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Short communication

Highly efficient propionylation and butyralation of cellulose in an ionic liquid catalyzed by 4-dimethylminopyridine

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ABSTRACT

Using 4-dimethylaminopyridine (DMAP) as the catalyst, highly efficient propionylation and butyralation of cellulose were successfully carried out in an ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) under mild conditions. Cellulose propionate (CP) and cellulose butyrate (CB) with a degree of substitution (DS) in the range from 0.89 to 2.89 were synthesized within only 30 min at 30 °C. The DS values of the products could be well controlled just by molar ratio of acid anhydride/anhydroglucose unit (AGU). More interestingly, the conversions of acid anhydrides in both propionylation and butyralation were as high as above 90%, even 96%. Therefore, this work provides a facile and highly efficient way for the synthesis of cellulose esters CP and CB.

1. Introduction

Cellulose esters are commercially important cellulose derivatives with a wide application in the field of plastics, film, fiber, coatings and pharmaceutical industries (Edgar, 2007; Edgar et al., 2001; Luo, Niang, & Schaetzel, 1997; Van Vlierberghe, Dubruel, & Schacht, 2011). Till now, heterogeneous methods are the actually applied ones for the production of most commercial cellulose esters. However, heterogeneous process often leads to some undesirable problems, such as non-uniform substitution of cellulose esters, high energy-consumption, excessive acylating reagents, and serious degradation of cellulose due to the usage of acidic catalysts. Therefore, homogeneous functionalization has been one focus of cellulose research for a long time. It not only provides opportunities to control DS value, but also creates more options to induce novel functional groups. Moreover, it may open up new avenues for the design of products with unconventional functional group in a controlled substitution pattern (El Seoud, Marson, Giacco, & Frollini, 2000; Saikia & Das, 2003). Over the past decades, some cellulose solvents, such as DMAc/LiCl (Nawaz, Casarano, & El Seoud, 2012; Williamson & McCormick, 1998), DMF/N_2O_4 (Wagenknecht, Nehls, & Philipp, 1993), DMSO/TBAF (Heinze et al., 2000; Hussain, Liebert, & Heinze, 2004), and some molten salt hydrate (Fischer, Voigt, & Fischer, 1999), have been employed for homogenous cellulose esterification. However, the above solvents have some limitations, such as toxicity, difficulty in solvent recovery, and the undesirable side reactions, which hamper their application on a large scale.

During the past several years, some room-temperature ionic liquids (ILs) proved to be novel and efficient solvents for cellulose, and considered as desirable green reaction media for cellulose homogenous derivatization (Swatloski, Spear, Holbrey, & Rogers, 2002; Zhang, Wu, Zhang, & He, 2005; Cao et al., 2009) As a new kind of aprotic solvents, ILs were found to be the very suitable reaction media for homogeneous cellulose esterification. Various cellulose esters, such as cellulose acetate (CA) (Heinze, Schwikal, & Barthel, 2005; Wu et al., 2004), cellulose acetate propionate (CAP) (Huang et al., 2011), cellulose acetate butyrate (CAB) (Cao, Li, & Zhang, 2011), cellulose laurate (Barthel & Heinze, 2006), cellulose furoate (Köhler & Heinze, 2007), and cellulose sulfates (Gericke, Liebert, & Heinze, 2009), have been homogenously synthesized in ILs. In the previous studies, without using any catalysts, cellulose acetates with a wide range of DS values could be readily obtained under the mild reaction conditions. However, synthesis of cellulose propionate (CP) and cellulose butyrate (CB) with relatively high DS is very difficult in ILs, because propionic anhydride and butyric anhydride are less reactive acylating reagents than acetic anhydride. For example, CP and CB were synthesized with acid anhydrides in ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl) at 80 °C, with a reaction time of 2 h and a molar ratio of

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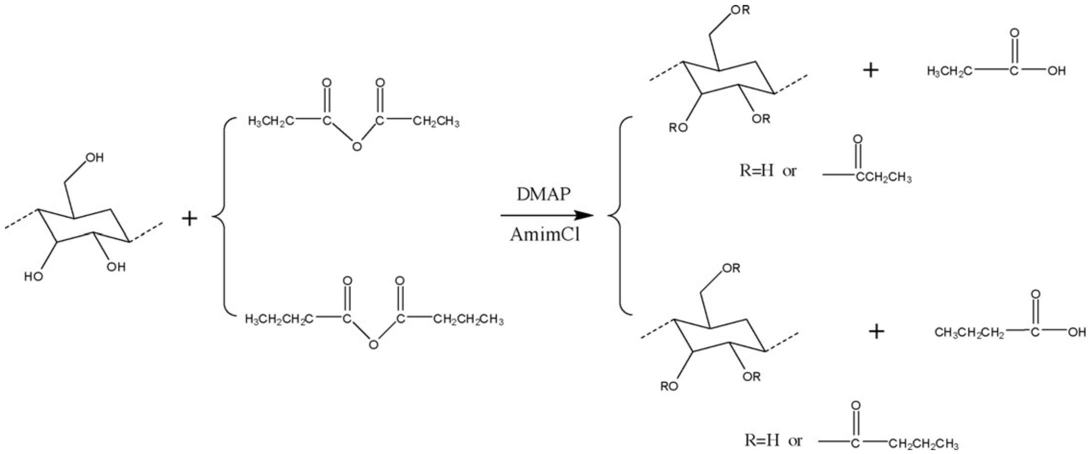

Scheme 1. Synthesis of CP and CB in AmimCl using DMAP as a catalyst.

1/3 (AGU/reagent). The maximal DS values of CP and CB obtained were 0.9 and 0.4, respectively (Heinze et al., 2008).

4-Dimethylaminopyridine (DMAP) is widely used as a nucleophilic catalyst for esterification with anhydrides (Sakakura, Kawajiri, Ohkubo, Kosugi, & Ishihara, 2007). In the present work, using DMAP as a catalyst and acid anhydrides as acylating agents, we explored an efficient procedure for the homogenous synthesis of CP and CB in ionic liquid AmimCl. CP and CB with DS in the range from 0.89 to 2.89 were synthesized under mild reaction conditions.

2. Experimental

2.1. Materials

Microcrystalline cellulose (MCC) with a degree of polymerization (DP) of 200 was obtained from Beijing Fengli Jingqiu Commerce and Trade Co., Ltd. and dried at 60 °C for 8 h in vacuum oven before use. AmimCl was synthesized according to the reported procedure (Wu et al., 2004). The water content in the obtained AmimCl was less than 500 ppm, as analyzed by Karl Fischer titration. DMAP (99.5%) was purchased from Haili Chemical Industry Co., Ltd. and dried at 50 °C for 8 h in vacuum oven before use. Propionic anhydride and butyric anhydride were purchased from Aladdin Reagent Co., Ltd. and used as received. All other chemicals were obtained from Beijing Chemical Company, and used as received.

2.2. Dissolution of cellulose in AmimCl

1 g of dried cellulose was dispersed in 24 g of AmimCl in a three-necked flask, and the mixture was heated to 80 °C for 1 h with mechanical stirring. A clear and viscous cellulose solution containing 4 wt% cellulose was obtained.

2.3. Synthesis of CP and CB in AmimCl

The temperature of the cellulose solution was held at desired temperature for 20 min. The required amount of DMAP (10 wt%, in DMF) solution and propionic anhydride or butyric anhydride was added to the solution under constant stirring. After the required elapsed time, the resultant products were precipitated in a 5-fold amount of deionized water, and filtered to separate the precipitate. The residue was washed three times with deionized water. Finally, the product was dried at 80 °C for 12 h. The synthesis of CP and CB in AmimCl is shown in Scheme 1.

2.4. Characterization

FTIR analysis was carried on a Perkin-Elmer spectrum 2000 instrument. The dried samples were tested by KBr pellet method. ^{1}H NMR spectra were recorded on a Bruker AV400 spectrometer with 16 scans in DMSO-d_6 containing a drop of trifluoroacetic acid-d, which shifted active hydrogen downfield. The signal peaks of CP were described as $\delta = 1.07$ ppm (methyl protons of propionyl, 3H), $\delta = 2.37$ ppm (methylene protons of propinyl, 2H), $\delta = 3.0$–5.5 ppm (protons of the cellulose backbone, 7H). Those for CB were $\delta = 0.92$ ppm (methyl protons of butyryl, 3H), $\delta = 1.57$ ppm and $\delta = 2.31$ ppm (methylene protons of butyryl, 2H) $\delta = 3.0$–5.5 ppm (protons of the cellulose backbone, 7H). The DS of CP and CB was calculated by Eq. (1):

$$DS = \frac{I_{CH_3} * 7}{I_{AGU} * 3}. \tag{1}$$

where I_{CH_3} is the peak integral of methyl protons and I_{AGU} is the peak integral of anhydroglucose unit.

The ^{13}C NMR spectra of cellulose ester in DMSO-d_6 were recorded at 100 °C on a Bruker AV-300 instrument. Each spectrum was obtained with an accumulation of 5000 scans.

3. Results and discussion

In our experiments, homogeneous propionylation and butyralation of cellulose CP and CB were carried out in the ionic liquid AmimCl with and without DMAP catalyst, and the detailed experiment conditions and results are presented in Table 1. In the absence of a catalyst, at a molar ratio (propionic anhydride/AGU) of 3:1 and 80 °C, only a relatively low substituted CP (DS = 0.53) was obtained after a reaction time of 3 h. In contrast, in the presence of catalyst DMAP (DMAP/AGU = 0.2), at the same molar ratio of acid anhydride/AGU and reaction temperature, the CP with a DS of 2.76 was obtained within only 30 min. More interestingly, a CP with a DS as high as 2.82 was obtained even at a reaction temperature of 30 °C within 30 min.

DMAP is also an efficient catalyst for the butyralation of cellulose. Without any catalyst, under a molar ratio of 5:1 (butyric anhydride/AGU), after reacting for 3 h, a low substituted CB ($DS_{CB} = 0.46$) was obtained, which is similar to that reported by Heinze et al. (2008). However, with the catalysis of DMAP, CB with high DS ($DS_{CB} = 2.76$) was obtained with a lower molar ratio of butyric anhydride/AGU (3:1) within a short time (30 min).

Investigation was conducted on the effect of reaction parameters, such as used amount of catalyst DMAP, reaction time, temperature, and the molar ratio of acid anhydride/AGU in

Table 1
DS of CP and CB homogenously synthesized in AmimCl under various conditions.

Sample	Acid anhydride	Temperature (°C)	Time (min)	DMAP/AGU (mol/mol)	Molar ratio of acid anhydride/ AGU	DS
CP-1	Propionic anhydride	80	180	–	3:1	0.53
CP-2	Propionic anhydride	100	180	–	3:1	1.24
CP-3	Propionic anhydride	80	30	0.6:1	3:1	2.72
CP-4	Propionic anhydride	80	30	0.4:1	3:1	2.72
CP-5	Propionic anhydride	80	30	0.2:1	3:1	2.76
CP-6	Propionic anhydride	80	30	0.1:1	3:1	2.55
CP-7	Propionic anhydride	50	30	0.4:1	3:1	2.80
CP-8	Propionic anhydride	30	30	0.4:1	3:1	2.82
CP-9	Propionic anhydride	20	30	0.4:1	3:1	2.89
CP-10	Propionic anhydride	30	2	0.4:1	3:1	1.09
CP-11	Propionic anhydride	30	5	0.4:1	3:1	1.54
CP-12	Propionic anhydride	30	10	0.4:1	3:1	2.31
CP-13	Propionic anhydride	30	20	0.4:1	3:1	2.53
CP-14	Propionic anhydride	30	30	0.4:1	1:1	0.89
CP-15	Propionic anhydride	30	30	0.4:1	1.5:1	1.36
CP-16	Propionic anhydride	30	30	0.4:1	2:1	1.90
CB-1	Butyric anhydride	80	180	-	5:1	0.46
CB-2	Butyric anhydride	80	180	0.4:1	1:1	0.91
CB-2	Butyric anhydride	80	30	0.4:1	1.5:1	1.41
CB-3	Butyric anhydride	80	30	0.4:1	2:1	1.84
CB-4	Butyric anhydride	80	30	0.4:1	2.5:1	2.43
CB-5	Butyric anhydride	80	30	0.4:1	3:1	2.76

cellulose, in the esterification of cellulose. From Table 1, it can be seen that the DS value of CP increased from 2.55 to 2.78 with an increment in dosage of DMAP/AGU from 0.1 to 0.2 under the same remaining conditions. However, further increasing the dosage of DMAP did not lead to substantial increments in DS. As the reaction time prolonged, the DS of CP dramatically increased at first, and became slow after 10 min. The DS of CP reached 1.09 within only 2 min, 1.54 within 5 min, 2.31 within 10 min, 2.53 within 20 min and 2.78 within 30 min. From Table 1, it can also be seen that the increase of reaction temperature from 20 to 80 °C did not lead to significant increase in DS, implying that the reaction temperature had little effect on this homogenous reaction system. The DS value of cellulose esters increased with increasing molar ratio of acid anhydride/AGU. By increasing the molar ratio of acid anhydride/AGU from 1:1 to 1:3 the DS of CP increased from 0.9 to 2.89, and the DS of CB from 0.91 to 2.76. Therefore, it is reasonable to speculate that the DS value of CP and CB can be well controlled just by controlling stoichiomeric ratio of acid anhydride/AGU.

From these results, it can be inferred that both the reaction rate and reaction efficiency of propionylation and butyralation of cellulose in AmimCl were greatly improved, when DMAP was used as a catalyst. Fig. 1 illustrates the theoretical and experimental DS as a function of the molar ratio of acid anhydride/AGU. Curve (a) represents the theoretical DS values at a 100% conversion rate of acid anhydride, in which acid anhydride is supposed to react completely with the cellulose. In other words, at the acid anhydride/AGU molar ratio of 1:1, 2:1, and 3:1, the DS values of the resulted cellulose esters will be 1, 2, and 3, respectively. Curves (b) and (c) depict the trend of experimental value. From Fig. 1, it can also be seen that the trend of experimental curves (b) and (c) were below but very close to the curve (a). The experimental DS values of both CP and CB were almost equal for all the molar ratios of acid anhydride/AGU. The conversion rate of acid anhydrides for the acid anhydride/AGU molar ratio ranging from 1:1 to 3:1 was above 90% or even 96%. The conversion rate of acid anhydride reacting with cellulose in ILs is much higher than ever reported (Bianchi, Marsano, Ricco, & Conio, 1997). Obviously, the propionylation and butyralation of cellulose in AmimCl catalyzed by DMAP is highly efficient. During the homogenous reaction, it is suggested that the acid anhydride reacts with DMAP to form activated acyl pyridinium that readily esterifies with the hydroxyl groups of cellulose (Besheer, Hause, Kressler, & Mader, 2007).

The FTIR spectra of cellulose, CP (DS = 1.36, DS = 2.82) and CB (DS = 1.41, DS = 2.76) are shown in Fig. 2. It can be seen that all cellulose esters show a very strong peak at 1733 cm^{-1}, indicating the existence of carboxylic acid ester. With increasing DS values of CP and CB, the intensity of esters peak increased, whereas that of the –OH stretching band at 3000–3600 cm^{-1} obviously decreased, indicating the decrease of hydroxyl groups in cellulose.

The ^{13}C NMR analysis was used to elucidate the molecular structure and evaluate the distribution of substituents in the synthesized cellulose esters. Fig. 3A shows the full-range ^{13}C NMR spectra of CP (DS = 1.52 and DS = 2.82). The peak at 172–173 ppm was assigned to the signal of the carbonyl carbon (C7), the peaks at 60–103 ppm were assigned to the signals of cellulose backbone carbon (C1–C6) (Cao et al., 2011), and the peaks at 7.9 ppm and 26.2 ppm were assigned to the signal of C9 and C8, respectively. In the signal region of cellulose backbone carbon, the peaks at 62.4 ppm and 60.1 ppm were assigned to the signal of C6 (unsubstituted hydroxyl group)

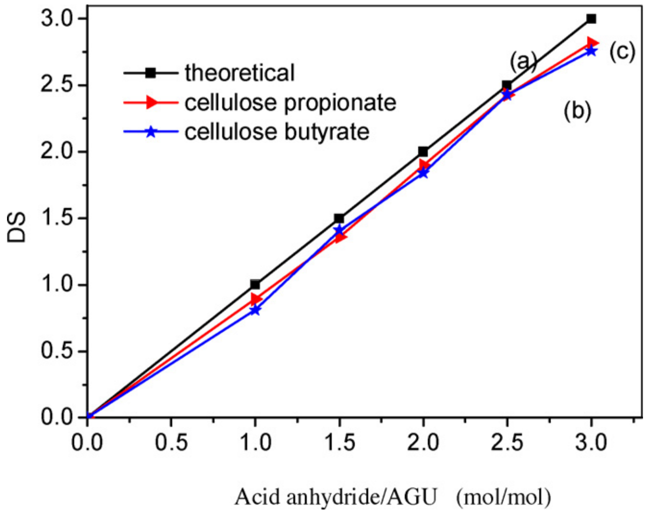

Fig. 1. Theoretical and experimental DS values of CP and CB versus the ratio of acid anhydride/AGU.

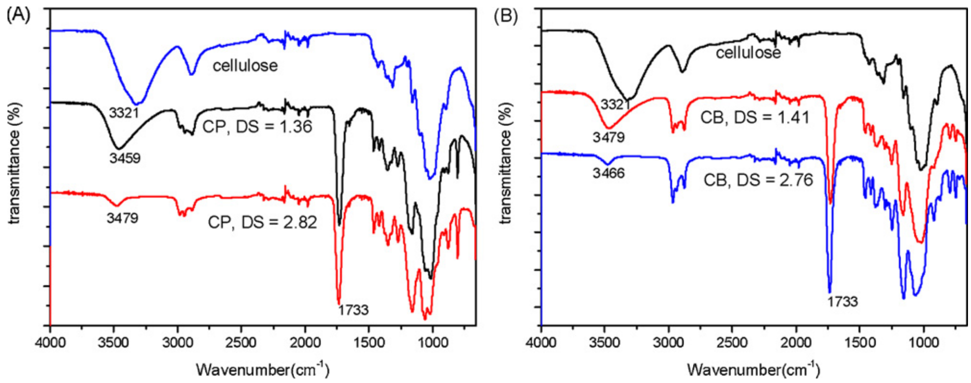

Fig. 2. FTIR spectra of cellulose, CP and CB.

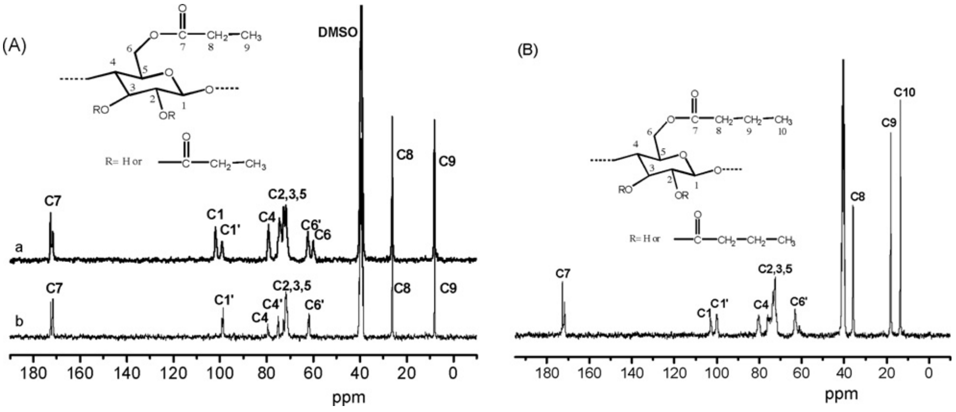

Fig. 3. ^{13}C NMR spectra of cellulose esters: (A) (a: CP-11 DS = 1.54, b: CP-8 DS = 2.82) and (B) CB (CB-3 DS = 1.84).

and C6′ (substituted hydroxyl group), 102.0 ppm and 99.1 ppm were assigned to the signal of C1 and C1′ (adjacent to C2 carbons bearing a substituted hydroxyl group). The peaks at 79.5 ppm and 75.0 ppm were assigned to C4 and C4′ (adjacent to C3 carbons bearing a substituted hydroxyl group). The signals of C2, C3 and C5 were heavily overlapped in 71.8–74.6 ppm range. In spectrum of sample CP-11 with DS of 1.54, no signal of C4′ was observed, and the intensity of signals C6 was smaller than that of C6′, and the intensity of signal C1 was smaller than that of C1′. The signals of C1 and C6 disappeared in the ^{13}C NMR spectrum for sample CP-8 with DS of 2.82, and the signal of C4′ appeared at 75.0 ppm. Obviously, the three hydroxyl groups at the C2, C3, and C6 exhibited different reaction activities, and the reactivity order is C6-OH > C2-OH > C3-OH. This result is different from that observed in acetylation of cellulose in AmimCl (Wu et al., 2004), in which the order of reactivity was C6-OH > C3-OH > C2-OH.

Fig. 3B presents the ^{13}C NMR spectrum of a CB with DS of 1.84. It can be clearly seen that the hydroxyl group at C6 was almost totally substituted, while the hydroxyl group at C2 was partly substituted. However, the signal of C4′ did not appear, indicating the hydroxyl group of C3 was unsubstituted. Therefore, for butyralation of cellulose in AmimCl, the reactivity order of the three hydroxyl groups at the C2, C3 and C6 positions is also in the order of C6-OH > C2-OH > C3-OH.

The solubility of CP and CB synthesized in some organic solvents was investigated. The results are presented in Table 2. It is clear that all the samples were soluble in DMSO and DMF. But, in other solvents, such as acetone, THF, toluene, chloroform, and ethyl acetate, the solubility of CP and CB depended greatly on the DS values. The CP with DS in 1.36–1.90 range, and CB with DS of 1.41–1.84 were swollen in THF, acetone, chloroform. However, the CP with DS above 2.55 and CB with DS above 2.43 were well dissolved in these

Table 2
Solubility of the cellulose propionate and cellulose butyrate synthesized in AmimCl.

Sample	DS	DMSO	DMF	Acetone	THF	Toluene	Chloroform	Ethyl acetate
CP-14	0.90	++	++	–	–	–	–	–
CP-15	1.36	++	++	+	+	+	+	–
CP-16	1.90	++	++	+	+	+	+	+
CP-6	2.55	++	++	++	++	++	++	+
CP-9	2.89	++	++	++	++	++	++	+
CB-1	0.46	++	++	–	–	–	–	–
CB-2	1.41	++	++	+	+	+	+	+
CB-3	1.84	++	++	+	+	+	+	+
CB-4	2.43	++	++	++	++	++	++	++
CB-5	2.76	++	++	++	++	++	++	++

++, soluble; +, swollen; –, insoluble.

three solvents. The solubility of CP (DS ≥ 2.55) and CB (DS ≥ 2.43) in ethyl acetate is different. CB with DS above 2.43 dissolved in ethyl acetate, whereas CP with DS above 2.55 was just swollen. Interestingly, we found that CP with DS above 2.55 and CB with DS above 2.43 were readily dissolved in non-polar solvent toluene, which might be due to the increased hydrophobic property of cellulose esters with increasing DS.

4. Conclusion

In the present work, we demonstrated that DMAP was an effective catalyst for both propionylation and butyralation of cellulose in an ionic liquid AmimCl. Cellulose propionate and cellulose butyrate with a wide range of DS were successfully synthesized in ionic liquid AmimCl by the reaction of cellulose with propionic anhydride and butyric anhydride. CP and CB with high DS ($DS_{CP} = 2.89$, $DS_{CB} = 2.76$) were obtained applying a molar ratio (acid anhydride/AGU) of 3:1 within only 30 min. The DS of CP and CB was easily controlled just by altering this molar ratio. Further, conversion of acid anhydride was very high, for instance, in the molar ratio (acid anhydride/AGU) range from 1:1 to 3:1, the conversion of propionic anhydride and butyric anhydride was above 90%. The products were characterized by FT-IR and NMR techniques. For both propionylation and butyralation of cellulose, the reactivity order of the three hydroxyl groups in each anhydroglucose unit was C6-OH > C2-OH > C3-OH. All the obtained cellulose esters with high DS values exhibited good solubility in some organic solvents. Therefore, this work provides a facile and highly efficient method for synthesis of CP and CB cellulose esters.

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