

Synthesis of cellulose benzoates under homogeneous conditions in an ionic liquid

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Abstract The ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) as a reaction medium was studied for the synthesis of cellulose benzoates by homogeneous acylation of dissolved cellulose with benzoyl chlorides in the absence of any catalysts. Cellulose benzoates with a degree of substitution (DS) in the range from about 1 to 3.0 were accessible under mild conditions. The DS of cellulose derivatives increased with the increase of the molar ratio of benzoyl chloride/anhydroglucose unit (AGU) in cellulose, reaction time, and reaction temperature. Benzoylation of cellulose with some 4-substituted benzoyl chlorides including 4-toluoyl chloride, 4-chlorobenzoyl chloride and 4-nitrobenzoyl chloride was also readily carried out under mild conditions. Furthermore, regioselectively substituted mixed cellulose esters were synthesized in this work. All products were characterized by means of FT-IR, ^1H -NMR, and ^{13}C -NMR spectroscopy. In addition, at the end of benzoylation of cellulose, the ionic liquid AmimCl was easily recycled. When the recycled AmimCl was used as the reaction media, the cellulose

benzoate with a similar DS was obtained under comparable reaction conditions.

Keywords Cellulose benzoates · Chiral stationary phases · Homogeneous acylation · Ionic liquid · Regioselectively substituted mixed cellulose esters

Introduction

Except for use as thermoplastic cellulose-based materials (Braun and Bahlig 1994), cellulose benzoates exhibit high chiral recognition ability and have been extensively used as chromatographic chiral selectors in chiral stationary phases (CSPs) for the separation of enantiomers by HPLC (Okamoto and Yashima 1998; Yashima 2001). The cellulose benzoates were often prepared by the reaction of cellulose with a large excess of the corresponding acid chloride in the presence of pyridine. In most cases, the synthesis of cellulose benzoates started from cellulose suspension in organic solvents and carried out heterogeneously (Rimböck et al. 1986; Francotte and Wolf 1992; Chen et al. 2003). The reaction initially involves the amorphous part and next the crystallites of cellulose. Therefore, in intermediate steps of reaction, the cellulose esters present an uneven substitution. As a consequence, it is generally difficult to control the structure of cellulose derivatives. In addition, to synthesize the

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task-specific cellulose benzoates for CSPs, such as bonded-type of CSPs and regioselectively substituted heterofunctional CSPs, it is often necessary to firstly protect the primary hydroxyl group at C-6 position using triphenylmethyl chloride and then remove the trityl group (Felix 2001; Franco et al. 2001; Chen et al. 2003). Although homogeneous synthesis of cellulose benzoates in LiCl/*N,N*-dimethylacetamide (DMAc) has also been reported (Okamoto et al. 1984, 1987; Ichida et al. 1984), there remain limitations such as difficulty for solvent recovery, using pyridine as the catalyst and time-consuming.

Room-temperature ionic liquids (ILs) are organic or organo-metal molten salts with melting points often below 100 °C. ILs are almost nonvolatile, non-flammable, thermally stable and reusable ‘green’ solvents. And polarity, melting point and other properties of ILs can be tuned by simple structural modifications of the cation and/or anion (Holbrey and Seddon 1999; Sheldon 2005; Welton 1999). Because of their unique properties, ILs are currently being explored as environmentally benign solvent substitutes for traditional volatile organic solvents in a variety of applications such as chemical synthesis, liquid/liquid separations, extractions, dissolution, catalysis, and polymerization (Welton 1999; Rogers and Seddon 2002; Wasserscheid and Welton 2003). Recently, it has been shown that cellulose can be readily dissolved in some ILs, such as, 1-butyl-3-methylimidazolium chloride (BmimCl) (Swatloski et al. 2002) and 1-allyl-3-methylimidazolium chloride (AmimCl) (Ren et al. 2003). As a new kind of aprotic solvents, ILs used as the ‘green’ reaction media for homogeneous cellulose derivations have also drawn much attention. In our previous studies, homogeneous acetylation of cellulose was carried out in AmimCl without any catalysts and cellulose acetates with a wide range of degree of substitution were obtained (Wu et al. 2004; Cao et al. 2007). Some other cellulose esters, such as cellulose carbanilate, phthalate, and furoate have also been successfully synthesized in ILs (Liu et al. 2007; Köhler and Heinze 2007; Barthel and Heinze 2006; El Seoud et al. 2007).

In the present study, the ionic liquid AmimCl was studied as a reaction medium for the synthesis of cellulose benzoates. The cellulose benzoates obtained were characterized by means of FT-IR and NMR spectroscopy and solubility test. Furthermore,

regioselectively substituted cellulose mixed ester was also synthesized under homogeneous reaction conditions. Finally, the recovery of the ionic liquid and the benzylation of cellulose in the recycled AmimCl were also discussed.

Experimental part

Materials

AmimCl was synthesized according to literature (Ren et al. 2003). Cellulose samples used included two kinds of microcrystalline cellulose, and dissolving pulp. The viscosity-average degree of polymerization (DP) of these three cellulose materials measured using an Ubbelohde viscometer in cupriethylenediamine hydroxide solution (CUEN) was 220, 300, and 650, respectively. They were dried in vacuum at 80 °C for 2 h prior to use. 4-Nitrobenzoyl chloride was purchased from Fluka. All other chemicals of analytical grade were obtained from Beijing Chemical Reagent Company, China, and used without further purification.

Dissolution of cellulose in AmimCl

For a typical preparation of cellulose solution in AmimCl (Zhang et al. 2005), the dried cellulose was added to a certain amount of AmimCl in a three-necked flask, and the mixture of cellulose/AmimCl was heated in oil bath for 30 min at 80 °C with mechanical stirring, yielding three different concentrations of cellulose/AmimCl solutions (containing 3.0, 5.0, and 7.0% of cellulose by weight). They were all clear and viscous solutions with light yellow color.

Synthesis of cellulose benzoates

At a given temperature, various benzylation agents (benzoyl chloride, 4-toluoyl chloride, 4-chlorobenzoyl chloride and 4-nitrobenzoyl chloride) were added into cellulose/AmimCl solutions under vigorous stirring. After the required time, the resultant products were isolated as methanol-insoluble fractions, filtered and washed three times with methanol. They were redissolved in DMSO, precipitated again into methanol and thoroughly washed with the same

solvent. Then these products were dried under vacuum at 80 °C.

Synthesis of cellulose-2,3-*bis*-O-(4-nitrobenzoate)-6-O-benzoate

Cellulose-2,3-*bis*-O-(4-nitrobenzoate)-6-O-benzoate was synthesized according to Scheme 1.

To a solution of 0.5 g cellulose in 9.5 g AmimCl, 3.6 mL benzoyl chloride were added at 60 °C for 20 min, the resultant product was isolated as methanol-insoluble fractions, filtered, washed three times with methanol, and dried under vacuum at 80 °C. Then the cellulose benzoate product was redissolved in AmimCl at 80 °C, and 2.3 g 4-nitrobenzoyl chloride was added into the solution with stirring for 2 h. The product was isolated as described above.

Measurements

The IR spectra were recorded with a Fourier transform IR spectrometer (FT-IR System 2000, Perkin Elmer). Cellulose and cellulose derivatives were tested via pressing with KBr to pellets. NMR spectra were acquired on a Bruker AV 400 spectrometer with 16 scans for ^1H -NMR and 8 000–18 000 scans for ^{13}C -NMR measurements (Bruker AV 400 and AV 600) at room-temperature in DMSO- d_6 .

The DS of cellulose benzoates was calculated from ^1H -NMR according to Goodlett et al. (1971) by equation:

$$\text{DS} = \frac{7I_{\text{phenyl}}}{5I_{\text{AGU}}}; \quad (1)$$

I_{phenyl} , peak integral of phenyl protons; I_{AGU} , peak integral of protons of anhydroglucose unit.

Results and discussion

Synthesis of cellulose benzoates

Investigation has been conducted on the effect of reaction parameters, such as temperature, reaction time, and the molar ratio of reactants, i.e., benzoyl chloride/anhydroglucose unit (AGU), in the synthesis of cellulose benzoates. The DS of cellulose benzoates synthesized in AmimCl under various conditions is listed in Table 1. The data show that the reaction was accelerated by raising the temperature. Under the conditions of a molar ratio of 10:1 and reaction time of 2 h, the increase of reaction temperature from 40 to 60, 80, and 100 °C led to an increase in the DS of the products from 1.13 to 1.34, 1.80, and 2.43, respectively. The DS of the products increased as reaction time prolonged. And increasing the molar ratio of benzoyl chloride/AGU from 2:1 to 5:1 also resulted in an increase in the DS of the products from 0.97 to 1.76. When the molar ratio increased from 5:1 to 10:1, the DS of the product was still the same. Thus, excess benzoyl chloride had no significant effect on the benzylation rate of cellulose in AmimCl. Furthermore, comparing the sample A22 with A2, we could find that, if the cellulose/AmimCl solution was continuously purged with gaseous N_2 , the DS was higher than that without N_2 . From Table 1, it can also be seen that, at different concentrations of cellulose/AmimCl solutions or using cellulose samples with different DPs, no significant difference in the DS values was observed. These results suggest that it is possible to control the DS value of cellulose benzoates by controlling stoichiometric ratio of benzoyl agent/AGU, reaction temperature, and reaction time, especially the last two conditions.

Scheme 1 The synthetic route of cellulose-2,3-*bis*-O-(4-nitrobenzoate)-6-O-benzoate

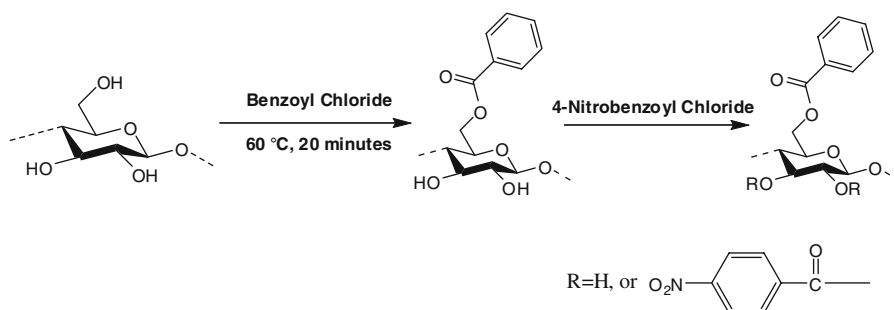


Table 1 DS of cellulose benzoates homogeneously prepared in AmimCl under various conditions

No	Cellulose			Molar ratio of benzoyl chloride/AGU	T (°C)	t (h)	DS
	Concentration (wt%)	Type	DP				
A1	5	MCC	220	10:1	100	2	2.43
A2	5	MCC	220	10:1	80	2	1.80
A3	5	MCC	220	10:1	70	2	1.63
A4	5	MCC	220	10:1	60	2	1.35
A5	5	MCC	220	10:1	50	2	1.15
A6	5	MCC	220	10:1	40	2	1.13
A7	5	MCC	220	10:1	100	1	2.21
A8	5	MCC	220	10:1	100	3	2.70
A9	5	MCC	220	10:1	100	4	3.0
A10	5	MCC	220	8:1	80	4	2.14
A11	5	MCC	220	8:1	80	2	1.77
A12	5	MCC	220	6:1	80	2	1.82
A13	5	MCC	220	5:1	80	2	1.76
A14	5	MCC	220	4:1	80	2	1.47
A15	5	MCC	220	3:1	80	2	1.22
A16	5	MCC	220	2:1	80	2	0.97
A17	7	MCC	220	10:1	80	1	1.56
A18	5	MCC	220	10:1	80	1	1.49
A19	3	MCC	220	10:1	80	1	1.61
A20	5	MCC-2	300	10:1	80	2	1.86
A21	5	Pulp	650	10:1	80	2	1.76
A22	5	MCC	220	10:1	80	2	1.98

Note: The sample A22 was synthesized when cellulose/AmimCl solution was continuously purged with gaseous N₂

FTIR spectra

FTIR spectra of unmodified cellulose (spectrum a), and the cellulose benzoate samples A16 with DS = 0.97 (spectrum b) and A7 with DS = 2.21 (spectrum c) are shown in Fig. 1. The spectra b and c provide a clear evidence of benzylation by showing the presence of some important peaks at 1,718 cm⁻¹ for C=O stretching in ester, 1,277 cm⁻¹ for stretching of (O) C–O, 3,067 cm⁻¹ for benzene ring C–H stretching, 1,604, 1,452 cm⁻¹ for aromatic C=C stretching and 713 cm⁻¹ for the out-of-plane C–H bending of the monosubstituted benzene. In addition, as the DS increased, the intensity of peaks at 3,348 (OH stretching) and 1,372 cm⁻¹ (OH bending) obviously decreased, and the absorption intensity at 1,718, 1,277 and 713 cm⁻¹ increased, and both peaks of ν_{OH} and $\nu_{\text{C=O}}$ shifted to higher frequencies (Sun et al. 2005; Chen et al. 2003; Acemoglu et al. 1998).

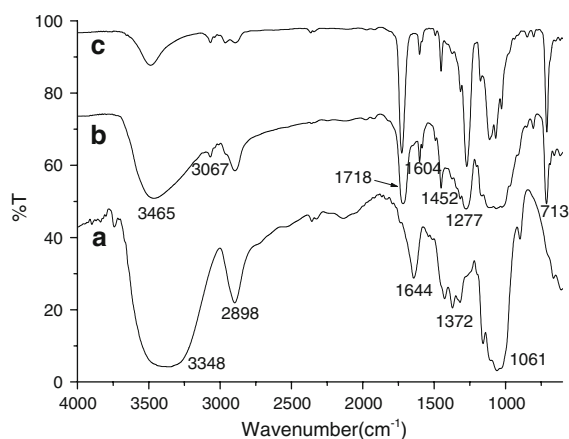
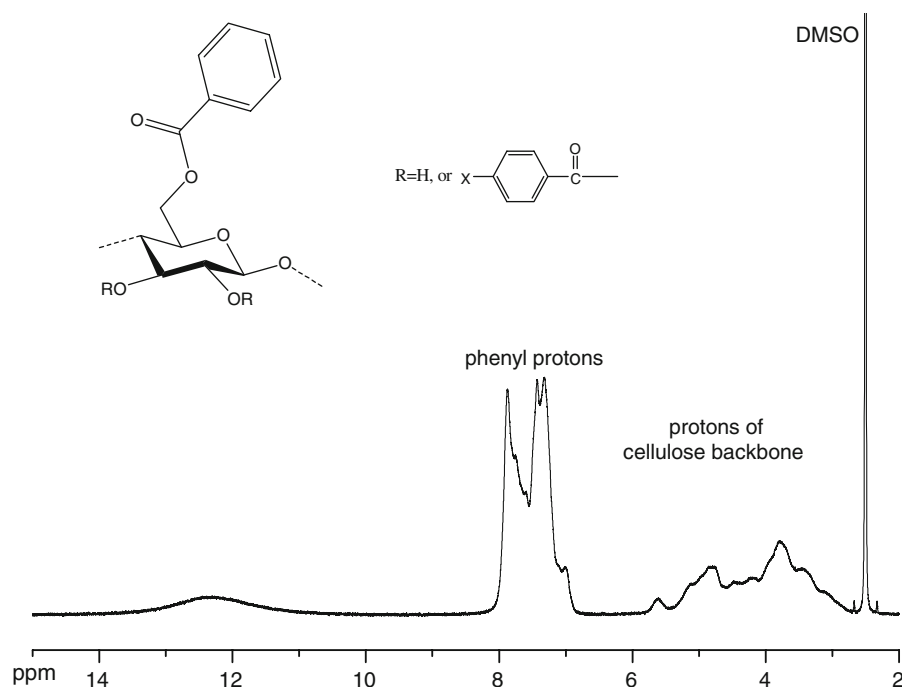


Fig. 1 FTIR spectra of unmodified cellulose (spectrum a), the cellulose benzoate sample A16 with DS = 0.97 (spectrum b), and the sample A7 with DS = 2.21 (spectrum c)

¹H-NMR spectra

The cellulose benzoate with DS 2.14 (Sample A10) was characterized by ¹H-NMR spectroscopy (Fig. 2). The results are described below.

Fig. 2 ^1H -NMR spectrum of the cellulose benzoate sample A10 with DS = 2.14



Cellulose benzoate: $\delta = 6.8\text{--}8.2$ (phenyl protons, 5H), $\delta = 2.8\text{--}5.9$ (protons of cellulose backbone, 7H) (Acemoglu et al. 1998).

^{13}C -NMR spectra

Structural analysis of cellulose benzoates by means of ^{13}C -NMR spectroscopy in $\text{DMSO-}d_6$ was performed (Fig. 3). It can be seen that at the DS value (A6) 1.13, all the signals of C-7, C-1, C-4, and C-6 are very sharp peaks and well resolved. In addition, the peak of C-6 influenced by esterification in O-6 appears at $\delta = 63.2$ ppm, exhibiting a downfield shift of about 3 ppm compared with the corresponding carbon of unmodified cellulose. All of these prove that the benzoyl chloride reacted specifically at the primary hydroxyl group C-6 and that reaction with secondary hydroxyl groups was almost nonexistent. In spectrum b for the sample A10 with DS of 2.14, the signal of C-7 becomes a broad peak. The signal of C-1 appears at 102.2 ppm while the signal at 99.2 ppm can be assigned to C-1' (C-1 atom influenced by an O-2 esterification). The C-4 and C-4' signals appear at 79.2 ppm and 76.7 ppm, respectively, indicating the influence of an O-3 functionalization. The signal of C-1 almost disappears in ^{13}C -NMR spectrum c for

the sample A8 with DS of 2.70. Therefore, the three hydroxyl groups at the C-2, C-3, and C-6 positions exhibited various reaction activities. Obviously, the benzylation reaction was exclusively preferred at C-6, and the order of reactivity was $\text{C6-OH} \gg \text{C2-OH} > \text{C3-OH}$.

Solubility of cellulose benzoates

The solubility of cellulose benzoates in some organic solvents is shown in Table 2. It is clear that all the samples are soluble in DMSO. When the DS is above 1.49, the samples dissolve rapidly in THF. In some polar solvents such as chloroform, acetone, and chlorinated solvents, samples of low DS can not dissolve, those samples with DS greater than 2.04 can be swollen, while those larger than 2.43 dissolve slowly.

Benzylation of cellulose with 4-substituted benzoyl chloride

Benzylation of cellulose with 4-toluoyl chloride, 4-chlorobenzoyl chloride and 4-nitrobenzoyl chloride were also investigated. The DS values of these products were determined by ^1H -NMR, as shown in

Fig. 3 ^{13}C -NMR spectra of cellulose benzoate sample A6 with DS = 1.13 (spectrum a), sample A10 with DS = 2.14 (spectrum b) and sample A8 with DS = 2.70 (spectrum c)

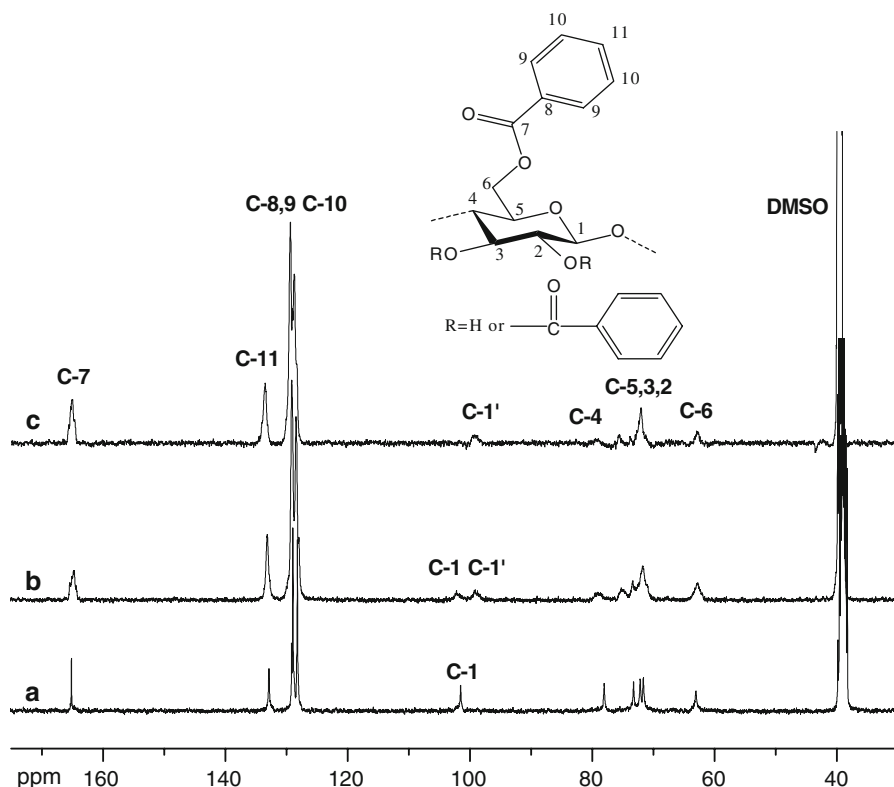


Table 2 Solubility of cellulose benzoate samples with different DS prepared in AmimCl

DS	Solvent						
	DMSO	THF	Acetone	Chloroform	Dichloromethane	1,2-Dichloroethane	Ethyl acetate
0.99	+	±	—	—	—	—	—
1.49	+	+	—	—	—	—	—
2.04	+	+	±	±	±	±	±
2.43	+	+	+	+	+	+	+
2.70	+	+	+	+	+	+	+

+, Soluble; —, Insoluble; ±, Wollen

Table 3. It is clear that the rule of reaction of cellulose with other phenyl chloride was the same as that of the synthesis of cellulose benzoate.

The products were characterized by ^1H -NMR spectroscopy, the results are described below:

Cellulose 4-nitrobenzoate: $\delta = 7.4\text{--}8.5$ (phenyl protons, 4H), $\delta = 2.8\text{--}6.0$ (protons of cellulose backbone, 7H);

Cellulose 4-chlorobenzate: $\delta = 7.1\text{--}8.1$ (phenyl protons, 4H), $\delta = 2.8\text{--}6.0$ (protons of cellulose backbone, 7H);

Cellulose 4-toluate: $\delta = 2.0\text{--}2.5$ (methyl protons, 3H), $\delta = 6.9\text{--}8.0$ (phenyl protons, 4H), $\delta = 2.9\text{--}5.9$ (protons of cellulose backbone, 7H).

The DS of cellulose 4-nitrobenzoate, 4-chlorobenzate, and 4-toluate was calculated from ^1H -NMR according to the equation (Goodlett et al. 1971):

$$\text{DS} = \frac{7I_{\text{phenyl}}}{4I_{\text{AGU}}}; \quad (2)$$

I_{phenyl} , peak integral of phenyl protons; I_{AGU} , peak integral of protons of anhydroglucose unit.

Table 3 DS of various cellulose benzoates homogeneously prepared in AmimCl under various conditions

No	4-Substituted benzoyl chloride	Cellulose (wt%)	Molar ratio of benzoyl chloride/AGU	T (°C)	Reaction time (h)	DS
B1	4-Toluoyl chloride	5	10:1	60	0.5	0.84
B2	4-Toluoyl chloride	5	10:1	80	0.5	1.23
B3	4-Toluoyl chloride	5	10:1	80	2.5	1.84
C1	4-Chlorobenzoyl chloride	5	10:1	60	0.5	1.11
C2	4-Chlorobenzoyl chloride	5	10:1	80	0.5	1.25
C3	4-Chlorobenzoyl chloride	5	10:1	80	2.5	2.00
D1	4-Nitrobenzoyl chloride	5	10:1	80	1	1.87
D2	4-Nitrobenzoyl chloride	5	10:1	80	1	2.88
D3	4-Nitrobenzoyl chloride	5	10:1	80	2	3.0

The products were also characterized by ^{13}C -NMR spectroscopy. Due to the steric hindrance effect, the benzylation reaction was also preferred at C-6.

Synthesis of regioselectively substituted cellulose mixed esters

It has been reported that some regioselectively substituted cellulose derivatives have exhibited a higher enantioselectivity than the homogeneously

substituted cellulose tribenzoates. In this work, some regioselectively modified cellulose mixed esters, such as cellulose-2,3-*bis*-O-(4-nitrobenzoate)-6-O-benzoate and cellulose-2,3-*bis*-O-(4-chlorobenzoate)-6-O-benzoate, were synthesized. For cellulose-2,3-*bis*-O-(4-nitrobenzoate)-6-O-benzoate, the DS values were determined from ^1H -NMR spectra and the regarding structure was characterized by ^{13}C -NMR spectroscopy. Figure 4 gives a ^{13}C -NMR spectrum of cellulose benzoate sample with DS of 0.99. It can

Fig. 4 ^{13}C -NMR spectrum of cellulose benzoate sample with DS of 0.99

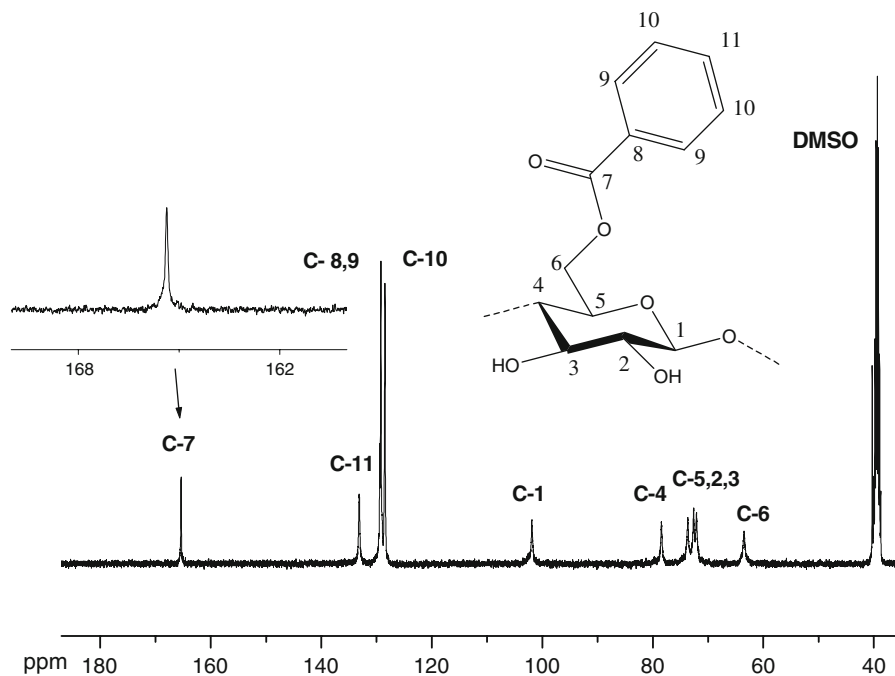
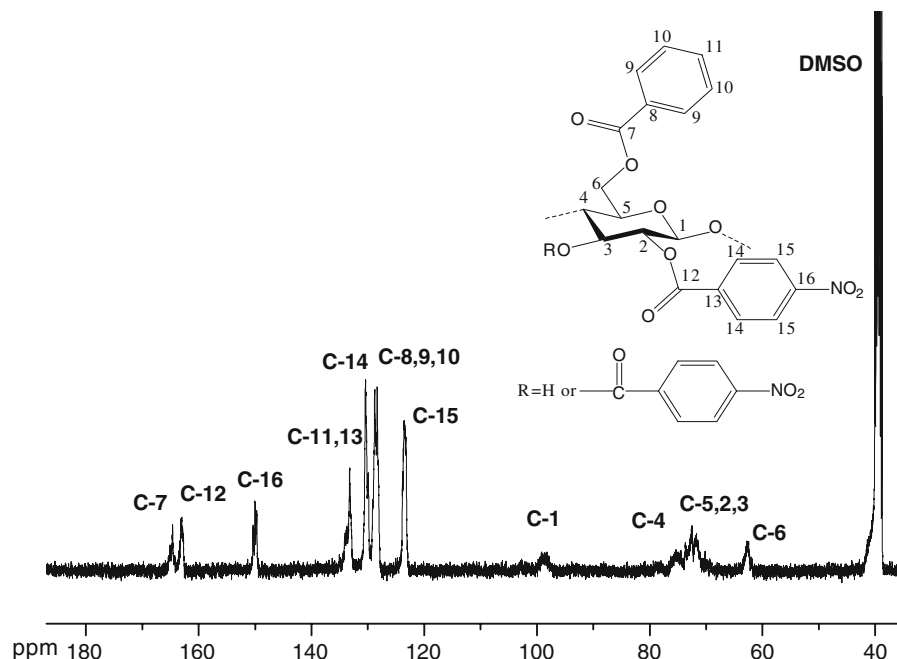


Fig. 5 ^{13}C -NMR spectrum of cellulose-2,3-*bis*-O-(4-nitrobenzoate)-6-O-benzoate in which DS of benzoate is 0.99 and DS of 4-nitrobenzoate is 1.82



be clearly seen that the benzoyl chloride reacted only with the primary hydroxyl group at C-6 and the substitution at secondary hydroxyl groups was almost nonexistent. Then 6-O-benzoate cellulose reacted with 4-nitrobenzoyl chloride and obtained cellulose-2,3-*bis*-O-(4-nitrobenzoate)-6-O-benzoate. In Fig. 5, the ^{13}C -NMR spectrum of the product exhibits a new characteristic signal at 163.1 ppm (C-12) due to the formation of the new benzoate bond. The other new signals at δ 150.0 ppm (C-16), 130.4 ppm (C-14) and 123.4 ppm (C-15) are attributed to the carbons of 4-nitrophenyl.

Recycling of the ionic liquid and synthesis of cellulose benzoates in the recycled AmimCl

At the end of benzylation of cellulose, 600 mL deionized water was poured into 1,200 mL the methanol/AmimCl solution, followed by stirring for 1 h and filtration. Then after a simple rotary evaporation, AmimCl with high purity was obtained (Fig. 6). Because of negligible vapor pressure and good thermostability, the recycling and isolation of this IL are very easily done. This advantage makes this IL potentially attractive for industrial applications.

The influence of freshness of AmimCl on the synthesis of cellulose benzoates was also studied.

When the recycled AmimCl was used as the benzylation media, cellulose benzoates with a comparable DS were obtained under the same reaction condition. The result was listed in Table 4.

Conclusion

It has been demonstrated that the ionic liquid AmimCl is a suitable reaction medium for the preparation of cellulose benzoates. Under the mild conditions, the homogeneous benzylation of cellulose was readily carried out in AmimCl without any catalyst. Cellulose benzoates with a DS in the range from about 1 to 3.0 were obtained, and the DS of cellulose derivatives were easily controlled by altering reaction temperature, reaction time, and the molar ratio of benzylation agent/AGU. The regioselectively substituted cellulose mixed esters were also synthesized in AmimCl. After reaction, the ionic liquid AmimCl was effectively recycled and reused. Therefore, this work provides a facile method to synthesize homofunctional, and regioselectively heterosubstituted cellulose benzoates. In other words, it provides a chance to develop a more efficient cellulose-based chiral stationary phases. Further investigation on the enantioselective ability

Fig. 6 ^1H -NMR spectra of the fresh and the recycled AmimCl after the reaction

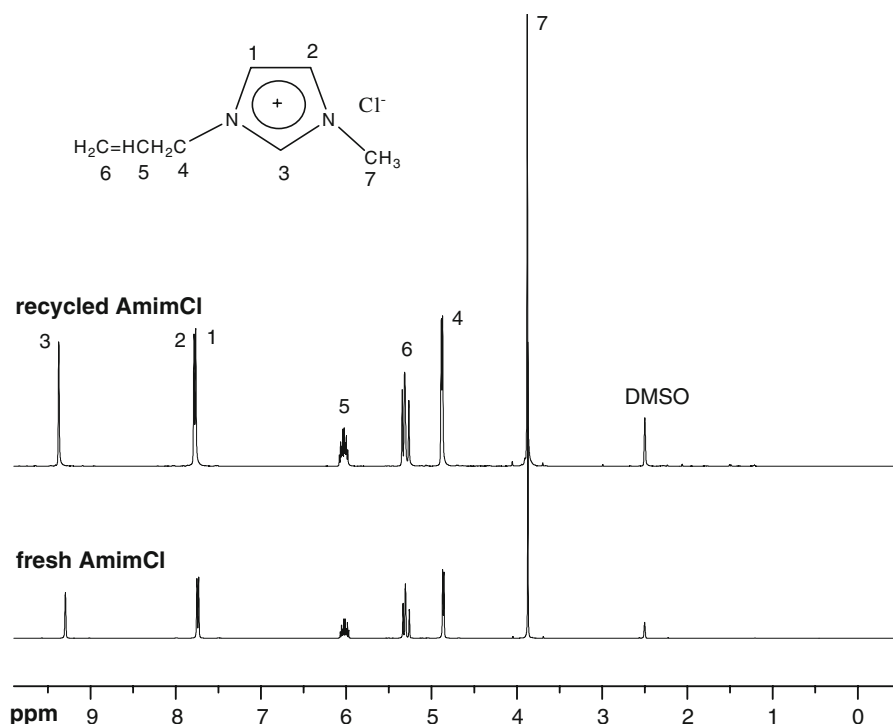


Table 4 DS of cellulose benzoates homogeneously prepared in the fresh and the recycled AmimCl

No	Ionic liquids	Molar ratio of benzoyl chloride/AGU	T (°C)	Reaction time (h)	DS
F1	Fresh AmimCl	10:1	60	1	1.17
F2	Fresh AmimCl	10:1	60	2	1.35
R1	Recycled AmimCl	10:1	60	1	1.15
R2	Recycled AmimCl	10:1	60	2	1.36
F3	Fresh AmimCl	10:1	80	1	1.49
F4	Fresh AmimCl	10:1	80	2	1.80
R3	Recycled AmimCl	10:1	80	1	1.52
R4	Recycled AmimCl	10:1	80	2	1.84

of cellulose benzoates synthesized in ILs will be conducted.

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