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Journal Name

Green Chemistry

ARTICLE TYPE

Acylation of cellulose in reversible ionic liquids

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1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), in conjunction of methanol after CO_2 capture in DMSO created a new solvent capable of dissolving up to 8 wt% of cellulose, which could be applied as a highly efficient reaction media for the synthesis of cellulose esters under mild conditions.

Cellulose esters are extremely commercially important materials of cellulose derivatives with a wide application in the field of plastics, film, fiber, membrane, coatings, textile and cigarette industries.[1-4] Although the synthesis of most commercial cellulose esters under heterogeneous conditions dominated the their production in the industry so far, homogeneous derivatation of cellulose has been obtained great interests for a long time, which has several advantages over the heterogeneous paths.[5, 6] Sulfuric acid was usually used as a catalyst for the production of cellulose esters in conventional heterogeneous processes, which usually resulted in considerable corrosion and degradation of cellulose; furthermore, it was impossible to synthesize partially substituted cellulose esters directly. While the homogeneous processes can produce cellulose esters with controllable degree of substitution (DS), physic-chemical properties directly by adjusting reaction conditions, such as reaction time, temperature and the molar ratio of derivatizing agents to cellulose.[7] Therefore, there is still an upsurge of interest in developing homogeneous derivation of cellulose for the production of cellulose esters, especially.[8, 9]

Towards a homogenous derivation of cellulose, one of the key issues is successful dissolution of cellulose.[10] However, due to the stiff molecule and close chain packing via numerous intermolecular hydrogen bonds, cellulose cannot be melt and is extremely difficult to dissolve. To date, a rather limited number of solvent systems are researched for cellulose derivatisation, such as N,N-dimethylacetamide (DMAc)/LiCl,[11-13] dimethyl sulfoxide (DMSO)/tetrabuthlammonium fluoride trihydrate (TBAF),[5, 14] $LiClO_4*3H_2O$ molten salt hydrate,[15, 16] and ionic liquids.[7, 17-22] Recently, the ionic liquids system has obtained extensively study due to their good solubility to cellulose, and significant progress has been achieved, especially in the field of homogeneous production of cellulose esters.[7] Although cellulose acetate with a wide range of DS values could be readily obtained under mild reaction conditions without using any other catalysts, it is very difficult to synthesize cellulose propionate (CP) and cellulose butyrate (CB) with high DS due to the less reactivity of propionic anhydride and butyric anhydride when 1-allyl-3-methylimidazolium chloride ionic liquids was used as a solvent.[23]

Catalysts are still needed for an efficient procedure for the homogeneous synthesis of CP and CB.[24]
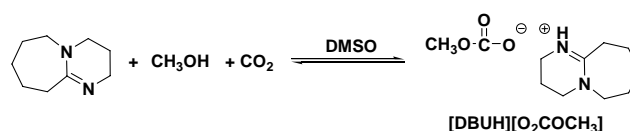
Scheme 1 *In situ* synthesis of CO_2-based reversible ionic liquids (RILs) in DMSO for cellulose dissolution and derivation

More recently, a novel mixed solvent based on a strong organic base in conjunction of an alcohol after CO_2 capture in DMSO was reported, and they were capable of dissolving up to 10 wt% of cellulose under mild conditions.[25] The design of this solvent system for cellulose dissolution and processing was based on the concept of switchable solvents triggered by CO_2 proposed by Jessop and co-workers[26] and stimulated by the potential shortages of ionic liquids for biomass processing and conversion in terms of high cost, high energy consumption for recycling and purification, etc. With the reversible compositional change under mild conditions from molecular liquids to ionic compounds, the proposed system introduced a variety of possible opportunities in catalysis and separation processes.[27] The strong organic bases played important role in this solvent system, and some of them were widely used as green organocatalysts for esterification of alcohols with anhydrides,[24, 28, 29] therefore, this mixed solvent system was expected to be a promising homogeneous system for acylation of cellulose acting as both of a solvent and a catalyst.[30]

Herein we report a homogeneous synthesis of cellulose esters stimulated by the successful dissolution of cellulose in this new solvent system. It was found that although the tetramethyl guanidine (TMG)-methanol/DMSO or TMG-ethylene glycol/DMSO systems after capturing CO_2 presented the best solubility to cellulose,[25] they were not suitable solvent systems for acetylation of cellulose when acetic anhydrate was used as the acylating reagent, which was evidenced by the low yields and low DS of cellulose acetate obtained. This may be due to the potential reaction of TMG with acetic anhydrate. When the system was designed by using 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) in conjunction of methanol in DMSO as $[DBUH][O_2COCH_3]$/DMSO (X_{RILs}=0.2, X_{RILs} is the molar fraction of formed ionic compounds in the mixture) in the presence of 0.5 MPa of CO_2 (Scheme 1), the system could dissolve 8 wt% cellulose in 3 h at 60 °C, and the as-prepared cellulose solution could be used for subsequent homogeneous synthesis of cellulose esters (Scheme 2) with satisfactory yields

and DS (Table 1).
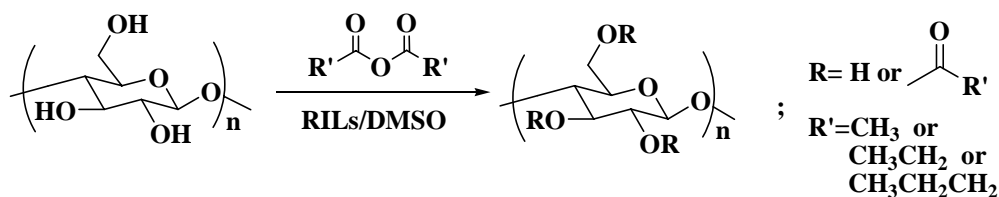
Scheme 2 Highly efficient synthesis of cellulose esters in [DBUH][O₂COCH₃]/DMSO (X_RILs=0.2) without adding any other catalysts

The formation and structure of [DBUH][O₂COCH₃] in DMSO was identified by NMR analysis (Supporting information, Fig. S1, 2). The satisfactory dissolution behavior of cellulose in this mixed solvent is evidenced by the viscous transparent cellulose solutions and the results of the transformation of cellulose I to cellulose II during the dissolution and regeneration process (Fig. 1). It is believed that with the assistant of DMSO, the *in-situ* formed carbonate ions acted as hydrogen bond acceptors in the mixed solution, which then interacted with the hydroxyl groups and ether bonds of the cellulose and by disrupting and breaking the intramolecular hydrogen-bonding network, thus leading to the dissolution of cellulose.[25]
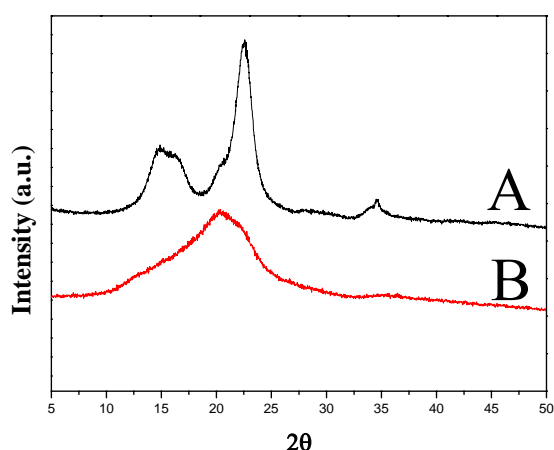

Fig.1 WAXD spectra of original cellulose and regenerated cellulose: (A) original cellulose (MCC); (B) regenerated cellulose by ethanol from 8 wt% of cellulose solution in [DBUH][O₂COCH₃]/DMSO (X_RILs=0.2, X_RILs is the molar fraction of formed reversible ionic liquids in the mixture)

With the new cellulose solution in our hands, we started the study with the synthesis of cellulose acetate, and the DS of all products were analyzed by NMR method in DMSO-d₆ according to previous publications.[19, 31] It is found that the reaction run much faster than that in ionic liquids, and a DS of 2.41 is achieved after only 0.083 h (5 min) at 80 °C when the molar ratio of acetic anhydride to hydroxyl groups (OHs) is set to 1.2 : 1 (Table 1, entry CA-1), while it took 3 h to achieve a DS of 2.3 at 100 °C when the molar ratio of acetic anhydride to hydroxyl groups was set to 1.7: 1 in ionic liquids,[21] whereas effective acetylation of cellulose with aliphatic anhydrides needs a catalyst, such as pyridine, sulfuric acid, or perchloric acid in other homogeneous solution, for example, only low DS of cellulose acetate could be obtained in DMAc/LiCl in the absence of a catalyst.[11] The findings demonstrate that the solvent system in this study is much more efficient than other solvent system for the acetylation of cellulose with acetic anhydride.

Table 1 gave the effects of various conditions such as reaction time, reaction temperature, and acid anhydride concentration on the DS of cellulose esters towards a better understanding of the acylation process. The results show that the reaction is running very fast in the first 5 min, and CA with a DS value of 2.41 is achieved (CA-1), and then becomes slow. The DS of CA reaches 2.63 (CA-2) within 10 min, 2.72 (CA-3) within 30 min, 2.91 (CA-4) within 1 h, 2.94 (CA-5) within 3 h. The reaction temperature only had slightly effect on the reaction, which was evidenced by the fact of products with DS of 2.51 (CA-6) and 2.71 (CA-7) when the reaction was performed at 25 °C and 50 °C in 5 h, respectively under identical conditions. CA with a high DS of 2.61 (CA-8) could be obtained in 1 h when the reaction was performed at 50 °C. These results show that this reaction system is extremely mild and efficient. Products with various DS were also obtained through modifying the molar ratio of acetic anhydride to the OHs (CA-9, 10 and 11). When the molar ratio of acetic anhydride/OHs was decreased from 1.1 and 1.0, the DS was slightly decreased from 2.82 (CA-11) and 2.25 (CA-10) under identical conditions, and a further decrease to 0.8 resulted in a significant decrease in the DS to 0.98 (CA-9). With these, it is reasonable to assume that the DS value of cellulose esters can be controlled by varying stoichiomeric ratio of acid anhydride/OHs, temperature, and reaction time. Commercially, it was hard to control the DS due to the heterogeneous nature of the reaction, and commonly used cellulose diacetate esters were obtained by hydrolyzing fully substituted cellulose acetate. The controllability to the DS of cellulose acetate of the new homogeneous acylation process will provide many opportunities in the design of cellulose acetate with various DS by simply varying the reaction conditions to meet the requirement of targeted applications.

Cellulose propionate and cellulose butyrate are also important cellulose derivatives, and a catalyst is usually needed for a highly efficient synthesis by using propionic anhydride and butyric anhydride as acylating reagents, even under homogeneous conditions.[24] The primary results show that highly efficient propionylation and buryralation of cellulose can be successfully carried out in this novel system under mild conditions without any other catalysts. Cellulose propionate (CP) and cellulose butyrate (CB) with DS of 2.91, and 2.59 were synthesized within 5 h at 80 °C (Table 1, CP, CB). The lower DS value of the CB than that of CP and CA obtained under identical conditions demonstrates that there is a relation between the DS and the length of the alkyl chain of the acid anhydride. From these results, it can be inferred that both of the reaction rate and reaction efficiency of acetylation, propionylation and butyralation of cellulose in [DBUH][O₂COCH₃]/DMSO (X_RILs=0.2) are greatly

improved. It is well recognized that during the homogeneous synthesis of CP and CB catalyzed by 4-Dimethylaminopyridine (DMAP), an activated acyl pyridinium intermediate is formed between the acid anhydride and DMAP, and the intermediate readily esterifies with the hydroxyl groups of cellulose.[28] The ionic liquids [DBUH][O₂COCH₃] can be reversed thermally to their molecular precursors under the reaction condition in this study,[26] therefore, it is reasonable to speculate that the *in-situ* formed DBU due to the degradation of [DBUH][O₂COCH₃] during the acylation process acts as a basic catalyst like DMAP to promote the reaction, thus achieving a higher reaction rate. However, further details still need to be identified in the future to support this hypothesis.

Table 1 Reaction parameters for the synthesis of cellulose derivatives.[a]

Entry	T (°C)	Time (h)	Reagent	Molar ratio [b]	DS[c]	Solubility [d]		
						DMSO	Acetone	CHCl₃
CA-1	80	0.083	Ac₂O	1.2/1	2.41	+	+	+
CA-2	80	0.17	Ac₂O	1.2/1	2.63	+	+	+
CA-3	80	0.5	Ac₂O	1.2/1	2.72	+	+	+
CA-4	80	1	Ac₂O	1.2/1	2.91	+	+	+
CA-5	80	3	Ac₂O	1.2/1	2.94	+	+	+
CA-6	25	5	Ac₂O	1.2/1	2.51	+	+	+
CA-7	50	5	Ac₂O	1.2/1	2.71	+	+	+
CA-8	50	1	Ac₂O	1.2/1	2.61	+	+	+
CA-9	80	5	Ac₂O	0.8/1	0.98	+	−	−
CA-10	80	5	Ac₂O	1/1	2.25	+	−	−
CA-11	80	5	Ac₂O	1.1/1	2.82	+	+	+
CP	80	5	(EtCO)₂O	1.2/1	2.91	+	+	+
CB	80	5	(PrCO)₂O	1.2/1	2.59	+	+	+

[a]All reactions of cellulose concentration were 5 wt%. [b].Molar ratio of acylation reagent to all of the hydroxyl groups in solution. [c]DS, degree of substitution calculated from ^{1}H NMR spectra according to a previous publication. [21] [d]"+" stands for soluble, and "−"stands for insoluble;
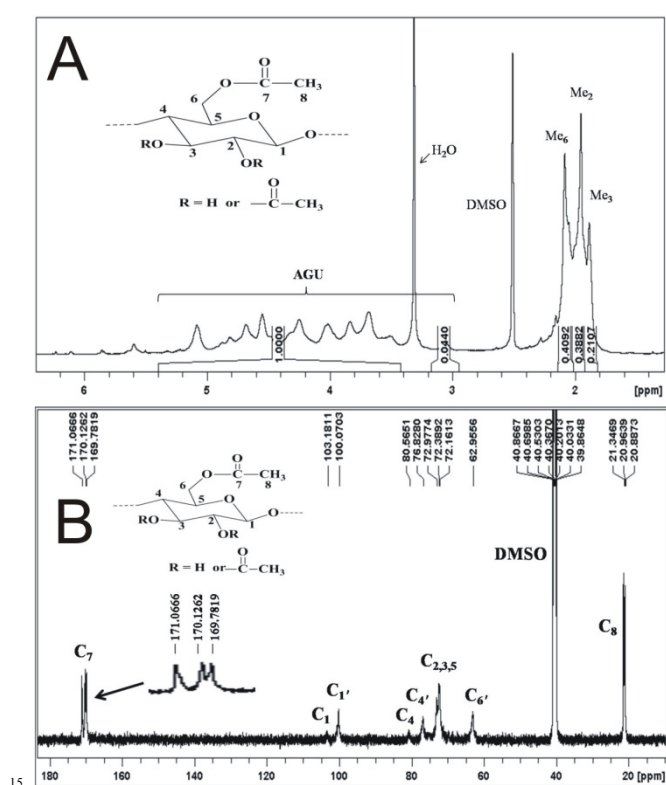

Fig.2 A: ^{1}H NMR spectrum of cellulose acetate sample (DS=2.25, CA-10) in DMSO-d₆; B: ^{13}C NMR spectrum of cellulose acetate sample (DS=2.25, CA-10) in DMSO-d₆

The ^{1}H NMR and ^{13}C NMR analysis were used to elucidate the molecular structure and evaluate the distribution of substituent in the synthesized cellulose esters. In the case of cellulose acetate, strong signals within the chemical shift range from 1.8 to 2.2 ppm assigned to methyl hydrogen in the ^{1}H NMR spectra (Figure 2A) and signals within the chemical shift range from 169 to 171 ppm assigned to carbonyl carbon in the ^{13}C NMR spectra (Figure 2B), were observed after the modification. The distribution of the acetyl moiety among the three OH groups (C₆-OH, C₃-OH, C₂-OH) in an AGU unit were calculated from the quantitative integration of acetyl methyl protons area of the ^{1}H NMR spectrum roughly, and the results were presented in Table S1. Although the error is large with this method, it does give possible the distribution trend of substituent among the three OH groups. It can be seen that the three hydroxyl groups at C₂, C₃, and C₆ position exhibit different reaction activities, and the order of reactivity is C₆-OH> C₂-OH > C₃-OH, which is similar to the acetylation in LiCl-1,3-dimethyl-2-imidazolidinone (DMI) solutions.[32] This result is different from those industrially synthesized through heterogeneous acetylation hydrolysis process,[33] whose partial DS order is C₃-OH > C₂-OH > C₆-OH, as well as those in ionic liquids.[21]

In Figure 2B, the peak at 63.0 ppm is assigned to C₆' carbon bearing a substituted acetyl group. However, an expected peak at 59.0 ppm assigned to the unmodified C₆ is not observed, indicating a fully substitution at C₆. The peaks at 80.6 ppm and 103.2 ppm are assigned to C₄ and C₁ bearing an unsubstituted hydroxyl group, respectively; and a peak around 100.1 ppm marked as C₁' is assigned to a C₁ carbon adjacent to C₂ carbons bearing a substituted hydroxyl group; and a peak around 76.8 ppm marked as C4' is assigned to C₄ carbon adjacent to C₃ carbons bearing a substituted hydroxyl group. The resonance peaks of C₂, C₃ and C₅ carbons heavily overlap as they give only a strong cluster around 71.0 ppm to 74.0 ppm for high DS sample. The signal at 171.1 ppm is assigned to the carbonyl carbons linked to C₆, 170.1 ppm to C₂, and 169.8 ppm to C₃. Quantitative evaluating the integration of C₁' and C₄' peaks demonstrate that

the degree of substitution at C_2 carbon is larger than that of C_3, which is consisted with the reactivity order of C_6-OH, C_2-OH and C_3-OH from ^{1}H NMR analysis in Table S1.
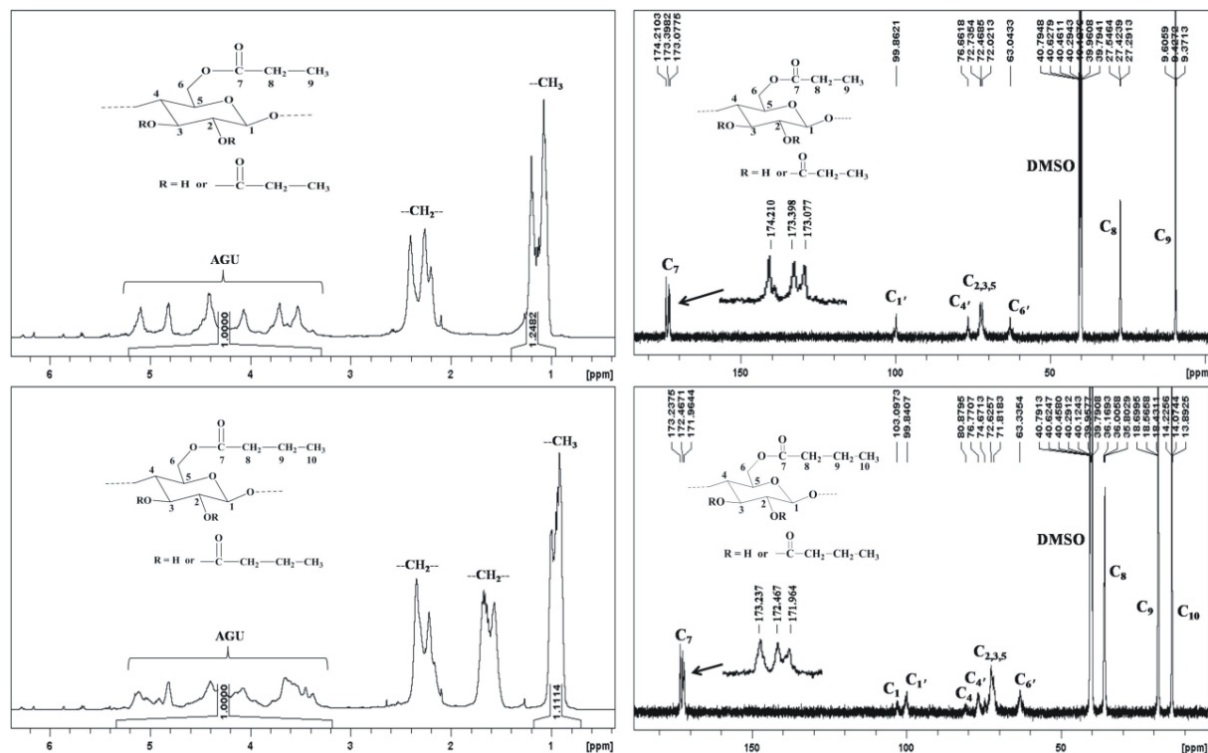
Fig.3 ^{1}H NMR and ^{13}C NMR results of CP (Top pattern, DS=2.91) and CB (Down pattern, DS=2.59)
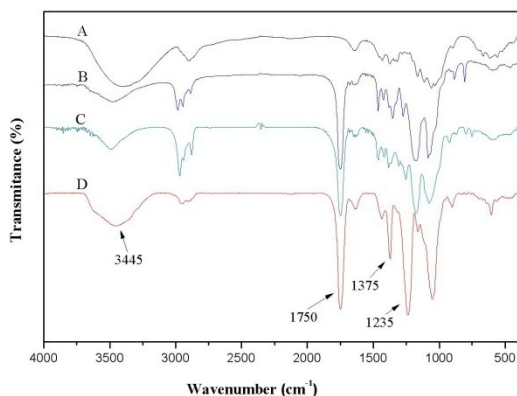

Fig.4 FTIR spectra of α-cellulose (spectrum A), CP (DS=2.91，spectrum B), CB (DS=2.59，spectrum C), CA (CA-10，spectrum D)

The results of ^{1}H NMR and ^{13}C NMR spectra of the as-prepared CP and CB also confirm their structures and the order of reaction activity of hydroxyl groups in this new homogeneous system (Fig. 3). For example, the ^{1}H NMR of CP clearly shows peaks from the propyl moieties esterified at 0.96-1.4 ppm (methyl proton) and 2.1-2.5 ppm (methyne proton), peaks due to the protons resonances on the anhydroglucose unit can also be observed at 3.2-5.2 ppm. The ^{1}H NMR spectrum of the CB also clearly shows peaks from the methyl protons of butyryl at 0.8-1.1 ppm, peaks at 3.2-5.3 ppm correspond to the protons resonance on the anhydroglucose (AGU) unit.

The FTIR spectra of α-cellulose and different cellulose esters (CA-10, CP, CB) were given in Figure 4. The successful and effective acylation of cellulose is evidenced by the appearance of characteristic bands assigned to ester group at 1750 cm^{-1} (C=O ester) and 1235 cm^{-1} (C-O stretching of acyl group) and decreasing intensity of characteristic bands assigned to hydroxyl groups at 3445 cm^{-1} (Figure 4). In addition, no bands assigned to acidic anhydride at 1840 cm^{-1} and 1760 cm^{-1} are observed, thus demonstrating the product free of unreacted acetic anhydride. These FTIR and NMR data are in accordance with those reported in the previous literatures.[5, 21, 24]

The difference in functionalization patterns is expected to lead to the difference in solubility of cellulose esters in conventional organic solvents. Table 1 also includes the solubility of the samples. The samples as-prepared were readily soluble in DMSO, but the solubility of CA in chloroform and acetone depends greatly on the total DS value. The samples with a DS (CA-1-8, CA-11) greater than 2.41 could dissolve rapidly in acetone and chloroform. The samples of CP (DS=2.91), CB (DS=2.59) are readily soluble in DMSO, acetone and chloroform.

The successful acylation of cellulose is also accompanied by the acylation of methanol to form esters, which is evidenced by the successful separation of methyl acetate with a satisfactory yield of 82% by simple distillation, an important reagent in chemical industry, in the case of synthesis of cellulose acetate. Its structure is confirmed by NMR analysis (Supporting information, Figure S3-4). The DMSO can be recycled by distillation after removing the methyl acetate and extra acids, while the DBU can be recycled by extraction with ethyl acetate after the system is neutralized by NaOH (4 wt%)-NaCl saturated aqueous solution (Figure S5). The structure and purity of the recycled DBU and

DMSO with this un-optimized procedure are identified by the comparative results of NMR analysis with those of fresh DBU and DMSO (Supporting information, Figure S6-9). Though there are minor contaminates in the recycled DBU, they are readily for subsequent application and no effect on the dissolution and reaction is observed, which primary demonstrates that the solvent in this study can be reused.

Conclusions

With the dissolution of cellulose in a new mixed solvent, [DBUH][O_2COCH_3]/DMSO (XR_{ILs}=0.2), synthesis of CA, CP and CB has been successfully accomplished without adding other catalysts. The DS of the products can be controlled by varying the reaction conditions. The recycling of the system, by distillation and extraction of components, is possible but full recyclability is not yet demonstrated. The findings demonstrated that the new solvent not only acted as a good solvent for cellulose, but also as an efficient media for its esterification reaction with acid anhydride under mild conditions. It is a very promising method to give relatively homogeneous cellulose esters, compared to the existing heterogeneous industrial process. Therefore, the authors predict that this new dissolution and reaction system can be extended to the versatile synthesis of other cellulose esters by using different acylating agents or other cellulose derivatives. Related studies are in progress.

Acknowledgment

Notes and references

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Graphical Abstract

Acylation of cellulose in reversible ionic liquids
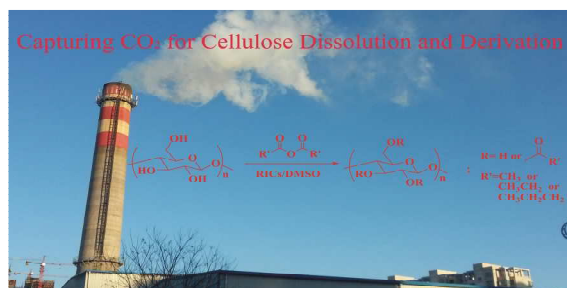
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