Homogeneous Acylation and Regioselectivity of Cellulose with 2-Chloro-2-Phenylacetyl Chloride in Ionic Liquid

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A cellulose acylate, cellulose-CPAC, was prepared homogeneously in the ionic liquid 1-butyl-3-methyl chloride imidazole ([Bmim]Cl) from cotton dissolving pulp. The pulp was first solubilized in the solvent system [Bmim]Cl/N,N-dimethyl formamide (DMF), and then reacted with 2-chloro-2-phenylacetyl chloride (CPAC) in the presence of an acid-binding agent. The effects of functional conditions including the molar ratio of CPAC/anhydroglucose unit (AGU), reaction time, reaction temperature, kind of acid-binding agent, and cellulose concentration on the degree of substitution (DS) were studied. The reactivities of the three hydroxyl groups in the homogeneous acylation of cellulose with CPAC were also investigated. The results showed that in homogeneous reaction medium, although all the C-6, C-3, and C-2 positions within the cellulose AGU could be substituted by CPAC, the reaction was quite selective for the C-6 OH. The successful synthesis of the cellulose-CPAC was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, XRD, and STA. Furthermore, the acylation of cellulose with CPAC decreased the thermal stability of cellulose.

Keywords: Cellulose; Homogeneous acylation; Ionic liquid; 2-chloro-2-phenylacetyl chloride; Regioselectivity

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INTRODUCTION

The high value-added utilization of glycans, which is one of the important focus areas for the development of an integrated forest products biorefinery, has been paid increasing attention due to the shortage of fossil resources and the environmental problems caused by the production and use of petrochemicals. Cellulose is the most abundant, inexpensive, biodegradable, renewable, and easily modified natural polymer in the world (Chen *et al.* 2009). By using its three hydroxyl groups as the reactive sites, cellulose can be easily converted into various high value-added products through chemical modifications such as acylation, etherification, and graft copolymerization.

The acylation of cellulose can be performed in both heterogeneous and homogeneous systems. Under heterogeneous conditions, the hydroxyl groups of the anhydro-glucose unit (AGU) have a low accessibility, and the reactions may mainly occur at the surface of the cellulose (Freire *et al.* 2006). In homogeneous medium, the three hydroxyl groups of the AGU are all accessible to the acylation agents, which can acquire a higher substitution degree (DS) and a uniform distribution of the functional groups along the polymer chain (Nagel and Heinze 2010). For example, Liu *et al.* (2009) investigated the homogeneous acylation of cellulose with succinic anhydride and acquired a succinylated cellulosic sample with a high DS of 2.31.

However, cellulose cannot dissolve in water and most common organic solvents due to its extensive intra- and inter-molecular hydrogen bonding and high crystallinity (Lan *et al.* 2011). Fortunately, the development of new solvents, such as DMAc/LiCl, N-methylmorpholine-N-oxide, DMF/N_2O_4, and ionic liquids has provided an opportunity to attempt homogeneous synthesis of cellulose derivatives (Lan *et al.* 2011). Among them, room-temperature ionic liquids (Huang *et al.* 2011; Liu *et al.* 2009; Possidonio *et al.* 2010), which are considered the most potential green solvents for the future, have been applied in the acylation modification of cellulose in recent years. Solvent ionic liquids can dissolve cellulose without reacting with it, providing a possibility for the functionalization of cellulose subsequently (Lan *et al.* 2011). A number of reports have demonstrated that the ionic liquids are excellent solvents of cellulose, especially [Bmim]Cl (Wang *et al.* 2014). A higher DS (2.72) could be obtained by using [Bmim]Cl as reaction medium for the reaction of cellulose with acetic anhydride than using 1-allyl-3-methyl imidazole chloride ([Amim]Cl) (1.86) under the same reaction conditions (Heinze *et al.* 2005).

The position of substitution has a powerful influence on the properties of cellulose derivatives such as solubility (Buchanan *et al.* 1991), crystallinity (Iwata *et al.* 1996), and thermal properties (Iwata *et al.* 1997). The three hydroxyl groups of AGU at C2, C3, and C6 positions exhibit different reaction activities. It is well known that the reaction activity of the three hydroxyl groups is in the order C6>C2>C3 for the esterification reaction owing to the lower steric hindrance of the primary OH at C-6. However, the order of reactivity for the etherification reaction is C2>C3>C6 due to the greater acidity of the OH group at C-2. The distribution of substitution groups of cellulose derivatives is also affected by reaction conditions and reagents. Huang *et al.* (2011) investigated the homogeneous acylation of sugarcane bagasse cellulose with propionic anhydride and butyric anhydride in [Amim]Cl. The results showed that the partial substitution of the synthesized cellulose acetate butyrate and cellulose acetate propionate satisfied the order of C6>C3>C2. Homogeneous acetylation of cellulose with acetic anhydride at relatively high concentration in ionic liquid also showed the reactivity order of C6-OH>C3-OH>C2-OH (Cao *et al.* 2010). However, a different partial substitution of C6>C2>C3 occurred in the homogeneous acylations of cellulose with bulky acid chlorides such as pivaloyl chloride and adamantoyl chloride in DMAc/LiCl, as reported by Xu *et al.* (2011). Furthermore, the difference of solvents also affects the distribution of substituents. The homogeneous acylation of cellulose with pivaloyl chloride in three different solvents, DMAc/LiCl, DMSO/TBAF, and [Amim]Cl under the same conditions, was also investigated by Xu *et al.* (2011). The results demonstrated that the partial DS of C6-OH accounted for 55%, 38%, and 60% of the total DS, respectively, indicating that the solvent of [Amim]Cl had a better regioselectivity for the C6 position than the two others. Therefore, it is vital to choose appropriate reaction conditions to synthetize cellulose derivatives having a certain distribution of substituents.

Recently, the ‘‘living’’/controlled radical polymerization methods such as atom transfer radical polymerization (ATRP) (Zhong *et al.* 2012) and reversible addition-fragmentation chain transfer (RAFT) polymerization (Grajales *et al.* 2012) have been used for grafting modification of cellulose due to their capability of molecular tailoring to well-defined graft polymers of predetermined molecular weight and narrow polydispersity (Roy *et al.* 2005; Chen *et al.* 2009). However, in order to graft polymer onto a cellulose backbone in a controlled manner, the synthesis of cellulose-based macro-initiators for ATRP and cellulose-based chain transfer agents for RAFT is the key process. The substituent distribution of the cellulose-based macro-initiators or chain transfer agents also is important for the evaluation of the structure of the graft modification polymer. The α-bromoisobutyryl bromide, chloroacetyl chloride, and 2-chloro-2-phenylacetyl chloride (CPAC) are the most important acylation reagents applied to react with cellulose to prepare cellulose-based macro-initiators or chain transfer agents (Chen *et al.* 2009; Hansson *et al.* 2009; Lin *et al.* 2013; Roy *et al.* 2005; Tastet *et al.* 2011; Zhong *et al.* 2012). The acylation of cellulose with α-bromoisobutyryl bromide has been widely investigated. However, the authors' search of the literature did not find any publications dealing with the detail about acylation modification of cellulose with CPAC. Furthermore, the substituent distribution along the cellulose backbone, the reaction kinetics, and the reaction conditions of cellulose with CPAC have not been illuminated. The acylation product of cellulose with CPAC, which has a benzene ring, will behave differently from α-bromoisobutyryl bromide and chloroacetyl chloride as the initiator of ATRP and the intermediate of RAFT chain transfer agent. In the present study, the hydroxyl groups of the cellulose were treated with CPAC in [Bmim]Cl to synthesize the cellulose acylate, cellulose-CPAC. Effects of reaction conditions on the DS value of cellulose-CPAC were investigated. An attempt was also made to clarify the reactivity difference between the two kinds of hydroxyl groups, primary and secondary.

EXPERIMENTAL

Materials

Cotton dissolved pulp (DP=500, cellulose content≥93%) obtained from Shandong Silver Hawk Chemical Fibre Co., Ltd. was dried in a vacuum drying oven for 24 h at 30 ^{o}C before use. 1-butyl-3-methyl chloride imidazole ([Bmim]Cl) purchased from Shanghai Chengjie Chemical Co., Ltd. was used without further purification. 2-chloro-2-phenylacetyl chloride (CPAC) and 4-dimethylaminopyridine (DMAP) were acquired from Sigma-Aldrich (Shanghai) Trading Co., Ltd. and used as received. N,N-dimethyl formamide (DMF), pyridine, and triethylamine were all analytic grade. Nitrogen was obtained from Jinan Deyang Special Gas Co., Ltd.

Dissolution of Cellulose in [Bmim]Cl

Ten grams of the ionic liquid [Bmim]Cl was weighed into a 250 mL, three-necked round bottom flask, and was heated to 80 ºC in an oil bath pan under stirring with a magnetic stir bar. After the [Bmim]Cl was molten, 0.3 g cotton dissolved pulp (1.852 mmol AGU) was added into the flask, and the mixture was continuously stirred for 2 h at 80 ºC until the pulp was completely dissolved in the [Bmim]Cl, obtaining a clear, slightly viscous cellulose solution.

The cellulose/[Bmim]Cl solution was added into deionized water and the cellulose was precipitated again. After being washed thoroughly, the regenerated cellulose was dried in a vacuum freezing drying oven for 48 h (referred to as "dissolved cellulose").

Acylation of Cellulose with CPAC in [Bmim]Cl/DMF

DMF, 10 mL, was added into the cellulose/[Bmim]Cl solution, and then the resulting cellulose solution was cooled down to 0 ºC using an ice-water bath. A required amount of CPAC dissolved in DMF (5 mL) was added dropwise into the cellulose solution via a constant pressure drop funnel under a nitrogen atmosphere. Then the acid-binding agent (pyridine, DMAP, or triethylamine) with the same moles as CPAC was added into the mixture. After the flask was sealed, the content was heated to a predetermined temperature in an oil bath pan and allowed to proceed for scheduled time under magnetic stirring. The reaction was halted by allowing the content to cool down to room temperature, and then the resulting mixture was slowly poured into deionized water with vigorous agitation. The precipitated acylation product, namely cellulose-CPAC, was then re-dissolved in DMF. After re-precipitating in deionized water and re-dissolving in DMF for two more times, the cellulose-CPAC was dialyzed for three days in deionized water, and then it was dried in a vacuum freezing drying oven for 48 h.

X-Ray Diffraction Analysis

The X-ray diffraction profiles of native cellulose, dissolved cellulose, and cellulose-CPAC were recorded using an X-ray diffractometer (D8-Advance, Germany Bruker AXS Corporation). Ni-filtered Cu Kα radiation (λ=0.1542 nm) generated at a voltage of 40 kV and a current of 40 mA was utilized, and a scan speed of 1-2°/min from 5° to 50° was used.

FT-IR

FT-IR spectra of native cellulose, dissolved cellulose, and cellulose-CPAC were recorded using an IRPrestige-21 FT-IR spectrophotometer. The samples were pressed into pellets with KBr before measuring. The spectra were collected at a resolution of 2 cm^{-1}, in the range of 500 to 4000 cm^{-1}.

^{1}H NMR and ^{13}C NMR Analysis

^{1}H NMR of the cellulose-CPAC was recorded on an AVANCE Ⅱ 400 spectrometer at room temperature in DMSO-*d6*. The DS value of the cellulose-CPAC was determined by the ratio of the integrals of the cellulose backbone protons and the protons of benzene ring. The DS of the cellulose-CPAC is calculated by Eq. (1) according to the method of Goodlett *et al.* (1971),

$$\mathrm{DS} = \frac{7\times S_1}{5\times S_2} \tag{1}$$

where S_1 is the integral of the resonances in the range of 7.0 to 8.0 ppm of the protons of the benzene ring, and S_2 is the integral of the resonances in the range of 3.0 to 6.0 ppm of the protons of AGU.

The ^{13}C NMR spectrum of the cellulose-CPAC was recorded on the spectrometer with a minimum of 5000 scans in DMSO-d6, a sample concentration of 60 $g\cdot L^{-1}$, a sweep width of 80 KHz, and a delay time of 3 s. The distribution of acyl groups among the three hydroxyl groups of the AGU was determined according to the method of Kamide and Okajima (1981). The total DS values were calculated according to Eq. 1, and the partial DS values were calculated based on the ratio of the integrals of the three carbonyl carbons at 167.5 ppm, 166.9 ppm, and 166.5 ppm in the ^{13}C NMR spectrum, respectively. The DS_{C6}, DS_{C3}, and DS_{C2} of the cellulose-CPAC were calculated using the following formulas,

$$\mathrm{DS_{C6}} = \frac{DS_{Total}\times S_{C6}}{S} \qquad \mathrm{DS_{C3}} = \frac{DS_{Total}\times S_{C3}}{S}$$

$$\mathrm{DS_{C2}} = \frac{DS_{Total}\times S_{C2}}{S} \qquad \mathrm{S} = S_{C6} + S_{C3} + S_{C2} \tag{2}$$

where DS_{C6}, DS_{C3}, and DS_{C2} are the DS of corresponding carbon atoms, DS_{Total} is the DS of the cellulose-CPAC calculated via ^{1}H NMR spectroscopy, and S_{C6}, S_{C3}, and S_{C2} are the integrals of the resonances of the peaks at 167.5 ppm, 166.9 ppm, and 166.5 ppm, respectively.

Simultaneous Thermal Analysis (STA)

A STA instrument SDTQ 600 STA was employed for simultaneous thermal analysis of native cellulose, dissolved cellulose, and cellulose-CPAC. The samples were heated from room temperature to 600 ºC at a heating rate of 10 ºC/min under a nitrogen atmosphere. The TA universal analysis software was used for dealing with the TG curves. The samples were all dried at 30 ºC for 24 h in vacuum drying oven prior to STA measurements.

RESULTS AND DISCUSSION

The synthesis route of cellulose-CPAC is shown in Fig. 1. [Bmim]Cl was chosen as the non-derivatizing solvent of cellulose and reaction medium of homogeneous acylation of cellulose with CPAC. Table 1 gives the effects of various conditions such as the molar equivalent of CPAC per AGU, reaction temperature, reaction time, kind of acid-binding agent, and cellulose concentration on the DS values of cellulose-CPAC.

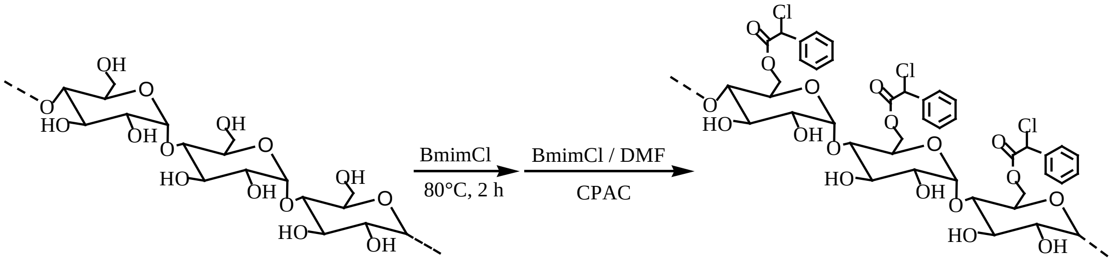


Fig. 1. Reaction scheme for the synthesis of cellulose-CPAC in [Bmim]Cl

Effects of Reaction Conditions on the DS of Cellulose-CPAC

The DS of cellulose-CPAC *versus* reaction time is illustrated in Table 1. The reaction was conducted at 35 °C with a molar ratio of 6:1 (CPAC/AGU). It is apparent that the DS of cellulose-CPAC increased with the reaction time, meaning that the extent of acylation increased appreciably with the reaction time. Moreover, only 4 h was needed to reach a DS value of 0.714, and the DS value was 0.734 at 8 h, meaning that most of the acylation reactions occurred in the first four hours due to higher collision probability, and then the acylation rate decreased markedly. Note that the DS of cellulose-CPAC was somewhat lower when the reaction time reached 36 h. Side effects might happen if the reaction time was too long, leading to the decline of the DS value. This may be due to the fact that an increasing number of HCl would be generated and the concentration of acid-binding agent would become smaller and smaller with the extension of reaction time, which probably led to the hydrolysis of a fraction of ester groups and the decreasing of DS.

As shown in Table 1, DS values of cellulose-CPAC ranging from 0.113 to 1.114 were acquired depending on the molar ratio of CPAC/AGU. At a molar ratio of 3:1, a low DS of 0.113 was attained with a reaction time of 24 h at 35°C, whereas a high DS of 1.114 was attained when the molar ratio of CPAC/AGU was 6:1, indicating that the DS of the cellulose derivatives can easily be adjusted by the molar ratio of the CPAC to the AGU. In order to prepare modified cellulose with a high DS, CPAC should be employed in large excess. The collision probability of CPAC with -OH in AGU increased with an increasing amount of CPAC, which increased the reaction probability resulting in higher DS of cellulose-CPAC. Compared with the results reported by Roy *et al.* (2005), in which a DS of 1.1 was obtained under the reaction conditions of CPAC/AGU molar ratio of 9:1, reaction temperature of 60 °C, and reaction time of 24 h using tetrahydrofuran (THF) as the reaction medium, the reaction had a higher activity in the homogeneous medium than in the heterogeneous medium.

Table 1 also shows the effect of temperature on the DS value of cellulose-CPAC. The DS values of 0.807, 1.114, and 0.795 were obtained when the reaction temperature was 25 ^{o}C, 35 ^{o}C, and 45 ^{o}C, respectively. This means that the acylation of cellulose with CPAC was more rapid at an appropriate temperature, and both lower and higher temperatures were unfavorable to the reaction. The high temperature can quicken the molecular motion of reactants and accelerate the reaction rate. However, the acylation reaction was an exothermic reaction, and the 2-chloro-2-phenylacetyl chloride is extremely unstable at high temperature. The decomposition of a small amount of 2-chloro-2-phenylacetyl chloride might occur at higher temperature, leading to a lower DS value. Based on these findings, the desirable temperature for the reaction was judged to be 35 ^{o}C.

Table 1. Reaction Conditions and Results of the Homogeneous Reaction of Cellulose with CPAC

Sample	Temperature (^{o}C)	Time (h)	Molar ratio[a]	Concentration[b] (%)	Acid-binding agent	DS
1	35	24	3.0: 1	3	pyridine	0.113
2	35	24	4.5: 1	3	pyridine	0.300
3	35	24	6.0: 1	3	pyridine	1.114
4	25	24	6.0: 1	3	pyridine	0.807
5	45	24	6.0: 1	3	pyridine	0.795
6	35	4	6.0: 1	3	pyridine	0.714
7	35	8	6.0: 1	3	pyridine	0.734
8	35	12	6.0: 1	3	pyridine	1.052
9	35	36	6.0: 1	3	pyridine	0.865
10	35	12	6.0: 1	3	triethylamine	0.432
11	35	12	6.0: 1	3	DMAP	0.360
12	35	12	6.0: 1	1	pyridine	0.359
13	35	12	6.0: 1	2	pyridine	0.516

[a]Molar ratio refers to Mol CPAC per mol AGU, [b]The concentration refers to the mass ratio of cellulose and [Bmim]Cl

The DS value of cellulose-CPAC gradually increased with the increase of cellulose concentration, as can be seen in Table 1, demonstrating that the reaction concentration had a significant effect on the reaction rate. The high reaction concentration can increase the collision probability of the acylation reagent CPAC with -OH, consequently improving the reaction efficiency and increasing the DS of the resulted cellulose-CPAC.

When the hydroxyl groups of AGU reacted with CPAC, HCl would be generated. Therefore, it is indispensable to add the acid-binding agent in the reaction process, which could promote the reaction and shorten the reaction time. In this study, three kinds of acid-binding agents *i.e.* pyridine, triethylamine, and DMAP were adopted. As can be seen from Table 1, the highest DS (1.052) was obtained when employing the pyridine as the acid-binding agent. The DS value of cellulose-CPAC was much lower when triethylamine or DMAP was used as acid-binding agent under the same molar ratio (1:2:2) of cellulose hydroxyl group, CPAC, and acid-binding agent.

XRD Analysis

The XRD spectra of native cellulose, dissolved cellulose, and cellulose-CPAC are shown in Fig. 2. As can be seen, the diffraction curve of the native cellulose exhibited strong characteristic peaks at around 15°, 17°, and 22.5°, and a weak characteristic peak at about 34.7°, coincident with the structure of cellulose I. By contrast, the diffraction curve of dissolved cellulose only had a small peak at around 19.8° and the crystallization peak at around 22.5° had almost disappeared, meaning that most of the crystalline structure of cellulose had been destroyed. The breakage of intra- and inter-molecular hydrogen bonds within the cellulose significantly improved the accessibility of acylation reagent with -OH of the AGU subsequently. As expected, the degree of crystallinity of cellulose-CPAC had completely disappeared after acylation reaction of cellulose with CPAC.

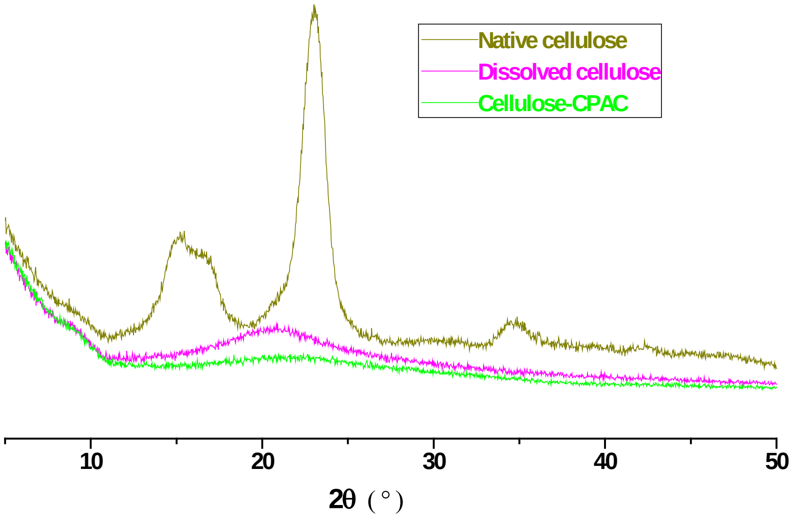


Fig. 2. XRD spectra of the native cellulose, dissolved cellulose, and cellulose-CPAC

FT-IR Analysis

Figure 3 compares the FT-IR spectra of cellulose before (a, b) and after (c, d, e, and f) the acylation process. Comparing the spectra of native cellulose (a) and dissolved cellulose (b), the absorption peaks in the two spectra were rather similar, indicating that the chemical structure of cellulose had not been changed in the process of dissolving in [Bmim]Cl. A similar result was reported by Lan *et al.* (2011), who reported that [Bmim]Cl acted as a direct solvent of cellulose and that no derivatization reaction occurred during dissolution.

The absorption bands at 1755 cm^{-1} in the infrared spectra of the cellulose-CPAC (c, d, e, and f) correspond to the stretching vibration of C=O in carboxyl groups. It is notable that these absorption bands were absent in the cases of the infrared spectra of the native cellulose (a) and the dissolved cellulose (b), indicating that the carboxyl groups are introduced into the cellulose in the course of the acylation modification with CPAC. Furthermore, the introduction of the stretching vibration absorption peak of C=C near 1500 cm^{-1}, which is the characteristic absorption peak of benzene ring and the stretching vibration absorption peak of C-Cl at 730 cm^{-1} in the spectra of cellulose-CPAC, demonstrates the successful formation of the cellulose-CPAC.

Comparing the FT-IR spectra of (c), (d), (e), and (f), the intensity of the absorption bands of C=O in carboxyl groups at 1755 cm^{-1} increased successively, which corresponded well with the increase of DS. Note that the intensity of the absorption bands of -OH at 3440 cm^{-1} were significantly reduced as the intensity of C=O was increased, indicating that a growing number of hydroxyl groups had been substituted by the acylation reagents.

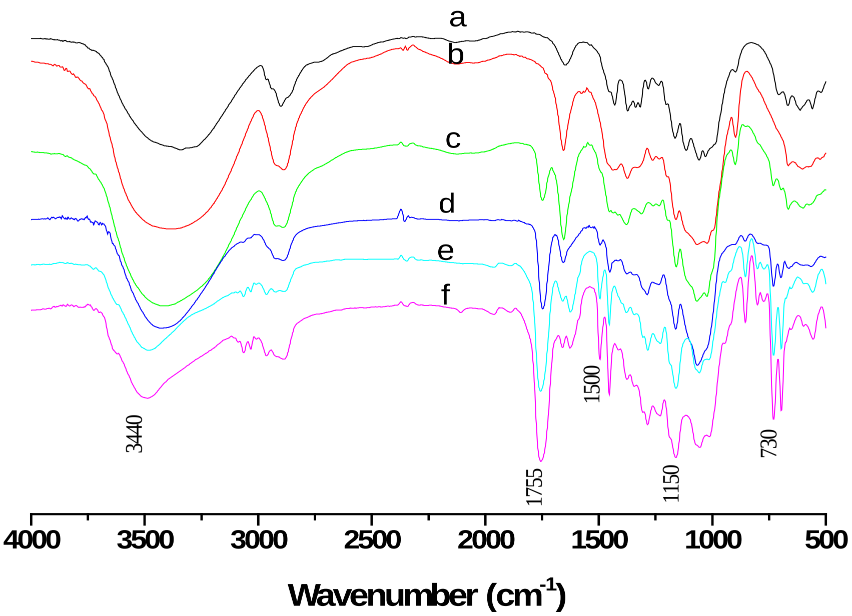


Fig. 3. FT-IR spectra of samples: (a), native cellulose; (b), dissolved cellulose; (c), (d), (e), and (f), cellulose-CPAC with the DS of 0.113 (sample 1), 0.359 (sample 12), 0.807 (sample 4), and 1.114 (sample 3), respectively

^{1}H NMR and ^{13}C NMR Analysis

The ^{1}H NMR spectrum of the cellulose-CPAC in DMSO-*d6* is shown in Fig. 4. The chemical shift in the range of 3.0 to 6.0 ppm (b, except H_2O) is attributed to the protons of the AGU. An obvious peak whose chemical shift was in the range of 7.0 to 8.0 ppm (a) should be ascribed to the protons of the benzene ring. This also demonstrates the successful substitution of OH groups on the cellulose backbone by CPAC.

Further confirmation was also obtained from ^{13}C NMR spectroscopy, and the full-range ^{13}C NMR spectrum of the cellulose-CPAC is shown in Fig. 5 (A). There are four main types of chemical shift of carbon atoms. The resonance peaks in the range of 60 to 110 ppm (b) are ascribed to the carbon atoms of the AGU. The shift δ 170 ppm (c) is assigned to the signals of the carbonyl carbon region. The chemical shift at 58 ppm (d) is attributed to the carbon atom adjacent to carbonyl group. Values of δ in the range 120 to140 ppm (a) are the typical chemical shifts of carbon atoms of benzene ring, of which peaks at 136.5 ppm (a_1), 129.9 ppm (a_2), 129.0 ppm (a_3), and 127.9 ppm (a_4) are ascribed to the four kinds of carbon atoms in the benzene ring, respectively.

In the AGU carbon region, the peaks at 102.4 ppm (b_1), 79.0 ppm (b_4), and 64.0 ppm (b_6) are attributed to C1, C4, and C6 carbons, respectively. The resonance peaks of C2, C3, and C5 carbons heavily overlap (Huang *et al.* 2011) and give only a strong cluster around 71.8 ppm.

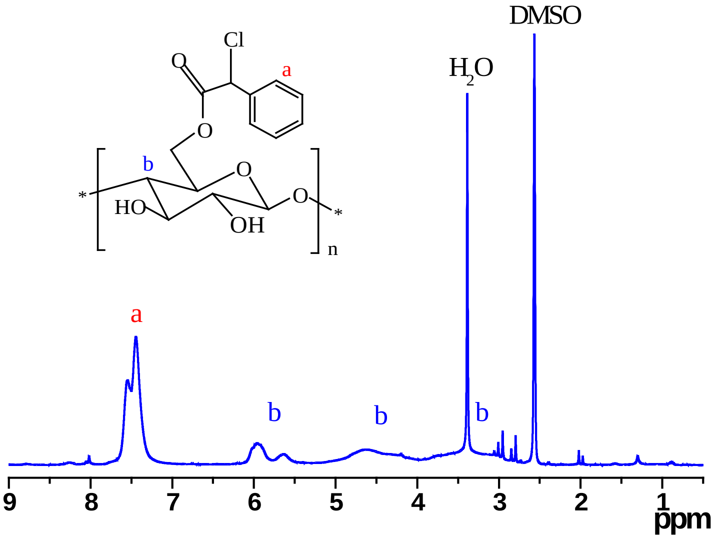
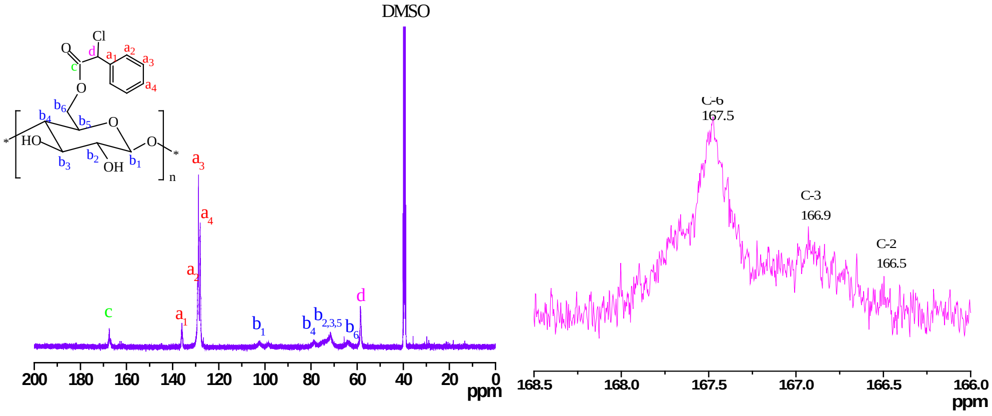


Fig. 4. ^{1}H NMR spectrum of cellulose-CPAC in DMSO-*d6*



(A) (B)

Fig. 5. ^{13}C NMR spectra of cellulose-CPAC (A) and the carbonyl carbon region (B)

The expanded carbonyl region spectrum of cellulose-CPAC is shown in Fig. 5 (B). The absorption peaks at 167.5 ppm, 166.9 ppm, and 166.5 ppm are attributed to the signals of C-6, C-3, and C-2 substitution groups, respectively. The partial DS values of the acyl moiety among the three OH groups are calculated from the integration of the carbonyl carbon area of the ^{13}C NMR spectrum, and the results are presented in Table 2.

Table 2. Distribution of the Acyl Groups among C-6, C-3, and C-2 of the Cellulose-CPAC

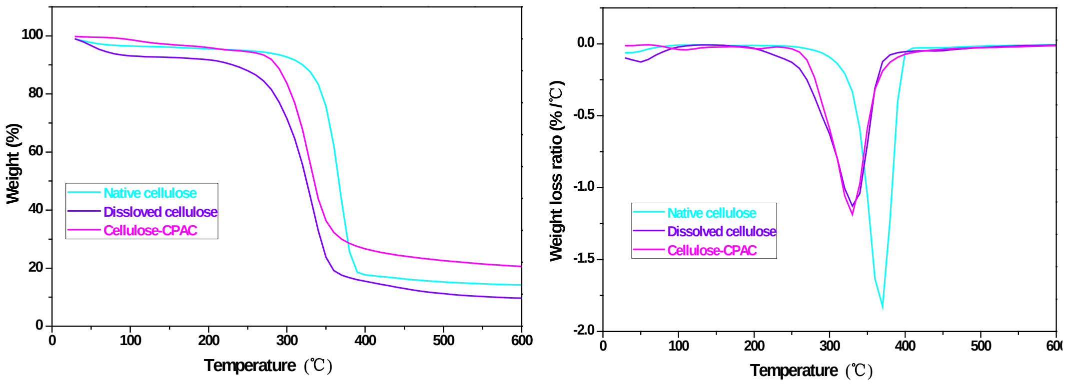
Sample	DS_{Total}	DS_{C6}	P_{C6} (%)	DS_{C3}	P_{C3} (%)	DS_{C2}	P_{C2} (%)
13	0.516	0.487	94.38	0.024	4.65	0.005	0.97
4	0.807	0.708	87.73	0.070	8.67	0.029	3.59
8	1.052	0.711	67.58	0.206	19.58	0.135	12.83
3	1.114	0.723	64.90	0.246	22.08	0.145	13.02

DS_{Total} refers to the DS of cellulose-CPAC determined by ^{1}H NMR spectroscopy, DS_{C6}, DS_{C3}, and DS_{C2} refer to the DS of corresponding carbon atom, P_{C6}, P_{C3}, P_{C2} refer to the percentage of DS of corresponding carbon atom

For sample 3 with DS equal to 1.114, the partial DS at O-6 was 0.723 while the DS at O-3 was 0.246 and the DS at O-2 was 0.145, revealing that the three hydroxyl groups at C2, C3, and C6 position exhibited different reaction activities. With regard to sample 13 with DS of 0.516, the partial DS at C-6, C-3, and C-2 were 0.487, 0.024, and 0.005, respectively, which also satisfied the order of reaction activity of C_6-OH>C_3-OH>C_2-OH. Furthermore, the other two samples exhibited the same trends, indicating that the CPAC is strongly inclined to react with primary hydroxyl groups, and the reaction activity of the C-2 hydroxyl groups is much lower than that of the C-3 hydroxyl groups. This is in good agreement with the results of Huang *et al.* (2011), who found that the reaction activity of the three hydroxyl groups satisfied the order of C6>C3>C2 when preparing cellulose derivatives via homogeneous reaction. In addition, the partial DS of the three OH groups all increased with the increasing of the total DS, illustrating that the three OH groups competed with each other to react with CPAC. However, at the beginning of the acylation, the reaction occurred almost exclusively at C6-OH, the acylation reaction began to occur at C3-OH and C2-OH only when the majority of primary hydroxyl groups had been substituted. The highest reactivity of the primary OH at C-6 may be attributed to its lower steric hindrance.

Thermal Analysis

The decomposition pattern and thermal stability of the native cellulose, dissolved cellulose, and cellulose-CPAC were evaluated using thermogravimetry (TG) and derivative thermogravimetry (DTG). Figure 6 shows the TG (a) and DTG (b) curves of the three samples, and their thermostability data are summarized in Table 3.



(a) (b)

Fig. 6. Thermogravimetry curves (a) and derivative thermogravimetry curves (b) of the native cellulose, dissolved cellulose, and cellulose-CPAC

Table 3. Thermostability of the Native Cellulose, Dissolved Cellulose, and Cellulose-CPAC

Sample	T_{di} (°C)	T_{dm} (°C)	T_{df} (°C)	residual mass (wt%)
Native cellulose	245	369	408	14.46
Dissolved cellulose	187	330	388	9.96
Cellulose-CPAC	239	331	400	20.83

The initial decomposition temperature, T_{di}, is the temperature at which the decomposition rate results in a significant weight loss; The maximum decomposition temperature, T_{dm}, is the temperature at which the highest decomposition rate is observed for the corresponding pattern; The final decomposition temperatures, T_{df}, corresponds to maximal decomposition of the sample

As can be seen, the native cellulose started to decompose at 245 °C, and its maximum decomposition temperature was 369 °C. Compared to the native cellulose, all the initial decomposition temperature (T_{di}), maximum decomposition temperatures (T_{dm}), and final decomposition temperatures (T_{df}) of dissolved cellulose decrease, indicating that the thermostability of cellulose decreases after dissolving in [Bmim]Cl, which is similar with the result reported by Lan *et al.* (2011). The decreasing of thermostability also indicates the breakage of intra- and inter-molecular hydrogen bonds in the dissolving process. The breakage of a large number of hydrogen bonds in the cellulose chain gives the chains more mobility under the thermal condition, which is similar with the results reported by Cao *et al.* (2010).

All the T_{di}, T_{dm}, and T_{df} values of the cellulose-CPAC were higher than that of the dissolved cellulose, but were lower than that of the native cellulose. This indicates that the thermal stability of cellulose was slightly decreased due to the introduction of the acyl group. Although the dissolution of cellulose can cause the decreasing of the thermostability, the introduction of CPAC which has a rigid benzene ring can improve the thermostability of cellulose-CPAC.

In addition, the residual masses above 600 °C are 14.46% for the native cellulose, 9.96% for the dissolved cellulose, and 20.83% for the cellulose-CPAC. The pyrolysis residues are primarily indecomposable inorganic salts (Lan *et al.* 2011). The higher pyrolysis residue of cellulose-CPAC indicates that more inorganic salts were incorporated into the cellulose derivative after acylation in ionic liquid.

CONCLUSIONS

1. The cellulose-CPAC can be produced by homogeneous acylation of cellulose with excess of 2-chloro-2-phenyl acetyl chloride (CPAC) in the presence of an acid-binding agent. The DS value can be controlled effectively by adjusting the reaction time, temperature, and the molar ratio of CPAC to AGU. The functionalization condition to achieve a high DS was: reaction temperature of 35 °C, reaction time of 24 h, molar ratio of 6:1 (CPAC/AGU), and reaction concentration of 3%, using pyridine as the acid-binding agent.
2. The reaction activity of the three hydroxyl groups was C6>C3>C2 in this homogeneous reaction system. At the beginning of the acylation, the reaction occurred mainly at the C_6-OH. When the majority of primary hydroxyl groups had been substituted, the C_3-OH and the C_2-OH began to react with CPAC. The acylation of cellulose with CPAC decreased the thermal stability of cellulose.

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