

Chlorine-free alternatives to the synthesis of ionic liquids for biomass processing*

Gabriela Gurau¹, Hui Wang¹, Yun Qiao², Xingmei Lu²,
Suojiang Zhang², and Robin D. Rogers^{1,2,‡}

¹*Department of Chemistry and Center for Green Manufacturing, The University of Alabama, Tuscaloosa, AL 35487, USA;* ²*Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China*

Abstract: Ionic liquids (ILs) are desirable for use in a large number of applications because of their unique properties; however, compositions comprising only a single IL are expensive to synthesize and difficult to purify, and the widely used chloride-based ILs can be toxic and corrosive. Therefore, there is a need for new IL compositions that minimize common disadvantages encountered with single IL composition and synthetic methods which avoid halide intermediates. In this study, IL mixtures, which are chloride-free, were synthesized by a one-pot process, and the mixtures were used to dissolve biopolymers. The synthesized IL mixtures show high capability to dissolve the two exemplary biopolymers, cellulose and chitin.

Keywords: cellulose; chitin; dissolution; halide-free synthesis; ionic liquids; one-pot synthesis.

INTRODUCTION

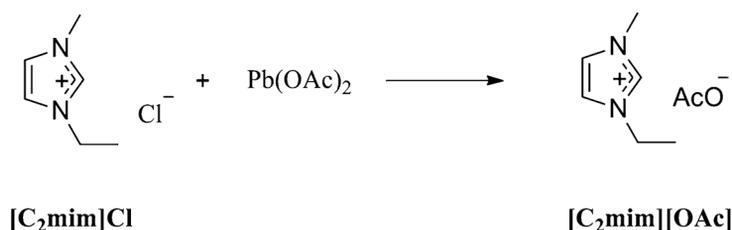
Biomass, as a renewable energy source, is now considered to be increasingly important owing to the worldwide emphasis on sustainable development and sharp increase in the demand for fuels and chemicals [1]. Ionic liquids (ILs, salts that melt below 100 °C) have attracted much interest in biomass processing [2]. This field emerged in 2002, when Swatloski et al. reported that imidazolium-based ILs can dissolve cellulose without degrading it, and 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) was shown to have the best dissolution ability [3]. Since then, studies on the application of ILs in the biomass field have made great progress, and it was found that ILs were able to dissolve many other kinds of biopolymers, including lignin [4,5], hemicellulose [6], chitin [7–9], silk fibroin [10], wool keratin [11], and even raw biomass materials, such as lignocellulosic biomass [12–15], and shrimp shells [9].

The first studies on the processing of biopolymers using ILs mainly centered on the chloride-based ILs. However, with the development of research on ILs, it was recognized that the chloride-based ILs can be toxic and corrosive [16,17], for example, the median lethal dose (LD₅₀) of [C₄mim]Cl was found to be in the range from 50 to 300 mg kg⁻¹ [18]. Later, the less toxic and corrosive acetate-based ILs, such as 1-ethyl-3-methylimidazolium acetate ([C₂mim][OAc]), were shown to have a much higher capability to dissolve cellulose [19], as well as very low melting points and viscosity [20].

Pure Appl. Chem.* **84, 411–860 (2012). A collection of invited papers for the IUPAC project 2008-016-1-300 “Chlorine-free Synthesis for Green Chemistry”.

‡Corresponding author: E-mail: rdrogers@as.ua.edu

Synthesis of the acetate ILs was initially based on metathesis of a chloride salt. Indeed, many new ILs were and still are synthesized by starting with a chloride salt [21,22]. For example, the acetate-based ILs have been synthesized from the corresponding chloride (or bromide)-based ILs and metal acetic acid salts, such as lead acetate or silver acetate [23], as shown in Scheme 1 for the synthesis of $[\text{C}_2\text{mim}][\text{OAc}]$.



Scheme 1 Synthesis of $[\text{C}_2\text{mim}][\text{OAc}]$.

Here, $[\text{C}_2\text{mim}]\text{Cl}$ was first prepared through the reaction of 1-methylimidazole with chloroethane and then $\text{Pb}(\text{OAc})_2$ was added into an aqueous solution of the $[\text{C}_2\text{mim}]\text{Cl}$. PbCl_2 produced in this process was separated from the IL solution by filtration. The whole synthetic process is quite complex, and impurities (e.g., starting materials and the residual organic solvents used for the synthesis) were still present in the IL, even after multiple purification steps [24].

In the synthesis of $[\text{C}_2\text{mim}][\text{OAc}]$ shown in Scheme 1, the impurities can include 1-methylimidazole, Cl^- , chloroethane, $\text{Pb}(\text{OAc})_2$, PbCl_2 , and water. The presence of impurities will influence the properties of ILs and their reactivity [25,26], for instance, deactivation of some catalysts can occur when chloride is present [27]. Different methods, including distillation under vacuum [28], extraction using organic solvents [29], use of sorbents [30,31], use of supercritical CO_2 [32], and zone melting [33] have been developed to purify ILs, however, our own experience shows that it is difficult to completely remove all the impurities from the ILs. In addition, the separation process will require a large volume of reagents and high energy consumption. Another issue addressed by the manufacturers of large-scale quantities of $[\text{C}_2\text{mim}][\text{OAc}]$ is the quality of the materials used in building the synthesis reactor: specific materials are required for the synthesis employing $[\text{C}_2\text{mim}]\text{Cl}$ as the intermediate, as the chloride-based ILs are reported to be corrosive, especially when water is present [34,35].

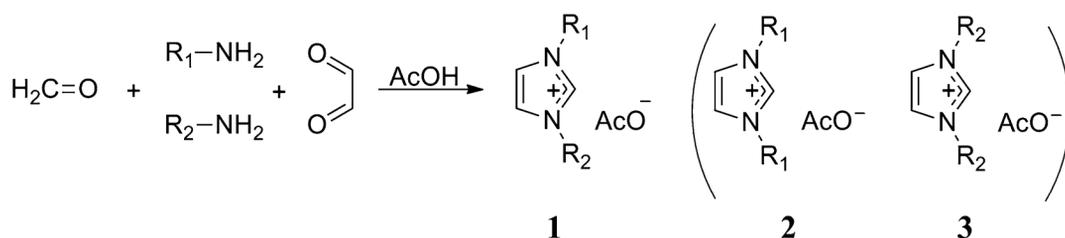
Another typical method for synthesizing ILs was reported by Bridges et al. [36] and Kalb et al. (the CBILS[®] route) [37]. In this process, the hydrocarbonate precursor ($[\text{Q}^+][\text{Y}^{n-}]$) containing the desired quaternary ammonium, phosphonium, or the analogous quaternary heteroaromatic cation, is treated with a Brønsted acid, resulting in the hydrocarbonate anion being given off as gaseous CO_2 and H_2O , and replaced by the desired anion. Although high-purity ILs can be synthesized via the CBILS route, there are some drawbacks that need to be considered; for example, water, as a byproduct, still needs to be removed, demanding more energy usage and thus leading to a more expensive process.

Ideally, the synthesis of ILs should involve a one step-process and neat conditions, thus minimizing the production cost. The one-pot synthesis of 1,3-disubstituted imidazolium salts [38–40] involves an α -dicarbonyl compound, an aldehyde, an alkylamine, and an acid as source of the anion (e.g., HCl , H_2SO_4 , H_3PO_4 for hydrophilic salts, or HPF_6 , HAsF_6 , CF_3COOH , $\text{CF}_3\text{SO}_3\text{H}$ for hydrophobic salts). While the symmetrically disubstituted imidazolium salts are obtained in fairly good yields, attempts to synthesize asymmetrically distributed salts produce a mixture of both symmetrically and asymmetrically imidazolium salts. Here we report the synthesis of ILs and IL mixtures using these one-pot synthetic methods to demonstrate both the methods eliminating halide and metathesis steps, and the utility of the IL mixtures themselves for low-cost biomass processing.

RESULTS AND DISCUSSION

The ILs 1,3-diethylimidazolium acetate ($[\text{C}_2\text{C}_2\text{im}][\text{OAc}]$), and 1,3-dimethylimidazolium acetate ($[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$) and the statistical mixtures 2:1:1 $[\text{C}_2\text{mim}]:[\text{C}_2\text{C}_2\text{im}]:[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$ and 2:1:1 $[\text{C}_4\text{mim}]:[\text{C}_4\text{C}_4\text{im}]:[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$, were synthesized using a one-pot synthetic process, where the ILs were prepared in situ from appropriate starting materials and in the desired ratio [38–41]. By simply mixing aqueous formaldehyde with an alkyl amine (e.g., methylamine, ethylamine, *n*-butylamine), an acid, and aqueous glyoxal solution, the hydrophilic ILs or mixtures were formed. The choice of the amine and the amount needed depend on the desired final product. For example, for the synthesis of $[\text{C}_2\text{C}_2\text{im}][\text{OAc}]$, 2 equiv of ethylamine was used, whereas in the case of 2:1:1 $[\text{C}_2\text{mim}]:[\text{C}_2\text{C}_2\text{im}]:[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$ mixture, 1 equiv of each, ethylamine and methylamine, was used.

The synthetic scheme for the imidazolium-based acetate ILs is illustrated in Scheme 2, and the ILs synthesized are shown in Fig. 1.



Scheme 2 One-pot synthesis of symmetrical 1,3-dialkylimidazolium acetate (**1**, $\text{R}_1 = \text{R}_2$) and statistical mixture of 1-alkyl-3-methyl-, 1,3-dialkyl-, 1,3-dimethylimidazolium acetates (**1 + 2 + 3**, $\text{R}_1 = \text{methyl}$, $\text{R}_1 \neq \text{R}_2$).

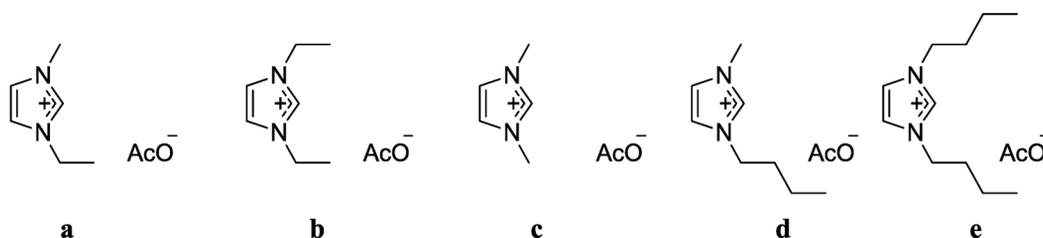


Fig. 1 IL structures: $[\text{C}_2\text{mim}][\text{OAc}]$ (a), $[\text{C}_2\text{C}_2\text{im}][\text{OAc}]$ (b), $[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$ (c), $[\text{C}_4\text{mim}][\text{OAc}]$ (d), and $[\text{C}_4\text{C}_4\text{im}][\text{OAc}]$ (e).

To achieve completion, the process requires about 24 h and temperatures around 70–75 °C, yielding a dark brown mixture, which is extracted several times with ethyl acetate in order to remove any unreacted starting materials. Water removal and drying (70–80 °C, 12–24 h, high vacuum) afford the desired product(s) in good yields (80–96 %, Table 1) and high purity (>97 %, determined by ^1H NMR spectroscopy). While NMR spectroscopy is a useful tool in confirming the product(s) structure(s), it is still a qualitative method, and has a limit of impurity detection of <3 mol %. For ultra-high-purity ILs, other methods for purity determination should be considered (e.g., UV–vis, HPLC). The product(s) can be further purified if needed, either by flash chromatography through a charcoal column [1], or by refluxing over charcoal in an appropriate solvent (miscible with the IL), followed by filtration through Celite®. Although mass loss is observed after charcoal purification (Table 1), this step is not necessary unless high-purity ILs are desired. Furthermore, to diminish or eliminate the formation of colored impurities, the reaction can be run at room temperature with an increased reaction time from 24 to 50 h.

Table 1 Yields of pure ILs and their mixtures obtained via the one-pot method before and after charcoal purification.

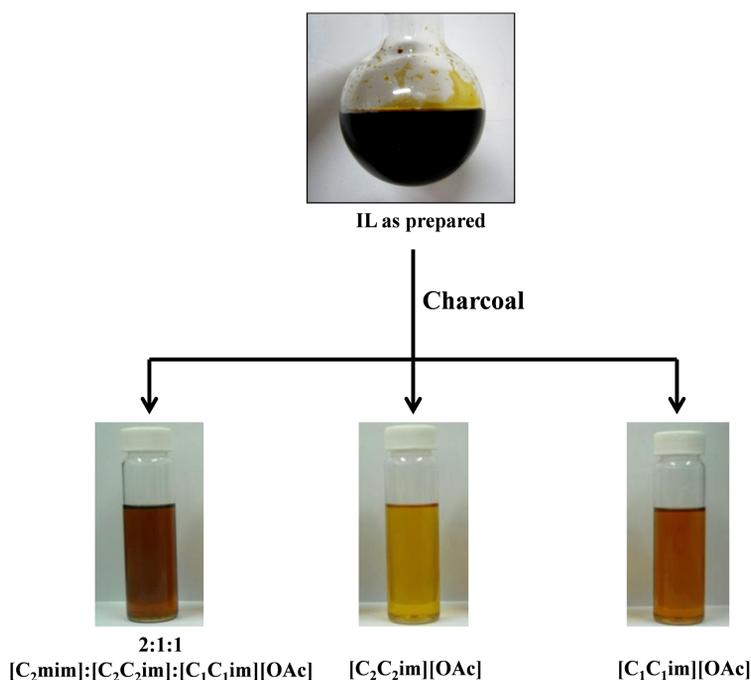
IL	Yield before purification (%)	Yield after purification (%)
[C ₁ C ₁ im][OAc]	96	nd ^a
[C ₂ C ₂ im][OAc]	89	82
2:1:1 [C ₂ mim]:[C ₂ C ₂ im]:[C ₁ C ₁ im][OAc]	87	70
2:1:1 [C ₄ mim]:[C ₄ C ₄ im]:[C ₁ C ₁ im][OAc]	80	68

^and: not determined.

Purification of ionic liquids

The dark color of the ILs prepared via the one-pot process can be attributed to the impurities present in the reaction media, mainly unreacted starting materials which will degrade or polymerize during the entire process. The colored impurities can be removed by running the ILs through a decolorizing charcoal column prior to use, as described in the literature [42]. (Caution: It should be pointed out that charcoal was reported to contaminate 1-butyl-3-methylimidazolium iodide with iodine species during the purification process using activated charcoal [43], however, we have not detected such impurities in our preparations.)

Pictures of the ILs before and after purification are illustrated in Fig. 2. To obtain a colorless IL, the crude solution needs to be passed several times through the charcoal column. Although the purification step might not seem feasible on a large-scale process, the purification process is needed only for

**Fig. 2** Pictures of the ILs before and after one elution through the charcoal column.

the synthesis of high-purity ILs used for high-end applications. Our experiments detailed below showed that the elimination of colored impurities had no effect on the use of these ILs for dissolution of biopolymers.

Properties of the IL statistical mixtures

Thermal characterization

An increase in the thermal stability of IL statistical mixtures has been observed as shown in Table 2. The onset decomposition temperatures ($T_{5\% \text{ onset}}$) of the IL mixtures are higher than the single ILs, 220 °C for the [C₂mim]:[C₂C₂im]:[C₁C₁im][OAc] statistical mixture vs. 150 °C for [C₂mim][OAc], 204 °C for [C₂C₂im][OAc], and 203 °C for [C₁C₁im][OAc]. The IL [C₄mim][OAc] has a $T_{5\% \text{ onset}}$ of 192 vs. 215 °C for the [C₄mim]:[C₄C₄im]:[C₁C₁im][OAc] statistical mixture. In addition, no melting points have been observed for the 2:1:1 statistical mixtures, whereas the individual ILs have measurable melting points (≤ -20 °C for [C₂mim][OAc] and [C₄mim][OAc], and 30 °C for [C₂C₂im][OAc]).

Table 2 $T_{5\% \text{ onset}}$ of pure ILs and their mixtures obtained via the one-pot method.

Ionic liquid	$T_{5\% \text{ onset}}$ (°C) ^a
[C ₂ mim][OAc] ^b	150
[C ₂ C ₂ im][OAc]	204
[C ₁ C ₁ im][OAc]	203
2:1:1	
[C ₂ mim]:[C ₂ C ₂ im]: [C ₁ C ₁ im][OAc]	220
[C ₄ mim][OAc] ^c	192
2:1:1	
[C ₄ mim]:[C ₄ C ₄ im]: [C ₁ C ₁ im][OAc]	215

^a $T_{5\% \text{ onset}}$ = onset temperature for 5 % decomposition.

^bPurchased from Iolitec GmbH.

^cData taken from IL Thermo Database.

Ionic conductivity

The IL mixtures have higher room temperature conductivity compared to the individual ILs (Table 3). For example, it was found that 2:1:1 [C₂mim]:[C₂C₂im]:[C₁C₁im][OAc] statistical mixture exhibits higher ionic conductivity than [C₂mim][OAc] itself. The [C₂mim][OAc] salt has a room temperature conductivity of 2.36 mS/cm, while that of the 2:1:1 mixture of [C₂mim]:[C₂C₂im]:[C₁C₁im][OAc] is 2.70 mS/cm (Table 3). It is known that higher ionic conductivities allow an electrochemical power source to deliver more power, in addition to enabling low-temperature applications.

Table 3 Conductivities of pure ILs and their mixtures obtained via the one-pot method.

Ionic liquid	Conductivity at RT (mS/cm)
[C ₂ mim][OAc] ^a	2.36
2:1:1 [C ₂ mim]:[C ₂ C ₂ im]:[C ₁ C ₁ im][OAc]	2.70
[C ₄ mim][OAc] ^b	1.10
2:1:1 [C ₄ mim]:[C ₄ C ₄ im]:[C ₁ C ₁ im][OAc]	2.88

^aPurchased from Iolitec GmbH.^bData from ref. [44].

Dissolution of biopolymers in the ionic liquid mixtures

Microcrystalline cellulose (MCC, Avicel PH-101) or practical-grade chitin was placed in the synthesized IL mixtures in a glass vial, and the resulting mixtures were stirred at room temperature or heated by oil bath to 100 °C until complete dissolution was observed and a clear solution was obtained as described in our previous publications [3,45]. It is common to find solubility data in the literature reported as weight percent (wt %). However, this term is often misused, and in reality is a mass ratio (g cellulose per g of IL) represented in percent. During our investigation of the role played by the IL ions in the dissolution process, we found that using g of cellulose per mol of IL instead of wt % is more beneficial in understanding the dissolution ability of the ILs.

Cellulose could be readily dissolved in the two IL mixtures even at room temperature. The solubility of cellulose in the 2:1:1 mixture of [C₂mim]:[C₂C₂im]:[C₁C₁im][OAc] reached 183.2 g/mol IL when heated to 100 °C, while the solubility in the 2:1:1 mixture of [C₄mim]:[C₄C₄im]:[C₁C₁im][OAc] was 132.3 g/mol IL, much higher than the solubility reported for [C₂mim][OAc] (30.1 g/mol IL) or [C₄mim][OAc] (27 g/mol IL) alone (Table 4). Although one might be inclined to correlate the IL mixture efficiency to the number of anions present, the same number of moles of OAc⁻ anions are present in 100 g of the mixture as are in 100 g of [C₂mim][OAc]. We believe that the lower viscosity of the IL mixtures (when compared to the pure IL), combined with the basicity of the anions, are responsible for the enhanced dissolution of biopolymers in the IL mixtures, and we will study this in future investigations.

Table 4 Dissolution of cellulose and chitin in ILs and IL mixtures.

ILs	MCC (Avicel PH-101)			
	Solubility (wt %)		Solubility (g/mol IL)	
	RT ^a	100 °C	RT ^a	100 °C
[C ₂ mim][OAc]	–	15 ^b	–	30.1
2:1:1 [C ₂ mim]:[C ₂ C ₂ im]:[C ₁ C ₁ im][OAc]	5	35	17.9	183.2
[C ₄ mim][OAc]	–	12 ^c	–	27
2:1:1 [C ₄ mim]:[C ₄ C ₄ im]:[C ₁ C ₁ im][OAc]	5	25	20.8	132.3

^aRoom temperature.^bData from ref. [46] (solubility reported at 110 °C).^cData from ref. [47].

Given the very high solubilities of cellulose in the statistical mixtures, it is not surprising that chitin will also readily dissolve in these IL mixtures. Practical-grade chitin was added portion-wise to the one-pot 2:1:1 mixture of [C₂mim]:[C₂C₂im]:[C₁C₁im][OAc]. A total of 0.032 g chitin could be completely dissolved in 2.0 g IL mixture after microwave heating (40 × 3 s pulses; 2 min total) as suggested in a prior publication [45]. [CAUTION: Care must be taken when using microwave heating

because ILs are efficient microwave absorbers and heating occurs rapidly, which can easily lead to degradation of the ILs, cellulose, and chitin, or even explosions of sealed systems.] The chitin solubility in the mixture is 5.4 g/mol IL, twice its solubility in commercially available [C₂mim][OAc] (2.6 g/mol IL) [45]. These results further confirmed that the IL mixtures containing the acetate anion are quite efficient in dissolving biopolymers, as well as easier and cheaper to synthesize.

CONCLUSIONS

Single acetate ILs and IL mixtures, free of chloride, were prepared via a one-pot synthetic process. This synthetic method overcomes the disadvantages of the routine preparation of ILs, such as use of chloride reagents, expensive to synthesize, difficulty in purification, and corrosivity to the reactor. Moreover, the IL mixtures, even unpurified, exhibit improved properties compared with the corresponding single ILs and even have higher dissolution ability for biopolymers, such as cellulose and chitin. By using aqueous, readily available, inexpensive raw materials, and therefore reducing or even eliminating the use of organic solvents, this one-pot process has potential environmental benefits and cost advantages over current technologies.

EXPERIMENTAL

Materials

Microcrystalline cellulose (Avicel PH-101) and practical-grade chitin were purchased from Sigma Aldrich and dried overnight in an oven (80 °C) prior to use. The IL 1-ethyl-3-methylimidazolium acetate was purchased from Iolitec GmbH with a nominal purity higher than 95 %, or synthesized using the CBILS route [48] and dried prior to use, under high vacuum (ca. 0.5 mbar) at ca. 60 °C, for at least 24 h.

Synthesis of 2:1:1 statistical mixture of [C₂mim]:[C₂C₂im]:[C₁C₁im][OAc]

Aqueous formaldehyde (37 %) (49.8 mL, 0.6 mol) was cooled in a 500-mL round-bottom flask in an ice-salt bath. Aqueous ethylamine (70 %) (57.7 mL, 0.6 mol) was added dropwise. The mixture was stirred for 30 min, followed by the addition of aqueous methylamine (40 %) (53.5 mL, 0.6 mol), while maintaining the temperature below 5 °C. Glacial acetic acid (99–100 %) (38.1 mL, 0.6 mol) was added in small portions while keeping the reaction temperature below 0 °C. After the addition was complete, aqueous glyoxal (40 %) (76.1 mL, 0.6 mol) was added dropwise and the resulting mixture was allowed to reach room temperature and stirred for 36 h. The mixture was extracted with ethyl acetate to remove any unreacted starting materials, and the water was removed under reduced pressure, yielding a light orange solution, which was purified as described in the literature [42]. After purification, 80 g (70 % yield) of a faint yellow liquid was obtained (98 % purity by NMR). The ¹H and ¹³C NMR confirmed the presence of a 2:1:1 mixture of 1-ethyl-3-methylimidazolium acetate, 1,3-diethylimidazolium acetate, and 1,3-dimethylimidazolium acetate. The reaction time can be reduced by increasing the temperature of the process, even though this will yield a darker mixture which will require successive purification. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 10.11 (s, 0.5H), 10.02 (s, 1H), 9.91 (s, 0.5H), 7.91–7.78 (m, 4H), 4.24 (q, *J* = 7.31 Hz, 2H), 4.23 (q, *J* = 7.31 Hz, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 1.58 (s, 6H), 1.43 (t, *J* = 7.31 Hz, 3H), 1.42 (t, *J* = 7.31 Hz, 3H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 174.2, 138.3, 137.6, 136.8, 123.9, 123.7, 122.4, 122.3, 44.4, 44.3, 35.9, 35.8, 26.1, 15.6, 15.5; *T*_{5% onset} = 220 °C; water content (Karl Fisher titration): 0.15 %.

Synthesis of 2:1:1 statistical mixture of [C₄mim]:[C₄C₄im]:[C₁C₁im][OAc]

Aqueous formaldehyde (37 %) (25 mL, 0.3 mol) was cooled in a 250-mL round-bottom flask in an ice-salt bath. Butylamine (99.5 %) (33.2 mL, 0.3 mol) was added dropwise. The mixture was heated to 70 °C, stirred for 15 min, and then cooled to 5 °C. Aqueous methylamine (40 %) (28 mL, 0.3 mol) was then added in small portions, while maintaining the temperature between 0–5 °C. After the addition was complete, the mixture was stirred for 1 h at 70 °C, and then cooled to 5 °C by means of an ice bath. Glacial acetic acid (99–100 %) (19.1 mL, 0.3 mol) was added dropwise while keeping the reaction temperature below 10 °C. The mixture was heated for additional 10 min, and after it was cooled to 5 °C, aqueous glyoxal (40 %) (38.0 mL, 0.3 mol) was added dropwise and the resulting mixture was heated at 75 °C for 12 h. The crude mixture was extracted with ethyl acetate to remove any unreacted starting materials, and the water was removed under reduced pressure yielding a dark brown solution, which was purified as described in the literature [42]. After purification, 45 g (68 % yield) of a light orange liquid was obtained (97 % purity by NMR). The ¹H and ¹³C NMR confirmed the presence of a 2:1:1 mixture of 1-butyl-3-methylimidazolium acetate, 1,3-dibutylimidazolium acetate, and 1,3-dimethylimidazolium acetate. The reaction can be optimized by working at low temperature, thus reducing the purification costs. ¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm) = 9.92 (s, 0.5H), 9.81 (s, 1H), 9.71 (s, 0.5H), 7.87 (d, *J* = 1.5 Hz, 1H), 7.84 (t, *J* = 1.79 Hz, 1H), 7.77 (t, *J* = 1.79 Hz, 1H), 7.74 (d, *J* = 1.5 Hz, 1H), 4.19 (t, *J* = 7.06 Hz, 2H), 4.18 (t, *J* = 7.15 Hz, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 1.76 (quintet, *J* = 7.35 Hz, 2H), 1.75 (quintet, *J* = 7.48 Hz, 2H), 1.62 (s, 6H) 1.23 (sext, *J* = 7.53 Hz, 2H), 1.22 (sext, *J* = 7.49 Hz, 2H), 0.87 (t, *J* = 7.34 Hz, 6H); *T*_{5% onset} = 215 °C; water content (Karl Fisher titration): 0.23 %.

Synthesis of 1,3-diethylimidazolium acetate

Aqueous formaldehyde (37 %) (99.6 mL, 1.33 mol) was cooled in a 500-mL round-bottom flask in an ice-salt bath. Aqueous ethylamine (70 %) (107.7 mL, 1.33 mol) was added dropwise. The mixture was stirred for 30 min, followed by the addition of aqueous ethylamine (70 %) (107.7 mL, 1.33 mol), while maintaining the temperature below 5 °C. Glacial acetic acid (99–100 %) (76.3 mL, 1.33 mol) was added in small portions while keeping the reaction temperature below 0 °C. After the addition was complete, aqueous glyoxal (40 %) (152.1 mL, 1.33 mol) was added dropwise and the resulting mixture was allowed to reach room temperature and stirred for 1.5 days. The mixture was extracted with ethyl acetate (3 times) to remove any unreacted starting materials, and the water was removed under reduced pressure, yielding a light orange solution which was purified as described in the literature [42]. After purification, 202 g (82 % yield) of a faint yellow liquid was obtained (98 % purity by ¹H NMR). The ¹H NMR and ¹³C NMR confirmed the formation of the desired imidazolium salt. The reaction time can be reduced by increasing the temperature of the process, even though this will yield a darker mixture which will require successive purification. ¹H NMR (500 MHz, DMSO-*d*₆) δ (ppm) = 9.91 (s, 1H), 7.87 (d, *J* = 1.5 Hz, 2H), 4.23 (q, *J* = 7.31 Hz, 4H), 1.63 (s, 3H), 1.42 (t, *J* = 7.31 Hz, 6H). ¹³C NMR (75 MHz, DMSO-*d*₆) δ (ppm) = 171.0, 137.2, 122.6, 44.5, 25.3, 15.7; *T*_{5% onset} = 204 °C; water content (thermogravimetric analysis): 0.70 %.

Synthesis of 1,3-dimethylimidazolium acetate

Aqueous formaldehyde (38.5 %) (24.5 mL, 0.40 mol) was cooled in a 250-mL round-bottom flask in an ice-salt bath. Aqueous methylamine (27.5 %) (78.0 mL, 0.89 mol) was added dropwise. The mixture was stirred with heating (70 °C) for 30 min. Glacial acetic acid (99.5 %) (25 mL, 0.51 mol) was added in small portions while keeping the reaction temperature below 0 °C. After the addition was complete, aqueous glyoxal (40 %) (36 mL, 0.40 mol) was added dropwise and the resulting mixture was heated at 70 °C for 10 h. The mixture was extracted with ethyl acetate (3 × 75 mL) to remove any unreacted starting materials, and the water was removed under reduced pressure, yielding a light orange

solution which was purified as described in the literature [42]. After purification, a faint yellow liquid was obtained (98 % purity by ^1H NMR). The ^1H NMR and ^{13}C NMR confirmed the formation of the desired imidazolium salt. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ (ppm) = 9.64(s, 1H), 7.80(d, 2H), 3.92(s, 6H, CH_3), 1.75(s, 3H, CH_3). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$) δ (ppm) = 174.3, 138.1, 123.9, 36.0, 24.4; $T_{5\% \text{ onset}} = 204$ °C; water content (thermogravimetric analysis): 3.05 %.

Dissolution of cellulose in 2:1:1 statistical mixtures of $[\text{C}_2\text{mim}]:[\text{C}_2\text{C}_2\text{im}]:[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$ and $[\text{C}_4\text{mim}]:[\text{C}_4\text{C}_4\text{im}]:[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$

Microcrystalline cellulose (0.002 g for the C_2 mixture or 0.01 g for the C_4 mixture) was placed in the title mixtures (2 g C_2 mixture or 1.5 g C_4 mixture) in a glass vial and the resulting mixture was stirred at room temperature until complete dissolution was observed. Solutions can be prepared in this manner with varying concentrations of up to 5 wt % cellulose. The viscous solution was heated (by means of an oil bath) at 100 °C and became clear. Small increments of cellulose were added gradually and stirred until complete dissolution was observed. The solution was increasingly viscous with cellulose concentration. At cellulose concentrations of 183.2 g/mol IL (C_2 mixture) or 132.3 g/mol IL (C_4 mixture), viscous gels formed. The solubility of cellulose and the rate of dissolution can be accelerated by microwave pulses using a standard home microwave oven as has been reported previously [45,49].

Dissolution of chitin in 2:1:1 statistical mixture of $[\text{C}_2\text{mim}]:[\text{C}_2\text{C}_2\text{im}]:[\text{C}_1\text{C}_1\text{im}][\text{OAc}]$

Practical-grade chitin (0.032 g) was added portion-wise to 2 g of the title mixture and subjected to microwave irradiation in a household microwave oven with stirring after every 3 s pulse. The viscosity of the solution increases with increasing chitin concentration. Complete dissolution was observed after 40×3 s pulses (2 min total) microwave heating as suggested in a prior publication [45].

REFERENCES

1. J. S. Kim, S. C. Park, J. W. Kim, J. C. Park, S. M. Park, J. S. Lee. *Bioresour. Technol.* **101**, 4801 (2010).
2. M. J. Earle, K. R. Seddon. *Pure Appl. Chem.* **72**, 1391 (2000).
3. R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers. *J. Am. Chem. Soc.* **124**, 4974 (2002).
4. Y. Q. Pu, N. Jiang, A. J. Ragauskas. *J. Wood Chem. Technol.* **27**, 23 (2007).
5. S. H. Lee, T. V. Doherty, R. J. Linhardt, J. S. Dordick. *Biotechnol. Bioeng.* **102**, 1368 (2009).
6. N. Sun, H. Rodríguez, M. Rahman, R. D. Rogers. *Chem. Commun.* **47**, 1405 (2011).
7. H. B. Xie, S. B. Zhang, S. H. Li. *Green Chem.* **8**, 630 (2006).
8. K. Prasad, M. Murakami, Y. Kaneko, A. Takada, Y. Nakamura, J. Kadokawa. *Int. J. Biol. Macromol.* **45**, 221 (2009).
9. Y. Qin, X. M. Lu, N. Sun, R. D. Rogers. *Green Chem.* **12**, 968 (2010).
10. D. M. Phillips, L. F. Drummy, D. G. Conrady, D. M. Fox, R. R. Naik, M. O. Stone, P. C. Trulove, H. C. De Long, R. A. Mantz. *J. Am. Chem. Soc.* **126**, 14350 (2004).
11. H. B. Xie, S. H. Li, S. B. Zhang. *Green Chem.* **7**, 606 (2005).
12. I. Kilpelainen, H. Xie, A. King, M. Granstrom, S. Heikkinen, D. S. Argyropoulos. *J. Agric. Food. Chem.* **55**, 9142 (2007).
13. D. A. Fort, R. C. Remsing, R. P. Swatloski, P. Moyna, G. Moyna, R. D. Rogers. *Green Chem.* **9**, 63 (2007).
14. N. Sun, M. Rahman, Y. Qin, M. L. Maxim, H. Rodríguez, R. D. Rogers. *Green Chem.* **11**, 646 (2009).
15. N. Sun, X. Y. Jiang, M. L. Maxim, A. Metlen, R. D. Rogers. *ChemSusChem* **4**, 65 (2011).

16. M. B. Turner, S. K. Spear, J. G. Huddleston, J. D. Holbrey, R. D. Rogers. *Green Chem.* **5**, 443 (2003).
17. K. M. Docherty, C. F. Kulpa. *Green Chem.* **7**, 185 (2005).
18. BASF, personal communication.
19. B. Kosan, C. Michels, F. Meister. *Cellulose* **15**, 59 (2008).
20. T. Welton. *Chem. Rev.* **99**, 2071 (1999).
21. W. Xu, L. M. Wang, R. A. Nieman, C. A. Angell. *J. Phys. Chem. B* **107**, 11749 (2003).
22. M. Camplo, M. Wathier, J. Chow, M. W. Grinstaff. *Chem. Commun.* **47**, 2128 (2011).
23. Y. Yang, L. B. Wang, Z. Zhang, C. M. Li, X. L. Fu, G. H. Gao. *Chem. Res. Chin. Univ.* **26**, 554 (2010).
24. B. Clare, A. Sirwardana, D. R. MacFarlane. *Top Curr. Chem.* **290**, 1 (2010).
25. S. Sarkar, R. Pramanik, C. Ghatak, P. Setua, N. Sarkar. *J. Phys. Chem. B* **114**, 2779 (2010).
26. A. Stark, M. Ajam, M. Green, H. G. Raubenheimer, A. Ranwell, B. Ondruschka. *Adv. Synth. Catal.* **348**, 1934 (2006).
27. B. Lindström, L. J. Pettersson. *Catal. Lett.* **74**, 27 (2001).
28. A. R. Hajipour, F. Rafiee. *J. Iran. Chem. Soc.* **6**, 647 (2009).
29. J. D. Holbrey, K. R. Seddon. *J. Chem. Soc., Dalton Trans.* **13**, 2133 (1999).
30. G. B. Appetecchi, S. Scaccia, C. Tizzani, F. Alessandrini, S. Passerini. *J. Electrochem. Soc.* **153**, A1685 (2006).
31. M. J. Earle, C. M. Gordon, N. V. Plechkova, K. R. Seddon, T. Weton. *Anal. Chem.* **79**, 758 (2007).
32. J. M. Andanson, F. Jutz, A. Baiker. *J. Supercrit. Fluids* **55**, 395 (2010).
33. A. R. Choudhury, N. Winterton, A. Steiner, A. I. Cooper, K. A. Johnson. *J. Am. Chem. Soc.* **127**, 16792 (2005).
34. R. G. Reddy, Z. J. Zhang, M. F. Arenas, D. M. Blake. *High Temp. Mater. Pr.-Isr.* **22**, 87 (2003).
35. M. Uerdingen, C. Treber, M. Balser, G. Schmitt, C. Werner. *Green Chem.* **7**, 321 (2005).
36. N. J. Bridges, C. C. Hines, M. Smiglak, R. D. Rogers. *Chem.—Eur. J.* **13**, 5207 (2007).
37. R. Kalb, W. Staber, M. Schelch, M. Kotschan, R. Hermann, W. Wesner. U.S. Patent 20080251759A1 (2008).
38. A. J. Arduengo. U.S. Patent 5077414 (1991).
39. R. X. Ren, V. R. Koch. U.S. Patent 7253289 B2 (2007).
40. J. Zimmermann, B. Ondruschka, A. Stark. *Org. Process Res. Dev.* **14**, 1102 (2010).
41. R. D. Rogers, D. T. Daly, G. Gurau. PCT, WO 2011/056924 A2 (2011).
42. M. J. Earle, C. M. Gordon, N. V. Plechkova. *Anal. Chem.* **79**, 758 (2007).
43. N. Srivastava, M. Shukla, S. Saha. *Ind. J. Chem.* **49**, 757 (2010).
44. E. S. Sterner, Z. P. Roslo, E. M. Gross, S. M. Gross. *J. Appl. Polym. Sci.* **114**, 2963 (2009).
45. Y. Qin, X. Lu, N. Sun, R. D. Rogers. *Green Chem.* **12**, 968 (2010).
46. H. Zhao, G. A. Baker, Z. Song, O. Olubajo, T. Crittle, D. Peters. *Green Chem.* **10**, 696 (2008).
47. J. Vitz, T. Erdmenger, C. Haensch, U. S. Schubert. *Green Chem.* **11**, 417 (2009).
48. R. Kalb, W. Wesner, R. Hermann, M. Kotschan, M. Schlech, W. Staber. WO2005021484 (2005).
49. N. Sun, W. Li, B. Stoner, X. Jiang, X. Lu, R. D. Rogers. *Green Chem.* **13**, 1158 (2011).