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Activating cellulose *via* its reversible reaction with CO_2 in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene for efficient synthesis of cellulose acetate

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The reversible reaction of cellulose pulp with CO_2 in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) resulted in a rapid and effective derivative dissolution of 10 cellulose in DMSO, which could be applied for subsequent derivatization of cellulose into cellulose acetate by using acetic anhydride as an acylation reagent under mild conditions. A serials of cellulose acetates with degree of substitution from 1.78 to 2.89 had been successfully synthesized without adding 15 external catalysts, and the structure and thermal properties of the products were characterized by various analytic technologies, such as NMR, FT-IR, TGA.

Recently, the dissolution & activation of cellulose for subsequent derivatization has been a focus of cellulose research with 20 opportunities to control degree of substitution (DS), design products with unconventional functional groups in a controlled substitution pattern.[1, 2] The promise of the efforts have been demonstrated by a larger number of studies after the successful dissolution of cellulose in various solvents, such as 25 DMAc/LiCl,[3,4] $LiClO_4 \cdot 3H_2O$ molten salt hydrate,[5,6] DMSO/TBAF,[5, 7] ionic liquids,[2, 8-15] and urea/NaOH aqueous solution.[16] Especially, the ionic liquids-based systems have been extensively studied due to their good solubility for cellulose and their thermo-chemical stability during the functionalization, 30 which was regarded as opening a new promising window for homogeneous derivatization of cellulose.[1] The homogeneous synthesis of cellulose esters in ionic liquids is of great interests because cellulose esters are extremely commercially important cellulose derivatives with wide application in various fields, such 35 as plastics, films, fibers, membranes, coatings, textiles and cigarette industries;[17-20] while currently, the commercial production of cellulose esters is dominated by heterogeneous processes, which are impossible to synthesize partially substituted cellulose esters directly.[2, 7] With the dissolution of cellulose in 40 ionic liquids, cellulose esters with a wide rage of DS and good solubility in traditional organic solvents could be readily obtained under mild reaction conditions with or without adding a catalyst. The promise was demonstrated, but challenges of ionic liquids were also recognized in terms of their high cost, difficulties in 45 purification and reusability from the practice point of view.[1] Furthermore, the chemistry of cellulose usually varies with solvents during the homogeneous derivatizations. Bearing the

significant promise and challenge of the current pathways for cellulose derivatization, there is still a high interest and demand 50 in new dissolution and activation strategy for functionalization of cellulose.
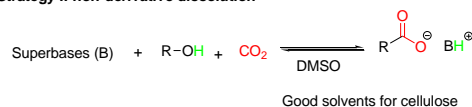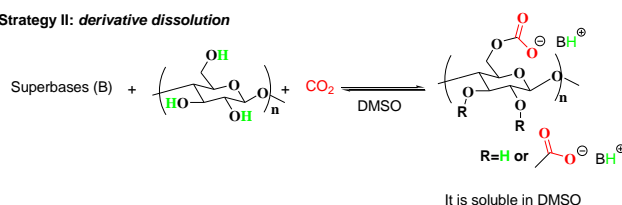

Scheme 1. The new strategies to dissolve cellulose by using CO_2 as a reagent

55 Recently, a novel strategy to dissolve cellulose by using CO_2 was proposed by Xie et al[21, 22] and Zhang et al[23] almost simultaneously based on a reversible reaction of hydroxyl group with CO_2 in the presence of strong organic bases, which was regarded as an important CO_2 triggered-strategy to construct 60 switchable solvents and materials (Scheme 1).[24-26] Under the concept, two strategies were developed for the dissolution of cellulose. The first strategy (non-derivative dissolution) is using reversible ionic liquids for dissolution of cellulose.[21] The second strategy (derivative dissolution) is based on the carbonation 65 reaction of cellulose with CO_2 in the presence of strong organic bases, leading to the dissolution of cellulose in DMSO (Scheme 1).[23] Further effort in this area demonstrated that the reversible ionic liquids system not only acted as a good solvent for cellulose, but also as an efficient media for acylation of cellulose with acid 70 anhydride to yield cellulose esters with tunable DS under mild conditions.[27, 28] The shortage of the process is the accompanied conversion of alcohols into ester during the acylation process. In contrast, the potential for cellulose functionalization stimulated by the novel derivative dissolution by using CO_2 has not been 75 developed so far. Herein, we firstly report a tunable synthesis of cellulose acetate stimulated by the successful dissolution of cellulose pulp (Scheme 2).
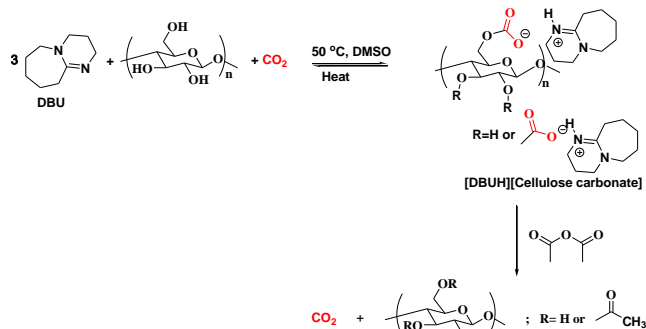
Scheme 2. The reversible reaction of cellulose pulp with CO_2 in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) results in a rapid and effective derivative dissolution of cellulose ([DBUH][Cellulose carbonate]) in DMSO and in situ efficient synthesis of cellulose acetate
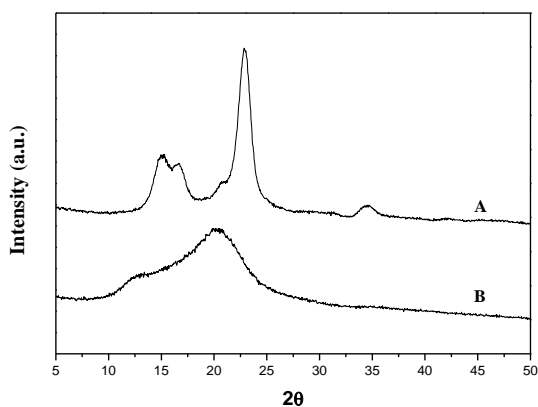
Results and Discussion

Fig.1 WAXD spectra of original cellulose and regenerated cellulose: (A) original cotton cellulose pulp; (B) regenerated cellulose by methanol from 8 wt% of cotton cellulose pulp solution

We started the study with using 1,8-Diazabicyclo[5.4.0] undec-7-ene (DBU) as the superbase to construct the solvent system for the dissolution of cotton cellulose pulp (DP=700), which has high molecular weight and is hard to dissolve than microcrystalline cellulose. Although over 10 wt% of microcrylstalline cellulose solution could be achieved,[23] the results show that it takes three hours to dissolve 8 wt% of cellulose pulp in DMSO under 0.2 MPa of CO_2 at 50 ^{o}C when chemical equivalence of DBU to the hydroxyl groups in the cellulose was used (Molar ratio of DBU to anhydroglucose unit (AGU) unit is 3:1). The satisfactory dissolution and activation behavior of cellulose in this system was evidenced by the viscous cellulose solution and the successful transformation of cellulose I to cellulose II during the dissolution and regeneration process (Fig. 1). When the CO_2 pressure was decreased from 0.2 MPa to 0.1 MPa or atmosphere, a non-full transformation of cellulose I to cellulose II was observed, which indicated that a proper CO_2 pressure was necessary to promote the carbonation reaction of cellulose towards a satisfactory dissolution and activation behavior.

The formation and existing state of the [DBUH][Cellulose carbonate] during the dissolution process were monitored by *in situ* IR (Fig. 2). A strong C=N-C stretching vibration absorption band of DBU was detected at 1615 cm^{-1} before the introduction of CO_2 and Cellulose. Newly formed asymmetric and symmetric carbonyl stretching bands at 1643 and 1671 cm^{-1}, asymmetric and

symmetric C-O-C stretching vibrations at 1278 and 1208 cm^{-1}, and promoted C=NH$^+$-C stretching vibrations at 1603 cm^{-1} were observed after 0.5 MPa of CO_2 was introduced into the DMSO–DBU–Cellulose mixture.[29] The results indicate that the carbonation reaction of cellulose in the presence of DBU occurs, which results in a CO_2-derivative dissolution of cellulose in DMSO. Given the fact of successful dissolution of cellulose, the potential applications of cellulose are of great interesting toward production of sustainable bioenergy, biochemicals and materials from biomass.[20, 30] The organic bases played an important role in this solvent system,[22,23] and some of them have been widely used as green organocatalysts for potential reactions of hydroxyl groups, for example, acylation, grafting polymerisation.[12, 14, 31, 32] Therefore, the newly designed solvent system was expected to be a promising homogeneous system for derivatization of cellulose acting as both a solvent and a catalyst.
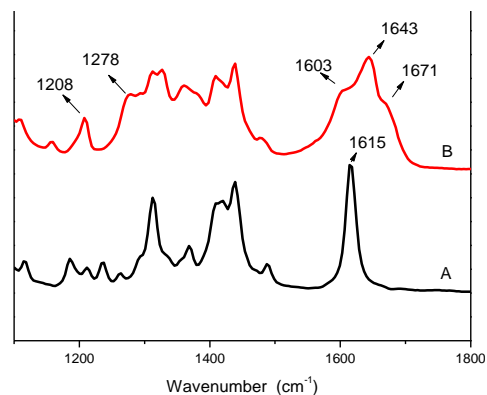

Fig. 2 Comparative infrared spectroscopy (IR) spectra A: DBU in DMSO; B: The formation of [DBUH][Cellulose carbonate] in DMSO at 50 ℃ when cellulose and 0.5 MPa CO_2 were introduced.

To our delight, serials of cellulose acetates (CA) with different DS can be obtained when acetic anhydride was added into the cellulose solution under various conditions. The DS of all the products were analyzed by the NMR method in DMSO-d$_6$ according to previous publications.[11, 13, 15] It was found that the reaction ran much faster, and a DS of 2.73 was achieved after only 0.5 h at 80 ^{o}C when the molar ratio of acetic anhydride to the AGU unit was set to 5:1 (Table 1, CA-3). While it took 3 h to achieve a DS of 2.3 at 100 ℃ when the molar ratio of acetic anhydride to AGU unit was set to 5 : 1 in ionic liquids.[13] Whereas effective acylation of cellulose with aliphatic anhydrides needs a catalyst in other solvents, for example, only a low DS of cellulose acetate could be obtained in DMAc–LiCl in the absence of a catalyst.[3] To identify the enhanced performance stimulated exactly by the dissolution and activation process, raw cellulose pulp was submitted to the acetylation reaction directly in the presence of DBU in DMSO without adding CO_2 to perform the dissolution process under identical conditions, and a product insoluble in DMSO, acetone, $CHCl_3$ was obtained. Further FT-IR analysis shows that it is a cellulose acetate with low substitution degree, which is evidenced by the strong absorbance band of OH (3420 cm^{-1}) in cellulose and weak absorbance band at 1750 cm^{-1} assigned to C=O functionality (Figure S1, spectrum D). The findings demonstrate that the solvent system in this study is an efficient protocol for the synthesis of CA and the dissolution

activation process plays an important role for subsequent derivatization of cellulose.

Table 1 shows the DS controllability of this system for the synthesis of CA by tuning reaction conditions such as reaction time, reaction temperature, and acid anhydride concentration. The results show that the reaction is running very fast in the first 0.5 h, and CA-3 with a DS value of 2.73 is achieved, and then becomes slow. But the as-prepared samples (CA-1, CA-2) become insoluble in DMSO when the reaction times are decreased from 0.5 h to 0.17 h (10 min) and 0.08 h (5 min). The DS of CA reaches 2.82 (CA-4) within 1 h, 2.87 (CA-8) within 5 h, 2.89 (CA-5) within 8 h, respectively. The reaction temperature has significant effect on the reaction, which was evidenced by the fact that a product with DS of 2.26 (CA-9) was obtained when the reaction was performed at 50 °C in 5 h. CA with various DS were

also obtained through modifying the molar ratio of acetic anhydride/AGU. When the molar ratio of acetic anhydride/AGU was decreased from 5:1 to 4:1 and 3: 1, the DS was decreased from 2.87 (CA-8) to 2.27 (CA-7) and 1.78 (CA-6) under identical conditions, respectively. Given these, it is reasonable to assume that the DS value of cellulose esters can be controlled by varying the stoichiometric ratio of acetic anhydride/AGU, temperature, and reaction time. Commercially, it was hard to control the DS due to the heterogeneous nature of the reaction directly, and commonly used cellulose diacetate esters were obtained by hydrolyzing fully substituted cellulose acetate. The DS controllability of CA in this study 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.

Table 1. Efficient synthesis of cellulose acetate under various conditions[a]

Code	T (℃)	Time (h)	reagent	Molar ratio of Ac₂O/AGU	DS[b]	Solubility[c]		
						DMSO	acetone	CHCl₃
CA-1	80	0.08	Ac₂O	5/1	N.D.[d]	−	−	−
CA-2	80	0.17	Ac₂O	5/1	N.D.[d]	−	−	−
CA-3	80	0.5	Ac₂O	5/1	2.73	+	+	+
CA-4	80	1	Ac₂O	5/1	2.82	+	+	+
CA-5	80	8	Ac₂O	5/1	2.89	+	+	+
CA-6	80	5	Ac₂O	3/1	1.78	+	−	−
CA-7	80	5	Ac₂O	4/1	2.27	+	−	−
CA-8	80	5	Ac₂O	5/1	2.87	+	+	+
CA-9	50	5	Ac₂O	5/1	2.26	+	−	−

[a] Cotton pulp concentration were 5wt% in all reactions; [b] DS was calculated from ^{1}H NMR spectra according to a previous publication. [c] "+" stands for soluble, and "−"stands for insoluble; [d] not detected.

^{1}H NMR and ^{13}C NMR analysis were used to elucidate the molecular structure and evaluate the distribution of substitutions in the as-prepared CA.[13] The results showed that strong signals within the chemical shift range from 1.8 to 2.2 ppm assigned to methyl hydrogen in the ^{1}H NMR spectra (Fig. 3A) and signals within the chemical shift range from 169 to 171 ppm assigned to carbonyl carbons in the ^{13}C NMR spectra (Fig. 3B) were observed after the modification, which were consistent with the results in previous publications.[13, 15, 27] The distribution of the acetyl moiety among the three OH groups (C6–OH, C3–OH, C2–OH) in an AGU unit was evaluated roughly from the quantitative integration of acetyl methyl protons area of the ^{1}H NMR spectrum, and the results are presented in Table S1. Although the results have any error by using this method, they do present a possible 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 of cellulose in LiCl–1,3-dimethyl-2-imidazolidinone (DMI) solutions[33] and CO₂-based reversible ionic liquids.[27,33] This result is different from those industrially synthesized through a heterogeneous acetylation hydrolysis process, whose partial DS order is C3–OH > C2–OH > C6–OH,[34] as well as those of C6–OH > C3–OH > C2–OH in ionic liquids.[13, 35]

In Fig. 3B, the peak at 63.0 ppm is assigned to the C6′ carbon bearing a substituted acetyl group. However, an expected peak at 59.0 ppm assigned to the unmodified C6 is not observed,

indicating full substitution at C6. The peaks at 80.3 ppm and 103.3 ppm are assigned to C4 and C1 bearing an unsubstituted hydroxyl group, respectively; and a peak around 100.0 ppm marked as C1′ is assigned to a C1 carbon adjacent to C2 carbons bearing a substituted hydroxyl group; and a peak around 76.9 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 72.2 ppm to 73.1 ppm for a 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. Given the reversible property of the formed [DBUH][Cellulose carbonate] at the reaction temperature, strictly speaking, the acetylation reactions in this system are not completely homogeneous because cellulose precipitates partially as active amorphous cellulosic gel from the reaction solution by adding acetic anhydride at atmosphere conditions, in associated with the releasing of CO₂.

Thus, at the early stage of the reaction the resulting solution is a kind of suspension. However, the suspended cellulosic gel is amorphous, which is more reactive with acetic anhydride in the presence of DBU than raw crystalline cellulose pulp, thus resulting in an efficient derivatization. Therefore, the distribution of substituents along the cellulose chain is different with those produced in ionic liquids, which is regarded as a homogeneous acetylation process. But the deviation process in this study is considered to be uniform relative to that in the heterogeneous reaction systems.

To identify the role of DBU during the acetylating process (Supporting information, section 1.5), at first, methanol was added into the obtained cellulose solution, and DBU free cellulose gel was obtained after washing with methanol and then DMSO thoroughly. Secondly, the DBU free cellulose gel was submitted to comparative experiments in the presence or the absence of DBU under identical conditions. In contrast, no reaction occurred in the absence of DBU (Figure S1, spectrum A, B), while CA (DS=2.19, Figure S1, spectrum C) was obtained when DBU was added. Although the DS is slightly lower than that (CA-4, DS=2.82) obtained under the *in situ* preparation process, the findings demonstrated that DBU not only acted as an reagent for the cellulose derivative dissolution process, but also acted as an organocatalyst and a scavenger of the acetic acid for the acetylating process. In fact, strong organic bases,[36, 37] such as DMAP, were widely investigated as organocatalysts for acylation of less reactive alcohols by using acid anhydrides under mild conditions, even the acylation of polyols.[32] It is well recognized that the reaction proceeds *via* acetylpyridinium intermediate.[38] It is reasonable to conjecture that similar intermediate were formed between DBU and acetic anhydride during the reaction in this study, but more details are needed to be addressed in the future.
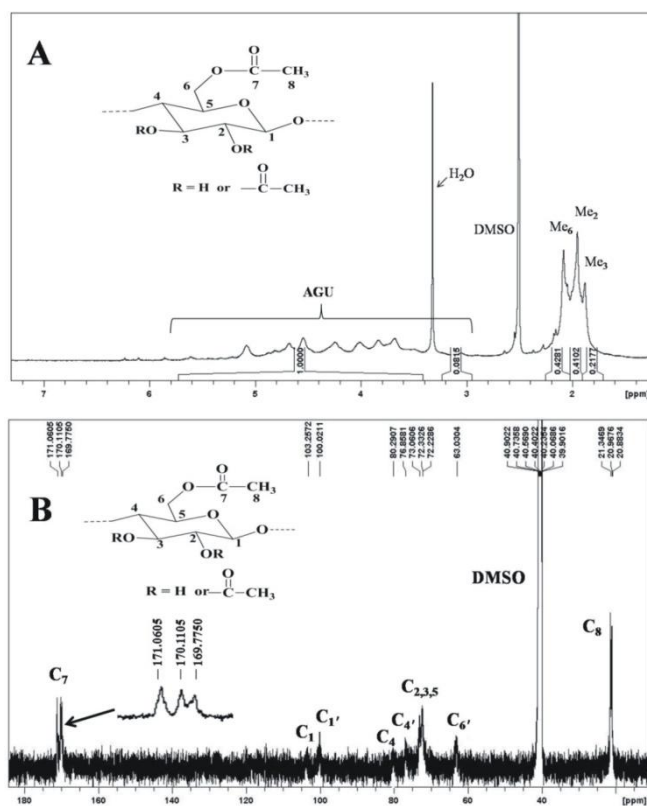

Fig. 3. ^{1}H NMR spectrum (A) and ^{13}C NMR spectrum (B) of cellulose acetate sample CA-7 (DS=2.27) in DMSO-d_6. Reaction condition (5 wt% cotton pulp，Ac_2O /AGU=4/1，80℃，5h).

The successful acetylation of cellulose was confirmed by examining the infrared spectra of native cellulose pulp and acetylated cellulose, and the results are shown in Fig. 4. In comparison, a decrease in the O-H band (3420 cm^{-1}) and increases in the three major ester bands of acetylated cellulosic

sample [i.e. the C=O band (1752 cm^{-1}), the C-O band (1233 cm^{-1}), and the C-CH$_3$ band (1372 cm^{-1})] provide evidence for acetylation. The intensity of the relative bands are increasing with the increase in the DS values. As expected, the absence of absorption region 1840-1760 cm^{-1} in the CAs demonstrates that the products are free of the unreacted acetic anhydride and the lack of peaks at 1700 cm^{-1} for carboxylic groups indicates that the products are also free of the by-product of acetic acid.
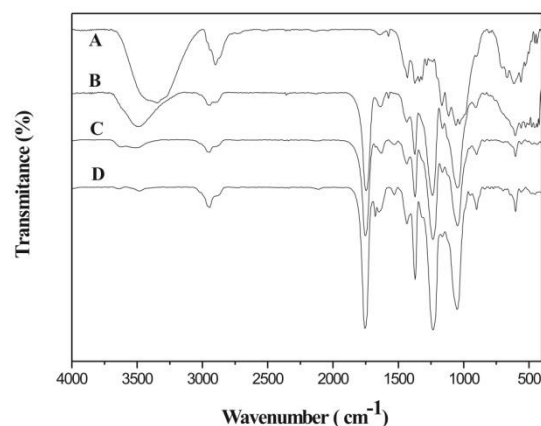

Fig. 4．FT-IR spectra of cotton pulp (spectrum A) and cellulose acetate CA-6, (spectrum B, DS=1.78) ; CA-9 (spectrum C，DS=2.27) ; CA-8 (spectrum C，DS=2.87).

The thermal properties of raw cellulose pulp and selected cellulose acetates were characterized by TGA and DSC measurements in N_2 atmosphere. Fig. 5 shows the thermogravimetric (TG) curves of raw cellulose and selected CAs. From these thermograms, it can be seen that the raw cellulose pulp starts to decompose at 320 °C, whereas the three CAs, CA-6, CA-9, CA-8, start to decompose at 284 °C, 275 °C, and 265 °C, respectively. This indicates the thermal stability of cellulose pulp is slightly decreased due to the acetylation. The DSC analysis (Fig. S2) shows that the cellulose pulp do not show the glass transition temperature (T_g) at standard heating scan under 200 °C, while the CA samples (CA-8, CA-9) exhibit very clear glass transition at 155 °C, 181 °C, respectively. The T_g of the CA decreases with an increase of DS, which is in accordance with the literature and can be explained by the fact that the higher DS leading to less hydrogen bonding and a lower T_g.[39]

The solubility of cellulose acetate in conventional organic solvents is one of the most important properties towards subsequent applications. Table 1 also includes the solubility of the samples, and the results show that the difference in functionalization patterns leads to the difference in the solubility of cellulose esters in conventional organic solvents. The as-prepared samples are readily soluble in DMSO except CA-1 and CA-2, and the solubility of CA in chloroform and acetone depends greatly on the total DS value. The samples with a DS (CA-3, CA-4, CA-5, CA-8) greater than 2.26 can dissolve rapidly in acetone and chloroform.

The recyclability of DMSO and DBU used in this study was primary investigated after precipitating the cellulose acetate by

using methanol after the reaction (Figure S3). DMSO with high purity (92%) can be distilled out directly after removing the low vapour point reagents by a rato-evaporator, while crude DBU can be recycled by extraction with ethyl acetate after the residual was [5] neutralized by NaOH (6 M) aqueous solution, and further purification through distillation is needed to get pure DBU (91%). 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 [10] (Fig. S4-7). They are readily suitable for subsequent application, which preliminarily demonstrates that the solvent in this study can be recycled, however, the reusability of the solvents need to be further investigated.
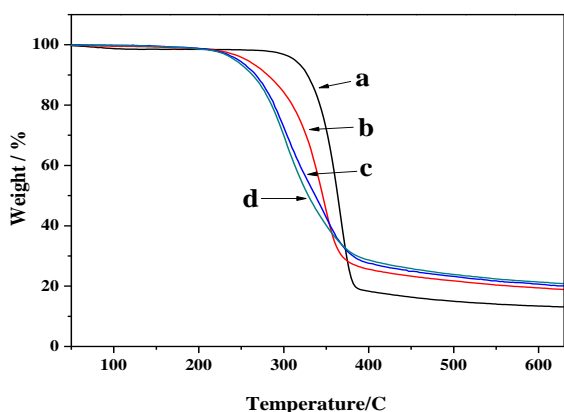

[15] Fig. 5. TG spectra of cotton pulp (spectrum a) and cellulose acetate CA-6, (spectrum b, DS=1.78) ; CA-7 (spectrum c，DS=2.27) ; CA-8 (spectrum d，DS=2.87).

Conclusions

The reversible reaction of cellulose pulp with CO_2 in the [20] presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) results in a rapid and effective derivative dissolution of cellulose in DMSO, on which, efficient synthesis of CA has been successfully accomplished without adding external other catalysts. The findings demonstrated that the DS of the products could be [25] controlled by varying the reaction conditions, the new solvent system not only acted as a good solvent for cellulose, but also as an efficient media for its acetylation with acetic anhydride under mild conditions. It is a very promising method to give relatively homogeneous cellulose esters, compared to the existing [30] heterogeneous industrial process. Therefore, the authors predict that present protocols could also be extended to the versatile synthesis of other cellulose esters by using different acylating agents or other cellulose derivatives. Related studies are in progress.

[35]

Acknowledgements

[40] **Notes and references**

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See [50] DOI: 10.1039/b000000x/

1. M. Gericke, P. Fardim and T. Heinze, *Molecules*, 2012, 17, 7458-7502.
2. T. Heinze, K. Schwikal and S. Barthel, *Macromolecular Biosci.*, 2005, 5, 520-525.
[55] 3. O. A. El Seoud, G. A. Marson, G. T. Giacco and E. Frollini, *Macromolecul. Chem. Phy.*, 2000, 201, 882-889.
4. G. A. Marson and O. A. El Seoud, *J. Appl. Polym. Sci.*, 1999, 74, 1355-1360.
5. S. Fischer, H. Leipner, K. Thummler, E. Brendler and J. Peters, [60] *Cellulose*, 2003, 10, 227-236.
6. S. Fischer, K. Thummler, K. Pfeiffer, T. Liebert and T. Heinze, *Cellulose*, 2002, 9, 293-300.
7. T. Heinze, R. Dicke, A. Koschella, A. H. Kull, E. A. Klohr and W. Koch, *Macromolecul. Chem. Phy.*, 2000, 201, 627-631.
[65] 8. A. P. Abbott, T. J. Bell, S. Handa and B. Stoddart, *Green Chem.*, 2005, 7, 705-707.
9. S. Barthel and T. Heinze, *Green Chem.*, 2006, 8, 301-306.
10. M. Gericke, T. Liebert and T. Heinze, *Macromolecul. Biosci.*, 2009, 9, 343-353.
[70] 11. K. Huang, B. Wang, Y. Cao, H. Li, J. Wang, W. Lin, C. Mu and D. Liao, *J. Agric. Food Chem.*, 2011, 59, 5376-5381.
12. Y. Luan, J. Zhang, M. Zhan, J. Wu, J. Zhang and J. He, *Carbohydr Polym*, 2013, 92, 307-311.
13. J. Wu, J. Zhang, H. Zhang, J. S. He, Q. Ren and M. Guo, [75] *Biomacromolecules*, 2004, 5, 266-268.
14. C. Yan, J. Zhang, Y. Lv, J. Yu, J. Wu, J. Zhang and J. He, *Biomacromolecules*, 2009, 10, 2013-2018.
15. H. Zhang, J. Wu, J. Zhang and J. S. He, *Macromolecules*, 2005, 38, 8272-8277.
[80] 16. J. Zhou, Q. Li, Y. Song, L. Zhang and X. Lin, *Polym. Chem.*, 2010, 1, 1662-1668.
17. K. J. Edgar, *Cellulose*, 2006, 14, 49-64.
18. K. J. Edgar, C. M. Buchanan, J. S. Debenham, P. A. Rundquist, B. D. Seiler, M. C. Shelton and D. Tindall, *Prog. Polym. Sci.*, 2001, 26, [85] 1605-1688.
19. O. A. El Seoud and T. Heinze, in Polysaccharides 1: Structure, Characterization and Use, ed. T. Heinze, 2005, vol. 186, pp. 103-149.
20. D. Klemm, B. Heublein, H. P. Fink and A. Bohn, *Angew. Chem.Int. Ed.*, 2005, 44, 3358-3393.
[90] 21. H. Xie, X. Yu, Y. Yang and Z. K. Zhao, *Green Chem.*, 2014, 16, 2422-2427.
22. China Pat., 201210374955.4, 2012.
23. Q. Zhang, N. S. Oztekin, J. Barrault, K. D. O. Vigier and F. Jerome, *ChemSusChem*, 2013, 6, 593-596.
[95] 24. P. G. Jessop, D. J. Heldebrant, X. W. Li, C. A. Eckert and C. L. Liotta, *Nature*, 2005, 436, 1102-1102.
25. P. G. Jessop, S. M. Mercer and D. J. Heldebrant, *Energy Environ. Sci.*, 2012, 5, 7240-7253.
26. Y. Liu, P. G. Jessop, M. Cunningham, C. A. Eckert and C. L. Liotta, [100] *Science*, 2006, 313, 958-960.
27. Y. Yang, H. Xie and E. Liu, *Green Chem.*, 2014, 16, 3018-3023.
28. China Pat., 201310278276.1, 2013.
29. S. Hardy, I. M. de Wispelaere, W. Leitner and M. A. Liauw, *Analyst*, 2013, 138, 819-824.
[105] 30. A. Ragauskas, Williams, CK, Davison, BH, Britovsek, G, Cairney, J, Eckert, CA, Frederick, WJ, Hallett, JP, Leak, DJ, Liotta, CL, Mielenz, JR, Murphy, R, Templer, R, Tschaplinski, T,, *Science*, 2006, 311, 484-489.
31. A. P. Dove, *ACS Macro Lett.*, 2012, 1, 1409-1412.

32. A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi and K. Ishihara, *J. Am. Chem. Soc.*, 2007, 129, 14775-14779.
33. A. Takaragi, M. Minoda, T. Miyamoto, H. Q. Liu and L. N. Zhang, *Cellulose*, 1999, 6, 93-102.
34. C. M. Buchanan, K. J. Edgar and A. K. Wilson, *Macromolecules*, 1991, 24, 3060-3064.
35. S. Koehler and T. Heinze, *Cellulose*, 2007, 14, 489-495.
36. E. Vedejs, N. S. Bennett, L. M. Conn, S. T. Diver, M. Gingras, S. Lin, P. A. Oliver and M. J. Peterson, *J. Org. Chem.*, 1993, 58, 7286-7288.
37. E. Vedejs and S. T. Diver, *J. Am. Chem. Soc.*, 1993, 115, 3358-3359.
38. S. J. Xu, I. Held, B. Kempf, H. Mayr, W. Steglich and H. Zipse, *Chem.-a Eur. J.*, 2005, 11, 4751-4757.
39. Y. Cao, J. Zhang, J. S. He, H. Q. Li and Y. Zhang, *Chin. J. Chem. Eng.*, 2010, 18, 515-522.

Graphical Abstract

Activating cellulose *via* its reversible reaction with CO$_2$ in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene for efficient synthesis of cellulose acetate
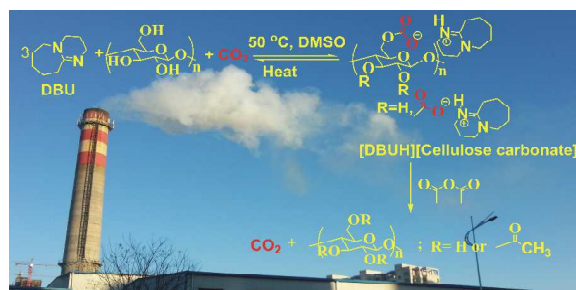
The reversible reaction of cellulose pulp with CO$_2$ in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) results in a rapid and effective derivative dissolution of cellulose in DMSO, which can be applied for efficient acetylation of cellulose to afford a serials of cellulose acetates with degree of substitution from 1.78-2.89 under mild conditions.