although ionic liquids possess a great potential, the solutions available today still have limitations that need to be taken into account.

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## REFERENCES

- [1] *The Outlook magazine* (1921) 129 162.
- [2] Eugene, S., Smith, A., *Life* (1972) 74-79.
- [3] Milnes, M., *Nature* (1971) 232 5310 395–396.
- [4] Bisarya, R., Puri, S., *Journal of Loss Prevention in the process industry* (2005) 18 209–212.
- [5] Dechy, N., Bourdeaux, T., Ayrault, N., Kordek, M., Le Coze, J., *Journal of Hazardous Materials* (2004) 111 131-138.
- [6] Enserink, M., <http://www.sciencemag.org/cgi/content/full/330/6003/432> *Science* (2010) 330 432–433.
- [7] Anastas, P.; Warner, J.; *Green Chemistry: Theory and Practice*, Oxford University Press: New York (1998) 30.
- [8] Lynd, L., Weimer, P., van Zyl, W., *Pretorius I.S.* (2002) 66 506–577.
- [9] D'andola, G., Szarvas, L., Massonne, K., Stegmann, V., *WO 2008/043837* (2008).
- [10] Argyropoulos, D., Xie, H., *WO/2008/098037* (2008).
- [11] Xu, A., Wang, J., Wang, H., *Green Chem.* (2010) 12 268-275.
- [12] Edgar, K., Buchanan, C., Debenham, J., Rundquist, P., Seiler, B., Shelton, M., Tindall, D., *Prog. Polym. Sci.* (2001) 26 1605.
- [13] Moutos, F., Freed, L., Guilak, F., *Nat. Mater.* (2007) 6 162.
- [14] Huser, G., Iborra, S.; Corma, A., *Chem. Rev.* (2006) 106 4044.
- [15] Barbosa, M., Granja, P., Barris, C., Amaral, I., *ITBM-RBM* (2005) 26 212.
- [16] Czaja, W., Young, D., Kawecki, M., Brown, R., *Biomolecules* (2007) 8 1.
- [17] Lee, K.; Mooney, D., *Chem. Rev.* (2001) 101 1869.
- [18] Li, Q.; He, Y.; Xian, M. Jun, G.; Xi, X.; Yang, J.; Li, L., *Biores. Technol.* (2009) 100 3570.
- [19] Pinkert, A., March, K., Pang, S., Staiger, M., *Chem. Rev.* (2009) 109 6712.
- [20] Nishiyama, Y.; Langan, P.; Chanzy, H., *J. Am. Chem. Soc.* (2002) 124 9074–9082.
- [21] Crawford, R., *Lignin biodegradation and transformation*. New York: John Wiley and Sons (1981).
- [22] Deguchi, S., Tsujii, K., Horikoshi, K., *Chem. Commun.* (2006) 3293.
- [23] Klemm, D., Heublein, B., Fink, H., Bohn, A., *Chem Inform* (2005) 36 36.
- [24] Turbak, A.F.. Newer cellulose solvent systems. In *Wood and Agricultural Residues*, ed. E.J. Soltes. New York: Academic Press (1983)
- [25] Philipp, B.; Lukanoff, B.; Schleicher, H.; Wagenknecht, W., *Chem.* (1986) 26 50.
- [26] Heinze, T.; Liebert, T. *Prog. Polym. Sci.* (2001) 26 1689.
- [27] Audemars, G., *British Patent* 283, 1855
- [28] <http://dissertations.ub.rug.nl/FILES/faculties/science/1998/h.boerstoel/thesis.pdf>.

- [29] Liebert, T., *Cellulose Solvents – Remarkable History, Bright Future, ACS Symposium Series Cellulose Solvents: For Analysis, Shaping and Chemical Modification* (2010) Vol. 1033 Chapter 1 3–54 <http://pubs.acs.org/isbn/9780841200067> - aff1#aff1.
- [30] Cross, C., Bevan, E., Beadle, C., *British Patent* 8,700, 1892.
- [31] Hermanutz, F., Gähr, F., Uerdingen, E., Meister, F., Kosan, B., *Macromol. Symp.* (2008) 262 23–27.
- [32] <http://www.afma.org/f-tutor/rayon.htm>.
- [33] Schuetzenberger, P., *Compt. Rend.* (1865) 61 485.
- [34] Philipp, B., Wagenknecht, W., Nehls, I., Ludwig, J., Schnabelrauch, M., Kim, H., Klemm, D., *Cellul. Chem. Technol.* (1990) 24 667.
- [35] Rudy, H. *Cellulosechemie* (1931) 13 49.
- [36] Fujimoto, T., Takahashi, S., Tsuji, M., Miyamoto, M., Inagaki, H., *J. Polym. Sci., Part C: Polym. Lett.* (1986) 24 495.
- [37] Takahashi, S., Fujimoto, T., Barua, B. M., Miyamoto, M., Inagaki, H., *J. Polym. Sci., Part A: Polym. Chem.* (1986) 24 2981.
- [38] Schnabelrauch, M., Vogt, S., Klemm, D., Nehls, I., Philipp, B., *Angew. Makromol. Chem.* (1992) 198 155.
- [39] Liebert, T., Klemm, D., Heinze, T., *J. Macromol. Sci., Part A: Pure Appl. Chem.* (1996) A33 613.
- [40] Vigo, T., Daighly, B., Welch, C., *J. Polym. Sci., Part B: Polym. Phys.* (1972) 10 397.
- [41] Liebert, T., *PhD Thesis*, University of Jena, German (1995).
- [42] Hasegawa, M., Isogai, A., Onabe, F., Usuda, M., *J. Appl. Polym. Sci.* (1992) 45 1857.
- [43] Nehls, I., Wagenknecht, W., Philipp, B., Stscherbina, D., *Prog. Polym. Sci.* (1994) 19 29.
- [44] Cemeris, M., Musko, N., Cemeris, N., *Khim. Drev.* (1986) 2 29.
- [45] Hawkinson, D., Kohout, E., Fornes, R., Gilbert, R., *J. Polym. Sci., Part B: Polym. Phys.* (1991) 29 1599.
- [46] Salin, B., Cemeris, M., Mironov, D., Zatsepin, A., *Khim. Drev.* (1991) 3 65.
- [47] Salin, B., Cemeris, M., Mironov, D., *Khim. Drev.* (1993) 5 3.
- [48] Liebert, T., Schnabelrauch, M., Klemm, D., Erler, U., *Cellulose* (1994) 1 249.
- [49] Liebert, T., Klemm, D., *Acta Polym.* (1998) 49 124.
- [50] Heinze, T., Liebert, T., Koschella, A., *Esterification of Polysaccharides*; Springer: Heidelberg, Berlin, (2006)
- [51] Klemm, D., Heinze, T., Stein, A., Liebert, T., *Macromol. Symp.* (1995) 99 129.
- [52] Liebert, T., Heinze, T., *Macromol. Symp.* (1998) 130 271.
- [53] Liebert, T., Heinze, T., *In Cellulose Derivatives; Modification, Characterization and Nanostructures*, Heinze, Th., Glasser, W. G., Eds.; ACS Symposium Series 688; American Chemical Society: Washington, DC, (1998) 61.
- [54] Koetz, J., Bogen, I., Heinze, U., Heinze, T., Klemm, D., Lange, S., Kulicke, W., *Papier* (1998) 52 704.
- [55] Carroll-Porczynski, C., "Natural polymer man-made fibers", Natural trade press, London (1961)
- [56] Sprague, B., Noether, H., *Text. Res. J.* (1961) 31 858
- [57] Northolt, M., Boerstoel, H., Maatman, H., Huisman, R., Veurink, J., Elzerman, H., *Polymer* (2001) 42 8249-8264
- [58] Villaine, P., Janin, C., *WO 851051 15*.

- [59] Schweitzer, E., *J. Prakt. Chem.* (1857) 72 109.
- [60] Despeissis, L. H., *French Patent* 203,741, 1890.
- [61] Fremerey, M., Urban, J., *German Patent* 111 313, 1899.
- [62] Fremerey, M., Urban, J., Bronnert, E., *German Patent* 119 098, 1899.
- [63] Ringsdorf, H., *Angew. Chem.* (2004) 116, 1082
- [64] Ahlrichs, R., Ballauff, M., Eichkorn, K., Hanemann, O., Kettenbach, G., Klufers, P., *Chem.-Eur. J.* (1998) 4 835.
- [65] Klufers, P., Kunte, T., *Angew. Chem., Int. Ed.* (2001) 40 4210.
- [66] Roy, C., Budtova, T., Navard, P., *Biomacromolecules* (2003) 4 259.
- [67] Isogai, A., Atalla, R., *Cellulose* (1998) 5 309–319.
- [68] Yamashiki, T., Matsui, T., Saitoh, M., Okajima, K., Kamide, K., Sawada British, T., *Polym. J.* (1990) 22 73–83.
- [69] Yamashiki, T. Kamide, K.; Okajima, K. *In Cellulose Sources and Exploitation*; Kennedy, J., Phillips, G., Williams, P., Eds.; Ellis Horwood: London, (1990) 197.
- [70] Yamashiki, T., Matsui, T., Kowsaka, K., Saitoh, M., Okajima, K., Kamide, K., *J. Appl. Polym. Sci* (1992) 44 691.
- [71] Yan, L., Gao, Z., *Cellulose* (2008) 15 789.
- [72] Zhou, J., Zhang, L., *Polym. J.* (2000) 32 866.
- [73] Cai, J., Zhang, L., *Macromol. Biosci.* (2005) 5 539.
- [74] Cai, J., Liu, Y., Zhang, L., *J. Polym. Sci., Part B: Polym. Phys.* (2006) 44 3093.
- [75] Egal, M.; Budtova, T.; Navard, P. *Cellulose* (2008) 15 361.
- [76] Cai, J.; Zhang, L.; Liu, S.; Liu, Y.; Xu, X.; Chen, X.; Chu, B.; Guo, X.; Xu, J.; Cheng, H.; Han, C.; Kuga, S., *Macromolecules* (2008) 41 9345.
- [77] Cai, J.; Zhang, L. *Biomacromolecules* (2006) 7 183.
- [78] Qi, H.; Chang, C.; Zhang, L., *Cellulose* (2008) 15 779.
- [79] Liu, S.; Zhang, L., *Cellulose* (2009) 16, 189.
- [80] Cai, J.; Zhang, L.; Chang, C.; Cheng, G.; Chen, X.; Chu, B., *ChemPhysChem* (2007) 8 1572.
- [81] Ruan, D., Lue, A., Zhang, L., *Polymer* (2008) 49 1027.
- [82] Klemm, D.; Philipp, B.; Heinze, T.; Heinze, U.; Wagenknecht, W., *Comprehensive Cellulose Chemistry*; Wiley VCH: New York, (1998) II 140.
- [83] Heinze, T.; Liebert, T., *Progress in Polymer Science* (2001) Volume 26, Number 9, November 2001 , pp. 1689-1762
- [84] Weimarn, P. P., *Kolloidzeitschrift* (1912) 11 41.
- [85] Letters, K., *Kolloidzeitschrift* (1932) 58, 229.
- [86] Chen, L., *U.S. Patent* 4999149 (1991).
- [87] Xu, Q.; Chen, L., *Textile Techn. Int.* (1996) 40 19.
- [88] Katz, J.; Derksen, J., *Rec. Trav. Chim.* (1930) 50 149.
- [89] Lukanoff, B.; Schleicher, H.; Philipp, B., *Cellul. Chem. Technol.* (1983) 17 593.
- [90] Fischer, S., Voigt, W., Fischer, K., *Cellulose* (1999) 6 213.
- [91] Leipner, H.; Fischer, S.; Brendler, E.; Voigt, W., *Macromol. Chem. Phys.* (2000) 201 2041.
- [92] Fischer, S.; Leipner, H.; Thuemmler, K.; Brendler, E.; Peters, J. *Cellulose* (2003) 10 227.
- [93] McCormick, C., Lichatowich, D., *J. Polym. Sci., Part B: Polym. Lett. Ed.* (1979) 17 479.

- [94] Nehls, I.; Wagenknecht, W.; Philipp, B., *Cellul. Chem. Technol.* (1995) 29 243.
- [95] El-Kafrawy, A., *J. Appl. Polym. Sci.* (1982) 27 2435.
- [96] Striegel, A.; Timpa, J.; Piotrowiak, P.; Cole, R., *Int. J. Mass Spectrom. Ion Proc.* (1997) 162 45.
- [97] Striegel, A.; Timpa, J., *Carbohydr. Res.* (1995) 267 271.
- [98] Silva, A., Laver, M., *TAPPI J.* (1997) 80 173.
- [99] Hasegawa, M., Isogai, A., Onabe, F., *J. Chromatogr.* (1993) 635 334.
- [100] Sjoeholm, E., Gustafsson, K., Eriksson, B., Brown, W., Colmsjoe, A., *Carbohydr. Polym.* (2000) 41 153.
- [101] El Seoud, O., Regiani, A., Frollini, E., *In Natural Polymers and Agrofibers Composites*; Frollini, E., Leao, A. L., Mattoso, L. H. C., Eds.; USP-IQSC: Sao Carlos, Brazil, (2000) 73.
- [102] Philipp, B., *J. Macromol. Sci., Part A: Pure Appl. Chem.* (1993) A30 703.
- [103] Spange, S., Reuter, A., Vilsmeier, E.; Heinze, T.; Keutel, D., Linert, W., *J. Polym. Sci., Part A: Polym. Chem.* (1998) 36 1945.
- [104] El-Kafrawy, A., *Lenzinger Ber.* (1983) 55 44.
- [105] Morgenstern, B., Kammer, H., *TRIP* (1996) 4 87.
- [106] Petrus, L., Grey, D., BeMiller, J., *Carbohydr. Res.* (1995) 268 319.
- [107] Helinger, H., Hengstberger, M., *Lenzinger Ber.* (1985) 59, 96.
- [108] Takaragi, A., Minoda, M., Miyamoto, T., Liu, H., Zhang, L., *Cellulose* (1999) 6 93.
- [109] Turbak, H., Sakthivel, A., *Chem. Tech.* (1990) 20 444.
- [110] McCormick, C., Dawsey, T., *Macromolecules* (1990) 23 3606.
- [111] McCormick, C.; Chen, T., *In Macromolecular Solutions, Solvent-Property Relationships in Polymers*; Symor, R. B., Stahl, G. A., Eds.; Pergamon Press: New York, (1982) 101.
- [112] Regiani, A., Frollini, E., Marson, G., Arantes, G., El Seoud, O., *J. Polym. Sci., Part A: Polym. Chem.* (1999) 37 1357.
- [113] Marson, G., El Seoud, O., *J. Appl. Polym. Sci.* (1999) 74 1355.
- [114] Graebner, D., Liebert, T., Heinze, T., *Cellulose* (2002) 9 193.
- [115] Hon, D., Yan, H., *J. Appl. Polym. Sci.* (2001) 81 2649.
- [116] Terbojevich, M., Cosani, A., Focher, B., Gastaldi, G., Wu, W., Marsano, E., Conio, G., *Cellulose* (1999) 6, 71.
- [117] Graenacher, C., Sallman, R., *U.S. Patent* 2179181 (1939).
- [118] Johnson, D., *U.S. Patent* 3447939 (1969) and 3508941 (1970).
- [119] Regenerated cellulose fibres, Ed. by Calvin Woodings, Woodhead Publishing Ltd, 2001. ISBN 1-85573-459-1
- [120] Franks, N., Varga, J. K., *U.S. Patent* 4145532 (1979).
- [121] Franks, N., Varga, J. K., *U.S. Patent* 4196282 (1980).
- [122] McCorsley, C., *Belgian Patent* 868735 (1978).
- [123] McCorsley, C., Varga, J. K., *U.S. Patent* 4142913 (1979).
- [124] McCorsley, C., *Belgian Patent* 875323 (1979).
- [125] McCorsley, C., *Belgian Patent* 871428 (1979).
- [126] McCorsley C., *US patent* 4246221 (1981).
- [127] Brandner, H., *Zengel, EP* 47929 (1981) (Akzo Nobel)
- [128] Buijtenhuijs, F., Abbas, M., Witteveen, A., *Das Papier* (1986) 40 615.

- [129] Konkin, A., Wendler, F., Meister, F., Roth, H.-K., Aganov, A.O., *Ambacher Spectroch. Acta Part A: Mol. Biomol. Spectr.* (2008) 69 1053.
- [130] Rosenau, T., Potthast, A., Sixta, H., Kosma, P., *Prog. Polym. Sci.* (2001) 26 1763.
- [131] Johnson, K., *What's an Ionic Liquid? The Electrochemical Society Interface.*, Spring (2007) 38-41.
- [132] Ngo, H., LeCompte, K., Hargens, L., McEwen, A., *Thermochimica Acta.* (2000) 357 97-102.
- [133] Carter, E., Culver, S., Fox, P., Goode, R., Ntai, I., Tickell, M., *Chem. Commun.* (2004) 6 630-631.
- [134] Abbott, A., Capper, G., Davies, D., Rasheed, R., Tambyrajah, V., *Chem. Commun.* (2003) 1 70-71.
- [135] Abbott, A., Boothby, D., Capper, G., Davies, D., Rasheed, R., *J. Am. Chem. Soc.* (2004) 126 9142-9147.
- [136] Lall, S., Mancheno, D., Castro, S., Behaj, V., Cohen, J., Engel, R., *Chem. Commun.* (2000) 2413-2414.
- [137] Handy, S., *Chem- Eur J.* (2003) 13 2938-2944.
- [138] Narita, A., Shibayama, W., Ohno, H., *J. Mat. Chem.* (2006) 16 1475-1482.
- [139] Smiglak, M., Reichert, W., Holbrey, J., Wilkes, J., Sun, L., Thrasher, J., *Chem. Commun.* (2006) 24 2554-2556.
- [140] Schneider, S., Hawkins T, Rosander M, Vaghjiani G, Chambreau S, Drake G., *Energy and Fuels.* (2008) 22 2871-2872.
- [141] Kosmulski, M., Gustafsson, J., Rosenholm, J., *Thermochimica Acta.* (2004) 412 47-53.
- [142] Earle, M., Esperanca, J., Gilea, M., Lopes, J., Rebelo, L., Magee, J. *Nature.* (2006) 439 831-4.
- [143] Armstrong, J., Hurst, C., Jones, R., Licence, P., Lovelock, K., Satterley, C., *Physical Chemistry Chemical Physics.* (2007) 9 982-90.
- [144] Rosamilia A., Strauss, C., Scott, J., *Pure and Applied Chemistry* (2007) 79 1869-1877.
- [145] Wasserscheid, P., *Nature* (2006) 439 797.
- [146] King, A., Asikkala, J., Mutikainen, I., Järvi P., Kilpeläinen, I., *Angew. Chem. Int. Ed.* (2011) 50 1 – 6.
- [147] Pham, T., Cho, C., Yun, Y., *Water Research* (2010) 44 352-372.
- [148] Imperato, G., Konig, B., Chiappe, C., *Eur. J. Org. Chem.* (2007) 7 1049-1058.
- [149] Gathergood, N., Scammells, P., Garcia, M., *Green Chem.* (2006) 8 156-160.
- [150] Garcia, M., Gathergood, N., Scammells, P., *Green Chem.* (2005) 7 9-14.
- [151] Schmid, A., Kollmer, A., Mathys, R., Witholt, B., *Extremophiles* (1998) 2 249-256.
- [152] [www.basf.com/group/corporate/en/innovations/innovation-award/2004/basil](http://www.basf.com/group/corporate/en/innovations/innovation-award/2004/basil), retrieved on 03.06.2011
- [153] Tan, S., MacFarlane, D., *Topics in current chemistry* (2010) 290 311-339.
- [154] Plechkova, N., Seddon, K., *Chem. Soc. Rev.* (2008) 37 123-150.
- [155] Seddon, K., *J. Chem. Tech. Biotech.* (1997) 68 351-6.
- [156] Jimenez, A., Bermudez, M., Carrion, F., Martinez-Nicolas, G., *Wear.* (2006) 261 347-59.
- [157] Mikkola, J.P., Kirilin, A., Tuuf, J., Pranovich, A., Holmbom, B., Kustov, L., *Green Chem.* (2007) 9 1229-37.
- [158] Heldebrant, D., Yonker, C., Jessop, P., Phan, L., *Energy and Environmental Science* (2008) 1 487-93.

- [159] Earle, M., McCormac, P., Seddon, K., *Green Chem.* (1999) 1 23-5.
- [160] Zayed, F., Greiner, L., Schulz, P., Lapkin, A., Leitner, W., *Chem. Commun.* (2008) 79-81.
- [161] Swatloski, R., Spear, S., Holbrey, J., Rogers R., *J. Am. Chem. Soc.* (2002) 124 4974-5.
- [162] Fukaya, Y., Hayashi, K., Wada, M., Ohno, H., *Green Chem.* (2008) 10 44-6.
- [163] Dadi, A., Varanasi, S., Schall, C., *Biotech. Bioeng.* (2006) 95 904-10.
- [164] Fort, D., Remsing, R., Swatloski, R., Moyna, P., Moyna, G., Rogers, R., *Green Chem.* (2007) 9 63-9.
- [165] Zhu, S., Wu, Y., Chen, Q., Yu, Z., Wang, C., Jin, S., *Green Chem.* (2006) 8 325-7.
- [166] Hermanutz, F., Gähr, F., Uerdingen, E., Meister, F., Kosan, B., *Macromol Symp.* (2008) 262 23-7.
- [167] Wu, J., Zhang, J., Zhang, H., He, J., Ren, Q., Guo, M., *Biomacromolecules* (2004) 5 266-8.
- [168] Zhang, H., Wu, J., Zhang, J., He, J., *Macromolecules* (2005) 38 8272-7.
- [169] Barthel, S., Heinze, T., *Green Chem.* (2006) 8 301-6.
- [170] Xu, A., Wang, J., Wang, H., *Green Chem.* (2010) 12 268-75.
- [171] Feng, L., Chen, Z., *J. Mol. Liq.* (2008) 142 1-5.
- [172] Varma, R., Namboodiri, V., *Chem. Commun.* (2001) 643-4.
- [173] Egorov, V., Smirnova, S., Formanovsky, A., Pletnev, I., Zolotov, Y., *Anal. Bioanal. Chem.* (2007) 387 2263-9.
- [174] Viswanathan, G., Murugesan, S., Pushparaj, V., Nalamasu, O., Ajayan, P., Linhardt R., *Biomacromolecules* (2006) 7 415-8.
- [175] Liu CF, Ren JL, Xu F, Liu JJ, Sun JX, Sun RC. *Journal of Agricultural and Food Chemistry* (2006) 54 5742-8.
- [176] Gholap, A., Venkatesan, K., Daniel, T., Lahoti, R., Srinivasan, K., *Green Chem.* (2003) 5693-6.
- [177] Gholap, A., Venkatesan, K., Daniel, T., Lahoti, R., Srinivasan, K., *Green Chem.* (2004) 6147-50.
- [178] Yadav, J., Reddy, B., Reddy, K., Raj, K., Prasad, A., *J. Chem. Soc.-Perkin Trans. 1.* (2001) 16 1939-41.
- [179] Mason T., *Chem. Soc. Rev.* (1997) 26 443-51.
- [180] Sun, N., Rahman, M., Qin, Y., Maxim, M., Rodriguez, H., Rogers, R., *Green Chem.* (2009) 11 646-55.
- [181] Yang, F., Li, L., Li, Q., Tan, W., Liu, W., Xian, M., *Carbohydrate Polymers* (2010) 81 311-6.
- [182] Sun, N., Rodriguez, H., Rahman, M., Rogers, R., *Chem. Commun.* (2011) 47 1405-21.
- [183] Graenacher, C., *U.S. Patent* 1943176 (1934).
- [184] Zavrel, M., Bross, D., Funke, M., Buchs, J., Spiess, A., *Bioresource Technology.* (2009) 100 2580-7.
- [185] Brandt, A., Hallett, J., Leak, D., Murphy, R., Welton, T., *Green Chem.* (2010) 12 672-9.
- [186] Vitz, J., Erdmenger, T., Haensch, C., Schubert, U., *Green Chem.* (2009) 11 417-424.
- [187] Kosan, B., Michels, C., Meister, F., *Cellulose.* (2008) 15 59-66.
- [188] Fukaya, Y., Sugimoto, A., Ohno, H., *Biomacromolecules.* (2006) 7 3295-7.
- [189] Pinkert, A., Marsh, K., Pang, S., Staiger, M., *Chem. Rev.* (2009) 109 6712-28.
- [190] Abe, M., Fukaya, Y., Ohno, H., *Green Chem.* (2010) 12 1274-80.
- [191] Brendler, E., Fischer, S., Leipner, H., *Cellulose* (2001) 8 283-8.

- [192] Rinaldi, R., *Chem. Commun.* (2011) 47 511-513.
- [193] Takaragi, A., Minoda, M., Miyamoto, T., Liu, H., Zhang, L., *Cellulose* (1999) 6 93-102.
- [194] Heinze, T., Schwikal, K., Barthel, S., *Macromol. Biosci.* (2005) 5 520-5.
- [195] Crosthwaite, J., Muldoon, M., Dixon, J., Anderson, J., Brennecke, J., *J. Chem. Thermo.* (2005) 37 559-68.
- [196] Miao, S., Miao, Z., Liu, Z., Han, B., Zhang, H., Zhang, J., *Microporous and Mesoporous Materials* (2006) 95 26-30.
- [197] Tsiopstias, C., Stefopoulos, A., Kokkinomalis, I., Papadopoulou, L., Panayiotou, C., *Green Chem.* (2008) 10 965-71.
- [198] Ma, H., Yoon, K., Rong, L., Mao, Y., Mo, Z., Fang, D., *J. Mat. Chem.* (2010) 20 4692-704.
- [199] Hines, J., Wanigasekara, E., Rudkevich, D., Rogers, R., *J. Mat. Chem.* (2008) 18 4050-4055.
- [200] Poplin, J., Swatloski, R., Holbrey, J., Spear, S., Metlen, A., Gratzel, M., *Chem. Commun.* (2007) 20 2025-2027.
- [201] Li, Z., Taubert, A., *Molecules* (2009) 14 4682-8.
- [202] Murakami, M., Kaneko, Y., Kadokawa, J., *Carbohydrate Polymers* (2007) 69 378-381.
- [203] Turner, M., Spear, S., Holbrey, J., Daly, D., Rogers, R., *Biomacromolecules.* (2005) 6 2497-2502.
- [204] Park, T., Lee, S., Simmons, T., Martin, J., Mousa, S., Snezhkova, E., *Chem. Commun.* (2008) 40 5022-5024.
- [205] Wu, R., Wang, X., Li, F., Li, H., Wang, Y., *Bioresource Tech.* (2009) 100 2569-2574.
- [206] Zhang, J., Wu, J., Cao, Y., Sang, S., Zhang, J., He, J., *Cellulose* (2009) 16 299-308.
- [207] Liebert, T., Heinze, T., *Biomacromolecule* (2001) 2 1124-32.
- [208] Edgar, K., Arnold, K., Blount, W., Lawniczak, J., Lowman, D., *Macromolecules* (1995) 28 4122-4128.
- [209] Heinze, T., Schaller, J., *Macromol. Chem. Phys.* (2000) 201 1214-1218.
- [210] Regiani, A., Frollini, E., Marson, G., Arantes, G., El Seoud, O., *J. Poly. Sci. Part a-Poly. Chem.* (1999) 37 1357-63.
- [211] Zhang, J., Wu, J., Cao, Y., Sang, S., Zhang, J., He, J., *Cellulose* (2009) 16 299-308.
- [212] Liu, C., Sun, R., Zhang, A., Qin, M., Ren, J., Wang, X., *J. Agricultural and Food Chem.* (2007) 55 2399-406.
- [213] Kohler, S., Heinze, T., *Cellulose.* (2007) 14 489-95.
- [214] Schluffer, K., Schmauder, H., Dorn, S., Heinze, T., *Macromol. Rapid Commun.* (2006) 27 1670-6.
- [215] El Seoud, O., Koschella, A., Fidale, L., Dorn, S., Heinze, T., *Biomacromolecules.* (2007) 8 2629-47.
- [216] Chheda, J., Huber, G., Dumesic, J., *Angew. Chem.It. Ed.* (2007) 46 7164-7183.
- [217] Huber, G., Chheda, J., Barrett, C., Dumesic, J., *Science.* (2005) 308 1446-50.
- [218] Roman-Leshkov, Y., Barrett, C., Liu, Z., Dumesic, J., *Nature* (2007) 447 982-U5.
- [219] Roman-Leshkov Y., Chheda, J., Dumesic J *Science* (2006) 312 1933-7.
- [220] Corma, A., Iborra, S., Velty, A., *Chem. Rev.* (2007) 107 2411-502.
- [221] Li, C., Zhao, Z., *Adv.Syn. Cat.* (2007) 349 1847-50.
- [222] Rinaldi, R., Palkovits, R., Schuth, F., *Angew. Chem. In. Ed.* (2008) 47 8047-50.
- [223] Zhang, Y., Du, H., Qian, X., Chen, E., *Energy and Fuels* (2010) 24 2410-7.

- [224] Amarasekara, A., Owereh, O., *Ind. Eng. Chem. Res.* (2009) 48 10152-5.
- [225] Liu, Q., Janssen, M., van Rantwijk, F., Sheldon, R., *Green Chem.* (2005) 7 39-42.
- [226] Lynd, L., Weimer, P., van Zyl, W., *Microbio. Mol. Bio. Rev.* (2002) 66 506.
- [227] Bayer, E., Lamed, R., Himmel, M., *Current Opinion in Biotechnology* (2007) 18 237-45.
- [228] Zhang, Y., Lynd, L., *Biotech. Bioeng.* (2004) 88 797-824.
- [229] Pottkamper, J., Barthen, P., Ilmberger, N., Schwaneberg, U., Schenk, A., Schulte, M., *Green Chem.* (2009) 11 957-65.
- [230] Turner, M., Spear S., Huddleston, J., Holbrey, J., Rogers, R., *Green Chem.* (2003) 5 443-7.
- [231] Zhao, H., Baker, G., Song, Z., Olubajo, O., Crittle, T., Peters, D., *Green Chem.* (2008) 10 696-705.
- [232] Remsing, R., Swatloski, R., Rogers, R., Moyna, G., *Chem. Commun.* (2006) 1271-3.
- [233] Toral, A., de los Rios, A., Hernandez, F., Janssen, M., Schoevaart, R., van Rantwijk, F., *Enzyme and Microbial Tech.* (2007) 40 1095-9.
- [234] De Los Rios, A., Hernandez-Fernandez, F., Martinez, F., Rubio, M., Villora, G., *Biocat. Biotrans.* (2007) 25 151-6.
- [235] Kuo, C., Lee, C., *Carb. Poly.* (2009) 77 41-6.
- [236] Dadi, A., Schall, C., Varanasi, S., *App. Biochem. Biotech.* (2007) 407-21.
- [237] Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y., Holtzapple, M., *Biores. Tech.* (2005) 96 673-86.
- [238] Zhao, H., Jones, C., Baker, G., Xia, S., Olubajo, O., Person, V., *J. Biotech.* (2009) 139 47-54.
- [239] Crosthwaite, J., Aki, S., Maginn, E., Brennecke, J., *Fluid Phase Equilibria.* (2005) 228 303-9.
- [240] Kilpelainen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., Argyropoulos, D., *Journal of Agricultural and Food Chemistry* (2007) 55 9142-8.
- [241] Liu, H., Sale, K., Holmes, B., Simmons, B., Singh, S., *J. Phys. Chem. B.* (2010) 114 4293-301.
- [242] Ragauskas, A., Williams, C., Davison, B., Britovsek, G., Cairney, J., Eckert, C., *Science* (2006) 311 484-9.
- [243] Aylward, G., Findlay, T., *SI Chemical Data.* 3rd ed: Jacaranda Wiley LTD (1994).
- [244] Visser, A., Swatloski, R., Rogers, R., *Green Chemistry.* (2000) 2 1-4.
- [245] Riisager, A., Fehrmann, R., Berg, R., van Hal, R., Wasserscheid P., *Phys. Chem. Chem. Phys.* (2005) 7 3052-8.
- [246] Gutowski, K., Broker, G., Willauer, H., Huddleston, J., Swatloski, R., Holbrey, J., *J. Am. Chem. Soc.* (2003) 125 6632-3.
- [247] *Organic Syntheses* (2004) 10 184.
- [248] Klemm, D., Heublein, B., Fink, H., Bohn, A., *Angew. Chem. Int. Ed.* (2005) 44 3358-93.
- [249] Burchard, W., *Cellulose* (2003) 10 213-25.
- [250] Roder, T., Morgenstern, B., *Polymer* (1999) 40 4143-7.
- [251] Mazza, M., Catana, D., Vaca-Garcia, C., Cecutti, C. *Cellulose* (2009) 16 207-15.
- [252] Kuang, Q., Zhao, J., Niu, Y., Zhang, J., Wang, Z., *J. Phys. Chem. B* (2008) 112 10234-40.

- [253] Gericke, M., Schluffer, K., Liebert, T., Heinze, T., Budtova, T., *Biomacromolecules* (2009) 10 1188-94.
- [254] Kasarova, S., Sultanova, N., Ivanov, C., Nikolov, I., *Optical Materials* (2007) 29 1481-90.
- [255] Froba, A., Kremer, H., Leipertz, A., *J. Phys. Chem. B.* (2008) 112 12420-30.
- [256] Hasse, B., Lehmann, J., Assenbaum, D., Wasserscheid, P., Leipertz, A., Froba, A., *J. Chem. Eng. Data* (2009) 54 2576-83.
- [257] Hirota, M., Tamura, N., Saito, T., Isogai, A., *Cellulose* (2010) 17 279-288.
- [258] Araki, J., Wada, M., Kuga, S., Okano, T., *Colloids and Surfaces A* (1998) 142 75-82.
- [259] Yokota, S., Ueno, T., Kitaoka, T., Wariishi, H., *Carbohydrate Research* (2007) 342 2593-2598.
- [260] Eichhorn, S., Dufresne, A., Aranguren, M., Marcovich, N., Capadona, J., Rowan, S., Weder, C., Thielemans, W., Roman, M., Renneckar, S., Gindl, W., Veigel, S., Keckes, J., Yano, H., Abe, K., Nogi, M., Nakagaito, A., Mangalam, A., Simonsen, J., Benight, A., Bismarck, A., Berglund, L., Peijs, T., *Journal of Materials Science* (2010) 45 1-33 and references therein.
- [261] Swalina, C., Zauhar, R., DeGrazia, M., Moyna, G., *J. Biomol Nmr* (2001) 21 49-61.
- [262] O'Brien, E., Moyna, G., *Carbohydrate Research* (2004) 339 87.
- [263] Moulthrop, J., Swatloski, R., Moyna, G., Rogers, R., *Chem. Commun.* (2005) 12 1557-9.
- [264] Zhang, L., Ruan, D., Gao, S., *J. Polymer Sci. Part B-Polymer Phys.* (2002) 40 1521-9.
- [265] Lindman, B., Karlstrom, G., Stigsson, L., *J. Mol. Liq.* (2010) 156 76-81.
- [266] Heinze, T., Dicke, R., Koschella, A., Kull, A., Klohr, E., Koch, W. *Macromol. Chem. Phys.* (2000) 201 627-31.
- [267] Yan, L., Chen, J., Bangal, P., *Macromol. Biosci.* (2007) 7 1139-48.
- [268] Yan, L., Gao, Z., *Cellulose* (2008) 15 789-96.
- [269] Liu, S., Zhang, L., *Cellulose* (2009) 16 189-98.
- [270] Biermann, O., Hadicke, E., Koltzenburg, S., Muller-Plathe, F., *Angew. Chem. In. Ed.* (2001) 40 3822.
- [271] Yamane, C., Aoyagi, T., Ago, M., Sato, K., Okajima, K., Takahashi, T., *Polymer Journal* (2006) 38 819-26.
- [272] Youngs, T., Hardacre, C., Holbrey, J., *J. Phys. Chem. B* (2007) 111 13765-74.
- [273] Zhang, J., Zhang, H., Wu, J., Zhang, J., He, J., Xiang, J., *Physical Chemistry Chemical Physics* (2010) 12 1941-7.
- [274] Terraneo, G., Potenza, D., Canales, A., Jimenez-Barbero, J., Baldrige, K., Bernardi, A., *J. Am. Chem. Soc.* (2007) 129 2890-900.
- [275] Pinkert, A., Marsh, K., Pang, S., *Ind. Eng. Chem. Res.* (2010) 49 11121-30.
- [276] Erdmenger, T., Haensch, C., Hoogenboom, R., Schubert, U., *Macromol. Biosci.* (2007) 7 440-5.
- [277] Novoselov, N., Sashina, E., Petrenko, V., Zaborsky, M., *Fibre Chemistry* (2007) 39 153-8.
- [278] Kahlen, J., Masuch, K., Leonhard, K., *Green Chem.* (2010) 12 2172-81.
- [279] Swatloski, R., Holbrey, J., Rogers, R., *Green Chem.* (2003) 5 361-3.
- [280] Wasserscheid, P., Keim, W., *Angew. Chem. Int. Ed.* (2000) 39 3772-89.
- [281] Ebner, G., Schiehser, S., Potthast, A., Rosenau, T., *Tet. Lett.* (2008) 49 7322-4.
- [282] Hsu, J., Yen, Y., Chu, Y., *Tet. Lett.* (2004) 45 4673-6.
- [283] Schobitz, M., Meister, F., Heinze, T., *Macromolecular Symposia.* (2009) 280 102-11.

[284] Wu, D., Wu, B., Zhang, Y., Wang, H., *J. Chem. Eng. Data* (2010) 55 621–624.

[285] Fukaya, Y., Iizuka, Y., Sekikawa, K., Ohno, H., *Green Chem.* (2007) 9 1155-1157.