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Effects of salt on homogeneous succinoylation of lignocellulosic fibers in dimethyl sulfoxide/tetraethylammonium chloride under mild condition

Jianqiang Chen,[1] Meng Su,[1] Rongping Chen,[1] Jianguo Hong,[1] Rongshi Cheng[2]

[1]College of Biology and the Environment, Nanjing Forestry University, Nanjing 210037, People's Republic of China

[2]Department of Polymer Science and Technology, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence to: J. Hong (E-mail: chenjq@njfu.edu.cn or jghongnj@163.com)

ABSTRACT: Effects of salt in the homogeneous succinoylation of ball milled mulberry wood in dimethyl sulfoxide (DMSO)/tetraethylammonium chloride (TEACl) was investigated using viscometry and two-dimensional nuclear overhauser effect NMR spectroscopy (2D NOESY). The intrinsic viscosity of mulberry wood solution strongly depends on the TEACl dosage indicating that the change in hydrodynamic size of polymers caused by the interactions between salt and polymers in solution. 2D NOESY spectra reveal that TEA^+ cations bind to the cellobiose in DMSO by the interactions between methenyl of TEA^+ and C(1)/C(1′) group of cellobiose and the intensities of the crosspeaks increased with an increase in TEACl dosage. Taking cellobiose as a model compound for cellulose, it can be expected that TEA^+ cations and cellulose forms a polyelectrolyte-like complex. The yields of homogeneous succinoylation of mulberry wood in DMSO/TEACl benefits from the interactions between TEA^+ cations and cellulose evidenced by weight percent gain, Fourier transform infrared spectra as well as CP/MAS ^{13}C-NMR spectra. © VC 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41912.

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INTRODUCTION

Biomass is the most abundant lignocellulosic resource in the earth, and it also presents an abundant resource for the production of biofuels, chemicals and new materials. As we know, the main components of lignocellulosic fibers are cellulose, hemicellulose, and lignin. Lignin, as a network polymer, binds with the carbohydrates (hemicelluloses and cellulose) to form a tight compact structure.[1] There are great amount of reactive hydroxyl groups in cellulose which can be used for functionalization of lignocellulosic fibers via certain substitution reactions.[2,3] Due to the high degree of crystallinity of cellulose and the rigid three-dimensional net structure of lignin, lignocellulosic fibers present insolubility in common molecular solvents. Consequently, chemical modifications of lignocellulosic fibers have been carried out in heterogeneous systems for a long time.[4–6] Compared to that in homogeneous system, it is very difficult for reactants and catalysts to break through the rigid structure of lignocellulosic fibers(such as wood and straw) and to react with reactive hydroxyl groups in heterogeneous systems. As a huge variety of non-derivatizing solvents for cellulose have been developed rapidly,[7] some original cellulose solvents have been applied to dissolve lignocellulosic fibers, among which Ionic liquids such as *N,N*-disubstituted imidazolines, with strong ability to disrupting hydrogen bonds can dissolve lignocellulosic fibers efficiently.[8–10] Other good solvents combine an organic solvent and a salt, such as dimethyl sulfoxide and *N*-methylimidazole (DMSO/NMI),[11] DMSO/lithium chloride (LiCl),[12] and DMSO/tetrabutylammonium (TBAF).[13] Meanwhile, homogeneous modifications of lignocellulosic fibers have been carried out in the solvents mentioned previously.[11,14,15]

The role of salt in the dissolution and homogenous modification for cellulose in salt-containing solvents has been intensively studied since the mixture of *N,N*-dimethylacetamide (DMAc) combined with LiCl,[16] first reported by McCormick showed an enormous potential for the preparation of a wide variety of derivatives. Although the mechanism of dissolution for cellulose in salt-containing solvents has remained ambiguous up to now,[7] it may be proposed that halide anions play a crucial role in the process. For instance, in TBAF·3H_2O/DMSO, fluoride ions act as strong hydrogen bond acceptors to break the cellulose-cellulose hydrogen bonds and thus dissolve the polymer.[17] Additionally, Östlund *et al.*[18] reported that the strong ion-dipole interactions between fluoride ions and OH-groups of cellulose could render cellulose chains effective negative charge. Without

Table I. The Solubility of Mulberry Wood in DMSO/TEACl Under Various Conditions

Dissolution conditions				
TEACl dosage (wt %)	Temperature (°C)	Stirring time (h)	Sample no.	Solubility (wt %)
3	40	3	1	1
6	40	3	2	2
10	40	3	3	5
15	40	3	4	6
20	40	3	5	10
10	25	3	6	2
10	70	3	7	8
10	40	1	8	2
10	40	6	9	7
10	40	9	10	8

or with small amount of water, cellulose is protected from self-association by the adsorbed fluoride ions. On the other hand, the degree of substitution (DS) of cellulose derivatives (e.g., cellulose acetate) is apparently influenced by salt when acetylation of cellulose was carried out in TBAF·3H_2O/DMSO.[19] The variation in DS values caused by TBAF concentration could be ascribed to the balance between aggregation of cellulose chains and complexation of cellulose OH groups by TBAF. However, such salt effect on the homogeneous modification of cellulose was based on the mechanism of dissolution of cellulose in the salt-containing solvent which is not known in detail,[7,19] yet.

High-resolution NMR is a powerful technique for studying and the molecular interactions among the components of a mixture under various conditions.[20,21] Particularly, two-dimensional (hetero) nuclear overhauser effect NMR spectroscopy (2D NOESY/HOESY) can provide detailed information on the proximity in space of two different components. Brendler *et al.*[22] reported the coordination of lithium cations and cellobiose dissolved in the molten salt hydrate solvent system by recording ^{7}Li-^{1}H HOESY spectra. In our previous works, the concentration effects of sodium *n*-dodecyl sulfate on the coil-to-globule transition of poly(*N*-isopropylacrylamide) have been systematically studied using 2D NOESY NMR.[23,24] In addition, intrinsic viscosity reflecting the hydrodynamic size of polymers in solution can be regarded as an important proof to indicate the interactions between ions and polymers.[25] In the current article, dissolution of mulberry wood in tetraethylammonium chloride (TEACl)/DMSO and homogeneous succinoylation were carried out as a function of TEACl concentration. With aims at exploring the role of TEACl in homogeneous succinoylation of mulberry wood in DMSO/TEACl, intrinsic viscosity and 2D NOESY NMR were employed to study the complex structures of TEACl and the cellulose of mulberry wood.

EXPERIMENTAL

Materials

Mulberry wood as agricultural residues was obtained from in Jiangsu province, China. The mulberry wood was dried in sunlight, peeled and pulverized into 40 mesh size and oven-dried at 60°C for 24 h, and further pulverized by planetary ball mill for 6 h in a stainless steel jar (QM-3SP2, Nanjing University affiliated Instrument Factory, Nanjing). The cellobiose and deuterated dimethyl sulfoxide (DMSO-d_6; 99.6 atom % D) were obtained from Sigma-Aldrich. All other chemicals in this study were analytical reagent grade and purchased from Nanjing Chemical Reagent Company, China.

Preparation of Mulberry Wood/DMSO/TEACl Solution

The excessive amount of ball-milled mulberry wood sample ($W1$, usually around 4.0 g) was put in the round flask with 40 mL DMSO for preswelling and dissolution after the addition of TEACl under various dissolution conditions in Table I. After dissolution, solid residues of the excess insoluble mulberry wood sample on the bottle of the round flask were filtered and weighted (W_{ex}). The solubility of mulberry wood sample was calculated:

$$\text{solubility wt \%} = \frac{W1 - W_{ex}}{W1}$$

Viscosity Measurement of Mulberry Wood/DMSO/TEACl Solution

The solution of sample No. 3 in Table I was selected for viscosity measurements using an Ubbelohde-type capillary viscometer 0.413 mm in diameter and 102.1 mm in length. The measured temperature at 40°C to was controlled by a circulating water bath. With continuous addition of TEACl to the solution, the $[\eta]$ at various TEACl concentrations can be calculated as shown in Figure 2. The efflux time t_u of the wood solutions with different TEACl concentrations from 10 to 38 wt % were measured. Blank TEACl solutions at corresponding concentrations without mulberry wood were used as respective solvents, and the efflux time t_v was measured carefully. The ratio of the flow time of the wood solution to that of the solvent, t_u/t_v, was regarded as the relative viscosity (η_r), and the intrinsic viscosity ($[\eta]$) was calculated by the following one-point method:

$$[\eta] = \frac{(2\times(\eta_{sp} - \ln(\eta_r)))^{0.5}}{C}$$

where C is the wood concentration in g/mL calculated by the solubility of sample No. 3 in Table I and the specific viscosity (η_{sp}) is equal to $\eta_r - 1$.

Table II. Chemical Shift in the ^{1}H-NMR Spectrum of Cellobiose in DMSO-d_6/TEACl

Chemical shift (ppm)					
1.13	2.50	3.21	3.39	3.55–3.65	4.27–4.34
Ta	DMSO	Tb	β-C(2′)-H	α,β-C(5)-H α-C(2)-H	α,β-C(1)-H β-C(1′)-H
4.63–4.67	4.74–4.78	4.89	4.90–4.92	5.29–5.32	6.8
α,β-C(6)-OH	α,β-C(3′,6′)-OH	α-C(1′)-H	α,β-C(3,4)-OH β-C(2′)-OH	α,β-C(2)-OH	β-C(1′)-OH

2D NOESY Experiments of Cellobiose/DMSO-d$_6$/TEACl Solution

In 2D NOESY experiments, two solution samples of cellobiose/DMSO-d_6/TEACl were carefully prepared to obtain an accurate concentration of cellobiose and TEACl. The concentrations of cellobiose in each sample were kept constant at 2 mg/mL, however, and those of TEACl in two solution samples were 5 and 10 mg/mL, respectively. 2D NOESY experiments of cellobiose/DMSO-d_6/TEACl solution were performed using a Varian 700 MHz spectrometer equipped with a 5-mm standard probe. 2D NOESY experiments were conducted at 40°C with 0.2 s mixing time.

Homogeneous Succinoylation of Mulberry Wood in DMSO/TEACl

The succinolyated mulberry wood was prepared by homogeneous reaction of dried ball-milled mulberry wood with succinic anhydride in DMSO/TEACl using DMAP as catalyst. Dried ball-milled mulberry wood (0.5 g) was entirely dissolved in the sufficient binary solvent of DMSO and TEACl. The mixture was mechanically stirred for sufficient time to ensure the complete dissolution of the wood sample. Succinoylation was carried out under conditions listed in Table II. After succinoylation, the mixture was slowly poured into 100 mL of isopropanol with agitation. The resultant solid was filtered and washed thoroughly with isopropanol to eliminate the DMSO, TEACl, unreacted succinic anhydride and catalyst DMAP, and then freeze dried. The dried products were weighed to determine the weight percent gain (WPG) on the basis of the weight of the dried ball-milled mulberry wood (WPG = [(weigh gain/original weight)] × 100%). Each experiment was performed at least in triplicate under the same conditions, and WPG represents the average value.

Characterization of the Succinolyated Mulberry Wood

The chemical structure of unmodified and succinolyated mulberry wood under various conditions were characterized by Fourier transform infrared spectroscopy (FT-IR) and solid-state CP/MAS ^{13}C-NMR spectroscopy. FT-IR spectra were obtained on FT-IR spectrophotometer (Nicolet 6700) from the finely ground sample (1%) in KBr pellets in the range 500–3800 cm^{-1}. Solid-state CP/MAS ^{13}C-NMR experiments were performed on a Bruker AVANCE III 300 MHz. The spin rate of the 4 mm rotor was 8 kHz for the CP/MAS experiments. The acquisition time was 0.0127 s. The delay time was 2 s.

RESULTS AND DISCUSSION

The Dissolution of Mulberry Wood in DMSO/TEACl

The mulberry wood was finely ball milled by planetary ball-milling, which is regarded as an effective way to improve the wood solubility in DMSO/LiCl at room temperature.[12] The dissolution of ball-milled mulberry wood in DMSO/TEACl under various conditions, such as TEACl dosage, temperature, stirring time is listed in Table I. Under gentle conditions of temperature at 40°C and dissolving time for 3 h, the solubility of mulberry wood in solution Samples 1–5 were apparently influenced by the dosage of TEACl. With the increased dosage of TEACl from 3 to 20 wt %, solubility of mulberry wood enhanced from 1(Sample 1) to 10 wt % (Sample 5). The appearance of wood solution (Sample 3 in Table I) is shown in Figure 1. When the dosage of TEACl was constant at 10 wt %, by comparing the results of solution Samples 6–10, it is obvious that the solubility of wood was augmented with the increased dissolving temperature and stirring time. As temperature raised to 70°C, the wood solubility was 8 wt % (Sample 7) after 3 h stirring time which is equivalent to the result of ball-milled wood powder dissolved in [amim]Cl.[10] Compared to complete wood dissolution in ionic liquids produced at high temperature (80–120°C within 8 h), comparable solubility in DMSO/TEACl can be achieved under much milder condition.

The viscosity behaviors of wood in solution in the presence of TEACl at various concentrations in Table I were systematically studied. Figure 2 shows the dependence of the intrinsic viscosity of the wood solution on TEACl concentration. In this study, the intrinsic viscosity was calculated according to the one-point

Figure 1. The appearance of suspension and solution of mulberry wood in TEACl/DMSO with dissolution condition of TEACl at 20 wt %, temperature at 40°C and stirring time for 3 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

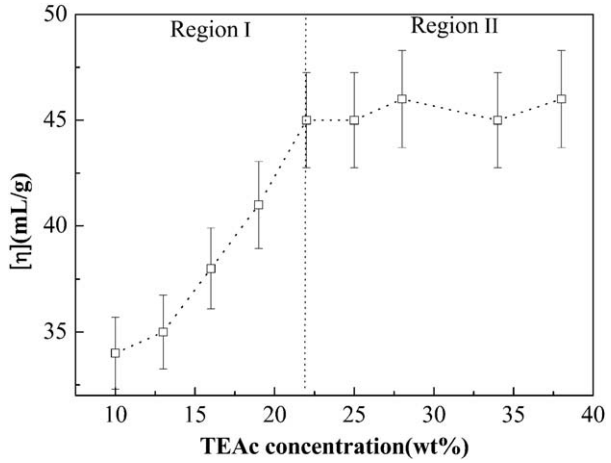

Figure 2. Dependence of the intrinsic viscosity of mulberry wood in DMSO/TEACl solution on the TEACl concentration at 40°C. The intrinsic viscosity was calculated according to the formula[24] $[\eta] = (2 \times (\eta_{sp} - \ln(\eta_r)))^{0.5}/C$.

method proposed by Cheng[26] to cancel the concentration effects in different experiments and reflect the hydrodynamic size of polymers in wood solution. It is necessary to point out that the *C* value of wood solubility is fixed, which indicates the interactions between constant amounts of dissolved wood with TEACl of various concentrations. Figure 2 shows two distinct regions in the intrinsic viscosity observed within the entire measured TEACl concentration range. In region I, TEACl addition from onset concentrations of 10 wt % obviously enhanced the intrinsic viscosity of wood in solution until the TEACl concentration increased to 22 wt %. The enhanced intrinsic viscosity reflected the increased hydrodynamic size of polymers in solution which can be explained by the aggregation of TEACl onto the cellulose chains. That result could be evidenced by 2D NOESY spectrum of cellobiose/DMSO-d_6/TEACl solution in the following section. Therefore, a polyelectrolyte-like complex of cellulose and TEACl was formed, resulting in increased intrinsic viscosity and hydrodynamic size of the polymers in wood solution for electrostatic repulsion. The interactions of TEACl and wood in solution were quite similar to the dissolution mechanism of cellulose in TBAF·3H_2O/DMSO where fluoride ions were absorbed to cellulose chains in DMSO.[19] The intrinsic viscosity increased from 33 to 45 mL/g as TEACl concentrations increased from 10 to 22 wt %, indicating the enhanced electrostatic repulsion of the charged complexes for more TEACl molecules bound to the polymers in wood solution. Connecting the dependence of wood solubility on TEACl dosage in Table I, the increase in the wood solubility probably arised from the effects of TEACl dosage on the conformation of polymers in wood solution. At TEACl concentrations higher than 22 wt %, i.e., in region II, the intrinsic viscosity increased slowly and gradually reached a plateau at around 45 mL/g. The result indicated that the hydrodynamic size of the charged complexes in solution was slightly changed due to the saturation of the wood fibers with TEACl in the wood solution.

2D NOESY Spectra of Cellobiose and TEA^+

2D NOESY spectroscopy is a powerful technique for investigating the interactions between two different components in close proximity (<0.5 nm).[27,28] In the present work, 2D NOESY spectroscopy was employed to study the interactions between cellobiose and TEA^+ in DMSO-d_6 where cellobiose was taken as a model compound to study the interactions between cellulose and TEA^+ in DMSO.[21,22,29] Before this measurement, the ^{1}H-NMR spectrum of the TEA^+ and cellobiose was first obtained, as shown in Figure 3(a). The proton signal of the external standard tetramethylsilane was used as the reference resonance. The precise assignments of cellobiose in DMSO-d_6/TEACl are shown in Table II. The ^{1}H-NMR spectrum exhibits sufficient resolution to separate the distinct proton signals of cellobiose which were consistent with the detailed assignments of the cellobiose peaks reported in Zhang's work.[29,30] The signals of methenyl protons of C(1) and C(1′) of cellobiose merge into one peat at 4.3 ppm, whereas strong peaks at 1.1 and 3.2 ppm corresponded to the methyl (Ta) and methenyl (Tb) protons on TEA^+, respectively. Therefore, the overlapping of proton signals of cellobiose and TEA^+ does not occur in 2D NOESY experiment. The distinct signal corresponding to DMSO-d_6 was at 2.5 ppm.

The 2D NOESY spectra of two samples of cellobiose/DMSO-d_6/TEACl with different TEACl dosage were showed in Figure 3(b). In both NOESY spectra of two solutions, strong positive cross-peaks appeared between the Tb and C(1)/C(1′) proton pairs. These cross-peaks revealed that TEA^+ was in close proximity (<0.5 nm) to cellobiose molecules and the complexation of TEA^+ and cellobiose were formed mainly via the interactions between the methenyl groups of TEA^+ and the C(1)/C(1′) of cellobiose. The interactions of Tb and C(1)/C(1′) could be a result of electrostatic interactions between the methenyl group of TEA^+ and the C(1)/C(1′) of cellobiose due to the electron-withdrawing and electron-donating properties of their adjacent groups. For TEA^+, the quaternary ammonium regarded as strong electron-withdrawing group endows the methenyl group electronegativity, while the C(1)/C(1′) of cellobiose has the electropositivity adjacent to the oxygen atoms as shown in Figure 4. Taking cellobiose as a model compound, it can be expected that charged TEA^+ binds to cellulose, which endows polyelectrolytic characteristics to the complexes of TEA^+ and cellulose in DMSO. Consequently, the hydrodynamic size of cellulose increased for electrostatic repulsion, as observed by the intrinsic viscosity measurements.

In terms of the intensity changes in the cross peaks with TEACl dosage, the signals of Tb and C(1)/C(1′) were obviously stronger with increased TEACl dosage. To analyze the 2D NOESY spectra further, 1D spectra extracted from the Tb signal of the 2D NOESY spectra at 3.2 ppm are listed on the right side of each set in Figure 3(b). The integrated intensity ratio of C(1)/C(1′) to Tb in each 1D spectrum was 0.02 and 0.13, respectively. The enhanced signals were ascribed to the increasing number of TEACl molecules binding to cellulose in wood solution. This finding well agreed with the results of viscosity measurement. It was worth noting that this complex model was different from that via hydrogen bonds between cations of ionic liquid and hydroxyls of cellobiose in EmimAc/cellobiose system.[29]

The Succinoylation of Mulberry Wood in DMSO/TEACl

Table III gives the effects of TEACl dosage and reaction temperature on the WPG value of succinolyated mulberry wood in DMSO/TEACl with other fixed variables. As shown in Table III,

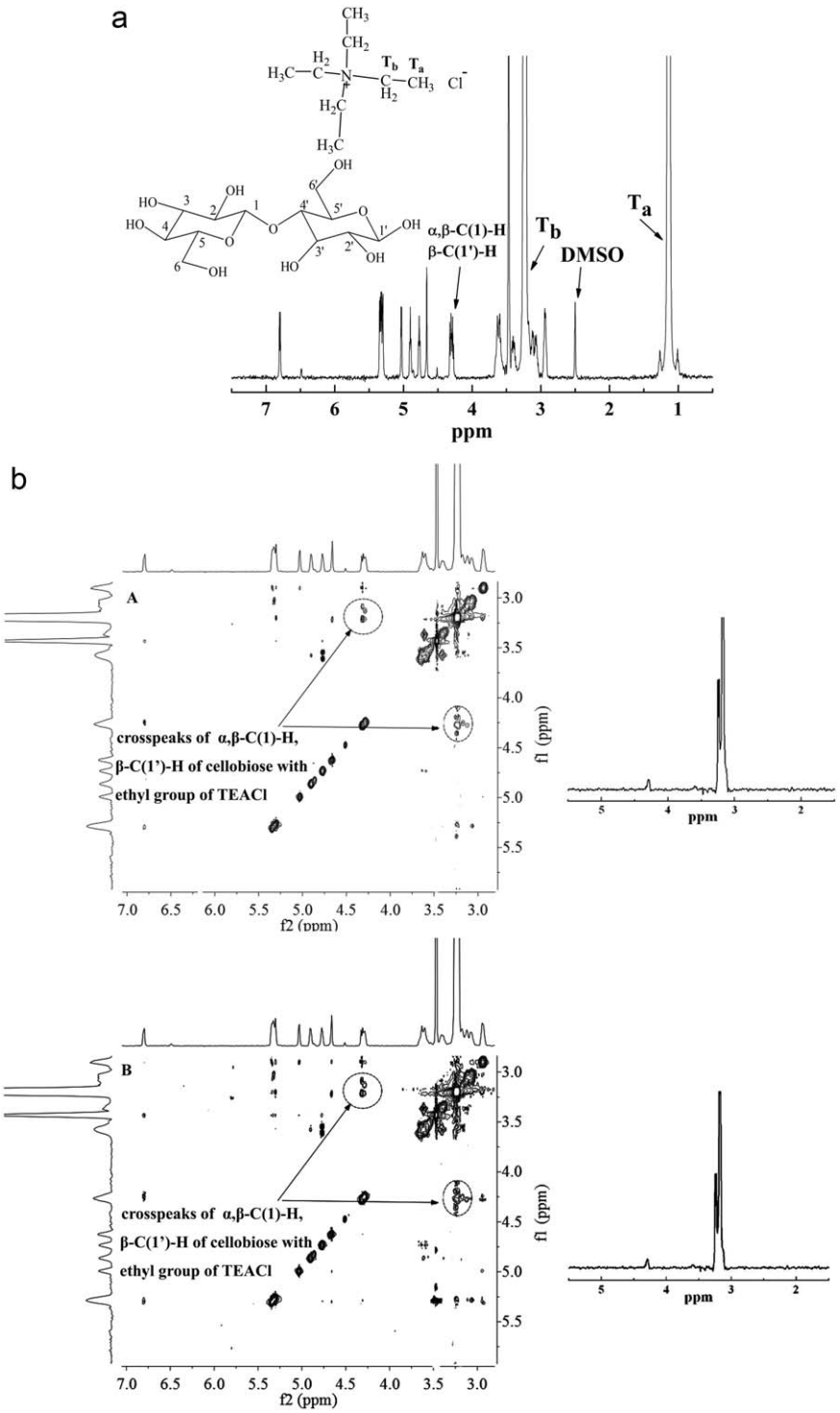

Figure 3. (a) ^{1}H-NMR spectra of the cellobiose in DMSO-d_6/TEACl, cellobiose at 2 mg/mL, TEACl at 5 mg/mL. (b) Left: ^{1}H–^{1}H 2D NOESY spectra TEACl at 5 mg/mL (A) and 10 mg/mL (B). Right: 1D spectra extracted from the underlined slices in the left spectra.

based on efficient dissolution in DMSO/TEACl, succinoylation of mulberry wood can be realized at temperature below 80°C, and even at room temperature, the succinoylation with a WPG of 31.2% can be produced (Sample 7).

As shown in Table III, TEACl dosage exerted considerable influence on the extents of homogeneous succinoylation in DMSO/TEACl. With the other same variables, the variation in TEACl dosage from 6 to 15 wt % led to obvious increase in WPG from 48.4% (Sample 1) to 65.2% (Sample 3). The TEACl dosage effect on WPG possibly arised from the enhanced accessibility of OH-groups of cellulose to reactants and catalyst in solution, when cellulose chains present extended conformation

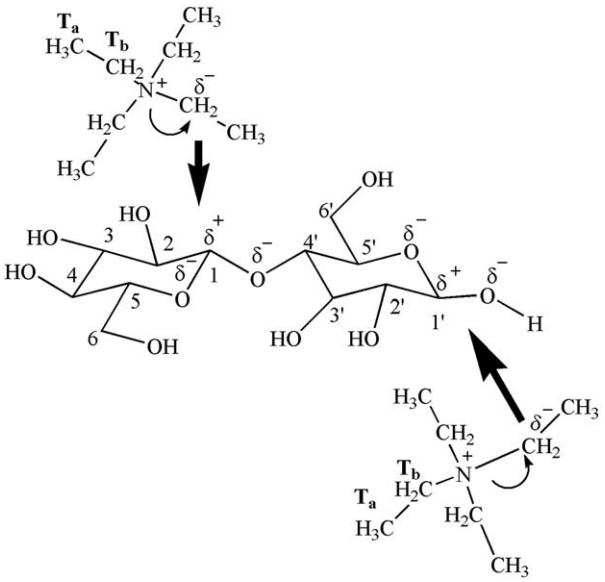

Figure 4. The schematic illustration of the mechanism for the interations of TEA^+ with cellobiose in DMSO.

due to electrostatic repulsion between polyelectrolyte-like complexes of TEA^+ cations and cellulose, reflected by the intrinsic viscosity behaviors in Figure 2 and 2D NOESY spectra in Figure 3(b). When TEACl dosage is more than 20 wt %, the WPG tended to reach a plateau (Samples 4–6), which was also consistent with the dependence of the intrinsic viscosity on TEACl dosage.

FT-IR Spectra

Figure 5 shows the FT-IR spectra of unmodified mulberry wood (Spectrum 1) and succinolyated Sample 2 (Spectrum 2) and 6 (Spectrum 3). For Spectrum 1 of unmodified sample, the strong absorption at 1045 cm^{-1} results from C–O stretching in cellulose, hemicellulose and lignin, or C–O–C stretching in cellulose and hemicellulose. The absorption at 2928 cm^{-1} corresponds to the C–H stretching. A strong band at 3430 cm^{-1} originates from hydroxyl groups in both unmodified and succinolyated

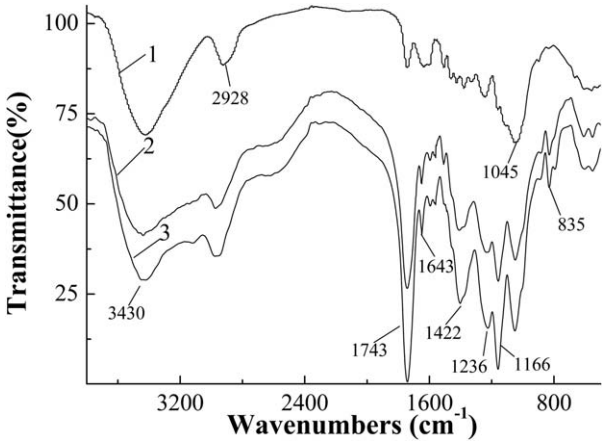

Figure 5. FT-IR spectra of unmodified mulberry wood (Spectrum 1), succinoylated Sample 2 (Spectrum 2) and 6 (Spectrum 3) in DMSO/TEACl with catalyst DMAP.

mulberry wood. In comparison, both the spectra 2 and 3 provide evidences for the succinoylation of mulberry wood indicated by the presence of two strong absorptions at 1166 and 1743 cm^{-1}.[31] In addition, the intensity of absorption bands at 1422 cm^{-1} assigned to the CH_2 was also enhanced after modification. By comparing Spectrum 2 and 3, the effects of TEACl dosage on the WPG of succinolyated mulberry wood could be studied by the peak intensities of above mentioned indicative peaks. A rise in TEACl dosage from 10 wt % (Spectrum 2, Sample 2) to 38 wt % (Spectrum 3, Sample 6) led to an increase in the intensity of the two ester bands at 1743 and 1166 cm^{-1}, suggesting that the TEACl dosage increased from 10 to 38 wt % has a positive effect on the extent of succinoylation, which is consistent with the trend of the WPG in Table III.

CP/MAS ^{13}C-NMR Spectra

Figure 6 shows the solid state CP/MAS ^{13}C-NMR spectra of unmodified (Spectrum a) and succinoylated wood Sample 2 (Spectrum b) and 6 (Spectrum c). In Spectrum a, all apparent signals between 55 and 105 ppm are assigned to the

Table III. Yield of Succinylated Mulberry Wood Obtained Under Various Conditions

Succinoylation conditions						
TEACl dosage (wt %)	DMAP dosage (wt %)	Anhydride dosage[a]	Temperature (°C)	Reaction time (h)	Sample no.	WPG (%)[b]
6	1.0	2 : 1	60	1.5	1	48.4
10	1.0	2 : 1	60	1.5	2	54.5
15	1.0	2 : 1	60	1.5	3	65.2
20	1.0	2 : 1	60	1.5	4	74.3
30	1.0	2 : 1	60	1.5	5	80.2
38	1.0	2 : 1	60	1.5	6	81.8
10	1.0	2 : 1	25	1.5	7	31.2
10	1.0	2 : 1	80	1.5	8	81.1

[a] Anhydride dosage represents the mass ratio of succinic anhydride to dried ball-milled mulberry wood (g/g).
[b] WPG represents the weight percent gain of ball-milled mulberry wood due to succinoylation and it was calculated according to: WPG = (weight gain/original weight) × 100%.

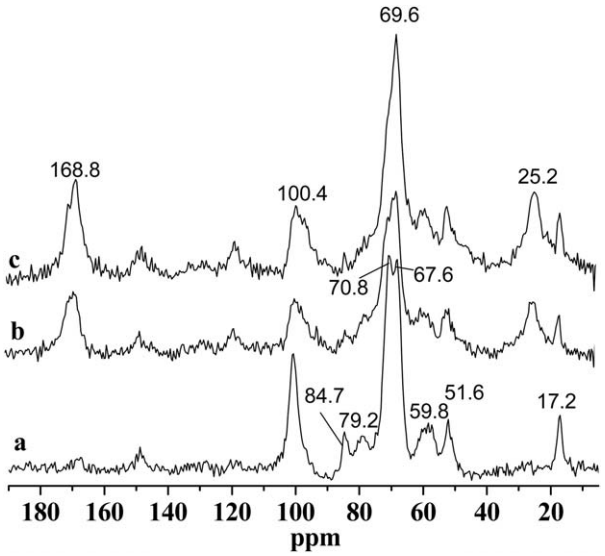

Figure 6. Solid-state CP/MAS ^{13}C-NMR spectra of unmodified mulberry wood (Spectrum a), succinoylated Sample 2 (Spectrum b), and 6 (Spectrum c).

carbohydrate carbons. The peaks at 100.4 [C(1) of cellulose and xylan], 84.7 and 79.2 [C(4) of crystal cellulose and amorphous cellulose, respectively], 70.8 [C(2), C(3) of cellulose] and 67.6 [C(5) of cellulose], and 59.8 [C(6) of cellulose and C(5) of xylan] were observed. The minor signals at 17.2 and 51.6 ppm, belonging to the CH_3 carbon of acetyl group in hemicelluloses and the methoxy group of aromatic moieties, respectively.[32] The presence of the peaks of the carboxylic group at 168.8 ppm and the methylene group at 25.2 ppm provide evidences of succinoylation. The increasing intensity of the two signals from b to c was consistent with the WPG data in Table III. It is worth noting that the sharp doublet over the broad cellulose signal at about 84 ppm over the C(4) region which has been assigned to the cellulose crystallite surface[33] decreased after succinoylation as shown in Spectrum b and almost disappeared in Spectrum c, which indicated that the crystalline structure of cellulose has been totally destroyed during succinoylation in DMSO/TEACl. The similar results were observed in the homogeneous modification of eucalyptus wood in DMSO/NMI.[10] Moreover, the originally splitting of signal at 70.8 and 67.6 ppm attributed to C(2), C(3), and C(5) of cellulose disappeared and a sharp peak at 69.6 appeared after succinoylation in connection with the slightly decreased signal at 59.8 ppm arising from C(6) of cellulose, which inferred the succinoylation might occur mainly at C(2), C(3) of cellulose rather than C(6) group.

CONCLUSION

In this work, the combination of intrinsic viscosity and 2D NOESY NMR was employed to study the effects of tetraethylammonium chloride (TEACl) on the homogeneous succinoylation of muberry wood in DMSO/TEACl. The interactions between TEACl and cellulose in the dissolution stage illustrated by the change in the hydrodynamic size of polymers and the spacial correlation between TEACl and cellubiose had strong effects on the succinoylation of muberry wood in solution. This study gave different interpretations for effects of salt in dissolution and modification of lignocellulosic fibers from the previous studies.

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