Effect of the Molecular Structure of Acylating Agents on the Regioselectivity of Cellulosic Hydroxyl Groups in Ionic Liquid

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Homogeneous functionalization of cellulose with chloroacetyl chloride (CAC), 2-bromoisobutyryl bromide (BrBiB), and 2-chloro-2-phenylacetyl chloride (CPAC) was performed in ionic liquid to evaluate the effect of the molecular structure of the reagents on the reactivity of the cellulosic hydroxyl groups. The results showed that the reaction was very selective for the less hindered C6-OH group, but the substitution of the secondary OH group still occurred, which indicated that the acylation of cellulose was only partly regioselective. The reaction extent and regioselectivity of the cellulosic hydroxyl groups partly depended on the molecular structure of the acylating agents. The reaction rate of the CAC was much faster than the relatively bulky BrBiB and CPAC, but the bulky acylating agents showed a higher C6-OH selectivity. Moreover, the BrBiB was less reactive than the CPAC, although they showed the same regioselectivity for the three hydroxyl groups. The acylation decreased the thermal stability of the cellulose, which decreased further as the bulk of the substituted groups increased.

Keywords: Cellulose; Homogeneous acylation; Regioselectivity; Cellulose-based macroinitiator; Ionic liquid

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INTRODUCTION

The chemical modification of cellulose, which is the major constituent of all plants, *via* reaction of the hydroxyl groups is the main method to generate the required application properties for biodegradable materials. In recent decades, with the clear understanding of the structure-property relationships, researchers have applied great effort toward the synthesis of regioselectively acylated cellulose derivatives (Zhang *et al*. 2009; Xu *et al*. 2012). Their physical, chemical, and biochemical properties are influenced not only by the degree of substitution (DS), but also by the position of the substitution and the distribution of the functional substituent groups in the anhydroglucose units (AGU) (Martin *et al*. 1999; Heinze *et al*. 2003; Xu *et al*. 2011; Fox and Edgar 2011; Ramos *et al*. 2011; Chen *et al*. 2014). However, the control of regiochemistry in the synthesis of cellulose-based materials is one of the most significant scientific challenges. Because there is not enough reactivity difference between the three hydroxyl groups, particularly between the C2-OH and C3-OH groups, the regioselective acylation of cellulose is extremely difficult (Xu *et al*. 2012). Consequently, the relative reactivity of the three hydroxyl groups in each repeating unit has been conducted with more and more detailed inspections (Martin *et al*. 1999; Fox *et al*.

2011).

Because of the relatively low steric hindrance of the primary hydroxyl groups at C6 and the relatively high acidity of the hydroxyl groups at C2 (Fox *et al*. 2011; Xu *et al*. 2011), the inherent reactivity of the three hydroxyl groups at the cellulose backbone is indeed different (Wu *et al*. 2004; Zhang *et al*. 2009). Regarding the reaction selectivity between the cellulosic hydroxyl groups, the derivatization of cellulose occurs preferentially at the primary hydroxyl groups (Zhang *et al*. 2009; Nagel and Heinze 2010). From esterification studies, it has been found that the C6-OH group can react ten times faster than the other groups. In etherification reactions, the C2-OH group has been observed to react twice as fast as the C3-OH group (Roy *et al*. 2009). Based on the different reactivities of the three OH groups, a common strategy to synthesize task-specific regioselectively acylated cellulose derivatives is first protecting the primary hydroxyl group at the C6 position, and then subsequently de-protecting the C6-OH group after derivatization of the secondary hydroxyl groups with stable functionalities occurs (Fox *et al*. 2011; Gericke *et al*. 2012).

The DS values of the cellulose derivatives depend on the nature of the reactants, such as the chain length of the acylating agents (Freire *et al*. 2006; Possidonio *et al*. 2009; Nagel and Heinze 2010; Uschanov *et al*. 2011). The efficiency of the cellulose esterification decreases as the chain length of the anhydrides increases (Liu *et al*. 2009). Uschanov *et al*. (2011) found that a longer fatty acid chain length and increased double bond content decreased the reactivity between the cellulose and fatty acid. The low reactivity of cellulose with vinyl esters with long aliphatic chains is due to their stronger steric hindrance effect (Cao *et al*. 2014). Nawaz *et al*. (2012) concluded that the DS values of the cellulose esters depended on the carbon atoms of the acyl group of the derivatizing agent because of a complex dependence of the activation enthalpy and entropy terms on the structural variable. Moreover, according to Dicke (2004), the formation of regioselective derivatives only succeeds by reaction with bulky groups, which primarily react with sterically favored hydroxyl groups. Zhang *et al*. (2009) synthesized regioselectively substituted mixed cellulose esters under homogeneous conditions and found that the benzoylation reaction was exclusively preferred at C6-OH; the order of reactivity was as follows: C6-OH >> C2-OH > C3-OH.

The relative distribution of the substituent between positions C6, C3, and C2 also depends on the reaction conditions. The advent of modern cellulose solvents that guarantee the equal accessibility among the OH groups in the amorphous and crystalline regions leads to the homogeneous functionalization of cellulose. Thus, better control of the DS values and a uniform distribution of the functional groups along the polymer chain are possible (Nagel and Heinze 2010). Moreover, controlled substitution along the biopolymer backbone can be achieved in a homogeneous reaction system (Possidonio *et al*. 2009; Fox *et al*. 2011; Nawaz *et al*. 2012). The OH group at position C6 is the most reactive under homogeneous conditions because it is sterically less hindered compared to the secondary OH groups at positions C2 and C3 (Ramos *et al*. 2005). Homogeneous acylation of sisal cellulose in dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride trihydrate (TBAF) showed the following distribution order for the acetyl groups: C6 > C2 > C3 (Ciacco *et al*. 2003). However, in most cases, the substituent distribution of the homogeneously synthesized cellulose derivatives occurs in the following order: C6 > C3 > C2 (Huang *et al*. 2011; Chen *et al*. 2014). Furthermore, the degree of aggregation of cellulose chains under homogeneous reaction conditions is influenced by the reaction medium and

influences the distribution of the functional groups (Ramos *et al*. 2005). Xu *et al*. (2011) compared the effect the reaction conditions had on the substitution of cellulose and found that DMAc/LiCl and [Amim]Cl were more useful than DMSO/TBAF for cellulose esterification with bulky acyl chlorides. The esterification showed a higher regioselectivity when DMAc/LiCl was used than in other systems.

Efficient and novel synthesis paths for the functionalization of cellulose have appeared over the past few decades. Graft copolymerization of vinyl monomers onto a cellulose backbone using the "living/control" radical polymerization technique has attracted the interest of many researchers. It is possible to produce macromolecules with various architectures and well-defined structures using atom transfer radical polymerization (ATRP) or reversible addition-fragmentation chain transfer polymerization (RAFT), in which introducing the necessary initiator sites is a very important step (Roy *et al*. 2005; Ifuku and Kadla 2008; Eichhorn *et al*. 2010; Moghaddam *et al*. 2014). Cellulose-based macroinitiators with carbon halide-type active sites resulting from the acylation of cellulose constitute a class of valuable polyfunctional macroinitiators that can lead to discovering new cellulose-based graft copolymers. By controlling the DS values of the macroinitiators, it is possible to control the grafting density of the final copolymer chains (Eichhorn *et al*. 2010). Furthermore, the cellulose-based macroinitiator with a controlled distribution of substituents is promising and allows for the design of novel cellulose graft copolymers with defined structures by ATRP polymerization (Ifuku and Kadla 2008). Chloroacetyl chloride (CAC), 2-bromoisobutyryl bromide (BrBiB), and 2-chloro-2-phenylacetyl chloride (CPAC) have been widely used as acylating agents for preparing the cellulose-based macroinitiators utilized to produce cellulose graft copolymers (Roy *et al*. 2005; Ifuku and Kadla 2008; Lin *et al*. 2009; Meng *et al*. 2009; Hiltunen *et al*. 2011; Gericke *et al.* 2012). Unfortunately, there is no information on the kinetics and activation parameters of these reactions, and also, no systematic study of the regioselectivity of the reaction of cellulose has been published. Moreover, until now, only little about how to accomplish regioselective substitution of cellulose, the most abundant, eco-friendly, renewable, and useful natural polymer, has been elucidated (Xu *et al*. 2011).

In the present paper, CAC, BrBiB, and CPAC were selected as acylating agents to react with cellulose in the ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) to investigate the relative reactivity of cellulosic hydroxyl groups at the C2, C3, and C6 positions. The aim of this work was to clarify the effect of the molecular structure of the acylating agents on the accessibilities and reactivities of the three cellulosic hydroxyl groups in the homogeneous system.

EXPERIMENTAL

Materials

Cotton dissolving pulp (DP = 500, cellulose content ≥ 93%), kindly donated by Shandong Silver Hawk Chemical Fibre Co., Ltd. (Weifang, China), was dried under reduced pressure for 12 h at 45 °C prior to use. The [Bmim]Cl and BrBiB were purchased from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China) and used without further purification. The CPAC was acquired from Sigma-Aldrich (Shanghai) Trading Co., Ltd. (Shanghai, China) and was used as received. The CAC, *N, N*-dimethylformamide (DMF), and pyridine were of analytical grade.

Methods

Acylation of cellulose in [Bmim]Cl/DMF

A 33.0 g sample of the [Bmim]Cl was weighed and put into a 250-mL three-necked round-bottom flask, which was then heated to 80 °C using an oil bath under magnetic stirring. After the [Bmim]Cl was molten, 1.0 g of cotton dissolving pulp (6.17 mmol AGU) was added, and the mixture was continuously stirred for an additional 2 h at 80 °C until the pulp was completely dissolved and a clear, slightly viscous, homogeneous cellulose solution was obtained.

To the cellulose solution, 15 mL of DMF was added, and then the resulting solution was cooled down to 0 °C using an ice-water bath. For a typical conversion, 4.18 g of the CAC (or 8.52 g of the BrBiB, or 7.0 g of the CPAC) previously dissolved in 15 mL of DMF was slowly dropped into the solution *via* a constant pressure drop funnel under a nitrogen atmosphere. Then, the pyridine with the same number of mol as the acylating reagent was added to the mixture. After the flask was sealed, the reaction mixture was heated to 35 °C in an oil bath to react for a set length of time with magnetic stirring. The resulting mixture was then slowly poured into deionized water while being vigorously stirred. The precipitated white or yellow products were the cellulose-based macroinitiators (namely, cellulose-CAC, cellulose-BiB, or cellulose-CPAC), which were then re-dissolved in DMF. After re-precipitating in deionized water and re-dissolving in DMF two more times, the cellulose-based macroinitiators were dialyzed for 3 d in deionized water and then dried in a vacuum freezing drying oven for 48 h.

FT-IR analysis

The Fourier transform infrared (FT-IR) spectra of the cellulose-based macroinitiators and unmodified cellulose were recorded with an FT-IR spectrophotometer (IRPrestige-21, Shimadzu, Kyoto, Japan) using the KBr pellet technique. The spectra were collected at a resolution of 2 cm^{-1}, in the range of 4000 to 500 cm^{-1}.

^{1}H NMR analysis

The ^{1}H nuclear magnetic resonance (NMR) spectra of the cellulose-based macroinitiators were recorded on an AVANCE II 400 spectrometer (Bruker, Karlsruhe, Germany) in DMSO-d6 at room temperature. The DS values of the cellulose-based macroinitiators were calculated from the integration ratios of the proton resonances of the acyl moieties to those of the cellulose backbone hydrogens (Xu *et al*. 2011), according to the method of Goodlett *et al*. (1971).

^{13}C NMR analysis

The ^{13}C nuclear magnetic resonance (NMR) spectra of the cellulose-based macroinitiators were recorded on the AVANCE II 400 spectrometer in DMSO-d6 with a minimum of 5000 scans, a sample concentration of 40 mg/mL, a sweep width of 80 kHz, and a delay time of 3 s. The distribution of the acyl moieties among the three OH groups of the AGU was calculated from the ^{13}C NMR spectrum by integrating the C=O peaks of the cellulose-based macroinitiators (Wang *et al*. 2014), according to the method of Kamide and Okajima (1981). The chemical shifts employed for C=O were 166.12 ppm (C2), 166.35 ppm (C3), and 166.93 ppm (C6) for cellulose-CAC; 169.19 ppm (C2), 169.43 ppm (C3), and 170.23 ppm (C6) for cellulose-BiB; and 166.61 ppm (C2), 166.83 ppm (C3), and 167.46 ppm (C6) for cellulose-CPAC.

Thermal analysis

The cellulose-based macroinitiators and unmodified cellulose were dried at room temperature for 24 h in a vacuum drying oven. Thermal gravimetric analysis (TGA) measurements were carried out using a TA Instruments TGA Q50 (New Castle, USA) to determine the decomposition temperature (T_d) of the prepared samples. The samples were measured under nitrogen atmosphere with a temperature increase rate of 10 °C/min from ambient temperature to 600 °C. The differential scanning calorimetry (DSC) analysis of the samples was performed on a TA Instruments DSC Q20 under nitrogen atmosphere. Approximately 3 mg of the sample was first heated from ambient temperature to 110 °C at a heating rate of 10 °C/min and was then immediately cooled to -50 °C. Subsequently, the sample was heated from -50 to 400 °C at a heating rate of 10 °C/min. The thermal behavior was analyzed based on the second heating traces.

RESULTS AND DISCUSSION

The cellulose from the cotton dissolving pulp was used as the starting material to prepare a series of polyfunctional macroinitiators, and acylating agents with different structures were employed. Figure 1 demonstrates the synthesis pathway for the cellulose-based macroinitiators in a homogeneous system. The cellulose was first dissolved in the ionic liquid [Bmim]Cl and then reacted with CAC, BrBiB, or CPAC. To understand the influence of the molecular structure of the acylating agents on the reactivities of the three cellulosic hydroxyl groups, the reaction was carried out under the same experimental conditions of 100% molar excess of acylating agents and a reaction temperature of 35 °C, using pyridine as the acid acceptor. The reaction products, cellulose-CAC, cellulose-BiB, and cellulose-CPAC, were characterized by FT-IR, and ^{1}H and ^{13}C NMR spectroscopies.

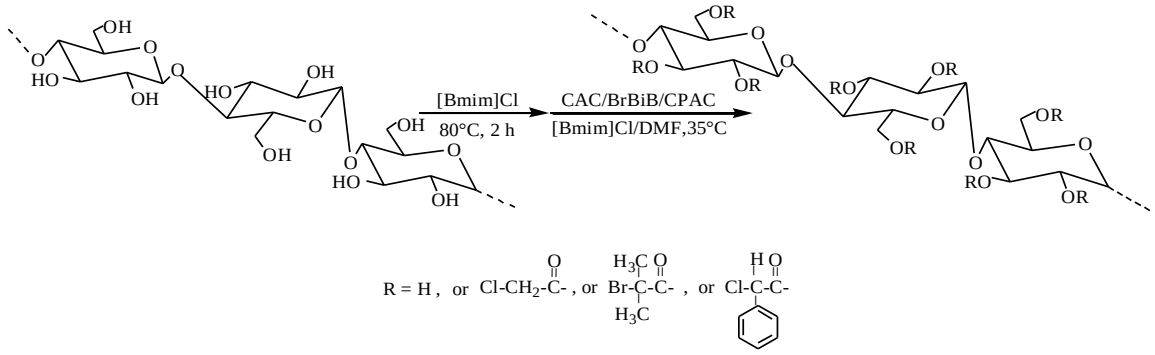


Fig. 1. Reaction scheme for the synthesis of cellulose-CAC, cellulose-BiB, or cellulose-CPAC in [Bmim]Cl/DMF

Structure Analysis

Typical examples of the FT-IR spectra of the unmodified cellulose and cellulose-based macroinitiators are shown in Fig. 2A. After comparing the FT-IR spectra of the cellulose-CAC (b), cellulose-BiB (c), and cellulose-CPAC (d), with that of the unmodified cellulose (a), the appearance of new strong absorption bands at 1756 cm^{-1} related to ester carbonyl groups (C=O) gave a clear-cut confirmation of the acylation of the cellulose (Ifuku and Kadla 2008). Moreover, by chloroacetylation of the OH groups, the peak related to the C-Cl bond was observable at 790 cm^{-1} in the spectrum for the cellulose-CAC (b)

(Martin *et al*. 1999). The stretching vibration band of the C-Br group in the 2-bromoisobutyryl moiety appeared at 664 cm^{-1} in the spectrum of the cellulose-BiB (c). An additional signal at 763 cm^{-1} indicated the presence of C-Cl in the cellulose-BiB, which was explained by the partial replacement of the bromide moieties by the chlorine anions from the solvent in a nucleophilic substitution reaction (Hufendiek *et al*. 2014). In the cellulose-CPAC spectrum (d), the presence of a peak at 3070 cm^{-1} for the benzene ring C-H stretching (Zhang *et al*. 2009) and the stretching vibration absorption peak of C-Cl at 730 cm^{-1} provided clear evidence of the introduction of 2-chloro-2-phenylacetyl moiety in the cellulose-CPAC. In addition, the shift of the peaks corresponding to the hydroxyl groups of cellulose from 3340 to around 3460 cm^{-1} and the decrease of these broad band intensities were additional proof of successful acylation.

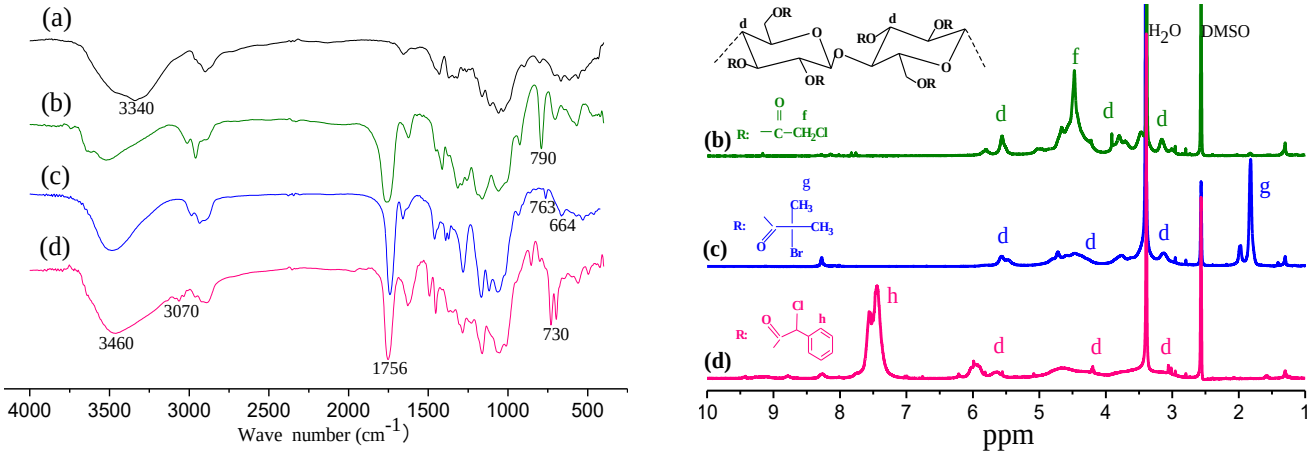


Fig. 2. (A) FT-IR spectra of the unmodified cellulose (a), cellulose-CAC (b, DS = 1.245), cellulose-BiB (c, DS = 0.910), and cellulose-CPAC (d, DS = 0.963); (B) ^{1}H NMR spectra of the cellulose-CAC (b, DS = 0.743), cellulose-BiB (c, DS = 0.503), and cellulose-CPAC (d, DS = 0.764)

Furthermore, the substitution of the hydroxyl groups on the cellulose backbone by the acylating agents was also confirmed by means of the ^{1}H and ^{13}C NMR analyses. Figure 2B shows the representative ^{1}H NMR spectroscopies of the cellulose-CAC, cellulose-BiB, and cellulose-CPAC recorded in DMSO-d_6. The signals for the protons of the cellulose backbone are located at 3.0 to 6.0 ppm (Zhang *et al*. 2009; Hiltunen *et al.* 2011). The ^{1}H NMR spectrum of the cellulose-CAC (b) showed a peak at 4.3 to 4.6 ppm, which was attributed to the methylene protons of the chloroacetyl groups (Martin *et al.* 1999). The protons of the CH_3 group of the 2-bromoisobutyryl moiety in the cellulose-BiB (c) appeared at 1.7 to 2.0 ppm (Hiltunen *et al*. 2011). The ^{1}H NMR spectrum of the cellulose-CPAC (d) showed a typical signal for the aromatic protons between 7.2 ppm and 7.9 ppm (Zhang *et al*. 2009).

The representative full-range ^{13}C NMR spectra of the cellulose-CAC, cellulose-BiB, and cellulose-CPAC are shown in Fig. 3. The resonances of the AGU carbon atoms were detectable in the region from 59.0 ppm to 104.0 ppm. The peaks at 102.4, 80.0, and 60.1 ppm were attributed to C1, C4, and C6 carbons bearing unsubstituted hydroxyl groups, respectively, and the peaks of the C2, C3, and C5 carbons heavily overlapped, which gave a strong cluster of peaks around 70.5 to 75.6 ppm. The peak near 98.5 ppm (designated 1')

was assigned to the C1 carbons adjacent to the C2 carbons bearing a substituted hydroxyl group, and the peak near 78.6 ppm (designated 4') was assigned to the C4 carbons adjacent to the C3 carbons bearing a substituted hydroxyl group. The peak at 64.2 ppm (designated 6') was attributed to the C6 carbons bearing a substituted hydroxyl group. The δ shift from 166.0 to 167.8 ppm (curve b) was assigned to the signal of the carbonyl carbon region in the cellulose-CAC, the δ shift from 169.0 to 170.7 ppm (curve c) was the butyryl carbonyl carbon signal in the cellulose-BiB, and the δ shift from 166.4 to 168.0 ppm (curve d) was the carbonyl carbon signal in the cellulose-CPAC. Furthermore, the presence of the signal at 40.9 ppm in curve b resulted from the chloromethyl of the cellulose-CAC (Martin *et al*. 1999). The peak at 29.3 ppm in curve c was assigned to the carbon of methyl group, and the peak at 65.6 ppm was the quaternary carbon of the 2-bromoisobutyryl moiety (Hiltunen *et al*. 2011). The signals of the aromatic carbons in the cellulose-CPAC appeared at 127.5 to 129.8 ppm and 135.6 to 136.4 ppm (Zhang *et al.* 2009), and the tertiary carbon of the 2-chloro-2-phenylacetyl moiety appeared at 57.8 to 59.0 ppm. These results supplied strong evidence of the successful acylation of cellulose.

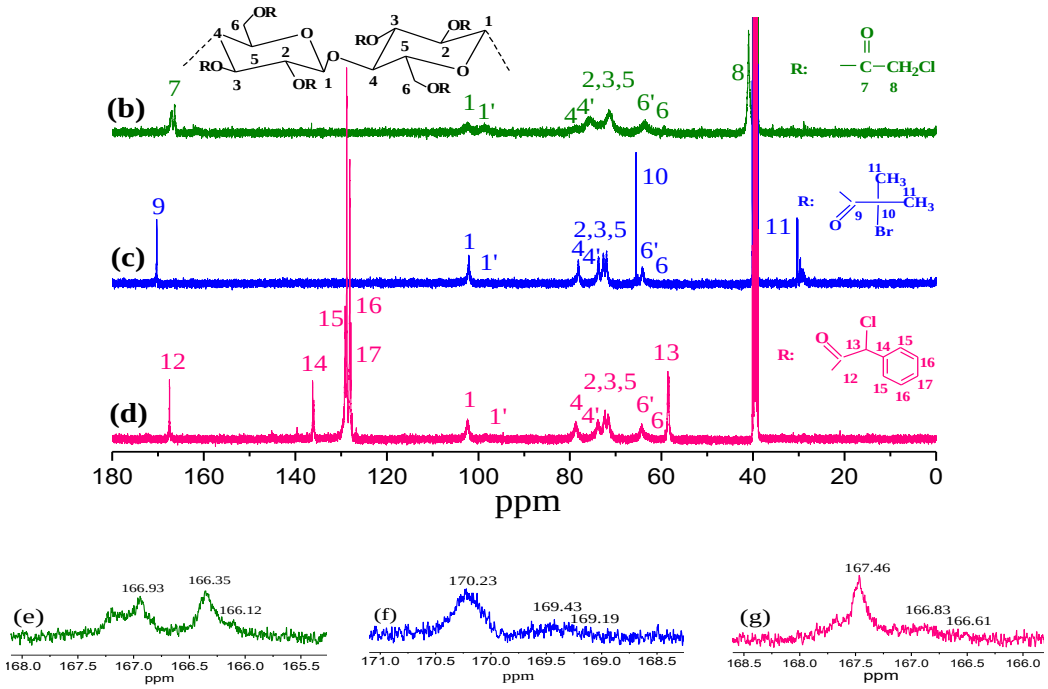


Fig. 3. ^{13}C NMR spectra of the cellulose-CAC (b, DS = 0.923), cellulose-BiB (c, DS = 0.526), and cellulose-CPAC (d, DS = 0.739), and the carbonyl carbon regions of the cellulose-CAC (e, DS = 1.245), cellulose-BiB (f, DS = 0.804), and cellulose-CPAC (g, DS = 0.963)

Acylation Extent *vs.* Molecular Structure of Reagents

The time courses of the cellulose acylation with CAC, BrBiB, and CPAC are shown in Fig. 4. Under the reaction conditions of 35 °C and 6 mol acylating agent/mol AGU, the acylation extent of the cellulose remarkably increased as the reaction time increased. This was due to the increased collision rate and time of the acylating agents with the cellulosic molecules in the solution (Liu *et al*. 2009). It should be mentioned that the relative reaction constants of the hydroxyl groups did not remain constant. At the beginning of the reaction, the acylation agents reacted very fast with the cellulose, and then the reaction speeds gradually slowed down. Moreover, the hydroxyl groups were not completely replaced by

the acylating agents, although the hydroxyl groups in the cellulose were readily accessible under the homogenous conditions. Figure 4 shows that in the reaction with CAC, BrBiB, and CPAC for 8 h, 12 h, and 24 h, respectively, the acylation extents of cellulose reached a maximum value, which was followed by a slight decrease, which meant that further treatment would not result in any increase in the extent of acylation. The introduction of steric crowding in the cellulose molecule, which might have affected the reactivity of the remaining free OH groups, did not lead to a further increase in the DS. Moreover, further increasing the reaction time had a detrimental effect on the cellulose acylation. A longer time period resulted in cellulose degradation and reverse reactions of acylation, such as partial hydrolysis of the formed ester groups, which therefore reduced the DS (Freire *et al*. 2006).

However, at the same reaction time, the acylation extent of cellulose using CAC was considerably higher than when BrBiB and CPAC were used, *i.e.*, longer reaction times were required to reach the same DS values for CPAC and particularly BrBiB. This indicated that the reactivity of the acylating agents was strongly affected by the molecular structure. Such a difference was accounted for by the steric hindrance of the substituents. The small molecules of CAC were easily able to reach the hydroxyl functions and react more rapidly with the OH groups, whereas the steric effect of the relatively bulky BrBiB and CPAC groups made the acylation of the cellulose more difficult.

BrBiB was less reactive than the other bulky acylating agent, CPAC. The reaction of cellulose with BrBiB at comparable reaction times led to acylated products with very low DS values (Table 1). To obtain a high DS (> 1.0), a long reaction time of up to 24 h needs to be applied for BrBiB. This may have been a result of both the steric hindrance and the electron donating effect of the two methyl groups in BrBiB, which decreased the electropositivity of the acyl carbon atom and increased the activation energy of acylation. While acting as an electron-withdrawing group, the benzene ring in the benzyl group can increase the electropositivity of the acyl carbon atom and decrease the activation energy of reaction to some extent, which would result in CPAC having a higher reaction rate with cellulose, although the 2-chloro-2-phenylacetyl is bulky and more hydrophobic. On the other hand, the lower reactivity of BrBiB than CPAC may also be due to the lower electron-withdrawing inductive effect of Br than Cl.

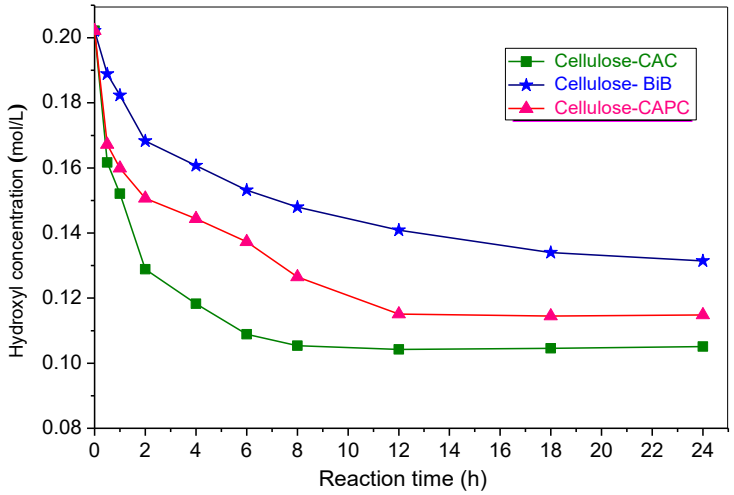


Fig. 4. Plot of the hydroxyl concentration *vs.* reaction time in the reaction between cellulose and different acylating agents (6 equiv/AGU, 35 °C)

Difference in Reactivity Among the Three OH Groups

The reactivity difference among the three OH groups (C6-, C3-, and C2-OH) in the AGU during acylation of cellulose with CAC, BrBiB, and CPAC in [Bmim]Cl was evaluated by ^{13}C NMR. The expanded carbonyl region spectra of the celluose-CAC, cellulose-BiB, and cellulose-CPAC are shown in Fig. 4. All of the carbonyl carbon signals were resolved into three peaks, which were assigned as carbonyl carbons linked to the C6, C3, and C2 carbons of the AGU. The partial degrees of substitution on the three reactive sites of the AGU were calculated by integrating the O−C=O peaks of the acylated products, and the results are presented in Table 1.

Table 1. Distribution of the Acyl Groups among C6, C3, and C2 of the AGU in the Cellulose-based Macroinitiators

Time (h)	DS_{Total}[a]	DS_{C6}[b]	P_{C6} (%)[c]	DS_{C3}[b]	P_{C3} (%)[c]	DS_{C2}[b]	P_{C2} (%)[c]
Cellulose-CAC							
0.5	0.601	0.470	78.2	0.092	15.3	0.039	6.5
1	0.743	0.507	68.2	0.149	20.1	0.087	11.7
2	1.087	0.636	58.6	0.317	29.1	0.134	12.3
4	1.245	0.692	55.6	0.385	30.9	0.168	13.5
6	1.384	0.701	50.7	0.470	33.9	0.213	15.4
8	1.436	0.707	49.2	0.485	33.9	0.244	16.9
Cellulose-BiB							
0.5	0.198	0.198	100	0	0	0	0
1	0.295	0.278	94.1	0.017	5.9	0	0
2	0.503	0.449	89.3	0.045	8.9	0.009	1.8
4	0.615	0.522	84.8	0.067	10.9	0.026	4.3
6	0.727	0.601	82.7	0.084	11.6	0.042	5.7
8	0.804	0.654	81.4	0.095	11.8	0.055	6.8
12	0.910	0.722	79.3	0.123	13.5	0.065	7.2
24	1.051	0.796	75.7	0.156	14.8	0.099	9.5
Cellulose-CPAC							
0.5	0.519	0.459	88.4	0.049	9.5	0.011	2.1
1	0.627	0.534	85.2	0.070	11.1	0.023	3.7
2	0.764	0.630	82.4	0.096	12.6	0.038	5.0
4	0.858	0.680	79.3	0.125	14.6	0.053	6.1
6	0.963	0.741	76.9	0.147	15.3	0.075	7.8
8	1.123	0.826	73.6	0.181	16.1	0.116	10.3

[a] DS_{Total} refers to the DS of cellulose-based macroinitiators determined by ^1H NMR spectroscopy.
[b] DS_{C6}, DS_{C3}, and DS_{C2} refer to the DS of the corresponding carbon atom.
[c] P_{C6}, P_{C3}, and P_{C2} refer to the percentages of the DS of the corresponding carbon atom.

As can be clearly seen, the acylation reaction of cellulose proceeded faster at the primary position compared to the secondary hydroxyl groups at positions C3 and C2, and there was a substantial difference in the reactivity between the C3-OH and C2-OH groups. At the beginning of the acylation, the substitution of cellulose hydroxyls mainly occurred at the more accessible position, the C6-OH groups. The acylation of the C3-OH groups proceeded at a slower rate following the acylation of the C6-OH groups, while the reaction activity of the C2-OH groups was the lowest amongst the three OH groups. The highest reactivity of the primary OH at the C6 carbon was attributed to its lower steric hindrance. The reason for the C3-OH groups being acylated slightly faster than the C2-OH groups seems to have been due to the substitution of C6-OH by the acyl group, which introduced

steric crowding in the cellulose molecule. This had a more adverse effect on the C2-OH group than the C3-OH group. The relative distribution of the acyl moiety among the carbon atoms of the AGU was in the following order: C6 > C3 > C2. This was consistent with the study by Martin *et al*. (1999), who partially functionalized the cellulose with chloroacetyl groups in a dimethylacetamide/LiCl system.

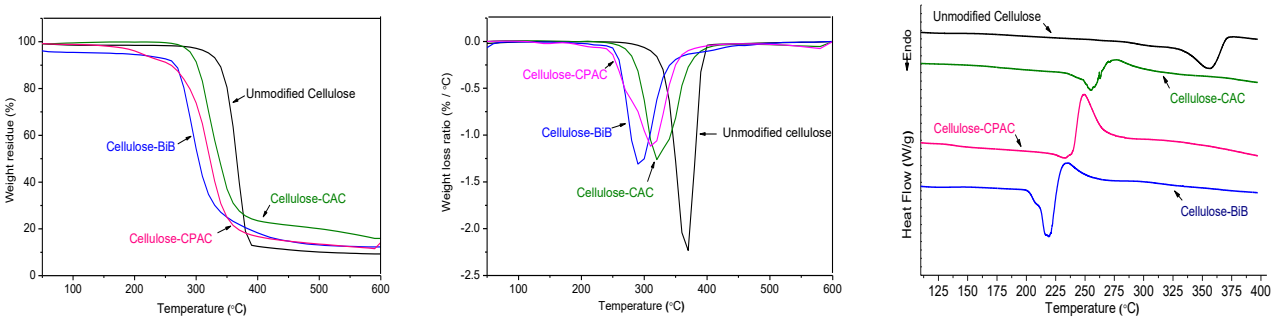
Table 1 also indicates that the structure of the substituents noticeably affected the regioselectivity of the cellulosic hydroxyl groups. When a DS_{Total} of approximately 0.6 was reached, the cellulose-CAC had a substituent distribution of 78.2% at position C6, 15.3% at C3, and 6.5% at C2, while both the cellulose-BiB and cellulose-CPAC had a substituent distribution of about 85% at C6, 11% at C3, and 4% at C2. As the acylation extent of cellulose increased, the regioselectivity of the three OH groups appreciably decreased. For the cellulose-CAC with a DS_{Total} of 1.087, the partial DS at C6 was 0.636, while at C3 it was 0.317 and at C2 it was 0.134. For the cellulose-BiB with a DS_{Total} of 1.051, the partial DS values at C6, C3, and C2 were 0.796, 0.156, and 0.099, respectively, and for the cellulose-CPAC with a DS_{Total} of 1.123, the partial DS values at C6, C3, and C2 were 0.826, 0.181, and 0.116, respectively. The data showed that the reaction of cellulose with the small reagent molecule, CAC, had a relatively low regioselectivity. At the same acylation extent, the regioselectivity of the three OH groups was much higher when using BrBiB and CPAC as the acylation agents than CAC. For the more voluminous reagent molecules, BrBiB and CPAC, the acylation reaction was preferential at the primary OH, and the secondary OH groups of the AGU underwent acylation only after most of the primary OH groups had been substituted. The reason for this result was that the higher steric hindrance of the two bulky substituents, BrBiB and CPAC, caused them to be unable to reach the secondary OH groups of cellulose, which had more steric hindrance. This result agreed with those of Nawaz *et al*. (2012), who found that the preference for the C6 position increased as a function of increasing molecular volume of the reagent.

Effect of Molecular Structure on Thermal Properties

A comparative study of the thermal properties was performed for unmodified cellulose, cellulose-CAC, cellulose-BiB, and cellulose-CPAC. The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves of these samples are shown in Fig. 5, and the data of the T_d and the residual weight at 600 °C are summarized in Table 2. The thermal decomposition of both the unmodified cellulose and cellulose-based macroinitiators described in Fig. 5 exhibited basically monomodal weight loss curves under a N_2 atmosphere. The presence of only one decomposition peak indicated the relative homogeneity of the cellulose-based macroinitiators. The unmodified cellulose started to decompose at 276 °C, whereas the cellulose-CAC, cellulose-BiB, and cellulose-CPAC began to decompose at 251, 239, and 228 °C, respectively. The decomposition temperatures at the largest decomposition rate (T_{dm}) were approximately 370, 320, 291, and 309 °C for the unmodified cellulose, cellulose-CAC, cellulose-BiB, and cellulose-CPAC, respectively. The noticeable decrease of the initial decomposition temperature (T_{di}), T_{dm}, and the final decomposition temperature (T_{df}) of the cellulose-based macroinitiators compared with the unmodified cellulose implied that the thermal stability of cellulose markedly declined after it was acylated. Evidently, this can be attributed to the introduced acyl moieties, which were the most active groups and were easily decomposed under those thermal conditions. In contrast, the possible occurrence of hydrogen halide during the heating process of the cellulose-based macroinitiators with carbon halide groups might

have promoted the thermal degradation reaction of the cellulose derivatives. Another reason was that the introduced acyl groups broke the intra- and inter-molecular hydrogen bonds in the cellulose chain and decreased the crystalline order after substitution of the cellulose hydroxyls, which made the chains more mobile under the thermal conditions (Cao *et al.* 2010). Furthermore, the ultimate percentages of the weight residue at 600 °C for the cellulose-based macroinitiators (12.29% to 15.92%) were considerably higher than that of the unmodified cellulose (9.3%). This was due to the introduced halogen elements, which are inorganic elements that are able to survive under the thermal conditions and increased the residual weight of the cellulose-based macroinitiators.

As can also be observed from Table 2, the molecular structure of the substituent groups had an important influence on the thermal stability of the cellulose-based macroinitiators. The cellulose-CAC was the most stable among the three cellulose-based macroinitiators, and the thermal stability of the cellulose-BiB seemed to be inferior to that of the cellulose-CPAC. The lower thermal stability of the cellulose-BiB and cellulose-CPAC than that of the cellulose-CAC may be explained by the comparatively bulky structure of the BiB and CPAC groups, which increased the inter-molecular distance (Cao *et al.* 2010). The somewhat less thermally stable behavior of the cellulose-BiB may have resulted from the fact that the BiB was slightly more active than the CPAC under the thermal conditions.



(a) (b) (c)

Fig. 5. (a) Thermogravimetric curves and (b) derivative thermogravimetric curves of the unmodified cellulose, cellulose-CAC (DS = 1.245), cellulose-BiB (DS = 0.910), and cellulose-CPAC (DS = 0.963), and (c) DSC thermograms of the unmodified cellulose, cellulose-CAC (DS = 0.743), cellulose-BiB (DS = 0.526), and cellulose-CPAC (DS = 0.739).

Table 2. Thermostability Results of the Unmodified Cellulose, Cellulose-CAC, Cellulose-BiB, and Cellulose-CPAC

Sample	T_{di} [a] (°C)	T_{dm} [b] (°C)	T_{df} [c] (°C)	T_m [d] (°C)	Residual mass (wt%)
Unmodified cellulose	276	370	394	355	9.30
Cellulose-CAC	251	320	375	254	15.92
Cellulose-BiB	239	291	338	219	12.29
Cellulose-CPAC	228	309	356	232	14.17

[a] T_{di} is the temperature at which the decomposition rate results in a remarkable weight loss.
[b] T_{dm} is the temperature at which the highest decomposition rate is observed for the corresponding pattern.
[c] T_{df} corresponds to the maximal decomposition of the sample.
[d] T_m is the temperature at which the endothermic peak reaches a maximum.

The effect of the molecular structure on the thermal properties was further investigated by DSC analysis. Figure 5c displays the DSC curves of the unmodified cellulose and acylated celluloses obtained in the second heating scan, and the T_m is summarized in Table 2. One obvious endothermic peak with a maximum value was seen at 355, 254, 219, and 232 °C for the unmodified cellulose, cellulose-CAC, cellulose-BiB, and cellulose-CPAC, respectively. The much lower T_m of the acylated celluloses than that of the unmodified cellulose revealed that the introduced acyl groups disrupted the intra- and inter-molecular hydrogen bonds in the cellulose main chain and decreased the crystalline order of the resulting acylated celluloses. The T_m values of the acylated celluloses clearly declined as the size of the acyl groups increased, which showed a strong correlation between the thermal properties and the molecular structure of the substituted groups. This is in agreement with the report by Jandura *et al*. (2000), where it was found that the thermal stability of the cellulose stearate was much lower than that of the cellulose undecanoate. Furthermore, the lower thermal stability of the cellulose-BiB than that of the cellulose-CPAC was confirmed by the DSC analysis, which meant that the substituted BiB groups were more beneficial in disrupting the hydrogen bonds of the cellulose chain than CPAC, resulting in a decrease in the T_m.

CONCLUSIONS

1. The acylation of cellulose with CAC, BrBiB, and CPAC in ionic liquid allowed for the introduction of acyl halide groups on to the cellulose backbone, which led to a series of homogeneous cellulose-based macroinitiators.
2. The small molecule, CAC, reacted much faster with cellulose than the relative bulky BrBiB and CPAC, and the reactivity of the BrBiB was clearly lower than that of the CPAC. The attachment of the substituents during the acylation of cellulose was preferred on the more accessible C6 position as expected, but it also occurred at the C3-OH and C2-OH groups. The substitution pattern of the acyl moieties on the anhydroglucose unit was in the following order: C6 > C3 > C2. Furthermore, the regioselectivity of cellulose reacting with the BrBiB and CPAC was much higher than that with the CAC, which indicated that the regioselectivity of cellulose also partly relied on the steric hindrance of the acylating agents.
3. The cellulose-based polyfunctional macroinitiators displayed a typical single weight-loss step degradation profile. The modification weakened the thermal stability of the cellulose-based macroinitiators, and the T_d was dependent on the molecular structure of the substituted groups.

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