

Review

Ionic Liquid as Reaction Media for the Production of Cellulose-Derived Polymers from Cellulosic Biomass

Joana Maria Lopes, María Dolores Bermejo *, Ángel Martín and María José Cocero

High Pressure Processes Group, Department of Chemical Engineering and Environmental Technology, University of Valladolid, C/ Doctor Mergelina s/n, 47011 Valladolid, Spain; joana.lopes@gmail.com (J.M.L.); mamaan@iq.uva.es (A.M.); mjcocero@iq.uva.es (M.J.C.)

* Correspondence: mdbermejo@iq.uva.es; Tel.: +34-983-184-077

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Abstract: The most frequent polymer on nature is cellulose that is present together with lignin and hemicellulose in vegetal biomass. Cellulose can be, in the future, sustainable raw matter for chemicals, fuels, and materials. Nevertheless, only 0.3% of cellulose is processed nowadays due to the difficulty in dissolving it, and only a small proportion is used for the production of synthetic cellulosic fibers especially esters and other cellulose derivatives, normally in extremely polluting processes. The efficient and clean dissolution of cellulose is a major objective in cellulose research and development. Ionic liquids (ILs) are considered “green” solvents due to their low vapor pressure, that prevents them evaporating into the atmosphere. In addition, these molten salts present advantages in process intensification, leading to more than 70 patents in lignocellulosic biomass in ILs being published since 2005, most of them related to the production of cellulose derived polymers, e.g., acetates, benzoates, sulfates, fluorates, phthalates, succinates, tritylates, or silylates. In this work, the use of ILs for production of cellulose derived polymers is thoroughly studied. To do so, in the first place, a brief summary of the state of the art in cellulose derivatives production is presented, as well as the main features of ILs in cellulose processing applications. Later, the main results in the production of cellulose derivatives using ILs are presented, followed by an analysis of the industrial viability of the process, considering aspects such as environmental concerns and ILs’ recyclability.

Keywords: cellulose; ionic liquids; cellulose derivatives; acetylation

1. Introduction

Cellulose is a natural biopolymer, being the most common organic polymer and main component of cell wall in plants. Natural global production is about 40 billion tons per year, of which three-tenths of a percent is used by the pulp industry [1]. Cellulose is a homopolysaccharide of $\beta(1\rightarrow4)$ D-glucosyl residues, resulting in a linear chain polymer composed of anhydrous glucose units (AGU) (Figure 1), each one containing three hydroxyl groups [2] able to form hydrogen bonds. Inner cohesion of crystalline regions is due to the van der Waals attraction between hydrogen-bonded sheets [3]. The crystal structure of cellulose varies with its origin (cellulose crystallinity can be 90–100 g/100 g cellulose in plant-based fibers and 60–70 g/100 g cellulose in wood-based fibers) and chemical or physical treatment (e.g., milling and hydrolysis) [4]. The chain length is expressed by the number of AGUs that is called degree of polymerization (DP). Therefore, cellulose of different origin, DP and index of crystallinity (Ic) is expected to require different dissolution/reaction conditions, due to the effect of these parameters on the accessibility to hydroxyl groups.

In nature, cellulose can be found as a part of lignocellulose, that mainly contains cellulose (40–50%), hemicellulose (20–40%), and lignin (20–30%) [5]. While cellulose and hemicellulose are composed of covalently linked and hydrogen bonded carbohydrate polymers, lignin consists of a net of phenolic polymers, forming a substance that is not soluble in water and conventional solvents.

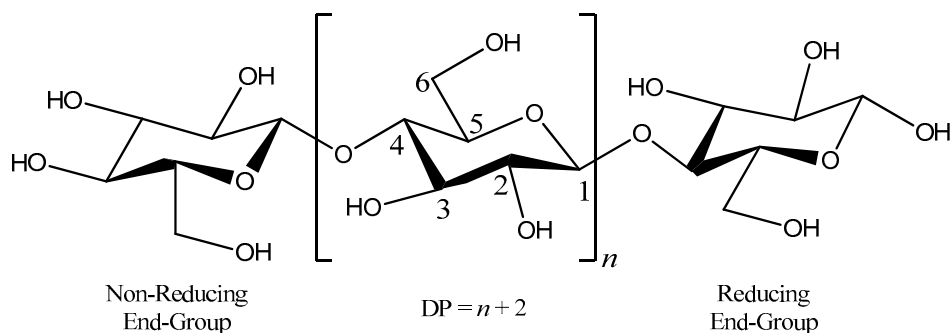


Figure 1. Cellulose structure.

The main cellulose resources are forestry, agriculture crops, industrial, food, and garden waste [6]. Wood pulp remains the main raw material source for the processing of cellulose, most of it being used for the production of paper and cardboard after partial removal of the non-cellulosic constituents from its original fiber form [7]. The use of organic solvents (e.g., ethanol, methanol, ethylene glycol, acetic acid, formic acid) for cellulose isolation and processing [8] is associated with higher pretreatment temperature, use of catalysts, toxicity, and inflammability issues. Thus, for the realistic use of cellulose as an extensive natural resource, it will be necessary to develop a platform that uses this natural polymer for the production of environmentally friendly and biocompatible products [9]. Therefore, development of alternative solvents for the efficient dissolution and transformation of lignocellulose into value-added products is necessary. Promising solvents for cellulose processing are the ionic liquids (ILs) [10–13].

2. Dissolution of Cellulose in ILs

2.1. ILs

ILs are organic salts containing only ions that are fluid at room temperature (usually defined as fluid below or around 100 °C) [14]. One of ILs' characteristics is their extremely low vapor pressure, below their decomposition temperature. Due to this property, they cannot pollute the environment by evaporation, unlike the organic solvents [15]. Furthermore, most ILs are non-flammable and have relatively high thermal stability, compared with organic solvents [16]. A number of studies about the properties of the ILs can be found in literature [17–20].

Different ILs with tunable properties can be synthesized by selection of their anion and cation. ILs present high solvation properties for a number of substances, e.g., water, methanol, acetone, chloroform, acetic anhydride, toluene, both polar and apolar, and even polymeric substances such as cellulose [21]. Many ILs present catalytic activity, and are able to stabilize catalysts and enzymes [22,23]. The properties of ILs can be adjusted by the variation of the size chain of the cation and variation of anion due to the changing polarity and size [24]. Several preparation procedures (e.g., direct quaternization, reaction of halide with Lewis acid, anion exchange) have been reviewed by Wasserscheid and Keim [25]. More recent reviews on synthesis of ILs can be found in literature, e.g., biocompatible ILs [26], ether, and alcohol functionalized ILs [27], or poly(ionic liquid)s [28]. It is worth noting that the label "green solvent" does not mean that all ILs are non-toxic [29]. An update on ILs use as solvents in synthesis and catalysis has been published by Hallett and Welton [30] and by Steinrück and Wasserscheid [31]. The structures of the main cations and anions described in literature are shown in Figure 2.

Salts based on the dialkylimidazolium, pyrrolidinium, and pyridinium cations have gained attention because of the wide spectrum of physicochemical properties [32–36], such as melting points, viscosities, densities, surface tension, refractive indices, and miscibilities with polar and nonpolar solvent. These properties can be affected by water, halides, and metals, which are the most prevalent

impurities present in ILs [37]. The presence of water can occur due to hygroscopicity, whereas other impurities mainly come from the mode of preparation of the IL. Thus, ILs prepared by identical reactions but provided by different suppliers can give different results, due to the presence of small concentrations of different impurities [38]. Methods for preparation of ILs and purity determination (in most cases by ^1H and ^{13}C NMR) are proposed in literature [39]. Additionally, methods for producing large quantities of high quality ILs propose simple techniques to determine the purity of the final product e.g., UV-vis spectroscopy for optical purity [40] and colorimetric determination of 1-methylimidazole in the range 0–3 mol % [41]. Recently, real-time monitoring of 1-methylimidazole concentration through LED-based optical sensor and photodiode detectors was achieved with detection limit of 4 mol % [42].

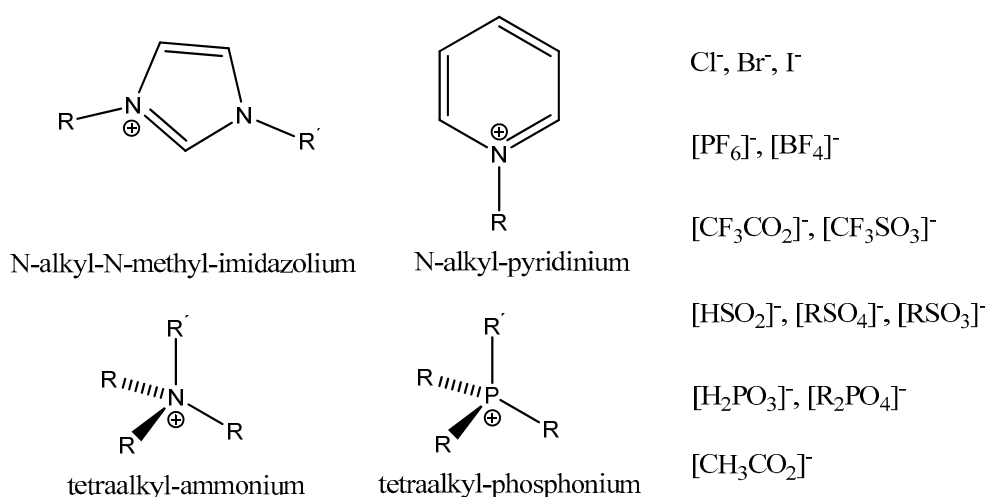


Figure 2. Typical cations and anions forming ionic liquids (ILs) described in literature [31].

2.2. Mechanism of Cellulose Dissolution

The first to dissolve cellulose in ILs were Swatloski et al. [43], opening new opportunities for the processing of this and other biopolymers, such as lignin [44–46] or chitin [47–49]. It was demonstrated that cellulose can be dissolved at concentrations up to 25% (*w/w*) in imidazolium-based ILs with chloride anions. Since then, a number of ILs have been found to be able to dissolve cellulose [50–54]. The most studied cations for cellulose dissolution are based on the imidazolium, pyridinium and pyrrolidinium cores, with allyl-, ethyl-, or butyl-side chains, and the most promising anions, apart from chloride, are acetate, formate, and alkylphosphate. However, chloride-based ILs with longer chain substituted imidazolium cations are less efficient in cellulose dissolution [43].

Cellulose dissolution results from the solvent's ability to eliminate the inter- and intra-molecular hydrogen bonds among biopolymer molecules. The predominant mechanism of this dissolution process is found to be the formation of hydrogen bonds between the anions of the ILs and the hydroxyl groups of the biopolymer, with no specific role for the cation [55–58]. However, it can also be found that the driving force of cellulose dissolution should be a result of the joint interactions of anions and cations with cellulose [59–61]. Computer simulations were carried out to support this [62].

Cellulose maintains its original chemical structure or forms a complex with the solvent only by intermolecular interactions (no covalent interactions occur) [63], thus, ILs are part of the so called non-derivatizing solvents [64] that include, for example, aqueous solution of sodium hydroxide [65], *N,N*-dimethylacetamide/lithium chloride (DMA/LiCl) [66,67], dimethylsulfoxide (DMSO) in combination with ammonium fluorides [68–71], and *N*-methylmorpholine-*N*-oxide (NMMO) [72]. There are a number of derivatizing solvents (able to dissolve cellulose with substitution, forming new covalent bonds) e.g., trifluoroacetic acid (TFA) [73], sodium hydroxide/carbon disulfide (NaOH/CS₂) [74], and *N,N*-dimethylformamide/dinitrogen tetroxide [75].

A number of works, including several reviews [76–82], have been already published on the cellulose dissolution process in ILs. Thus, this subject will not be discussed in depth in this review. However, for understanding of the dissolution process of cellulose in ILs in relation with its industrial application, it is important to mention the solvent properties: hydrogen bond basicity, viscosity, and water content.

2.3. Hydrogen Bond Basicity of Cellulose Dissolving ILs

ILs with high ability to form hydrogen bonds (hydrogen bond basicity) weaken the inter- and intra- molecular hydrogen bonds of cellulose structure, causing its dissolution [83]. Thus, the efficiency of these processes is usually improved with increased basicity of the ILs. The hydrogen bonding ability can be quantified by the Kamlet–Taft parameters [84], which specify three distinct polarities: hydrogen-bonding acidity (α), hydrogen-bonding basicity (β), and dipolarity/polarizability (π^*). All three protons of the imidazolium ring are acidic, with the 2-position proton being the one that contributes more to the hydrogen-bonding acidity [85]. A study [86] on imidazolium-based ILs reported π^* variation with both anion and cation, α dependence mainly on the cation and β value, in general, affected mainly by the nature of the anion species. β values of ILs with the same cations vary with the anion structure, as shown in Table 1. Chloride-based ILs are potential solvents for cellulose (e.g., $\beta_{[\text{Bmim}]\text{Cl}} = 0.95$), as the chloride anion is a strong proton acceptor in the interaction between hydroxyl groups of cellulose. Nevertheless, the high melting temperature and high viscosity makes their use expensive and inefficient. As an alternative to conventional ILs, polar ILs with low melting points and relatively low viscosities, such as dialkylimidazolium salts with phosphate-, acetate-, and formate-derived anions have been studied [87]. Some [Bmim]-based ILs containing carboxylic anions (Ac and HCO₂) were reported [88] to show stronger hydrogen-bonding basicity ($\beta_{[\text{Bmim}]\text{OAc}} = 1.09$, $\beta_{[\text{Bmim}]\text{HCO}_2} = 1.01$) than chloride anion. The methylphosphonate anion salts with stronger hydrogen bond basicity than conventional ILs are able to dissolve 2.0 wt % of cellulose powder within 3 h at room temperature [88] (25 °C) and within 30 min at 45 °C [89]. In general, polar ILs are very hygroscopic, however, almost no correlation has been found between π^* and hygroscopicity of [mim]-based ILs [90]. ILs with other anions presenting low basicity, such as those with bromide ($\beta_{[\text{Emim}]\text{Br}} = 0.87$), trifluoroacetate ($\beta_{[\text{Emim}]\text{CF}_3\text{CO}_2} = 0.74$), thiocyanate ($\beta_{[\text{Emim}]\text{SCN}} = 0.71$), methanesulfonate ($\beta_{[\text{Emim}]\text{MeSO}_3} = 0.70$), or tetrafluoroborate ($\beta_{[\text{Bmim}]\text{BF}_4} = 0.38$) anions show [83] cellulose solubilities <1% in mass.

Table 1. ILs capable of dissolving cellulose (modified from [83] and molecular-microscopic properties measured at 25 °C: hydrogen-bonding acidity (α), hydrogen-bonding basicity (β), dipolarity/polarizability (π^*) and physical properties: viscosity at 25 °C (η), melting temperature (Tm), decomposition temperature (Tdec).

ILs (Cellulose Solubility > 1%) ^{1,2}	η (mPa·s)	Tm (°C)	Tdec (°C)	Kamlet–Taft Parameters ³			Ref.	ILs (Cellulose Solubility < 1%)	β	Ref.
				β	α	π^*				
[Amim]Cl	2090		256	0.83	0.46	1.17	[87]	[Bmim]BF ₄	0.38	[86]
[Emim]HCO ₂		52	212				[87]	[Bmim]PF ₆	0.21	[86]
[Prmim]HCO ₂	117			0.99	0.48	1.08	[87]	[Emim]MeOSO ₃	0.61	[89]
[Amim]HCO ₂	66		205	0.99	0.48	1.08	[87]	[Emim]MeSO ₃	0.70	[89]

Table 1. Cont.

ILs (Cellulose Solubility > 1%) ^{1,2}	η (mPa·s)	T _m (°C)	T _{dec} (°C)	Kamlet–Taft Parameters ³			Ref.	ILs (Cellulose Solubility < 1%)	β	Ref.
				β	α	π^*				
[Bmim]OAc				1.09	0.55	0.99	[88]	[Emim]CF ₃ CO ₂	0.74	[91] ⁴
[Bmim]Cl		66	254	0.95	0.47	1.10	[91]	[Emim]SCN	0.71	[91]
[Bmim]HCO ₂				1.01	0.56	1.03	[88]	[Emim]BF ₄	0.55	[91,92] ⁵
[Emim](MeO) ₂ PO ₂	265	21	289	1.00	0.51	1.06	[89]	[Emim]N(CN) ₂	0.64	[91]
[Emim](MeO)HPO ₂	107		275	1.00	0.52	1.06	[89]	[Emim]I	0.75	[91]
[Emim](MeO)MePO ₂	510		262	1.07	0.50	1.04	[89]	[Emim]PF ₆	0.44	[91]
[Emim](EtO) ₂ PO ₂						1.00	[89]	[Bmim]CH ₃ SO ₃	0.85	[91]
[Emim]Cl		89	285				[92]	[Bmim]Br	0.87	[91]
[Emim]H ₂ PO ₂		17	260	0.97	0.52	1.09	[93]			
[Amim](MeO)HPO ₂	123		265	0.99	0.51	1.06	[93]			
[Prmim](MeO)HPO ₂	219		277	1.00	0.54	1.02	[93]			
[Bmim](MeO)HPO ₂	287		277	1.02	0.52	1.01	[93]			
[Emim]OAc ^{6,7}	162			0.95	0.40	1.09	[94,95]			

¹ 1-Allyl-3-methylimidazolium chloride, [Amim]Cl;
Ethyl-3-methylimidazolium formate, [Emim]HCO₂;
1-Propyl-3-methylimidazolium formate, [Prmim]HCO₂;
1-Allyl-3-methylimidazolium formate, [Amim]HCO₂;
1-Butyl-3-methylimidazolium acetate, [Bmim]OAc;
1-Butyl-3-methylimidazolium chloride, [Bmim]Cl;
1-Butyl-3-methylimidazolium formate, [Bmim]HCO₂;
1-Ethyl-3-methylimidazolium dimethylphosphate, [Emim](MeO)₂PO₂;
1-Ethyl-3-methylimidazolium methylphosphonate, [Emim](MeO)HPO₂;
1-Ethyl-3-methylimidazolium methyl methylphosphonate, [Emim](MeO)MePO₂;
1-Ethyl-3-methylimidazolium diethylphosphate, [Emim](EtO)₂PO₂;
1-Ethyl-3-methylimidazolium chloride, [Emim]Cl;
1-Ethyl-3-methylimidazolium dihydrogenphosphate, [Emim]H₂PO₂;
1-Allyl-3-methylimidazolium methylphosphonate, [Amim](MeO)HPO₂;
1-Propyl-3-methylimidazolium methylphosphonate, [Prmim](MeO)HPO₂;
1-Butyl-3-methylimidazolium methylphosphonate, [Bmim](MeO)HPO₂;
1-Ethyl-3-methylimidazolium acetate, [Emim]OAc;

² Solubility conditions: 2–8 wt % of cellulose in IL, temperature of dissolution from 100 °C to 130 °C;
³ Kamlet–Taft parameters values measured at 25 °C using a single set of dyes: Reichardt's dye, 4-nitroaniline and *N,N*-diethyl-4-nitroaniline;
⁴ β value obtained using the 3-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-di-one dye;
⁵ Solubility conditions: 5 wt % of cellulose in IL, temperature of dissolution 50 °C;
⁶ Kamlet–Taft parameters measured using Reichardt's dye 2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino) phenolate;
⁷ Viscosity measured at 20 °C.

The β parameter is considered an excellent predictor of lignocellulosic biomass pretreatment efficacy [96]. Cellulose dissolving ILs present β values between 0.83 and 1.09, while non-cellulose dissolving IL β values range from 0.21 to 0.87, as shown in Table 1. Strong hydrogen-bonding basicity alkyl methylimidazolium-based ILs can be designed using various anions: Ac, (MeO)MePO₂, (MeO)HPO₂, HCO₂, (MeO)₂PO₂, Cl, H₂PO₂. Furthermore, the dipolarity/polarizability studied [97] as a function of cation–anion interaction strength indicates an increase with stronger ion pairing effect i.e., the resulting cation effect on π^* is different with weakly coordinating anion compared to the strongly coordinating anion (e.g., chloride). It is expected that 1-alkyl-3-methylimidazolium cations show larger values of π^* [98], even when compared with different cations sharing the same anion, such that imidazolium > pyridinium > pyrrolidinium [99].

2.4. Viscosity of Concentrated Cellulose Solutions in ILs

The viscosity of ILs depends on their molecular structure and interactions between ions: electrostatic, Van der Waals, and hydrogen bonds [100]. To obtain low viscosity ILs, it is necessary to select asymmetrical cations and anions (irregular packing) or increase their size. Increasing the distance between the cation and anion, the ionic interaction become weaker [101]. In ILs having a common anion and a similar alkyl chain length on the cation, the viscosity increases when increasing the cation size, in the following order: imidazolium < pyridinium < pyrrolidinium [102]. In general, viscosities increase with the increasing number and length of alkyl substituents on the cation. Pyridinium salts are, in general, more viscous than the equivalent imidazolium compounds [103], as shown in Table 2.

Table 2. Viscosity (η), density (ρ), and water content (wt %) of ILs.

IL ¹	T (°C)	η (mPa·s)	ρ (kg/m ³)	Water (wt %) ²	Ref.
<i>Methylimidazolium</i>					
[Bmim]OAc	20	646		1.100	[103]
ECOENG 41M	20	1676		0.083	[103]
[Bmim]OAc	20	429	1055	0.085	[104]
[Bmim]Cl	25		1080	0.220	[105]
[Amim]Cl	25	821	1166	0.180	[106]
[Emim]OAc	20	202	1102	0.124	[107]
[Emim](MeO)HPO ₂	20	286	1212	0.078	[107]
[Emim]CH ₃ SO ₃	20	232	1246	0.029	[107]
[Emim]CF ₃ SO ₃	20	52	1390	0.002	[107]
[Emim]Tos	30	1417	1223	0.056	[107]
[Emim](MeO) ₂ PO ₂	30	193	1214	0.014	[107]
[Emim]EtSO ₄	20	125	1240	0.105	[108]
<i>Pyridinium</i>					
[Empy]EtSO ₄	20	204		0.026	[103]
[Epy]EtSO ₄	20	183		0.068	[103]
[EEpy]EtSO ₄	25	325	1220	<0.08	[109]
[Mpy]CH ₃ SO ₄	25	116	1345	<0.06	[109]
[MMPy]CH ₃ SO ₄	25	129	1302	<0.06	[109]
[EMpy]CH ₃ SO ₄	25	456	1285	<0.08	[109]
<i>Pyrrolidinium</i>					
[Bmpyr]OAc	25	107	1021	0.070	[104]
[Bmpyr]CF ₃ SO ₃	20	222	1256	0.072	[100]
[Bmpyr](BtO)HPO ₂	25	321	1082	0.025	[110]
[Empyr](EtO)HPO ₂	25	320	1123	0.021	[110]

- ¹ Butyl-3-methylimidazolium acetate, [Bmim]OAc;
 1-Butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethylsulfate, ECOENG 41M;
 1-Butyl-3-methylimidazolium chloride, [Bmim]Cl;
 1-Allyl-3-methylimidazolium chloride, [Amim]Cl;
 1-Ethyl-3-methylimidazolium acetate, [Emim]OAc;
 1-Ethyl-3-methylimidazolium methylphosphonate, [Emim](MeO)HPO₂;
 1-Ethyl-3-methylimidazolium methanesulfonate, [Emim]CH₃SO₃;
 1-Ethyl-3-methylimidazolium: trifluoromethanesulfonate, [Emim]CF₃SO₃;
 1-Ethyl-3-methylimidazolium tosylate, [Emim]Tos;
 1-Ethyl-3-methylimidazolium dimethylphosphate, [Emim](MeO)₂PO₂;
 1-Ethyl-3-methylimidazolium ethylsulfate, [Emim]EtSO₄;
 1-Ethyl-3-methylpyridinium ethylsulfate, [Empy]EtSO₄;
 1-Ethylpyridinium ethylsulfate, [Epy]EtSO₄;
 1,2-Diethylpyridinium ethylsulfate, [EEpy]EtSO₄;
 1-methylpyridinium methylsulfate, [Mpy]CH₃SO₄;
 2-ethyl-1-methylpyridinium methylsulfate, [EMpy]CH₃SO₄;
 1-Butyl-1-methylpyrrolidinium acetate, [Bmpyr]OAc;
 1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate, [Bmpyr]CF₃SO₃;
 1-Butyl-1-methylpyrrolidinium butylphosphonate, [Bmpyr](BtO)HPO₂;
 1-Ethyl-1-methylpyrrolidinium ethylphosphonate, [Empyr](EtO)HPO₂;

- ² Water content (weight fraction percentage) of IL before the measurements of viscosity and density.

From the alkylmethylimidazolium-based ILs viscosities, it is clear that chloride anion increases the value of that property, as reported in literature [111]. In addition, even the presence of very low concentrations of chloride as an impurity in non-chloride-based alkylimidazolium ILs increases the viscosity. Seddon et al. [111] related this issue to an increase in the cohesive forces via hydrogen bonding between the chloride and the protons of the imidazolium ring. In the same work, it was also concluded that the presence of water and other molecular co-solvents reduces the viscosity of ILs. For example, viscosities of binary mixtures [112] of water + [Amim]Cl and ethanol + [Amim]Cl

measured in the range of 20–60 °C with water molar fraction up to 0.8 and ethanol of 0.55 are up to 85% lower than the viscosity of the pure IL.

While the addition of molecular solvents to an IL decreases the solution viscosity, the addition of cellulose increases drastically the viscosity of the mixture. Concentrated cellulose/IL solutions show non-Newtonian behavior. The Newtonian behavior is lost progressively with increasing polymer concentration [113] explained by the increase of interactions between polymer chains and restriction of the motion of individual chains. Concentrated cellulose solutions (cellulose mass concentrations between 4 and 12%) usually require dissolution temperature of 100 °C [114,115]. The zero shear viscosity of concentrated cellulose solutions in [Amim]Cl, in the range of 10 to 25 wt % at 100 °C, presents values between 2209 and 125,700 Pa·s [113]. These values represent a challenge for cellulose processing with ILs with high viscosity. The viscosities of mixtures IL + cellulose were compared at 85 °C by Kosan [116], and were found to increase in the following order: [Emim]OAc (2281 Pa·s) < [Bmim]OAc (9690 Pa·s) < [Emim]Cl (24,900 Pa·s) < [Bmim]Cl (47,540 Pa·s) < [Bdmim]Cl (188,400 Pa·s), with cellulose concentrations between 12.8% and 15.8%. The viscosity of solutions of 4 and 8 wt % cellulose fibers (DP = 650) in [Amim]Cl at 80 °C reported by Zhang et al. [59] was respectively 110 and 1480 Pa·s. In order to improve the processability of cellulose, a co-solvent can be added to reduce the viscosity of the solution, but the co-solvent must be chosen in order that it does not reduce the solubility of cellulose in water. The most frequent co-solvent used in cellulose processing is DMSO. The maximal amount of cellulose dissolved in [Emim]OAc + 10 wt % DMSO is five times higher than at [Emim]OAc + 10 wt % water [117]. The cellulose intrinsic viscosity of the solution does not depend on DMSO content, but the addition of water higher than 10–15% in cellulose/[Emim]OAc solution leads to cellulose coagulation [117]. Although, cellulose/IL/DMSO solutions behave as Newtonian fluids at very low cellulose concentration (<0.80 wt %), the solution viscosity increases with cellulose concentration and exhibits a shear-thinning behavior at higher shear rates [118]. Additionally, shear thinning behavior can be detected, as well with dimethylacetamide (DMAc) and dimethylformamide (DMF), at high fractions of IL [119]. As an alternative to water or organic solvents, viscosity reduction can be provided by carbon dioxide (CO₂) [120]. Using CO₂ as a co-solvent has the advantages of being cheap, non-toxic, and can be easily separated of the IL when decreasing the pressure. In biphasic mixtures of IL–CO₂ at moderate or high pressure, CO₂ can dissolve significantly into the IL-rich liquid phase, up to concentrations round 30–40% in mol [121] in the case of imidazolium chloride ILs. CO₂ is not causing the precipitation of cellulose, except in ILs with acetate anion, in which a reversible carboxylate reaction occurs that cause cellulose precipitation [122,123].

To the best of our knowledge, only a few viscosity data of mixtures CO₂ + IL can be found in literature [124–126] for non-cellulose dissolving ILs, and for the mixture CO₂ + [Amim]Cl [127]. In general, the reduction in viscosity is between 85% and 45% at moderate pressures of 10–12 MPa, but with molar fractions as low as 10% of CO₂, viscosity can decrease 30–40% with respect to the viscosity of the pure IL. In all cases, the effect in viscosity reduction with CO₂ is more important at lower temperatures, where both viscosities and CO₂ solubilities are higher.

The effect of CO₂ in IL + cellulose mixtures was only studied by Iguchi et al. [128], with and acetate anion IL, using low concentrations of cellulose to avoid its precipitation with CO₂. At 4 MPa and 39 °C, viscosity can be reduced of 1.2 wt % cellulose + [Bmim]OAc solution by about 80%.

2.5. Water Effect on the Anion Interaction with Cellulose

The presence of water or alcohol in an IL decreases the solubility of cellulose, so they can cause cellulose precipitation from IL solutions. Nevertheless, in the case of water, it can be a serious challenge for the cellulose processing in ILs, because even partially water-immiscible ILs are hygroscopic, and are able to absorb up to 1%, by weight, of water from the environment [129]. Absorbed water interacts with the anions, and these interactions can cause changes in the structure of water [130]. Cammarata et al. [131] showed that for low coordinating anion (low basicity), water is associated with the anion of the ILs via hydrogen bonding, instead of being self-associated. In those cases,

the concentrations of the dissolved water are typically in the range of 0.2 ± 1.0 mol/L. In ILs with strongly coordinating anion (highly basic, that is, those able to dissolve cellulose), water molecules can self-associate, being able to dissolve much higher water amounts that may exceed 1.0 mol/L.

Adding water to the solution cellulose/IL means that the water-anion interactions saturate the hydrogen-bonding ability of the anions, allowing the water molecules to form hydrogen bonds with cellulose [132], meanwhile, the cations are maintained in a second solvation shell of cellulose, due to strong interactions with anions. Computer simulations [133] using 1-alkyl-3-methylimidazolium cations ($n = 1, 2, 3, 4, 5$) paired with chloride, acetate, or dimethylphosphate, showed that water crowds the hydrogen-accepting sites of the anions, preventing interactions with cellulose.

3. Industrial Cellulose Derivative Production Methods

Fibers are divided into two groups: natural fibers and chemical fibers (man-made fibers). Natural materials are dissolved to make cellulose fibers, such as wood pulp or cellulose. The market is focusing on using cellulose fibers through renewable sources [134]. Most fibers made from cellulose derivatives are produced by replacing the hydrogen atoms of hydroxyl groups in the AGUs of cellulose with alkyl or substituted alkyl groups [135]. Cellulose derivatives can be cellulose esters and ethers. They are generally synthesized by esterification of cellulose with inorganic or organic acids, or by etherification or Michael addition in heterogeneous or homogeneous media, respectively [135]. Cellulose derivatives production mechanism using ILs is schematized in Figure 3.

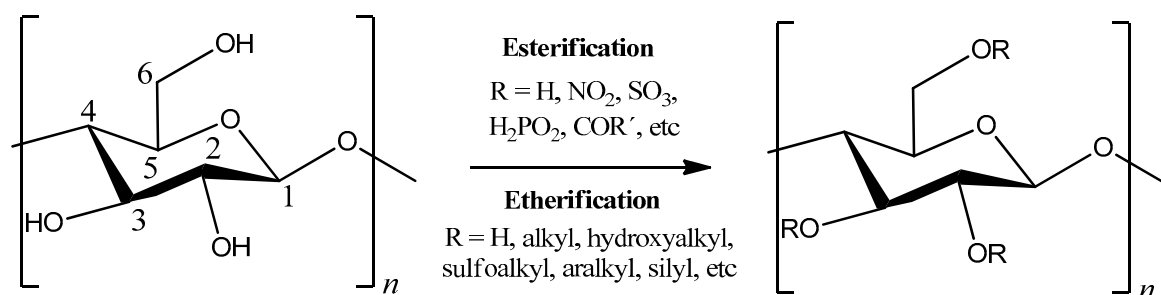


Figure 3. Synthesis of cellulose esters and ethers. Reprinted with permission from [135]. Copyright 2013 John Wiley and Sons.

Depending on the number of hydroxyl groups substituted, cellulose derivatives may have low or high degree of substitution (DS). The degree of substitution is a measure of the average number of hydroxyl groups on each AGU unit which are derivatized by substituent groups. As each AGU has three hydroxyl groups available for substitution, the maximum possible DS is 3. Cellulose contains 31.48% by weight of hydroxyl groups (one primary and two secondary per AGU) and the reactivity of these hydroxyl groups varies according to the reaction medium in which functionalization is done [136].

Since 1944, cellulose esters have been produced [137] by a simple heterogeneous process consisting of pouring a mixture containing the acetylation agent into water, filtering, washing, and drying. The polymers have been produced in different shapes: films, fibers, plastics, and coating applications. Several organic cellulose esters have been used in commercial products or in pharmaceutical investigations, such as cellulose acetate (CA), cellulose acetate phthalate (CAP), cellulose acetate butyrate (CAB), and cellulose esters based on inorganic acids, e.g., cellulose nitrate, and silylated celluloses, such as trimethylcellulose and others [138].

Commercially marketed cellulose acetates have versatile applications [139]. Besides their traditional applications as additives in the food industry, in coatings, printing, cosmetic, textile, and in the pharmaceuticals industry, new cellulose derivatives have also been investigated for their applications, such as drug delivery systems [140], in chiral separation and recognition [141], as

photoactive materials [142], as antioxidant agents [143], in memory of electronic devices [144], and graft copolymers [145].

The properties of cellulose ethers important for their commercialization are determined by their molecular weights, chemical structure, and distribution of the substituent groups, degree of substitution, and molar substitution [146]. Examples of mostly used cellulose ethers are methyl cellulose (MC), ethyl cellulose (EC), hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), hydroxypropylmethyl cellulose (HPMC), and carboxymethyl cellulose (CMC). Cellulose ethers act as thickeners, binders, film formers, and water retention agents in construction applications, although they function also as suspension aids, surfactants, lubricants, protective colloids, and emulsifiers [147]. HPC and HEC, in particular, have been investigated for production of antibiotics [148].

Natural cellulose has highly crystalline regions, in which a highly branched hydrogen bonding network makes it insoluble in water and many organic solvents. This explains why standard commercial methods for producing cellulose derivatives begin as heterogeneous reactions, followed, in the case of esters, by a subsequent back-hydrolysis reaction [149]. In the case of cellulose ethers, an activation of the cellulose prior to the heterogeneous etherification is required, and the produced cellulose ethers exhibit non-uniform mixtures [150]. Cellulose must be activated to break its crystallinity before etherification to obtain a soluble product. A common method of cellulose activation is to mercerize it with NaOH [151].

Cellulose derivatives synthesized in homogeneous reaction media could have different properties from those of cellulose derivatives synthesized in heterogeneous media with similar chemical compositions. When the reactions proceed in homogeneous solutions, the regioselectivity depends on the reactivity differences among the free hydroxyl groups on the cellulose molecules [152], not by their accessibility [153].

The most prominent example for the utilization of ILs as cellulose solvent are the Ioncell-F fibers. The process to make lyocell [154] fibers is a solvent spinning process (dry-jet wet spinning). The cellulose is directly dissolved in the solvent NMMO/water or ILs (Ioncell-F fibers) such as [Bmim]Cl, [Bmim]OAc, [Emim]Cl, [Emim]OAc, and [DBNH]OAc [155], spun through an air gap and precipitated in water. Thus, this fiber is composed of cellulose because it has not suffered substitution reactions. The Table 3 compares the structure and mechanical properties of the viscose fiber [156] to cellulose fibers prepared from NMMO and ILs [157]. Viscose fiber is a cellulose fiber made from wood pulp, however, has several drawbacks due to the use of highly toxic carbon disulfide (CS₂) and precipitate formation, owing to chemical degradation of polysaccharides [158].

Table 3. Comparison of mechanical properties of regenerated cellulose fibers from viscose process [156] to NMMO and ILs [157].

Fiber/Solvent ¹	Cross-Section Shape	Tenacity Cond. (cN/tex)	Elongation Cond. (%)	Commercial/Experimental Fiber	Ref.
Viscose	Lobate	22		com.	[156]
NMMO	Round	40.2	13.0	com.	[157]
[Emim]Cl	Round	43.0	9.6	exp.	[157]
[Bmim]Cl	Round	50.1	9.3	exp.	[157]
[Emim]OAc	Round	44.7	10.4	exp.	[157]

¹ N-methylmorpholine-N-oxide, NMMO;

Ethyl-3-methylimidazolium chloride, [Emim]Cl;

1-Butyl-3-methylimidazolium chloride, [Bmim]Cl;

1-Ethyl-3-methylimidazolium acetate, [Emim]OAc.

Fiber characterization is normally done by measuring the tenacity and the elongation at break. Furthermore, titer, modulus and cross-section can be determined [157]. The level of stretching determines the tenacity and elongation level. A high degree of stretching results in a relatively tear-resistant and low strain fiber. A higher elastic modulus means a higher resistance of the fiber against deformation. The same cross-section can be obtained for different solvent systems assuming the use of similar spinnerets. NMMO and ILs present fiber properties in the same range (Table 3) and the same cross-section (round). Higher tenacity, crystallinity, and molecular weight can be obtained using the lyocell process [159]. Degradation during the lyocell process should be less than 10%, thus similar fiber properties of lyocell fibers spun from ILs compared to NMMO suggest similar solution structures of cellulose [159]. Additionally, the mechanical properties of the regenerated fibers, such as tensile strength and elongation at break, can be strongly dependent on the DP of the original cellulose [160].

Despite many advantages, the lyocell process still produces fibers with severe fibrillation. Fibrillation is the peeling away of fibrils of the fiber surface by applying mechanical stress to fibers which are swollen in water [161]. This is undesired, especially in the processing from fiber to fabric. Methods for fibrillation reduction have been published [162–164]. The use of NMMO, which is a thermally unstable solvent, could lead to uncontrolled thermal degradation. From the thermodynamic point of view, the state of a thermal explosion is reached that requires a major investment in safety technology [165]. Additionally, the use of high melting point alkylmethylimidazolium based ILs shows spinning dopes containing high cellulose concentration (e.g., 16.5 wt %), however, the decomposition and the viscosity remain a challenge [166]. A new cellulose spinning solvent, consisting of a superbase-based IL, [DBNH]OAc, was reported to present high dissolution power and a low viscosity [155], and to produce high tenacity fibers (over 50 cN/tex).

It has been demonstrated that chemical modification of cellulose may be carried out under homogenous conditions using ILs in a commercial scale towards high-value cellulose derivatives, as published in a patents review [167]. The substitution reaction using ILs does not require an inorganic base in order to activate cellulose [168]. The performance of the homogeneous reaction in IL media presents a number of advantages, the main one being the existence of different options in introducing functional groups, and the better control of the DP and in the degree of substitution (DS). An overview over cellulose derivatives from ILs is reported [169]. The conditions of homogeneous substitution reactions in order to prepare cellulose derivatives are shown in Table 4.

Table 4. Conditions of reaction media for the homogeneous esterification of cellulose and DS of the cellulose derivatives.

IL ¹	Co-Solvent ²	Catalyst	Base	wt % ³	Reagent	Conditions ⁴	DS ⁵	Ref.
[Amim]Cl		DMAP		4	Propionic anhydride, butyric anhydride	1:1–5:1; 2–180 min; 20–100 °C	Prop: 0.89–2.89, But: 0.91–2.76	[168]
[Amim]Cl				4	Propionic anhydride, acetic anhydride, butyric anhydride	5:1, 9:1, 13:1; 60–300 min; 80–100 °C	Prop: 0.93–2.46, But: 0.86–2.07	[170]
[Bmim]Cl			Py	11	Acetyl chloride	3:1, 5:1, 10:1; 2 h; 80 °C	Ac < 3.00	[171]
[Amim]Cl			Py/Et ₃ N	10	Acetic anhydride, tosyl chloride	3:1, 8:1; 48 h, r.t.	Ac: 2.99, Tos: 0.84	[172]
[Emim]OAc			IM	3	Tosyl chloride	2:1; 300 min; 7 °C	Tos: 0.55	[173]
[Bmim]Cl	DMI		Py, BIM	11	Tosyl chloride	1:1–5:1; 1–48 h; 25 °C	Tos: 1.14, Cl: 0.16	[174]
[Bmim]Cl			Py	11	2-furoyl chloride	1:1, 3:1, 5:1; 0.5–17 h; 65 °C	0.46–3.00	[175]
[Bmim]Cl					Acetyl chloride	3:1, 5:1, 10:1;	Ac: 2.81–3.0	[176]
[Emim]Cl			Py	11	Phenyl isocyanate	15–120 min; 80 °C	Carb: 0.26–3.0	
[Admim]Br				6	Phenyl isocyanate	1:1–10:1;	Carb: 0.29–3.0	[177]
[Bmim]Cl					Acetic anhydride	120–240 min; 80 °C	Ac: 0.69–3.0	
[Bmim]Cl				3	Chloroacetyl chloride	3:1, 5:1; 60–300 min; 30–50 °C	0.33–1.87	[178]
[Amim]Cl	DMF			4	2-bromopropionyl bromide	5:1; 480 min; r.t.	0.7	[179]
[Amim]Cl				3–7	Benzoyl chloride, 4-toluoyl chloride, 4-chlorobenzoyl chloride, 4-nitrobenzoyl chloride	2:1–10:1; 60–240 min; 40–100 °C	1–3.0	[180]
[Bmim]Cl			Py	10–12	Acetic anhydride, Propionic anhydride, Butyric anhydride, Pentanoic anhydride, Hexanoic anhydride	1:1, 3:1, 5:1; 2 h; 80 °C	0.4–3.0	[181]
[Bmim]Cl, [Amim]Cl, [Emim]OAc	DMF			11	Sulfur trioxide, chlorosulfonic acid	1.3:1–3:1; 120–240 min; 25 °C	0.22–0.89	[182]
[Bmim]Cl				2.35	Phthalic anhydride	2:1–10:1; 20–120 min; 85–105 °C	0.12–2.54	[183]
[Bmim]Cl				2	Succinic anhydride	1:1–12:1; 5–120 min; 85–105 °C	0.037–0.53	[184]
[Bmim]Cl	DMSO	NBS		2	Succinic anhydride	4:1; 30–240 min; 90–120 °C	0.24–2.31	[185]
[Bmim]Cl		DMAP		2	Succinic anhydride	4:1; 30–120 min; 60–110 °C	0.24–2.34	[186]
[Bmim]Cl		Iodine			Succinic anhydride	4:1; 30–120 min; 85–110 °C	0.56–1.54	[187]
[Bmim]Oac [Bmim]Cl [Bmim]OPr					Carboxylic anhydrides, carboxylic acid halides, diketene, or acetoacetic acid esters	<0.2 (molar ratio)	0.1–3.0	[188]

Table 4. Cont.

IL ¹	Co-Solvent ²	Catalyst	Base	wt % ³	Reagent	Conditions ⁴	DS ⁵	Ref.
6					C1 to C20 straight- or branched-chain alkyl or aryl carboxylic anhydrides, carboxylic acid halides, diketene, or acetoacetic acid esters		0.1–3.0	[189]
7					Acetic anhydride, Propionic anhydride, Butyric anhydride, 2-ethylhexanoic anhydride, Nonanoic anhydride		≤3.0	[190]
6				0.1–50	Thionyl chloride, Methanesulfonyl chloride, Chlorodimethyliminium chloride, Phosphoryl chloride, Tosyl chloride	30–150 °C	0.5–3.0	[191]
6			Py	5–10	Chlorosulfonic acid, Sulfur trioxide, Sulphuric acid, Sulfamic acid	1:1–6:1; 1–720 min; 130 °C	0.05–2.5	[192]

¹ [Amim]Cl: 1-Allyl-3-methylimidazolium chloride,
 [Bmim]Cl: 1-Butyl-3-methylimidazolium chloride,
 [Emim]OAc: 1-Ethyl-3-methylimidazolium acetate,
 [Emim]Cl: 1-Ethyl-3-methylimidazolium chloride,
 [Bdmim]Cl: 1-Butyl-2,3-methylimidazolium chloride,
 [Admim]Br: 1-Allyl-2,3-methylimidazolium bromide,
 [Bmim]Opr: 1-butyl-3-methylimidazolium propionate;

² DMAP: 4-dimethylaminopyridine, Py: Pyridine, BIM: 1-Butylimidazole,
 Et₃N Triethylamine, IM: Imidazole, DMI: 1,3-dimethyl-2-imidazolidinone,
 DMF: Dimethylformamide, NBS: N-bromosuccinimide;

³ Concentration of cellulose in IL during dissolution by weight;

⁴ Reaction conditions: molar ratio of reagent per mol of anhydroglucose unit (AGU) in cellulose; reaction time; reaction temperature;

⁵ Range of degrees of substitution (DS);

⁶ Cation: imidazolium, pyrazolium, oxazolium, 1,2,4-triazolium, 1,2,3-triazolium, and/or thiazolium, quinolinium, isoquinolinium, piperdinium, pyrrolidinium, pyridazinium, pyrimidinium, pyrazinium, pyrazolinium;
 Anion: C1 to C20 straight- or branched-chain carboxylate or substituted carbonylate, or alkylphosphates
 (e.g., chloride, formate, acetate, propionate, butyrate, valorate, hexanoate, lactate, oxalate, chloro-, bromo-, fluoro-substituted acetate, propionate and butyrate);

⁷ Carboxylated ILs containing sulfur, halide or transition metals

3.1. Esterification

Conversion of cellulose, dissolved in different ILs, with carboxylic acid chlorides or anhydrides is very efficient for the preparation of cellulose esters (Table 4). General synthesis route and molecular structure of cellulose esters homogeneously prepared in ILs were thoroughly reviewed elsewhere [193].

Cellulose acetate butyrate and cellulose acetate propionate can be prepared homogeneously in [Amim]Cl from sugarcane bagasse [170]. The cellulose acetate content was affected by reaction temperature, reaction time, and molar ratio reagent/AGUs. With propionic anhydride, the DS obtained was between 0.89 and 2.89, and with butyric anhydride, from 0.91 to 2.76. The most common methods for determination of DS include ^1H NMR, ^{13}C NMR in DMSO- d_6 , CDCl_3 , or D_2O .

Heinze et al. [171] used [Bmim]Cl as reaction medium and synthesized cellulose acetates with high DS values in good yield (85.9%) within a short time (2 h). DS was controlled by the amount of reagent added. The acetylating reagent acetic anhydride proved to be less effective than acetyl chloride. Cellulose fluorates can be synthesized with yields of 84.4% and 90.2% and with a DS range of 0.46–3.0; thus, as [Bmim]Cl is a very efficient medium for reaction, short reaction times and low amounts of acylation reagent are needed [175]. Cellulose benzoates with different moieties at the aromatic ring are prepared homogeneously in [Amim]Cl by conversion of cellulose with the corresponding benzoyl chlorides [180]. An excess of reagent of 5 mol per mol of AGU leads to completely substituted cellulose derivatives [181], such as cellulose pentanoates, cellulose hexanoates, with DS above 0.9 soluble in DMSO, and for DS of 2.3 soluble in DMSO, acetone, and chloroform (CHCl_3).

Cellulose sulfates were prepared through homogeneous conversion of cellulose with different sulfating reagents in [Bmim]Cl, [Amim]Cl, and [Emim]OAc and DMF as dipolar aprotic co-solvent [182]. The sulfation of cellulose in [Bmim]Cl proceeded in 30 min and the prolongation of the reaction time to 2 h did not change the DS values significantly. In contrast, after 24 h, the DS of the products decreased from 0.83 to 0.66, which is most likely due to acidic cleavage of the sulfate ester bond. The sulfation was investigated at 25 °C and higher temperatures. The results show that sulfation at higher temperature does not give the desired DS, indicating decomposition of polymer chain. Production of cellulose sulfates with DS up to 2.5 was patented by Procter & Gamble Company [192].

The *p*-toluenesulfonic acid esters of cellulose (cellulose tosylates) are versatile intermediates for the preparation of several cellulose derivatives. Homogeneous reaction yielding tosylated cellulose can be carried out in [Amim]Cl, and aspects such as the degree of tosylation, the reaction temperature and the base can be varied, e.g., trimethylamine is not fully mixed with [Amim]Cl, however, pyridine works efficiently [172]. The homogeneous reaction produces a predominant conversion of primary hydroxyl groups at DS values up to 1 [173,174]. However, derivatization with tosyl chloride generates additional chloride as a second reaction product, thus, chlorination of cellulose occurs due to the presence of chloride ions in the reaction media (Figure 4). Additionally, a tosylated AGU can react as well with hydroxyl groups of the same or another cellulose chain, resulting in crosslinking, and thus, insoluble products. To prevent these side reactions, the temperature is kept at 8–10 °C [174].

Preparation of cellulose carbanilates with DS up to 3.0 could be prepared in [Bmim]Cl. The synthesis of cellulose carbanilates was carried out without any catalysts. Higher DS were accessible by increasing molar ratio and reaction time. Heinze [176] and Schluffer [177] showed that bacterial cellulose with DP ~6500 could be efficiently converted with phenyl isocyanate under homogeneous reaction conditions. Heinze and co-workers have investigated the acylation of cellulose in four types of ILs with lauroyl chloride, leading to cellulose laurates with DS ranging from 0.34 to 1.54. The reaction was found to start homogeneously and then continue heterogeneously. DS values slightly increased with addition of a base such as pyridine and with shorter reaction time (2 h). Additionally, the acetates were soluble in DMSO, but not in acetone, and for DS higher than 2.85, were soluble in CHCl_3 . Schluffer compared DS of acetylated bacterial cellulose (BC) to the DS from the reaction with cellulose from plants (lower DP) and a lower reactivity was found. Highly substituted BC phenyl urethanes were soluble in DMSO, DMF, and in THF, depending on the DS.

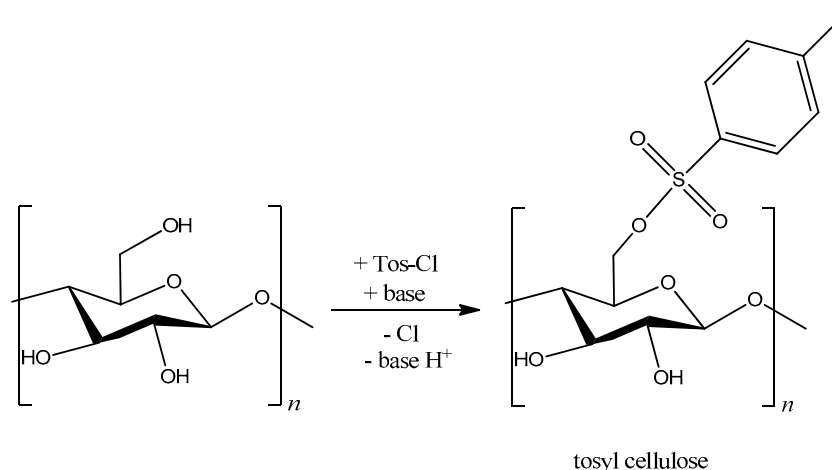


Figure 4. Tosylation of cellulose with tosyl chloride. Reprinted with permission from [174]. Copyright 2012 Elsevier.

Cellulose chloroacetates and bromoacetates were synthesized by acylation of cellulose with chloroacetyl chloride and 2-bromopropionyl bromide under mild conditions, in [Bmim]Cl and [Amim]Cl, respectively [178,179]. The cellulose acetates (macroinitiators) have been applied for subsequent preparation of methacrylate graft copolymers by atom transfer radical polymerization (ATRP).

[Bmim]Cl have been also applied as reaction media for the homogeneous preparation of dicarboxylic acid esters, such as cellulose phthalates [183] that can be prepared with DS ranging from 0.12 to 2.54. DS increases with reaction temperature from 85 to 100 °C, molar ratio of phthalic anhydride/AGU in cellulose from 2:1 to 10:1, and reaction time from 20 to 120 min. Cellulose succinates are produced by succinylation of cellulose using succinic anhydride and [Bmim]Cl (DS up to 2.18) [184], and with addition of catalysts: *N*-bromosuccinimide (DS up to 2.31) [185], 4-dimethylaminopyridine (DS up to 2.34) [186], and iodide (DS up to 1.54) [187].

Eastman Chemical Company have several patents that describe the homogeneous preparation of cellulose esters and mixed esters, and the recycling of the ILs by evaporation of precipitation agent as well as residues of the volatile acylation reagents [188–190,194]. In some of these inventions, the produced cellulose esters were used as protective and compensation films for liquid crystalline displays. A patent for chlorinating polysaccharides with DS up to 3 is also found in literature [191].

3.2. Etherification

In Millymaki and Aksela [195], there is an invention of a method for preparing cellulose ethers, where the derivatives have been divided into aliphatic cellulose ethers, comprising alkyl ethers, substituted alkyl ethers, hydroxyalkyl ethers, and mixed aliphatic ethers of cellulose. The second group comprises aryl and aralkyl ethers of cellulose, and the third group silyl ethers of cellulose. Table 5 presents some examples of etherification reactions of cellulose dissolved in different ILs.

Homogenous silylation of cellulose has been reported under mild conditions, within short reaction time at low temperature (1 h, 80 °C) and low excess of reagent [181]. Trimethylsilyl cellulose was obtained through reaction of cellulose dissolved in [Emim]OAc and [Emim]Cl, with etherifying reagent hexamethyldisilazane (HMDS). [Emim]OAc is more efficient than [Emim]Cl in this reaction. It has been reported [196] that carboxylate and diethylphosphate counter-ions give better results than chloride. Furthermore, the solubility of HMDS in the IL increases with the increasing extent of CH_x groups in the anion. Additionally, because of HMDS insolubility in the IL, trimethylsilyl cellulose precipitates, thus, the reaction starts homogeneously and ends heterogeneously. To keep it homogenous, a solvent is added (DMSO or DMAc).

Table 5. Conditions of reaction media for the homogeneous etherification of cellulose and DS of the cellulose derivatives.

IL ¹	Co-Solvent ²	Base	Cellulose (wt %) ³	Reagent	Conditions ⁴	DS ⁵	Ref.
[Emim]OAc [Emim]Cl [Emim]Cl [Bmim]Cl [Emim]OAc [Bmim]OAc [Bmim]PrO [Bmim]Cl [Amim]Cl	DMSO/DMA		10	Hexamethyldisilazane	3:1, 5:1, 8:1; 1 h; 80 °C	1.6–2.9	[181]
[Emim]OAc [Bmim]OAc [Bmim]PrO [Bmim]Cl [Amim]Cl		Py	11	Hexamethyldisilazane	1.8:1–9.2:1; 16 h, 80–120 °C	1.2–2.9	[196]
[Amim]Cl		Py	10	Trityl chloride 4-methoxytrityl chloride	1–14 h, 100 °C 3:1, 6 h, 60 °C	0.80–1.37 ~2	[197] [198]
[Amim]Cl		Py/BIM	10	Trityl chloride	3:1, 6:1; 1–20 h; 90 °C	0.02–0.95	[199]
[Emim]OAc	DMSO		4–11.5	Propylene oxide, ethylene oxide Propylene oxide, ethylene oxide,	5:1–50:1; 19 h; 80 °C	0.09–1.34	[200]
[Emim]OAc, [Bmim]Cl	H ₂ O, DMSO, DMF, DME, CHCl ₃			1-allyloxy-2,3-epoxypropane, 2,3-epoxypropyl isopropyl, etherepichlorohydrine, 2,3-epoxypropyltrimethylammonium chloride, phenylglycidylether, 2,3-epoxypropyl isopropyl ether	5:1, 10:1, 30:1; 3–72 h; 21–100 °C	0.09–2.16 ⁶	[201]

¹ [Emim]OAc: 1-Ethyl-3-methylimidazolium acetate,
[Emim]Cl: 1-Ethyl-3-methylimidazolium chloride,
[Bmim]Cl: 1-Butyl-3-methylimidazolium chloride,
[Bmim]OAc: 1-Butyl-3-methylimidazolium acetate,
[Bmim]PrO: 1-butyl-3-methylimidazolium propionate,
[Amim]Cl: 1-Allyl-3-methylimidazolium chloride;

² DMSO: Dimethylsulfoxide, DMA: Dimethylacetamide, Py: Pyridine, BIM: 1-Butylimidazole,
DMF: Dimethylformamide, DME: Dimethoxyethane, CHCl₃: Chloroform,

³ Concentration of cellulose in IL during dissolution by weight;

⁴ Molar ratio of reagent per mol of anhydroglucose unit (AGU) in cellulose; reaction time; reaction temperature;

⁵ Range of degrees of substitution (DS);

⁶ Molar substitution (MS).

Tritylation of cellulose with trityl chloride is an effective protecting group strategy for synthesizing regioselectively modified cellulose derivatives [199]. Homogeneous tritylation of cellulose in [Amim]Cl with trityl chloride (TrCl) showed that DS can be influenced by the type of base used in the reaction (pyridine or 1-butylimidazole). The reaction with pyridine started heterogeneously, then changed to homogeneous finishing heterogeneous, and produced trityl cellulose with higher DS ~1. Despite the homogeneous reaction in the presence of 1-butylimidazole (BIM), the higher DS was 0.22. BIM is not considered suitable for tritylation of cellulose in ILs.

Köhler [200] reported the homogeneous hydroxyalkylation of cellulose without additional inorganic bases under completely homogeneous reaction conditions in [Emim]OAc at 80 °C for 19 h. The reagents propylene oxide and ethylene oxide produced derivatives with a DS from 0.09 to 1.34. Addition of co-solvent (DMSO) to a higher concentrated solution of cellulose/IL changed the DS to higher value.

Patented [201] homogeneous reaction without addition of organic or inorganic bases with lower IL load prepares high DP (from 1000 to 6500) cellulose ethers. The cellulose ethers produced by this invention include 2-hydroxyethyl cellulose, 2-hydroxypropyl cellulose, 2-hydroxybutyl cellulose, 2-hydroxy-3-isopropoxy-propyl cellulose, 3-allyloxy-2-hydroxypropyl cellulose, 3-chloro-2-hydroxypropyl cellulose, (2-hydroxy-3-trimethylammoniumpropyl)-cellulose chloride, and 2-hydroxy-3-phenoxypropyl cellulose. These products are soluble in H₂O and DMSO depending on the molar substitution (MS). MS values of hydroxyalkyl celluloses were determined by the method of Zeisel. Homogeneous synthesis of cellulose ethers [201] has been patented by Tylose GmbH & Co. in ILs, such as [Bmim]Cl, [Emim]OAc, and co-solvents: DMSO, DMF, dimethoxyethane (DME), and CHCl₃.

Patents of cellulose etherification process carried out under heterogeneous reactions conditions in [Bmim]Cl or [Emim]Cl are found in literature [202,203]. In contrast to the homogeneous process, the heterogeneous etherification method requires an activation of the cellulose prior to the etherification.

The reaction mixture can progress as heterogeneous–homogeneous–heterogeneous. As an example, trimethylsilylcellulose can be produced by heterogeneous reaction of microcrystalline cellulose with [Bmim]Cl and silylating agent 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (mol reagent/molAGU up to 5.6) at high temperature (125 °C), although with low DS up to 0.9 [202].

Commercially available hydroxyalkyl celluloses are prepared heterogeneously. This process requires activation of the cellulose which is a cause for higher costs and energy consumption. Additionally, because of the solid state of cellulose and intermediates, the product quality depends on the quality of the stirring and geometry of the reaction vessel [204]. In contrast, homogeneous production of cellulose derivatives allows the development of methods for synthesis of cellulose ethers without activation of cellulose, and high yields of products with new and better properties.

4. Cellulose Precipitation

Regeneration of cellulose from IL systems occurs by contact of the cellulose solution with a coagulation bath of protic polar solvents such as water or alcohols. Cellulose regeneration mechanisms for selected solvents have been reviewed elsewhere [205]. The yield of regenerated wood and the yield of recycled IL are affected by the choice of anti-solvent. Regeneration of 8 wt % solution of wood dissolved in [Amim]Cl yielded >95% (weight percent from the original amount of wood) and practically all the IL could be recovered (under vacuum at 40 °C) using water as anti-solvent. Moreover, the yield of regenerated wood with water was reported to be higher than that of methanol at the same number of IL recycle uses (up to 3). Conventional precipitation can be achieved with anti-solvents, such as water (e.g., water concentration in IL > 20% [117]), ethanol, methanol, and acetonitrile show high yields above 90%. Precipitation with compressed CO₂ has been reported as a “greener” alternative [206]. Precipitation of cellulose dissolved in IL with acetate anion is produced by CO₂ addition because the CO₂ reacts with the acetate anion, forming another compound, a carboxylate zwitterion. With the formation of that compound, the bonds between cellulose and the acetate anion are broken, causing cellulose precipitation. The ILs can be regenerated by adding water in stoichiometric proportion, which destroys the zwitterion. The cellulose precipitated by this method presents a decrease of crystallinity and stability. At pressures between 6–18 MPa of CO₂, 60% of the cellulose dissolved in [Bmim]OAc is precipitated, resulting in relatively low yield compared to that of protic solvent. Despite the low yield, CO₂ could be a sustainable method to regenerate cellulose from ILs.

The cellulose can be regenerated in the shape of powder, fibers, or films, but these last two forms are especially interesting. The fabrication of regenerated cellulose fiber/film involves two steps: dissolution of cellulose in IL to make the spinning dope, and extrusion of the spinning dope to form regenerated cellulose fiber and film. The influence of spinning conditions on cellulose crystallization that takes place during fiber/film precipitation with water, is of great importance in fiber and film processing, and has been studied in several works.

Sun and coworkers [207] studied the crystalline characteristics of regeneration of cellulose fiber, extrudate, and film from 6% cellulose/[Bmim]Cl solution with different spinning conditions. The degree of crystallinity, crystal size, and crystallite orientation of the regenerated cellulose fiber and film, were evaluated using wide angle X-ray diffraction (WAXD).

WAXD data showed that cellulose regenerated from [Bmim]Cl solution was transformed from a cellulose I to cellulose II structure, and amorphous regions increased in the regenerated cellulose. Crystalline characteristics of regenerated cellulose are affected by the die shapes. A reduction of die diameter does not cause a significant change in fiber crystallinity, but results in an increase in crystallite size and crystal orientation factor. Additionally, fiber drawing speed was shown to be a main effect to improve fiber crystal orientation.

Airgap- and wet spinning of eucalypt dissolving grade pulp in [Emim]OAc and methylimidazole (MIM) was investigated by Olsson et al. [208]. Pure [Emim]OAc/cellulose solution was spun at 2.8 m min⁻¹ through 150 μm capillaries. For samples with co-solvent MIM, an 80 μm holes spinneret was used due to lower viscosity. Coagulation took place in water, and fibers were drawn by rotating

take-off rollers to desired extent. The fibers were then immersed in pure water for 1 week before drying at 105 °C for 1 h. The crystallinity of the fiber using only [Emim]OAc as solvent is lower than in fibers produced with co-solvent. However, fibers with higher tenacity cannot be achieved with high amount of co-solvent i.e., $x_{IL} = 0.5$ in 15% pulp solutions.

Michud and coworkers [209] produced regenerated cellulose fibers by dry-jet spinning from cellulose/[DBNH]OAc solutions to study the influence of cellulose molecular structure on the spinnability and the mechanical properties of the resulting fibers. The solutions were extruded through a multi-hole spinneret (36 holes, diameter of 100 μm , and capillary length of 20 μm) via 1 cm air gap into a cold (10–15 °C) aqueous coagulation bath at a constant extrusion velocity of 16 cm^3/min . High spinnability with high stretching was found for a proportion of cellulose chain having DP > 2000 larger than 20 wt % and DP < 100 between 5 and 10 wt %. The final properties of the fibers are directly affected by the draw of the fluid filaments in the air gap.

The effect of altering the coagulation medium during regeneration of cellulose dissolved in [Emim]OAc was also studied [210]. Cellulose solutions (4 wt %) were coagulated in water, ethanol, and 1-propanol. For films coagulated in water, a higher degree of cellulose II was found, compared to the films coagulated in alcohols. The decreased preference of [Emim]OAc to diffuse into the coagulation bath could explain the lower conversion to cellulose II in alcohols.

Diffusion of [Bmim]Cl from cellulose filament during coagulation process was studied [211], and the factors affecting it: polymer concentration, concentration, and temperature of the coagulation bath. The diffusion rate of [Bmim]Cl decreased with increasing polymer content (5, 8, 10, and 12 wt %) in the spinning solution, and the initial concentration of [Bmim]Cl in the coagulation bath (0–20 wt %), while the diffusion coefficients increased largely with the coagulation temperature becoming higher (5–70 °C).

5. Recycling of ILs after Cellulose Processing

In general, synthesis of ILs is a polluting and energy intensive process that frequently involves the use of halide and/or sulfur intermediates, conventional organic solvents, or the use of metal oxide catalysts. Chlorinated organic compounds are undesired, due to the difficulties and safety issues in their disposal. For environmental and economic issues, it is important to recover and recycle ILs after the regeneration or derivatization of cellulose [212]. If these solvents are efficiently recycled, the overall waste production of the process will be decreased.

Methods used for recovery and recycling of ILs such as distillation, extraction, adsorption, induced phase separation, and membrane-based methods, were thoroughly reviewed elsewhere [213]. Thus, only a few considerations about this point will be treated here.

In cellulose processing, the most frequent impurities in ILs at the end of the process are heavy impurities due to the decomposition or incomplete precipitation of cellulose, and volatile impurities such as water or alcohols used to cause cellulose precipitation. Due to the negligible vapor pressure of ILs, volatile impurities can be removed from the IL mixture by evaporation without loss of the ILs. Nevertheless, this process can be energy intensive. Traditional methods like evaporation and extraction were applied to remove the impurities from [Emim]OAc, which had been previously used as medium for cellulose acetylation [214]. Impurities like ethyl acetate, *n*-propyl acetate, isopropyl acetate, and THF could be reduced from 40 wt % to 5 wt % within less than 1 h using these methods. However, acetic acid was found not to be easily removed from [Emim]OAc or [Emim]Cl by evaporation, and a residual level of about 20% and 8% was respectively achieved, due to the high normal boiling point of acetic acid (118 °C). Liquid–liquid extraction for acetic acid removal was also unsuccessful due to the slow mass transfer, despite the extraction ability for acetic acid of the tested solvents. Esterification of acetic acid with alcohol in large excess at elevated temperature and pressure with subsequent distillation was found to be the best method to purify [Emim]OAc. Molecular distillation was used to recover [Amim]Cl used in homogeneous cellulose acetylation [215]. The IL was recovered with a combination of two techniques: conventional vacuum, to remove most of the water, and then the small amounts of acetic acid and water (less than 10% by mass) that are difficult to remove were disposed

through molecular distillation. The IL was recycled and reused five times in the reaction, and the purity of recycled IL (for the fifth time) was as high as 99.56%.

In theory, ILs can be reused, but after many cycles, heavy impurities can accumulate, or degradation can be suffered by the ILs. Moreover, in the derivatization processes, the use of organic or inorganic bases and the addition of stabilizers results in degradation of the biopolymer, and exhibits an enormous drawback for IL recycling and its repeated application [190]. An object of further investigation in cellulose processing is to develop a simple process for the preparation of cellulose derivatives which does not require the addition of any organic and/or inorganic bases, and which reduces the salt load and where the IL can be easily recycled and reused after purification.

6. Conclusions

Several aspects of cellulose processing in ILs have been reviewed. Cellulose has strong inter- and intramolecular hydrogen bonds, which limits the efficient application of this bio-polymer. Progress has been made on understanding the mechanism of cellulose dissolution in ILs, however, many details remain unknown. The advantages and disadvantages of using ILs in cellulose derivatization were discussed for esterification and etherification of cellulose. Key problems, such as the high cost of ILs and high viscosity of the reaction mixture, have been delaying their use in industrial cellulose processing. The chemicals (solvents and/or catalysts) employed should be carefully assessed regarding their biodegradability. Moreover, sustainability of cellulose processing with ILs could be given priority using effective recyclability and reuse of ILs, which is required for industrial implementation.

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Abbreviations

[Amim]Cl	1-Allyl-3-methylimidazolium chloride
[Bmim]BF ₄	1-Butyl-3-methylimidazolium tetrafluoroborate
[Emim]HCO ₂	1-Ethyl-3-methylimidazolium formate
[Bmim]PF ₆	1-Butyl-3-methylimidazolium hexafluorophosphate
[Prmim]HCO ₂	1-Propyl-3-methylimidazolium formate
[Emim]MeOSO ₃	1-ethyl-3-methylimidazolium methylsulfate
[Amim]HCO ₂	1-Allyl-3-methylimidazolium formate
[Emim]MeSO ₃	1-Ethyl-3-methylimidazolium methanesulfonate
[Bmim]OAc	1-Butyl-3-methylimidazolium acetate
[Emim]CF ₃ CO ₂	1-Ethyl-3-methylimidazolium trifluoroacetate
[Bmim]Cl	1-Butyl-3-methylimidazolium chloride
[Emim]SCN	1-Ethyl-3-methylimidazolium thiocyanate
[Bmim]HCO ₂	1-Butyl-3-methylimidazolium formate
[Emim]BF ₄	1-Ethyl-3-methylimidazolium tetrafluoroborate
[Emim](MeO) ₂ PO ₂	1-Ethyl-3-methylimidazolium dimethylphosphate
[Emim]N(CN) ₂	1-Ethyl-3-methylimidazolium dicyanamide
[Emim](MeO)HPO ₂	1-Ethyl-3-methylimidazolium methylphosphonate
[Emim]I	1-Ethyl-3-methylimidazolium iodide

[Emim](MeO)MePO ₂	1-Ethyl-3-methylimidazolium methyl methylphosphonate
[Emim]PF ₆	1-Ethyl-3-methylimidazolium hexafluorophosphate
[Emim](EtO) ₂ PO ₂	1-Ethyl-3-methylimidazolium diethylphosphate
[Bmim]CH ₃ SO ₃	1-Butyl-3-methylimidazolium methanesulfonate
[Emim]Cl	1-Ethyl-3-methylimidazolium chloride
[Bmim]Br	1-Butyl-3-methylimidazolium bromide
[Emim]H ₂ PO ₂	1-Ethyl-3-methylimidazolium dihydrogenphosphate
[Amim](MeO)HPO ₂	1-Allyl-3-methylimidazolium methylphosphonate
[Prmim](MeO)HPO ₂	1-Propyl-3-methylimidazolium methylphosphonate
[Bmim](MeO)HPO ₂	1-Butyl-3-methylimidazolium methylphosphonate
[Emim]OAc	1-Ethyl-3-methylimidazolium acetate
ECOENG 41M	1-Butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethylsulfate
[Emim]CH ₃ SO ₃	1-Ethyl-3-methylimidazolium methanesulfonate
[Emim]CF ₃ SO ₃	1-Ethyl-3-methylimidazolium: trifluoromethanesulfonate
[Emim]Tos	1-Ethyl-3-methylimidazolium tosylate
[Emim]EtSO ₄	1-Ethyl-3-methylimidazolium ethylsulfate
[Empy]EtSO ₄	1-Ethyl-3-methylpyridinium ethylsulfate
[Epy]EtSO ₄	1-Ethylpyridinium ethylsulfate
[EEpy]EtSO ₄	1,2-Diethylpyridinium ethylsulfate
[Mpy]CH ₃ SO ₄	1-methylpyridinium methylsulfate
[MMpy]CH ₃ SO ₄	1,3-Dimethylpyridinium methylsulfate
[EMpy]CH ₃ SO ₄	2-ethyl-1-methylpyridinium methylsulfate
[Bmpyr]OAc	1-Butyl-1-methylpyrrolidinium acetate
[Bmpyr]CF ₃ SO ₃	1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate
[Bmpyr](BtO)HPO ₂	1-Butyl-1-methylpyrrolidinium butylphosphonate
[Empyr](EtO)HPO ₂	1-Ethyl-1-methylpyrrolidinium ethylphosphonate
[DBNH]OAc	1,5-diaza-bicyclo[4.3.0]non-5-enium acetate
[Emim]DEP	1-Ethyl-3-methylimidazolium diethylphosphate
[Bdmim]Cl	1-Butyl-2,3-methylimidazolium chloride
[Admim]Br	1-Allyl-2,3-methylimidazolium bromide
[Bmim]OPr	1-butyl-3-methylimidazolium propionate

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