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ORIGINAL PAPER

Activation of cellulose by 1,4-dioxane for dissolution in *N,N*-dimethylacetamide/LiCl

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Abstract *N,N*-Dimethylacetamide/lithium chloride (DMAc/LiCl) mixture is a popular solvent system used for cellulose dissolution, analysis, and derivatization. However, a pre-treatment (activation) procedure is needed for most celluloses to dissolve readily in DMAc/LiCl. Here, an optimized version of the activation protocol based on solvent exchange to 1,4-dioxane was introduced. Its universality was demonstrated by successful activation and dissolution of six different celluloses (AVICEL, Sigmacell, cotton linters, Encell, Lincell, and Whatman paper). Dissolution times varied significantly for different cellulose types and also depended on factors such as the drying method employed or the water removal step inclusion/omission. Dioxane-activated celluloses were analyzed with a variety of methods. SEC measurements indicated low destructivity of the dioxane activation method. The infrared spectroscopy analysis showed that dioxane remained adsorbed on cellulose even after rigorous drying. In addition, upon dioxane activation, stagnation or a slight increase in the total order index of celluloses was observed. This observation was in accordance with the crystallinity index changes determined by solid-state NMR. Finally, scanning electron microscopy revealed disintegration of AVICEL particles and defibrillation of fibrous celluloses upon dioxane activation; Sigmacell remained apparently unchanged.

Keywords Cellulose activation · Cellulose dissolution · 1,4-Dioxane · Solvent exchange · *N,N*-Dimethylacetamide/lithium chloride

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Introduction

Due to its high abundance and specific properties, cellulose ranks among the most important renewable resources. However, cellulose processing is complicated by the biopolymer's peculiar supramolecular structure, comprising a complex network of hydrogen bonds, which efficiently suppresses cellulose solubility in a majority of standard organic solvents. As a result, cellulose dissolution has become one of the cellulose chemistry leading topics. The dissolution process is extremely important in both industry and academia. For example, in the textile industry cellulose dissolution is a prerequisite for production of regenerated fibers. In addition, we can also witness a growing interest in controlled preparation of cellulose derivatives via the homogenous reaction conditions (HRC) scheme (El Seoud and Heinze 2005).

The HRC scheme represents an interesting alternative to the widely industrially used heterogeneous modification of cellulose mainly because it overcomes

some of the drawbacks associated with the latter approach. These drawbacks include non-uniform substitution patterns caused by different accessibility of crystalline and amorphous regions in cellulose, poor control of the degree of substitution (DS), and possible degradation reactions (El Seoud and Heinze 2005; Ramos et al. 2005; Marson and El Seoud 1999a; Ramos et al. 2011). Lately, HRC has also been utilized in controlled synthesis of more complex structures such as cellulose-based graft copolymers. Indeed, a combination of the HRC scheme and controlled radical polymerization methods, e.g., atom transfer radical polymerization (ATRP) or single-electron transfer living radical polymerization (SET-LRP), proved to be a powerful tool in controlling the graft copolymer architecture as it allows product tailoring to specific applications (Vlček et al. 2006, 2008, 2011; Yan and Ishihara 2008; Raus et al. 2011). The HRC scheme use is crucial here since it enables stoichiometric control of the DS and, in turn, of the grafting density (Raus et al. 2011).

During the past decades, many cellulose solvents have been developed (El Seoud and Heinze 2005; Liebert 2010). They can be classified according to different criteria. Based on the type of interaction between the solvent and cellulose, the most common classification distinguishes derivatizing and non-derivatizing solvents. Further, cellulose solvents can be divided into aqueous and non-aqueous groups. Obviously, water presence influences the scope of use of aqueous cellulose solvents; for instance, it limits the derivatizing reagent selection. From this point of view, non-derivatizing, non-aqueous solvents appear to be the most universal class. For example, ionic liquids (ILs), especially those of 1-alkyl-3-methylimidazolium type, emerged as efficient, non-derivatizing solvents for cellulose in recent years (Swatloski et al. 2002; El Seoud et al. 2007; Pinkert et al. 2009). Nevertheless, it might prove necessary to use ILs as a mixture with other solvent(s) in order to overcome their drawbacks such as high viscosity at standard reaction temperatures (Gericke et al. 2011).

The mixture of *N,N*-dimethylacetamide and lithium chloride (DMAc/LiCl) represents a well established non-derivatizing, non-aqueous solvent system that has been widely employed for cellulose modification under HRC to prepare a wide range of derivatives (El Seoud and Heinze 2005; Heinze and Liebert 2001; Liebert 2010; Heinze 1998). Moreover, the colorless nature of DMAc/LiCl and also its ability to dissolve different cellulose types without significant degradation (Liebert 2010; Henniges et al. 2010; Strlič and Kolar 2003; Röder et al. 2001) make the solvent system an important medium for cellulose analysis by various methods (e.g., SEC, NMR, or light scattering). Cellulose modification in DMAc/LiCl typically comprises three steps: activation, dissolution, and a reaction with a suitable derivatizing agent.

Activation is a pre-treatment process facilitating cellulose dissolution. Apart from specific treatments (e.g., mercerization) sometimes employed for certain cellulose types, two general approaches to the activation can be found in literature: solvent exchange to DMAc and thermal activation. The procedure of solvent exchange to DMAc involves repeated cellulose immersion in a series of solvents, such as water, methanol and, finally, DMAc (El Seoud and Heinze 2005; McCormick et al. 1985). This procedure can become laborious for larger cellulose quantities because it involves multiple filtrations that can be rather time-consuming, especially for finely powdered samples. Further, quite large volumes of solvents are typically employed (Regiani et al. 1999). Nevertheless, for analytical purposes, solvent exchange to DMAc is still the method of choice mainly due to its experimental simplicity and non-destructivity (Henniges et al. 2010, 2011). The second approach to cellulose activation uses cellulose heating in DMAc/LiCl at elevated temperatures. Various modifications of this thermal activation method can be found in literature, for example, a distillation of a part of the solvent volume from the cellulose–DMAc/LiCl slurry to partially remove water (Regiani et al. 1999; Edgar et al. 1995) or carrying out the key steps under reduced pressure (Marson and El Seoud 1999b; El Seoud et al. 2000). Unfortunately, the activation conditions usually lead to more or less pronounced cellulose degradation, resulting in a decreased molecular weight of cellulose and in solution discoloration (Potthast et al. 2002a, 2003).

Recently, we have reported on a new, promising activation procedure based on solvent exchange to 1,4-dioxane. The method was successfully used for dissolution of microcrystalline cellulose AVICEL PH-101, which was in turn transformed into a range of cellulose graft copolymers with variable architecture and composition (Raus et al. 2011). The dioxane-based procedure was found to compare favorably to other activation protocols; thus, its synthetic utility

was demonstrated. Nevertheless, due to the different aims of the report, the comments on other than synthetic aspects of the dioxane activation were rather limited. Therefore, we present here a follow-up study providing deeper discussion of the dioxane activation nature and benefits.

In this paper, an optimized version of the dioxane procedure has been used to activate six different celluloses/pulps in order to manifest the universality of the method. In addition, the activated cellulose samples have been studied by a variety of methods to reveal changes in cellulose structure associated with the activation process.

Materials and methods

Materials

Highly purified powder celluloses Sigmacell Cellulose Type 101 and microcrystalline cellulose AVICEL PH-101 (Fluka Biochemika) were bought from Aldrich. Other cellulose samples had fibrous form and were kindly provided by Prof. Antje Potthast from University of Natural Resources and Life Sciences, Vienna. These included cotton linters, Whatman filter paper, Encell (bleached paper-grade eucalyptus kraft pulp; manufactured by Ence, Spain), and Lincell (non-blended, ECF bleached flax pulp; manufactured by Celesa S.A., Spain). Cellulose samples were used as received and were not pre-dried, unless otherwise stated. Alpha-cellulose content (DIN 54355) in the fibrous celluloses was as follows: cotton linters, 98.5 %; Whatman paper, >98 %; Encell, 92 %; Lincell, 93.6 %. *N,N*-dimethylacetamide (Aldrich) was dried according to the literature procedure (Potthast et al. 2002b) and kept over an activated molecular sieve (4 Å; Fluka) under argon. 1,4-Dioxane (Lach-Ner, Czech Republic) was distilled before use. Lithium chloride (Fluka) was dried at 190 °C in vacuum for 8 h prior to use.

Cellulose activation by solvent exchange to DMAc

Activation of cellulose was carried out according to the published method (McCormick et al. 1985). Cellulose was stirred in distilled water (30 ml g^{-1}) for 1 h and then filtered off. This was repeated two times, followed by three identical cycles with methanol and, subsequently, with DMAc.

Cellulose activation by solvent exchange to 1,4-dioxane

Cellulose was activated by an optimized version of the procedure published recently (Raus et al. 2011). In a 500 ml round bottom flask equipped with a magnetic stirring bar and a distillation head, cellulose (5 g) was mixed with distilled water (300 ml), and the stirred mixture was refluxed for 1 h. Then, cellulose was filtered off on a glass frit and dispersed in dioxane (300 ml). The resulting mixture was refluxed for 1 h using the same setup into which a distillation column (50 cm length, packed with HELI-PAK packing material) was incorporated. Afterwards, condensate had been collected until the temperature reached the boiling point of pure dioxane (101 °C). Further, ca. 150 ml of dioxane was added into the distillation flask, and the distillation column and head were replaced with the custom-made drying loop charged with an activated 4 Å molecular sieve (see Fig. 1 for details). In the loop, the cellulose/dioxane mixture was refluxed for 8 h. Finally, cellulose was collected by filtration and dried in vacuum (80 °C), or freeze dried, for 6 h Note: all the procedure parts involving dioxane were carried out under argon atmosphere.

Determination of dioxane-activated cellulose dissolution time

Dioxane-activated cellulose (25 mg) was introduced into a 10 ml flask equipped with a magnetic stirring bar and a three-way stopcock, and the flask was three times evacuated and back-filled with argon. Then, 7.7 % DMAc/LiCl stock solution (5 ml) was added into the flask through an argon-flushed syringe, and the mixture was stirred at room temperature. Dissolution of cellulose was followed visually by a comparison with a clear cellulose solution sample. For cellulose samples that had a tendency to produce highly viscous solutions (e.g., Sigmacell), the concentration of cellulose in DMAc/LiCl was halved.

Characterization

Size exclusion chromatography with multiple-angle laser light scattering detection (SEC MALLS)

SEC MALLS analysis of cellulose samples was carried out in 0.9 % (v/w) DMAc/LiCl with the use

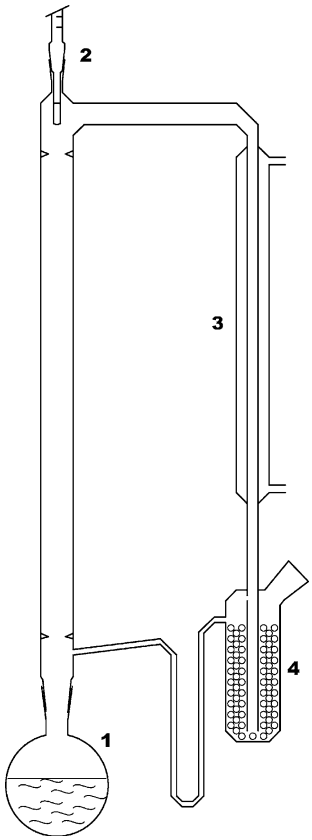


Fig. 1 Distillation loop used for water removal from cellulose. *1* Distillation flask containing cellulose suspension in dioxane, *2* thermometer, *3* water-cooled condenser, *4* drying flask filled with an activated 4 Å molecular sieve

of the following system: an online degasser Dionex DG-2410, a Kontron 420 pump, a column oven Gynkotek STH 585, a MALLS detector Wyatt Dawn DSP with argon ion laser ($\lambda_0 = 488$ nm), and a refractive index (RI) detector Shodex RI-71. Data evaluation was performed with standard Astra, GRAMS/32, and Origin software. The following parameters were used in the GPC measurements: flow: 1.00 ml min^{-1}; columns: four PL gel mixedA LS, 20 µm, 7.5 × 300 mm; injection volume: 100 µL; run time: 45 min. The amount of dissolved material was determined from the RI signal (d*n*/dc value of 0.136 ml g^{-1} and a detector constant of 5.3200e-5 V^{-1}).

Attenuated total reflectance (ATR) FTIR spectroscopy

Infrared spectra were acquired on a Nexus Nicolet 870 FTIR spectrometer purged with dry air and equipped with a liquid nitrogen cooled MCT (mercury cadmium telluride) detector. Spectra of powder polymer samples were acquired using a Golden Gate single reflection ATR cell (Specac), equipped with a diamond internal reflection element. When a powder sample was placed onto the crystal area, the force applied to the sample (by means of the pressure arm of the ATR accessory) was adjusted until the strongest spectral band at about 1,030 cm^{-1} reached intensity of about 0.4 units. Such practice ensured good contact of the sample material with the ATR crystal and good sample to sample reproducibility. Spectra were recorded with a resolution of 4 cm^{-1}; 256 scans were averaged per spectrum. After subtraction of the spectrum of atmosphere, baselines were corrected (linear baseline correction) and an advanced ATR correction was applied.

Solid-state nuclear magnetic resonance (SS NMR)

1D solid-state NMR spectra of untreated and dioxane-activated cellulose samples were measured with a Bruker Avance 500 NMR spectrometer using a 4 mm MAS probe. Magic angle spinning (MAS) frequency of the sample was 11 kHz. Amplitude modulated cross-polarization (CP) with duration 1,750 µs was used to obtain ^{13}C CP/MAS NMR spectra with 2 s recycle delay. The number of scans for the accumulation of ^{13}C CP/MAS NMR spectra was 2,048. During detection, a high-power dipolar decoupling was used to eliminate the strong heteronuclear dipolar coupling. The isotropic chemical shift of ^{13}C scale was calibrated with glycine as an external standard (176.03 ppm—low-field carbonyl signal). Taking into account frictional heating of the samples during fast rotation, all NMR experiments were carried out at 308 K. Temperature calibration was performed with $Pb(NO_3)_2$ as described in literature (Brus 2000). Prior to the analysis, the untreated cellulose samples were dried at 80 °C for 6 h in vacuum. The crystallinity index was calculated from the deconvoluted (Lorentzian/Gaussian = 0.2) C4 signal (Park et al. 2010).

Scanning electron microscopy (SEM)

SEM analysis was carried out with a Vega Plus TS 5135 microscope (Tescan). A cellulose sample was fixed on a conductive, double adhesive carbon tape that was covered with 4 nm platinum layer by a vacuum sputter coater SCD 050 (Balzers) in order to

limit sample damage and electron beam-caused charging. All samples were observed in a secondary electron mode (SE) at accelerating voltage 30 kV.

Light microscopy

Light microscopy was performed with a DM6000 M microscope (Leica). On a microscopic support glass, a small amount of cellulose was mixed with a drop of 7.7 % DMAc/LiCl stock solution and covered with a cover glass. The sample was observed in transmitted light using bright field imaging.

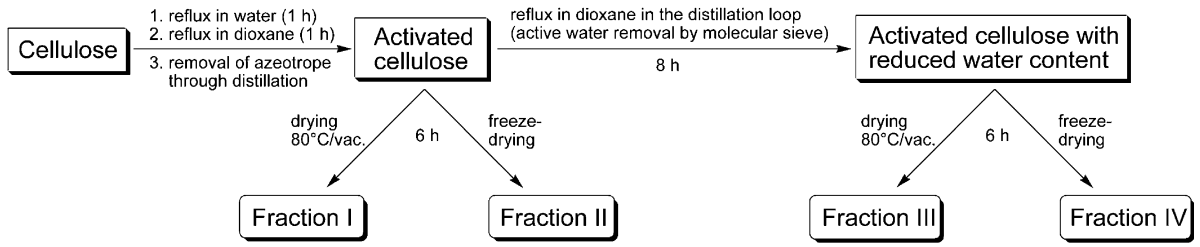
Results and discussion

Dioxane activation procedure and cellulose dissolution in DMAc/LiCl

Recently, we have shown that solvent exchange to 1,4-dioxane can be used for activation of low-molecular weight, microcrystalline cellulose AVICEL PH-101 (Raus et al. 2011). Resulting activated cellulose dissolved readily in the DMAc/LiCl solvent system. Nevertheless, due to wide variance of cellulose samples, finding a universal activation scheme that would give identical results for different celluloses is very unlikely (El Seoud and Heinze 2005; Ramos et al. 2005). Actually, there is a wide range of factors that might influence the process of cellulose dissolution and, indirectly, also the course of subsequent derivatization. These include, for example, the cellulose origin, purity, molecular weight, crystallinity, pore structure, water content, and, of course, the solvent type, the concentration of solvent components (for solvent systems), the dissolution temperature, etc. Therefore, universality of the dioxane activation method needed to be verified by activation and dissolution of different cellulose samples. The celluloses tested here included AVICEL PH-101, Sigmacell Type 101, cotton linters, eucalyptus pulp (Encell), flax pulp (Lincell), and Whatman paper. These samples represent a rather diverse group containing celluloses of different origin (wood, annual plants), molecular weight, crystallinity, processing history, physical form (powder, fibers), and purity (highly purified cellulose versus pulps with considerable residual hemicellulose/lignin content). We also took the opportunity and optimized the dioxane-based activation protocol to make it faster and more efficient.

The activation method presented here is based on cellulose swelling with water and subsequent efficient replacement of water with 1,4-dioxane. Compared to the traditional procedure of solvent exchange to DMAc, the current method differs in two important aspects. Firstly, 1,4-dioxane is used as an activation agent. Besides dioxane, we also tested acetone, benzene, and methanol as activation agents in preliminary solvent-exchange experiments. However, only dioxane treatment led to clear enhancement of cellulose solubility in DMAc/LiCl. The inefficiency of acetone in this regard was previously mentioned by Ishii et al. (2008). Secondly, a different experimental setup is employed that exploits unique properties of the water-dioxane mixture, namely its ability to form an azeotropic mixture with a minimum of boiling point (88 °C) and a relatively high water content (18 %) (Horsley 1947). Hence, water can be conveniently removed from the system by a simple distillation of the azeotrope, which helps drive the solvent exchange process forward. Moreover, when needed, it is easy to employ an additional water removal step in order to minimize the water content in cellulose.

The updated dioxane activation procedure introduced in this paper differs from the recently reported version (Raus et al. 2011) in several aspects. The changes include shorter reflux time (1 h instead of 2.5 h), the use of a packed distillation column, and utilization of a different setup in the additional water removal step (a distillation loop/molecular sieve instead of a Soxhlet extractor/CaH_2) (Scheme 1). These changes bring a host of advantages. Firstly, the activation time is decreased. Secondly, more efficient azeotropic distillation is achieved, which is reflected in lower consumption of dioxane. Thirdly, the distillation loop/molecular sieve combination (Fig. 1) represents a more convenient setup for activation of larger cellulose quantities. In the loop, cellulose suspension in dioxane is heated; the distillate, after cooling, passes through a bed of an activated molecular sieve before returning back to the distillation flask. Traces of water are thus gradually removed. The drying progress can be conveniently followed by observation of temperature changes on a thermometer. Finally, the activation protocol becomes virtually waste-free. The easy-to-reactivate molecular sieve can



Scheme 1 The procedure for activation of cellulose by 1,4-dioxane

also be used for drying of wet dioxane resulting from the azeotropic distillation.

Scheme 1 depicts the complete activation procedure, the additional water removal step included. Four samples were acquired for every cellulose type (designated as Fractions I–IV). Two samples were removed after the azeotropic distillation and dried in vacuum at 80 °C (Fraction I) or freeze-dried (Fraction II). The remaining two samples, acquired after the additional water removal step, were dried accordingly (Fractions III and IV). Such an arrangement was employed to study how the cellulose dissolution time is influenced by (1) use of different drying methods, and (2) inclusion of the additional water removal step.

Table 1 provides the dissolution times of dioxane-activated samples of the six celluloses studied here; mass average molecular weight (M_w) and dispersity (M_w/M_n) values determined by SEC MALLS are also presented. Considering these data, several important observations can be made. Firstly, substantial differences in the dissolution times of different celluloses exist; the values range from 5 min to 5 days. Further, in most cases, additional reflux in dioxane with active water removal (Fractions III and IV, Scheme 1) leads to somewhat faster dissolution. This effect was most significant in the case of Sigmacell; on the other hand, cotton linters did not seem to be influenced at all. Finally, the freeze-dried fractions of some of the celluloses (AVICEL, Sigmacell, and cotton linters) dissolved noticeably faster than the thermally dried ones.

Various factors can contribute to the observed dissolution time differences. Probably the most obvious one is the molecular weight as its values are vastly different for different celluloses. However, the molecular weight did not appear to be the sole determining factor influencing the dissolution times. For example, cellulose with the highest measured M_w (Encell) took considerably shorter time to dissolve than some samples of lower M_w (Whatman, Lincell, Sigmacell). Nevertheless, the relatively low M_w of cotton linters can be used as an explanation for its surprisingly fast dissolution, especially when compared to Whatman paper behavior (i.e., cellulose of similar origin). It should be noted that cotton cellulose often requires a specific pre-treatment (mercerization) to go readily into DMAc/LiCl solution (El Seoud and Heinze 2005). Sample purity is likely to be another important factor determining the dissolution time. It is known that impurities such as hemicelluloses or lignin can have a

Table 1 Mass average molecular weight, dispersity (SEC MALLS) and dissolution times (7.7 % DMAc/LiCl) of dioxane-activated celluloses

Cellulose	M_w	M_w/M_n	Dissolution times[a]			
			Fraction I	Fraction II	Fraction III	Fraction IV
AVICEL	35,000	1.94	2 h	15 min	1.5 h	5 min
Sigmacell	360,000	6.50	36 h	3.5 h	12 h	2.5 h
Encell	566,000	6.26	8 h	8 h	6 h	6 h
Whatman	468,000	2.38	5 days	5 days	4 days	4 days
Cotton linters	237,000	5.69	3.5 h	1 h	3.5 h	1 h
Lincell	384,000	3.33	2 days	2 days	30 h	30 h

[a] The designation of fractions corresponds to Scheme 1

detrimental effect on cellulose dissolution in DMAc/LiCl, e.g., by decreasing cellulose swellability and hindering surface accessibility (Henniges et al. 2010). It is well possible that similar effects play a role during cellulose activation by dioxane. Indeed, the samples of the highest purity (AVICEL and Sigmacell) generally showed a better response to prolonged activation times (Fractions III and IV), compared to pulps with a comparatively lower alpha-cellulose content (Encell, Lincell). The noticeable difference in dissolution times of Encell and Lincell could be ascribed to the different origin of these samples. It was previously reported that celluloses from annual plants generally take longer to dissolve than these isolated from wood (Henniges et al. 2011). Finally, the expectable differences in the pore structure of the studied celluloses cannot be neglected as they could also contribute to the diverse dissolution behavior.

Individual cellulose types differed in their dissolution behavior. For example, freeze-dried AVICEL showed, on contact with solvent, almost instant dissolution of the finely powdered part of the material while bigger conglomerates did not get dispersed; instead, they swelled on the surface and dissolved more slowly. The rest of cellulose samples showed quite fast dispersion in DMAc/LiCl, followed by gradual clearing of the milky suspension. In the case of Encell, Whatman, Lincell, and (to a lesser extent) cotton linters, the bulk of the sample dissolved noticeably faster than suggested in Table 1, but the clear solution contained a small quantity of well-defined ~ 1 mm fibers that disintegrated and dissolved only slowly and thus became the limiting factor of the dissolution process. The gradual breaking and disintegration of individual fibers of fibrous celluloses is illustrated in Fig. 2 where light microscopy images of cotton linters dissolution are given.

The dioxane-based activation procedure presented here is highly customizable and can be tailored to specific needs. For instance, the thermal or freeze drying of samples can be left out when needed. Although the dissolution times of non-dried, activated samples were not systematically studied, they appeared to be very close to those of freeze-dried samples. Furthermore, the additional water removal step can be skipped if low water content in activated cellulose is not critical. On the other hand, it is advisable to include the additional water removal step

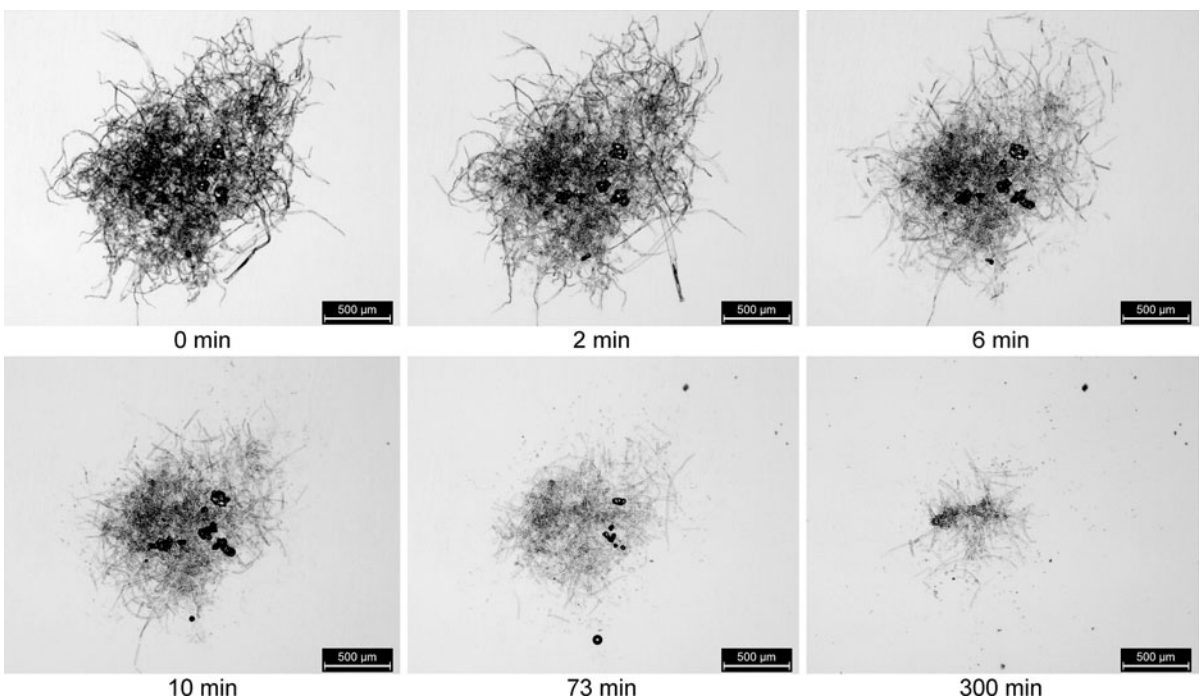


Fig. 2 Light microscopy images of cotton linters (Fraction III, Table 1) at different stages of dissolution in DMAc/LiCl

if the dissolved cellulose substrate is used for an acylation reaction. This assumption was confirmed in control derivatization experiments (data not shown here) where the four fractions of AVICEL were acylated by 2-bromoisobutyryl bromide under the same reaction conditions as these used in our previous work (Raus et al. 2011). While Fractions III and IV gave acylation efficiency in line with the best previously reported results, acylation of fractions that did not undergo the water removal step (Fractions I and II) led to about 15 % lower acylation efficiency values.

To further illustrate the efficiency of the activation experimental setup used here, we tested the traditional solvent exchange approach on AVICEL, that is, simple immersion of cellulose in water overnight, followed with three 1-h cycles in dioxane. Indeed, this treatment made AVICEL soluble in DMAc/LiCl; however, overnight stirring was needed to achieve a clear solution.

SEC MALLS analysis

As was already mentioned, thermal activation in DMAc/LiCl can result in degradation of cellulose chains and, consequently, in a molecular weight decrease and molecular weights distribution (MWD) changes. Moreover, discolored, amber, or brownish cellulose solutions are typically obtained. In contrast, dioxane activation leads to clear, colorless cellulose solutions. This observation indicates that degradation processes might not play such a significant role here. To support this hypothesis, dioxane-activated cellulose samples were analyzed by SEC MALLS and the acquired data were compared with those of samples activated by the reportedly non-destructive solvent exchange to DMAc, which was used as a benchmark in the comparison.

In Fig. 3, representative MWD traces of AVICEL, Sigmacell, and Lincell are given as examples. As

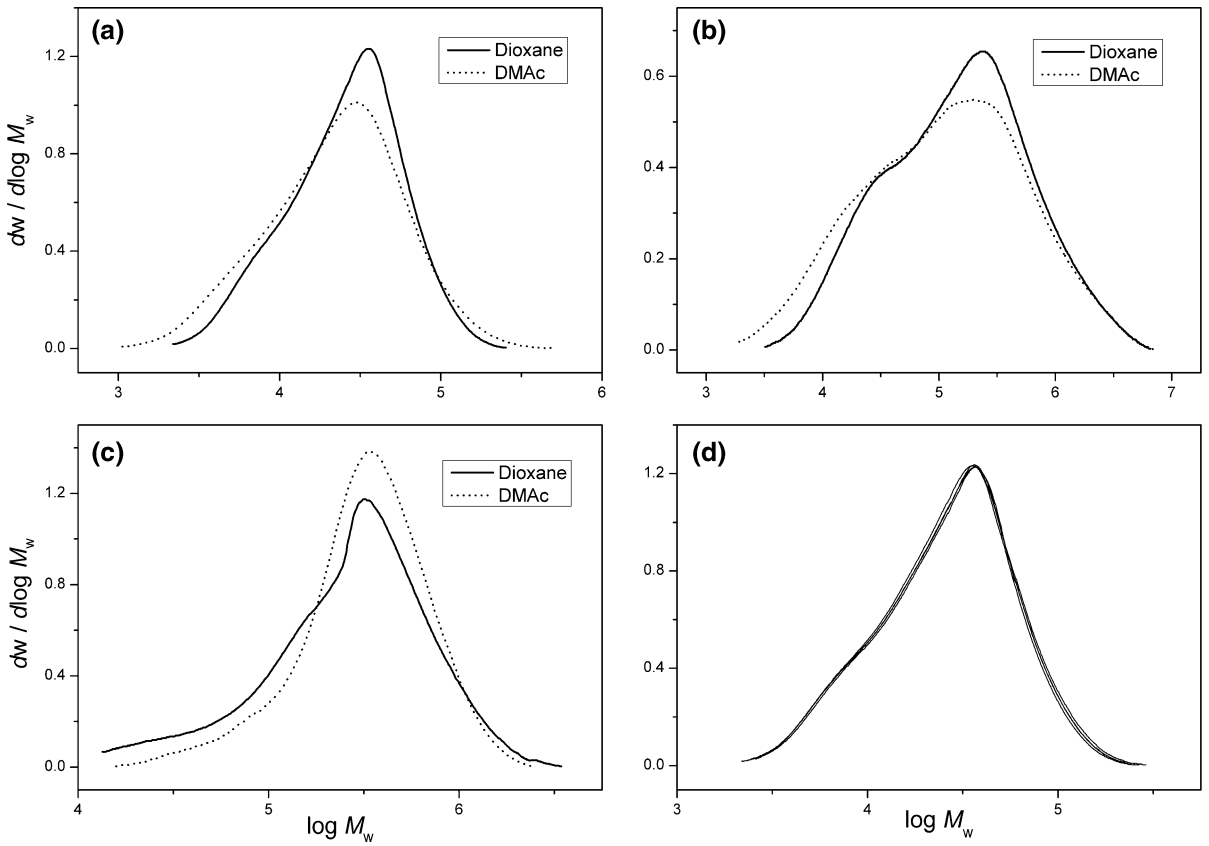


Fig. 3 MWD traces of celluloses activated by solvent exchange to dioxane (*solid line*) or to DMAc (*dashed line*): **a** AVICEL, **b** Sigmacell, **c** Lincell, **d** AVICEL (MWDs of the four isolated fractions as depicted in Scheme 1). In **a**, **b**, and **c**, traces of Fraction II, Scheme 1, are shown

discussed above, these celluloses differ in several aspects, such as the physical form, purity, crystallinity, a source, or molecular weight. The differences between DMAc-activated and dioxane-activated samples seemed to be only minor, especially for purified celluloses AVICEL and Sigmacell (Fig. 3a, b). MWDs of pulps could show certain deviations as illustrated by Lincell MWDs (Fig. 3c); however, various factors can possibly play a role here. For instance, slight mechanical degradation during the activation procedure cannot be completely ruled out. Furthermore, impurities such as hemicelluloses present in industrial pulps can respond differently to DMAc- and dioxane-based protocols because of different solubility in these media. Apparently, even the relatively pure samples such as cotton linters can be affected. For example, in the course of cotton linters activation by solvent exchange to DMAc, presence of a fine waxy fraction was observed during the sample filtration. On the other hand, this waxy fraction dissolved in hot dioxane when the dioxane activation was employed. On the whole, the dioxane chemical stability and the SEC MALLS analysis of pure cellulose samples (AVICEL, Sigmacell) indicate that (chemical) degradation does not pose a problem in dioxane-based activation.

Figure 3d compares the MWD traces of the four fractions acquired throughout the dioxane activation of AVICEL as depicted in Scheme 1. The perfect overlap of the MWD traces demonstrates that the additional water removal step and different drying methods do not lead to any significant MWD changes.

ATR FTIR analysis

Untreated as well as dioxane-activated (Fractions III and IV, Scheme 1) cellulose samples were analyzed by ATR FTIR. Characteristic spectroscopic features (Liang and Marchessault 1959a, b; Nelson and O'Connor 1964a; Sugiyama et al. 1991) suggest that all the samples are predominantly composed of Iβ crystalline allomorph, with only a small content of cellulose Iα and traces of cellulose II. The composition did not appear to be altered by the dioxane activation.

For all the dioxane-activated cellulose samples, slight changes in the shapes and intensities of the bands were detected; however, no band shifts were observed. The band shape changes were most pronounced in the C–O stretching region of the spectra; this region is depicted in Fig. 4 for AVICEL and Lincell to illustrate the differences. The apparent narrowing of the bands indicates somewhat more ordered structure (at molecular level) of the activated samples. This observation is consistent with the changes in the total order index. The total order index is known to correlate with crystallinity of cellulose determined by X-ray diffraction, by density measurements, or from accessibility derived from moisture sorption (Nelson and O'Connor 1964b). The index values were calculated from the ratio of the intensities

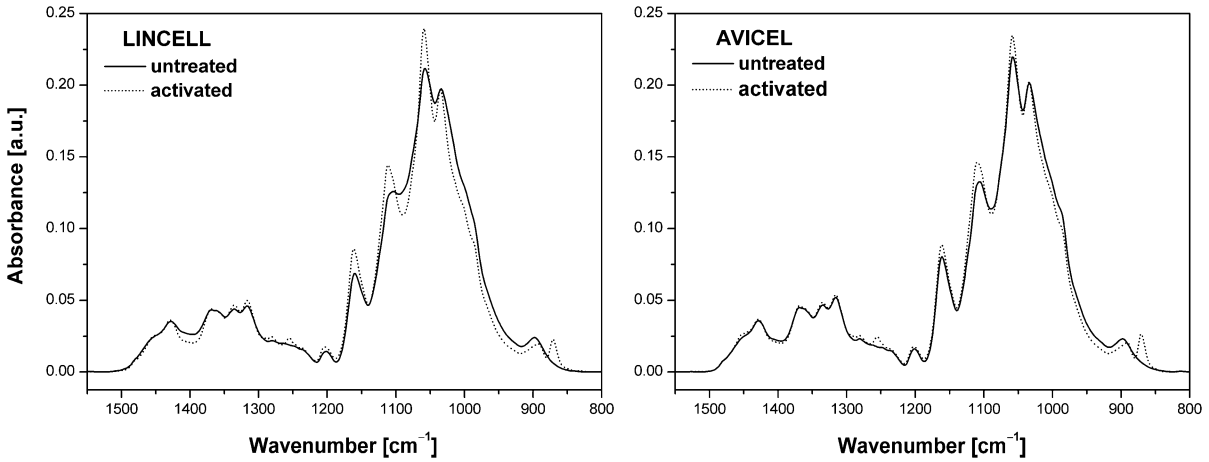


Fig. 4 The C–O stretching regions of the ATR FTIR spectra of Lincell and AVICEL. Spectra of Fraction IV (Scheme 1) of the dioxane-activated samples are shown

of the bands at 1,372 and at 2,900 cm^{-1} (Nelson and O'Connor 1964b), where the band at 1,372 cm^{-1} represents the C–H bending mode along the direction of the chain (Liang and Marchessault 1959b), and the band at 2,900 cm^{-1} represents the C–H and CH_2 stretching (Nelson and O'Connor 1964b).

Table 2 compares the total order index values with the values of the crystallinity index determined from solid-state NMR (SS NMR) spectra of the celluloses (Park et al. 2010); numbers for both untreated and dioxane-activated (complete procedure) cellulose samples are shown. There were only marginal differences between freeze-dried and thermally dried activated samples; values for the latter are shown in Table 2. Stagnation or a slight increase in the total order index of activated samples, compared to untreated samples, can be seen. The same picture is revealed when analyzing the crystallinity index values. It is noteworthy that the numerical values of the total order index and the crystallinity index cannot be directly compared. In principle, SS NMR analyzes the bulk of the sample while ATR FTIR is limited to a surface layer of certain depth. The layer thickness was calculated to be about 2 μm for the wavenumber region shown in Fig. 4 (Urban 1996). On the whole, the results are in accordance with previous studies that contended that there is no apparent correlation between crystallinity and cellulose solubility (Lennholm et al. 1994; Sjöholm et al. 1997).

Interestingly, ATR FTIR spectra of all the activated cellulose samples clearly show the presence of dioxane with bands at around 890 and 870 cm^{-1} (Malherbe and Bernstein 1952). Dioxane can be detected even after prolonged (12 h) drying of the samples in vacuum at 80 °C. The accurate ATR FTIR spectra-based calculation of dioxane content in activated samples is complicated by the factors discussed above as well as other aspects (e.g., the advanced ATR correction applied, optical properties of the samples involved, or the molar absorption coefficient differences). Nevertheless, the weight fraction of dioxane in the dried activated cellulose samples was estimated to be about 2–3 %. It should be noted that analogous presence of DMAc in dried DMAc-activated cellulose samples was recently reported by Ishii et al. (Ishii et al. 2008; Ishii and Isogai 2008). The authors found that DMAc stayed adsorbed on the cellulose surface even after vacuum-drying and suggested that the solvent presence affected the molecular mobility and hydrogen bonding network of cellulose.

Table 2 Total order index (ATR FTIR) and crystallinity index (SS NMR) of untreated (thermally dried) and dioxane-activated (complete procedure) cellulose samples

Cellulose	Total order index		Crystallinity index	
	Untreated	Activated	Untreated	Activated
AVICEL	0.47	0.50	0.54	0.55
Cotton linters	0.43	0.46	0.43	0.45
Sigmacell	0.36	0.43	0.18	0.28
Encell	0.41	0.46	0.41	0.42
Whatman	0.42	0.49	0.60	0.70
Lincell	0.38	0.47	0.57	0.57

The infrared spectra did not indicate any substantial changes to the hydrogen bonding pattern of cellulose upon dioxane activation. However, it should be emphasized that the presence of cellulose-dioxane hydrogen bonds might not be readily apparent in the infrared spectra due to the overlap of the corresponding bands with the bands of hydroxyl groups participating in the intermolecular cellulose–cellulose hydrogen bonding. For instance, density functional theory [DFT B3LYP/6-31G(d)] (Frisch et al. 2004) calculations predict only a small difference between the wavenumbers of the O–H stretching vibration of cellulose's primary hydroxyl group interacting with C3 oxygen from different cellulose chain (3,393 cm^{-1}) and with the dioxane oxygen (3,387 cm^{-1}). Therefore, the possibility of dioxane-cellulose hydrogen bonds formation cannot be disregarded. Analogous hydrogen bonding interactions between hydroxy compounds and 1,4-dioxane in liquid phase are well known and have been a subject of numerous studies (Johari and Smyth 1969; Sengwa and Sankhla 2007; Kumbharkhane et al. 2009).

SEM analysis

Scanning electron microscopy was utilized to study morphology changes associated with the cellulose activation by dioxane. For every cellulose, the following samples were evaluated: (1) untreated, (2) untreated, thermally dried, (3) dioxane-activated, thermally dried (Fraction III, Scheme 1), and (4) dioxane-activated, freeze-dried (Fraction IV, Scheme 1).

Figure 5 compares selected dioxane-activated samples with untreated ones. Generally, there were

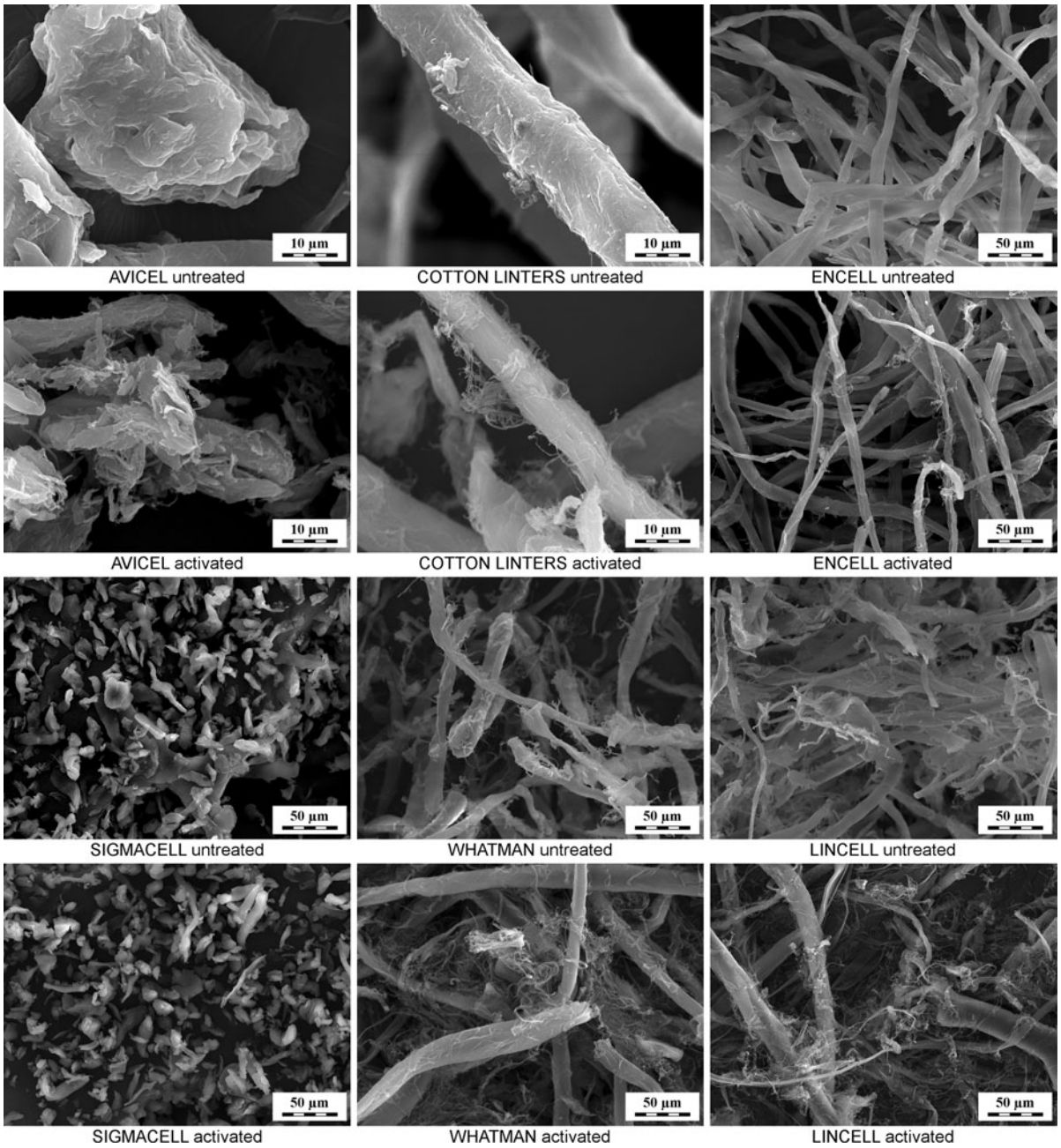


Fig. 5 SEM micrographs of untreated and dioxane-activated cellulose samples

no significant differences between the non-dried and dried untreated samples; micrographs of non-dried samples are shown in Fig. 5. Similarly, the micrographs of thermally dried and freeze-dried activated samples were virtually identical; the thermally dried samples are shown for Encell and Sigmacell, with the rest being freeze-dried celluloses.

The dioxane activation procedure resulted in various changes in the morphological structure of cellulose particles or fibers. In the case of AVICEL, significant disintegration of the particles (or their agglomerates) occurred, which led to formation of smaller fragments. In the process, some of the interstices observable in untreated AVICEL were

apparently lost. Fibrous celluloses, that is, cotton linters, Encell, Lincell, and Whatman, showed more or less pronounced defibrillation as thin fibers were peeled away from the original fiber surface. It can be also noticed that Whatman and Lincell samples contain thicker, better-developed fibers along with finer ones, which might be the cause of their somewhat problematic dissolution behavior discussed above. Surprisingly, Sigmacell did not respond to the activation procedure with any noticeable surface changes. Nevertheless, it can be concluded that for some of the cellulose types studied here, the observed morphological changes are quite pronounced and may contribute to easier penetration of the solvent into cellulose structure and thus faster dissolution.

Conclusions

In this paper, an optimized version of the recently introduced cellulose activation method, based on solvent exchange from water to dioxane, was presented. The modified procedure is faster than the previously reported version, suitable for larger quantities of cellulose, easy to tailor to specific needs, and virtually waste-free.

Universality of the activation method was demonstrated by the successful activation and dissolution of six celluloses of diverse origin, purity, molecular weight, and crystallinity. Dissolution times of cellulose fractions acquired at different stages of the activation procedure and dried differently were determined. In this regard, celluloses varied in their response to factors such as the type of sample drying or the inclusion of an additional water removal step. As expected, dissolution time differed significantly among the celluloses studied here. Besides molecular weight, other factors, such as sample purity or cellulose source, presumably influenced the dissolution rate.

The activated cellulose samples were analyzed by SEC MALLS, ATR FTIR, SS NMR, and SEM. The SEC MALLS analysis was used to determine molecular weights and MWDs of the studied celluloses. Relatively small differences in MWDs of cellulose samples activated by dioxane and by solvent exchange to DMAc were found. This observation indicated non-destructivity of the dioxane activation method. The ATR FTIR analysis revealed that dioxane activation caused only minor changes in the spectra of the studied celluloses; the changes suggested presence of more ordered structures compared to the untreated samples. This finding was consistent with the stagnation or a slight increase in the total order index of the studied celluloses upon their activation by dioxane. The crystallinity index calculated from the SS NMR spectra of untreated and dioxane-activated samples showed very similar trends. Further, ATR FTIR confirmed that dioxane stayed adsorbed on cellulose even after rigorous drying. The amount of adsorbed dioxane was estimated to be approximately 2–3 % (w/w). Finally, the SEM analysis of activated and untreated samples revealed disintegration of cellulose particles (AVICEL) or defibrillation of fibrous celluloses (Encell, Lincell, cotton linters, Whatman); Sigmacell remained apparently unchanged. The observed structural changes might enhance solvent complex diffusion into the cellulose structure and thus facilitate cellulose dissolution.

On the whole, the results presented in this study help to establish the dioxane-based activation method as a reasonably universal alternative to the presently used activation protocols.

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