Chapter from the book *Ionic Liquids: Applications and Perspectives*
Downloaded from: [http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives](http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives)

Interested in publishing with InTechOpen?
Contact us at book.department@intechopen.com
Chemical Modification of Cellulose with Succinic Anhydride in Ionic Liquid with or without Catalysts

CF Liu¹, AP Zhang²,³, WY Li¹ and RC Sun¹,⁴

¹State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, China
²Institute of New Energy and New Material, South China Agricultural University, China
³Biomass Energy Key Laboratory of Guangdong Regular Higher Education Institutions, South China Agricultural University, China
⁴Institute of Biomass Chemistry and Technology, Beijing Forestry University, China

1. Introduction

Currently, environmental problems such as global warming and dwindling energy resources are becoming increasingly critical issues. Utilization of biomass, especially inedible lignocelluloses to create fuels, energy, chemicals, composites and a host of other products is highly desirable for the construction of sustainable society (Zhang et al., 2007; Ogaki et al., 2009; Zhang et al., 2010). U.S. Department of Energy has targeted to achieve 10% of basic chemical building blocks arising from lignocellulosic biomass by 2020, and achieve a further increase to 50% by 2050 (Mohanty et al., 2002). At the same time, the European Union has developed a scenario for supplying 25% of the E.U.’s gasoline demand with biofuels by 2030 (Himmel et al., 2007).

The integrated utilization and multi-product biorefinery of lignocellulosic biomass is becoming the significant issue and development tendency. In this promising pattern, the lignocellulosic biomass is firstly fractionated to three main components, that is, lignin, hemicelluloses, and cellulose, then the isolated components are independently utilized to produce different products according to their own properties. Cellulose, the most abundant natural polymer, is a homopolymer composed of D-glucopyranose units linked by β (1→4) glycosidic bonds (Pandey et al., 2000). It is non-toxic, renewable, biodegradable and modifiable, and has great potential for an excellent industrial material (Richardson & Gorton, 2003). The promising applications of cellulose include biofibers, biopolymers, biofuels, and biocomposites (Reddy & Yang, 2005; Clark et al., 2009). Due to three hydroxyl groups available within one anhydroglucose units (AGU), a great variety of chemical modifications of cellulose are possible (Potthast et al., 2006). Chemical modifications of cellulose can introduce functional groups into the macromolecules in heterogeneous phase or homogeneous phase to improve the overall utilization of cellulosic polymers. Homogeneous functionalization has been one focus of cellulose research for a long time because more uniform and stable products can be obtained in homogeneous phase than heterogeneous phase (Regrini et al., 1999; El Seoud et al.,...
The intrinsic lack of solubility of native cellulose in water and most organic solvent systems constitutes a major obstacle for cellulose utilization. The efficient dissolution of cellulose is a long-standing goal in cellulose research and development and still of great importance (Heinze et al., 2005).

Recently, due to their unique physico-chemical properties, such as chemical and thermal stability, non-flammability and immeasurably low vapor pressure, ionic liquids (ILs) have been considered as the most potential green solvents in the future, which have attracted a great deal of scientific attention in many fields (Forsyth et al., 2002; Turner et al., 2003). Many kinds of ILs with a variety of structures have been reported as novel solvents for cellulose dissolution, including a series of alkylimidazolium salts containing chloride (Swatloski et al., 2002; Luo et al., 2005; Heinze et al., 2005; Zhang et al., 2005), formate (Fukaya et al., 2006), acetate (Hermanutz et al., 2007; Kosan et al., 2008; de Maria & Martinsson, 2009), and alkylphosphate (Fukaya et al., 2006; Fukaya et al., 2008; Kamiya et al., 2008; Mazza et al., 2009).

Based on the dissolution of cellulose in ILs, the investigation into the use of ILs as reaction media for cellulose functionalization has also been reported. Modification of cellulose represents one of the most versatile transformations as it provides access to a variety of biobased materials with valuable properties. Acylation of cellulose with linear chain acylation reagents such as anhydride or chloride is the most common method to produce cellulose bioproducts. Because of the wide application of cellulose acetate, cellulose acetylation with acetic anhydride or acetyl chloride in ILs has been extensively studied, and cellulose acetates with high degree of substitution (DS) were easily prepared (Wu et al., 2004; Abbott et al., 2005; Heinze et al., 2005; Barthel & Heinze, 2006; Granstrom et al., 2008). Furthermore, ILs were also be reported as reaction media for cellulose modification with other liquid reagents, such as carbanilation with phenyl isocyanate (Barthel & Heinze, 2006; Schlufter et al., 2006), acylation with lauroyl chloride (Barthel & Heinze, 2006), and perpropionylation with propionic anhydride (Schlufter et al., 2006). However, an undesired byproduct, namely, the corresponding carboxylic acid, is undoubtedly produced. This acid must be removed from the reaction after modification.

On the other hand, cellulose derivatives obtained with solid reagents such as cyclic anhydrides have also been widely used in various applications such as water absorbents for soil in agriculture, natural absorbents for the removal of heavy metal ions in wastewater treatment, medicine for drug delivery systems, and thermoplastic materials (Hadano et al., 2003; Yoshimura et al., 2006). More importantly, modification with cyclic anhydrides such SA does not yield such a byproduct. Moreover, the reaction results in a pendant carboxylic moiety attached to the cellulose via a covalent ester bond, providing a site upon which further reactive chemistry is possible. In the present study, we investigated the possibility of cellulose succinoylation in ILs without any catalysts. Three catalysts were also explored to increase cellulose modification efficiency. The cellulosic derivatives were then characterized by Fourier transform infrared (FT-IR), and solid-state CP/MAS $^{13}$C nuclear magnetic resonance (NMR) spectroscopies as well as thermal analysis.

2. Experimental

2.1 Materials

Rice straw (RS) was obtained from Guangzhou, China. It was dried in sunlight and then cut into small pieces. The cut RS was ground and screened to prepare 20-40 mesh size particles
(450-900 μm). Ionic liquid [C₄mim]Cl was obtained from the Chemer Chemical Co., Ltd., Hangzhou, China, and used as received. All of other chemicals used were of analytical grade and purchased from Sigma-Aldrich, Guangzhou, China.

2.2 Isolation of cellulose from RS
The dried RS powder was first dewaxed with toluene-ethanol (2:1, v/v) in a Soxhlet apparatus for 6 h. The dewaxed RS was oven-dried and then soaked in distilled water (800 mL) at 80 °C for 2 h. The insoluble residue was then dewaxed and water-soluble-free sample was delignified with sodium chlorite at pH 3.8-4.0, adjusted by 10% acetic acid, at 75 °C for 2 h. The residue was collected by filtration, washed with distilled water and ethanol, and then dried in a cabinet oven for 16 h at 50 °C. The holocellulose obtained was extracted with 10% KOH (600 mL) at 20 °C for 10 h. After filtration, the residue was washed thoroughly with distilled water until the filtrate was neutral, and then suspended in 95% ethanol (liquor to solid ratio 25:1) for 10 h. After filtration, the solid residue was dried in an oven at 50 °C for 16 h.

2.3 Succinoylation of cellulose in ionic liquid
The succinylated cellulosic derivatives containing free carboxylic groups were prepared by homogeneous reaction of RS cellulose without any catalysts or with three different catalysts including iodine (I₂), N-bromosuccimide (NBS), and 4-dimethylaminopyridine (DMAP) in the solvent system containing [C₄mim]Cl and DMSO. Dried cellulose was added to [C₄mim]Cl in three-necked flask continuously purged with gaseous N₂, and the mixture of cellulose/[C₄mim]Cl was stirred at 80 °C up to 3 h to guarantee the complete dissolution of cellulose. To reduce viscosity and achieve suitable mixing, 5 mL DMSO was added to this mixture. The succinoylation reaction was carried out according to the following procedures.

2.3.1 Succinoylation without any catalysts
To the cellulose solution in [C₄mim]Cl/DMSO system, SA, previously dissolved in 5 mL DMSO, was added at the corresponding reaction temperature with the 4:1 molar ratio of SA/AGU in cellulose in Table 1. The mixture was heated in oil bath under N₂ atmosphere with magnetic stirring for the desired time. After the required time, the resulting mixture was slowly poured into 150 mL of isopropanol with stirring, washed thoroughly with isopropanol to eliminate ILs, un-reacted anhydride, and byproducts, and then dried in a vacuum at 50 °C for 16 h.

2.3.2 Succinoylation catalyzed with iodine
To the cellulose solution in [C₄mim]Cl/DMSO system, SA and I₂, previously dissolved in 5 mL DMSO, were added at the corresponding reaction temperature with the 4:1 molar ratio of SA/AGU in cellulose and the corresponding weight ratio of I₂/SA shown in Table 2. The mixture was heated in oil bath under N₂ atmosphere with magnetic stirring for the desired time. Then the reaction mixture was treated with a saturated solution of sodium thiosulfate (2 mL) with stirring, and then vigorously shaken for 2 min to guarantee complete transformation of iodine to iodide. The resulting mixture was slowly poured into 150 mL of isopropanol with continuous stirring. The solid was filtered, washed thoroughly with isopropanol to eliminate ILs, un-reacted anhydride, and byproducts, and then dried in vacuum at 50 °C for 16 h.
2.3.3 Succinoylation catalyzed with N-bromosuccimide
To the cellulose solution in [C₄mim]Cl/DMSO system, SA and NBS, previously dissolved in 5 mL DMSO, were added at the corresponding reaction temperature with the 4:1 molar ratio of SA/AGU in cellulose and the corresponding weight ratio of NBS/SA shown in Table 2. The mixture was heated in oil bath under N₂ atmosphere with magnetic stirring for the desired time. After the required time, the resulting mixture was slowly poured into 150 mL of isopropanol with stirring, washed thoroughly with isopropanol to eliminate ILs, unreacted anhydride, NBS, and byproducts, and then dried in a vacuum at 50 °C for 16 h.

2.3.4 Succinoylation catalyzed with 4-dimethylaminopyridine
To the cellulose solution in [C₄mim]Cl/DMSO system, SA and DMAP, previously dissolved in 5 mL DMSO, were added at the corresponding reaction temperature with the 4:1 molar ratio of SA/AGU in cellulose and the corresponding weight ratio of DMAP/SA shown in Table 2. The mixture was heated in oil bath under N₂ atmosphere with magnetic stirring for the desired time. After the required time, the resulting mixture was slowly poured into 150 mL of isopropanol with stirring, washed thoroughly with isopropanol to eliminate ILs, unreacted anhydride, DMAP, and byproducts, and then dried in a vacuum at 50 °C for 16 h.

2.4 Determination of degree of substitution
The DS of cellulosic preparations was determined by direct titration method (Jeon et al., 1999; Stojanovic et al., 2005). A known weight of the sample was dissolved in 10 mL of DMSO by stirring at 75 °C for 30 min. After cooling, 5-6 drops of phenolphthalein indicator were added. This solution was titrated against 0.01 mol/L standard NaOH solution until a permanent pale pink color was seen. The DS was calculated by using the following equation:

\[ DS = \frac{162 \times (V_{NaOH} \times c_{NaOH})}{m - 100 \times (V_{NaOH} \times c_{NaOH})} \]

where: 162 g/mol is the molar mass of an AGU, 100 g/mol is the net increase in the mass of an AGU for each succinoyl substituted, m is the weight of sample analyzed, \( V_{NaOH} \) is the volume of standard NaOH solution consumed in the titration, and \( c_{NaOH} \) is the molarity of standard NaOH solution.

2.5 Characterization of the native and succinylated cellulose
Viscosity of the cellulose was measured by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, Part 1, cupriethylenediamine (CED) method (BS 6306, Part 1, 1982). The viscosity average DP (degree of polymerization) of cellulose was estimated from their intrinsic viscosity \([\eta]\) in CED hydroxide solution, \( P^{0.90} = 1.65[\eta] \), where P is an indeterminate average DP (Evans & Wallis, 1989). Molecular weight (Mw) of cellulose was then calculated from P by multiplied by 162, the Mw of an AGU. The FT-IR spectra of the cellulose and succinylated cellulosic derivatives were recorded on an FT-IR spectrophotometer (Nicolet 510) from finely ground samples (1%) in KBr pellets in the range 4000-400 cm⁻¹. Thirty-two scans were taken for each sample with a resolution of 2 cm⁻¹ in the transmission mode. The solid-state CP/MAS ¹³C NMR spectra were obtained on a Bruker DRX-400 spectrometer with 5 mm MAS BBO probe employing both Cross Polarization and Magic Angle Spinning and each experiment was recorded at ambient temperature. The spectrometer operated at 100 MHz. Acquisition time was 0.034 s, the delay
time 2 s, and the proton 90° pulse time 4.85 μs. Each spectrum was obtained with an accumulation of 5000 scans.
Thermal analysis of the cellulose and succinylated cellulosic samples was performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The apparatus was continually flushed with nitrogen. The sample weighed between 8 and 12 mg and the scans were run from room temperature to 550°C at a rate of 10°C per minute.

3. Results and discussion

3.1 Modification without any catalysts

Delignification of dewaxed and water-soluble-free RS followed by alkaline extraction yielded 44.6% cellulose (based on the dry weight of RS). The intrinsic viscosity, degree of polymerization, and molecular weight of the native cellulosic preparation were determined to be 348 mL·g⁻¹, 1165, and 188730 g·mol⁻¹, respectively.
Due to three hydroxyl groups available within one anhydroglucose units (AGU), a great variety of chemical modifications of cellulose are possible. In the present study, succinoylation of the cellulose isolated from RS in [C₄mim]Cl/DMSO system was investigated with or without catalysts. Usually, SA reacts with cellulose O-H groups to form the monoester as shown in Fig. 1. After cellulose was dissolved in [C₄mim]Cl, the viscous solution obtained was diluted by DMSO to achieve a suitable and clear mixture. Solid SA and catalyst previously dissolved in DMSO were added to the solution to achieve homogeneous reaction. Table 1 shows the effects of reaction conditions including the molar ratio of SA/anhydroglucose units (AGU) in cellulose, reaction time, and reaction temperature on DS of the cellulose succinylated without any catalysts.

As shown in Table 1, an increase of molar ratio of SA/AGU in cellulose from 1:1 to 2:1, 3:1, 4:1, 6:1, 8:1, and 10:1 resulted in the improvement of the DS of succinylated cellulose from 0.02 to 0.04, 0.07, 0.11, 0.15, 0.22, and 0.31, respectively, which was due to the greater availability of succinic anhydride molecules in the proximity of the cellulosic molecules at higher concentration of succinic anhydride. The DS increased from 0.08 to 0.12, 0.15, 0.16, and 0.20 with the enhancement of reaction temperature from 90 to 100, 110, 120, and 130°C, respectively. The reason for this enhancement of succinoylation was presumed to be due to the favourable effect of temperature on succinoylation reaction. A higher reaction temperature would enhance the mobility of the molecules, the diffusion of succinic anhydride into the cellulosic molecules, and the swell ability of cellulose, therefore, increasing succinoylation rates. The rate and time of collisions of succinic anhydride with

![Fig. 1. Reaction of cellulose with succinic anhydride in ionic liquid.](www.intechopen.com)
3.2 Iodine-catalysed succinoylation

Recently, it has been demonstrated that iodine (I\(_2\)) is an effective catalyst for acetylation of alcohols and polysaccharides without solvents (Biswa et al., 2005; Ren et al., 2007). In the present study, we investigated the possibility of cellulose succinoylation catalyzed with I\(_2\) in [C\(_4\) mim]Cl/DMSO system to increase cellulose modification efficiency. As shown in Table 2, the increase of the dosage of I\(_2\) from 2% to 4%, 6%, 8%, 10%, and 15% resulted the improved DS from 0.74 to 0.92, 1.13, 1.25, 1.29, and 1.30, respectively. In comparison to the sample 5 obtained without any catalyst under the same conditions (DS=0.15), the succinoylation efficiency clearly increased. The possible mechanism of succinoylation and the actual role of iodine are not clear. However, a plausible explanation is that iodine might be ionized into I\(^+\) and I\(^-\) in ILs. I\(^+\) in turn activates the carbonyl groups of succinic anhydride to form as the acylation reagent for further reaction, as shown in Fig. 2.

3.3 NBS-catalysed succinoylation

It has been demonstrated that NBS is a novel, highly effective catalyst for acetylation of alcohols under mild reaction conditions. It is an inexpensive and commercially available reagent that is traditionally used as an oxidizing agent or brominating agent (Karimi & Seradj, 2001). In the present study, the possibility of cellulose succinoylation catalyzed with NBS was explored in [C\(_4\) mim]Cl/DMSO system to increase cellulose modification efficiency. As shown in Table 2, the DS was enhanced from 1.14 to 1.76, 1.95, 2.11, 2.17, and 2.18 with...
the improvement of NBS dosage from 1% to 3%, 5%, 7%, 10% and 15%, respectively, indicating the highly efficient succinoylation catalysed with NBS compared with that without any catalyst. The possible mechanism of NBS-catalysed succinoylation is shown in Fig. 3. NBS might act as a source for Br\(^+\), which in turn activates the carbonyl groups of SA to produce the highly reactive acetylating agent. This acetylating agent reacts with hydroxyl groups of cellulose, which upon elimination of NBS, produce succinoylated cellulose.

| SA/AGU | Catalyst | Catalyst/SA(%) | T/°C | t/min | Sample | DS  |
|--------|----------|----------------|------|-------|--------|-----|
| 6:1    | I\(_2\)  | 2              | 110  | 60    | 16     | 0.74|
| 6:1    | I\(_2\)  | 4              | 110  | 60    | 17     | 0.92|
| 6:1    | I\(_2\)  | 6              | 110  | 60    | 18     | 1.13|
| 6:1    | I\(_2\)  | 8              | 110  | 60    | 19     | 1.25|
| 6:1    | I\(_2\)  | 10             | 110  | 60    | 20     | 1.29|
| 6:1    | I\(_2\)  | 15             | 110  | 60    | 21     | 1.30|
| 6:1    | NBS      | 1              | 110  | 60    | 22     | 1.14|
| 6:1    | NBS      | 3              | 110  | 60    | 23     | 1.76|
| 6:1    | NBS      | 5              | 110  | 60    | 24     | 1.95|
| 6:1    | NBS      | 7              | 110  | 60    | 25     | 2.11|
| 6:1    | NBS      | 10             | 110  | 60    | 26     | 2.17|
| 6:1    | NBS      | 15             | 110  | 60    | 27     | 2.18|
| 6:1    | DMAP     | 1              | 110  | 60    | 28     | 1.26|
| 6:1    | DMAP     | 2              | 110  | 60    | 29     | 1.54|
| 6:1    | DMAP     | 3              | 110  | 60    | 30     | 1.85|
| 6:1    | DMAP     | 5              | 110  | 60    | 31     | 1.92|
| 6:1    | DMAP     | 8              | 110  | 60    | 32     | 1.99|
| 6:1    | DMAP     | 15             | 110  | 60    | 33     | 2.27|

Table 2. The DS of succinylated cellulose with different catalysts in [C\(_4\)mim]Cl/DMSO system.

\[ I_2 \rightarrow I^+ + I^- \]

\[ I^+ + \text{SA} \rightarrow \text{I-SA} \]

\[ \text{I-SA} + \text{OH} \rightarrow \text{IOH} + \text{SA} \]

\[ \text{IOH} + \text{RG} \rightarrow \text{IO-RG} + \text{H} \]

[2] Possible mechanism of succinoylation of cellulose using I\(_2\) as a catalyst.
Fig. 3. Possible mechanism of succinoylation of cellulose using NBS as a catalyst.

### 3.4 DMAP-catalysed succinoylation

Pyridine has been found to be effective in the modification of wood with various long chain anhydrides, because it serves not only to swell the wood structure, thereby permitting effective ingress of reagent, but also catalyses the reaction via nucleophilic mediated catalysis (Sun et al., 2001). In comparison to pyridine, DMAP was found to be approximately $10^4$ times more active when used as acylation catalyst (Hill et al., 2000). In the present study, we studied the succinoylation of cellulose in [C$_4$mim]Cl/DMSO system using DMAP as a catalyst. As shown in Table 2, the improvement of DMAP dosage from 1% to 2%, 3%, 5%, 8%, and 15% led to the increment in DS of succinylated cellulose from 1.26 to 1.54, 1.85, 1.92, 1.99, and 2.27, respectively. The possible mechanism of DMAP-catalysed succinoylation is shown in Fig. 3. The nucleophilic attack of DMAP on a carbonyl group of succinic anhydride leads to intermediate, which could react with cellulose hydroxyl groups and produce cellulose ester.

### 3.5 FT-IR

Fig. 4 illustrates the FT-IR spectra of native cellulose (spectrum 1) and succinylated samples 9 (spectrum 2, without any catalysts) and 24 (spectrum 3, 5% NBS). In spectrum 1, the absorbances at 3431, 2923, 1629, 1381, 1165, and 1048 cm$^{-1}$ are associated with native cellulose. The strong adsorption at 3431 cm$^{-1}$ is due to the stretching of hydroxyl groups and that at 2923 cm$^{-1}$ to the C-H stretching. The band at 1629 cm$^{-1}$ relates to the bending mode of the absorbed water. The peak at 1381 cm$^{-1}$ is attributed to the O-H bending. The absorption band at 1165 cm$^{-1}$ corresponds to C-O antisymmetric bridge stretching. A strong peak at 1048 cm$^{-1}$ arises from C-O-C pyranose ring skeletal vibration.

Compared with spectrum 1, the spectra 2 and 3 of succinylated cellulose provide evidence of succinoylation by the occurrence of the absorbance at 1732 and 1573 cm$^{-1}$. In general, the absorption by carbonyl bonds in esters gives peaks at 1750 cm$^{-1}$, and one in carboxylic acids exhibits a band at 1712 cm$^{-1}$ (Jayakumar et al., 2000). The overlapping band at 1732 cm$^{-1}$ is indicative of absorption by carbonyl group in carboxyl and esters. The absorption band at
Fig. 4. Possible mechanism of succinoylation of cellulose using DMAP as a catalyst.

Fig. 5. FT-IR spectra of native cellulose (spectrum 1) and succinylated cellulose samples 9 (spectrum 2) and 24 (spectrum 3)

1573 cm$^{-1}$ is associated with the antisymmetric stretching of carboxylic anions (Yoshimura et al., 2006), indicating the formation of monoester. In addition, the intensity of the absorption band at 1165 cm$^{-1}$ for C-O antisymmetric stretching increased after succinoylation, suggesting that the esterification reaction does occur. These significant changes of the absorption bands indicated that the monoester of succinylated cellulose was formed in [C$_4$ mim]Cl/DMSO system under the conditions given. It should be noted that the intensities of the bands at 1732, 1573, and 1165 cm$^{-1}$ are significantly improved from spectrum 2 to spectrum 3, indicating the enhanced succinoylation of cellulose. It suggested that NBS is a high efficient catalyst of cellulose succinoylation in [C$_4$ mim]Cl/DMSO. As expected, the absence of peaks at 1850 and 1780 cm$^{-1}$ in spectra 2 and 3 for succinylated cellulose confirmed that the products are free of the unreacted SA.
3.6 Solid-state CP/MAS $^{13}$C-NMR

CP/MAS $^{13}$C-NMR spectroscopy is the most effective of the few methods for the characterization of the lignocellulosic materials directly and is capable of providing detailed information directly on solid samples (Maunu, 2002). In the present study, the succinoylation reaction of cellulose with or without catalysts was also studied by solid-state CP/MAS $^{13}$C-NMR spectroscopy, and the corresponding spectra are illustrated in Fig. 6.

![Fig. 6. Solid-state CP/MAS $^{13}$C-NMR spectra of native cellulose (spectrum a) and succinylated cellulose without catalysts (sample 5, spectrum b) and with catalyst NBS (sample 24, spectrum c), DMAP (sample 31, spectrum d), and iodine (sample 17, spectrum e).](image)

In spectrum a, all noticeable signals are distributed in the region between 50 and 110 ppm for the carbon atoms of the carbohydrate moiety. The typical signals at 101.4 (C-1), 85.2 (C-4 of crystalline cellulose), 79.7 (C-4 of amorphous cellulose), 71.2 (C-5), 67.8 (C-2 and C-3), 61.1 (C-6 of crystalline cellulose), and 59.8 ppm (C-6 of amorphous cellulose) have all been reported before (Chang & Chang, 2001; Maunu, 2002). Evidently, the presence of the signals of the carboxylic group at 171.0 ppm and the methylene group at 26.4 ppm provided evidence of succinoylation, which indicated that the reaction shown in Fig. 1 does occur. The signals at 85.2 ppm for C-4 of crystalline cellulose and 61.1 ppm for C-6 of crystalline cellulose disappeared in spectra b to e after succinoylation, suggesting the complete
disruption of cellulose crystalline structure during the dissolution and functionalization, which indicated that succinoylation reaction occurs in homogeneous phase. The intensity of the signal for C-6 significantly decreased after succinoylation, and that at 67.8 ppm for C-2 and C-3 also decreased, which indicated the succinoylation reaction at C-6, C-2, and C-3 positions does occur. Obviously, the succinoylation reaction is preferred at C-6. The significant decrease of the signal for C-6 indicated that the reactivity of C-6 is higher than that of C-2 and C-3.

3.7 Thermal analysis

Fig. 7 illustrates TGA curves of native cellulose (curve a) and succinylated cellulose without catalyst (sample 6, curve b) and with NBS catalyst (sample 22, curve 3). The native cellulose starts to decompose at 226°C, whereas the regenerated cellulose begins to decompose at 205°C and 202°C for samples 6 and 10, respectively. At 50% weight loss, the decomposition temperature occurs at 338°C for native cellulose, 330°C for sample 6, and 285°C for sample 22. These decreasing trends of decomposition temperature suggested that thermal stability of cellulose decreased after succinoylation, especially true for high DS samples.

![TGA curves](image)

Fig. 7. The thermograms of native cellulose (a) and succinylated cellulose samples 6 (b) and 22 (c)

4. Conclusion

The succinylated cellulosic derivatives with low DS were prepared without any catalysts. The increase of reaction temperature, molar ratio of SA/AGU in cellulose, and reaction time led to an increase in DS of cellulose samples. DS of cellulosic derivatives obtained with iodine, NBS, and DMAP catalysts was significantly improved compared with the products without any catalysts, indicating that these three catalysts were effective catalysts for cellulose succinoylation in ILs. The possible mechanism of homogeneous succinoylation catalyzed with these catalysts and the actual role of these catalysts were also proposed. Fourier transform infrared and solid-state cross-polarization/magic angle spinning $^{13}$C-NMR spectroscopies also provided evidence of catalyzed homogeneous succinoylation reaction. The results indicated that the reaction of hydroxyl groups at C-6, C-2, and C-3...
positions in cellulose all occurred. The thermal stability of the succinylated cellulose was found to decrease upon chemical modification.

5. Acknowledgements

The authors are grateful for the financial support of this research from the National Natural Science Foundation of China (Nos. 30871994, 30972325, and 30710103906), the Guangdong Natural Science Foundation (No. 8451064101000409), Specialized Research Fund for the Doctoral Program of Higher Education (No. 20070561040), Chinese Universities Scientific Fund (No. 2009ZZ0024), and National Basic Research Program of China (No. 2010CB732201)

6. References

Abbott, A.P., Bell, T.J., Handa, S. & Stoddart, B. (2005). O-acetylation of cellulose and monosaccharides using a zinc based ionic liquid, Green Chemistry 7(10): 705-707.

Barthel, S. & Heinze, T. (2006). Acylation and carbamimation of cellulose in ionic liquids, Green Chemistry 8(3): 301-306.

Biswas, A., Shogren, R.L. & Willett, J.L. (2005). Solvent-free process to esterify polysaccharides, Biomacromolecules 6(4): 1843-1845.

Chang, S.T. & Chang, H.T. (2001). Comparisons of the photostability of esterified wood, Polymer Degradation and Stability 71(2): 261-266.

Clark, J.H., Deswarte, F.E.I. & Farmer, T.J. (2009). The integration of green chemistry into future biorefineries, Biofuels Bioproducts & Biorefining-Biofpr 3(1): 72-90.

de Maria, D. & Martinsson, A. (2009). Ionic-liquid-based method to determine the degree of esterification in cellulose fibers, Analyst 134(3): 493-496.

Evans, R. & Wallis, A.F.A. (1989). Cellulose molecular-weights determined by viscometry, Journal of Applied Polymer Science 37: 2331-2340.

Forsyth, S.A., MacFarlane, D.R., Thomson, R.J. & von Itzstein, M. (2002). Rapid, clean, and mild o-acetylation of alcohols and carbohydrates in an ionic liquid, Chemical Communications 7(7): 714-715.

Fukaya, Y., Sugimoto, A. & Ohno, H. (2006). Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates, Biomacromolecules 7(12): 3295-3297.

Fukaya, Y., Hayashi, K., Wada, M. & Ohno, H. (2008). Cellulose dissolution with polar ionic liquids under mild conditions: Required factors for anions, Green Chemistry 10(1): 44-46.

Granstrom, M., Kavakka, J., King, A., Majoimen, J., Makela, V., Helaja, J., Hietala, S., Virtanen, T., Maunu, S.L., Argyropoulos, D.S. & Kilpelainen, I. (2008). Tosylation and acylation of cellulose in 1-allyl-3-methylimidazolium chloride, Cellulose 15(3): 481-488.

Hadano, S., Onimura, K., Tsutsumi, H., Yamasaki, H. & Oishi, T. (2003). Syntheses of chemical-modified cellulose obtained from waste pulp, Journal of Applied Polymer Science 90(8): 2059-2065.

Heinze, T., Schwickal, K. & Barthel, S. (2005). Ionic liquids as reaction medium in cellulose functionalization, Macromolecular Bioscience 5(6): 520-525.
Chemical Modification of Cellulose with Succinic Anhydride in Ionic Liquid with or without Catalysts

Hermanutz, F., Gaehr, F., Uerdingen, E., Meister, F. & Kosan, B. (2007). New developments in dissolving and processing of cellulose in ionic liquids, *Macromolecular Symposia* 262(1): 23-27.

Hill, C.A.S., Cetin, N.S. & Ozmen, N. (2000). Potential catalysts for the acetylation of wood, *Holzforschung* 54(3): 269-272.

Himmel, M.E., Ding, S.Y., Johnson, D.K., Adney, W.S., Nimlos, M.R., Brady, J.W. & Foust, T.D. (2007). Biomass recalcitrance: Engineering plants and enzymes for biofuels production, *Science* 315(5813): 804-807.

Jayakumar, R., Balaji, R. & Nanjundan, S. (2000). Studies on copolymers of 2-(n-phthalimido)ethyl methacrylate with methyl methacrylate, *European Polymer Journal* 36(8): 1659-1666.

Jeon, Y.S., Viswanathan, A. & Gross, R.A. (1999). Studies of starch esterification: Reactions with alkenyl-succinates in aqueous slurry systems, *Starch-stärke* 51(2-3): 90-93.

Kamiya, N., Matsushita, Y., Hanaki, M., Nakashima, K., Narita, M., Goto, M. & Takahashi, H. (2008). Enzymatic in situ saccharification of cellulose in aqueous-ionic liquid media, *Biotechnology Letters* 30(6): 1037-1040.

Karimi, B. & Seradj, H. (2001). N-bromosuccinimide (NBS), a novel and highly effective catalyst for acetylation of alcohols under mild reaction conditions, *Synlett* (4): 519-520.

Kosan, B., Michels, C. & Meister, F. (2008). Dissolution and forming of cellulose with ionic liquids, *Cellulose* 15(1): 59-66.

Luo, H.M., Li, Y.Q. & Zhou, C.R. (2005). Study on the dissolubility of the cellulose in the functionalized ionic liquid, *Polymeric Materials Science & Engineering* 21(2): 233-235.

Maunu, S.L. (2002). NMR studies of wood and wood products, *Progress in Nuclear Magnetic Resonance Spectroscopy* 40(2): 151-174.

Mazza, M., Catana, D.A., Vaca-Garcia, C. & Cecutti, C. (2009). Influence of water on the dissolution of cellulose in selected ionic liquids, *Cellulose* 16(2): 207-215.

Mohanty, A.K., Misra, M. & Drzal, L.T. (2002). Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world, *Journal of Polymers and the Environment* 10(1-2): 19-26.

Ogaki, Y., Shinozuka, Y., Hatakeyama, M., Hara, T., Ichikuni, N. & Shimazu, S. (2009). Selective production of xylose and xylo-oligosaccharides from bamboo biomass by sulfonated aliphane solid acid catalyst, *Chemistry Letters* 38(12): 1176-1177.

Pandey, A., Soccol, C.R., Nigam, P. & Soccol, V.T. (2000). Biotechnological potential of agro-industrial residues. I: Sugarcane bagasse, *Bioresource Technology* 74(1): 69-80.

Reddy, N. & Yang, Y. (2005). Biofibers from agricultural byproducts for industrial applications, *Trends in Biotechnology* 23(1): 22-27.

Ren, J.L., Sun, R.C., Liu, C.F., Cao, Z.N. & Luo, W. (2007). Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst, *Carbohydrate Polymers* 70(4): 406-414.

Richardson, S. & Gorton, L. (2003). Characterisation of the substituent distribution in starch and cellulose derivatives, *Analytica Chimica Acta* 497(1-2): 27-65.

Schlufter, K., Schmuerer, H.P., Dorn, S. & Heinze, T. (2006). Efficient homogeneous chemical modification of bacterial cellulose in the ionic liquid 1-n-butyl-3-methylimidazolium chloride, *Macromolecular Rapid Communications* 27(19): 1670-1676.
Stojanovic, Z., Jeremic, K., Jovanovic, S. & Lechner, M.D. (2005). A comparison of some methods for the determination of the degree of substitution of carboxymethyl starch, *Starch-stärke* 57(2): 79-83.

Sun, R.C., Sun, X.F. & Zhang, F.Y. (2001). Succinoylation of wheat straw hemicelluloses in n,n-dimethylformamide/lithium chloride systems, *Polymer International* 50(7): 803-811.

Swatloski, R.P., Spear, S.K., Holbrey, J.D. & Rogers, R.D. (2002). Dissolution of cellulose with ionic liquids, *Journal of the American Chemical Society* 124(18): 4974-4975.

Turner, M.B., Spear, S.K., Huddleston, J.G., Holbrey, J.D. & Rogers, R.D. (2003). Ionic liquid salt-induced inactivation and unfolding of cellulase from *Trichoderma reesei*, *Green Chemistry* 5(4): 443-447.

Wu, J., Zhang, J., Zhang, H., He, J.S., Ren, Q. & Guo, M. (2004). Homogeneous acetylation of cellulose in a new ionic liquid, *Biomacromolecules* 5(2): 266-268.

Yoshimura, T., Matsuo, K. & Fujioka, R. (2006). Novel biodegradable superabsorbent hydrogels derived from cotton cellulose and succinic anhydride: Synthesis and characterization, *Journal of Applied Polymer Science* 99(6): 3251-3256.

Zhang, H., Wu, J., Zhang, J. & He, J.S. (2005). 1-allyl-3-methylimidazolium chloride room temperature ionic liquid: A new and powerful nonderivatizing solvent for cellulose, *Macromolecules* 38(20): 8272-8277.

Zhang, M.J., Qi, W., Liu, R., Su, R.X., Wu, S.M. & He, Z.M. (2010). Fractionating lignocellulose by formic acid: Characterization of major components, *Biomass & Bioenergy* 34(4): 525-532.

Zhang, Y.H.P., Ding, S.Y., Mielenz, J.R., Cui, J.B., Elander, R.T., Laser, M., Himmel, M.E., McMillan, J.R. & Lynd, L.R. (2007). Fractionating recalcitrant lignocellulose at modest reaction conditions, *Biotechnology and Bioengineering* 97(2): 214-223.
This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

How to reference
In order to correctly reference this scholarly work, feel free to copy and paste the following:

CF Liu, AP Zhang, WY Li and RC Sun (2011). Chemical Modification of Cellulose with Succinic Anhydride in Ionic Liquid with or without Catalysts, Ionic Liquids: Applications and Perspectives, Prof. Alexander Kokorin (Ed.), ISBN: 978-953-307-248-7, InTech, Available from: http://www.intechopen.com/books/ionic-liquids-applications-and-perspectives/chemical-modification-of-cellulose-with-succinic-anhydride-in-ionic-liquid-with-or-without-catalysts