A Novel, Efficient Procedure for Acylation of Cellulose Under Homogeneous Solution Conditions

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ABSTRACT: Commercially available cellulose (Avicel PH101) was successfully acylated under homogeneous solution conditions by the following novel procedure: 2.0 g of cellulose and 5.0 g of LiCl were introduced into a glass reactor, magnetic stirring was started, the pressure was reduced to 2 mmHg, the temperature was raised to 110°C in 30 min, and the reactor was kept under these conditions for another 30 min. *N,N*-Dimethylacetamide, 60 mL, was introduced, atmospheric pressure was restored, and the temperature was raised to 150°C in 30 min. The system was kept under these conditions for 1 h, then the temperature was decreased to 40°C; in 2 h a clear cellulose solution was obtained. Acid anhydride was added, and the solution was stirred at 60°C for additional 18 h. Acetates, propionates, butyrates, and acetate/butyrate mixed ester were prepared with excellent reproducibility of the degree of substitution, from 1 to 3. The degree of polymerization of cellulose is negligibly affected by these reaction conditions. The distribution of the acetyl moiety among the three OH groups of the anhydroglucose unit follows the order $C_6 > C_2 > C_3$. Features relevant to the industrial application of this novel procedure are discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1355–1360, 1999

Key words: cellulose, acylation of; cellulose acetate; cellulose propionate; cellulose butyrate; cellulose acetate/butyrate

INTRODUCTION

Interest in derivatization of cellulose under homogeneous solution conditions is due to the following: (a) the degree of substitution, DS, of the cellulose derivative can be effectively controlled by adjusting the molar ratio of derivatizing agent to cellulose; (b) the substituent groups are introduced regularly along the natural polymer backbone; (c) the physico-chemical properties of products thus obtained are much better controlled than those that are prepared under heterogeneous solution conditions. These features are of prime importance for applications of cellulose derivatives.[1–9]

The solvent system LiCl/*N,N*-dimethylacetamide, DMAC, has proven to be most suitable for preparation of a wide variety of cellulose derivatives, for example, organic esters and mixed esters. These have been prepared by using acyl chloride/tertiary amine catalyst,[1–4,8] acid anhydride/tertiary amine catalyst,[5–7] and acid anhydride without a catalyst.[10]

Our aim is to contribute to the industrial feasibility of homogeneous acylation, for example, by introducing modifications that increase the rate at which cellulose becomes accessible to the derivatizing reagent. This requires a better understanding of the different steps of the reaction, namely, cellulose activation, dissolution, and derivatization.

We present here an efficient procedure for the synthesis of cellulose esters (acetates, propionates, and butyrates) and mixed esters (acetate/butyrate) under homogeneous solution conditions. The method is simple, faster than those reported elsewhere,[1–8,10] requires no tertiary amine catalyst,[1–5,8] uses a convenient acylating agent , acid anhydride , and does not result in degradation of the natural polymer.

EXPERIMENTAL

Reagents

Avicel PH-101 microcrystalline cellulose (hereafter designated as Avicel cellulose) was obtained from FMC Inc. (Philadelphia) and was used as received. Other reagents were obtained from Aldrich or Merck. DMAC was distilled from CaH_2 under reduced pressure and kept over activated type 4 Å molecular sieves. Acid anhydrides were distilled from P_2O_5. Diketene and 2,2,6 trimethyl-1,3-dioxin-*4H*-4-one were distilled under reduced pressure prior to use. LiCl was dried at 200°C, then cooled under reduced pressure and kept in a tightly stoppered bottle.

Acylation of Avicel Cellulose

To a 100-mL three-necked round-bottom flask, equipped with a stopcock, a 100-mL graduated cylindrical funnel (no equilibration side arm) and a magnetic stirrer, were added 2.0 g of Avicel cellulose (12.3 mmol) and 5.0 g of LiCl. The flask was connected to a vacuum pump, the pressure was reduced to 2 mmHg, the system was heated from room temperature to 110°C in 30 min, then kept under these conditions for another 30 min. The vacuum pump was turned off, and 60 mL of DMAC were slowly added. The system was then brought to atmospheric pressure with dry, oxygen-free nitrogen, the graduated funnel was removed, and the reactor was quickly equipped with an efficient mechanical stirrer and a condenser with a drying tube. The temperature was then raised to 150°C in 30 min, and the cellulose slurry was vigorously stirred for 1 h at that temperature. The mixture was slowly cooled to 40°C in 2 h, and a clear cellulose solution was obtained. After raising the solution temperature to 60°C, acid anhydride was added dropwise and the solution was stirred at 60°C for an additional 18 h. Sample work up was similar to that given else-

where.[8,10] The same procedure was used for the preparation of cellulose acetate/butyrate mixed ester, with acetic anhydride added first.

In acetoacetylation with diketene, after dissolution of cellulose at 40°C, the temperature was raised to 110°C in 30 min. A solution of diketene in 10 mL DMAC was added dropwise, and the temperature was kept at 110°C for additional 30 min. The same procedure was employed for acetoacetylation with 2,2,6 trimethyl-1,3-dioxin-*4H*-4-one, except that the system was attached to a water pump (via a cold trap) to remove produced acetone, *vide infra*.

Characterization of Cellulose and its Esters

Determination of Molecular Weights from Solution Viscosity Measurement

Molecular weights (M_w) of Avicel cellulose and its triacetate were determined at 25.0°C from intrinsic viscosities, η, of their solutions in cupriethylenediamine and DMAC, respectively. We used an Ubbelohde shear dilution viscosimeter, connected to a Schott AVS 360 measuring unit, model 1200 titration controller and model T200 Titronic piston burette. Values of M_w were obtained from the Mark-Houwink-Sakurada relationships:[11]

$$[\eta]_{\text{cellulose}} = (1.01 \times 10^{-4})M_w^{0.9} \quad (1)$$

$$[\eta]_{\text{cellulose triacetate}} = (2.71 \times 10^{-2})M_w^{0.75} \quad (2)$$

Determination of the Degree of Cellulose Crystallinity by X-Ray Diffraction

X-ray diffraction was recorded with a Phillips X'PERT MPD diffractometer in the reflection geometry in the angular range of 10– 40° (2θ), with a scan step size of 0.02°. The CuK radiation from the anode (operating at 40 kV and 40 mA) was monochromatized by using a 15-μm Ni foil. The crystallinity index of cellulose, I_c, was calculated by the formula:[12]

$$I_c = 1 - (I_{\text{min}}/I_{\text{max}}) \quad (3)$$

where I_{min} is the intensity minimum between 2θ = 18 and 19°, and I_{max} is the intensity of the crystalline peak at the maximum between 2θ = 22 and 23°. I_c of the Avicel cellulose sample used was found to be 0.79.

I_c was also measured during cellulose dissolution, as follows: aliquots were withdrawn and un-

dissolved cellulose was quickly filtered in a sintered glass funnel, washed with DMAC, and then with ethanol. The undissolved fraction was extracted with ethanol, then dried at room temperature, under reduced pressure until constant weight.

Acyl Content of Cellulose Esters

The DS of cellulose derivatives was determined either by the ASTM volumetric method,[13] or by ^{1}H-NMR spectroscopy,[14] by using a Bruker DRX-500 spectrometer (operating at 500.13 MHz for ^{1}H). Samples were dissolved in DMSO-d_6, and the spectra were recorded at 80°C.

Determination of the Distribution of the Acyl Moiety among the OH Groups of the Anhydroglucose Unit, AGU, of Cellulose

This was carried out by integrating the ^{13}C-NMR spectrum of a solution of cellulose ester in DMSO-d_6 (Bruker DRX-500 spectrometer, experiment temperature 80°C). To ensure fast relaxation of the carbonyl carbon atom of the acyl group, the solution contained 20 mg Cr(III) acetylacetonate/0.5 mL cellulose solution.[15] The inverse gated decoupling program, Invgate, was used with a 5-s pulse delay. The acquisition parameters were adjusted to give a digital resolution of 0.02 ppm/data point. Attribution of the ^{13}C-NMR chemical shifts of the CO group of the acetyl moiety at C_2, C_3, and C_6 of AGU of cellulose is given elsewhere.[16] Peak deconvolution and the corresponding peak area calculation was carried out with a commercial software.

Other Analysis

The water content of Avicel cellulose was determined by weight after drying the sample for 2 h at 105°C. The Karl Fisher titration method was used to determine the water content of DMAC; a Schott model 1200 titration controller and PT 1400 electrode were employed. The purity of regenerated DMAC was determined by a Shimadzu GC-17A gas chromatograph, equipped with a flame ionization detector, and a Supleco SPB5 glass capillary column, operating at 110°C (injector temperature 230°C).

RESULTS AND DISCUSSION

The procedure introduced is shown in the following scheme:
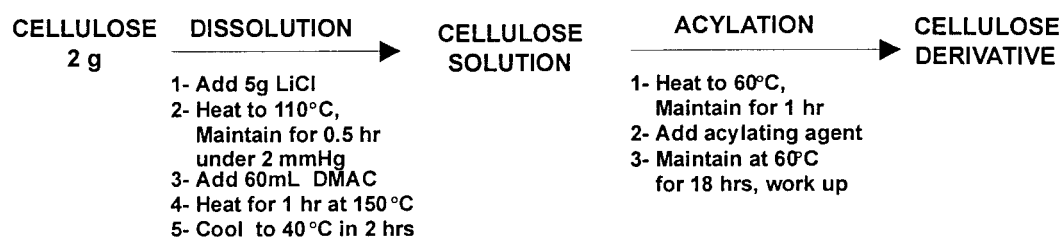
This procedure has the following attractive features.

Simplicity and Speed of the Activation/Dissolution Step

Derivatization of cellulose under homogeneous solution conditions usually involves three steps, namely activation, dissolution, and subsequent reaction with the derivatizing agent. The objective of the activation step is to decrease the crystallininty of cellulose, for example, by disrupting the strong, water-mediated H-bonding of the natural polymer chains. Activation has been carried out by a three-step solvent exchange treatment, namely water, methanol, and DMAC.[1–3] This procedure, however, is slow (ca. 1 day), and requires large volumes of solvents, 25 mL of water; 64 mL of methanol and 80 mL of DMAC per gram of cellulose.[2] Activation has also been carried out by boiling cellulose slurry in LiCl/DMAC, followed by distillation of 25% of the solvent volume.[7,10] Despite elimination of the solvent exchange step, polymer degradation may occur for some celluloses at the boiling point of the mixture (ca. 170°C).[17] Additionally, the efficiency of water removal by this procedure is rather limited.[10] Once activated, complete dissolution of cellulose is usually achieved

Table I   Acylation of Avicel PH101 Cellulose

Cellulose Ester	Equivalents of Anhydride/OH Group of AGU	DS[a]
Monoacetate	1	1.0 ± 0.1
Diacetate	2	1.8 ± 0.2
Triacetate	3	2.7 ± 0.2
Monopropionate	1.25	1.2 ± 0.2
Dipropionate	2	1.7 ± 0.2
Tripropionate	3	2.7 ± 0.2
Monobutyrate	1	0.8 ± 0.2
Dibutyrate	2	1.7 ± 0.2
Tributyrate	3	2.7 ± 0.2

[a] Degree of substitution of cellulose, determined by volumetric procedure or by ^{1}H-NMR spectroscopy, average of four runs.

by stirring its slurry in LiCl/DMAC for up to 48 h (for cotton linter)[1–3, 7,10]

In the present procedure, cellulose and LiCl are dried under reduced pressure. After complete dissolution of Avicel cellulose, aliquots were withdrawn, and the solvent was distilled under atmospheric pressure. No water has been detected in this DMAC by Karl-Fisher titration method, i.e., complete removal of water is achieved during the drying step. The whole drying, activation/dissolution sequence is completed within 4 h, i.e., we employ the time that is usually required to dissolve activated cellulose to carry out its acylation.

Suitability to Prepare Esters and Mixed Esters

Table I shows the results of acylation of Avicel cellulose by acetic, propionic, and butyric anhydrides. Our results show that the experimental conditions used are suitable to obtain the desired DS, by using stoichiometric quantities of acid anhydride/AGU in the absence of tertiary amine catalyst. These results contrast favorably with acetylation of cellulose from sugar cane bagasse with acetyl chloride/pyridine (molar excess of acyl halide = 25%),[8] and with the reaction of Whatman CF-11 cellulose with propionic anhydride/ tertiary amine catalyst (molar excess of anhydride from 88 to 114%) and butyric anhydride/ tertiary amine catalyst (molar excess of anhydride from 25 to 67%).[5] Our acylation scheme can also be used to prepare mixed esters, as shown by the following example: Avicel cellulose was triacylated with a mixture of acetic anhydride (0.5 mol/AGU) and butyric anhydride (2.5

mol/AGU). The total DS was found to be 2.5, the individual DS were found to be 0.4 and 2.1 for the acetyl and the butyryl moiety, respectively.

Reproducibility of DS

Although the question of reproducibility of DS is crucial for industrial applications, it has received little attention in acylation under homogeneous solution conditions.[8,10] The easy control of the reaction leads to highly reproducible results, as shown by the small variation of DS within *four runs*, as shown in Table I. Reproducibility of DS is not easily attainable under heterogeneous solution conditions, because it is rather difficult to control the reaction.[9]

To fully asses the present procedure, the following experiments have been carried out. (a) Effect of activation/dissolution on the DP of cellulose—after complete dissolution of Avicel cellulose, aliquots were withdrawn, the cellulose was precipitated with ethanol, extracted with ethanol then water, and air dried. The DP of the starting material (155 ± 5), and that of several regenerated samples (150 ± 5) showed that there is no degradation during this step. (b) Effect of acylation on the DP of products—The DP of four cellulose triacetate samples was found to be 143 ± 3, showing negligible degradation during the acetylation step. This is an important result because cellulose degradation can be a serious problem during acylation under both heterogeneous,[9] and
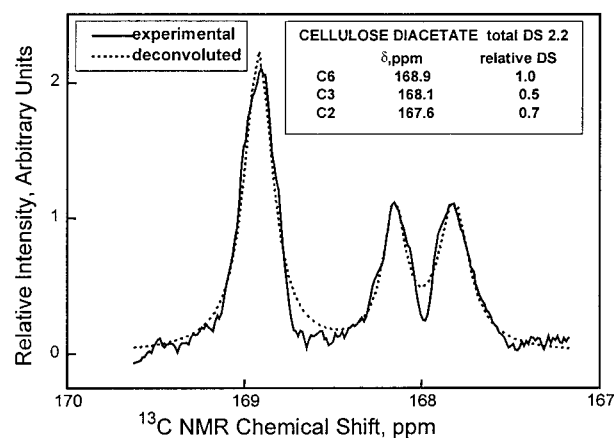

Figure 1 Carbonyl carbon region of ^{13}C-NMR spectrum of a cellulose diacetate solution in DMSO-d$_6$, sample DS = 2.2. The order of the peaks from left to right is: C$_6$, C$_3$, and C$_2$, respectively. The solid line is experimental, and the dashed one is calculated by a (Lorentzian) peak deconvolution program.

homogeneous solution conditions.[18] (c) Acyl distribution among different positions of the AGU—The O-acetyl carbonyl carbons appear at 168.71 to 168.93 ppm, 169.11 to 169.60 ppm, and 169.83 to 170.04 ppm for C_2, C_3, and C_6, respectively.[16] The DS at each carbon atom was determined from the corresponding area after peak deconvolution of the ^{13}C-NMR spectrum, as shown in Figure 1 for a diacetate sample, DS = 2.2. The calculated DS are 0.7, 0.5, and 1.0, for C_2, C_3, and C_6, respectively. For a dipropionate sample, DS = 2.2, the individual DS were 0.8, 0.4, and 1.0 for C_2, C_3, and C_6, respectively (spectrum not shown). The order of reactivity, $C_6 > C_2 > C_3$, is similar to that observed for acylation of several cellulose samples, both under heterogeneous and homogeneous solution conditions.[19,20] Substitution at C_6-OH position is favored because this group is the least sterically hindered one of the AGU. The reason for lower reactivity of C_3-OH, relative to that of C_2-OH, is that the oxygen atom of the former group is less reactive as a nucleophile due to bonding to the Li^+ ion.[21]

Finally, we address some additional relevant points: (d) Solvent recycling—Environmental regulations, and the relatively high cost of DMAC require its recycling in the process. After the reaction has been completed, the solvent was distilled under reduced pressure (10 mmHg) to give ca. 50% of a 99% pure DMAC. Although the yield of this distillation has not been optimized, the high purity of recovered solvent indicates the feasibility of solvent recycling without further purification. (e) Synthesis of cellulose triacetoacetate—We have attempted the preparation of the triacetoacetate ester by reacting Avicel cellulose with substances whose thermal decomposition generates acetylketene, namely, diketene, or the more convenient diketene-acetone adduct, 2,2,6-trimethyl-4H-1,3-dioxin-4-one.[22–24] Despite the high reactivity of acetylketene toward nucleophilic attack (by the OH groups of cellulose),[22–24] the DS obtained, 2.0 ± 0.3, was always lower than the targeted one. Because drying under reduced pressure has proven to be efficient, vide (a) supra, this result cannot be attributed to loss of acetylketene due to its reaction with adventitious water. We attribute the low DS obtained to side reactions of acetylketene that lead to the formation of stable products, namely dehydroaceticacid and 2,6-dimethyl-4-pyrone, as shown in the following reaction scheme:[22–24]
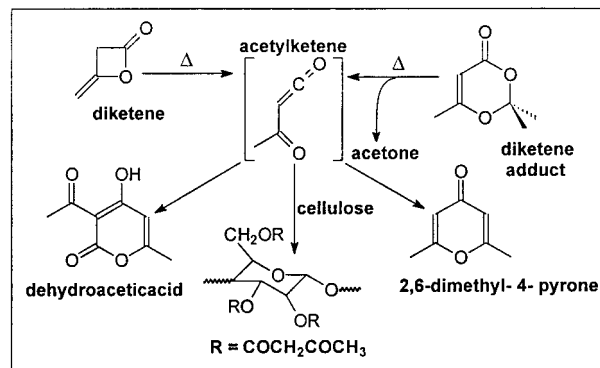
(f) Dissolution behavior of Avicel cellulose—Several trial runs have showed that formation of a clear cellulose solution requires 2 h when the system is cooled to 40°C and more than 8 h when the temperature is kept at 70°C! During cooling, the crystallinity of undissolved cellulose decreases as a function of temperature/time, for example, it was found to be 0.70 at 112°C (80 min) and 0.58 at 78°C (100 min). This temperature effect can be explained by considering the three stages of dissolution of polysaccharides having amorphous/crystalline regions. The first involves transition of the solid polymer to a hypothetical liquid amorphous state, the second is associated with dissolution and solvation of the macromolecule, whereas the third involves mixing of the solvated polymer molecules with the solvent to give an infinitely dilute solution.[25] The corresponding enthalpy of solution, $\Delta H_{solution}$, is given by:[26]

$$\Delta H_{solution} = \Delta H_{fusion} + \Delta H_{transition} \\ + \Delta H_{interaction} + \Delta H_{mixing} \quad (4)$$

where ΔH_{fusion}, $\Delta H_{transition}$, $\Delta H_{interaction}$, and ΔH_{mixing}, refer to the enthalpies of: fusion of the cellulose crystalline regions; solvent-mediated transition of the amorphous component from vitreous to highly elastic state; interaction between cellulose and the solvent system; and thermochemical effects of the mixing process, respectively. Not all terms of eq. (4) are experimentally accessible. For example, because cellulose decomposes before it melts, various approaches have been employed to estimate ΔH_{fusion}, for example, from enthalpies of solution of β-glucosan (1,6-anhydro-β-glucopyranose, a model for cellulose).[26] Analysis of the right-hand side of eq. (4) indicates that the only positive term is the enthalpy of fusion.[26] Note that $\Delta H_{interaction}$ includes enthal-

pies of interaction of DMAC with cellulose and LiCl, both are negative quantities.[27] That is, the overall cellulose dissolution process is exothermic, cellulose dissolution by complexation with LiCl being more favorable at a lower temperature, 40°C. Heating the sample at 150°C is required, however, for its activation, i.e., for penetration of the solvent into the fiber wall; breaking of the fiber and the fibril structure; and dissolution of the latter.[28]

CONCLUSIONS

The method reported here contributes to industrial application of the LiCl/DMAC cellulose dissolution/reaction solvent system. The method is simple, uses stochiometric concentrations of acid anhydride/AGU, requires no catalyst, causes negligible degradation of cellulose, can be used for the preparation of esters and mixed esters, permits solvent recovery, and the results (in terms of DS) are highly reproducible. The complex cellulose dissolution process seems to be exothermic.

REFERENCES

1. McCormick, C. I.; Callais, P. A.; Huchinson, B. H., Jr. Macromolecules 1985, 18, 2394.
2. McCormick, C. I.; Callais, P. A. Polym Prepr 1986, 27, 91.
3. McCormick, C. I.; Callais, P. A. Polymer 1987, 28, 2317.
4. Suzuki, K.; Kurata, S.; Ikeda, I. Polym Int 1992, 29, 1.
5. Samaranayake, G.; Glasser, W. G. Carbohydr Polym 1993, 22, 1.
6. Petrus, L.; Gray, D. G.; Miller, J. N. Carbohydr Res 1995, 268, 319.
7. Edgar, K. J.; Arnold, K. M.; Blount, W. W.; Lawniczak, J. E.; Lowman, D. W. Macromolecules 1995, 28, 4122.
8. Ibrahim, A. A.; Nada, A. M. A.; Hagemann, U.; El Seoud, O. A. Holzforschung 1996, 50, 221.
9. Toyoshima, I. In Cellulosics: Chemical, Biochemical and Material Aspects; Kennedy, J. F.; Phillips, G. O.; Williams, P. A., Eds.; Ellis Horwood: New York, 1993, p. 125.
10. Regiani, A. M.; Frollini, E.; Marson, G. A.; Arantes, G. M.; El Seoud, O. A. J Polym Sci Polym Chem, 1999, 37, 1357.
11. (a) Marx-Figini, M.; Schultz, G. V. In Polymer Handbook; Brandrup, J.; Immergut, E. H., Eds.; Wiley: New York, 1975, p. V-107; (b) Kamide, K.; Miyazaki, Y.; Abe, T. Makromol Chem 1979, 180, 2801.
12. Buschle-Diller, G.; Zeronian, S. H. J Appl Polym Sci 1992, 45, 967.
13. American Society for Testing and Materials, Philadelphia, method D-871 (1983).
14. (a) Kamide, K.; Okajima, K.; Saito, M. Polym J 1981, 13, 115; (b) Kamide, K.; Okajima, K. Ibid 1981, 13, 127; (c) Iwata, T.; Azuma, J.-I.; Okamura, K.; Muramoto, M.; Chun, B. Carbohydr Res 1992, 224, 277.
15. Braun, S.; Kalinowski, H.-O.; Berger, S. 100 and More Basic NMR Experiments; VCH: Weinheim, 1996, p. 99.
16. Kowsaka, K.; Okajima, K.; Kamide, K. Polym J 1988, 20, 827.
17. Callais, P. A. Derivatization and Characterization of Cellulose in Lithium Chloride and N,N-Dimethylacetamide Solutions. Ph.D. Thesis,University of Southern Mississippi (1986).
18. Sealey, J. E.; Samaranayake, G.; Todd, J. G.; Glasser, W. G. J Polym Sci Part B 1996, 34, 1613.
19. Deus, C.; Friebolin, H.; Siefert, E. Makromol Chem 1991, 192, 75.
20. (a) Malm, C. J.; Tanghe, L. J.; Laird, B. C.; Smith, G. D. J Am Chem Soc 1953, 75, 80; (b) Dawsey, T. R.; McCormick, C. L. J Macromol Sci Rev Macromol Chem Phys 1990, C30, 405.
21. Saint-Germain, J.; Vincendon, M. Org Mag Res 1983, 21, 371.
22. Clemens, R. J.; Hyatt, A. J Org Chem 1985, 50, 2431.
23. Clemens, R. J. Chem Rev 1986, 86, 241.
24. Clemens, R. J.; Witzeman, J. S. J Am Chem Soc 1989, 111, 2186.
25. Myasoedova, V. V.; Pokrovskii, S. A.; Zav'yalov, N. A.; Krestov, G. A. Russ Chem Rev 1991, 60, 954, and references cited therein.
26. (a) Paul, R. C.; Banait, J. C.; Narula, S. P. J Electroanal Chem 1975, 66, 111; (b) Taniewska-Osinska, S.; Wozincka, J. Thermochim Acta 1981, 47, 57.
27. Pionteck, H.; Berger, W.; Morgenstein, B.; Fengel, D. Cellulose 1996, 3, 127.