Research Article

Homogeneous Esterification of Cellulose in the Mixture N-Butylpyridinium Chloride/Dimethylsulfoxide

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Received 9 February 2016; Revised 3 May 2016; Accepted 26 May 2016

Academic Editor: Haisong Qi

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The present study deals with the homogeneous acylation of cellulose with *p*-nitrobenzoyl chloride in a reaction medium composed of a mixture of 1-butylpyridinium chloride and dimethylsulfoxide (BPyCl/DMSO), in the presence of different bases and under mild conditions. The preparation of cellulose *p*-nitrobenzoate depending on the reaction conditions, the influences of reaction parameters such as the base type, and the types of cellulose (kraft and microcrystalline) on the products were investigated. Cellulose *p*-nitrobenzoate with a degree of substitution (DS) in the range from 0.12 to 1.5 was accessible, with a low excess of reagent and for a short reaction time. The cellulose esters were characterized by ¹H-NMR, ¹³C NMR, and FT-IR spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and solubility tests.

1. Introduction

Cellulose is the most abundant natural polymer; its derivative products have many important applications in fiber, membrane, paper, polymer, and paint industries [1–3]. The structure of cellulose consists of both crystalline and amorphous regions, and this construction makes it difficult to be dissolved in normal solvents. Cellulose modification, under homogeneous conditions, particularly esterification, has received increased attention during the last several decades, aiming for better conversion and distribution. The mostly applied solvents in this modification process are N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) [4], a mixture of dimethylsulfoxide (DMSO) and tetrabutylammonium fluoride trihydrate (TBAF × 3H₂O) [5], various ionic liquids (ILs), namely, 1-N-butyl-3-methylimidazolium chloride ([Bmim]Cl), and 1-allyl-3-methylimidazolium chloride ([Amim]Cl) [6, 7]. The 3-methyl-N-butyl-pyridinium chloride and benzyldimethyltetradecylammonium chloride were also investigated as a new kind of solvents for cellulose. The ILs used have the ability to dissolve cellulose with a degree of polymerization (DP) in the range from 290 to 1200 to a very

high concentration [8, 9]. Homogeneous esterification of cellulose with acyl-1H-benzotriazole and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride and N-alkyl-2-halopyridinium salts as activating agents in DMSO/TBAF was carried out. It has been found that N,N-carbonyldiimidazole (CDI) is most effective regarding the degree of substitution (DS) values [10]. In order to expand the scope of ILs used for cellulose esterification and explore the possibility of using nonimidazolium type of ILs, the dissolution and homogeneous acetylation of cellulose into the novel protic IL 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]) with a dispersing agent such as acetone, acetonitrile, DBN, or DMSO under mild conditions were reported [11]. Also, acetylation of xylan in [DBNH][OAc], followed by acetic anhydride/1,5-diazabicyclo[4.3.0]non-5-ene (Ac₂O/DBN) and no cosolvent added, was investigated [12]. Room-temperature ionic liquids, being considered as desirable green solvents for a wide range of separation and as reaction media for processes including catalysis, have recently received significant attention [13, 14]. Synthesis and structural characterizations of *p*-bromobenzoate and *p*-phenylbenzoate of kraft and microcrystalline cellulose in

[Bmim]Cl were carried out [15]. ILs are almost nonvolatile, nonflammable, thermally stable, and reusable “green” solvents. Particularly, used as reaction media, ILs have several advantages such as enhancement of reaction rates, improvement of selectivity and yields, or ease of recycling catalysts [16, 17]. For example, acetylation of alcohols and saccharides was conducted in a dicyanamide based ionic liquid [18]. 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 [19, 20].

In the present study, we describe the homogeneous esterification of cellulose in BPyCl/DMSO solvent system, applying *p*-nitrobenzoyl chloride as acylation agent. The cellulose *p*-nitrobenzoate obtained was characterized by means of FT-IR, NMR spectroscopy, and solubility tests. Thermogravimetric analysis (TGA) was used for degradation and char content information of the modified celluloses by measuring the change in mass as a function of temperature. The scanning electron microscopy (SEM) was used to monitor the morphology changes. The main objective of this work is to develop novel sustainable ionic liquid-based systems (IL/cosolvent) with the capability to dissolve cellulose of high molecular weight and to carry out the homogeneous esterification of cellulose. In order to develop an efficient, commercially and environmentally viable IL-based process, recycling of ILs is of crucial importance.

2. Experimental

2.1. Materials. Commercial microcrystalline cellulose with a degree of polymerization ($DP \approx 200$) (Powder Aldrich Chemical) and bleached kraft cellulose ($DP \approx 1200$) provided by Cellulose of Morocco Company were used as initial cellulose. The cellulose was dried for 6 h at 60°C until constant weight before use. All other standard chemicals were purchased from ACROS chemicals or Aldrich chemical and used as is received without further purification. The IL 1-butylpyridinium chloride (BPyCl) was synthesized in accordance with the literature [6].

2.2. Synthesis of 1-Butylpyridinium Chloride. The pyridine (8, 21 g) and butane chloride (20 g) at a molar ratio 1:2 were added to a round-bottom flask fitted with a reflux condenser for 48 h at 80°C with stirring. The solid is washed with ethyl acetate (3×20 mL) and dried under vacuum. The obtained product (BPyCl) had a solid bright white color, yield 84%. Synthesis of 1-butylpyridinium chloride is shown in Scheme 1.

2.3. Dissolution of Cellulose in (BPyCl)/DMSO. Cellulose (2 w%) was suspended in a mixture of 1-butylpyridinium chloride/DMSO (70 w/30 w) in a round-bottom flask. This mixture was stirred with a magnetic stirrer at 80°C for a maximum of 12 h. The solubility of cellulose in BPyCl/DMSO mixture was checked visually.

2.4. Synthesis of Cellulose *p*-Nitrobenzoate (General Procedure). A mixture of cellulose (2 w%), 1-butylpyridinium chloride/dimethylsulfoxide (70 w/30 w), *p*-nitrobenzoyl

SCHEME 1: Reaction scheme for the synthesis of 1-butylpyridinium chloride.

chloride (5 mol equivalent), and the base (5 mol equivalent) was heated in an oil bath to 80°C and kept at this temperature for 1.30 h. The reaction mixture was precipitated in 100 mL isopropanol. The obtained cellulose *p*-nitrobenzoate was filtered and washed several times with methanol and then dried at 40°C in vacuum.

IR (KBr): 3378.66 cm^{-1} $\nu(\text{OH})$, 2914 cm^{-1} $\nu(\text{CH}$ cellulose), 1730 cm^{-1} $\nu(\text{C=O}$ ester), 1628 cm^{-1} $\nu(\text{C=C})$, 1260 cm^{-1} $\nu(\text{C-O})$, 1100 cm^{-1} $\nu(\text{C-O-C})$, 1528 cm^{-1} $\nu(\text{NO}_2)$, and 850 cm^{-1} $\nu(\text{CN})$.

^{13}C -NMR (DMSO- d_6): $\delta = 60.5$ (C-6), $\delta = 73\text{--}75.3$ (C-5, 3, 2), $\delta = 83.5$ (C-4), $\delta = 103$ (C-1), $\delta = 130$ (C-10), $\delta = 133.5$ (C-8, 9), $\delta = 152$ (C-11), and $\delta = 170$ ppm (C-7).

^1H -NMR (DMSO- d_6): cellulose *p*-nitrobenzoate: $\delta = 7.3\text{--}8$ (phenyl protons, 4H) and $\delta = 3.3\text{--}5$ (protons of kraft cellulose, 7H).

^1H -NMR is usually convenient and is widely used for DS determination of cellulose derivatives. The peaks for *p*-nitrobenzoyl at around 7.3–8.2 ppm strongly overlap with signals for the protons of the cellulose AGU in the range 3.3–5 ppm. The partial DS value of the acetyl moiety among the three OH groups can be inferred from the integration of the ^{13}C NMR spectra of a solution of cellulose ester in DMSO- d_6 .

The DS of cellulose ester was calculated from the ^1H -NMR spectra [21] by equation

$$DS = \frac{7I_{\text{phenyl}}}{4I_{\text{AGU}}}, \quad (1)$$

where I_{phenyl} is the peak integral of phenyl protons at 7.3–8.2 ppm and I_{AGU} is the peak integral of protons of anhydroglucose unit at 3.3–5 ppm.

2.5. Spectroscopic Measurements. The chemical structure of cellulose and cellulose ester samples was analyzed by FT-IR, ^{13}C NMR, and ^1H -NMR spectroscopy techniques.

FT-IR. A mass of 1 mg of the substrate is crushed and mixed with 50 mg of potassium bromide KBr (99%). The obtained powder is then pelletized under a pressure of 6 bars. The spectra were recorded on Vertex 70 spectrometer at room temperature. All spectra were recorded by accumulating 64 scans at a resolution of 4 cm^{-1} in the range of 4000 to 400 cm^{-1} .

NMR spectra were acquired on a Bruker Advance 300 MHz spectrometer with 16 scans for ^1H -NMR and up to 81920 scans for ^{13}C NMR at 60°C in deuterated dimethylsulfoxide (DMSO- d_6) and a sample concentration of 60 mg/mL.

SCHEME 2: General synthesis of cellulose *p*-nitrobenzoate.

2.6. Thermal Analysis. The analysis of the kraft cellulose and grafted cellulose samples was performed using thermogravimetric analysis (TGA) on a simultaneous thermal analyzer SETARAM LABSYS EVO (1F). The apparatus was continually flushed with nitrogen. The 10 to 13 mg samples were heated from room temperature up to 600°C in aluminum pan with a constant heating rate of 10°C/min. Three samples were used to characterize each material.

2.7. Morphological Surface Analysis. SEM analyses were performed with a FEI Quanta 200 microscope to observe the morphology of cellulose and cellulose derivatives. Before SEM analysis, the dried cellulose samples were coated with a carbon layer to increase their conductivity. All samples were examined using an accelerating voltage of 30 kV.

2.8. Solubility. The solubility of cellulose ester at room temperature was checked in the following solvents: N,N-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), dimethylformamide (DMF), and water, considering a concentration of 0.02 g/mL solvent.

3. Results and Discussion

3.1. Synthesis of Cellulose *p*-Nitrobenzoate. Recently, the solubility of cellulose in various ionic liquids has been reported [6, 22–24]. Even better cellulose solvents than the ILs with chloride as their anion are ILs with acetate as an anion. The homogeneous dissolution of cellulose in ionic liquid 1-butylpyridinium chloride (BPyCl) with cosolvent dimethylsulfoxide (DMSO) can be used to perform functionalization reactions to introduce functionalities to the cellulose backbone. As a model reaction, the esterification with *p*-nitrobenzoyl chloride was chosen; since it is a regioselective protection reaction for the more reactive primary hydroxyl group. The cellulose *p*-nitrobenzoate could be used as raw material for the preparation of other cellulose derivatives by modification of nitro groups (NO_2). The general reaction scheme of the nitrobenzoylation is shown in Scheme 2.

3.2. Structure Characterization

3.2.1. FT-IR Spectroscopy. FT-IR spectra of the kraft cellulose, the regenerated kraft cellulose, and the kraft cellulose *p*-nitrobenzoate sample from (BPyCl)/DMSO are shown in

FIGURE 1: IR spectra of kraft cellulose (a), regenerated cellulose, (b) and grafted cellulose (c).

Figure 1. It can be seen that spectra (a) and (b) are quite similar and no new peaks appear in the regenerated sample, indicating no chemical reaction occurred during the cellulose dissolution and regeneration processes. In other words, (BPyCl)/DMSO is a nonderivatizing solvent for cellulose. Spectrum (c) provides a clear evidence of acetylation by showing the presence of some important peaks at 1730 cm^{-1} for (C=O) stretching ester, 1260 cm^{-1} for stretching of (C-O), 3053 cm^{-1} for aromatic ring (C-H) stretching, 1628 cm^{-1} for aromatic (C=C) stretching, 3378 cm^{-1} for group (OH) stretching of cellulose, 2914 cm^{-1} for (C-H) cellulose, and 1100 cm^{-1} for (C-O-C) asymmetric stretching and ring asymmetric stretching for cellulose. The strong absorption peaks at 1528 cm^{-1} and 850 cm^{-1} correspond, respectively, to NO_2 symmetric stretching and (C-N) stretching. These differential FT-IR results confirmed the reactions of esterification of cellulose by *p*-nitrobenzoyl chloride in a mixture (BPyCl)/DMSO.

The results of the homogeneous reaction of cellulose with *p*-nitrobenzoyl chloride (5 eq.) in a mixture (BPyCl)/DMSO with 2% (w/w) cellulose were allowed to react at 80°C. Reaction conditions, DS values of the obtained cellulose esters, and their solubility are summarized in Table 1.

Initial attempts at the homogeneous esterification of kraft and microcrystalline cellulose in (BPyCl)/DMSO mixture were carried out at 80°C for 12 h without any base. The obtained outcome was a black mixture, which indicates a

TABLE 1: Reaction conditions, DS, and solubility for obtained cellulose *p*-nitrobenzoate.

Entry	Cellulose type	Base	Reaction time (h)	DS ^a	Solubility			
					DMSO	DMF	DMAc	H ₂ O
1	Microcrystalline	DMAP	1.30	0.4	+	–	–	–
2	Microcrystalline	Pyridine	1.30	0.23	+	–	–	–
3	Microcrystalline	Triethylamine	1.30	0.19	+	–	–	–
4	Microcrystalline	DMAP	3.0	1.50	+	+	+	–
5	Kraft	DMAP	1.30	0.35	+	–	–	–
6	Kraft	Pyridine	1.30	0.19	+	–	–	–
7	Kraft	Triethylamine	1.30	0.12	+	–	–	–
8	Kraft	DMAP	3.0	1.42	+	+	+	–

^aDS was determined with ¹H-NMR method.

+, soluble; –, insoluble.

degradation of the cellulose. No precipitated product resulted from the addition of isopropanol, ethanol, or methanol to the black mixture. This confirms again that the cellulose has been degraded. It is assumed that the black color is caused by a combination of the released hydrogen chloride and the decomposition products of cellulose.

On another occasion, the esterification was performed on (BPyCl)/DMSO mixture, using tertiary bases such as triethylamine, pyridine, and 4-dimethylaminopyridine (DMAP) and reducing the reaction time to 3 h with the intention of capturing the released hydrogen chloride and suppressing the degradation of cellulose. The finding was that the brown color replaced the black one.

The effect of reaction parameters such as reaction time and base type on the synthesis of cellulose *p*-nitrobenzoate in a mixture (BPyCl)/DMSO has been studied. The DS of the products increases as reaction time prolongs (entries 1, 4 and 5, 8). Table 1 shows that, under conditions of 80°C and DMAP (5 eq.), the DS of the acylated product reaches 0.4 for microcrystalline cellulose and 0.35 for kraft cellulose within a period of 1.30 h, whereas it increases to 1.5 and 1.42 within 3 h for the microcrystalline cellulose and kraft cellulose, respectively.

Further investigation on the influence of the bases was carried out (entries 1, 2, and 3) keeping the ratio of *p*-nitrobenzoyl chloride to cellulose at 5 mol equivalent, and adding 5 mol equivalent of various bases. The DS of the obtained cellulose *p*-nitrobenzoate has reached 0.19, 0.23, and 0.4 for triethylamine, pyridine, and DMAP, respectively. It is clear that, by using DMAP and pyridine, the reactivity of acylation systems increases. This might be due to the stabilization of the acylpyridinium ion, which plays an important role in the catalytic cycle and results in an increasing rate of the reaction.

The results presented in Table 1 also show that the DS of kraft cellulose is lower than that of the MCC, and the degree of substitution of obtained products increased with decrease in the degree of polymerization. This is due to the fact that, with the decrease in molecular weight, more numbers of hydroxyl groups become available to undergo esterification reaction giving higher DS values in comparison to high molecular mass cellulose. These results suggest that it

is possible to control the DS value of cellulose *p*-nitrobenzoate by controlling reaction time and the choice of the used base. The three hydroxyl groups at the C2, C3, and C6 positions exhibit various reaction activities. In fact, Figure 2 shows a ¹³C NMR spectrum of sample (4) with a DS of 1.5 in which the signal at 170.2 ppm was attributed to the carbonyl carbon at C-6, the signal at 167.4 ppm to carbon at C-2, and the signal at 166.2 ppm to carbon at C-3. Obviously, the nitrobenzoylation reaction is favored at C-6, and the order of reactivity is C6-OH > C2-OH > C3-OH. This result is similar to that observed in [Amim]Cl solution [25].

3.3. Solubility. In this work, the solubility of synthesized cellulose *p*-nitrobenzoate in a mixture ionic liquid/cosolvent (BPyCl/DMSO), DMAc, DMF, DMSO, and water was investigated, and the results are summarized in Table 1. All esters products are readily soluble in DMSO and insoluble in the water, but the solubility of the ester in dimethylformamide and N,N-dimethylacetamide depends greatly on the total DS value.

3.4. Thermogravimetric Analysis. During the TGA study of the thermal behavior of kraft cellulose, *p*-nitrobenzoyl chloride, and cellulose ester (DS ≈ 1), the temperature was increased from 25 to 600°C, according to a heating speed of 10°C/min, and maintained constant at 95°C for 15 min to remove adsorbed water. The results of the analysis are summarized in Figure 3. The main thermal characteristics from the TGA-DTG curves, such as the temperature of the beginning of the degradation T_0 corresponding to 1% mass loss, the temperature of maximum mass loss T_{max} , and the percentage of carbon residue (CR%) at T_{max} and at 400°C, are given in Table 2.

Results of the TGA and the DTG represented in Figure 3 show that kraft cellulose (a) degrades between 280 and 360°C and the speed of mass loss has a peak around 350°C (mass loss 42%). These results are consistent with those of the literature [26–28]. The TGA and DTG spectra for *p*-nitrobenzoyl chloride (b) can be decomposed into two zones. The first one is located between 110 and 280°C with a DTG peak centered at 254°C (mass loss 35%). The second zone, which takes place between 280 and 375°C with a maximal

FIGURE 2: NMR spectra of kraft cellulose *p*-nitrobenzoate. FIGURE 3: Thermogravimetric analysis TGA-DTG for kraft cellulose (a), *p*-nitrobenzoyl chloride (b), and cellulose *p*-nitrobenzoate (c).TABLE 2: Thermal characteristics of samples kraft cellulose (a), *p*-nitrobenzoyl chloride (b), and cellulose *p*-nitrobenzoate (c).

Samples	T_0 (°C)	T_{max} (°C)	CR ^a (%) (at T_{max})	CR ^b (%) (at 400°C)
(a)	280	350	58	34
(b)	100	254–360	65–24	12
(c)	80	264	45	20

T_0 : temperature of the beginning of the degradation to 1% mass loss.

T_{max} : temperature of maximum mass loss.

CR^a (%): percentage of carbon residue at T_{max} .

CR^b (%): percentage of carbon residue at 400°C.

mass loss speed at 360°C (mass loss 76%), is related to slower decomposition processes. The TGA and DTG curves of the cellulose ester (c) are fundamentally different from those of the other various constituents. DTG peaks observed for the *p*-nitrobenzoyl chloride (254°C and 360°C) and the cellulose (350°C) disappeared. DTG peak of the final compound presents only one main peak at 264°C (mass loss 55%), at a

lower temperature than the main peak of decomposition of the cellulose (350°C) and at a temperature between the two peaks of the *p*-nitrobenzoyl chloride. DTG peak of the cellulose ester becomes wider and shifts to lower temperature, and the amount of carbon residue at 400°C and at T_{max} decreases by ~14% and is observed as compared to the unmodified kraft cellulose. These results showed decreased thermal stability for cellulose *p*-nitrobenzoate due to a decrease in crystallinity of cellulose modified by esterification and to the in situ formation of nitrogen containing NO₂, which accelerate cellulose decomposition. Even if the interpretation is difficult, it can be concluded that there is a significant chemical modification of initial substrates and thus the formation of a chemical bond between these molecules, confirming the occurrence of grafting.

3.5. Morphological Surface Analysis. SEM analysis was mainly employed to determine the surface properties of the samples. Figure 4 shows the SEM micrograph illustrating the morphology of microcrystalline cellulose (a), kraft cellulose (d), and their corresponding regenerated (b, e) and grafted (c, f) celluloses.

The analysis of the SEM pictures reveals a number of things: First, the microcrystalline cellulose (MCC) is mainly composed of rod-like and platelet-like cellulose micro-fibrils, shaped into a spherical agglomeration. Second, the kraft cellulose has a three-dimensional structure made of nanometric fibers. Before their treatment, these fibrils are identifiable almost one by one, but this distinction becomes very difficult after the regeneration and esterification treatments. Initially and before treatments the fibrils exist at an elementary level with a variable size within 3–20 nm, depending on the source of cellulose (a, d) [29]. Third, under the electron microscopic examination, the regenerated celluloses obtained from the microcrystalline (b) and kraft (e) cellulose are nonporous, with a plain texture and a surface structure that is smooth, compact, and homogeneous. Fourth, the morphology of the cellulose nitrobenzoate derivative ($DS \approx 1$) is clearly different from the morphologies of microcrystalline and kraft celluloses, which indicates successful grafting.

FIGURE 4: SEM micrographs of microcrystalline cellulose (a), regenerated microcrystalline cellulose (b), grafted microcrystalline cellulose (c), kraft cellulose (d), regenerated kraft cellulose (e), and grafted kraft cellulose (f).

4. Conclusion

The results show that (BPyCl)/DMSO is a direct solvent to dissolve cellulose. In general, it was found that cellulose dissolved very well in (BPyCl)/DMSO and the solubility can reach 5 wt% at 80°C. Mixture of IL with a cosolvent was successfully applied for the synthesis of cellulose *p*-nitrobenzoate by reacting cellulose with *p*-nitrobenzoyl chloride in the presence of base under mild conditions. The resulted compounds were characterized by spectroscopy techniques (FT-IR, NMR). The DS values were obtained by ¹H-NMR technique.

It was shown that cellulose esters with different DS can be obtained by varying the reaction time in a completely homogeneous synthesis. The products dissolve in some organic solvents such as DMSO, DMAc, and DMF, depending on their DS values. The detailed studies about the interaction cellulose/solvent are still under investigation. The thermal behaviors were investigated by thermogravimetric analysis (TGA) under nitrogen. The results indicated some differences between thermal degradation of cellulose and cellulose *p*-nitrobenzoate. The cellulose derivatives exhibited less heat resistance compared to cellulose, meaning that cellulose is a thermally more stable material than cellulose

p-nitrobenzoate. Surface morphology of grafting cellulose is clearly different from the surface morphologies of cellulose, which proves the grafting success.

Competing Interests

The authors declare that they have no competing interests.

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