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Homogeneous tritylation of cellulose in 1-allyl-3-methylimidazolium chloride and subsequent acetylation: The influence of base

Yuxia Lv[a,b], Yaliang Chen[a,b], Ziqiang Shao[a,b,*], Renxu Zhang[c], Libin Zhao[c]

[a] College of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, PR China
[b] Beijing Engineering Technology Research Center for Cellulose and Its Derivative Materials, Beijing 100081, PR China
[c] Sichun Nitrocell Corp. Ltd., Luzhou 646605, PR China

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ABSTRACT

Homogeneous tritylation of cellulose in 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid with triphenylmethy chloride as regents, pyridine or 1-butylimidazole (BIM) as base was investigated, and subsequent acetylation of the 6-*O*-functionalized products was further studied. The structure of products was analyzed by FTIR and ^{13}C NMR spectroscopy and base influences on the structure were discussed as well. The solution with pyridine as base underwent heterogeneous–homogeneous–heterogeneous process and the obtained trityl cellulose (TC) had organized structure with trityl group located completely at C-6 position of cellulose with maximum DS_{trityl} of nearly 1. In the case of BIM as base, the solution was homogeneous for the whole reaction, but the highest DS_{trityl} was about 0.22, with trityl group located not only at position 6 but also partially at position 2. Subsequent acetylation of the TC led to products with a preferred functionalization of the unprotected secondary OH-groups.

1. Introduction

Cellulose, as the most abundant polymer on earth, has attracted much attention in more expanded application areas such as in field of nanoscience, nanotechnology, functionalized materials apart from in fiber, paper, membrane, polymer and paint industries (Klemm, Heublein, Fink, & Bohn, 2005; Qiu & Hu, 2013). However, cellulose can not be melted and extremely difficult to be dissolved in common solvents because of its stiff molecules and close packing via numerous intermolecular and intramolecular hydrogen bonds (De Souza Lima & Borsali, 2004; Nishiyama, Langan, Wada, & Forsyth, 2010). Ionic liquids (ILs) exhibit a powerful capacity to dissolve cellulose and received considerable attention as alternatives to the traditional organic solvents due to their excellent dissolving capability, negligible vapor pressure, ease of recycling and high thermal stability (Forsyth, Pringle, & MacFarlane, 2004; Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). Recently, studies on the application of ILs in cellulose chemistry have studied extensively, including homogeneous derivation in ILs, like esterification and etherification of cellulose (Ohno & Fukaya, 2009; Gericke, Fardim, & Heinze, 2012a).

Chemical modification of cellulose has been exploited even before its polymeric nature was determined and well understood. Cellulose derivatives with different functions provide a means of altering the physical and chemical properties of cellulose and increasing its functionality and scope of their use (Heinze & Liebert, 2001; Liebert, 2008). To develop new applications or to better predict the performance of cellulose derivatives in current application, it is critical to understand structure property relationship in detail. However, preparation of these derivatives with well-defined structures is usually difficult owing to the polyhydroxy of cellulose and its insolubility in ordinary solvents (Klemm, Heinze, Philipp, & Wagenknecht, 1997; Fox, Li, Xu, & Edgar, 2011). Organized structure products can be achieved when cellulose intermediates

* Corresponding author at: College of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, PR China. Tel.: +86 10 68940942; fax: +86 10 51704616.
E-mail address: Shaoziqiang@263.net (Z. Shao).

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with proper protecting groups are able to carry out regioselective reactions in solution under mild conditions. Development of such intermediates is so essential for constructing molecular architectures that many studies have been done and some protecting groups have proved effectual for preparing soluble cellulose intermediates (Koschella, Fenn, Illy, & Heinze, 2006; Liu, Xia, & Yang, 2012).

Trityl group is a common and important protecting group for many functional groups because of its easy installation and cleavage (Koschella et al., 2006; Fox et al., 2011). They have long been extensively exploited to achieve regioselectivity in protecting primary hydroxyl of cellulose. The trityl group is introduced on hydroxyl by many homogeneous procedures, in order to obtain products with uniform distribution of trityl moieties along the polysaccharide chain. The regioselective substituting accuracy and efficiency of protecting group are influenced by solvent mediums (e.g. DMAc/LiCl or ILs), catalysts (e.g. pyridine or triethylamine), molar ratio of protecting group and so on (Takahashi, Fujimoto, Barua, Miyamoto, & Inagaki, 1986; Gómez, Erler, & Klemm, 1996; Erdmenger, Haensch, Hoogenboom, & Schubert, 2007; Granström, Olszewska, Mäkelä, Heikkinen, & Kilpeläinen, 2009). In past years many studies had reported that this protecting reaction was popularly carried out in DMAc/LiCl solvent at temperatures of 100–150 °C (Gómez et al., 1996; Welcke, Kötteritzsch, & Heinze, 2010). Compared to harsh conditions resulted from solvent of DMAc/LiCl, ILs are of special interest, because they can give a milder condition for regioselective substituting primary hydroxyl of cellulose, and achieve higher degree of distribution (DS) and substituting efficiency (Erdmenger et al., 2007; Granström et al., 2009). For example, after 3 h reaction trityl cellulose (TC) with DS of 1.09 was obtained in 1-butyl-3-methylimidazolium chloride (BmimCl), while for DMAc/LiCl system 24 h were required to obtain TC with a comparable DS at same reaction reagent and molar ratio of protecting group (Takahashi et al., 1986; Erdmenger et al., 2007). Furthermore, the fact that DS did not exceed 1.3 in the tritylation of cellulose with a *p*-methoxytrityl group in DMAc/LiCl was reported, whereas the DS reached about 2.0 in ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) (Gómez et al., 1996; Granström et al., 2009).

It is widely accepted that the tritylation reaction predominantly consists of an attack by the triphenylmethylcarbenium ion Tr^+ on the hydroxyl site through a S_N1 mechanism (Granström et al., 2009; Fox et al., 2011). The process rate depends on the capability of its components to favor the heterolytic cleavage of the Tr—X bond and the competition between Tr^+ and H^+. Generally, trityl chloride (TrCl) are used in association with an organic base such as pyridine, triethylamine etc (Erdmenger et al., 2007). In fact, the base acts as a proton scavenger when the substrate hydroxyls release protons, thus avoiding *O*-detritylation of trityl-ethers by the released HCl and promoting the competition of Tr^+ ions on the hydroxyl site as well. Therefore, the DS of TC would increase with the concentration of pyridine until the solution would easily become turbid and heterogeneous (Erdmenger et al., 2007). Although triethylamine is more basic and less toxic than pyridine, and it is reported to be more favored for the tritylation of cellulose than that of pyridine in DMAc/LiCl, it could not be applied for homogeneous tritylation of cellulose in ILs because the base neither dissolved in the ILs nor in cellulose/IL solution (Erdmenger et al., 2007; Gericke et al., 2012b). Thus, a more basic and miscible solvent with ILs might be more suitable in homogeneous cellulose/ILs solutions. Gericke et al. (2012b) has reported that mixtures of ILs with co-solvent turned out to be an efficient media for the homogeneous tosylation of cellulose, and application of 1-butylimidazole (BIM) as base would increase the reactivity and efficiency. As an effective base in cellulose tosylation, BIM might be available for tritylation of cellulose in ILs as well.

In the present work we studied the homogeneous reaction of cellulose in AmimCl with TrCl as regents, pyridine or BIM as base. The purpose was to evaluate the effect of base on homogeneous tritylation of cellulose in AmimCl. Moreover, subsequent acetylation reactions of TC including the final detritylation step were investigated. The functionalization patterns of the cellulose derivatives were examined using ^{13}C- and ^{1}H NMR spectroscopy.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC, Vivapur 101) with a degree of polymerization (DP) of 220 was used. AmimCl was synthesized according to the literature (Zhang, Wu, Zhang, & He, 2005). Pyridine (AR grade) was supplied by Beijing Chemical Reagent Factory and purified by distillation before use. Triphenylmethy chloride (CP grade), acetic anhydride (AR grade), hydrobromic acid aqueous solution (40 wt%), and other organic solvents were obtained from Beijing Chemical Reagent Factory and used as received. Propionic anhydride (AR grade) and 1-butylimidazole (AR grade) were purchased from Aladdin Reagent Co. Ltd. and used as received.

2.2. Characterization

Fourier-Transform Infrared (FTIR) spectra were recorded on a Nicolet is50 infrared spectrometer (TA). Cellulose and cellulose derivatives were tested via pressing with KBr to pellets. The data was collected after 16 scans at a resolution of 2 cm^{-1} within wave number range 4000–500 cm^{-1}. NMR spectra were acquired on a Bruker AV 400 spectrometer with 16 scans for ^{1}H NMR and 8000–18,000 scans for ^{13}C NMR measurements (Bruker AV 600) at room temperature, or 5000–8000 scans for ^{13}C NMR measurements (Bruker AV 300) at 100 °C in DMSO-d_6. Elemental analysis was done on vario EL cube Elemental Analyzer (Elementar). The instrument determined total carbon, hydrogen, and nitrogen contents, while oxygen content was determined by difference.

2.3. Synthesis of trityl cellulose

2.0 g of dried cellulose (12.3 mmol) was dispersed in 18.0 g AmimCl (113.6 mmol) in a three necked flask, and the mixture was heated to 90 °C for 8 h with continuous mechanical stirring. A clear and viscous solution was obtained with 10 wt% cellulose concentration. TrCl (10.3–20.6 g, 36.9–73.8 mmol) and BIM (9.7–32.3 mL, 73.8–246.0 mmol) or dried pyridine (5.9–13.9 mL, 73.8–172.2 mmol) were added in cellulose solution under continuous stirring at 90 °C and reacted for 1–20 h. The reaction mixture was precipitated in 200 mL methanol. After filtered, the TC was washed several times with methanol and finally dried in vacuum at 60 °C. The yield was 90–93%.

Elemental analysis found (sample P10): C% 73.68, H% 5.84, N% 0.08, and O% 20.40 (calculated).

2.4. Acetylation of trityl cellulose

Acetic anhydride (0.25–12.5 mL, 2.6–132.2 mmol) was added to a solution of 1 g (2.5 mmol) of sample P10 in 16 mL pyridine under mechanical stirring at 90 °C and reacted for 12–48 h. After reaction, the mixture was cooled to room temperature and then poured into 200 mL methanol. The precipitate (AP10) was filtrated off and washed with methanol for several times and finally dried in vacuum at 60 °C.

Elemental analysis found (sample AP10): C% 69.50, H% 5.61, N% 0.02, and O% 24.87 (calculated).

^{1}H NMR (sample AP10, 10 mg/mL in DMSO-d_6, 293 K): δ (ppm) = 7.5–6.3 (H-trityl), 5.5–2.7 (H-AGU), 2.1–1.6 (H-acetyl).

2.5. Detritylation of 2,3-O-acetyl-6-O-trityl-cellulose

For the detritylation step, 1 g (2.2 mmol) 2,3-*O*-acetyl-6-*O*-trityl-cellulose (sample AP10) was first dissolved in 50 mL chloroform and then 1.3 mL of hydrobromic acid solution (8.9 mmol) was added drop wise under vigorous stirring at room temperature. After 30 min the solution was poured into 1 L of 70% aqueous methanol solution to obtain a white precipitate. The polymer (CA10) was washed several times with 200 mL methanol and dried in vacuum at 60 °C.

FTIR (sample CA10): $\nu_{C–OH}$ 3470, $\nu_{C–Haliphatic}$ 2920, $\nu_{C=O}$ 1756, $\nu_{H–O–H}$ 1620, δ_{CH} 1370, $\nu_{C–O–Cacetyl}$ 1240, $\delta_{C–OH}$ 1227, $\nu_{CC\ pyranose\ ring}$ 1155, $\nu_{C–OH}$ 1050 cm^{-1}.

2.6. Propionylation of cellulose acetate samples

2,3-*O*-acetyl-cellulose (CA10) was proprionated to estimate the degree of acetylation at the C-2, C-3 and C-6 positions of the AGU. In general, 1 g of CA10 (4.0 mmol) was dissolved in 25 mL anhydrous pyridine and 22.5 mL (174.6 mmol) propionic anhydride was added. The solution was heated to 90 °C and stirred for 2 h, and then it was cooled to room temperature and poured into 500 mL methanol. The precipitate, cellulose acetate propanoate (CAP10), was repeatedly washed with methanol and dried under vacuum at 60 °C to obtain a white powder.

^{1}H NMR (sample CAP10, 10 mg/mL in DMSO-d_6, 293 K): δ (ppm) = 5.5–2.7 (H-AGU), 2.4–1.6 (CH_3-acetyl and CH_2-propionate), 1.23–0.61 (CH_3-propionate).

3. Results and discussion

3.1. Homogeneous tritylation of cellulose

3.1.1. Pyridine as base for reaction

MCC was dissolved in AmimCl and converted with TrCl at 90 °C in the presence of pyridine as base. The results of TC synthesized in AmimCl/pyridine under various conditions were listed in Table 1. In the reaction, pyridine with TrCl was added drop by drop into the cellulose solution. Upon the addition of pyridine, the reaction mixture became turbid forming a heterogeneous system because the local concentration of base at the drop-in zone exceeded the maximum limit. After 30 min reaction time with continuous mixing, a clear solution was obtained. But shortly after the reaction, the systems became turbid and heterogeneous again. For example, when the molar ration of AGU/TrCl/pyridine was 1:3:10, the solution became turbid after 4 h, and phase separation even occurred after 12 h reaction. This transformation from homogeneous to heterogeneous reaction advanced by increasing concentration of TrCl and pyridine showed in Table 1, because of increasingly hydrophobic of tritylated products with increasing DS. It was reasonable to assume that at a certain stage, the amount of compounds with rather low polarity (i.e. TC, excess TrCl and base) exceeded the limit that can be solubilized by the rather polar IL system.

The reaction parameters, such as reaction time, molar ratio of reactants, and amount of pyridine, would affect the DS_{trityl} of TC. A successive increase in reaction time from 1 to 12 h resulted in an increasing DS_{trityl} from 0.28 to 0.61 (P1-5). Further prolonging of the reaction time to 20 h, the DS_{trityl} decreased to 0.18 (P7). It was assumed that the decrease of the DS_{trityl} might be caused by a combination of the released chloride anions, thus the cleavage of trityl group from cellulose would occur with increasing acidic environment in the solution after persistent reaction. As can be seen from the results listed in Table 1, the tritylation in AmimCl with pyridine yielded products with a maximum DS_{trityl} of 0.61 (P5) at a molar ratio of TrCl to AGU of 3 to 1 (reaction time 12 h). When the molar ratio of TrCl to AGU increased to 6:1, the DS_{trityl} of 1 (P10) in a one-step procedure in AmimCl/pyridine was obtained after 8 h reaction. However, according to references, higher DS_{trityl} and substituting efficiency of cellulose tritylation were achieved in BmimCl with pyridine as base. Erdmenger et al. (2007) had reported in his study that tritylation of cellulose with a 6 fold excess of TrCl and 10 fold excess of pyridine per cellulose monomer in BmimCl, a DS of 1.09 was obtained after 3 h reaction time at 100 °C. Granström had explained the higher substituting efficiency in ILs than that in DMAc/LiCl (Granström et al., 2009). They considered that the activation effect is brought about by the decreasing released chloride anion which may be bound by the imidazolium cation in the ILs. In comparison with BmimCl, the cation $[Amim]^+$ had a smaller ion size and a double bond in *N*-substituted methylimidazolium cation of AmimCl (Zhang et al., 2005). Therefore, the reason of higher reaction efficiency in BmimCl/pyridine was speculated that cation $[Amim]^+$ had relatively more electronic chemical structure caused by the conjugative effect of double bond in *N*-substituted methylimidazolium cation of AmimCl, while the $[Bmim]^+$ had stronger polarizing cation with lengthy alkyl group as week electron-donor group, thus $[Bmim]^+$ was able to bind much more released chloride anions. These could be confirmed by their ^{1}H NMR spectrogram of AmimCl and BmimCl, as the H peaks of BmimCl cation appeared at downfield regions (Ren, Wu, Zhang, He, & Guo, 2003; Gericke et al., 2012b). The other reason might be that ion pair or hydrogen bonding of AmimCl might have dissociated when temperature was higher than 43 °C, thus the ability of binding the released chloride anions of imidazolium cation in the IL decreased (Zhang et al., 2005).

The influence of the amount of pyridine was carried out keeping the ratio of TrCl to cellulose at six mol equivalent. When the mol equivalents of pyridine were increased, the resulting DS_{trityl} increased firstly and then decreased. The lower excess of base would reduce the reaction, while more excess of base would promote the substituting efficiency until the base exceeded the limit which could easily induce the cellulose solution to become turbid and heterogeneous. With 14 mol equivalent pyridine, the cellulose solution was turbid in the whole reaction process because of the excess lower polar base in the solution.

3.1.2. BIM as base for reaction

The results of TC synthesized in AmimCl/BIM under various conditions were also listed in Table 1. BIM with TrCl gave quickly homogeneous mixture even at the drop-in zone of cellulose/AmimCl solutions when it was added into the solution drop by drop. And tritylation of cellulose in AmimCl/BIM proceeded completely homogeneously from the beginning and no precipitation or phase separation occurred even after 16 h reaction time. When the mol equivalent of base BIM was 20, the solution was still homogenous at beginning but phase separation happened after 4 h reaction. Compared to pyridine ($pK_a = 5.37$, $E_T^N = 0.30$), BIM possessed a comparably high basicity ($pK_a = 7.18$) and polarity ($E_T^N = 0.35$) (Gericke et al., 2012b). BIM was well miscible with IL than pyridine because AmimCl was a rather polar solvent with $E_T^N = 0.64$ (Gericke, Liebert, Seoud, & Heinze, 2011; Rinaldi, 2011). Therefore, the cellulose/AmimCl solution with BIM was homogeneous at the beginning, while the solution with pyridine could yet become clear after 30 min mixing. Although BIM had high polarity, the solution of cellulose/AmimCl/BIM kept homogeneously in the whole reaction process. After calculating the DS_{trityl} from the elemental composition, the reason for homogeneous reaction was found.

Table 1
Conditions and results of the tritylation of cellulose in AmimCl and base, reaction temperature 90 °C.

No	Base	Molar ratio of AGU/trityl chloride/base	*t* (h)	Reaction course	Product				
					DS[a]	Solubility[b]			
						DMSO	DMF	DMAc	Pyridine
P1	Pyridine	1:3:10	1	Hom	0.28	–	–	–	–
P2	Pyridine	1:3:10	2	Hom	0.36	–	+	+	+
P3	Pyridine	1:3:10	4	Het > hom	0.48	–	++	++	++
P4	Pyridine	1:3:10	8	Gel	0.59	+	++	++	++
P5	Pyridine	1:3:10	12	Het	0.61	+	++	++	++
P6	Pyridine	1:3:10	16	Het	0.39	–	+	+	+
P7	Pyridine	1:3:10	20	Het	0.18	–	–	–	–
P8	Pyridine	1:6:10	1	Hom	0.62	+	++	++	++
P9	Pyridine	1:6:10	4	Gel	0.81	++	++	++	++
P10	Pyridine	1:6:10	8	Het	0.95	++	++	++	++
P11	Pyridine	1:6:10	12	Het	0.75	++	++	++	++
P12	Pyridine	1:6:6	8	Het	0.80	++	++	++	++
P13	Pyridine	1:6:14	8	Het	0.91	++	++	++	++
B1	BIM	1:3:10	1	Hom	0.02	–	–	–	–
B2	BIM	1:3:10	2	Hom	0.02	–	–	–	–
B3	BIM	1:3:10	4	Hom	0.03	–	+	+	+
B4	BIM	1:3:10	8	Hom	0.17	++	++	++	++
B5	BIM	1:3:10	12	Hom	0.18	++	++	++	++
B6	BIM	1:3:10	16	Hom	0.20	++	++	++	++
B7	BIM	1:6:10	8	Het	0.22	++	++	++	++
B8	BIM	1:3:6	8	Hom	0.15	++	++	++	++
B9	BIM	1:3:14	8	Hom	0.16	++	++	++	++
B10	BIM	1:3:20	8	Het	0.14	++	++	++	++

[a] Determined by elemental analysis.
[b] ++, Soluble; –, Insoluble; +, Swollen.

As can be seen from Table 1, the DS_{trityl} was very low for every tritylation production. As expected, the DS_{trityl} increased with increasing molar ration of reagent:AGU and reaction time. However, a molar ratio of TrCl to AGU of 6 to 1 and reaction time of up to 8 h could not increase the DS_{trityl} values beyond 0.22. These results were in contrast to those obtained for homogeneous tosylation of cellulose in ILs with BIM as base. In their study, they found that higher basic base BIM would increase the reactivity and efficiency of tosylation reaction (Gericke et al., 2012b). Although Erdmenger et al. had pointed out that strong base triethylamine would promote the reaction efficiency of cellulose tritylation in BmimCl, BIM was not found this similar function (Erdmenger et al., 2007).

As already stated, it might be concluded from the results that direct tritylation with BIM as base to products with a DS_{trityl} of 1 was not possible under the homogeneous reaction conditions applied. It might be assumed that BIM was an amphoteric solvent which exhibited acidity and basicity at the same time, thus it could react with inorganic acid but hardly to bind the free chloride ions (Cassidy, Reinhardt, Cleland, & Frey, 1999; Gericke et al., 2012b). Considering the tritylation reaction mechanism, which was S_N1-type, the reasons for lower DS_{trityl} with BIM as base would be explained as follows. As the tritylation reaction consisted of two steps, the first one was the heterolytic cleavage of the Tr—Cl bond, leaving Tr^+ and Cl^- ions in the solvent, and the second step was an attack by the Tr^+ ion on the hydroxyl site. For these two steps, the reaction efficiency was dominated predominantly by the first step. Therefore, at the beginning of reaction, comparable more free chloride ions were existed in AmimCl/BIM solutions because the amphoteric character BIM could not bind the released chloride ions, and thus it would prevent further heterolytic cleavage of the Tr—X bond. For tosylation of cellulose, which was S_N2-type, the attack of tosyl chloride on the hydroxyl site and the cleavage of chloride ions were happened simultaneously, thus the leaving inorganic acid HCl could be bound by BIM (Gericke et al., 2012b). Therefore, BIM was a suitable base for tosylation of cellulose but not for tritylation of cellulose in ILs. However, the nitrogen on pyridine ring could react with strong alkaline by a nucleophilic displacement reaction. As a strong alkaline, chloride ion would react with pyridine and form quaternary ammonium salt. Therefore, a DS_{trityl} of 1 for tritylation of cellulose in ILs with pyridine could be obtained. Although using BIM as base higher DS of TC could not achieved, other possible base was still needed further investigation for homogeneous tritylation in ILs.

3.2. Characterization of trityl cellulose

The TC samples were soluble in various organic solvents such as DMSO, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, and pyridine. Especially samples obtained in solution with BIM as base exhibited excellent solubility in solvents, for example, products with DS_{trityl} upward of 0.14 could be dissolved well in the above-mentioned organic solvents. These samples showed typical bands in the FTIR spectra. Fig. 1 showed the spectra of unmodified cellulose (spectrum a), TC sample B5 with DS_{trityl} = 0.18 (spectrum

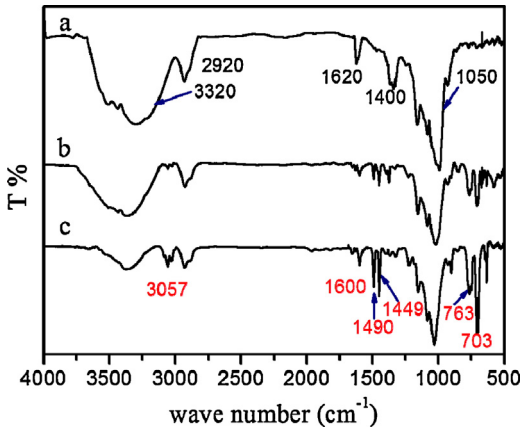

Fig. 1. FTIR spectra of unmodified cellulose (spectrum a) and trityl cellulose samples B5 with DS_{trityl} = 0.18 (spectrum b) and P10 with DS_{trityl} = 0.95 (spectrum c).

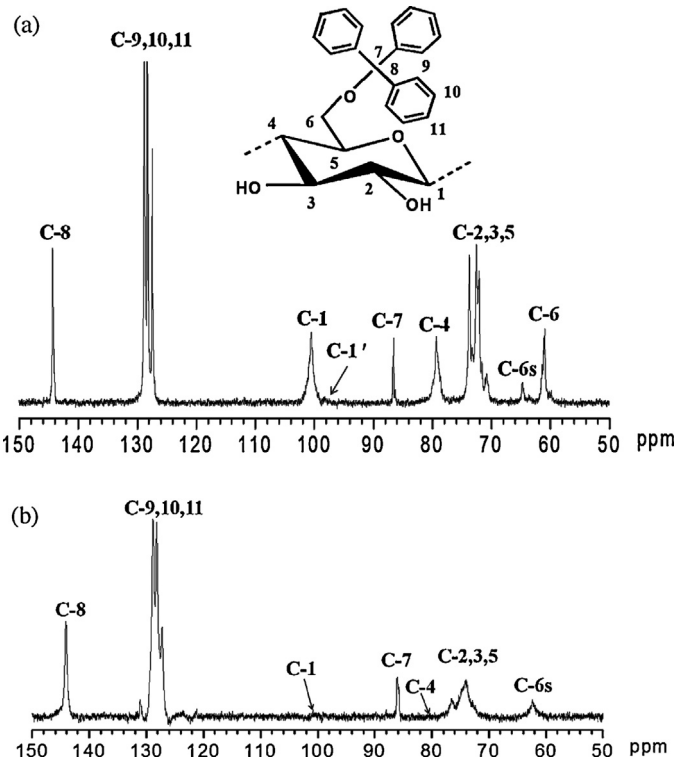

Fig. 2. ^{13}C NMR spectra of trityl cellulose sample B5 with DS_{trityl} = 0.18 (a) and sample P10 with DS_{trityl} = 0.95 (b) in dimethyl sulfoxide-d_6 at room temperature.

b) and P10 with DS_{trityl} = 0.95 (spectrum c). The spectra b and c provided a clear evidence of tritylation by showing the presence of some important peaks at 3057 cm^{-1} for benzene ring C—H stretching, 1600, 1449 cm^{-1} for aromatic C=C stretching and 703 cm^{-1} for the out-of-plane C—H bending of the monosubstituted benzene. In addition, as the DS_{trityl} increased, the intensity of peaks at 3320 (OH stretching) and 1370 cm^{-1} (OH bending) obviously decreased, and the absorption intensity at 3057 and 703 cm^{-1} increased.

Fig. 2 showed the ^{13}C NMR spectra of two TC samples dissolved in DMSO-d_6. The peak assignment was carried out on the basis of the results of the literature data (Erdmenger et al., 2007). In the case of B5, the aromatic C-atoms 9, 10 and 11 of trityl substituent gave a group of peaks in the region from 128.8 to 127.5 ppm. A separate peak for C-7 and C-8 at 86.6 and 144.3 ppm could be detected, respectively. In the ring carbon spectrum of the AGU of sample B5, the peak of C-6 influenced by substitution of trityl in C-6 appeared at 64.7 ppm, exhibiting a downfield shift compared with the corresponding carbon of unmodified cellulose at 61.1 ppm. In addition, an unnoticeable splitting of the peak of C-1 carbon (100.6 and 98.3 ppm) could be observed. From this peak splitting it might be concluded that this TC obtained in solutions with BIM as base was not only tritylated at position 6 but also partially at position 2. This might be the reason for their excellent solubility in solvents. Moreover, using this TC as raw material some cellulose derivatives could be synthesized in common organic solvents without much influence on their structures, when homogeneous modification of cellulose could not be accomplished in cellulose nonderivative solvents.

In Fig. 2(b) for sample P10, the signals of the ring carbon spectrum of the AGU became broad peaks, and the peaks of C-1, 4 and C-2, 3, 5 moved downfield because of their electron cloud changes caused by the increasing DS_{trityl}. Moreover, only a signal for the tritylated C-6 atom at 62.5 ppm and C-1 atom at 100.8 ppm could be observed for P10. All of these proved that the TrCl reacted mainly at the primary hydroxyl group C-6 and the reaction with secondary

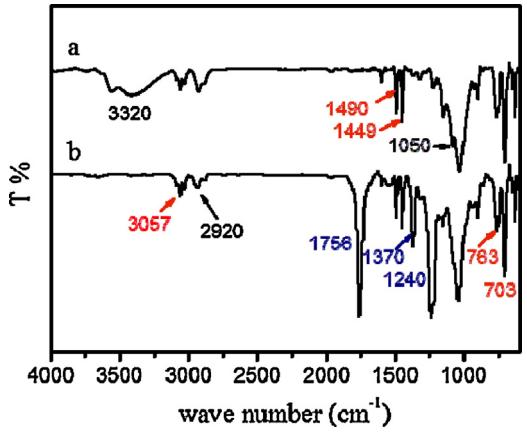

Fig. 3. FTIR spectra of trityl cellulose samples P10 with DS_{trityl} = 0.95 (spectrum a) and peracetylated trityl cellulose AP10 with DS_{AC} = 1.92 (spectrum b).

hydroxyl groups was almost nonexistent for samples obtained in solutions with pyridine as base. However, due to the bulky trityl group the NMR spectra were relatively poor resolved and the peak resolution was even more deteriorating with increasing DS_{trityl}. Therefore, the signals for C-1, C-4 and C-6 in P10 spectrum could not be clearly distinguished. More experiments were needed for understanding their exact structure.

3.3. Acetylation of 6-O-trityl-cellulose

Cellulose acetate (CA) was one of the most commercially relevant and widely utilized cellulose derivatives. The distribution of acetyl groups along the backbone of cellulose was random for CA no matter prepared by typically homogeneous or heterogeneous acetylation. A well-defined structure of CA would be achieved with TC as raw materials. In this study, sample B5 and P10 were used to react with acetic anhydride in pyridine within 48 h at 90 °C, thus the peracetylated TC products AB5 and AP10 were obtained. From Fig. 3 it could be seen that these peracetylated TC samples showed the typical FTIR signals of the TC moieties, and two high-intensity bands appeared at about 1756 and 1240 cm^{-1}, indicating the presence of the acetyl ester functions. The DS of acetyl groups were 2.78 and 1.92 for AB5 and AP10, calculated from the elemental composition.

The peracetylated TC dissolved well in dipolar, aprotic solvents like DMSO, *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, pyridine, THF, chloroform and 1,2-dichloroethane and so on. The structure characterization of the peracetylated TC was also carried out by ^{13}C NMR in order to determine the molecular structure as well as the distribution of trityl group and acety group. Fig. 4 showed the ^{13}C NMR spectra of samples AB5 and AP10. For AB5, apart from the peaks of the carbons from TC, the typical peaks of carbons from acetyl group were found locating at 170.4 and 20.8 ppm, corresponding to C-12 and C-13 atom, respectively. In addition, a separate peak for the substituted C-6 atom at 63.4 ppm, C-1′ atom (adjacent to C-2 carbons bearing a substituted hydroxyl group) at 96.0 ppm and C-4′ atom (adjacent to C-3 carbons bearing a substituted hydroxyl group) at 74.4 ppm could be observed, indicating that the hydroxyl groups of C-2, C-3 and C-6 were almost totally substituted. The inset in Fig. 4(a) showed the acetyl carbonyl peaks, which attributed to the carbonyl carbon at C-6, C-3 and C-2. Due to the existence of trityl group with DS_{trityl} of 0.18, the carbonyl carbon peak at C-6 overlapped with that of C-3. Although Fig. 2(a) showed that trityl group was not only tritylated at position 6 but also partially at position 2 for B5 sample, the tritylated C-2 and C-6 atom peaks were not showed in Fig. 4(a) probably because of the much lower trityl group at AGU. The ^{13}C NMR spectrum of AP10 in Fig. 4(b) represented similar signals

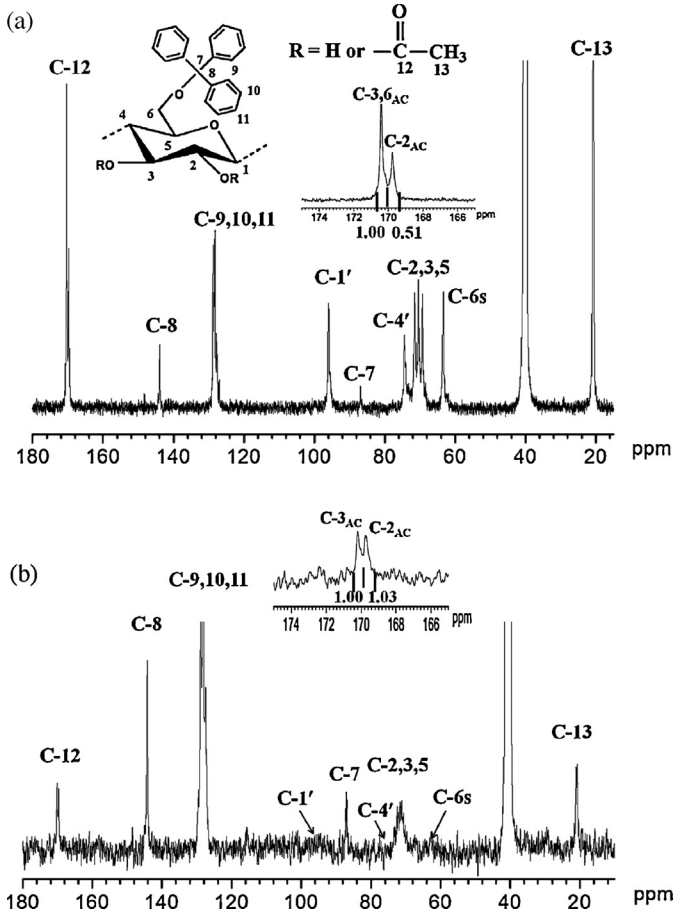

Fig. 4. ^{13}C NMR spectra of peracetylated trityl cellulose sample AB5 with DS_{trityl} = 0.18, DS_{AC} = 2.78 in dimethyl sulfoxide-d_6 at room temperature (a) and sample AP10 with DS_{trityl} = 0.95, DS_{AC} = 1.92 in dimethyl sulfoxide-d_6 at 100 °C (b).

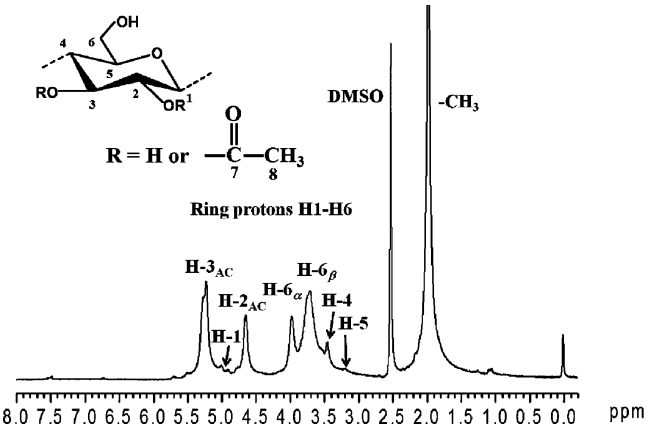

Fig. 5. ^{1}H NMR spectrum of detritylated product regioselective cellulose acetate CA10 in dimethyl sulfoxide-d_6 at room temperature.

of carbon as that of AB5. The acetyl carbonyl signals at 170 ppm showed two nearly equal integrated peaks, which attributed to the carbonyl carbon at C-3 and C-2, respectively, indicating that the hydroxyl groups at C-2 and C-3 were almost substituted by acetyl groups (Hsieh & Kadla, 2012). However, due to the bulky trityl group and higher DS_{trityl} in the AP10, the signals for carbons of cellulose backbone could not be clearly distinguished in the ^{13}C NMR spectrum. In order to decrease the effect of trityl group, AP10 was treated by firstly detritylation and then followed by propionylation (Tsunashima & Hattori, 2000; Gräbner, Liebert, & Heinze, 2002).

The regioselective CA10 was obtained by detritylation of AP10 according to procedures in Section 2.5. In the FTIR spectrum of the detritylated product, the signals of the aromatic region disappeared (see Section 2.5). The structure of CA10 could be confirmed further by ^{1}H NMR spectroscopy showed in Fig. 5. It can be seen that the signals of phenyl protons were nonexistence in the ^{1}H NMR spectrum, and the signals of acetyl protons and anhydroglucose unit protons located at 2.1–1.6 and 5.5–2.7 ppm, respectively (Kono, 2013). The DS of CA10 was 2.02 calculated from the ratio of peak integral of phenyl protons and anhydroglucose unit, and this value was comparable to the DS of 1.92 calculated from the elemental composition.

The distribution of acetyl group along the cellulose backbone was determined via propionylation for CA10. This method allowed for the quantification of the carbonyl carbons associated with the C-2, C-3 and C-6 positions of AGU as well as the specific distribution of acetyl groups and propanoyl groups in the cellulose. From Fig. 6 it could be seen that the acetyl groups located only at C-2 and C-3, while the propanoyl groups located just at C-6. The DS at C-2, C-3 and C-6 positions was approximately equivalent to 1, indicating that the trityl group totally protected the primary hydroxyl group C-6 and 2,3-di-*O*-acetyl-cellulose was obtained.

Based on TC with different DS_{trityl}, regioselective 2,3-*O*-acetyl-cellulose could be obtained. Although the total DS were identical,

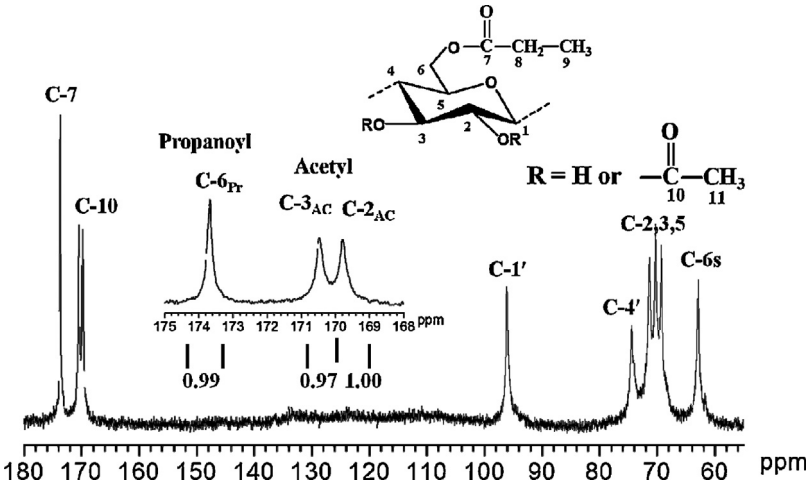

Fig. 6. ^{13}C NMR spectrum of perpropionylated regioselective cellulose acetate sample (CA10) in dimethyl sulfoxide-d_6 at room temperature.

the physical properties of these regioselective CAs were different from those of random distribution CA. Therefore, the regioselective CAs were synthesized to study the influence of acetyl group distribution on their properties. Future work will investigate the properties of CA obtained by heterogeneous reaction, homogeneous reaction and regioselective reaction.

4. Conclusion

The synthesis of TC in AmimCl with TrCl as regents, pyridine or BIM as base was studied in this paper. When pyridine was used as base, the solution converted from heterogeneity to homogeneity and then to heterogeneity because of the low polarity pyridine and increasingly hydrophobic of tritylated products with increasing DS_{trityl}. It was demonstrated by ^{13}C NMR that the obtained TC had organized structure and the trityl group located just at C-6 position with maximum DS_{trityl} of nearly 1. The tritylation of cellulose had higher reaction efficiency in BmimCl/pyridine than that in AmimCl/pyridine because of the relatively more electronic chemical structure of cation $[Amim]^+$. On the other hand, the cellulose solution with BIM was homogeneous for the whole reaction, but the DS_{trityl} values of obtained TC could not exceed 0.22 owing to the amphoteric property of BIM and S_N1-reaction mechanism of tritylation. TC obtained with BIM as base was not only tritylated at position 6 but also partially at position 2, thus they had excellent solubility in solvents.

A preferred functionalization of the secondary positions was found in peracetylated TC products. In case of products with $DS_{trityl} < 1$ a partial substitution of the primary OH group took place as well. Under controlled acidic conditions the trityl moieties could be removed, yielding regioselective 2,3-*O*-acetyl-cellulose. The information about the regioselective structure was studied by FTIR and ^{13}C NMR spectroscopy, and the structure property relationship between heterogeneous and homogeneous productions as well as regioselective and homogeneous productions will be investigated in future work.

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