

Demonstrating Sustainable Biomass Utilization and Processing Using Ionic Liquids – An Introduction to Undergraduate Chemistry Laboratories

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Abstract A more sustainable, greener chemistry aiming at the utilization of renewable resources is a main research focus to reduce human environmental impact. Unfortunately, there is a lack of powerful, environmentally benign solvents for the two most abundant renewable biopolymers, cellulose and lignin. Ionic liquids are here introduced to undergraduate chemistry laboratories as recyclable, tunable solvents for the dissolution and processing of biomass in the form of wood and its components to create alternative processes that are safer as well as waste- and additive-free. These experiments emphasize the principles of green chemistry and demonstrate the scope and potential of ionic liquids for the production of novel, biodegradable materials from renewable resources.

Keywords: ionic liquids, biomass, polymer chemistry, hands-on learning, green chemistry, material science, solvents

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1. Introduction and Background

The enhanced usage of renewable resources, the reduction of energy expenditure, chemicals and waste in chemical processing as well as the generation of environmentally benign materials are main topics in green chemistry [1] and should be included in chemical education [2,3]. These strategies for sustainable development are highly demanded as petroleum feedstocks are expiring and environmental pollution along with the anthropogenic climate change are becoming critical issues [4]. The sustainable utilization of the renewable biopolymers lignin and cellulose, that are the major components of woody plants, might be a contribution to achieve these goals. Both are already industrially generated and processed on very large scale although these processes offer a high potential for enhanced sustainability [5]. The localization of lignin and cellulose in plants along with the chemical structure of the biopolymers and the monolignols that form the highly heterogeneous lignin structure [6] are schematically shown in Figure 1. The wood pulping techniques, such as the kraft, sulfide or organosolv processes, that are currently applied for the generation of cellulose by separation from lignin, are highly energy-intensive and demand a variety of additives [7]. The lignin produced this way as byproduct is mainly used as a low grade fuel to compensate the energy demands of the pulping industry

[8]. A more sustainable process for the pretreatment of wood to separate lignin and cellulose is therefore highly desirable from economic and ecological points of view [9,10]. Furthermore a material usage of lignin in form of biodegradable polymers could reduce the environmental problems compared to mineral oil based polymers and minimize resource underutilization [11,12]. Cellulose is currently mainly processed through the viscose route to generate cellulose fibers (viscose fiber/ rayon) or foils (known under the tradename cellophane) [13].

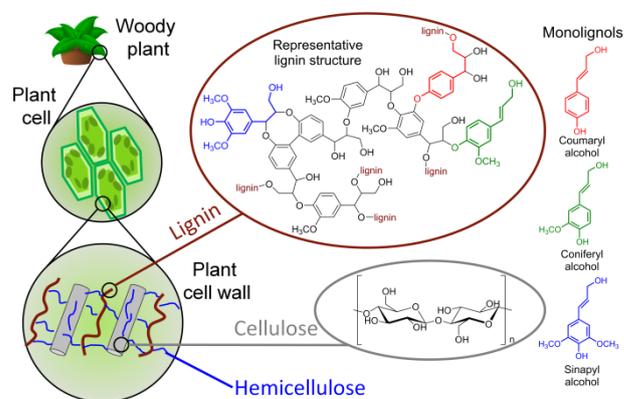


Figure 1. Localization and representative molecular structure of lignin and cellulose in woody plants that are used in the experiments along with three monolignols that form the heterogeneous lignin structure

The processing requires large quantities of the corrosive sodium hydroxide and sulfuric acid along with the toxic,

volatile and highly flammable carbon disulfide that could bring about serious environmental threats [14]. A safer, waste-free cellulose processing could therefore reduce environmental impact and even the costs of this large scale industrial process [15]. Especially the lack of appropriate solvents hampered the processing of cellulose and lignin in the past. The high chemical and biochemical resistance of lignin towards cracking currently prevents its material usage for the formation of low molecular weight compounds, but might be beneficial for its use as macromonomer. The problem of the insolubility of these biopolymers could be overcome by the novel solvent class of ionic liquids (ILs).

Ionic liquids are organic salts with low melting points (per arbitrary definition lower than 100°C) that are tunable in a very wide range due to their chemical composition so that they can accomplish a broad variety of different tasks [16]. ILs have promising characteristics that could lead to an overall greener, more benign chemistry with impact to several other disciplines, such as material science, energy conversion, as well as in the improvement of the sustainability of a wide range of applications. Especially the insignificant vapor pressure, that prevents exposure through evaporation and flammability, the high thermal stability and the recyclability are huge advantages compared to conventional molecular solvents for creating safer and waste-reduced processes. A range of ILs were found to selectively dissolve biopolymers and even pure wood [17,18] in comparably high weight percentages at moderate temperatures without the demand for further additives. This offers capabilities for a more environmental friendly isolation and processing of biomass with easy recovery of hydrophilic ILs via the aqueous phase while precipitating the water-insoluble biopolymers at the same time [19]. In this way ILs may serve as an alternative solvent for cellulose processing or as a reaction medium to generate bio-based polymers, for example. There are already a number of publications about ILs in undergraduate chemistry laboratories but mainly focusing on their synthesis and general properties [20,21,22]. This contribution is aimed at demonstrating the practical applications that ILs could enable in future operations such as biorefineries [23,24], the further utilization of renewable feedstocks, alternative processing and more benign chemical products, and the occurring synergistic effects. We present laboratory instructions for processing the biopolymers cellulose and lignin by

utilizing pure, simple to obtain ILs as efficient, safe, waste-reduced and recyclable media. The ability of ILs for selective dissolution of biomass compounds, the regeneration of biopolymers and the production of biodegradable polymers from lignin as underutilized renewable feedstock is demonstrated to students. This contribution is also aimed to introduce ILs as diverse, tunable substance class that has attracted researchers from various disciplines. Simultaneously the twelve principles of green chemistry [25] are taught to undergraduate teaching laboratories. The students become aware of the advantages of the ILs in processing biopolymers if the current industrial processes are discussed in terms of their sustainability and how ILs could help to improve this factor. Moreover, the students learn hands-on the possibilities for novel sustainable materials like synthetic wood and lignin-based polymers. Three lignin-based semi-synthetic polymers are synthesized via polycondensation and polyaddition, respectively. Remarkably, the large-scale waste product lignin can be used as a substitute for industrially applied polyols to generate biodegradable polymers that are not persistent in the environment such as most polymers based on mineral oil.

2. Experimental Instructions

In the experiments presented below the two ILs 1-butyl-3-methyl-imidazolium chloride ([C₄-mim][Cl]) and triethylammonium methanesulfonate ([Et₃NH][SO₃Me]) are used to solve, regenerate and process the biopolymers. Their molecular structures are shown in Figure 2a. Both chosen ILs can be synthesized in a one-step reaction from comparable cheap precursors. Furthermore, [C₄-mim][Cl] is commercially available. Full details about the synthesis protocols are given in the supporting information. The handling process is divided into three parts with three different didactic aims showing hands-on. First the unique dissolution ability of ionic liquids for biopolymers is shown, followed by the regeneration of cellulose-based polymers in the desired shapes as more sustainable alternative to the industrial processing. In the third part the generation of lignin-based polymers is demonstrated that may help to substitute the polymers made from mineral oil which often suffer from the problem of limited biodegradability. Thus the experiments can individually be scheduled according to timeframe or didactic goals.

Table 1. Solutions of the biopolymers in the ILs

Solution no.	Ionic Liquid	Weight of components / g				Comment
		IL	Cellulose ^{a)}	Lig-nin ^{b)}	Wood ^{c)}	
1	[C ₄ -mim][Cl]	5.00	-	-	0.15	Ability of ILs to dissolve pure wood
2	[C ₄ -mim][Cl]	5.00	0.20	-	-	Dissolution of pure cellulose
3	[C ₄ -mim][Cl]	5.00	0.20	0.25	-	Dissolution of wood-components to obtain "synthetic wood"
4	[Et ₃ NH][SO ₃ Me]	5.00	0.20	0.50	-	Selective dissolution of lignin (cellulose separation from biomass)
5	[Et ₃ NH][SO ₃ Me]	30.0	-	4.50	-	Stock solution of pure lignin for lignin-based polymers

a) Commercially available cosmetic cotton balls.

b) Hydrophobic lignin obtained by the kraft process is recommended.

c) Untreated dry wood chips.

2.1. Preparation of the Biopolymer Solutions

To demonstrate the exceptional dissolution ability of ILs for biomass the solutions of pure wood, cellulose, lignin and cellulose-lignin mixtures, respectively, are prepared by mixing the weighted amounts according to Table 1. The solutions are heated to 80°C in an oil bath and kept at this temperature over a period of 2 hours under intense stirring. The students can directly observe the advantages and disadvantages of the two ILs for processing biopolymers. The resulting biopolymer solutions are displayed in Figure 2b.

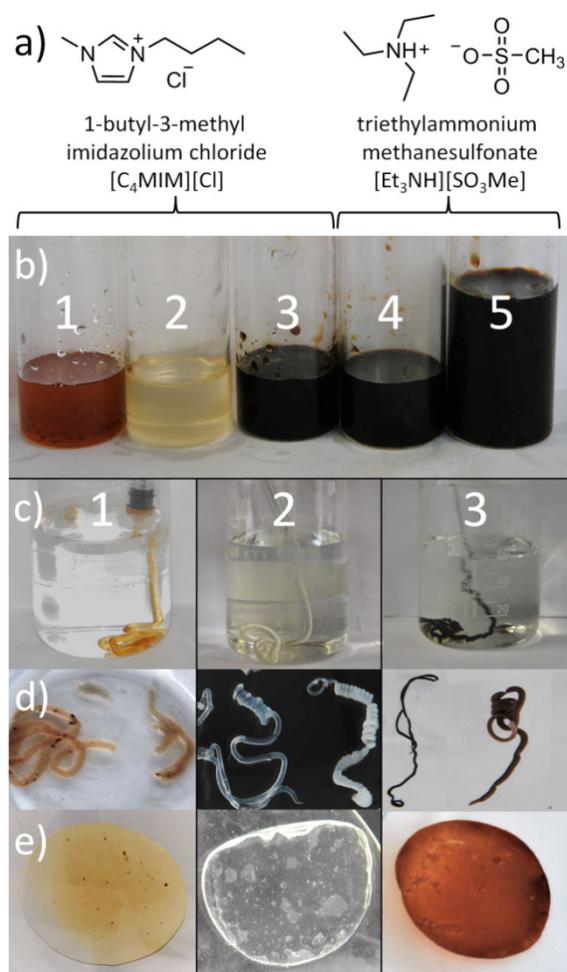


Figure 2. a) Molecular structures of the two ILs used for biopolymer treatment. b) Prepared solutions 1-5 of the dissolved biopolymers in the ionic liquids. c) Spinning of the solutions 1-3 by injection of the hot biopolymer solutions via syringe into distilled water. d) Obtained fibers after removing the IL dissolved in water. e) Obtained foils of the biopolymers after drying

2.2. Cellulose Processing and Generation of Synthetic Wood

The cellulose containing solution 1-3 can be used to demonstrate the regeneration of the biopolymers and ILs. Therefore the hot solutions (about 0.3 mL) are raised by a syringe with screw thread and equipped with an injection needle. The hot, viscous solutions are then injected into a beaker containing distilled water (Figure 2c) under constant pressure. Stable filaments are obtained from the solutions 2 and 3, while solution 1 produces only fibers of

minor quality and mechanical stability. Stable films of polymers can be obtained by putting about 0.2 mL of the solution 2 or 3 between two watch glasses and then placing in distilled water. From solution 1 only non-stable foils are obtained. The resulting fibers and films are shown in Figure 2d and Figure 2e. After immersing in the water for about 30 min the IL is fully dissolved as seen by the shrinkage of the fibers. The ionic liquid [C₄-mim][Cl] can now be regenerated by first removing the precipitated polymers and afterwards evaporating water under reduced pressure to generate a closed, waste-free cycle.

2.3. Production of Lignin-Based Biodegradable Polymers

Solution 5 containing 15 wt% lignin in [Et₃NH][SO₃Me] is used to produce a variety of more sustainable, biodegradable polymers based on lignin to demonstrate the versatility of lignin as macromonomer.

First the students prepare a copolymer I of lignin and adipoyl dichloride as linker. For this purpose about 10 g of the lignin solution in [Et₃NH][SO₃Me] is placed in an small beaker mold and 3.0 ml of the adipoyl dichloride is slowly added dropwise. During the addition of the adipoyl dichloride the solution is mixed after every few drops using a disposable spatula. After the addition is complete the polymer-solution is stirred for additional 5 minutes and the beaker filled with water. The mixture is stirred, the polymer filtered off and the filter washed with additional water. After drying in air the solid precipitate is placed in an appropriate mold and dried in a compartment dryer at 90°C. Additional pressure on the polymer improves thereby the mechanical stability and yields non-brittle polymers. The mechanical stability of the final polymer can also be improved by the addition of 10 wt% starch that is dissolved in the ionic liquid prior to the polymerization reaction.

The second produced copolymer (polymer II) is an epoxy resin produced from lignin and a di-epoxide. Therefore about 10 g of the lignin solution and about 2.5 g of 2,2-bis(4-glycidyloxyphenyl)propane (bisphenol A diglycidyl ether) are combined and heated to 90°C for three hours under intensive stirring. After cooling down, the reaction mixture is poured into about 150 mL distilled water and stirred for 5 minutes to dissolve the IL in the aqueous phase. The precipitate is filtered off and washed three times with 20 mL distilled water. The obtained polymer II can either be dried in air or in a compartment drier at 80°C using a mold to obtain a shaped polymer.

For the generation of polymer III about 10 g of the lignin solution in [Et₃NH][SO₃Me] is placed in a beaker or test tube and 3 g of diphenylmethane-1,4-diisocyanate are added and stirred in the mixture. The reaction is placed in an oil bath and slowly heated to 90°C. Upon temperature increase, the reaction starts which is visibly observed by foaming: a brown foam is formed in the reaction vessel. After the gas evolution has ended the mixture is cooled down and distilled water is added to the reaction flask. After 30 minutes the water is decanted and the polymer washed three additional times with water before the polymer is dried in air or a compartment drier at 80°C.

The three semi-synthetic, biodegradable polymers based on lignin created this way are displayed in Figure 3a.

2.4. Hazards

[C₄-mim][Cl] (GHS06, GHS09) is toxic if swallowed and toxic to aquatic life. [Et₃NH][SO₃Me] has no finished hazardous evaluation. Because of the very low vapor pressure and high thermal stability the ILs are non-flammable and an exposition via the air is minimized. Lignin and cellulose do not have any hazard or precautionary statements. Adipoyl chloride (GHS05) is corrosive and releases hydrogen chloride upon reaction with lignin. Although only small quantities are used the reaction should be performed in a fume hood. 2,2-bis(4-glycidyloxyphenyl) propane (bisphenol A diglycidyl ether) (GHS07) can cause allergic reactions with the skin and is harmful for water organisms. 4,4'-methylene diphenyl diisocyanate is rated as toxic and possibly carcinogen (GHS06, GHS08). Any contact with the skin or any exposition through the air has to be avoided. Complete hazard and precautionary statements are given in the supporting information. All substances should be used in a well-ventilating fume hood; appropriate safety equipment including gloves, lab coat and safety goggles should be worn throughout the whole experiments to do not risk any harms. All used chemicals should be disposed correctly according to local regulations.

3. Results and Discussion

3.1. Use of ILs in Biomass Pretreatment

The direct advantages of ILs for the selective and non-selective dissolution of biopolymers from woody plants are demonstrated by the dissolution ability of ILs for the two most abundant biopolymers, cellulose and lignin. [C₄-mim][Cl] is able to dissolve even pure, untreated wood at moderate temperatures and times with only few suspended particles left over. However, this IL shows no selectivity for either lignin or cellulose as observed from solution 1. [C₄-mim][Cl] is therefore a powerful solvent for the dissolution and processing of wood-derived biopolymers to certain products but of lower interest for an alternative separation process for the isolation of cellulose. As seen from solution 2 the IL can also be used to dissolve pure, untreated cellulose. The direct cellulose dissolution using ILs is considered as an interesting alternative to the processing of cellulose without time consuming, chemical-intensive derivatizations and hazardous chemicals, like applied in the viscose process on large industrial scale. A more detailed comparison is given in the supporting information. As [C₄-mim][Cl] dissolves both lignin and cellulose (solution 3) it can be used to create polymer blends as some kind of "synthetic wood" which has individually controllable amounts of the two biopolymers. This gives interesting possibilities for material science, to obtain uncritical, biodegradable polymers, polymer composites or semi-synthetic polymers, respectively. All solutions using [C₄-mim][Cl] are highly viscous at room temperature but remain in their liquid state although they are cooled below the melting point of the IL. As seen from solution 4 the [Et₃NH][SO₃Me] is unable to dissolve cellulose but can dissolve lignin in comparably high amounts resulting in solutions of

moderate viscosity.

The selective dissolution ability of some ILs [26] such as [Et₃NH][SO₃Me] for lignin enables alternative biomass pretreatment and conversion processes at moderate temperatures and ambient pressure. The use of ILs could possibly offer a cellulose isolation method that is less energy-intensive, with no demand for further additives unlike the industrially applied techniques such as the kraft, sulfite or organosolv processes. Especially the much lower viscosity of the observed [Et₃NH][SO₃Me] solutions compared to those with [C₄-mim][Cl] as solvent makes them easier to handle for further processing. The usage of well-designed ILs for biomass pretreatment in bio-refineries may offer an interesting approach for the effective utilization of this renewable feedstock in the near future.

3.2. Sustainable Biomass Processing Using ILs

The regeneration of the biopolymers is demonstrated to be facile by simply adding water to the biopolymer solutions. The water-soluble, hydrophilic ILs dissolve readily in water, whereas the insoluble biopolymers are precipitating upon addition of the antisolvent water. By using a selective geometry for the precipitation of the biopolymers and their blends different shapes could be obtained as observed by the fibers and foils. The regeneration of cellulose (solution 2) is comparable to the technical viscose process which results in the formation of regenerated cellulose filaments (rayon) or foils (cellophane) but our process demands less energy and no additional derivatization or additives. The recovery of the ILs can be achieved by simple evaporation of water to create an effective recycling thus achieving a more sustainable, waste-free processing. Furthermore the application of ILs in cellulose processing increases the safety of the process appreciably as no corrosive chemicals such as sodium hydroxide or sulfuric acid, respectively, are needed; the toxic, flammable and highly volatile derivatization agent carbon disulfide is avoided. The biopolymer regeneration is not limited to celluloses but can also be applied to the dissolved wood (solution 1) and to "synthetic wood"-mixtures of cellulose and lignin (solution 3) in variable amounts. In this way it becomes feasible to obtain new biodegradable, environmental benign polymer blends with tunable properties from renewable resources.

3.3. Biodegradable Semi-Synthetic Polymers Based on Lignin

Solution 5 shows the dissolution ability of [Et₃NH][SO₃Me] for even high weight percentages of lignin; the obtained solutions can be utilized as a reaction medium for polymerizations to obtain sustainable lignin-based macromolecules. The incorporation of the lignin units facilitates the biodegradation to smaller fragments that are subject to faster decomposition. The usage of ionic liquids as solvent for polymerization has, alongside with the direct accessibility of lignin, the general advantages of the solution polymerization that is widely applied in chemical industry. These include the controllable reaction rate and depression of auto-

acceleration through heat absorption by the solvent and reduced viscosity compared to polymerizations in the bulk. The polymerization reactions are similar to industrially applied polymer syntheses of widely distributed synthetic polymers but are tailored (down-scaled) to the didactic demands. In these experiments the lignin substitutes the industrially applied polyols and acts as crosslinking macromonomer. For the polymerizations the hydroxyl-units act as reactive groups for the polycondensation or polyaddition, respectively. The reaction schemes of the polymerizations are shown in Figure 3b. The presented polymer types produced in the experiments are also commercially produced in high volume so the theoretical backgrounds about the mechanisms are connected to relevant, daily-life products. It should be noted that the highly heterogeneous structure of lignin containing lots of different hydroxyl-groups always leads to crosslinking so that elastomers or thermosets are obtained depending on the degree of crosslinking. The addition of adipoyl chloride to the lignin solution produces hardly deformable polyester (polymer I) in a polycondensation reaction. Polymer II is a polyether and generated in a polyaddition of the diepoxide. After the removal of water the polymer is obtained as a thermoset whereas the diisocyanate produces a polyurethane (polymer III) that has a large degree of elasticity. The foaming during the polymerization of the polyurethane results from marginal CO₂-evolution that is the result of the reaction of the isocyanate with traces of water. All three semi-synthetic polymers are solids after workup but have different mechanical properties as a result of the different chemical composition and amount of crosslinking. These three reactions show the great potential of the direct material use of lignin as polyol instead of its current use as low grade fuel.

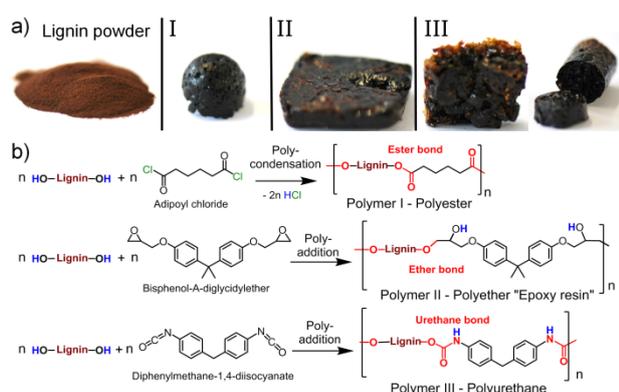


Figure 3. a) Photograph of the initial lignin powder and the obtained lignin based polymers I-III. b) Schematic reaction mechanism for the formation of the three lignin-based polymers via poly-condensation (Polymer I) or poly-addition (polymer II and III)

3.4. Context of the Green Chemistry Principles in Science Education – Education for Sustainability

The necessity to integrate sustainability in science education was recognized a few years ago. One of the goals of Education for Sustainable Development (ESD) is the training for better decision-making ability in the fields of a sustainable development. Beside this a main

focus lies on the “developing critical and educated citizens who, in making decisions, are aware of the influence of ideological, cultural, and historical contexts. Decisions in these fields require knowledge from and understanding about science in general and chemistry in particular” [27].

For the context of ionic liquids in school, in the Schülerlabor [28,29] or undergraduate studies it is indispensable that the students learn more about these solvents as well as polymers in an experimental way to have a direct transfer of up-to-date research in scientific disciplines. For this purpose the students should be confronted with the 12 principles of green chemistry [25]. These principles are a guideline how to achieve a more sustainable and environmental friendly chemistry and help to become aware of the factors of reactions and processes that should be optimized. [30] The 12 principles of green chemistry and how the usage of ionic liquids can improve the sustainability of biomass-pretreatment, cellulose processing as well as the benefits of lignin-based polymers are discussed in detail in the supporting information. The combination of the intensively discussed green chemistry concepts of ionic liquids as neoteric solvents, the development of sustainable resources as well as products designed for biodegradability offers a broad range of synergetic effects. Especially the treatment and processing of the two highly abundant natural polymers cellulose and lignin has a great potential for future developments.

4. Conclusion

The vivid hands-on experiments introduce the new substance class of ionic liquids to the students and show their possible contribution to a more sustainable development in selected technical applications that further benefit from synergetic effects. These include novel techniques for biomass pretreatment and processing as well as the fabrication of biodegradable polymers from the large-scale waste product lignin. The students learn that ILs, as powerful solvents for biomass, can dissolve even pure wood, allow the generation of “synthetic wood” and replace conventional methods for cellulose processing that demand large amounts of harmful chemicals. Furthermore, it is shown how ILs can contribute to the generation of diverse lignin-based polymers that reduce the consumption of mineral oil and address the problem of limited biodegradability of most conventional polymers. All the discussed topics are intensively investigated in the current scientific research; our contribution aims to build a bridge between academic research via chemical didactics to the chemical education and the education for sustainable development. The students should become aware of the advantages of the introduced concepts, especially in the context of the 12 principles of green chemistry.

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