

## Preparation and Characterization of Phthalated Cellulose Derivatives in Room-Temperature Ionic Liquid without Catalysts

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Homogeneous modification of cellulose, isolated with 10% KOH from delignified sugarcane bagasse, was performed in room-temperature ionic liquid 1-allyl-3-methylimidazolium chloride with phthalic anhydride in the absence of catalyst. The results showed the degree of substitution of phthalated cellulosic derivatives, ranging from 0.10 to 0.73, increased with the increment of reaction temperature, reaction time, and the molar ratio of phthalic anhydride/anhydroglucose units in cellulose under the conditions given. The products were characterized by FT-IR and solid-state CP/MAS <sup>13</sup>C NMR spectroscopy as well as thermal analysis, and the results revealed that the phthalation reaction at C-6, C-2, and C-3 positions of the cellulose all occurred. The thermal stability of the phthalated cellulose was found to decrease upon chemical modification. However, this thermal stability of the phthalated cellulose over 200 °C is rather satisfactory.

**KEYWORDS:** Cellulose; bagasse; ionic liquid; phthalic anhydride; homogeneous modification

### INTRODUCTION

In recent years, there has been an increasing trend in society toward more efficient utilization of agro-industrial residues for the production of various products (1, 2). One of these residues is the sugarcane bagasse, a fibrous residue of cane stalks left over after the crushing and extraction of the juice from the sugarcane. Bagasse consists of approximately 50% cellulose, which makes it possible to use this residue by producing cellulose derivatives (3). Cellulose is the most abundant of all naturally occurring substances and widely used as a raw material in numerous industrial applications (4, 5). Chemical modification of cellulose, introducing functional groups into the macromolecules to substitute the free hydroxyl groups in heterogeneous phase or homogeneous phase, is one of the methods for the production of value-added products. Homogeneous functionalization has been one focus of cellulose research for a long time because more uniform and stable products could be obtained (6–8). However, due to its high crystallinity, cellulose is insoluble in water and most of the traditional organic solvents, which is a major obstacle for cellulose homogeneous modifica-

tion. Suitable cellulose solvents, which can efficiently dissolve cellulose and provide feasible reaction environment for cellulose functionalization, are eagerly needed in cellulose utilization. To date, a number of solvent systems, such as DMAc/LiCl, DMF/N<sub>2</sub>O<sub>4</sub>, NMNO, and some molten salt hydrates like LiClO<sub>4</sub>·3H<sub>2</sub>O, have been found efficient for cellulose dissolution (9–12). However, there remain limitations such as toxicity, cost, difficulty for solvent recovery, or instability.

Room-temperature ionic liquids (ILs), being considered as desirable green solvents and reaction media for a wide range of processes, have recently received significant attention (13, 14). In 2002, dissolution of cellulose with ILs was first reported by Swatloski et al. (15). The authors found that ILs including 1-butyl-3-methylimidazolium chloride ([C<sub>4</sub>mim]Cl) could be used as non-derivatizing solvents for cellulose. They pointed out that the high chloride concentration and activity in ILs play an important role in cellulose dissolution. However, the relatively high melting point of [C<sub>4</sub>mim]Cl, about 80 °C, limits its application as a solvent or reaction medium for cellulose research and development. One year later, 1-allyl-3-methylimidazolium chloride (AmimCl), a room-temperature IL with low melting point (about 17 °C), was synthesized and proved to have outstanding capability for dissolving cellulose (16). The alkenyl substituent on nitrogen instead of saturated alkyl makes the IL have a lower melting point and keep higher thermal stability as compared to other ILs substituted by saturated alkyl containing the same number of carbon atoms, which makes AmimCl a promising reaction medium for cellulose function-

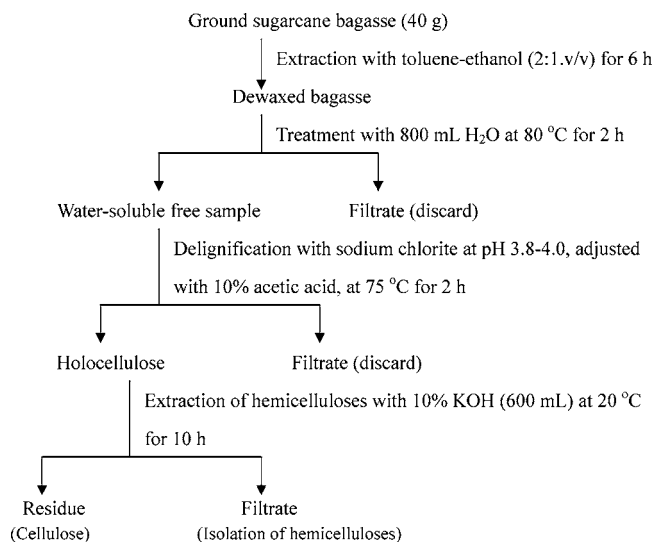
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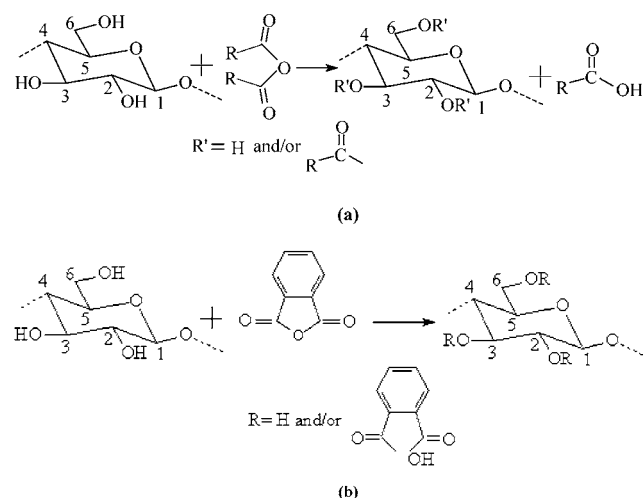
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**Figure 1.** Scheme for isolation of cellulose from sugarcane bagasse.

**Scheme 1.** Reaction of Cellulose with Linear Chain Anhydride (a) and Phthalic Anhydride (b)



alization. Homogeneous acetylation of cellulose with acetic anhydride in room-temperature IL AmimCl has been successfully accomplished by Wu et al. (17), and the authors suggested that the cellulose functionalizations, including esterification, etherification, alkylation, silylation, grafting, and halogenation, were all possible in homogeneous cellulose/ionic liquid solutions (17, 18). As far as the authors are aware, phthalation of cellulose using room-temperature ILs as reaction media has not been reported.

In this work, cellulose was first isolated with potassium hydroxide from sugarcane bagasse (SCB) after delignification with sodium chlorite. Homogeneous modification conditions of obtained cellulose with phthalic anhydride in room-temperature IL AmimCl, including molar ratio of phthalic anhydride/anhydroglucose units (AGU) in cellulose, reaction temperature, and reaction time, were investigated. The extent of phthalation was measured by the DS (degree of substitution) of cellulose derivatives. The modified cellulosic samples were then characterized by Fourier transform infrared (FT-IR) and solid-state cross-polarization magic angle spinning (CP/MAS) carbon-13 NMR as well as thermal analysis.

## MATERIALS AND METHODS

**Materials.** Sugarcane bagasse (SCB) was obtained from a local sugar factory (Guangzhou, China). It was dried in sunlight and then cut into

**Table 1.** Degree of Substitution (DS) of Phthalated Cellulose in Room-Temperature Ionic Liquid AmimCl

cellulose (%) <sup>a</sup>	phthalation conditions			phthalated cellulose	
	molar ratio <sup>b</sup>	temperature (°C)	reaction time (h)	sample no.	DS
2.5	1:1	80	1	1	0.10
2.5	2:1	80	1	2	0.12
2.5	3:1	80	1	3	0.17
2.5	4:1	80	1	4	0.21
2.5	6:1	80	1	5	0.32
2.5	8:1	80	1	6	0.62
2.5	4:1	80	0.5	7	0.15
2.5	4:1	80	0.75	8	0.18
2.5	4:1	80	1.5	9	0.29
2.5	4:1	80	2	10	0.38
2.5	4:1	80	5	11	0.56
2.5	4:1	80	9	12	0.73
2.5	4:1	70	1	13	0.12
2.5	4:1	90	1	14	0.30
2.5	4:1	100	1	15	0.56
2.5	4:1	105	1	16	0.62

<sup>a</sup> Represents the cellulose in AmimCl by weight (w/w) during dissolution of cellulose. <sup>b</sup> Represents the molar ratio of phthalic anhydride/AGU in cellulose.

small pieces. The cut SCB was ground and screened to prepare 20–40 mesh size particles (450–900  $\mu\text{m}$ ). Room-temperature ionic liquid AmimCl was obtained from the Institute of Chemistry and Chemical Engineering, Hebei Normal University, and used as received. All other chemicals used were of analytical grade and obtained from Guangzhou Chemical Reagent Factory, China.

**Isolation of Cellulose.** A scheme for the isolation of cellulose from SCB is shown in **Figure 1**. The dried SCB powder was first dewaxed with toluene–ethanol (2:1 v/v) in a Soxhlet apparatus for 6 h. The dewaxed SCB was then soaked in distilled water (800 mL) at 80 °C for 2 h. The insoluble residue was delignified with sodium chlorite at pH 3.8–4.0, adjusted by 10% acetic acid, at 75 °C for 2 h. The residue was collected by filtration, washed with distilled water and ethanol, and then dried in a cabinet oven for 16 h at 50 °C. The holocellulose obtained was extracted with 10% KOH (600 mL) at 20 °C for 10 h to release the hemicelluloses. After filtration, the residue was washed thoroughly with distilled water until the filtrate was neutral, then washed with 95% ethanol and dried in an oven at 50 °C for 16 h.

**Physicochemical Characterization of Cellulose.** The neutral sugar composition of the cellulose obtained was determined by gas chromatography (GC) analysis of the corresponding alditol acetates. The sample (10 mg) was treated with 72%  $\text{H}_2\text{SO}_4$  (0.125 mL) for 45 min at room temperature by agitation on a vortex mixture. The solution was then diluted to 1.475 mL, heated to 100 °C for 2.5 h, cooled, and neutralized with 0.32 mL of 15 M ammonia. After reduction, the resulting alditols were acetylated for GC analysis as described by Blakeney et al. (19).

The viscosity of the cellulose obtained was determined by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, Part 1, cupriethylenediamine (CED) method (BS 6306, Part 1, 1982). The viscosity average DP (degree of polymerization) of cellulose was estimated from their intrinsic viscosity  $[\eta]$  in CED hydroxide solution using the following equation (20).

$$P^{0.90} = 1.65[\eta]/\text{mL g}^{-1}$$

where  $P$  is an indeterminate average DP. Molecular weight ( $M_w$ ) of crude cellulose was then calculated from  $P$  multiplied by 162, the  $M_w$  of an AGU.

**Homogeneous Modification of Cellulose in AmimCl.** The phthalated cellulosic derivatives containing free carboxylic groups were prepared by homogeneous reaction of SCB cellulose with phthalic anhydride in room-temperature IL AmimCl. Dried cellulose (0.405 g) was added to AmimCl in a three-necked flask, and the mixture of cellulose/AmimCl was stirred at 80 °C up to 10 h to guarantee the complete dissolution of cellulose. Next, the flask was continuously

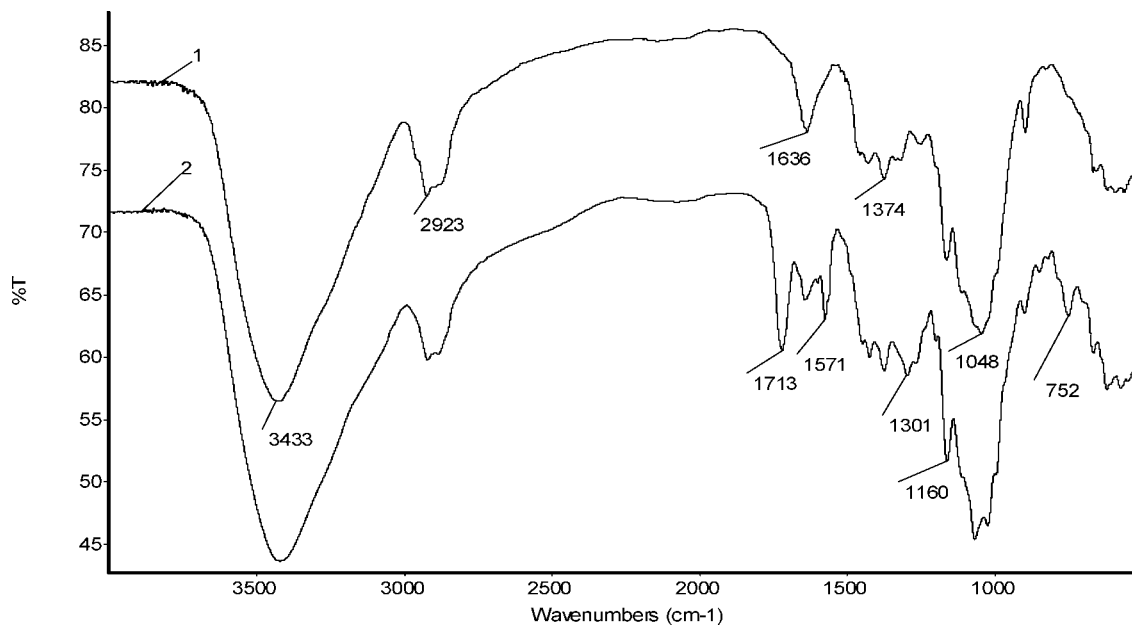


Figure 2. FT-IR spectra of unmodified cellulose (spectrum 1) and phthalated cellulose sample 14 (spectrum 2).

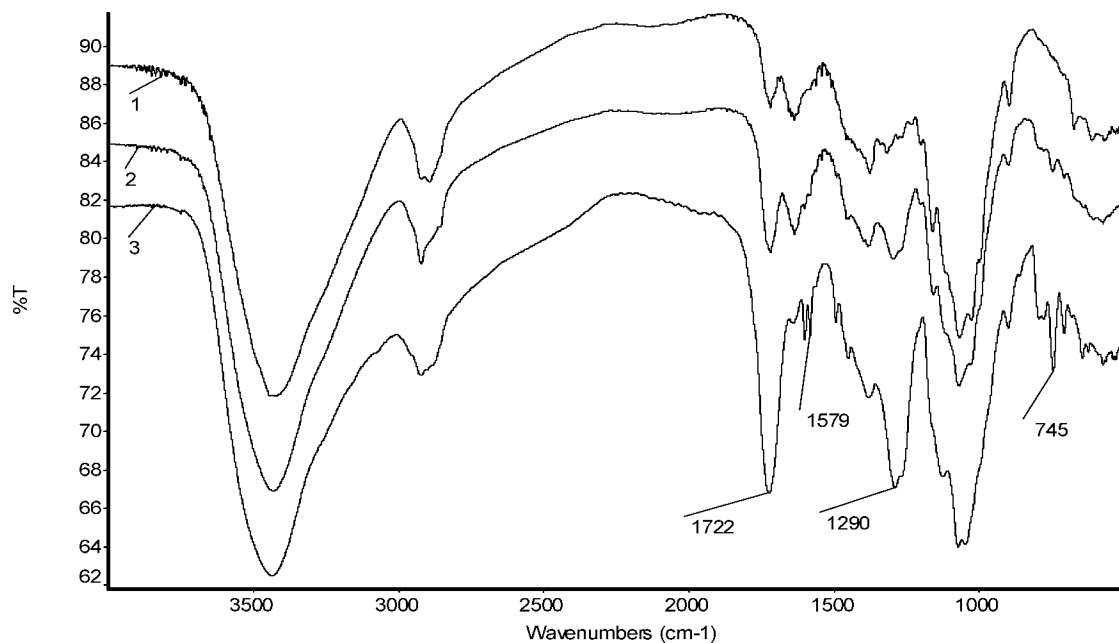


Figure 3. FT-IR spectra of phthalated cellulose samples prepared with molar ratios of phthalic anhydride/AGU 2:1 (spectrum 1, sample 2), 6:1 (spectrum 2, sample 5), and 8:1 (spectrum 3, sample 6).

purged with gaseous  $N_2$ . To the cellulose/AmimCl solution, phthalic anhydride, previously dissolved in 5 mL of AmimCl, was added at the temperature of 70, 80, 90, 100, and 105 °C with the molar ratio of phthalic anhydride/AGU in cellulose at 1:1, 2:1, 3:1, 4:1, 6:1, and 8:1, respectively. The mixture was heated in an oil bath under  $N_2$  atmosphere with stirring for 0.5, 0.75, 1, 1.5, 2, 5, and 9 h, respectively. After the required time, the resulting mixture was slowly poured into 300 mL of ethanol with stirring to stop the reaction. The solid was filtered, washed thoroughly with ethanol to eliminate ILs, unreacted anhydride, and byproducts, and then dried in vacuum at 50 °C for 16 h.

**Determination of the Degree of Substitution (DS).** The degree of substitution of the modified cellulosic preparations was determined by the back-titration method (21, 22). A known weight of the sample was dissolved in 10 mL of 0.1 M NaOH by stirring at 50 °C for 30 min. The excess of NaOH was back-titrated with standard 0.025 M HCl using phenolphthalein as the indicator. The titration was repeated three times, and the average value of the HCl volume was

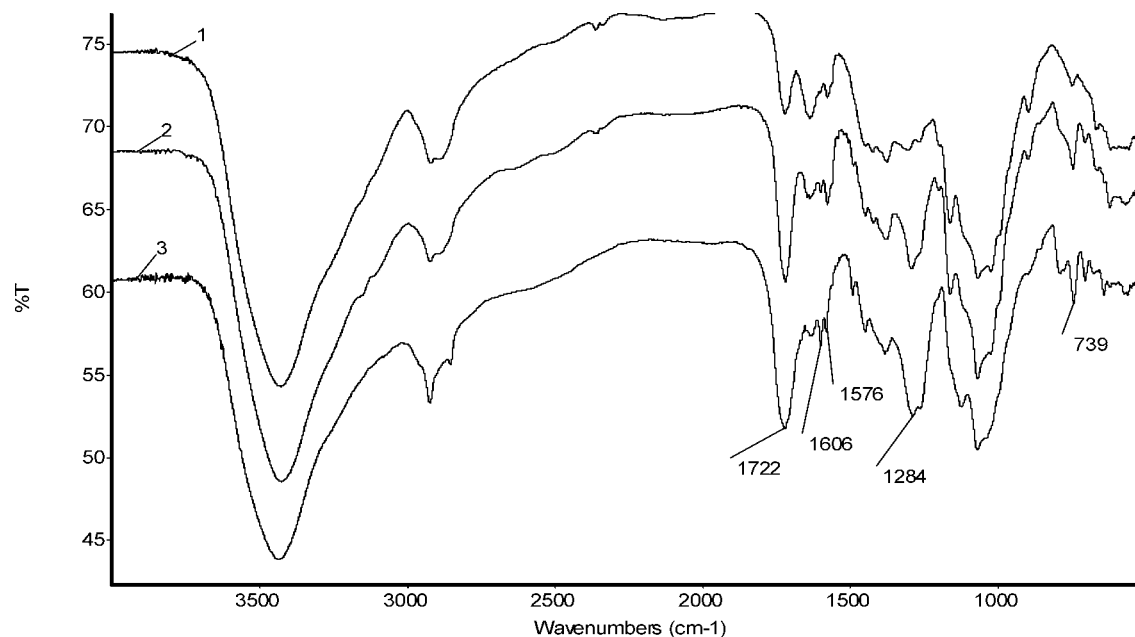
used for the calculations. The DS was calculated by using the following equation:

$$DS = \frac{162 \times n_{COOH}}{m - 148 \times n_{COOH}}$$

where 162 g/mol is the molar mass of an AGU, 148 g/mol is the net increase in the mass of an AGU for each phthaloyl substituted,  $m$  is the weight of sample analyzed, and  $n_{COOH}$  is the amount of COOH calculated from the obtained value of the equivalent volume of known molarity HCl according to the following equation:

$$n_{COOH} = (V_{NaOH} \times C_{NaOH} - V_{HCl} \times C_{HCl})/2$$

**Spectroscopic and Thermal Characterization.** The FT-IR spectra of the cellulose and the phthalated cellulosic derivatives were recorded on an FT-IR spectrophotometer (Nicolet 510) from finely ground



**Figure 4.** FT-IR spectra of phthalated cellulose samples prepared at 80 °C for 0.75 h (spectrum 1, sample 8), 1.5 h (spectrum 2, sample 9), and 2 h (spectrum 3, sample 10).

samples (1%) in KBr pellets in the range 4000–400  $\text{cm}^{-1}$ . Thirty-two scans were taken for each sample with a resolution of 2  $\text{cm}^{-1}$  in the transmission mode. The solid-state CP/MAS  $^{13}\text{C}$  NMR spectra were obtained on a Bruker DRX-400 spectrometer with 5 mm MAS BBO probe employing both cross polarization and magic angle spinning, and each experiment was recorded at ambient temperature ( $293 \pm 1$  K). The spectrometer was operated at 100 MHz. Acquisition time was 0.034 s, the delay time 2 s, and the proton  $90^\circ$  pulse time 4.85 s. Each spectrum was obtained with an accumulation of 5000 scans.

Thermal analysis of the cellulose and the phthalated cellulosic samples was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The apparatus was continually flushed with nitrogen. The sample weighed between 8 and 12 mg, and the scans were run from room temperature to 500 °C at a rate of 10 °C per min.

## RESULTS AND DISCUSSION

**Native Cellulose.** On the basis of the dry weight of sugarcane bagasse, the treatment of holocellulose, obtained after delignification with sodium chlorite, with 10% KOH at 20 °C for 10 h yielded 49.6% cellulose. The neutral sugar composition of the cellulose showed that glucose was the predominant sugar component, which comprised 94.8% of the total sugars, indicating a relatively high content of cellulose. Small amounts of non-cellulosic sugars, such as xylose (2.8%), galactose (1.5%), mannose (0.8%), and arabinose (0.6%), were also observed, indicating that the cellulosic preparation contained minor quantities of residual hemicelluloses. The intrinsic viscosity, degree of polymerization, and molecular weight of the native cellulosic preparation were determined to be 378  $\text{mL g}^{-1}$ , 1277, and 206 800  $\text{g mol}^{-1}$ , respectively.

**Modification and the Degree of Substitution.** Prior to modification, dissolution of the cellulose in AmimCl at 80 °C for 10 h with a cellulose to AmimCl weight ratio of 2.5% resulted in a noticeable degradation of the cellulose macromolecules under the conditions given as shown by reducing its intrinsic viscosity, degree of polymerization, and molecular weight to 286  $\text{mL g}^{-1}$ , 934, and 151 300  $\text{g mol}^{-1}$ , respectively. In this case, the high chloride concentration and its activity in ILs play an important role in cellulose dissolution, which is

highly effective in breaking the extensive hydrogen-bonding network present in cellulose (15, 16). In addition, the DP of the cellulose was also found to decrease from 1310 to 751 (data not shown) when  $[\text{C}_4\text{mim}]\text{Cl}$  was used as a solvent, which suggested that the extent of degradation of cellulose in AmimCl was lower than that in  $[\text{C}_4\text{mim}]\text{Cl}$ . This degradation of cellulose during dissolution in ILs has also been reported by Heinze et al. (23). They found that the dissolution of spruce sulfite pulp and cotton linters in  $[\text{C}_4\text{mim}]\text{Cl}$  led to slight degradation, and DP of cellulose after regeneration decreased from 593 to 544 for spruce sulfite pulp and from 1198 to 812 for cotton linters, respectively.

Of all chemical modification reactions of cellulose, acetylation using acetic anhydride remains the most widely studied (24–27). In addition, there have been a few papers published dealing with modification using the other linear chain anhydrides (28). It is worth noticing that modification with linear chain anhydrides produces an undesired byproduct, the corresponding carboxylic acid, as shown in **Scheme 1a**. However, modification with cyclic anhydrides such as succinic anhydride or phthalic anhydride does not yield a byproduct. Furthermore, the reaction results in products containing carboxylic groups, providing a site upon which further reactive chemistry is possible (29). **Scheme 1b** shows the reaction for phthalation of cellulose with phthalic anhydride. Solid phthalic anhydride, cellulose, and the resulting products could all be dissolved in room-temperature IL AmimCl, and, therefore, homogeneous modification of cellulose with phthalic anhydride could be achieved in AmimCl. **Table 1** lists the degree of substitution (DS) of the phthalated cellulose derivatives under various conditions. Clearly, the DS of the products depended on the molar ratio of phthalic anhydride/AGU, reaction duration, and reaction temperature used. The increase in molar ratio of phthalic anhydride/AUG in cellulose from 1:1 (sample 1) to 2:1 (sample 2), 3:1 (sample 3), 4:1 (sample 4), 6:1 (sample 5), and 8:1 (sample 6) resulted in a DS increase from 0.10 to 0.12, 0.17, 0.21, 0.32, and 0.62, respectively, which could be interpreted in terms of greater availability of phthalic anhydride molecules in the proximity of the cellulose molecules at higher concentration of phthalic anhydride. This observed phenomenon was consistent with the

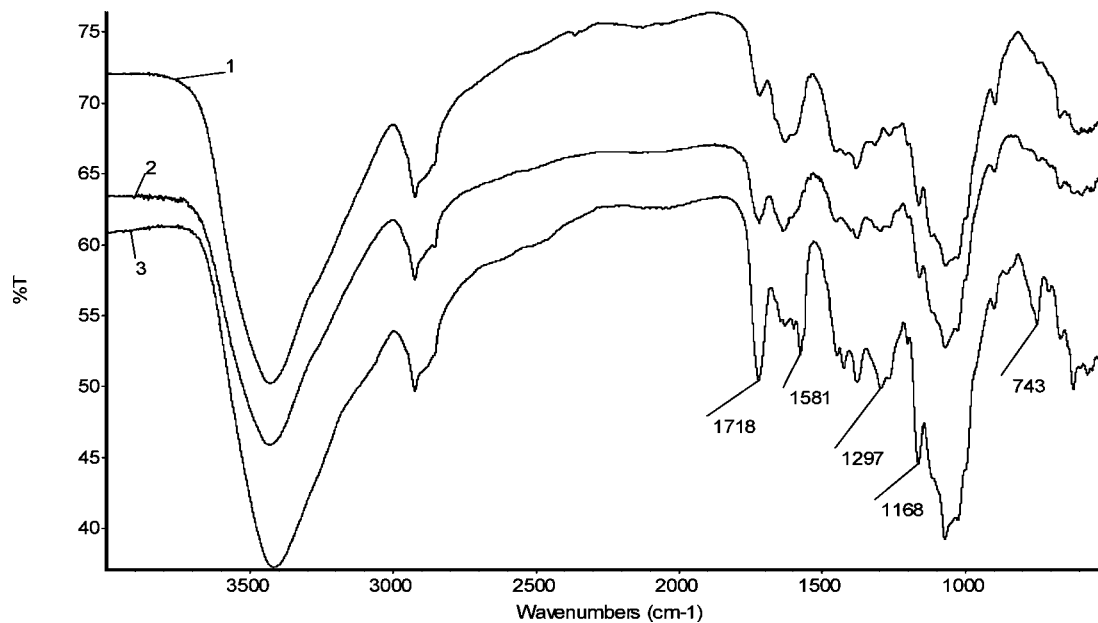


Figure 5. FT-IR spectra of phthalated cellulose samples prepared at 70 °C (spectrum 1, sample 13), 80 °C (spectrum 2, sample 4), and 100 °C (spectrum 3, sample 15).

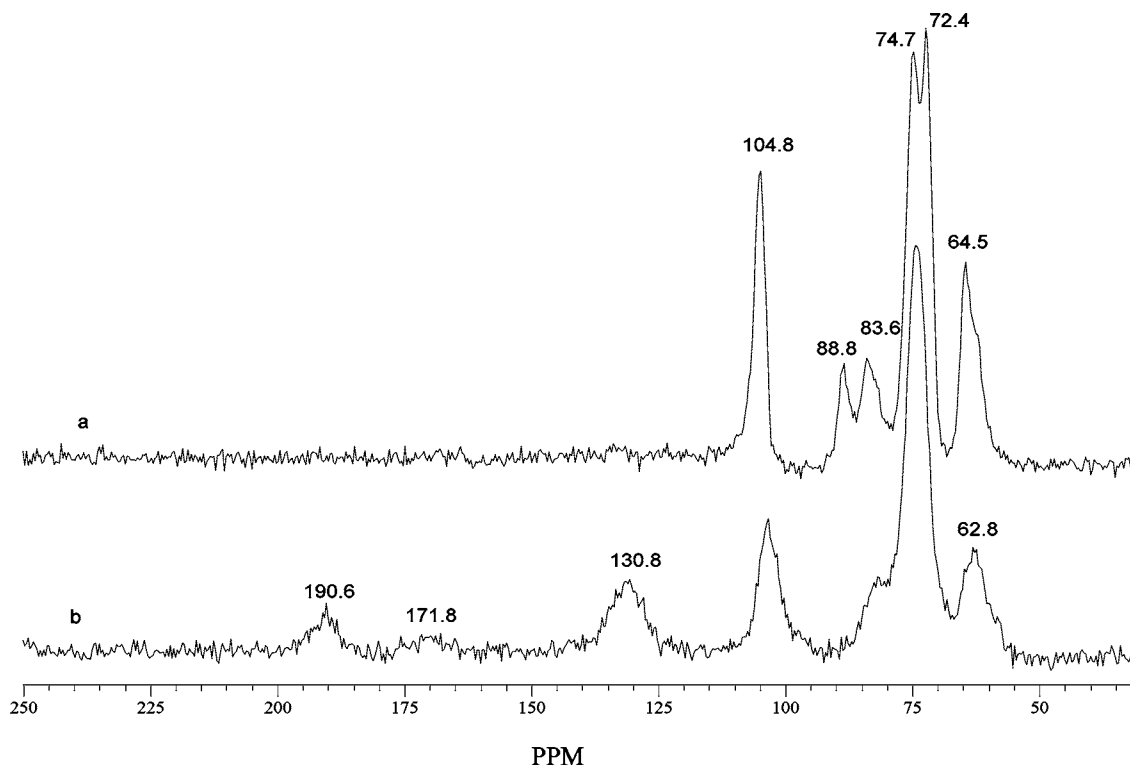


Figure 6. Solid-state CP/MAS  $^{13}\text{C}$  NMR spectra of unmodified cellulose (spectrum a) and phthalated cellulose sample 6 (spectrum b).

study on the reaction of cellulose with succinic anhydride in LiCl/NMP and in TBAF/DMSO by Yoshimura et al. (30). As can be seen from **Table 1**, holding the molar ratio of phthalic anhydride/AGU at 4:1 and reaction temperature at 80 °C, the DS of the cellulosic derivatives reached 0.15 within only 0.5 h (sample 7), 0.18 within 0.75 h (sample 8), 0.21 within 1 h (sample 4), 0.29 within 1.5 h (sample 9), 0.38 in 2 h (sample 10), 0.56 in 5 h (sample 11), and 0.73 in 9 h (sample 12). This increment in DS of the phthalated cellulose with reaction time could be due to the increased rate and time of collisions of phthalic anhydride with cellulosic molecules. Furthermore, raising the reaction temperature from 70 °C (sample 13) to 80 °C (sample 4), 90 °C (sample 14), 100 °C (sample 15), and

105 °C (sample 16) resulted in an increase in the DS of the products from 0.12 to 0.21, 0.30, 0.56, and 0.62, respectively. The reason for this enhancement of phthalation was presumed to be due to the favorable effect of temperature on the reaction. A higher reaction temperature would enhance the mobility of the molecules, the diffusion of phthalic anhydride into the cellulosic molecules, and the swellability of cellulose, therefore increasing phthalation rates.

**FT-IR Spectra.** The FT-IR spectra of unmodified cellulose (spectrum 1) and phthalated cellulose sample 14 (spectrum 2) are given in **Figure 2**. The absorbances at 3433, 2923, 1636, 1374, 1160, and 1048  $\text{cm}^{-1}$  seen in spectrum 1 are associated with native cellulose. A strong band at 3433  $\text{cm}^{-1}$  is originated



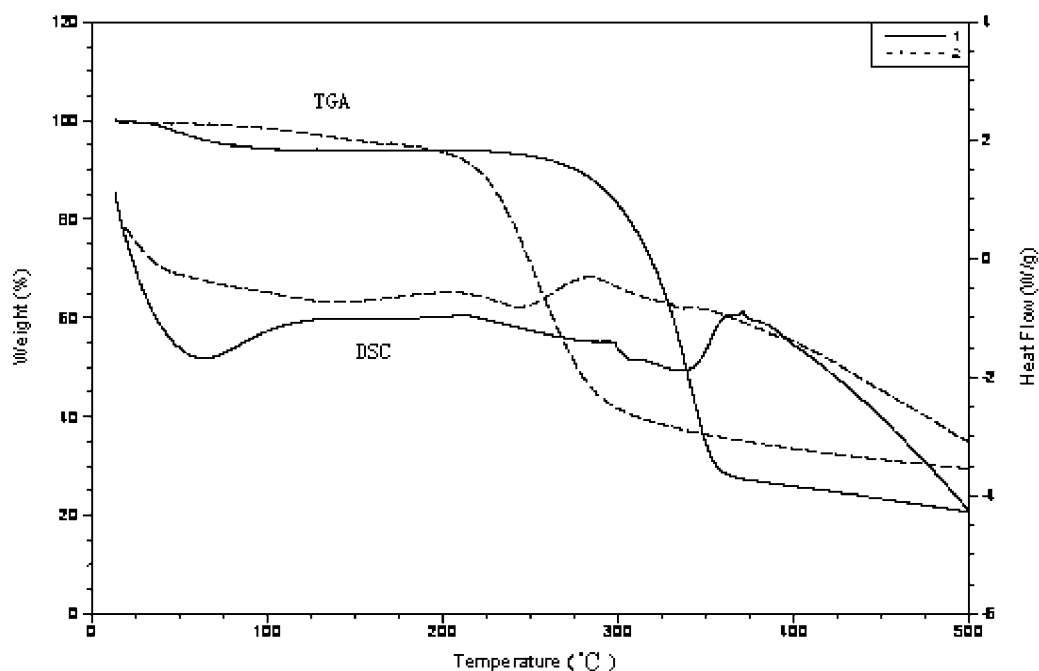


Figure 7. The thermograms of unmodified cellulose (1) and phthalated cellulose sample 10 (2).

from OH stretching, and that at  $2923\text{ cm}^{-1}$  is attributed to the C–H stretching. The band at  $1636\text{ cm}^{-1}$  corresponds to the bending mode of the absorbed water. The peak at  $1374\text{ cm}^{-1}$  is attributed to the O–H bending. The absorption band at  $1165\text{ cm}^{-1}$  corresponds to C–O antisymmetric bridge stretching (31). A strong peak at  $1048\text{ cm}^{-1}$  arises from C–O–C pyranose ring skeletal vibration. In comparison, the spectrum of phthalated cellulose (spectrum 2) provides evidence of phthalation by showing the presence of three bands at  $1713$ ,  $1571$ , and  $752\text{ cm}^{-1}$ . The band at  $1713\text{ cm}^{-1}$  is indicative of absorption by carbonyl group in carboxyl and esters. In general, the absorption by carbonyl bonds in esters gives peaks at  $1740\text{ cm}^{-1}$ , and one in carboxylic acids exhibits a band at  $1700\text{ cm}^{-1}$ . The two bands are strongly overlapped and therefore resulted in a peak centered at  $1713\text{ cm}^{-1}$  (32). The band at  $1571\text{ cm}^{-1}$  corresponds to the antisymmetric stretching of carboxylic anions (30). The band at  $752\text{ cm}^{-1}$  relates to out-of-plane C–H bending of the ortho disubstituted benzene (32). Moreover, the peak intensity at  $1160\text{ cm}^{-1}$  for C–O antisymmetric stretching in ester and  $1301\text{ cm}^{-1}$  for C–O symmetric stretching in ester and carboxyl also increased. These changes suggested that carboxylic groups and phthalyl group were introduced into the cellulosic molecules and the esterification reaction occurred, indicating the occurrence of phthalation reaction in cellulose as illustrated in Scheme 1b. As expected, the absence of peaks at  $1850$  and  $1780\text{ cm}^{-1}$  in spectrum 2 of the phthalated cellulose sample 14 confirmed that the products are free of the unreacted phthalic anhydride (33). In addition, the intensity of the peak at  $1048\text{ cm}^{-1}$  for C–O–C stretching in spectrum 2 slightly decreased due to the degradation of the cellulose macromolecules during dissolution and modification, corresponding to the decreasing trend of DP from 1277 in native cellulose to 934 in dissolved cellulose in the IL.

Figures 3–5 show the effect of the molar ratio of phthalic anhydride/AGU, reaction time, and reaction temperature on the peak intensity of phthalated cellulose samples. As shown in Figure 3, an increase in molar ratio of phthalic anhydride/AGU from 2:1 (spectrum 1, sample 2) to 6:1 (spectrum 2, sample 5), and to 8:1 (spectrum 3, sample 6) resulted in an obvious increment in the intensity of the peaks at  $1722\text{ cm}^{-1}$  for C=O

stretching,  $1579\text{ cm}^{-1}$  for antisymmetric stretching of carboxylic anions,  $1290\text{ cm}^{-1}$  for C–O symmetric stretching, and  $745\text{ cm}^{-1}$  for the out-of-plane C–H bending of the ortho disubstituted benzene, which is parallel to the increasing data of DS in Table 1. In Figure 4, the intensity of peaks at  $1722$ ,  $1576$ ,  $1284$ , and  $739\text{ cm}^{-1}$  obviously increased with an increase of reaction time from 0.75 h (spectrum 1, sample 8) to 1.5 h (spectrum 2, sample 9), and to 2 h (spectrum 3, sample 10), corresponding to an increase of the DS. Similarly, noticeably increasing trends of the bands at  $1718$ ,  $1581$ ,  $1297$ , and  $743\text{ cm}^{-1}$  observed in Figure 5 with the increment in reaction temperature from  $70\text{ }^{\circ}\text{C}$  (spectrum 1, sample 13) to  $80\text{ }^{\circ}\text{C}$  (spectrum 2, sample 4), and to  $100\text{ }^{\circ}\text{C}$  (spectrum 3, sample 15) are parallel to the increasing data of DS in Table 1.

**CP/MAS  $^{13}\text{C}$  NMR Spectra.** The phthalation reaction of cellulose was also studied by solid-state CP/MAS  $^{13}\text{C}$  NMR spectroscopy, and the spectra of unmodified cellulose (spectrum a) and phthalated cellulose sample 6 (spectrum b) are shown in Figure 6. Evidently, the signals at  $130.8\text{ ppm}$  for benzene ring,  $190.6\text{ ppm}$  for carbonyl group, and  $171.8\text{ ppm}$  for carboxylic group (34, 35) in spectrum b revealed the occurrence of esterification and the presence of phthaloyl group and carboxylic group in sample 6, indicating that the reaction shown in Scheme 1b does occur. Moreover, the signal at  $88.8\text{ ppm}$  for C-4 of crystal cellulose disappeared in spectrum b, and the signal for C-6 shifted from  $64.5\text{ ppm}$  in spectrum a to  $62.8\text{ ppm}$  in spectrum b, which indicated that the crystalline structure of the cellulose was completely disrupted by breaking hydrogen bonds in  $\alpha$ -cellulose during the dissolution and functionalization in IL (36). In addition, the three free hydroxyl groups at C-6, C-2, and C-3 positions are the main reactive sites in cellulose. As shown in Figure 6, the intensity of the signal at  $62.8\text{ ppm}$  for C-6 decreased after phthalation, and that at  $72.4\text{ ppm}$  for C-2 and C-3 also decreased, which indicated the phthalation reaction occurred at C-6, C-2, and C-3 positions.

**Thermal Analysis.** The thermal behavior of native cellulose and phthalated cellulosic derivatives was also studied by TGA and DSC in  $\text{N}_2$  atmosphere. Figure 7 illustrates the TGA and DSC thermograms of unmodified cellulose (1) and phthalated

cellulose sample 10 (2). The TGA curves give an initial decrease below 100 °C due to loss of moisture. After that, the native cellulose starts to decompose at 253 °C, whereas the phthalated cellulose sample 10 begins to decompose at 208 °C. At 50% weight loss, the decomposition temperature occurs at 339 °C for native cellulose and 278 °C for the phthalated cellulose. This decreasing trend of decomposition temperature indicated that the thermal stability of the phthalated cellulose is lower than that of the native cellulose. However, the thermal stability of the phthalated cellulose over 200 °C is rather satisfactory to use as a biodegradable material for absorbing heavy metals from industrial wastewater, because high densities of phthalated cellulose with carboxylic groups provide useful properties such as metal chelation.

DSC is generally used to investigate the possibility of interaction between components and measure the extent of disruption of the hydrogen bonds as well as quantify the heat energy flows (37). From the DSC curves in **Figure 7**, the exothermic peak, which represents heat released from the product, was observed at a maximum temperature of 362 °C for unmodified cellulose and 283 °C for phthalated cellulose, respectively, which indicated again that a noticeable degradation of cellulose occurred during the dissolution and modification.

In conclusion, the above results indicated that the homogeneous modification of cellulose with phthalic anhydride could be successfully achieved in room-temperature ionic liquid 1-allyl-3-methylimidazolium chloride without any catalysts, and carboxylic groups were introduced into cellulose. The DS of cellulose derivatives ranged from 0.10 to 0.73 under the conditions given, and it increased with the increment of the molar ratio of phthalic anhydride/AGU in cellulose, reaction time, and reaction temperature. Solid-state CP/MAS <sup>13</sup>C NMR spectroscopy confirmed that the phthalation at C-6, C-2, and C-3 positions all occurred. The thermal stability of phthalated cellulose was found to be lower than that of the native cellulose. However, this thermal stability of the phthalated cellulose over 200 °C is rather satisfactory to use as a biodegradable material for absorbing heavy metals from industrial wastewater. In addition, it should be noted that the macromolecular polymer was substantially degraded and the crystalline structure was completely converted into amorphous state during dissolution and derivatization processes.

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