Regioselectively Functionalized Cellulose Derivatives: A Mini Review

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Summary: The paper reviews recent developments in synthesis and characterization of regioselectively functionalized cellulose derivatives. It demonstrates the importance of protecting groups like triphenylmethyl- and thexyldimethylsilyl (TDMS) ethers in cellulose chemistry. The protected cellulose derivatives can be used for the preparation of 2,3-*O*-functionalized polymers. Moreover, the TDMS group opens up the synthesis of 3-*O*-ethers of cellulose that possess interesting properties in terms of structure in solution, water-solubility, and thermoreversible gelation.

Keywords: cellulose; NMR; properties; protecting groups; synthesis

Introduction

Cellulose ethers are prepared in technical scale by the conversion of alkali cellulose with alkylating reagents, e.g., epoxides, alkyl- and carboxyalkyl halides.[1] The reaction of cellulose with reagents of low steric demand leads to a random distribution of substituents within the anhydroglucose unit (AGU) and along the polymer chain. It is well known that not only the degree of substitution (DS) but also the distribution of functional groups may influence the properties of cellulose ethers.[2] However, to gain detailed information about the influence of the structures on properties not only a comprehensive structure characterization but also cellulose ethers with a defined functionalization pattern are indispensable for the establishment of the structure-property- relationships.

The paper reviews synthesis pathways for the preparation of cellulose ethers with controlled functionalization pattern considering adequately own research results. The influence of a pulp treatment with NaOH (mercerization) or H_3PO_4 prior to the introduction of the protecting groups is discussed as well. Moreover, the synthesis and characterization of novel 3-*O*-functionalized cellulose ethers will be described.

Regioselective Functionalization of Cellulose

The preparation of regioselectively functionalized cellulose ethers is still a challenge in polymer chemistry. Up to now, the most important approach for the synthesis of cellulose derivatives with controlled functionalization pattern is the application of protecting groups (Figure 1a). Other methods comprising, e.g., selective cleavage of primary substituents play a minor role. Examples are the deacetylation of cellulose acetate under aqueous acidic or alkaline conditions or in the presence of amines (Figure 1b).[3,4] In addition, activating groups may also be exploited for selective reactions (Figure 1c). However, sulfonic acid ester moieties can not be introduced in a selective manner. *p*-Toluenesulfonic acid chloride reacts preferably but not selectively with the primary OH groups of the AGU up to a DS of about 1. Secondary OH functions react as well resulting in a total DS of up to 2.3 applying excess reagent. It has been shown that bulky substituents like isopropyl moieties at the aromatic ring do not improve the regioselectivity of the sulfonic acid ester

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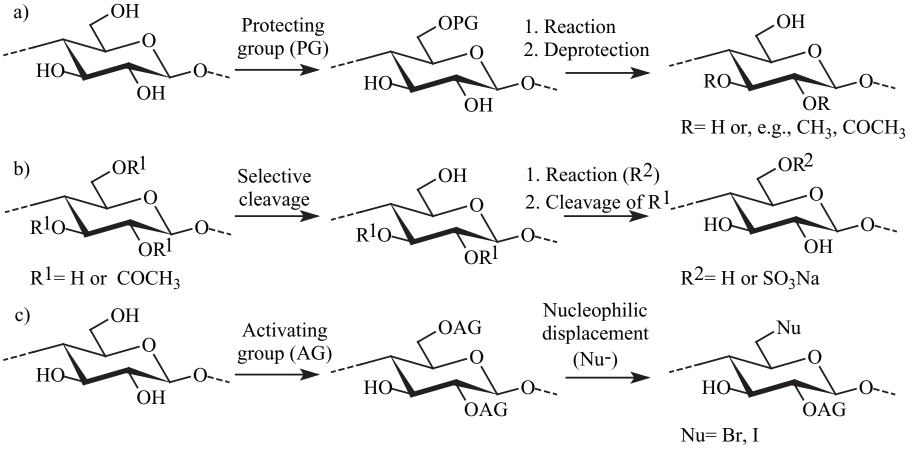


Figure 1.
Pathways for the regioselective functionalization: (a) protecting group technique, (b) selective cleavage of primary substituents, and (c) activating groups.

formation.[5] On the contrary, the selectivity of subsequent nucleophilic displacement (S_N) reactions can be controlled by the reactivity of the nucleophile applied. Although it occurs directly at a carbon atom of the AGU, a major drawback is that the S_N reaction may not be complete and sulfonic acid esters located at the secondary OH groups can not be displaced easily.

In order to achieve selective etherification, blocking group reagents must consist of at least one bulky alkyl- or aryl moiety.

In this regard triphenylmethyl- and trialkylsilyl ethers are of special interest.[6] A blocking group must meet requirements related to selective introduction, stability during subsequent reactions, and removability without loss of other substituents.

Triphenylmethyl Ethers and Subsequent Products

Triphenylmethyl (trityl) chloride reacts preferably with the primary OH group of cellulose due to its steric demand. The resulting triphenylmethyl moiety is one of the oldest and cheapest protecting groups in polysaccharide chemistry as it can be introduced and removed easily. Tritylation can be achieved by the treatment of the polymer in pyridine slurry.[7] Prior to tritylation, the cellulose is treated with aqueous NaOH or the synthesis starts with cellulose acetate, which is deacetylated and transferred to pyridine in order to increase the reactivity of the biopolymer. More conveniently, a homogeneous synthesis applying *N,N*-dimethylacetamide (DMA)/LiCl as cellulose solvent is recommended (Figure 2). Due to its stability under alkaline conditions, it is widely used for the preparation of 2,3-*O*-functionalized cellulose derivatives.[8] It has been found that the rate of formation and cleavage of the trityl ether is remarkably increased by introduction of substituents, in particular methoxy groups, at the aromatic ring

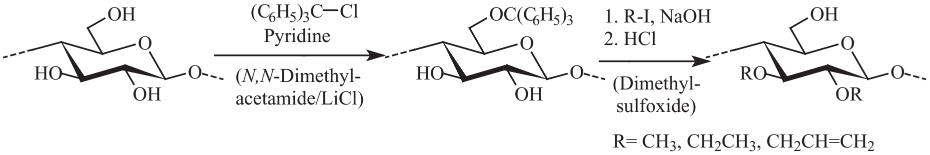


Figure 2.
Synthesis and subsequent reactions of 6-*O*-triphenylmethyl cellulose.

(Table 1). The reactivity of trityl chloride is comparably low, and hence, a reaction time of at least 48 h is required to achieve a DS of 1. Monomethoxytrityl chloride reacts more quickly and the desired DS of 1 is obtained already after few hours.

It must be mentioned that a certain amount of trityl functions is located at position 2 of the AGU. A total DS of 1.06 corresponds to a partial DS at position 6 of 0.96 and a partial DS at position 2 of 0.10.[8] This deviation from the ideal structure of 6-mono-*O*-trityl cellulose may cause distinct differences of the properties of the resulting polymers.

Conversion of 6-*O*-trityl cellulose with acetic acid anhydride or propionic acid anhydride yields the corresponding 2,3-*O*-functionalized acetates or propionates.[9] Detritylation was achieved by treatment with HBr in acetic acid.

Subsequent acylation yields the peracylated cellulose esters with inverse functionalization pattern useful for the peak assignment of NMR spectra. The cellulose esters can form single crystals that are visualized by means of atomic force microscopy.[10] In addition, investigations of the structure in solution revealed large differences to cellulose esters with random distribution of substituents, e.g., the chain conformation, solubility, and clustering mechanism may be different.[11,12]

In a comparable way, the preparation of cellulose sulfuric acid half esters with preferred functionalization of the secondary OH functions was achieved.[13] Sulfur trioxide pyridine complex was used as reagent followed by detritylation. DS values up to 0.99 were realized.

Regioselectively functionalized 2,3-*O*-methyl- and 2,3-*O*-ethyl celluloses were prepared via 6-*O*-trityl cellulose.[7]. Alkylation was achieved by conversion of the 6-*O*-trityl cellulose dissolved in dimethyl sulfoxide (DMSO) with solid NaOH as base and the corresponding alkyl iodides at 70 °C within several hours. It is worth to note that a small amount of water in the mixture (about 1 ml per 60 ml DMSO) increases the conversion drastically up to almost complete etherification of the OH groups.

A fairly difficult synthesis path is the preparation of 6-*O*-alkyl celluloses shown in Figure 3.[14] This procedure comprises the application of two different protecting groups. First, 6-*O*-trityl cellulose is converted with allyl chloride in the presence of NaOH yielding allylation of position 2 and 3. After detritylation, isomerization of the 2,3-*O*-allyl cellulose to 2,3-*O*-(1-propenyl) cellulose with potassium tert.-butoxide is carried out. Position 6 is alkylated and the 1-propenyl groups at the secondary positions are cleaved off with HCl in methanol.

The 6-*O*- and 2,3-*O*-functionalized alkyl cellulose samples were subjected to a number of investigations, e.g., study of gelation effects,[15] behavior in blends with synthetic polymers,[16] hydrogen bond system,[17] and enzymatic degradation.[18]

Cellulose ethers may exhibit the phenomenon of thermoreversible gelation that

Table 1.
Conversion of Cellulose with Different Triphenylmethyl Chlorides (3 mol/mol Anhydroglucose Unit in *N*,*N*-dimethylacetamide/LiCl, 4 h at 70 °C, Detritylation with 37% Aqueous HCl in Tetrahydrofuran, Adapted from[8]).

Protecting group	DS[a]	Reaction rate	
		Formation	Cleavage
Triphenylmethyl ether	0.41	1	1
Triphenylmethyl ether	1.05[b]	–	–
Monomethoxytriphenylmethyl ether	0.96	2	18

[a] Degree of substitution.
[b] After 48 h.

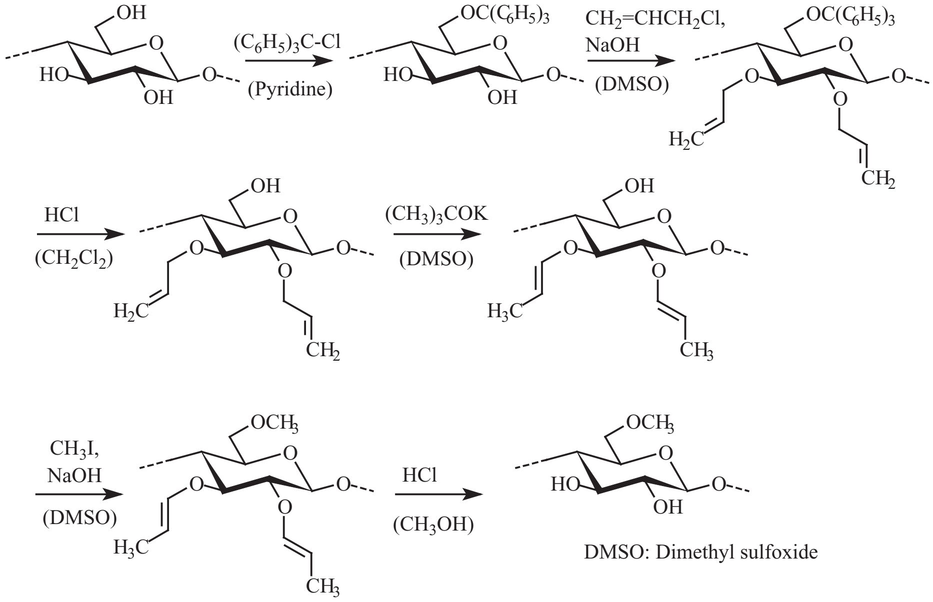
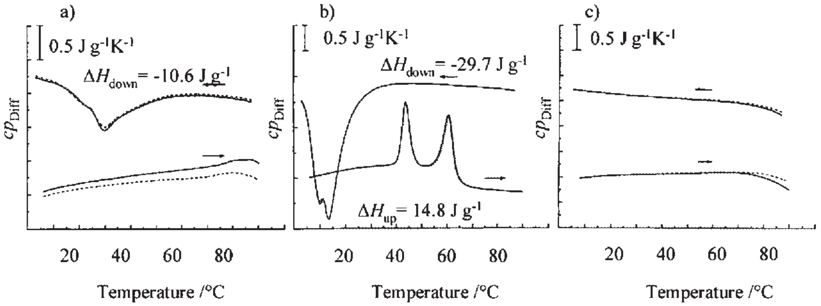


Figure 3.
Preparation of 6-*O*-methyl cellulose.[14]

strongly depends on the functionalization pattern as shown for selectively methylated cellulose.[19] It was found that slight differences in the polymer composition result in remarkable changes of the thermal behavior. A set of 2,3-*O*-methyl celluloses was prepared starting from 6-*O*-trityl- and 6-*O*-monomethoxytrityl cellulose.[20] Due to varied reaction conditions, the total DS and composition of the repeating units are slightly different. Typical samples are summarized in Figure 4, which are water-soluble and studied as aqueous solutions by DSC measurements. It can be clearly seen that thermal events are in strong correlation with the polymer composition regarding differently functionalized repeating units. If the polymer contains tri-*O*-methylated glucose units in combination with monomethylated ones, a distinct thermal behavior is observed, i.e., the methyl cellulose exhibits thermoreversible gelation (Figure 4a and b). In contrast, a uniform 2,3-*O*-methyl cellulose shows no thermal gelation. It becomes obvious that 2,3-*O*-methyl glucose units do not cause significant intermolecular interactions that are necessary for the gelation (Figure 4c).

Ionic 2,3-*O*-carboxymethyl cellulose (CMC) was synthesized via 6-O-trityl cellulose applying sodium monochloroacetate as etherifying reagent with solid NaOH as base in DMSO.[21,22] After a reaction time of 29 h at 70 °C, the product was detritylated with gaseous HCl in dichloromethane for 45 min at 0 °C. Alternatively, the detritylation can be carried out in ethanol slurry with aqueous hydrochloric acid. The 2,3–*O*-CMC synthesized possess a DS of up to 1.91. ^{13}C NMR spectra revealed the structural uniformity (Figure 5). The polymer is water soluble starting with DS 0.3.[23]

Very recently, 2,3-*O*-hydroxyalkyl ethers of cellulose could be prepared starting from 6-*O*-monomethoxytrityl cellulose.[24] Homogeneous reaction conditions can not be applied because the epoxides react with DMSO in the presence of NaOH. Other reaction media like alcohols, which are useful for carboxymethylation reactions, did not work because they do not moisten the hydro-



Repeating unit	Molar fraction (%)		
	Sample a	Sample b	Sample c
Glucose	5.79	3.04	3.09
mono-*O*-methyl	26.08	2.14	7.17
di-*O*-methyl	67.26	84.05	87.94
tri-*O*-methyl	2.78	10.77	1.81
Total DS	1.69	2.03	1.89

Figure 4.

Thermal behavior of 2,3-O-functionalized methyl celluloses dependent on the polymer composition (differential heat capacity, cp_{Diff}, degree of substitution, DS, reprinted from Carbohydr. Res., Vol. 326, Kern et al., Synthesis, control of substitution pattern and phase transitions of 2,3-di-O-methylcellulose, 67-79 (2000) with permission from Elsevier [20]).

phobic monomethoxytrityl cellulose. It has been shown that tensides, in particular mixtures of nonionic and anionic ones, are able to mediate the conversion.

The reaction of monomethoxytrityl cellulose with ethylene- and propylene oxide in isopropanol/water mixtures containing sodium dodecyl sulfate and polyethyleneglycol C_{11}–C_{15}-ether (IMBENTIN AGS-35) afforded 2,3-*O*hydroxyalkyl celluloses with a molar substitution (MS) of up to 2.0 after detritylation. Interestingly, the polymers become water-soluble starting with a MS 0.25 (hydroxyethyl cellulose) and 0.5 (hydroxypropyl cellulose, HPC), while a conventional HPC is water-soluble with MS >4. ^{13}C NMR spectroscopy revealed the etherification of the secondary hydroxyl groups of the AGU. As it is shown in Figure 6, only one signal can be observed for the CH_2 group of position 6. In addition, the peaks of the etherified positions 2 and 3 appear in the range from 80–83 ppm.

Trialkylsilyl Ethers and Subsequent Products

Trialkylsilyl ethers with at least one bulky alkyl moiety are valuable protecting groups. Typical examples are the tert.-butyl- and thexyldimethylsilyl (TDMS) ethers. With respect to its performance, the TDMS ether is the most versatile protecting group in terms of selectivity. It can be used for the preparation of two different types of protected cellulose derivatives because the regioselectivity of the silylation depends on the state of dispersity of cellulose in the reaction mixture, i.e., the selectivity is medium controlled (Figure 7). Starting from cellulose that is swollen in a mixture of ammonia and aprotic-dipolar solvents, in particular *N*-methylpyrrolidone (NMP) at −15 to −25 °C, the conversion with TDMS-Cl leads to an exclusive silylation of the primary OH group.[25,26]

TDMS-NH_2 acting as silylating reagent is immediately formed after addition of

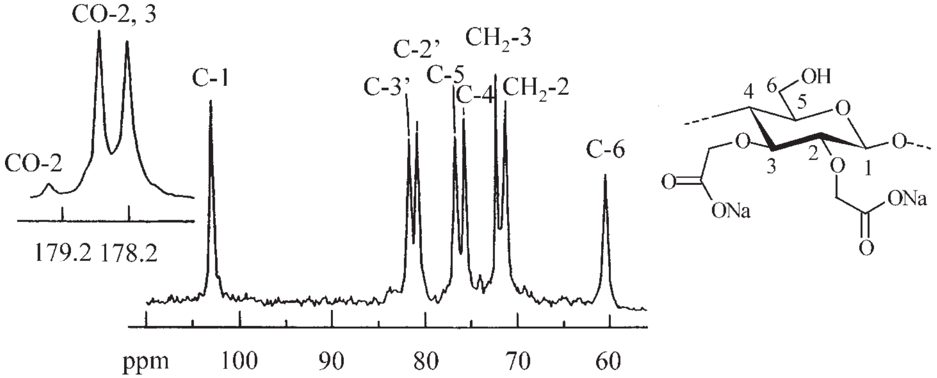


Figure 5.
^{13}C NMR spectrum of 2,3-*O*-carboxymethyl cellulose with degree of substitution of 1.75 recorded in D_2O (reprinted with permission from Wiley-VCH).[21]

TDMS-Cl to the reaction mixture. The conversion of cellulose with TDMS-NH_2 in DMA/LiCl solution at 80 °C leads to products with DS up to 1.6 indicating silylation of the secondary OH functions.

This result shows in comparison to the conversion of the swollen cellulose that the state of dispersity of the polymer determines the pronounced *O*-6 selectivity under heterogeneous conditions.[27]

In contrast, silylation of cellulose dissolved in DMA/LiCl with TDMS-Cl in the presence of pyridine afforded TDMS-celluloses with DS up to 1.8.[26] Imidazole is a more effective base than pyridine. It forms the highly reactive TDMS imidazo-

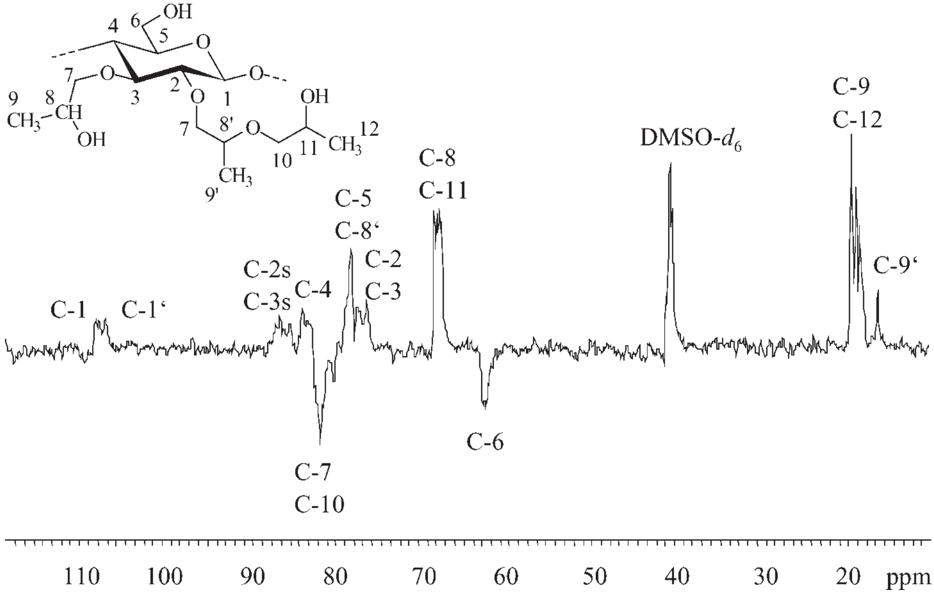


Figure 6.
^{13}C DEPT 135 NMR spectrum of 2,3-*O*-hydroxypropyl cellulose (molar substitution 0.33) recorded in dimethyl sulfoxide (DMSO)-d_6 at 40 °C (reprinted with permission from Wiley-VCH).[24]

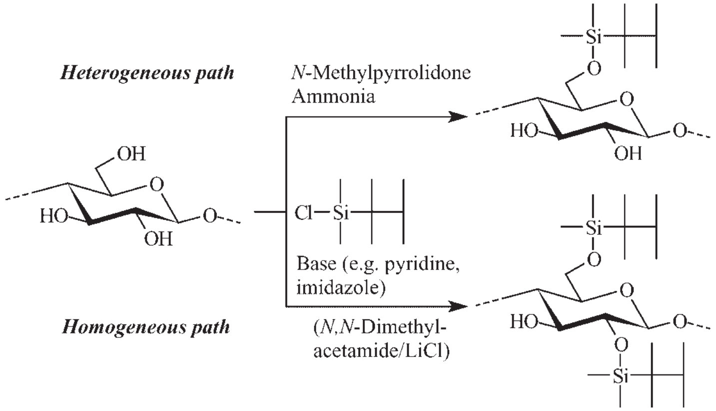


Figure 7.
Heterogeneous and homogeneous path of silylation leading to cellulose selectively protected at position 6 and position 2 and 6.

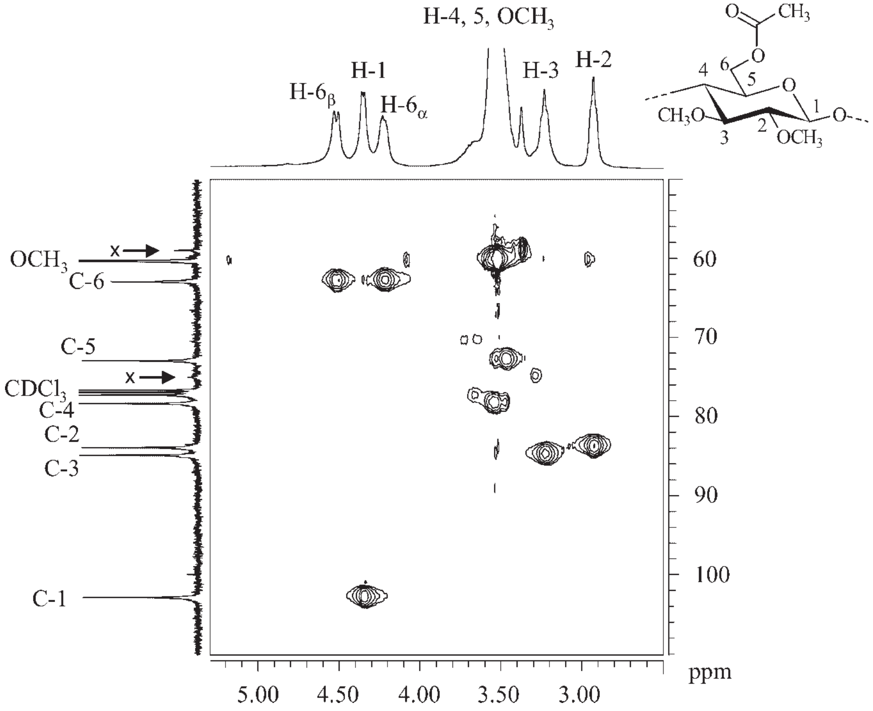


Figure 8.
Heteronuclear multiple bond quantum coherence NMR spectrum of 2,3-di-O-methyl-6-mono-O-acetyl cellulose with degree of substitution 2.0 recorded in $CDCl_3$. The arrows (x) mark signals probably corresponding to methyl groups at position 6.

lide, and TDMS celluloses with DS up to 2 can be synthesized.[28] Extensive washing with ethanol removes all silicon-based by-products resulting in a correct gravimetric DS-determination. The OH group at position 3 does not react under heterogeneous and homogeneous conditions.

2,3-O-Methyl Celluloses

A 2,3-di-*O*-methyl cellulose was prepared starting from 6-*O*-TDMS cellulose with DS 0.91 using methyl iodide as etherifying reagent and sodium hydride as base in tetrahydrofuran (THF). In order to achieve etherification of all hydroxyl groups, the reaction was carried out over 3 days at 50 °C. The protecting group was removed with tetrabutylammonium fluoride trihydrate (TBAF) within 24 h at 50 °C followed by reprecipitation of the polymer from methanol/chloroform solution into acetone. A DS of 2.0 was determined by means of ^{1}H NMR spectroscopy of the peracetylated sample. In contrast to a 2,3-*O*-methyl cellulose prepared via 6-*O*-trityl cellulose, this polymer is water insoluble and dissolves only in NMP and methanol/chloroform. Therefore, it is concluded thatthe structure is more uniform compared with sampled prepared via tritylation.

The heteronuclear multiple bond quantum coherence (HMQC) NMR spectrum shows cross-peaks that correspond to a 2,3-di-*O*-methyl-6-*O*-acetyl cellulose (Figure 8). Peaks in the ^{1}H NMR spectrum that can be assigned are: 2.91 (H-2), 3.23 (H-3), 3.52 (H-4, 5, OCH_3), 4.27 (H-6_α), 4.36 (H-1), 4.52 ppm (H-6_β). The signals in the ^{13}C NMR spectrum correspond to: 60.4 (OCH_3), 63.0 (C-6), 73.0 (C-5), 78.2 (C-4), 83.8 (C-2), 84.9 (C-3), 102.7 ppm (C-1). The spectrum shows also peaks of low intensity, e.g., at 3.36 ppm in the ^{1}H- and at 58.9 and 74.9 ppm. Due to the DS of 0.91 of the TDMS cellulose a reason may be the presence of methyl groups at position 6. In this case, the very weak signal at 74.9 ppm corresponds to position 6 of the AGU bearing a methyl group and the peak at 58.9 ppm is caused by the OCH_3 moiety.

Decrease of both the molar excess of the reagents and the reaction time yielded a 2,3-*O*-methyl cellulose with DS 0.20. Due to the low DS of 0.2, the sample is water

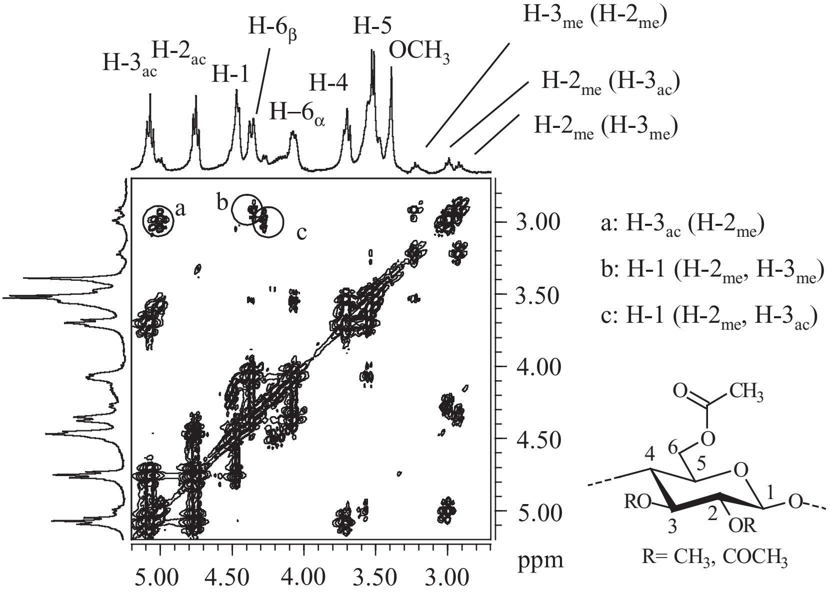


Figure 9.
COSY NMR spectrum of peracetylated 2,3-*O*-methyl cellulose (degree of substitution 0.2) in the range from 2.5 to 5.5 ppm recorded in $CDCl_3$. Index "ac" means acetyl groups and index "me" means methyl groups.

Table 2.
3-Mono-O-Functionalized Cellulose Ethers Synthesized and their Solubility.

Substituent at position 3	Soluble in[a]					Ref.
	Ethanol	DMSO	DMA	THF	H_2O	
Methyl	−	−	−	−	−	[28]
Ethyl	−	+	+	−	+	[29]
Allyl	−	+	+	−	−	[28]
n-Pentyl	+	+	+	+	−	[30]
iso-Pentyl	+	+	+	+	−	[30]
Dodecyl	−	−	−	+	−	[30]

[a] *N*,*N*-Dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), soluble (+), insoluble (−).

insoluble and different repeating units occur in the polymer, i.e., in addition to glucose, dimethylated repeating units as well as monomethylated ones functionalized at position 2 or 3 may be present after peracetylation. The COSY NMR spectrum shows main signals that correspond to a cellulose triacetate with peaks at 5.08 (H-3), 4.75 (H-2), 4.47 (H-1), 4.36 (H-6_β), 4.06 (H-6_α), 3.71 (H-4), and 3.52 ppm (H-5) (Figure 9). The resonance of the methoxy function appears at 3.39 ppm. Moreover, peaks of low intensity in the range from 2.9 to 3.3 ppm are detected. One signal is assigned to the methylated position 3 ($\delta = 3.22$ ppm). The two other signals belong to the methylated position 2 depending on the substituents on position 3; 2.98 ppm (position 3 is acetylated) and 2.90 (position 3 is methylated).

The resonance of H-1 is also sensitive to the structure of the repeating unit, i.e., in addition to the H-1 signal of the triacetate structure, two other peaks are visible at 4.30 ppm (position 2 and 3 methylated) and 4.27 ppm (position 2 methylated, position 3 acetylated). Finally, a cross-peak at 4.98 ppm is detected for H-3 neighboring to a methylated position 2.

3-Mono-O-functionalized cellulose ethers

A variety of 3-mono-*O*-alkyl celluloses was synthesized (Table 2). Conversion of 2,6-di-*O*-TDMS cellulose with excess methyl iodide or allyl chloride in THF in the presence of NaH afforded the

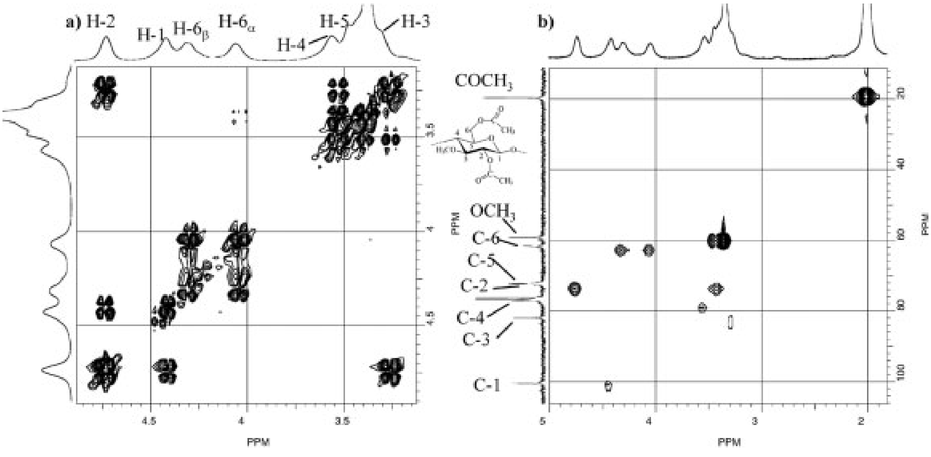


Figure 10.
COSY (**a**) and HMQC NMR spectra (**b**) of 3-O-methyl-2,6-di-O-acetyl cellulose recorded in $CDCl_3$.

Table 3.
Structure Parameters of 3-*O*-alkyl Celluloses (adapted from[30]).

Cellulose ether	Molar mass (g/mol)	Degree of polymerization	Aggregation number
3-*O*-dodecyl	61 880	200	1
3-*O*-*n*-pentyl	$3.8\,10^6$	16 478	82
3-*O*-*iso*-pentyl	301 000	1 309	6.5

fully etherified polymers.[28] Repeated treatment with TBAF yielded the 3-mono-*O*-functionalized cellulose ethers. While the 3-mono-*O*-allyl cellulose is free of silicon, traces of silicon containing by-products remained in the 3-mono-*O*-methyl cellulose even after extensive purification.

The 3-mono-*O*-methyl cellulose is insoluble and swells in aprotic-dipolar solvents indicating a strong network of hydrogen bonds. Dissolution occurred only after addition of LiCl that destroys intra- and intermolecular interactions.

3-Mono-*O*-allyl cellulose is soluble in DMSO and *N*,*N*-dimethylformamide. Other organic solvents and water do not dissolve 3-mono-*O*-methyl- and 3-mono-*O*- allyl cellulose. The structure was characterized by means of two-dimensional NMR spectroscopy of the peracetylated polymers (3-mono-*O*-methyl-2,6-di-*O*-acetyl cellulose, Figure 10). The signals detected in the ^{1}H NMR spectrum are: 0.04–1.23 ppm (not shown in Figure 10, CH$_3$, Si-CH$_3$), 2.03, 2.05 (COCH$_3$), 3.37 (H-3), 3.48 (H-5), 3.57 (H-4), 4.08 (H-6$_\beta$), 4.35 (H-6$_\alpha$), 4.46 (H-1), 4.77 (H-2) and in the ^{13}C NMR spectrum: 20.70, 20.79 (CO$\underline{C}$H$_3$), 59.86 (O$\underline{C}$H$_3$), 62.34 (C-6), 72.76 (C-5), 72.98 (C-2), 77.64 (C-4), 82.49 (C-3), 100.88 (C-1), 169.34, 170.36 (C=O).

Increase of the alkyl chain length changes the solubility of the polymers (see Table 2). For instance, 3-*O*-*n*-pentyl-, 3-*O*-*iso*-pentyl- and 3-*O*-dodecyl ethers are soluble in THF. Light scattering investigations of the polymer solution revealed a different aggregation behavior. Aggregation numbers of 6.5 (*iso*-pentyl) and 83 (*n*-pentyl) were calculated. The 3-*O*-dodecyl ether forms molecularly dispersed solutions if the concentration is less than 2 mg/l (Table 3).[30]

3-Mono-*O*-ethyl cellulose dissolves in aprotic-dipolar solvents and is, in contrast to other 3-*O*-ethers, soluble in water.[29,31] Also in the case of samples with high

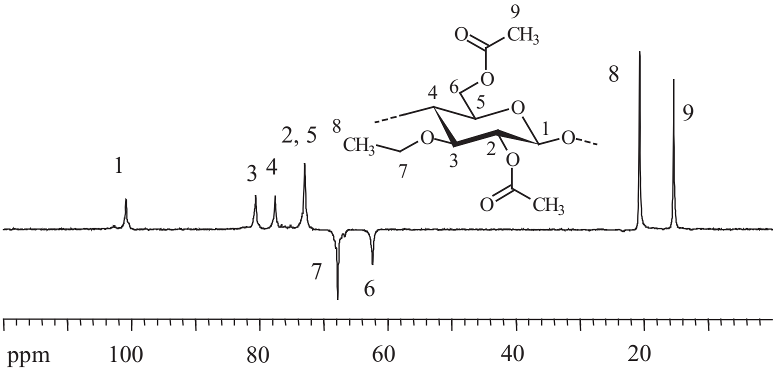


Figure 11.
DEPT 135 NMR spectrum of 3-mono-*O*-ethyl-2,6-di-*O*-acetyl cellulose (degree of substitution of ethyl groups = 1.05) prepared from spruce sulfite pulp.

Table 4.
Thermoreversible Gelation of Ethyl Cellulose Depending on the Functionalization Pattern.

Functionalization pattern	Cellulose	DP[a]	DS[b]	Cloud point (°C, 4% in H_2O)
Statistic	–[c]	–[c]	1.3	33
	–[c]	–[c]	1.1–1.6[d]	≈30[d]
Non-statistic	Avicel	300	0.67	56
3-Mono-*O*-ethyl	SSP[e]	590	1.05	63
	Avicel	300	1.00	63

[a] Degree of polymerization of the starting material.
[b] Degree of substitution, determined by means of ^{1}H NMR spectroscopy of the peracetylated samples.
[c] Not known.
[d] Values taken from.[32]
[e] Spruce sulfite pulp.

degree of polymerization (DP), NMR spectroscopy of the peracetylated samples revealed the uniform structure (Figure 11).

Several cellulose ethers exhibit the phenomenon of thermoreversible gelation. It is known that ethyl cellulose with DS 0.7–1.7 becomes water insoluble already at about 30 °C (Table 4).[32]

In contrast, an ethyl cellulose, which was prepared via induced phase separation (conversion of cellulose dissolved in DMA/LiCl with solid NaOH and ethyl iodide), possesses a distinct higher cloud point temperature of 56 °C. A block-like distribution of substituents along the polymer chain is assumed for this polymer.[33] A similar value (63 °C) was determined for the structural uniform 3-mono-*O*-ethyl cellulose independent of the DP.

Influence of a Pulp Treatment with NaOH or H_3PO_4 prior to the Reaction

The influence of NaOH- and H_3PO_4 treatments on the DP, hemicellulose content, the crystallinity, and reactivity regarding the TDMS protecting group technique was studied.[34] Table 5 gives an overview of the pulps used. The pulps were mercerized with aqueous NaOH (18%, w/v) for 1 h and washed extensively with water[37] or treated with 85% H_3PO_4 for 20 min and washed with THF and water.[38] The wet samples were freeze-dried in order to preserve the crystalline structure. For comparison, the untreated pulps were dried in the same manner.

Figure 12 shows the change of DP by the treatment. The mercerization has no effect on the chain-length of the cellulose. In contrast, the treatment with H_3PO_4 leads to significant polymer degradation. Starting from DP 1433 (cellulose **A**) DP values of about 300 result.

NaOH and H_3PO_4 reduce the content of hemicellulose (Figure 13, celluloses **B**, **C** and **D**, except sample **A** that is free of hemicellulose).

It must be pointed out that both treatments lead to a significant decrease of the hemicellulose content. Whereas H_3PO_4 leads to a decrease of hemicelluloses of about 40 to 60%, NaOH solution can be

Table 5.
Specifications of the Celluloses Used for the Investigation.

Cellulose	Code	DP_{Cu}[a]	Hemicellulose content (%)[b]
Cotton Linters	**A**	1433	0
Beech sulfite pulp	**B**	1157	14.80
Beech sulfite pulp	**C**	604	5.40
Spruce sulfite pulp	**D**	504	3.40

[a] Degree of polymerization determined by viscometry in cupriethylenediamine solution.[35]
[b] Determined by means of HPLC after complete chain degradation.[36]

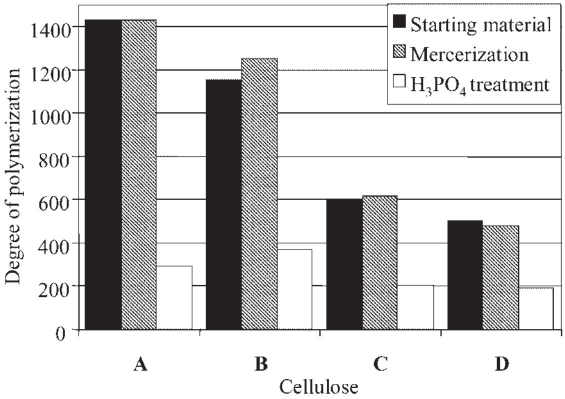


Figure 12.
Dependence of the degree of polymerization of the cellulose samples on the treatment with NaOH or H_3PO_4.

considered to be more effective. It removes from about 70% to almost 100% of hemicelluloses (pulp **D**).

^{13}C CP/MAS NMR spectra were used to determine the crystallinity of the samples. Figure 14 exemplarily shows the spectra of cellulose **A**. The peak of C-4 consists of an amorphous and a crystalline part and was used for the calculation of the crystallinity. The ratio of the two signals was determined by a line-fitting method.[39]

It becomes obvious that the treatment of the pulps with NaOH or H_3PO_4 leads to a decrease of the crystallinity (Table 6). However, the efficiency depends on the type of pulp. For instance, cotton linters **A** with a degree of crystallinity of 61.5% possesses a degree of crystallinity of 29.6% after mercerization and of 33.2% after H_3PO_4 treatment. The decrystallizing effect is less pronounced in case of the pulps **B**-**C**. The crystallinity of pulp **B** (45.4%) can be reduced to 31.1% by mercerization and to 36.2% by H_3PO_4. A more drastic difference was found for pulp **C** with a degree of crystallinity of 46.1%. The decrystallizing effect of NaOH is higher (25.7%) than the effect of H_3PO_4 (38.0%). Mercerization and H_3PO_4 treatment pulp **D** result only in small changes of the crystallinity.

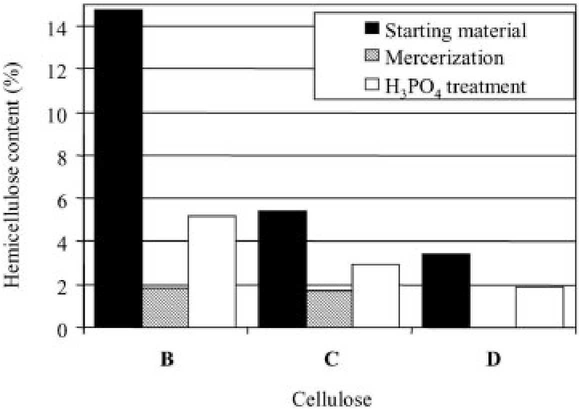


Figure 13.
Dependence of the hemicellulose content of the celluloses on the treatment with NaOH or H_3PO_4.

Assessment of the reactivity by conversion of the pulps with thexyldimethylchlorosilane

The DS realized by conversion of the pulps dissolved in DMA/LiCl with TDMS-Cl in the presence of imidazole was used to assess the reactivity. The reaction was carried out for 24 h at 100 °C, as applied for the conversion of low-DP cellulose (Figure 7). Due to the strong depolymerization of pulp by H_3PO_4, only the mercerized samples were subjected to the silylation experiments. Already the dissolution of the pulps in DMA/LiCl showed remarkable differences. Before mercerization the pulps give turbid solutions (Figure 15).

Table 6.
Change of the Crystallinity of the Different Celluloses According to the Treatment with NaOH and H_3PO_4.

Cellulose	Crystallinity (%)		
		Treated with	
		NaOH	H_3PO_4
A	61.5	29.6	33.2
B	45.4	31.1	36.2
C	46.1	25.7	38.0
D	45.0	37.0	43.6

On the contrary, a clear solution is obtained after mercerization. A cellulose of low DP, e.g. Avicel, yields a DS of 2.0 under comparable conditions.[28] The silylation experiments revealed that DS 2 can not be

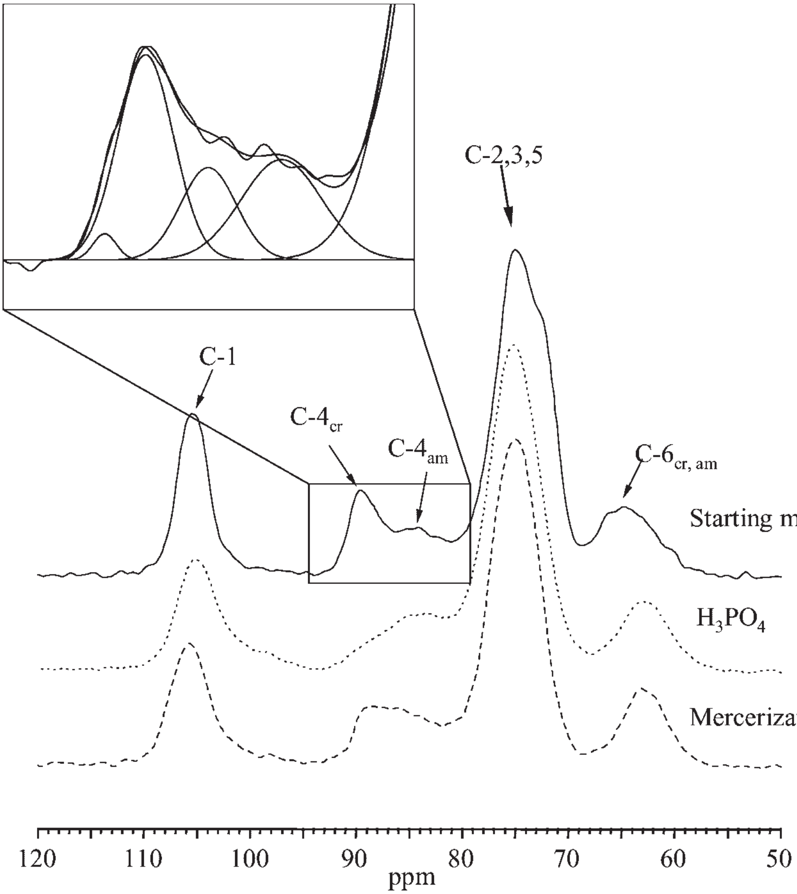


Figure 14.
^{13}C cross-polarization/magic angle spinning NMR spectra of cotton linters **A** and the mercerized- and H_3PO_4 treated samples. The amorphous (index am) and crystalline (index cr) parts of the C-4 peak were used for the calculation of the crystallinity.

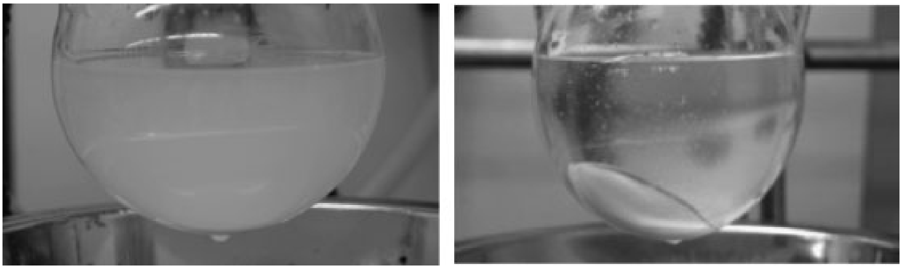


Figure 15.
Solutions of cotton linters (**A**, Table 5) in *N*,*N*-dimethylacetamide/LiCl before (left) and after mercerization (right).

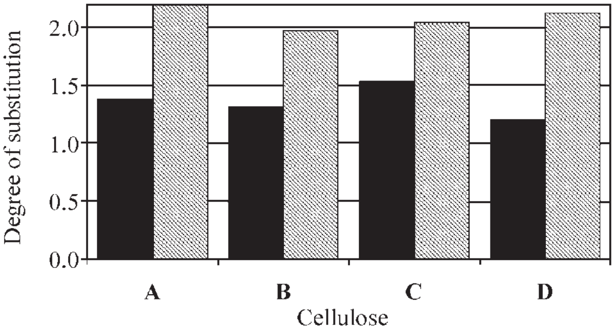


Figure 16.
Silylation of different celluloses in *N*,*N*-dimethylacetamide/LiCl before (■) and after (▨) NaOH treatment.

achieved with the pulps before the pretreatment (Figure 16). The maximum DS obtained is 1.53 (pulp **C**). Pulp **D** yields a TDMS cellulose with DS as low as 1.20. The TDMS celluloses are insoluble in common organic solvents, which may be caused by inhomogeneous polymer composition. They swell in THF, hexane, toluene, and chloroform. After mercerisation and subsequent silylation, a DS of 2 was realized with all pulps. These samples are completely soluble in THF and chloroform. This indicates the activating effect of the mercerization and enables the synthesis of 2,6-di-*O*-TDMS cellulose of high DP.

Conclusion

The synthesis of regioselectively functionalized cellulose derivatives is still a challenge in research of this important class of biopolymers. It has been shown that the primary OH group and the secondary OH group at position 2 can be selectively protected. Subsequent functionalization and deprotection afforded polymers with controlled functionalization pattern. Such derivatives are valuable for the establishment of structure-property relationships. NMR spectroscopy is a powerful tool to characterize the structure of regioselectively functionalized derivatives and is able to detect also structural features of low extent. The results showed that further studies are still needed. For instance, no simultaneous protection of both secondary OH groups of cellulose could be achieved up to now.

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