

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Chemical modification of cellulose
New possibilities of some classical routes

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Cover: Picture of an Erlenmeyer flask containig a never-dried TCF-bleached (peroxide-based bleaching) Scandinavian softwood kraft pulp supplied by Södra Cell used in this work as a starting material for some of studied modification reactions

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Abstract

Owing to its unique structure, along with the inexhaustible renewability, cellulose has been a subject of scientific and commercial interest for over 150 years. However, given attractive structural properties, such as stiffness, hydrophilicity, stereoregularity, potential for chemical modifications and ability to form superstructures, utilization of this biopolymer is far below its potential. The prospect of improving it is closely connected with chemical modification possibilities.

The research presented in this thesis explores these possibilities with the emphasis on reactive groups employed for substitution of cellulose backbone in different modification systems. Under homogeneous conditions, in the system dimethyl sulfoxide/tetrabutylammonium fluoride four new esterification agents for *in situ* activation of carboxylic acids were successfully employed in preparation of cellulose esters.

In heterogeneous aqueous systems, focus was on readily quantified cationizations of cellulose accomplished by oxirane mediated etherifications. Reactions of two new etherification agents, 2-oxiranylpiperidine and N-oxiranylmethyl-N-methylmorpholinium chloride were explored. Etherification with the former provided cellulose with reactive piperidine moieties that could be utilized in further functionalizations, *i.e.* quaternizations of the piperidine nitrogen yielding cationic celluloses. Further, etherification with N-oxiranylmethyl-N-methylmorpholinium chloride introduced good leaving groups, N-methylmorpholine moieties, which could be employed in subsequent self-crosslinking reactions. Obtained crosslinked materials exhibited remarkably altered structure accessibility, highly defined by choice of crosslinking conditions. Oxirane mediated cationization was further applied on surface cationization of cellulose nanocrystals. Reaction with N-oxiranylmethyltrimethylammonium chloride yielded sufficient surface cationization required to provide electrostatic colloidal stabilization of their aqueous suspensions. Interestingly, these suspensions exhibited thixotropic gelling along with the typical tendencies to self-order.

Another cationization method applied on cellulose nanocrystals was studied, as well. It was based on intermediate esterification of cellulose nanocrystals with chloroacetylchloride in a non-aqueous system, followed by subsequent substitution with a tertiary amine. This procedure yielded highly cationized cellulose nanocrystals with varying extent of surface and bulk modification. In spite of overall high surface cationization the modified nanocrystals lacked colloidal stabilization in aqueous suspensions, which is likely an effect of strong interactions between introduced groups.

Key words: Cellulose esters, Cellulose ethers, Cellulose characterization, Crosslinking of cellulose, Cationization, Cellulose nanocrystals

List of publications

The thesis is based on results contained in the following papers, referred to by Roman numerals in the text.

- I New coupling reagents for homogeneous esterification of cellulose
Hasani M, Westman G
Cellulose 14(4), 347-356, 2007

- II Cationization of cellulose by employing N-oxiranylmethyl-N-methylmorpholinium chloride and 2-oxiranylpyridine as etherification agents
Hasani M, Westman G, Potthast A, Rosenau T
Journal of Applied Polymer Science 114 (3), 1449–1456, 2009

- III Self-crosslinking of 2-hydroxypropyl-N-methylmorpholinium chloride cellulose fibres
Hasani M, Westman G
Submitted to Cellulose

- IV Cationic surface functionalization of cellulose nanocrystals
Hasani M, Cranston ED, Westman G, Gray DG
Soft Matter 4, 2238-2244, 2008

- V Cationization of cellulose nanocrystals through introduction of betaine esters
Hasani M, Westman G
Submitted to Cellulose

Contributing report

The author has made the following contributions to the papers:

- Paper I Main author. Responsible for experimental work and manuscript writing.
- Paper II Main author. Main part of the experimental work; manuscript writing. The molecular weight distribution analysis was performed by Dr. Antje Potthast.
- Paper III Main author. Responsible for experimental work and manuscript writing.
- Paper IV Main author. Responsible for the synthetic work and the main part of the characterization work; contributed to manuscript writing. Characterization work and manuscript writing were performed in collaboration with Dr. Emily D. Cranston and Dr. Derek G. Gray.
- Paper V Main author. Responsible for experimental work and manuscript writing. AFM imaging was performed by Anders Mårtensson.

Abbreviations

AFM	atomic force microscopy
AGU	anhydroglucose unit
BET	Brunauer, Emmett, Teller
CDI	N,N'-carbonyldiimidazole
CNC	cellulose nanocrystals
CDCl ₃	deuterated chloroform
DABCO	1,4-diazabicyclo[2.2.2]octane
DCC	1,3-dicyclohexylcarbodiimide
DMAc	dimethylacetamide
DMF	dimethylformamide
DS	degree of substitution
DP	degree of polymerization
DMSO	dimethylsulfoxide
DMT-MM	4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride
EPTMAC	2,3-epoxypropyltrimethylammonium chloride
FSP	fibre saturation point
FTIR	Fourier transformed infrared
LiCl	lithium chloride
MDS	molar degree of substitution
M _w	weight average molar mass
NMM	N-methylmorpholine
NMMO	N-methylmorpholine oxide
NMR	nuclear magnetic resonance
4-PP	4-pyrrolidinopyridine
TBAF	tetrabutylammonium fluoride
TEA	triethylamine
TFA	trifluoroacetic acid
WRV	water retention value

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1. INTRODUCTION

1.1 Background

The history of cellulose utilization is as old as that of mankind. It has its origins in the indispensable use of wood as construction material and fuel and comprises thousands of years utilization of fibre plant cellulose in clothing and papermaking. However, development of methods for large-scale isolation of cellulose from wood in the 19th century, along with contemporary advances in chemical reagents manufacture opened up for new applications, such as starting material for chemical modifications. As the chemical industry advanced and efforts on elucidation of cellulose structure gained increased understanding for modification processes, there was a growing excitement in utilization of cellulose for new value-added products. As a result, new cellulosic materials emerged, including cellulose nitrates, acetates, carboxymethylcellulose and new regenerated fibres. However, only a couple of decades later many of these materials were gradually displaced by cheaper petroleum-based polymers when focus shifted from cellulose to the more profitable petroleum chemistry.

It took another couple of decades before cellulose research received new impetus. This time due to the increased awareness about limited nature of petroleum resources and a growing urge to provide a sustainable alternative based on renewable materials. Again, cellulose as the most abundant renewable polymer came in focus. And again, chemical modification was recognized as the main tool in broadening its utilization, stimulating research towards new modification methods. As a result, cellulose chemistry issues, such as introduction of new structures to the cellulose backbone, improved reaction selectivity and development of new modification media have become the subject of intensified research. These efforts contribute constantly to improved application and characterization possibilities.

Some of them will be highlighted in forthcoming chapters in order to give a background to the present cellulose research and to introduce the reader to the objectives and findings of this work.

1.2 Aim and outline of the thesis

In general, the present thesis is aimed towards new cellulose derivatives and new modification pathways for cellulose. The work covers etherifications and esterifications, modification of different cellulose substrates and employment of both heterogeneous and homogeneous conditions, along with characterization efforts. Cationization reactions stand out here as easily quantified modifications adding interesting and readily detectable material properties. They thus dominate as reactions of choice primarily due to the characterization benefits, but also as efficient tools in affecting material features. While, possibilities and challenges of chemical modifications of cellulose are in the focus, characterization - even though essential for comprehensive

understanding of chemical modifications - is limited to estimations of average chemical conversion and analysis of the obtained material properties, mainly due to the lack of accessible analytical methods during these studies.

The overall work can be divided into three parts: the first part dealing with homogeneous esterification through the action of new esterification agents, the second part exploring preparation of cationic ethers under aqueous alkali conditions including further application of this chemistry to crosslinking possibilities, and the third part focusing on cationization of nanocrystalline cellulose.

As an introduction to the field, Chapter 2 describes cellulose structure and the principles of its chemical modification, followed by a short account of the characteristic analytical methods used in this work, in Chapter 3. Further, Chapter 4 presents the study of new esterification agents employed under homogeneous conditions. Chapter 5 reports on our findings on cellulose cationization in aqueous media, using oxirane functionalized reagents, with further applications to self-crosslinking reactions. In Chapter 6 studies on the modification of cellulose nanocrystals are presented, including further implementation of the cationization chemistry explored in Chapter 5. General conclusions and outlook are discussed in Chapter 7.

2. CELLULOSE

2.1 Cellulose sources

Approximately half of the biomass produced continuously by nature through the photosynthetic fixation of carbon dioxide is cellulose. The largest quantities are incorporated into the cell wall of higher plants, especially woody plants, where cellulose is embedded in the matrix of hemicelluloses, lignin and comparably small amounts of pectins and proteins. Wood pulp, produced by the large-scale isolation of cellulose through chemical digestion of surrounding cell wall components is, thus, the most important commercial source of this polymer.

Cellulose occurs also as the seed hairs of cotton, the extracellular product of some bacteria, e.g. *Acetobacter xylinum* and *Acanthamoeba castellani* (Jonas, Farah, 1998; Vandamme *et al.*, 1998), as a cell wall component of fungi and some algae, e.g. *Valonia ventricosa* (Horikawa, Sugiyama, 2007) and in marine animals such as tunicates (Kimura, Itoh, 2001).

Cotton and cellulose producing bacteria are important as sources providing cellulose in essentially pure form, the latter being only of scientific interest so far.

2.2 Structure

Structurally, cellulose is a carbohydrate polymer with characteristic structure regularity and possibilities for strong intra- and intermolecular interactions. One of the main consequences of this structure, as will be explored in the following chapters, is the striking tendency to self-order, giving rise to a specific supramolecular arrangement, which is in many aspects decisive for physical and chemical properties of cellulose. Depending on the biological origin, supramolecular structures are further organized in a well-defined gross architecture defined as cellulose morphology. Here a short description of the morphology of woody plants cellulose, as the most abundant cellulose form, will be given. Figure 1 illustrates different hierarchical levels of cellulose structure.

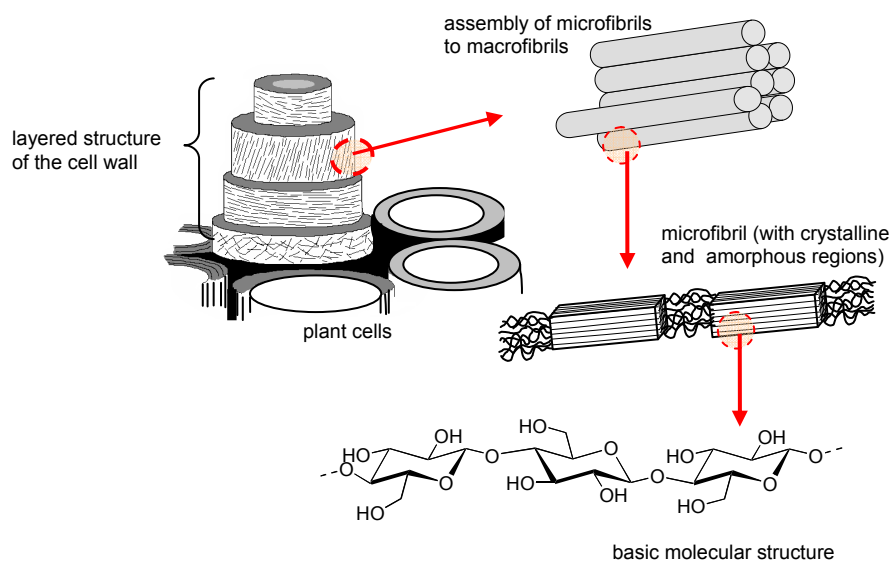


Figure 1. Schematic presentation of different structural levels of cellulose

2.2.1 Basic molecular structure

The term cellulose can be traced back to 1838 and the French chemist Anselme Payen who used it for purified fibrous plant tissues that according to his findings consisted of a glucose based material, similar to starch (Zugenmaier, 2008). Indeed, cellulose is, just like starch a carbohydrate polymer built up of glucose units. However it took several decades of basic carbohydrate research combined with crystallographical studies to reveal that the glucose Payen discovered in his extractions is in the form of D-anhydroglucose pyranose units, AGUs, adopting chair conformation (Ferrier, 1963) and being linked in straight chains by 1,4- β -glycosidic bonds (Irvine, Hirst, 1923; Chu, Jeffrey, 1968; Klemm *et al.*, 1998a; Pérez, Mazeau, 2005) (Figure 2).

The number of AGUs in the chain, referred to as the degree of polymerization, DP, varies with cellulose source. Using a mild nitration of cellulose combined with light scattering Goring and Timell (Goring, Timell, 1962) could estimate DP for wood cellulose to 9000-10 000. Significantly lower values are typical for processed forms such as regenerated cellulose and cellulose powders.

Due to the 1,4- β -glycosidic linkages each AGU contains free hydroxyl groups at C-2, C-3 and C-6 positions. They are placed equatorially creating a hydrophilic site in a ring plane, whereas hydrogen atoms adopt axial positions.

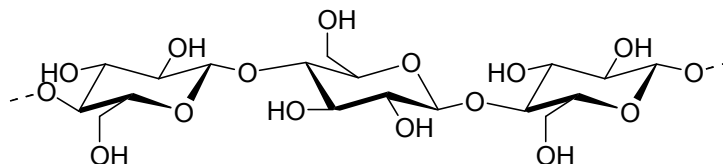


Figure 2. Basic molecular structure of cellulose.

This structure provides the basis for characteristic hydrogen bonding having decisive influence on chain conformation and further on supramolecular organization (Kondo, 2005). As a consequence of the optimization of bonding angles, primarily with respect to hydrogen bonds, every second

AGU ring is rotated approximately 180° in the plane imposing two-fold-helical conformation of the chain.

Another factor affecting hydrogen bonding is the rotational conformation of the hydroxyl group at C-6. As shown by ^{13}C NMR and X-ray experiments (Horri, Hirai, 1983), there are three possible conformations that differ in the position of the C-6 hydroxyl group with respect to O-5 and C-4, shown in Figure 3. According to recent studies the *tg* conformation occurs in native cellulose crystals, (Nishiyama *et al.*, 2002) while *get* is characteristic of the crystalline structure of regenerated polymer (Isogai *et al.*, 1989; Langan *et al.*, 2001). *gg* conformation together with mixed *gt* and *tg* can be found in non-ordered regions.

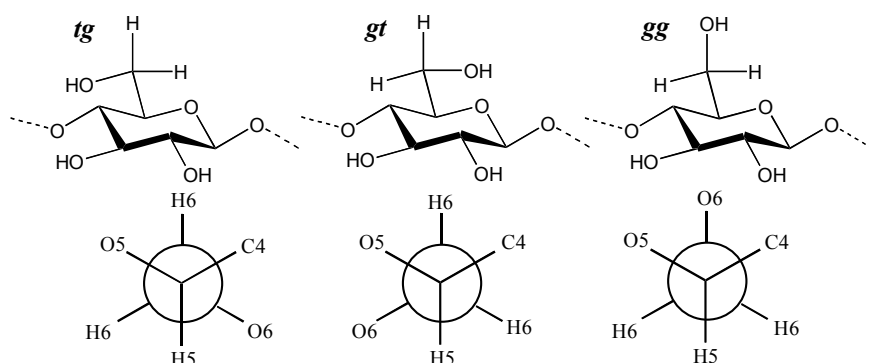


Figure 3. Rotational conformations of the cellulose hydroxymethyl group. *t* and *g* denote trans and gauche conformations corresponding to the dihedral angles of 180° and 60° , respectively. The first latter denotes configuration relative to O-5, the second letter denotes that relative to C-4.

At last, the directional chemical asymmetry of the cellulose chain should be mentioned. It originates from the fact that the two chain ends are chemically different. The anhydroglucose end unit containing a free hydroxyl group at the C-1 position is reducing, since it is in equilibrium with the aldehyde structure. The other end containing a free 4-OH group is non-reducing (Figure 4). This asymmetry is translated to isolated cellulose crystallites showing a clear distinction between the two ends of the rodlike crystalline particles (Kuga, Brown, 1988).

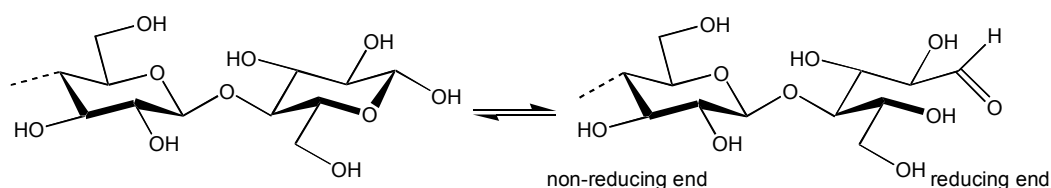


Figure 4. Directional chemical asymmetry of the cellulose chain due to the existence of a reducing and non-reducing end.

2.2.2 Supramolecular structure

Determined by hydrogen bonding and van der Waals interactions

The supramolecular structure of cellulose is a result of strong hydrogen bonding leading to self-ordering of cellulose chains in partially crystalline microfibrils, usually seen as basic units of cellulose fibrillar structure.

As a consequence of the equatorial position of hydroxyl groups, imposing strong hydrogen bonding parallel to the AGU ring plane, cellulose chains in microfibrils are arranged in sheets. Here both intra- and interchain interactions are important, the former contributing to the regularity of the structure and the latter being responsible for the chain interactions in sheets. A standard intrachain hydrogen bond, found in practically all cellulose structures, exists between the 3-OH and O-5 of the adjacent AGU. According to Kondo this bond often remains even in the dissolved state (Kondo, 1994). Interchain bonds are generally assumed to involve the 6-OH of one chain and the 2-OH and/or 3-OH of the neighbouring chain. However, 6-OH and 2-OH are often involved in intermolecular bonds as well. For instance, the intramolecular bond between the 2-OH and 6-OH of the adjacent AGU is typical for crystalline portions of native cellulose (Gilbert, Kadla, 1998; Kondo, 2005), facilitating the *tg* conformation of the hydroxymethyl group. Sheets of cellulose chains are further organized in layered structures held together primarily by van der Waals bonds arising from the interactions of axially placed C-H bonds (Kondo, 2005).

Facilitated by biosynthesis but not perfect

The above described self-ordering of cellulose is highly facilitated by the manner of biosynthesis proceeding in transmembrane enzymatic complexes responsible for the simultaneous extrusion of several parallel chains that can spontaneously aggregate. The exact morphology of these complexes is genetically determined and displays thus a significant variety.

The morphology observed in algae and land plants is usually referred to as rosette and is built up of six subunits organized in rings (Brown *et al.*, 2000; Kimura, Kondo, 2002; Cosgrove, 2008). Although the biosynthesis of cellulose has been investigated for several decades, there are still a lot of uncertainties, many of them concerning number of synthesizing complexes in the rosette subunits and possible aggregation of individual rosettes. Recent studies imply existence of 3-4 synthesizing enzymes per rosette subunit (in contrast to the commonly suggested 6) and possibility of cocrystallization of chains produced by two or more individual rosettes (Haigler, Roberts, 2009).

However, the order of the aggregated chains is not perfect along the whole chain length and apart from crystalline, there are also non-ordered regions. The content of these regions depends on the cellulose source and the treatment of the material.

Crystalline portions can appear in different arrangements

Depending on the source and/or treatment, crystalline portions of microfibrils can principally exhibit five different crystalline modifications: cellulose I – occurring as α and β allomorph, cellulose II, cellulose III and cellulose IV. Generally, deviations among crystalline allomorphs arise from alterations in hydrogen bonding, usually involving a change in the rotational conformation of the 6-OH. Accompanying alteration in the chain conformation results in a shift of intrasheets within the cellulose fibril and leads to formation of a new crystalline arrangement (Klemm *et al.* 1998a; Horii, 2001; Zugenmaier, 2001).

Cellulose I is native cellulose and can occur as α and β allomorph. It is characterized by the *tg* conformation of 6-OH, parallel chain arrangement and generally less dense interchain hydrogen bonding (Nishiyama, 2002), as compared to the thermodynamically more stable regenerated form, cellulose II. Apart from the regeneration of cellulose I, cellulose II can be readily obtained by treatment of native cellulose with sufficiently strong alkali, a commercial process known as mercerization. For the cellulose II predominant *gt* conformation of 6-OH groups is suggested – a conformation contributing to the more efficient interchain bonding – along with the antiparallel chain arrangement (Gessler *et al.*, 1995; Kroon-Batenburg, Kroon, 1997; Langan *et al.*, 2001).

Cellulose III is prepared by treating cellulose I or II with liquid ammonia. Heating cellulose III with glycerol yields in turn cellulose IV. Both treatments are reversible and result in severe decrystallization (Isogai *et al.*, 1989).

2.2.3 Morphological structure

The morphological structure of cellulose is defined by further organization of cellulose micro- and macrofibrils as parts of biological functional units in various organisms.

Typical for native plant cellulose is the arrangement in layers of different density and texture. This reflects the basic morphology of the fibre cell wall (Figure 5), where layered structures of parallel cellulose fibrils are embedded in a matrix of other polysaccharides (hemicelluloses) and lignin (Kerr, Goring, 1975; Burgert, 2006).

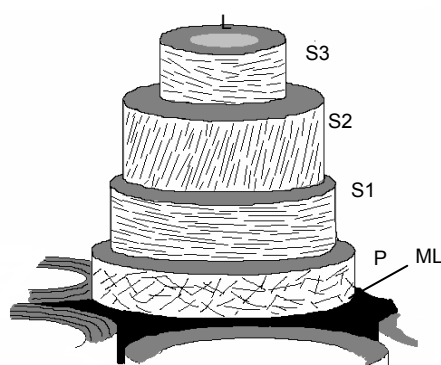


Figure 5. Schematic representation of the layered structure of the woody plants cell wall. *P* denotes layers forming the primary cell wall; *S1*, *S2*, *S3* layers of the secondary cell wall. Lumen – the rest of the cytoplasmic channel – is denoted by *L*; and middle lamella – the pectin rich intracellular material – by *ML*.

Upon removal of the main part of other cell wall components during the isolation of cellulose (pulping), pores of varying sizes ranging from nano to micro dimensions are created (Stone, Scallan, 1968; Fahlen, Salmén, 2003; Fahlen, Salmén, 2005). Their presence expands drastically the total surface area of cellulose fibres and is thus of crucial importance for accessibility in chemical modifications. The pore volume is highly sensitive to drying and swelling. The former is known to cause almost irreversible closure of pores, resulting in a remarkable reduction of accessibility (Häggkvist, Ödberg, 1998; Fernandes *et al.*, 2004). Swelling, on the other hand, is the opposite process and refers to the uptake of water or other swelling agent upon considerable disruption of intermolecular hydrogen bonds. Depending on the swelling agent this process can be limited to non-ordered regions only, or can affect the crystalline regions as well. In each case enhanced structure accessibility is obtained (Stone, Scallan, 1968; Klemm *et al.* 1998a; Jaturapiree *et al.*, 2008).

As a comparison, the morphology of cotton and especially bacterial cellulose is significantly different due to the absence of the cell wall polymers. This dictates a more compact morphology characterized by significantly lower accessibility.

2.3 Chemical modification of cellulose

2.3.1 General features – reactivity, accessibility and reaction products

Chemical modification of cellulose is mainly based on conversions of its alcohol groups, comprising a broad spectrum of chemical reactions applicable on alcohols, *e.g.* etherifications, esterifications, oxidations, along with corresponding crosslinking reactions based on the cellulose polyfunctionality. Furthermore grafting and formation of addition compounds through complexation mechanisms should also be mentioned. In a broader sense hydrophilic cleavage of glycosidic bonds by the action of acids, as well as base catalyzed peeling reactions at reducing ends may be seen as chemical modifications employed in the preparation of cellulose powders and crystallites (Isogai, 2001; Heinze, 2005).

Properties of the obtained products are defined by the nature, amount and distribution of introduced substituents. In some reactions the consequences of accompanying chain degradation have to be taken into account as well, since the molecular weight of the product usually has an important role. The extent of chemical conversion is expressed by the average number of substituted hydroxyl groups per AGU, referred to as the degree of substitution, DS. In the case of cascade reactions, the chemical conversion is further quantified by molar degree of substitution, MDS, defined as the average number of substituents attached to AGU. Uniform substituent distribution usually enhances the effect of modification and is recognized as an important factor in governing end-product properties (Ithagaki *et al.*, 1997; Kondo, 1997; Sekiguchi *et al.*, 2003).

However, the intrinsic reactivity of the present alcohols and acetals is often of minor importance for the outcome of modifications, as the supramolecular structure strongly controls their accessibility for chemical reagents. This is especially important for reactions performed in cellulose suspensions, *i.e.* heterogeneous systems, where the gross structure of the polymer is principally maintained (Klemm *et al.*, 1998a). In the case of complete dissolution the supramolecular structure is erased and conditions for chemical conversion are remarkably altered compared to heterogeneous reactions.

There is, thus, a distinction between heterogeneous and homogeneous modifications in cellulose chemistry. In spite of numerous solvent systems for cellulose developed through the years, all commercial derivatizations of cellulose are still based on heterogeneous processes, associated with low costs and low environmental impact (Klemm, 1998a). Nevertheless, the potential of the homogeneous processes is today widely recognized and a variety of cellulose derivatives is prepared through homogeneous reactions on the lab-scale with the advantage of good product control.

As the work in this thesis embraces both homogeneous and heterogeneous procedures, some main features of both approaches will be highlighted in the following text. Subsequently, a short introduction to cellulose modification through esterification, etherification and crosslinking will be given, as a background for the studied reactions. For an overview on cellulose modification through oxidation, which has not been included in this study, the reader is referred to the respective literature (*e.g.* Jackson, Hudson, 1937; Yackel, Kenyon, 1942; Isogai, Kato, 1998; Kim, 2000; Tahiri, Vignon, 2000; Potthast *et al.*, 2007).

2.3.2 Heterogeneous processes – accessibility and reaction media

In heterogeneous systems accessibility is the crucial factor determining the course of chemical modifications, usually leading to non-uniform conversions with the preference for easily accessible low ordered regions. Structurally, as already mentioned, accessibility is determined by the supramolecular structure and the hierarchical organization of cellulose. However, from the reactivity point of view it highly depends on the type and conditions of chemical modification (Schleicher *et al.*, 1989; Klemm *et al.*, 1998a). Generally, reaction media with the ability to disrupt interchain hydrogen bonds and enhance structure accessibility are referred to as swelling agents. They are known to promote the uniformity and effectiveness of chemical reactions (Mantanis *et al.*, 1995; Fidale *et al.*, 2008). Non-swelling media, on the other hand, are characterized by inherently poor interaction with cellulose and therefore generally restrict chemical modification to the fibril surface and low ordered areas (Baiardo *et al.*, 2000; Freire *et al.*, 2006; Viera *et al.*, 2007).

Moreover, the chemical reaction itself often has a significant impact on accessibility, as it disrupts hydrogen bonds by the chemical conversion of cellulose hydroxyls. As a result, some reactions start under heterogeneous conditions that gradually, as the conversion proceeds, transform into homogeneous (Liebert *et al.*, 2005). Still, most common heterogeneous reactions are conducted under conditions of limited swelling, associated with the overall retention of fibrous solid state structure.

Methods commonly employed to enhance accessibility in these systems rely on decrystallization and conversion to more porous arrangements (Schleicher, Kunze, 1988), including e.g. treatment with aqueous alkali solutions, ammonia and amines (Wagenknecht *et al.*, 1992; Nishiyama, Okano, 1998; Mormann *et al.*, 2001; da Silva Perez *et al.*, 2003). For instance, prior to etherification reactions treatment with aqueous alkali is performed both as a necessary activation of cellulose hydroxyls and as a swelling step opening up the structure. Due to this advantageous combination of chemical activation and structure “widening”, aqueous alkali is typically the media of choice in heterogeneous conversions. In lab-scale non-aqueous swelling agents, such as DMF and DMSO in combination with organic bases, are often employed as an alternative in order to eliminate competing reaction with water hydroxyls.

Furthermore, different degradative methods, including ultrasonic treatment, enzymatic degradation and chemical depolymerization are usually employed as pre-treatments enhancing further chemical conversions (Engström *et al.*, 2006; Wang *et al.*, 2008).

Turning to structure reactivity in heterogeneous systems, it has been shown that modification takes place predominantly in the non- or low-ordered regions and at the surface of crystalline portions. Relative conversions of hydroxyl groups within the AGU are determined by combining effects of applied reaction conditions (reaction media, reagent concentration, etc.), the type of chemical conversion and intrinsic reactivity of individual hydroxyls (Tezuka, Imai, 1987; Tezuka, Imai, 1990; Kondo, 2005; Adden *et al.*, 2006a; Adden *et al.*, 2006b).

2.3.3 Solvent systems for homogeneous modifications

In solutions, full and equal accessibility of all hydroxyl groups is usually assumed, facilitating good reaction control. However, possible solvation effects of different solvent systems have to be taken into account, as they may result in enhanced blocking or activation of certain hydroxyl groups (Wagenknecht, 2008). Typically, the degree of chemical modification here is controlled

stoichiometrically and regioselective modifications are readily performed through the utilization of protecting groups. Nevertheless, the impact of cellulose accessibility is evident in these systems as well. Characteristic supramolecular organization makes specific demands on solvent systems with regard to their chemical composition and concentrations of cellulose that can be dissolved. By these means it indirectly affects the homogeneous modification as well, limiting it to a rather small group of solvent systems, and with few exceptions, to small-scale reactions.

Generally, cellulose can be dissolved in strongly polar systems capable of overcoming intermolecular interactions of cellulose chains or by the formation of easily decomposed soluble derivatives (Heinze, Koschella, 2005). Among the solvents working through intermolecular interactions only (so called non-derivatizing solvents) of the highest commercial and scientific relevance are N-methylmorpholine oxide (NMMO), used in a commercial Lyocell process - an alternative to the viscose process (Niekraszewicz, Czarnecki, 2002), N,N-dimethylacetamide / lithium chloride, (DMAc/LiCl), utilized widely in cellulose analytics and in lab-scale modifications (McCormick, Callais, 1987), dimethylsulfoxide/tetrabutyl ammonium fluoride, (DMSO/TBAF), with potential to dissolve celluloses of relatively high chain length without pre-treatment (Heinze *et al.*, 2000; Ciacco *et al.*, 2003) and ionic liquids, i.e. liquid organic salts that have gained attention as environmentally friendly solvents exhibiting high stability and low vapour pressure (Swatloski, 2002; Heinze *et al.*, 2005; Zhu *et al.*, 2006). Here examples of aqueous non-derivatizing solvents should also be mentioned including aqueous solutions of transition metal complexes with amines, such as copper complexes with ammonia (Cuoxam), and ethylenediamine (Cuen) and nickel complex with tris(2-aminoethyl)amine, Ni(tren)(OH)₂ (Heinze *et al.*, 1999), as well as NaOH/urea/water, recently used as modification media (Zhou *et al.*, 2004; Zhou *et al.*, 2005).

The dissolution of cellulose through formation of soluble derivatives suffers usually from occurrence of ill-defined side reactions. Nevertheless, dissolution of alkali treated cellulose by carbon disulphide going through the formation of cellulose xanthogenate has been used for over a century as the key step of the viscose process. Furthermore, systems such as N,N-dimethylformamide (DMF)/N₂O₄ (Wagenknecht *et al.*, 1993), DMSO/paraformaldehyde and trifluoroacetic acid (TFA) in combination with various organic solvents are of considerable scientific importance (Klemm *et al.*, 1998a).

2.3.4 Esterification

Esterification of cellulose is based on reactions of cellulose hydroxyl groups with acids and their derivatives. Among the wide variety of cellulose esters, comprising both organic and inorganic acid esters, some of the oldest and commercially most important cellulose derivatives are found, such as cellulose nitrates, xanthogenates and acetates. However, in this subchapter the emphasis will be on cellulose esters of organic acids as an introduction to the work presented in the thesis.

In the lab-scale they are commonly prepared through action of carboxylic acid chlorides or anhydrides in the presence of an appropriate tertiary amine (Heinze, 2005; Freire *et al.*, 2006), which promotes the formation of an acyl cation, generally proposed as the active intermediate in esterifications (Klemm *et al.*, 1998c). Rarely the acid itself is sufficiently reactive to bring about esterification with cellulose hydroxyls. In that case the formation of the acyl cation intermediate is favoured by acidic conditions.

As a more versatile approach, so called *in situ* activation is often employed, based on the transformation of either acids or cellulose hydroxyls to highly activated structures that are subsequently easily reacted to desired esters. By analogy to esterifications of low molecular

alcohols a number of agents for *in situ* activation have been used (Morooka *et al.*, 1984; Sealey *et al.*, 1996; Glasser *et al.*, 2000).

The introduction of the solvent systems LiCl/DMAc and more recently DMSO/TBAF as well as ionic liquids opened up for a wide range of homogeneous esterification systems offering good control of DS values and uniform substituent distribution (Gräbner *et al.*, 2002; Heinze *et al.*, 2003; Liebert, Heinze 2005). Classical esterifications with acid chlorides and anhydrides in the presence of pyridine (Vaca-Garcia *et al.* 1998; Hon, Yan, 2001; Gräbner *et al.*, 2002), as well as reactions including *in situ* activation (Heinze *et al.*, 2003; Hussain *et al.*, 2004) have been successfully performed in these systems.

Esterifications mediated by *in situ* activation of carboxylic acids in the solvent system DMSO/TBAF will be discussed in Chapter 4, where studies on new esterification agents prepared in this work will be presented.

The properties of cellulose esters are typically governed by the nature and amount of introduced carboxyl compound. Since the esterifications are equilibrium reactions between the ester bond formation and its hydrolytic cleavage, esters are susceptible to hydrolysis. As a consequence, DS can be regulated by the water content in the reaction media, with structure accessibility for water being often of significant importance (Ludwig, Philipp, 1990; Klemm *et al.*, 1998c). In the case of commercially prepared cellulose acetates, DS is usually regulated by the subsequent controlled acetate hydrolysis of the fully acetylated cellulose.

Cellulose nitrates, xanthogenates and acetates have already been mentioned as commercially important cellulose esters – nitrates as lacquers and explosives, acetates as plastics and xanthogenates as the key intermediates in the viscose production. Of special scientific importance are cellulose esters of *p*-toluenesulfonic acid, offering possibilities for regioselective modifications. These ester groups can be easily introduced by reaction with *p*-toluenesulfonyl chloride in pyridine and are employed both as protecting groups in subsequent esterifications or as leaving groups in reaction with nucleophiles (Heinze *et al.*, 2001; Koschella, Heinze, 2001).

2.3.5 Etherification

Due to the chemically stable ether linkage and structural versatility of the etherification agents available, a large variety of cellulose ethers is produced both on lab- and industrial scale.

Etherification routes rely typically on Williamson ether synthesis, ring opening reactions of oxirane functionalized reagents or Michael addition of activated double bond structures.

As usually being performed in aqueous medium, starting from alkali swollen cellulose, these processes are associated with a considerable consumption of etherifying agent by competing reactions with water (Viera, 2007). Adjusting the cellulose-to-alkali and cellulose-to-water ratio with regard to amount etherification agent is therefore of great importance.

Even though etherifications can be conducted in non-aqueous media including swelling agents such as DMF and DMSO (Baouab *et al.*, 2000) and common solvent systems for cellulose (Isogai, 1986; Isogai, 2001; Ramos *et al.*, 2005) only reactions in aqueous alkali systems are commercially relevant.

Depending mainly on the nature of etherifying agent and the degree of substitution, cellulose ethers with broad variation of properties can be produced. Most attractive characteristics are controlled water interactions such as swelling, gelation and solubility (Zhang, 2001). Applications of the commercially most important cellulose ethers - carboxymethyl cellulose, alkyl- and hydroxyalkyl celluloses – rely on these very properties, especially beneficial in controlling the

rheology of water systems. Hydroxyalkylation is due to the spacer activity of hydroxyalkyl groups commonly employed to loosen up the cellulose structure, often as a pre-treatment prior to chemical modifications.

From the scientific point of view especially interesting are silyl and trityl cellulose ethers valuable as intermediates in the synthesis of regioselectively substituted cellulose. Silyl ethers render cellulose more hydrophobic and may be retained in the structure or removed in subsequent reactions, depending on the chemical procedure applied (Wagenknecht *et al.*, 1992; Mormann *et al.* 1999). Tritylation of cellulose occurs preferably at the primary hydroxyl group and is a common functionalization step in the preparation of 2,3-O-cellulose ethers (Kondo, Gray, 1991; Kondo, 1993; Schaller, Heinze, 2005).

In this work special attention has been given to preparation of cationic cellulose ethers, compounds with good and readily quantified interactions with water and anions.

2.3.6 Crosslinking

Crosslinking of cellulose relies on action of di- or polyfunctional agents capable of reacting with two or more cellulose hydroxyls upon formation of covalent bridges, usually composed of acetal (Smith, 1972; Meyer *et al.*, 1976; Frick, Harper, 1982), ether (Tasker, Badyal 1994; Guo, Ruckenstein, 2002), ester (Welch, 1988; Caulifield, 1994; Yang, Xu, 1998), sulfone (Esposito *et al.* 1996), disulfide (Sakamoto *et al.*, 1970), urethane (Verburg, Snowden, 1967; Morak, Ward, 1970) or urea linkages (Stevens, Smith, 1970; Vail, 1972). Crosslinks may also be of electrostatic nature based on at least divalent metal cations connecting anionic sites of the polymer.

Traditionally, crosslinking via formaldehyde and its derivatives, employed in textile finishing, has been the most important commercial application of this type of chemical modification. However, due to the health hazards associated with these compounds, focus has shifted to development of formaldehyde-free agents, including dialdehydes, diepoxides, epichlorohydrin, polycarboxylic acids, etc. Dialdehydes, such as glyoxale and its derivatives are frequently used in the textile industry, whereas crosslinking through esterification with polycarboxylic acids has found its main application in paper stabilization. Epichlorohydrin combines the halide and the oxirane function and is today the crosslinker of choice in numerous research and industrial applications (Smith, 1972; Frick, Harper, 1982; Welch 1992).

Properties of the crosslinked celluloses are dependent on the nature and distribution of the crosslinks, but are also affected by the supramolecular and morphological state of cellulose during reaction.

Extensive crosslinking leads generally to decreased accessibility and reduced interaction possibilities (Tasker, Badyal, 1994). However, flexible hydrophilic crosslinks introduced in small quantities can often have a “spacer effect” contributing to a more open structure. A typical example is crosslinking with epichlorohydrin that enhances water retention ability at low crosslinking degrees, but causes the opposite effect when structure tightening due to more pronounced crosslinking overcomes the initial spacer effect (Klemm *et al.*, 1998c).

2.3.7 Cellulose nanocrystals

As already mentioned, the biosynthesis of cellulose is responsible for the alignment of cellulose chains in highly crystalline structures that are insoluble in water and resistant to a wide variety of chemical reagents. However, cellulose fibrils also contain imperfectly packed non-ordered regions that are more accessible and susceptible to chemical conversions. Applying strongly acidic aqueous

conditions they can be removed yielding a highly crystalline residual of cellulose fibres (Beck-Candanedo *et al.*, 2005; Samir *et al.*, 2005). These isolated crystallites are referred to as cellulose nanocrystals, CNC, and are typically rigid rod-shaped particles with colloidal dimensions determined by source and preparation method. For the wood crystallites typical dimensions are 3-5 x 100-200 nm. High surface area, low density and good mechanical strength are some of attractive properties associated with the high interest in these particles (Samir *et al.*, 2004; Cao *et al.*, 2007).

From the application point of view, greatly advantageous is the ability of CNC to form stable suspensions in water and other media if sufficient steric (Araki *et al.*, 2001) or electrostatic stabilization (Araki, 1999; Montanari, 2005) is provided. Sulphuric acid hydrolysis is commonly employed as the preparation method providing electrostatic stabilization through the introduction of anionic half sulphate esters to the surface of CNC.

A striking property of stable aqueous CNC suspensions is a tendency to self-order into so called chiral nematic structures at sufficiently high concentrations (Gray 1994; Dong *et al.*, 1996; Dong *et al.*, 1998). This means the organization of CNC rods in stacked planes, each plane consisting of parallelly aligned nanocrystals, with the orientation being slightly rotated relative to the previous plane around a perpendicular axis. The driving force is believed to be minimization of increasing electrostatic repulsion at high concentrations, as observed for other rodlike particles aligning in planes. The occurrence of chirality in the intrinsic ordering of planes, in the case of cellulose nanocrystals, has been attributed to the twist in the morphology of CNC-rods. It originates either from the inherent structure of CNC-rods or surface charge effects imposing a twisted shape of the effective particle volume (Revol *et al.*, 1992; Araki, Kuga, 2001). The most efficient packing of such twisted rods is obviously through the formation of chiral nematic structures, i.e. through the alignment of the thread of one rod with the groove of the next one, which might account for observations of chiral nematic ordering at high concentrations.

Chemical modification of cellulose nanocrystals as an important tool in improving their applications will be discussed in Chapter 6.

3. MATERIALS AND METHODS

3.1 Cellulose substrates

The microcrystalline cellulose used in Paper I, Avicel® PH 101, degree of polymerization 260, was obtained from Fluka and treated in vacuum at 110° C for 8 h prior to use.

Cotton linters cellulose employed in the preparation of cationic cellulose ethers (Paper II) was supplied by Munktell Filter AB and used without further purification.

A never-dried TCF-bleached (peroxide-based bleaching) Scandinavian softwood kraft pulp supplied by Södra Cell was used for the crosslinking studies in Paper III, as well as the starting material in preparation of cellulose nanocrystals in Paper V.

The cellulose nanocrystals studied in Paper IV were prepared from cotton filter aid supplied by Whatman.

3.2 Analytical methods

One of the central issues of this work has been the characterization of obtained cellulose derivatives, as a tool to elucidate the course of studied chemical conversions. The analytical methods employed in cellulose chemistry are adjusted to the special requirements of cellulose as a macromolecule and usually differ from the conventional procedures. Here the principles of some of the analytical method used in this work will be briefly described.

3.2.1 ¹H NMR characterization of cellulose derivatives via subsequent modification

Subsequent modification of cellulose derivatives as a prerequisite for NMR analysis has been reported by several groups (Goodlett *et al.*, 1971; Tezuka, Tsuchiya, 1995; Liebert *et al.*, 2005).

Chemical conversion of unsubstituted hydroxyl groups provides the solubility necessary for obtaining sufficiently resolved NMR spectra, where the magnitude of obtained spectral integrals can be used in estimating DS values. Typically, the spectral integrals of AGU signals are compared to those of introduced substituents. Whether the signals of original or subsequently introduced substituents are used depends on the composition of the spectra, considering the importance of obtaining accurate integral values originating from non-overlapping signals. In the case of indirect estimations, where signals of subsequently introduced groups are used to quantify free hydroxyl groups in the original derivative, and thus determine the amount of original substituent, a complete functionalization is, of course, required.

Peracetylation, perpropionylation, per-4-nitrobenzoylation, pertrifluoroacetylation and permethylation are examples of suitable modifications.

In this work perpropionylation is employed providing chloroform soluble cellulose esters. Assuming the complete propionylation of free hydroxyl groups of the original esters (as confirmed by FTIR), the DS of the esters is calculated from the ratio of the spectral integrals of the AGU protons and the methyl protons of the propionate moiety by equation:

$$DS_{\text{ester}} = 3 - \frac{7 \times I_{H,\text{propyl}}}{3 \times I_{H,\text{AGU}}}$$

$I_{H,\text{propyl}}$ = Spectral integral of methyl protons of propionate moieties

$I_{H,\text{AGU}}$ = Spectral integral of all protons of AGU.

3.2.2 Methyl orange sorption

It has been shown that the sorption capacity of cationic celluloses with regard to anionic dyes typically reflects their degree of cationization. Several previous reports explore the sorption of different anionic species to celluloses of varying cation content (Bradley, Rich, 1956; Baouab *et al.*, 2000; Bouzaida, Rammah, 2002; Zghida *et al.*, 2006).

In this work the interaction of cationic cellulose ethers with the anionic dye methyl orange (shown in Figure 6) was studied in order to demonstrate and compare their cationic characters.

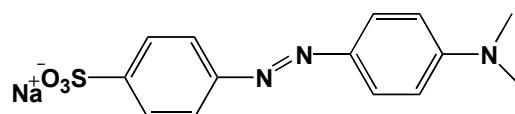


Figure 6. Chemical structure of methyl orange.

Typically, cellulose ethers of known weight are suspended in a water solution of known methyl orange concentration and stirred for a sufficiently long time to reach equilibrium between the dye molecules sorbed to the cationic sites of cellulose and those remaining dissolved in the water.

The remaining concentration of dissolved methyl orange at equilibrium is then determined by measuring solution absorbance at the wavelength corresponding to the absorbance maximum ($\lambda_{\text{max}} = 463 \text{ nm}$). Consequently, the amount of dye sorbed to the cellulose ether is calculated as the difference between the initial and the final dye concentration in the water. The concentration of the sorbed methyl orange is plotted as a function of the concentration in water in order to construct sorption isotherms, illustrating the equilibrium saturation of cationic sites.

3.2.3 Determination of fibre saturation point, FSP

Determination of fibre saturation point is a technique for estimation of the amount of water held within the fibre. In a practical sense, it measures the ability of water saturated fibres to dilute a solution of large non-interacting probe molecules. From these measurements, the amount of inaccessible water held within the fibre can be determined. In a typical procedure, according to the method reported by Stone and Scallan (Stone, Scallan, 1968), water saturated fibres of known dry weight and water content are combined with a known solution of probe molecules and agitated until reaching the equilibrium. Dextran of effective diameter of 560 \AA , exceeding the typical diameter of the largest macropores in fibres, is a suitable probe molecule. The dilution of

the dextran solution upon interaction with aqueous fibres is determined by measuring refraction index of the solution before and after the addition of fibres. It is then used to calculate the amount of water available for dilution and subsequently inaccessible water held in the fibre wall per dry weight. The latter is defined as the fibre saturation point and is highly indicative of fibre wall accessibility. As such, it is sensitive to structural changes within the fibre wall, especially crosslinking and variations in ion content.

3.2.4 Water retention value, WRV

Water retention value is a common measure of a cellulose sample ability to retain water after controlled centrifugation (Maloney *et al.*, 1999; Hubbe, Heitmann 2007). Typically, a sample of water saturated fibres is centrifuged, weighted and then oven-dried and reweighted in order to estimate the amount of water retained after centrifugation. Expressed as the ratio of water to dry fibre weight this water amount is known as the water retention value. It is mainly determined by the balance between the osmotic pressure within the fibre and the restraining effect of the fibre wall architecture and can therefore reflect structural changes of the fibres. However, centrifugation of the sample imposes also a significant impact of the whole fibre network. Consequently, factors affecting fibre packing during centrifugation, such as fibre length distribution and flexibility may be of considerable importance. Furthermore, depending on the centrifugation rate different amounts of water can be pressed out from the fibres strongly affecting the obtained water retention values.

In this work water retention values of the studied cellulose derivatives were used as an indication of structural changes in terms of hydrophilicity, accessibility or ion content. When necessary, WRV was combined with FSP measurements in order to obtain more complete information on changes within a single fibre.

3.2.5 Fibre surface area

The so called Brunauer, Emmett and Teller model, BET, (Brunauer *et al.*, 1938) describing the physical adsorption of gas molecules on the available surface of a dry sample is widely used for estimation of the surface area of porous materials. Essentially, it measures the amount adsorbed gas as a function of the relative gas pressure. Here the adsorption of nitrogen at room temperature is used as a tool to study changes in the available surface area of cellulose samples.

Cellulose materials are susceptible to pore collapse upon drying leading to a dramatic loss of the available area. For this reason, the main challenge in applying the BET model to cellulose samples is obtaining dry samples with preserved original structure porosity.

Gradual solvent exchange from water to a non-polar medium (water-acetone-cyclohexane) followed by drying in a stream of nitrogen gas is beneficially employed in order to completely exclude moisture that could facilitate the structure collapse during drying (Thode *et al.*, 1958).

4. NEW COUPLING REAGENTS FOR HOMOGENEOUS ESTERIFICATION OF CELLULOSE

(Paper I)

4.1 Background

Appropriate activation of acids for esterification reactions has been one of the main objectives of esterification chemistry, not the least of which is cellulose chemistry, where structural features of the macromolecule make special demands on reagents and reaction conditions.

Cellulose esterification through *in situ* activation of carboxylic acids has emerged from the recent efforts to broaden the spectrum of esterification routes and circumvent the shortcomings of the classical methods based on acid anhydrides and chlorides – compounds associated with limited availability. Moreover, applying homogeneous reaction conditions is expected to provide good control of DS and uniform substituent distribution. In this part of the work we thus turned our attention to homogeneous esterification through *in situ* activation of carboxylic acids as a promising route towards new cellulose materials.

Previously used coupling reagents for *in situ* activation of carboxylic acids in cellulose chemistry include *p*-toluenesulfonyl chloride (Shimizu, Hayashi, 1988; Sealey *et al.*, 1996; Glasser *et al.*, 2000; Heinze *et al.*, 2000;), 1,3-dicyclohexylcarbodiimide (DCC) combined with 4-pyrrolidinopyridine (4-PP) (Dave *et al.*, 1993; Samaranayake, Glasser, 1993) and N,N'-carbonyldiimidazole (CDI) (Gräbner *et al.*, 2002; Heinze *et al.*, 2003; Hussain *et al.*, 2004).

Our aim was to explore new routes for *in situ* activation of carboxylic acids by investigating two groups coupling reagents structurally different from the previously used compounds: N-alkyl-2-halopyridinium salts and alkoxychloro-1,3,5-triazines. Both are well-known in the organic synthesis of small molecules, but have never been employed in the esterification of cellulose. The most common N-alkyl-2-halopyridinium reagent is the so called Mukaiyama reagent (N-methyl-2-chloropyridinium iodide), known as a coupling agent for the preparation of esters, amides, lactones, lactams and carbodiimides (Mukaiyama *et al.* 1975; Mukaiyama 1979). In this work we investigated the Mukaiyama reagent and its two analogues, N-methyl-2-bromopyridinium iodide and N-methyl-2-bromopyridinium tosylate.

As a representative of alkoxychloro-1,3,5-triazines, the most commonly employed DMT-MM, (4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride) was studied (Kunishima *et al.* 1999a; Kunishima *et al.* 1999b; Armitt, 2001).

These four compounds were investigated as acid-activating agents in homogeneous esterifications of microcrystalline cellulose with the bulky easily detected (NMR) adamantane-1-carboxylic acid. The cationic character of the reagents and considerable structural resemblance to ionic liquid molecules in the case of Mukaiyama reagents were expected to be advantageous in retaining homogeneous conditions during esterifications. As the reaction media the system DMSO/TBAF was used offering fast and straightforward dissolution procedure.

The product esters were characterized by NMR and FTIR spectroscopy and in terms of DS compared to the reference esterification afforded with the already known CDI.

4.2 Results and discussion

4.2.1 Esterification reactions

The studied esterification agents were synthesized by simple synthetic procedures, according to the reaction scheme in Figure 7.

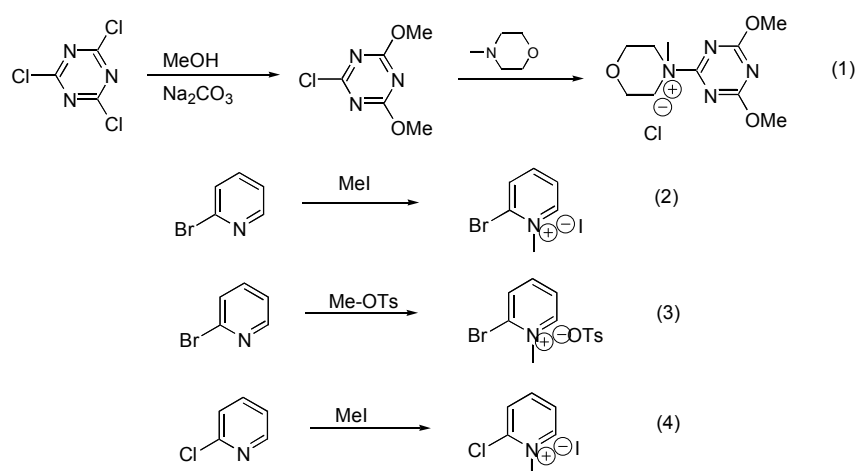


Figure 7. Synthesis of DMT-MM, (1) and N-Alkyl-2-halopyridinium salts (2-4).

The esterifications of cellulose with adamantane-1-carboxylic acid mediated by these compounds were, as mentioned, conducted under homogeneous conditions after dissolving microcrystalline cellulose in DMSO/TBAF. The dissolution takes place at room temperature and yields within less than 15 min of stirring a viscous yellowish solution (Heinze *et al.*, 2000).

Two esterification series were performed. In the first series each reagent was employed in the quantity optimal for the corresponding classical alcohol esterification: 2 equiv./alcohol group for the DMT-MM and 1.1 equiv./alcohol group for the N-alkyl-2-halopyridinium salts. In the second series all the reagents, including the reference CDI, were used in the same quantities (0.5 equiv./cellulose hydroxyl) in order to study their relative efficiencies. All other conditions were identical to those reported for CDI mediated cellulose esterifications (i.e. 80°C, 48h).

The esterification of cellulose mediated by DMT-MM proceeds according to the reaction scheme in Figure 8. As shown, the reagent allows the addition of a carboxylate anion under the displacement of N-methylmorpholine moiety and the subsequent formation of an active ester (Kunishima *et al.* 1999a; Kunishima *et al.* 1999b; Armitt, 2001). The presence of an initial amount of N-methylmorpholine catalyst, NMM (2) is required in order to facilitate the formation of the carboxylate. According to the previous investigations on low molecular alcohols, the best yields were obtained with 1.2 equiv. NMM/alcohol group. Consequently, the same amount was employed in the first esterification series, while being reduced to 0.3 equiv./alcohol (corresponding to 0.5 equiv. DMT MM) in the second series. The obtained cellulose esters were easily purified by washing with water and ethanol.

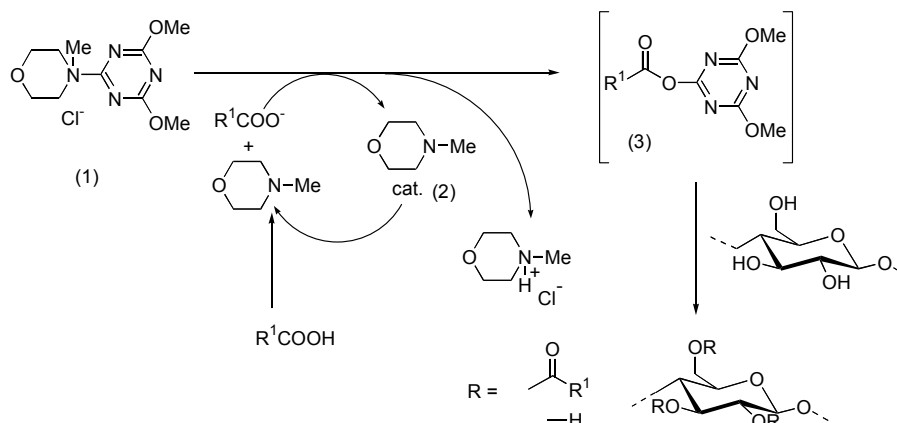


Figure 8. Scheme for cellulose esterification applying in-situ activation of carboxylic acids with DMT-MM.

The corresponding reaction scheme for the action of Mukaiyama reagents, under same reaction conditions, is shown in Figure 9. The readily displaced halogen atom at the 2-position facilitates the formation of an activated ester (Mukaiyama *et al.* 1975; Mukaiyama 1979). Here as well, an organic base (Et_3N) is used as a catalyst and a counterion captor forming triethylammonium halides, ($\text{Et}_3\text{NH}^+\text{X}$).

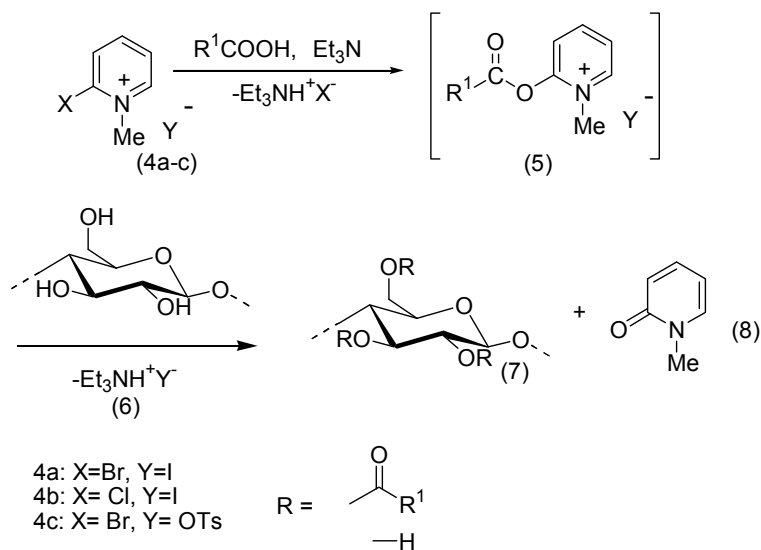


Figure 9. Scheme for cellulose esterification applying in-situ activation of carboxylic acids with Mukaiyama reagents.

The formation of triethylammonium halides leads in the case of N-methyl-2-bromopyridinium iodide (Figure 9, 4a) and N-methyl-2-chloropyridinium iodide (4b) to discoloration of the product esters. However, both the halide salts and pyridones (8), also liberated under esterification, are easily removed by aqueous ethanol wash.

In contrast, removal of the solvent salt residuals (TBAF) present in all obtained esters proved to be more demanding, requiring boiling and washing in aqueous ethanol. This purification could be

followed by the disappearance of residual TBAF signals at 1.0, 1.47, 1.68, 2.91 and 3.36 ppm on ^1H NMR spectra in DMSO.

A constant challenge of this type of modifications is to maintain homogeneous conditions even after the addition of reagents to the DMSO/TBAF-cellulose system, as cellulose solutions are highly sensitive to content changes. In the case of CDI, DMT-MM and the two Mukaiyama agents (4a and 4c) the homogeneity seems to be easily restored upon heating of the reaction mixture. However, the esterification mediated with (4b) suffers from extensive gelation when a high concentration of the agent is employed (1.1 equiv. (4b), the first esterification series). Consequently, the conditions in this reaction cannot be considered as homogeneous.

4.2.2 Characterization

The obtained cellulose esters were not soluble in water, but could be dissolved in DMSO upon stirring for 20-60 min, yielding clear viscous solutions. Hence, ^{13}C NMR spectra of the esters could be recorded in DMSO- d_6 . Figure 10. shows a representative ^{13}C NMR spectrum of an adamantoyl cellulose ester.

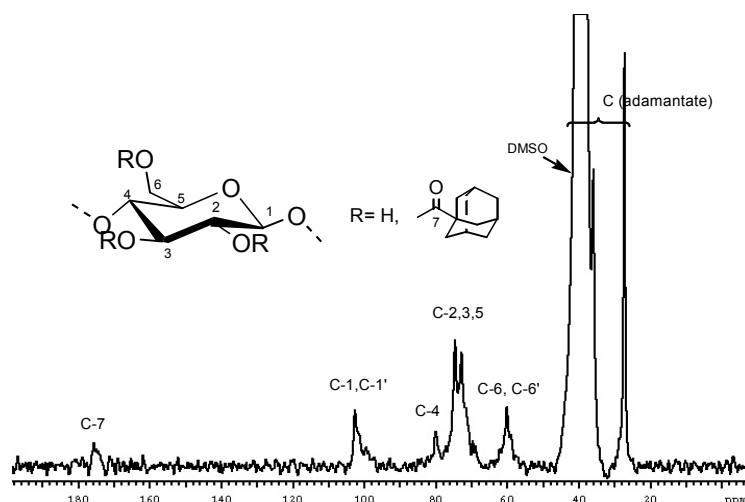


Figure 10. ^{13}C NMR spectrum of cellulose adamantate (adamantoyl ester formation mediated with *N*-methyl-2-bromopyridinium tosylate) recorded in DMSO- d_6 at 25°C (50 000 scans accumulated).

The signal of the carbonyl carbon of the ester linkage is observed at 176-179 ppm, confirming ester formation. The adamantane moiety signals are found between 46 and 26 ppm, partly overlapped by the DMSO signal. Further, the carbons of the anhydroglucose units of cellulose are visible between 104 and 60 ppm. C-1' and C-6' in the spectrum indicate carbons influenced by the esterification. Unfortunately these signals are not sufficiently resolved.

Characterization by ^1H NMR in DMSO was highly limited due to the broadening of cellulose proton signals, as a consequence of interactions with the water content in DMSO.

The formation of cellulose esters mediated with the studied coupling reagents was also confirmed by FTIR. As shown in Figure 11 a new band at 1735-1750 cm^{-1} assigned to the absorption of ester carbonyl groups emerges in all FTIR spectra. An increase in intensity of the band at 2910-2950 cm^{-1} originating from the aliphatic C-H-stretches is also observed indicating the introduction of the adamantane moieties.

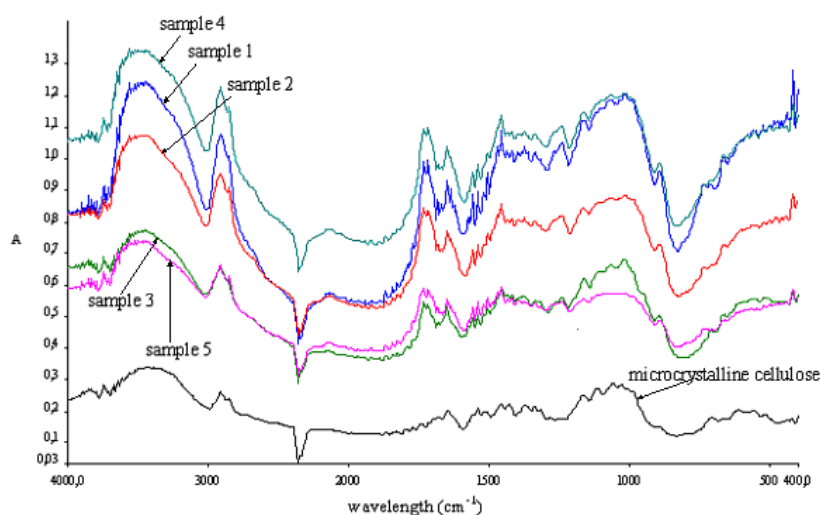


Figure 11. FTIR spectra of cellulose before and after esterification with adamantane-1- carboxylic acid mediated with different esterification agents (DMT-MM, sample **1**, *N*-methyl-2-bromopyridinium iodide, sample **2**, *N*-methyl-2-chloropyridinium iodide, sample **3**, *N*-methyl-2-bromopyridinium tosylate, sample **4**, CDI, sample **5**).

Additional evidence for ester formations was provided by thermogravimetric analysis (Figure 12). Whereas unmodified cellulose decomposes in one step, all the obtained adamantoyl cellulose esters exhibit a two-stage degradation typical of cellulose monoesters. They also show a typical decrease in thermal stability and a slightly lower rate of decomposition.

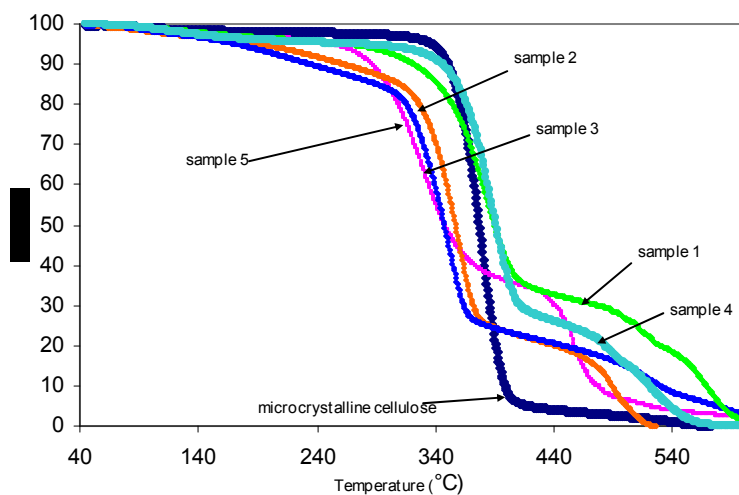


Figure 12. TGA curves of microcrystalline cellulose before and after esterification with adamantane-1- carboxylic acid mediated with different esterification agents (DMT-MM, sample **1**, *N*-methyl-2-bromopyridinium iodide, sample **2**, *N*-methyl-2-chloropyridinium iodide, sample **3**, *N*-methyl-2-bromopyridinium tosylate, sample **4**, CDI, sample **5**).

When the occurrence of the esterifications by action of the studied coupling reagents was established, it was of great interest to determine the DS of the different esters in order to compare the efficiency of the employed reagents. For this purpose ^1H NMR spectroscopy in combination with subsequent derivatization of obtained esters was employed. Liebert *et.al.* have reported on perpropionylation as an efficient method to transform similar cellulose derivatives to CDCl_3 -

soluble compounds (Liebert *et.al.*, 2005) that could further be analyzed by ^1H NMR spectroscopy. According to this method ^1H NMR spectrum of fully perpropionylated cellulose adamantate in CDCl_3 could be obtained, as shown in Figure 13.

The DS could be determined indirectly, from the spectral integrals of the methyl protons of the propionate moiety ($\delta = 0.9 - 1.3$), as compared to the integrals of the AGU protons ($\delta = 3.4 - 5.0$), (see Methods 3.2.1). The adamantoyl signals were partly overlapped with those from the methylene protons of the propionate and could not be used for a more direct estimation of DS.

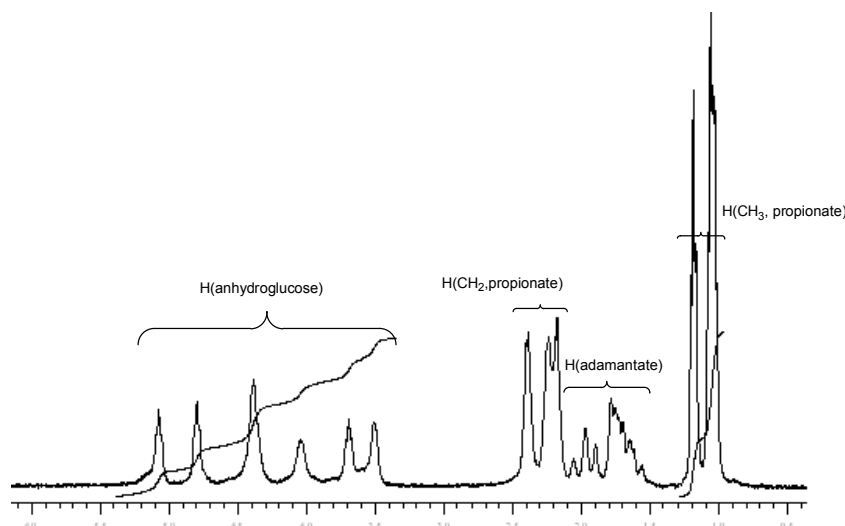


Figure 13. ^1H NMR spectrum of cellulose adamantate propionate (adamantate formation mediated with DMT-MM) recorded in CDCl_3 at 20°C (19 scans accumulated).

Results are shown in Table 1.

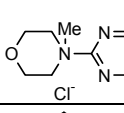
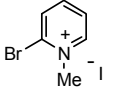
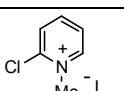
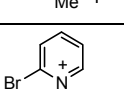
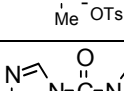
Sample	Esterification agent	Esterification agent/OH group	Substituent / AGU
1	 DMT-MM	2 : 1	0.67
		0.5 : 1	0.32
2	 N-methyl-2-bromopyridinium iodide	1.1 : 1	0.90
		0.5 : 1	0.27
3	 N-methyl-2-chloropyridinium iodide	1.1 : 1	0.43
		0.5 : 1	0.40
4	 N-methyl-2-bromopyridinium tosylate	1.1 : 1	0.67
		0.5 : 1	0.27
5	 CDI	1.1 : 1	1.00
		0.5 : 1	0.29

Table 1. Results for the homogeneous esterification of cellulose mediated with four new esterification agents and the commonly used CDI.

Interestingly, changing the reagent quantity leads to varying changes in the DS for different reagents, revealing their different concentration-efficiency relationships in the cellulose-DMSO/TBAF system.

For instance, N-methyl-2-bromopyridinium tosylate seems to be a more efficient coupling reagent at high concentrations than DMT-MM, since it takes 2.1 equiv. of DMT-MM to obtain the same DS as with 1.1 equiv. of the N-methyl-2-bromopyridinium tosylate. On the other hand, when the both reagents are employed in 0.5 equiv., the DMT-MM shows a slightly better reactivity (DS=0.32 compared to 0.27).

4.3. Conclusions

Studies of model esterifications of cellulose with adamantane-1-carboxylic acid in DMSO/TBAF point out the N-alkyl-2-halopyridinium salts and the DMT-MM as valuable esterification agents, providing a new entry to the chemical tools for cellulose esterifications.

They all yield esters with DS values comparable to those obtained with the commonly used CDI. However, depending on the concentration, the N-methyl-2-chloropyridinium iodide exhibits varying efficiency. At high concentrations this reagent gives rise to an extensive gelation leading to non-homogeneous conditions and low DS. Esterification at low reagent concentration, on the other hand, retains homogeneous character and yields rather high DS, significantly exceeding the corresponding DS obtained by CDI. Consequently, this compound may be useful as a coupling reagent in the synthesis of low substituted cellulose esters.

5. CATIONIC CELLULOSE ETHERS

(Paper II-III)

5.1. Background

Cationization of cellulose is commercially recognized as a modification enhancing cellulose interaction with water, adding affinity toward anions and often providing antibacterial activity. Main cationization strategies comprise the attachment of pre-built quaternary nitrogen structures to the cellulose backbone or quaternization of previously attached amino groups. The introduction of the pre-built quaternary structures by means of etherification is currently the preferred route. It usually employs N-oxiranylmethyl- or 3-chloro-2-hydroxypropyl trialkylammonium salts as etherification agents combined with the alkaline activation of cellulose hydroxyl groups (McKelvey, Benerito, 1967; Gangneux *et al.* 1976; Baouab *et al.*, 2000; Gruber, 1996).

Etherification with N-oxiranylmethyltrialkylammonium salts has been known for a long time and is based on the reactivity of the oxirane functionality. Under alkaline conditions the oxirane ring is readily opened by the nucleophilic attack of alkali activated cellulose hydroxyls creating an ether bond to the cellulose backbone. Ever since the early work of Benedict and Fresco (Benedict, Fresco, 1955) and Bradley and Rich (Bradley, Rich, 1956) the oxirane ring opening chemistry has been commonly employed in cationization of cellulose (Gruber, 1996; Baouab *et al.*, 2000; Gruber, 2002).

However, studies on these reactions have almost exclusively focused on reagents containing methyl or/and ethyl substituted quaternary nitrogen.

The objective of the present work was to explore the employment of new oxirane functionalized compounds for the introduction of cationic substituents to cellulose, with the emphasis on reactivity and resulting material properties. Reactivity was studied in terms of the DS of the obtained ethers, while interactions with water (WRV) and the anionic dye methyl orange were investigated as representative material properties.

Hence, two new compounds, N-oxiranylmethyl-N-methylmorpholinium chloride, and 2-oxiranylpiperidine were synthesized and used as etherification agents. The cellulose ether yielded from the etherification with 2-oxiranylpiperidine could be subsequently quaternized to afford different cationic ethers. Etherification with the commonly used N-oxiranylmethyltrimethylammonium chloride – here abbreviated as EPTMAC according to the commercial name, 2,3-epoxypropyltrimethylammonium chloride – was also performed and used as a reference reaction. Similarly to the commercial oxirane-mediated etherifications of cellulose, etherifications in this study were performed under heterogeneous aqueous alkaline conditions.

Furthermore, as etherification with N-oxiranylmethyl-N-methylmorpholinium chloride provided cellulose structure with the N-methylmorpholine moiety – known from previous studies as a good leaving group (Kunishima *et al.*, 1999b, Armitt, 2001) – it could be used as a basis for the crosslinking of cellulose. For instance, the action of the commonly used esterification reagent,

DMT-MM, is based on a substitution reaction with the appropriate carboxylate upon release of N-methylmorpholine. In our previous studies this reagent was successfully employed in the preparation of cellulose esters with adamantane-1-carboxylic acid (see Chapter 4). Consequently, the cationic cellulose ether obtained from reaction with N-oxiranylmethyl-N-methylmorpholinium chloride could be considered as a reactive cellulose derivative prone to substitution reactions, not the least of which is crosslinking by action of cellulose nucleophiles (hydroxyls, carboxylates, etc.). Here, we investigated the self-crosslinking of this cellulose ether with regard to reactivity, activation and the effects of crosslinking conditions on obtained material properties.

5.2 Results and discussion

5.2.1. Synthesis of etherification agents

Both N-oxiranylmethyl-N-methylmorpholinium chloride (1) and 2-oxiranylpipridine (2) were prepared by efficient synthetic routes illustrated in Figure 14.

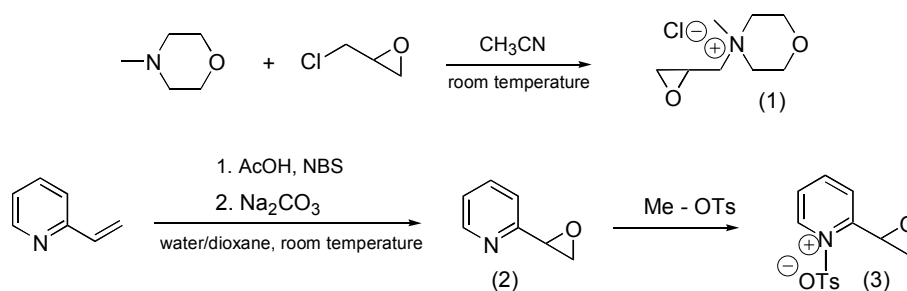


Figure 14. *Synthesis of oxirane functionalized cations for etherification of cellulose.*

N-oxiranylmethyl-N-methylmorpholinium chloride is synthesized by the quaternization of N-methylmorpholine with epichlorohydrin, in the presence of small amount of acetonitrile. The product was easily isolated by filtration and washed with diethyl ether.

The synthesis of 2-oxiranylpipridine is a simple one-pot reaction, where the double bond of 2-vinylpyridine was treated with acetic acid/N-bromosuccinimide, (NBS) and finally Na_2CO_3 in order to yield an oxirane. Pure 2-oxiranylpipridine, a colourless liquid, was obtained in high yield by distillation. It could be further easily quaternized by reaction with methyl-*p*-toluenesulfonate resulting in N-methyl-2-oxiranylpipridinium tosylate (3).

5.2.2 Etherification of cellulose (Paper II)

The etherifications of cellulose with the above described oxirane structures were performed under aqueous alkaline conditions, according to the reaction scheme in Figure 15.

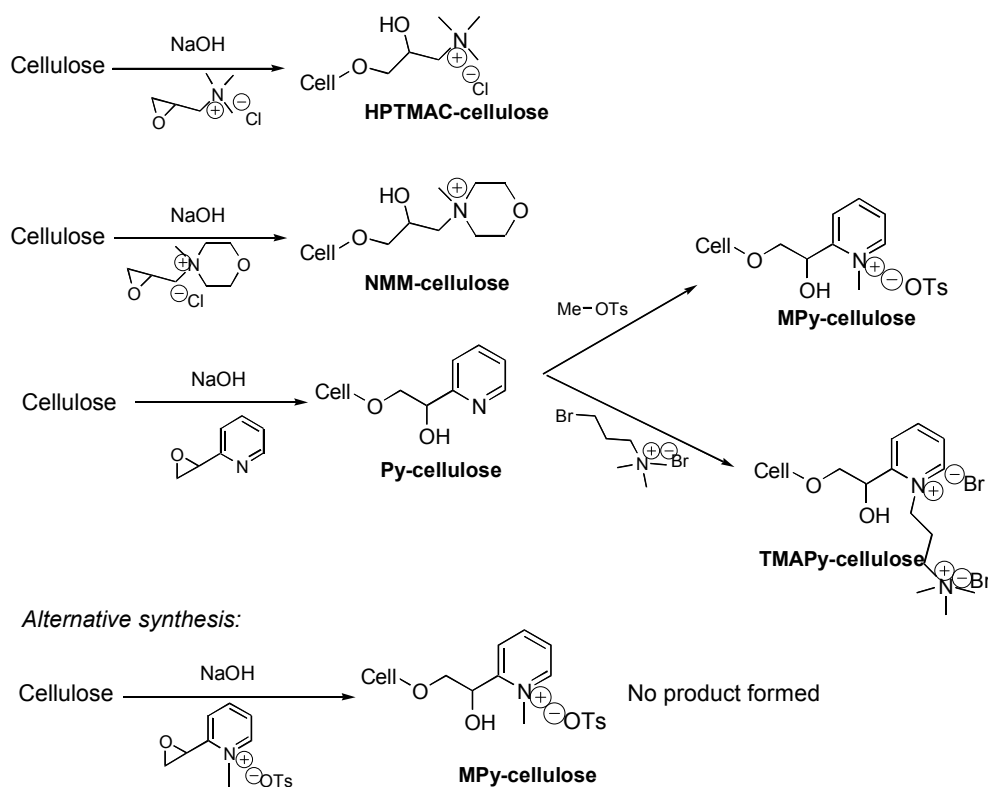


Figure 15. Reaction scheme for synthesis of cationic cellulose ethers with *N*-oxiranylmethyl-*N*-methylmorpholinium chloride and 2-oxiranypyridine as etherification agents.

By varying the water content in etherification reactions two different groups of cellulose ethers were prepared: in the first group (series I) etherifications were conducted in diluted water suspensions (7% w/w), whereas in the second group (series II) reactant concentrations were raised by reducing the amount of water (11%w/w suspensions).

The reaction with 2-oxiranypyridine yielded a slightly discoloured cellulose material, Py-cellulose, whereas *N*-oxiranylmethyl-*N*-methylmorpholinium chloride and the reference compound EPTMAC formed white cellulose derivatives, NMM-cellulose and HPTMAC-cellulose, respectively. During the work up, including extensive filtration with water, NMM- and HPTMAC-cellulose showed a tendency to gel, typical of cationized celluloses. As expected, the gelation was more pronounced in the second etherification series, where due to the increased reactant concentrations higher degrees of etherification were expected. Of course, in all these etherifications there is a possibility of tandem reactions, since the alkoxide formed upon addition of an oxirane can react further with another oxirane leading to formation of an oligoether chain. Occurrence and extent of these reactions have not been investigated in this study, but are considered as a possible parameter affecting outcome of studied etherifications.

Subsequent quaternizations of Py-cellulose obtained in the series II with methyl-*p*-toluenesulfonate and bromopropyltrimethylammonium bromide at elevated temperatures in DMSO afforded MPy- and TMAPy-cellulose, respectively (Figure 15).

Table 2 summarizes structures of all the synthesized cellulose ethers.

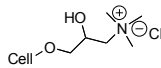
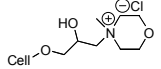
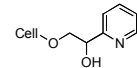
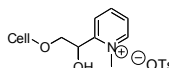
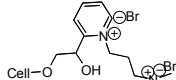
Structure	Name
	HPTMAC-cellulose
	NMM-cellulose
	Py-cellulose
	MPy-cellulose
	TMAPy-cellulose

Table 2. Chemical structure of the studied cellulose ethers.

Interestingly, an attempt to make the quaternization of Py-cellulose with bromopropyltrimethylammonium bromide more efficient by raising the reaction temperature from 80°C to 110 °C resulted in severe degradation of the Py-cellulose.

DMSO-mediated degradation of cellulose has been previously reported, mainly as a side reaction during carbanilations in DMSO. Proposed mechanisms include the oxidation of cellulose with DMSO with subsequent β -elimination and require the presence of carbonyl groups in the starting cellulose material (Henniges *et al.*, 2007). Here, further investigation of quaternization reactions including separate treatments of Py-cellulose and quaternization agents with DMSO, revealed that DMSO and the quaternization agents generate extremely acidic conditions at high temperatures. The depolymerization of cellulose is thus probably a result of acidic hydrolysis of the glycosidic bonds. DMSO is well known for its oxidizing abilities and in this case acidification of the reaction mixture might have its origin in the oxidation of the alkylating agent by DMSO, a process generating H^+ (Kornblum *et al.*, 1959; Nace, Monagle, 1959).

It is also interesting that the attempts to obtain the MPy-cellulose by one step etherification with the quaternized 2-oxiranylpriidine failed (Figure 15). Since an NMR-study of the alkaline hydrolysis of the studied oxirane reagents did not indicate any drastic differences in degradation rates, the failed etherification could not be a result of a too fast hydrolysis of the reagent. Instead it might be explained by sterical hindrances induced by the close proximity of the oxirane to the quaternized nitrogen atom of the pyridine ring bearing a methyl group and a counterion.

5.2.3 Characterization of the cationic cellulose ethers (Paper II)

Characterization by means of FTIR spectroscopy, elemental- and molecular weight distribution analysis, as well as water and methyl orange interactions confirms the formation of the desired cellulose ethers.

FTIR-spectroscopy

FTIR spectra of unmodified cellulose and synthesised cellulose ethers are shown in Figure 16.

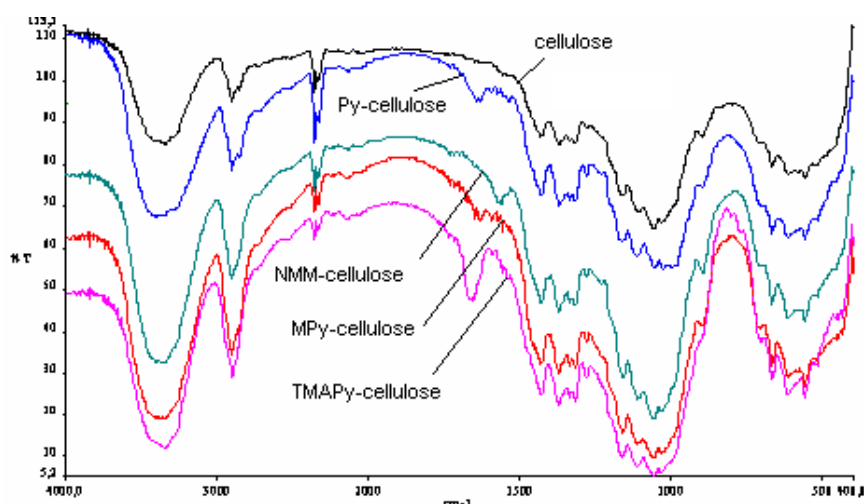


Figure 16. FTIR spectra of unmodified cellulose and the studied cellulose ethers.

FTIR-spectra of Py-, MPy- and TMAPy-celluloses show characteristic bands at 1630-1650 cm^{-1} assigned to C-N vibrations in the pyridinium groups. Furthermore, all the spectra also show an increase in signal from C-H stretching, indicating presence of the substituent structures in the obtained cellulose ethers. Absorption bands at $\sim 1540 \text{ cm}^{-1}$ in the spectrum of NMM- and HPTMAC-cellulose can be attributed to C-N vibrations in methylmorpholinium and trimethylammonium moieties of these ethers.

Estimation of DS

The nitrogen content of the studied ethers was determined through elemental analysis and used to estimate the degrees of substitution, assuming absence of tandem reactions and complete removal of unreacted reagents and bi-products. The results are given in Table 3.

Cellulose ether	Serie I		Serie II	
	Etherification on 7% w/w cellulose suspension		Etherification on 11% w/w cellulose suspension	
	Nitrogen content (%)	DS	Nitrogen content (%)	DS
HPTMAC-cellulose	0.33	0.040	0.47	0.057
NMM-cellulose	0.40	0.049	0.61	0.077
Py-cellulose	0.23	0.027	0.32	0.038
MPy-cellulose			0.22	-
TMAPy-cellulose			0.18	-

Table 3. Nitrogen content and DS of studied cellulose ethers.

In spite of employing 1 equiv. of a cationic reagent per cellulose hydroxyl, etherification reactions yielded a very modest substitution of cellulose, with DS ranging from 0.027 to 0.077 (Table 3). According to the NMR-studies performed on the reagents under similar conditions, these low

values may be mainly attributed to the competing alkaline hydrolysis of the reagents. Poor accessibility of the cellulose structure combined with dilution in the heterogeneous system and hydrolysis of the reagents renders a very low rate of etherification. Under such conditions the alkaline hydrolysis of the reagent is probably the dominating reaction leading to rather low DS values.

As expected, the degrees of etherification were significantly raised by reducing the water content of the reaction slurry in the series II (Table 3).

For the ethers prepared in one step, HPTMAC-, NMM- and Py-cellulose, DS could be estimated from the nitrogen content data. MPy- and TMAPy-cellulose are prepared from Py-cellulose and thus probably contain the same quantity of pyridyl moieties. However, estimation of their cation content based on the above data is troublesome. Unreasonable changes in nitrogen content during quaternizations (Table 3) indicate side reactions of the quaternizing agents with cellulose hydroxyls that might have been activated by alkali during the previous etherification step.

Still, based on these results it might be concluded that N-oxiranylmethyl-N-methylmorpholinium chloride exhibits higher etherification reactivity towards cellulose than both 2-oxiranylpyridine and EPTMAC under aqueous alkaline conditions. As mentioned above, a rather low reactivity of 2-oxiranylpyridine might be explained by sterical hindrances arising from the close proximity of the oxirane and the pyridine ring, as well as by the modest solubility of the 2-oxiranylpyridine in water and the lack of beneficial electrostatic interactions with cellulose possible in the case of the cationic reagents.

Methyl orange sorption

Obtained results are further confirmed by the methyl orange sorption studies, as shown in Figure 17 displaying dye concentration sorbed to the cellulose ether (mg dye/g cellulose ether, Y_e) as a function of the equilibrium dye concentration in the water solution (mg dye/L water, C_e).

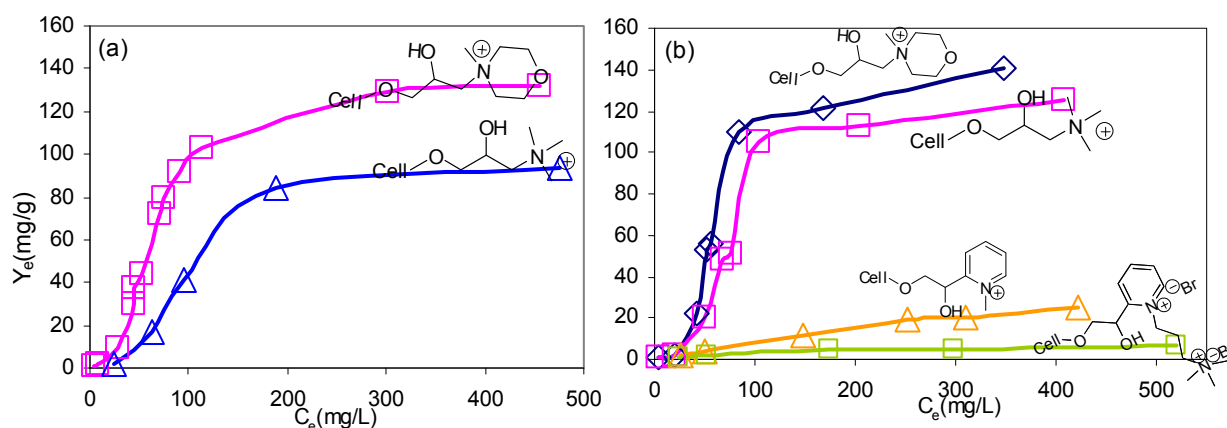


Figure 17. Sorption of methyl orange on the synthesized cellulose ethers: (a) series I, etherification in 7% w/w cellulose suspension and (b) series II, etherification in 11% w/w cellulose suspension.

In Table 4, the maximum observed sorption values are listed along with the number of available cationic sites calculated from the degrees of substitution as mmol/g cellulose ether.

Sample	Number of available cationic sites (mmol/g)	Maximum observed sorption of methyl orange (mmol/g)
Series I		
NMM-cellulose	0,30	0,40
HPTMAC-cellulose	0,25	0,28
Series II		
NMM-cellulose	0,48	0,43
HPTMAC-cellulose	0,35	0,38
MPy-cellulose	-	0,06
TMAPy-cellulose	-	0,02

Table 4. *Maximum sorption of methyl orange for the two series of cationic ethers (mmol/g).*

As shown from the sorption isotherms, NMM-cellulose displays the highest methyl orange sorption in both etherification series. On the other hand, a significantly lower dye sorption could be observed for both cationic ethers synthesized from Py-cellulose. Different reactivities of the N-oxiranylmethyl-N-methylmorpholinium chloride and 2-oxiranylpyridine towards cellulose, as well as the incomplete quaternization of pyridine nitrogen account partly for these observations. Further, different basicity and consequently different ion exchange potential of the quaternary ammonium salts and pyridine salts have to be taken into account as well. The occurrence and extent of tandem reactions might also have impact on the dye sorption, since it affects cation distribution.

Furthermore, it is difficult to draw a parallel between the nitrogen content and methyl orange sorption of the TMAPy- and MPy-cellulose, since their nitrogen percentages contain different types nitrogen (quaternized and non-quaternized pyridine nitrogen, as well as quaternized trimethylammonium nitrogens that are introduced to the pyridinium moieties or reacted with cellulose hydroxyls). In addition, all these cationic sites probably display a variation in sorption capacities depending on their position and structure. For these reasons, no estimation of the amount of available cationic sites could be done for these two ethers (Table 4).

It is interesting that the methyl orange sorption on NMM-cellulose only to a very limited extent reflects an increase in nitrogen content between the two series, whereas HPTMAC-cellulose seems to sorb an excess of the dye compared to the number available sites. This probably originates from the different ion exchange potentials of the substituents and possible variations in their distribution combined with the possibility of dimeric and non-electrostatic dye adsorption.

Molecular weight distributions

Molecular weight distributions after performed one-step cationizations indicate no significant depolymerization of the starting material. On the other hand, the two-step preparation of MPy- and TMAPy-cellulose involving quaternization of the pyridine nitrogen in DMSO evidently leads to a significant depolymerization of the cellulose backbone (Figure 18). As discussed above, this is most likely a consequence of acidic hydrolysis resulting from a side reaction between DMSO and the quaternizing agents.

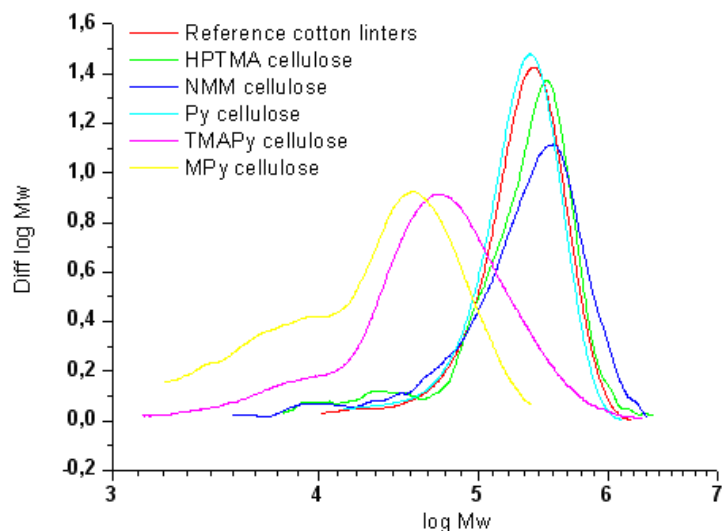


Figure 18. *Molecular weight distribution for the studied cellulose ethers.*

WRV

As observed during the work up of the obtained ethers, cationization rendered significantly improved interaction with water. When in water the cationized celluloses displayed a strong tendency to gel, an observation confirmed by studying swelling in water, measured as water retention values (WRV). These values reflect the cationic nature of the ethers and follow variations in DS (Figure 19).

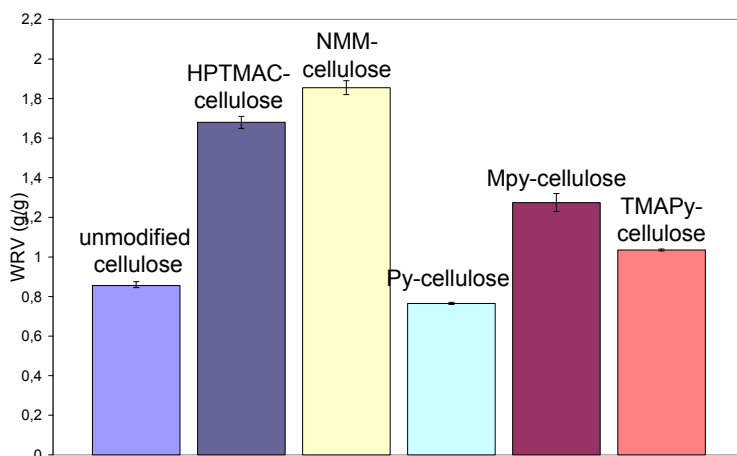


Figure 19. *Water retention values of the cellulose ethers (series II) and unmodified cellulose.*

Apparently cationization results in a significant increase of water retention, with NMM- and HPTMAC-cellulose being able to retain about twice the amount of the water retained by unmodified cellulose. A slightly higher water retention value for NMM-cellulose reflects the higher degree of cationization of this ether compared to HPTMAC-cellulose. The less cationized MPy- and TMAPy-celluloses exhibit, as expected, a lower increase in WRV, whereas substitution with the rather hydrophobic pyridinium moiety slightly reduces swelling capacity of the fibres.

5.2.4 Self-crosslinking of NMM-cellulose (Paper III)

Measuring water retention values of samples dried at 105°C (6 h) gave, as expected, lower values and revealed a striking deviation in the case of NMM-cellulose.

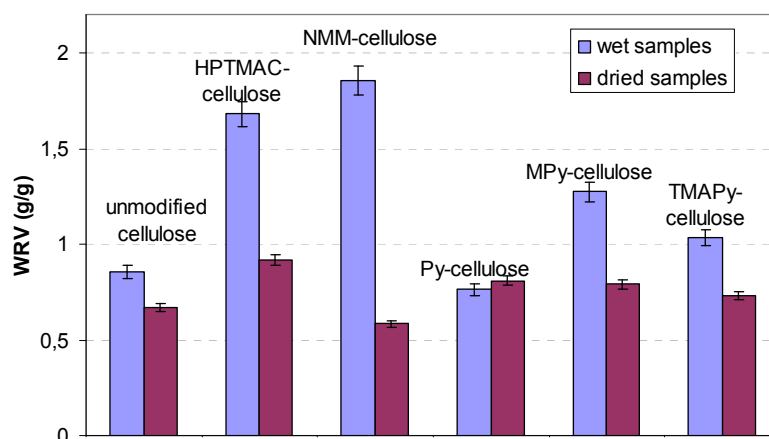


Figure 20. Comparison of water retention values for the cationic cellulose ethers and unmodified cellulose before and after drying at 105°C.

As illustrated in Figure 20, NMM-cellulose displayed a significantly higher reduction of water retention value upon drying than the other studied cationic ethers. In fact, the water retention value of thermally treated NMM-cellulose decreased below that of unmodified cellulose. Considering the cationic nature of this ether – a characteristic expected to be retained upon drying – this behaviour was highly unexpected. It indicated a probable loss of cationicity. Moreover, it also indicated further structural changes associated with decreased accessibility as a consequence of a possible crosslinking process.

In the following our efforts to elucidate the process behind the structural changes observed in NMM-cellulose will be described.

At first, efforts were made to shed light on the presumed crosslinking mechanism by analysing the compound released during the thermal treatment of NMM-cellulose. Further, it was of great interest to investigate simple activation routes feasible with the idea of straightforward crosslinking, such as thermal activation in the presence and absence of base. Furthermore, we examined the outcome of crosslinking from water versus acetone in order to elucidate aspects of intra- and inter-fibre crosslinking of NMM-cellulose.

NMR analysis

¹H NMR spectrum of the compound released upon heating of NMM-cellulose shows typical N-methylmorpholine signals with two wide bands centred at 2.70 ppm (4H, -CH₂N-) and 3.87 ppm (4H, -CH₂O-) and a methyl group signal appearing at 2.38 ppm (Figure 21).

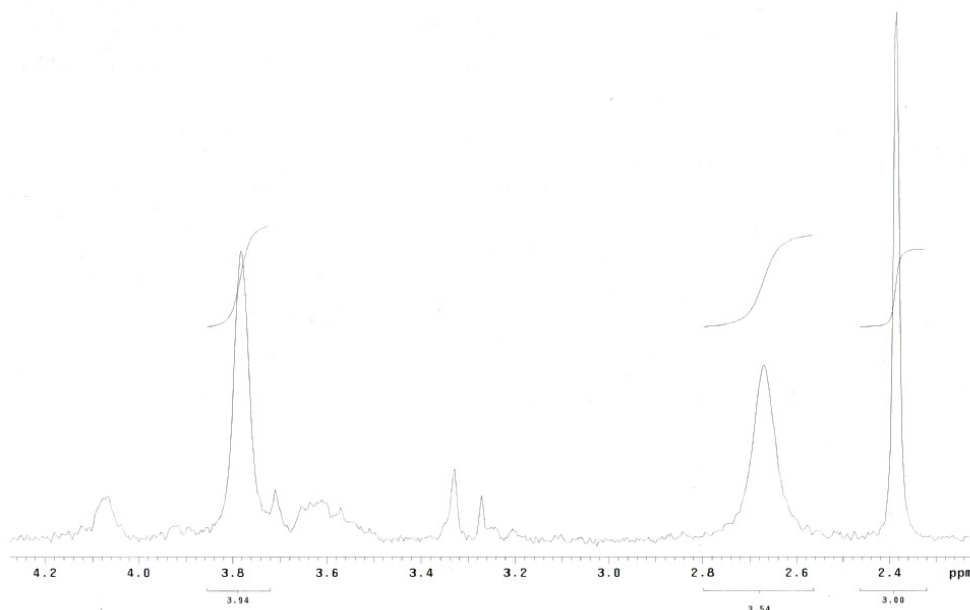


Figure 21. ^1H NMR spectrum of compound released during heating of NMM-cellulose at 105°C for 6 h. The spectrum is recorded in D_2O at room temperature with 20 scans accumulated.

These results imply a crosslinking mechanism involving release of N-methylmorpholine and proceeding probably according to the reaction scheme shown in Figure 22. Crosslinking is, thus, presumably accompanied by the loss of nitrogen content and cationicity, which is beneficially used in the assessment of crosslinking reactions and the characterization of obtained materials.

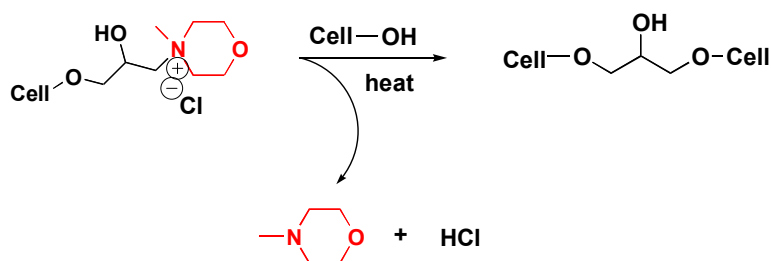


Figure 22. Suggested reaction scheme for heat induced self-crosslinking of NMM-cellulose.

Reactivity, crosslinking and resulting material properties

In order to investigate applicability of the suggested crosslinking reaction on cellulose pulp fibres, the synthesis of NMM-cellulose was performed on bleached kraft pulp and the resulting NMM-cellulose was used in the crosslinking studies as presented in the following.

a) Reactivity studies through elemental analysis

In agreement with the suggested crosslinking mechanism, the elemental analysis of the NMM-cellulose after different thermal treatments shows a decrease in nitrogen content as a consequence of N-methyl morpholine release (Figure 23).

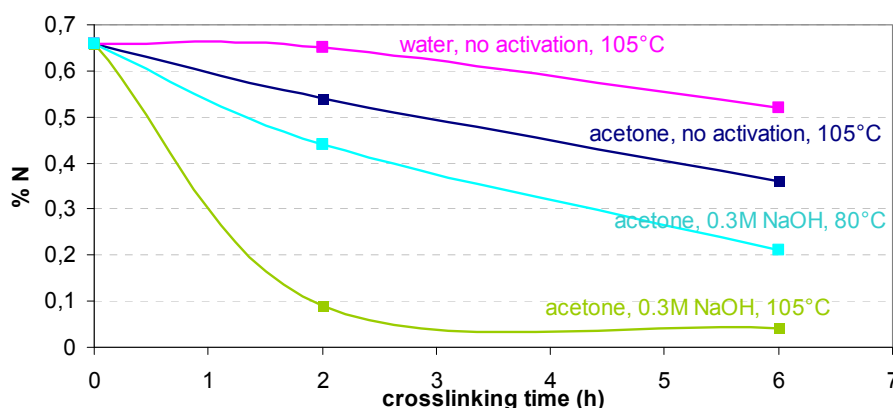


Figure 23. Elemental analysis results of thermally treated NMM-cellulose, showing N-content as a function of reaction conditions.

Evidently, temperature increase, acetone rinsing and especially activation with base enhance the NMM-cellulose reactivity. No appreciable reaction could be detected after drying at 80°C, either from water or acetone. However, almost two thirds of substituents were released after 6h at the same temperature when the base treatment (0.3M NaOH_(aq)) in combination with acetone rinsing was employed. A similar effect of base activation was illustrated for samples treated at 105°C. Here the role of acetone rinsing itself became obvious. Even though this treatment is too quick for complete solvent exchange, it replaces an appreciable amount of water with the low boiling acetone, facilitating faster contact between fibrils during the heating. Heating aqueous samples at 105°C for 6 h could bring about 25% substituents to react. When rinsed with acetone prior to thermal treatment this number was more than doubled and increased dramatically above 90% when activation with sodium hydroxide was included as well. The observed impact of base activation is in line with the assumed reaction mechanism involving the action of cellulose nucleophiles on N-methylmorpholine substituents. It increases nucleophilicity of cellulose hydroxyls, thus, enhancing the overall substitution reaction. Prolonging reaction time from 2 to 6 h results in a conversion increase varying from approximately 7% for base- and acetone-treated sample dried at 105°C to 33% for a corresponding sample dried at 80°C.

After clarifying reactivity and activation issues the samples prepared at 105°C were studied closer in order to elucidate the impact of crosslinking media and base activation on the resulting structure accessibility. The studied samples with corresponding crosslinking conditions are listed in Table 5.

Crosslinking conditions	Sample name
No treatment	NMM-cellulose
Heating of aqueous sample, no alkali treatment	NMM-W-cellulose
Heating of acetone rinsed sample, no alkali treatment	NMM-A-cellulose
Heating of alkali activated, acetone rinsed sample	NMM-AA-cellulose

Table 5. Samples obtained by heating of NMM-cellulose (105°C, 6 h) in combination with different pre-treatments.

b) Accessibility and cationicity through methyl orange sorption

Interestingly, the sorption of the anionic dye, methyl orange, does not completely follow the reactivity pattern observed by the elemental analysis (Figure 24). As expected, the original NMM-cellulose exhibits, by far, the highest sorption in accordance with its unreduced cationic character. Sorption abilities of the thermally treated samples reflect, on the other hand, decrease in cationic charge combined with reduced accessibility due to crosslinking and hornification. Consequently, all thermally treated samples sorb only modest amounts of methyl orange, especially NMM-AA, being highly decationized by the action of base.

The contradictory low methyl orange sorption of NMM-W in comparison to the apparently less cationic NMM-A (compare elemental analysis results) suggests that this should be interpreted in terms of structure accessibility. Applying different reaction conditions promotes crosslinking at different morphological and supramolecular levels, thus leading to dramatic variations in accessibility. Here, reduced anion sorption of the obviously more cationic NMM-W indicates a severe reduction of accessibility upon crosslinking, probably associated with the crosslinking between fibre surfaces.

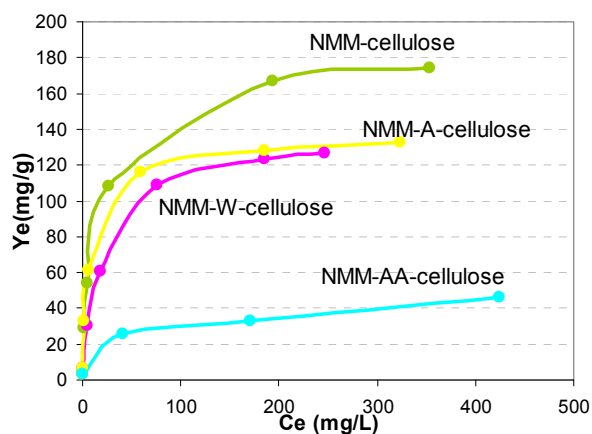


Figure 24. Sorption of methyl orange on NMM-cellulose and samples prepared by different treatments of it.

c) Studies of water interactions by means of WRV

All the water retention values were studied in comparison to a reference sample consisting of unmodified cellulose fibres subjected to identical thermal treatment. Assuming the same hornification progress for the sample and corresponding reference, the effect of hornification could largely be ruled out and the observed difference in WRV interpreted as a result of the crosslinking reaction only.

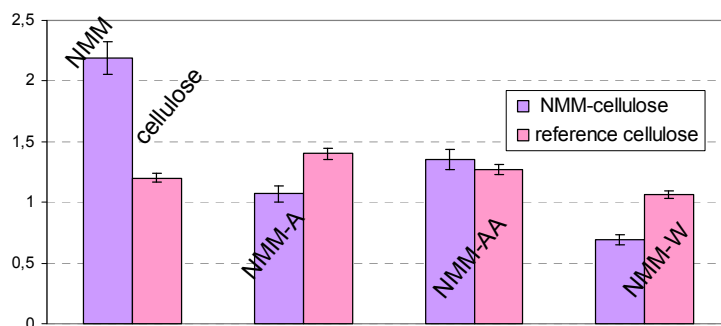


Figure 25. Water retention values for NMM-cellulose and thermally treated NMM-celluloses in comparison to identically treated unmodified cellulose.

As previously observed, NMM-cellulose retains significantly more water per dry weight than unmodified pulp. This WRV difference is of course a result of the cationic character of NMM-cellulose and is dramatically reduced or even reversed (NMM-A and NMM-W) upon thermal treatment, as shown in Figure 25. Usually no such behaviour is observed for cellulose derivatives and is in this case indicative of extensive structural changes within NMM-cellulose, apart from the underlying hornification. This structure alteration is obviously associated with reduced accessibility and wettability and is probably a result of the crosslinking reaction on NMM-substituents.

Variations in WRV after drying reveal some interesting features of the reaction-property relationship. As shown in Figure 25, more pronounced reduction of WRV could be observed when aqueous NMM was dried compared to the acetone rinsed sample, even though the elemental analysis shows clearly higher reactivity of the acetone treated NMM-cellulose.

Such disagreement indicates significantly different impacts of crosslinking on structure accessibility. Consequently, it also indicates varying course of crosslinking with regard to cellulose morphology. In the case of NMM-A, acetone treatment suppresses fibre-fibre interactions resulting in highly reduced crosslinking at fibre-fibre interfaces. On the other hand, presence of water during preparation of NMM-W facilitates both intra- and inter- fibre crosslinking and leads to a more drastic decrease in accessibility, which is clearly reflected in the observed water retention values.

Unlike both NMM-A and NMM-W celluloses, NMM-AA does not exhibit a reversal in WRV difference relative to the starting material, NMM-cellulose. Indeed, it shows a significant decrease in WRV, indicating certain crosslinking, but this effect is obviously not sufficient to suppress WRV below that of the reference sample. The remaining cations in the structure of NMM-AA probably cause the observed increase in WRV compared to the reference. Of course, the presence of cations is essential for all studied samples, with NMM-W and NMM-A being even more cationic than NMM-AA. However, crosslinking in these samples is obviously extensive enough to overcome contribution of the cations and sufficiently reduce WRV, which is not case with NMM-AA. At first glance, this result is in sharp contrast with what might be expected for NMM-AA cellulose, being alkali activated and thus probably highly crosslinked, as indicated by elemental analysis. Still this points out additional structural changes.

Low remaining nitrogen content (elemental analysis) and absence of expected WRV reduction indicates in this case the release of N-methylmorpholine without accompanying crosslinking. The introduction of hydroxide ions apparently promotes a substitution reaction at NMM-substituents, but not substitution by activated cellulose hydroxyls that would result in crosslinking. Most likely, hydroxide ions introduced during alkali activation act as nucleophiles and cause the release of NMM-moieties. Only a small part of the remaining NMM-structures can, thus, contribute to crosslinking. This explains the relatively modest reduction of WRV in combination with the low remaining nitrogen content observed for this sample.

d) Further insights in water interaction by FSP

In order to obtain a more complete picture of structural changes within a fibre during thermal treatments of NMM-cellulose, WRV measurements were combined with fibre saturation point measurements – a technique more sensitive to structural changes within the fibre wall (see Methods, 3.2.3). As can be seen in Figure 26, the FSP of NMM-cellulose decreases dramatically after thermal treatment.

To a certain extent this is of course a consequence of hornification, but the reduction of FSP compared to the identically heated reference samples (subjected presumably to same hornification process) indicates crosslinking of the fibre wall.

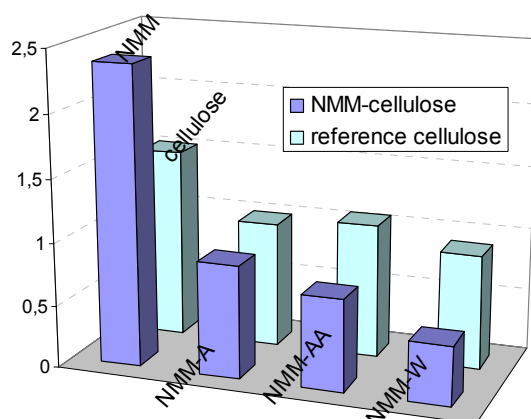


Figure 26. *FSP values for NMM-cellulose and thermally treated NMM-celluloses in comparison to identically treated reference pulps.*

As being sensitive to structural features of the fibre wall, FSP is highly affected by the level of crosslinking and the amount of remaining cations within the fibre. In fact, in this case the water uptake measured by FSP may be seen as a balance between the restraining effect of crosslinking due to reduced fibre wall elasticity and the enhancing effect of cations due to increased osmotic pressure. The high level of crosslinking associated with a low amount of remaining cations consequently results in a significant reduction of FSP.

Only a modest change observed for NMM-A-cellulose is a consequence of a relatively high cation content due to a moderate extent of crosslinking (compare to elemental analysis results). Still, the NMM-W cellulose shows a dramatic decrease in FSP in spite of poor reactivity. This can be explained by severe reduction in fibre wall elasticity due to both inter- and intra-fibre crosslinking, facilitated by water presence during heating. This process creates a highly restrained structure that significantly limits the elasticity of the fibre wall.

Furthermore, a high reduction of FSP could be observed for NMM-AA-cellulose. This is, however, evidence of certain crosslinking in this sample, in spite of a severe alkali mediated loss of N-methyl morpholine. Without the crosslinking effect deviation from the reference sample would probably be insignificant. In fact, with the majority of NMM-moieties removed by alkali this sample would without crosslinking greatly resemble the reference structure.

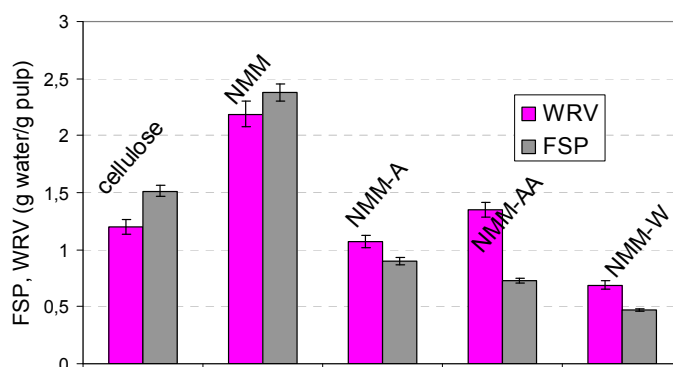


Figure 27. *Comparison between WRV and FSP values for studied NMM-samples.*

FSP values of non-crosslinked fibres (cellulose and NMM-cellulose) are higher than their WRV. This is usually attributed to partial removal of water from the fibre wall by centrifugation. Upon crosslinking this difference is reversed and reflects reduced fibre wall elasticity, as shown in

Figure 27. The highest difference was observed for the poorly crosslinked NMM-AA-cellulose. As discussed above, this sample displays a relatively high WRV as a consequence of low crosslinking and a relatively low FSP as a result of a very low cation content compared to the other samples. However, as showed above even low level of crosslinking has a significant impact on FSP. The observed decrease in the FSP of NMM-AA compared to the reference sample (Figure 26) is an effect of crosslinking. In the case of FSP (compare to WRV results) this effect is obviously sufficient to overcome the opposite contribution of remaining cations and clearly illustrates sensitivity of FSP to crosslinking. The low FSP value of NMM-AA cellulose thus is the result of a low cation content in combination with the crosslinking effect.

e) Fibre surface area

The surface area of the studied samples and references is presented in Figure 28. Percentages in the figure express the relative change compared to the reference.

A dramatic decrease in the surface area of all three prepared samples compared to the identically treated references once again confirms the occurrence of the crosslinking reaction within the structure. As expected, a maximum decrease in surface area was observed for NMM-W due to crosslinking at both inter- and intrafibre levels.

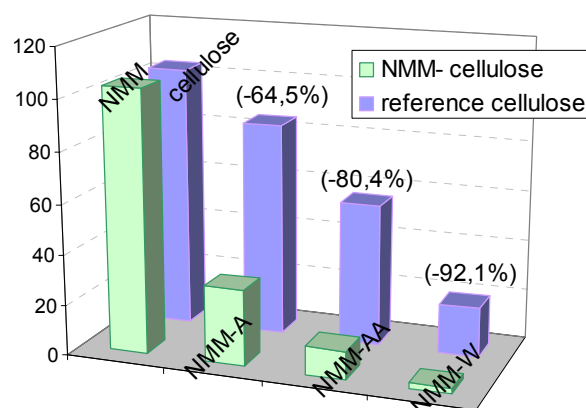


Figure 28. Surface area of studied NMM-cellulose and corresponding references determined by nitrogen adsorption. Percentages in the brackets express the relative change compared to the reference.

NMM-A cellulose shows an unexpectedly low reduction of the surface as compared to the less crosslinked NMM-AA (elemental analysis). Again, this can be ascribed the relatively high cation content of NMM-A resulting in the increased swelling associated with the de-bonding of the structural elements. The pre-treatment of the samples including gradual solvent exchanged from polar to non-polar and subsequent drying in the stream of nitrogen aims to preserve the surface area of the water-swollen cellulose. Increased swelling in the case of the cation-rich NMM-A, as observed by WRV, is thus translated into increased internal surface area, which is not case with the severely decationized NMM-AA. The effect of cations in NMM-W was suppressed by crosslinking at both intra- and interfibre levels.

5.2.5 Conclusions

A group of cationic cellulose ethers has been synthesized employing N-oxiranylmethyl-N-methylmorpholinium chloride and 2-oxiranylpuridine under aqueous alkaline conditions.

The water content in the reaction mixture and sterical hindrances at the oxirane moieties proved to be important factors in governing etherification efficiency.

Even though the 2-oxiranylpuridine exhibited somewhat lower etherification reactivity, it is a valuable chemical anchor, since it introduces reactive pyridine moieties to the cellulose structure. The pyridine substituted cellulose might be used as a starting material for numerous further modifications, where quaternization of pyridine nitrogen with alkyl halides or *p*-toluenesulfonates is one example, shown in this work. Quaternization conditions need to be adjusted in order to obtain maximum quaternization with minimized side-reactions of quaternizing agents, especially those leading to depolymerization of cellulose. Furthermore, possibility of tandem reactions needs to be taken into account, since it would lead to enrichment of N-methylmorpholine and pyridine substituents in the oligoether chains with probable consequences for products properties. In the case of 2-oxiranylpuridine etherification, this tendency is most likely reduced due to the significant sterical hindrance around the *in situ* formed alkoxide groups.

Cationized celluloses exhibit a significant improvement in swelling capacity. The introduction of the cationic N-methylmorpholinium chloride at a DS of 0.077, for instance, results in more than a 2-fold increase in the water retention value. As a much more striking consequence of this functionalization (introduction of N-methylmorpholinium chloride) the cellulose structure is rendered prone to self-crosslink due to the good leaving group properties of the N-methylmorpholine moiety. The substitution reaction between fibre nucleophiles and N-methylmorpholine bearing carbon occurs readily upon heating at 105°C. The reaction can take place at a lower temperature as well if alkali activation is employed. However, the action of hydroxide ions as nucleophiles causes the release of N-methylmorpholine moieties without any accompanying crosslinking, resulting in low-crosslinked samples with low cation content. On the contrary, without alkali activation, the low level of crosslinking corresponds to a high cation content and vice versa, which is in line with the assumed crosslinking mechanism (Figure 29). These variations are reflected by the WRV-and FSP- values of the samples and by their adsorption capacities for anions and nitrogen gas.

Employing an acetone wash prior to thermal treatment raises reactivity and promotes intra-fibre crosslinking. On the other hand, heating of aqueous samples facilitates both inter- and intra-fibre crosslinking. This treatment yields highly collapsed structures, which in spite of a low crosslinking level (compared to acetone washed samples) display very poor accessibility (Figure 29).

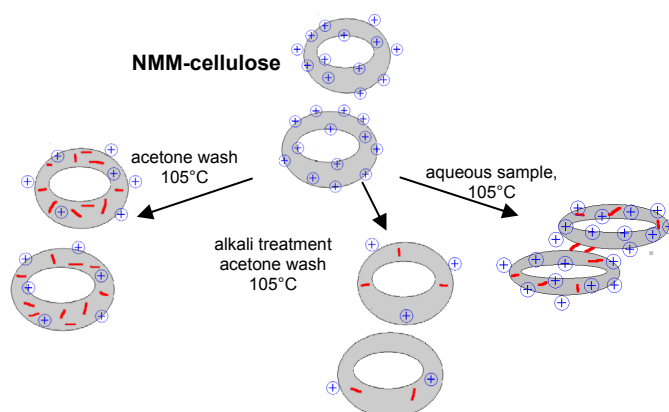


Figure 29. Schematic illustration of suggested course of crosslinking of NMM-cellulose viewed at fibre cross-section. Gray surfaces represent the fibre cross-section. Positive charge symbols represent the cationic NMM-substituents; red lines depict covalent crosslinks introduced upon release of NMM-groups.

6. CHEMICAL MODIFICATION OF CELLULOSE NANOCRYSTALS

(Papers IV-V)

6.1 Background

Controlled acid hydrolysis of cellulose yields rodlike, highly crystalline cellulose nanoparticles, known as cellulose nanocrystals (CNC). They exhibit superior mechanical properties and have as such attracted increasing attention as reinforcing fillers in polymer composites. Their ability to form stable water suspensions with characteristic self-ordering at high concentrations has opened up for further applications based on the optical properties of the solidified liquid crystals.

Chemical modification of these particles has recently received considerable interest as a route towards their broader utilization, aiming primarily for improved compatibility with non-polar polymer matrices (Grunert, Winter, 2002; Yuan *et al.*, 2006) and increased stability in various solvent systems (Araki *et al.*, 2001; Montanari *et al.*, 2005; Habibi *et al.*, 2006). It relies on classical reactions applied in cellulose chemistry, taking into account the consequences of the crystalline nature and large surface area of CNC on reactivity, as well as the risk of disturbing the crystalline structure during chemical reactions. The latter may occur as a result of intracrystalline swelling (e.g. upon treatment with strong aqueous alkali solutions) or extensive modification resulting in a gradual dissolution of cellulose chains.

Cationization of cellulose nanocrystals has not been studied before, even though it is desired in order to increase their affinity for anions and, thus, open up for new applications involving adsorption on anionic polymers, preparation of polyelectrolytic multilayers, etc.

In this work we have explored two cationization methods applied on this cellulose substrate.

Based on the previous experiences of oxirane functionalized cations (Chapter 5), the reaction with N-oxiranylmethyltrimethylammonium chloride (EPTMAC), used in functionalization of e.g. cotton linters (Baouab *et al.*, 2000), starch (Bendoraitiene *et al.*, 2006), xylan (Schwikal *et al.*, 2006) and chitosan (Spinelli *et al.*, 2004), was employed as an example of surface cationization of CNC in aqueous suspension. Further, searching for more versatile cationization methods, another, completely different chemical procedure was studied as well. It involves esterification of cellulose nanocrystals with the highly reactive chloroacetyl chloride as an intermediate reaction, followed by quaternization with an appropriate tertiary amine. Chloroacetylation of cellulose has been previously reported by Pikler *et al.* (Pikler *et al.*, 1980) and Martin *et al.* (Martin *et al.*, 1999) as a route for the introduction of chlorine into cellulose structure. The presence of this functionality has been further utilized by Krouit *et al.* (Krouit *et al.*, 2008) employing it in a nucleophilic substitution reaction with a tertiary amine, similar to procedures investigated in this work applied on CNC.

The obtained cationized nanocrystals were characterized by means of elemental analysis, electrophoretic mobility measurements (Z-potential), conductometric titration and atomic force microscopy (AFM).

6.2 Results and discussion

6.2.1 Surface cationization of CNC with EPTMAC (Paper IV)

Cationization reaction

Surface cationization of CNC with EPTMAC proceeds through a nucleophilic addition of the alkali-activated cellulose hydroxyl groups to the oxirane moiety of EPTMAC, according to the reaction scheme shown in Figure 30.

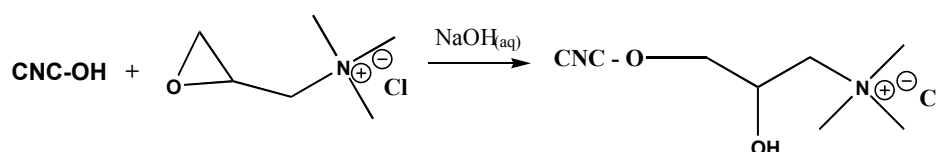


Figure 30. Reaction scheme for surface cationization of CNC with EPTMAC.

In this reaction, the amount of base must provide sufficient activation of the surface hydroxyl groups while avoiding a base induced conversion of the crystalline structure. Besides, the concentration of the base should also be high enough to completely hydrolyze the anionic surface sulfate ester groups during the cationization, to ensure the pure cationic character of the resulting CNC. The 2 M NaOH accomplished this charge reversal as seen by Z-potential measurements. Under these conditions, hydrolysis appears to have completely removed the surface sulfate ester groups without disrupting the crystal morphology. (The removal of sulfate esters could be confirmed by conductometric titration with NaOH.) After extensive dialysis and sonication a stable aqueous suspension of 2-hydroxypropyltrimethylammonium-chloride-CNC (HPTMAC-CNC) was obtained.

Structural characterization of HPTMAC-CNC

The main surface properties obtained for HPTMAC-CNC are listed in Table 6.

Measurement	Unmodified CNC	HPTMAC-CNC
Z-potential	-39 ± 3 mV	$+30 \pm 5$ mV
Surface charge density	0.41 e/nm^2	0.26 e/nm^2
Nanocrystal dimensions	$13 \pm 3 \times 176 \pm 21$ nm	$11 \pm 2 \times 174 \pm 18$ nm
Degree of substitution	N/A	0.02 /AGU

Table 6. Surface properties of HPTMAC-CNC compared with unmodified CNC.

The Z-potential measurements confirmed the cationization of CNC with EPTMAC showing a charge reversal from -39 ± 3 mV before to $+30 \pm 5$ mV after treatment with EPTMAC. This

magnitude of Z-potential indicates a stable suspension before and after functionalization. The DS was determined by conductometric titration of chloride ions with AgNO_3 and found to be 0.112 mmol/g corresponding to a degree of substitution of 0.02 per bulk AGU, neglecting possible occurrence of tandem reactions. Assuming predominantly surface cationization, this gives a surface charge density of 0.26 e/nm^2 , compared to 0.41 e/nm^2 for the starting material. Both the Z-potential and the conductometric titrations indicate that the modification introduced fewer cationic substituents than the original number of sulfate esters groups that were present on the CNC surface.

Investigation of the surface morphology of CNC and HPTMAC-CNC by AFM confirmed that the functionalization did not affect the size or shape of the nanocrystals, as shown in Figure 31 a, b.

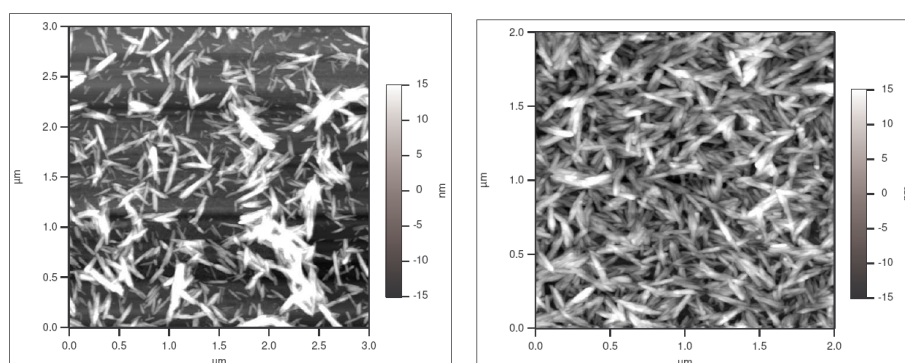


Figure 31. *AFM height images of CNC on mica (a) before and (b) after functionalization with EPTMAC.*

Self-ordering and flow properties

Shear birefringence was observed in the stable aqueous suspensions of HPTMAC-CNC, as expected for CNC. Figure 32 is a photograph of a 1.9% w/w HPTMAC-CNC suspension taken through crossed polarizers while shaking the vial. On standing, the birefringence disappeared. Even after freeze drying, HPTMAC-CNC was easily re-dispersed in water with retained shear birefringence.

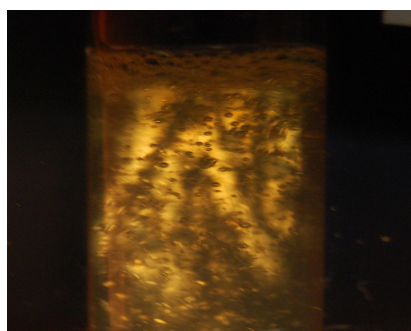


Figure 32. *Shear-induced birefringence in a 1.9% w/w HPTMAC-CNC suspension in water, viewed through crossed polarizers.*

On increasing the concentration, we expected to observe the formation of a liquid crystalline chiral nematic phase, as displayed by the initial anionic CNC suspension. However, at above 3.5% w/w, the HPTMAC-CNC suspension formed an isotropic gel, which apparently inhibited the formation of an ordered liquid crystalline phase. However, ordered regions, characteristic of a

liquid crystal, did appear as the water evaporated from the edges of the solidifying sample. When stress was applied to the drying suspension, the ordered regions deformed, but again, no chiral nematic texture was observed. Polarized light microscopy images of the ordered region close to the edge of the sample are shown in Figure 33.

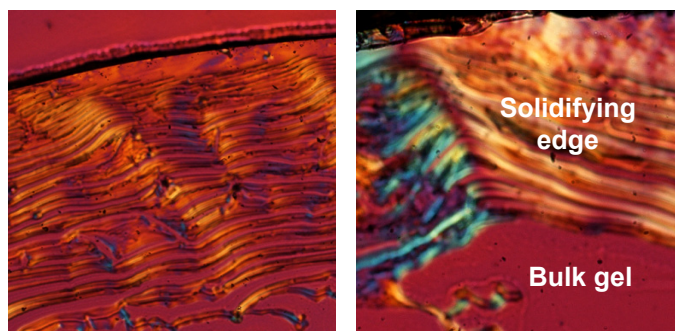


Figure 33. Photomicrographs ($1 \times 1 \text{ mm}$) between crossed polarizers of the solidifying edge of a HPTMAC-CNC suspension.

Furthermore, the HPTMAC-CNC hydrogels exhibited thixotropy. This is illustrated for a 4.9% w/w gel in Figure 34, which shows that the gel is stable when the vial is inverted (Figure 34a), but readily flows after agitation (Figure 34b).

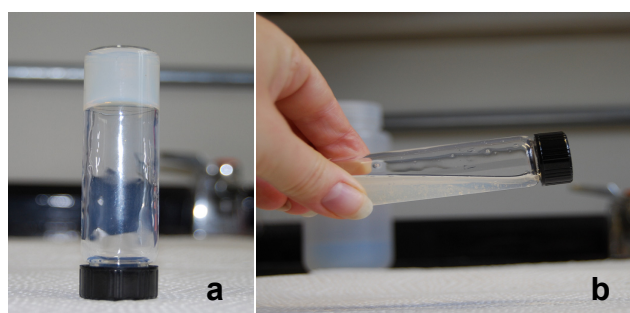


Figure 34. Thixotropic behaviour of HPTMAC-CNC hydrogels: 4.9% w/w gel, (a) before and (b) immediately after agitation.

Rheological evidence for thixotropy was obtained from viscosity measurements at increasing and decreasing shear rates resulting in a hysteresis shown in Figure 35. Previous studies of CNC suspension thixotropy point out the surface charge density as an important factor in governing gel properties (Araki *et al.*, 1998). The effect is attributed to reduced charge and inter-particle aggregation in the HCl system. In the present study, the lower concentration range was not examined for HPTMAC-CNC, however, the presence of thixotropy in the functionalized system does correspond to a slight decrease in Z-potential (from -39 mV to $+30 \text{ mV}$). At a shear rate of 10 s^{-1} the viscosity for 1.9% w/w HPTMAC-CNC is 0.06 Pas , i.e. 20 times larger than for 1.6% w/w CNC from H_2SO_4 -hydrolysis and comparable to 0.7% w/w CNC from HCl hydrolysis (Araki *et al.*, 1998).

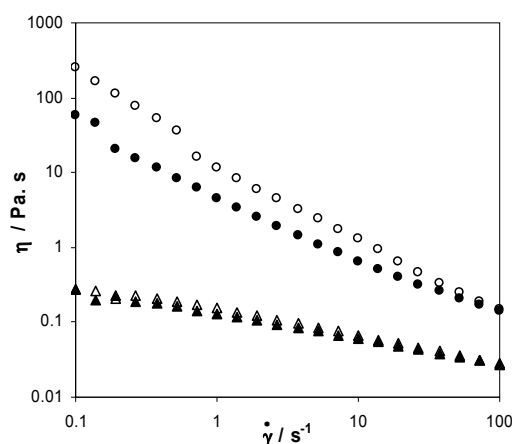


Figure 35. *Thixotropy loop showing shear viscosity as a function of shear rate for HPTMAC-CNC 5.0% w/w (circles) and 1.9% w/w (triangles). Open symbols are for increasing shear rate and closed are for decreasing shear rate.*

Ion-exchange and desulfation studies.

When desulfated prior to the EPTMAC treatment, HPTMAC-CNC suspensions exhibited the same gelation behaviour as the corresponding suspensions functionalized without the desulfation step. This indicates that possible residual anionic groups on CNC do not contribute to the gelation mechanism.

Exchanging the chloride counterions with hydroxide ions, on the other hand, resulted in suspensions with remarkably different behaviour. (Complete exchange of chloride ions for hydroxide ions was confirmed by conductometric titration with hydrochloric acid.) Unlike the strong-gelling original HPTMAC-CNC suspensions which gelled at 3.5% w/w, the ion-exchanged suspensions displayed a weaker tendency to gel; the onset was evident around 5% w/w. The nature of the counterion, in addition to the reduced charge effect mentioned above, is thus very likely an important factor in the formation of functionalized-CNC gels.

6.2.2 Cationization of cellulose nanocrystals through introduction of betaine esters (Paper V)

Cationization of cellulose nanocrystals through introduction of betaine esters proceeds according to the reaction scheme in Figure 36.

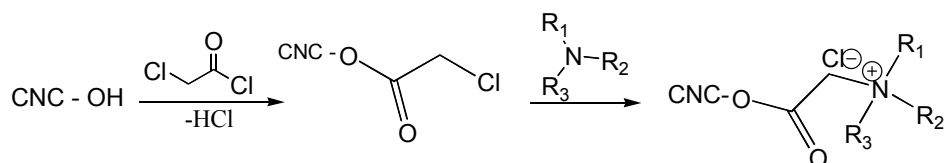


Figure 36. *Cationization of cellulose nanocrystals through introduction of betaine esters.*

Due to the activating action of the chloride substituent in the acetyl group, chloroacetyl chloride is a highly reactive compound undergoing vigorous esterification with cellulose hydroxyls already at room temperature. Esterifications could proceed without any further activation of the acid chloride, i.e. the presence of a tertiary amine typically employed as activating agents for acids, acid

chlorides and anhydrides was not required. Furthermore, the advantage of conducting reaction at room temperature significantly reduced the risk of acidic chain degradation upon formation of HCl during esterification. Consequently, no acid scavenger was required either and the reaction could be performed by simply adding chloroacetyl chloride to the suspension of cellulose nanocrystals.

In order to avoid competing reactions with water, DMSO was used as a reaction medium. Since the reactions were performed at room temperature no side-reactions of the solvent were expected (compare to side-reactions of DMSO discussed in Chapter 5). This fast introduction of chloroacetyl groups to the cellulose backbone was followed by the addition of various tertiary amines, resulting in a nucleophilic displacement reaction at the chlorinated acetyl group carbon and the formation of betaine esters attached to CNC, as shown in Figure 36.

Adjusting the amount of the highly reactive chloroacetyl chloride in this procedure turned out to be of crucial importance in order to prevent disruption of the crystalline structure of CNC and at the same time ensure sufficient introduction of reactive chloroacetate intermediates.

Employing amounts corresponding to 3 equiv. or higher per cellulose hydroxyl group resulted in an obvious destruction of crystalline structure through dissolution and subsequent aggregation of cellulose chains. As shown in Figure 37 no crystalline particles could be detected on AFM images of cellulose aggregates formed during reaction with 3 equiv. reagent per bulk hydroxyl group.

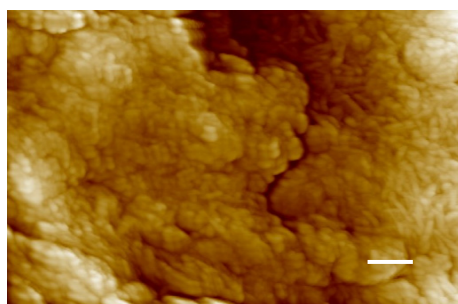


Figure 37. *AFM image of aggregates created during treatment of CNC with the excess of chloroacetylchloride corresponding to 3 equiv./bulk hydroxyl group. Scale bar 200 nm.*

On the other hand, after the reduction of the reagent content to 2 equiv. per hydroxyl group no essential alteration of size and shape of cellulose nanocrystals upon the chemical treatment could be observed on AFM (Figure 38.)

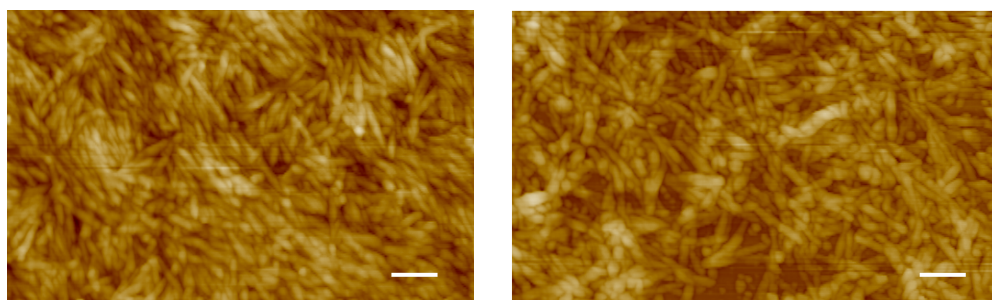


Figure 38. *AFM images of CNC on mica before and after surface modification with chloroacetyl chloride (2 equiv./hydroxyl group) and N-methylmorpholine. Scale bar 200 nm.*

Since the further reduction of reagent content resulted in significantly lower cationization level and a dramatic decrease in electrophoretic mobility (treatment with 1 equiv. or less per hydroxyl group could not provide sufficient surface cationization detectable as electrophoretic mobility of the particles), 2 equiv. per hydroxyl group was chosen as an appropriate amount of chloroacetyl chloride for all cationizations reported here.

Characterization of CNC-betaine esters

Formation of CNC betaine esters could be confirmed by FTIR, showing the characteristic ester band at 1760 cm^{-1} . As an example FTIR spectra of CNC modified with quinoline betaine esters (Q-CNC) and N-methylmorpholine betaine esters (NMM-CNC) together with the spectra of unmodified CNC are shown in Figure 39.

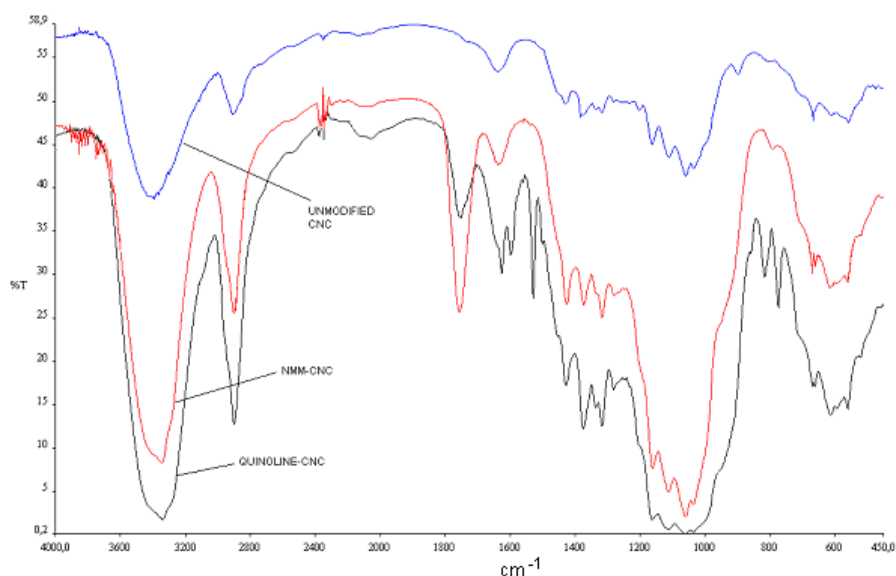


Figure 39. FTIR spectra of CNC betaine esters of N-methylmorpholine and quinoline.

The quinoline betaine ester of CNC gives rise to additional bands in the $1600\text{--}1500\text{ cm}^{-1}$ region typical of its aromatic ring system. The N-methylmorpholine group, on the other hand, contains no significantly IR-active structures distinct from the signals of pure cellulose.

Table 7 summarizes prepared betaine esters of CNC with corresponding degrees of substitution (calculated from elemental analysis results) and electrophoretic mobilities (Z-potential) in water. It should be mentioned that the anionic sulfate groups, attached to the CNC surface during the preparation of these nanocrystals, were hydrolyzed off upon heating in water, prior to modification with betaine esters. Desulfation could be confirmed by Z-potential measurements indicating neutral particle surface. Hence, the observed Z-potentials contain no contribution from the anionic sulphate groups.

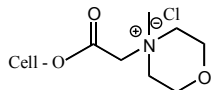
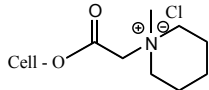
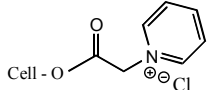
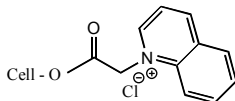
Cationized CNC	Z-potential (mV)	DS
NMM-CNC 	27 ± 3	0.03
PIP-CNC 	31 ± 3	0.18
Py-CNC 	32 ± 2	0.13
Q-CNC 	38 ± 4	0.12

Table 7. Structures of prepared CNC-betaine esters with measured electrophoretic mobilities and degrees of substitution.

Since all CNC-betaine esters are prepared from the same intermediate, the obtained DS values reflect the reactivity of employed amines towards displacement of chloride from the acetylchloride moiety.

It is well known that N-methylpiperidine with its sp^3 hybridized nitrogen atom is a stronger base and a stronger nucleophile compared to the pyridine having its lone electron pair in resonance with the aromatic ring system (Hutchinson, Tarbell, 1969). The same trend is expressed by the DS of the three CNC-betaine esters: PIP-NCC, Py-NCC and Q-NCC. Further, N-methylmorpholine is known as a mild non-nucleophilic base, which could be attributed to the conformational and electron withdrawing effects of the oxygen containing ring combined with the bulkiness around the N-atom. This is clearly mirrored in the low substitution level of NMM-CNC. Even though N-methylpiperidine possesses the same substitution at the N atom, the effect of the oxygen in the ring is apparently of decisive importance, reflected also in the well-documented reactivity order of the corresponding secondary amines: morpholine and piperidine (Arnett *et al.*, 1951; Vuljanic *et al.*, 1996).

As expected, attempts to prepare analogous betaine esters with 1,4-diazabicyclo[2,2,2]octane (DABCO) and triethylamine (TEA) failed. DABCO is known as an efficient dechloroacetylation agent in carbohydrate chemistry (Lefeber *et al.*, 2000). Initially it forms an unstable betaine ester that is rapidly degraded, in this case probably by the traces of water present in the reaction medium. TEA on the other hand, represents an extremely poor nucleophile due to the shielding effect of the ethyl chains.

As shown in Table 7, variations in the Z-potential of the synthesized CNC betaine esters do not follow variations in DS, which can be attributed to the influence of other factors affecting electrophoretic mobility, such as substituent distribution, charge delocalization etc. Moreover, since electrophoretic mobility measures surface charge, these deviations might indicate certain introduction of betaine esters in the bulk of nanocrystals, as well. The comparably low Z-potential of the apparently most substituted PIP-CNC would, in that case, be a sign of significant bulk

modification of CNC. Similarly, the highest observed Z-potential of Q-CNC in combination with relatively low DS could be indicative of a predominant surface modification in this case.

Self-ordering and suspension properties

As exemplified in Figure 40 with the photograph of NMM-CNC in water suspension taken through crossed polarizers while shaking (concentration < 0.05 %), shear birefringence could be observed in aqueous suspensions of CNC betaine esters, illustrating pronounced self-ordering of the modified particles. The occurrence of shear birefringence at so low concentrations indicate pronounced interaction between the particles, facilitated presumably by the hydrophobic interaction of organic substituents and possible electrostatic interactions of their cationic sites and polarized carbonyl groups.



Figure 40. *Shear-induced birefringence in the aqueous suspension of N-methylmorpholine betaine ester of CNC viewed through crossed polarizers, concentration ~0.05% w/w.*

Unexpectedly, none of modifications described provided sufficient stabilization in water suspensions, in spite of the appreciably high content of cations introduced to the surface, as confirmed by Z-potential measurements. After couple of hours standing all CNC betaine esters eventually precipitated from their water suspensions. As suggested by Dong and Gray, (Dong, Gray, 1997) who studied the effects of organic counterions on ordering of charged CNC, this might be to some extent attributed to the hydrophobic interactions between the organic substituents. These attractive interactions weaken the electrostatic repulsive forces and thus reduce stabilization in water suspensions. Indeed, Q-CNC with the largest organic portion showed the lowest stability precipitating after less than an hour on standing. Moreover, betaine esters contain both cationic sites and polarized carbonyl moieties bearing a partial negative charge at the oxygen atom. Possible electrostatic interactions between these groups are another factor likely to facilitate aggregation of the particles.

6.3 Conclusions

Both EPTMAC and chloroacetyl chloride combined with an appropriate tertiary amine can be employed to introduce cationic substituents to cellulose nanocrystals.

Reaction with EPTMAC under aqueous alkaline conditions (corresponding to 1.5 equiv. NaOH/cellulose hydroxyl and 1equiv. EPTMAC/cellulose hydroxyl) results in aqueous suspensions that are electrostatically stabilized by cationic trimethylammonium chloride groups. Mild alkaline cationization conditions preserve the morphology and geometry of cellulose nanocrystals, while resulting in an extensive hydrolysis of the anionic sulfate esters originally present at the surface of nanocrystals. The applied conditions also lead to a slight decrease in total surface charge density, as compared to the initial (anionic) charge of CNC. Aqueous suspensions of these cationic

nanocrystals show a pronounced tendency to form thixotropic gels, which inhibits the formation of chiral nematic liquid crystalline phases at concentrations where they are readily observed for the original anionic nanocrystals. Factors governing the tendencies of rod-like colloidal species to gel rather than form ordered phases are not well understood. However, in this system, the relatively low electrostatic repulsion, the nature of the quaternary ammonium substituent and the nature of the counterion most likely contribute to the observed gelation.

On the other hand, chloroacetylation of CNC suspensions in DMSO followed by treatment with tertiary amines yields the cationic betaine esters of CNC, that in spite of high surface cationization lack colloidal stabilization in water. Attractive interactions of organic cations presumably contribute to the relatively fast precipitation of these particles from water suspensions.

Both the amount of chloroacetyl chloride and the choice of amine are crucial for the outcome of the reaction. The former should not exceed 2 equiv. per cellulose hydroxyl in order to retain the structure of cellulose nanocrystals, while the latter is limited to relatively non-hindered tertiary amines such as cyclic structures and those forming sufficiently stable betaine esters. Deviations in the electrophoretic mobilities of modified CNC particles from the corresponding DS values indicate varying extents of surface and bulk substitution. Z-potential measurements confirmed efficient surface cationization. However, in order to obtain a more complete picture of the course of modification, the extent of the surface reaction versus that taking place within the crystalline bulk is to be investigated in future work.

7. CONCLUDING REMARKS AND OUTLOOK

Functionalization of cellulose requires reactive groups that will ensure an efficient and controlled attachment of desired structures to the macromolecule backbone. This work has focused on reactive groups mediating etherification reactions – **oxirane groups** – and those mediating esterifications – **DMT-MM**, **N-alkyl-2-halo pyridinium salts** and **chloroacetyl chloride**. The presented reactions are adjusted to different cellulose substrates ranging from dissolved cellulose, over highly swollen pulp, to cellulose nanocrystals, where limited swelling is a priority in retaining the original crystalline arrangement. This spectrum of conditions reflects the diversity of modification approaches as determined by cellulose substrate, available chemistry and, of course, by the necessity to adapt them to the desired end-products.

In the homogeneous system DMSO/TBAF, **DMT-MM** and **N-alkyl-2-halo pyridinium salts** have been proven useful as esterification agents comparable to the commonly used CDI. In fact, at low reagent concentrations (0.5 equiv.) the efficiency of **N-methyl-2-chloropyridinium iodide** significantly exceeded that of CDI, while at higher concentrations this effect was suppressed by the extensive gelation of the reagent. **N-methyl-2-chloropyridinium iodide** could, thus be suitable for preparation of low substituted cellulose esters or possibly for esterifications in diluted heterogeneous systems. Indeed, in order to obtain a more complete picture of the potential of these reagents, it would be of great interest to extend the study to other systems – homogeneous and heterogeneous, as well as to a broad variety of carboxylic acids and cellulose substrates. Furthermore, **N-alkyl-2-halo pyridinium salts** structurally resemble to compounds behaving as ionic liquids, known for their potential as cellulose solvents. Compounds combining ionic liquid behaviour with esterification agent abilities would be highly attractive in creating new esterification systems for cellulose. Thus, an investigation of the potential ionic liquid properties of **N-alkyl-2-halo pyridinium salts** and their applicability on cellulose activation/dissolution would be of interest in the further studies of these reagents.

In the presented studies, relatively high degrees of substitution were obtained indicative of the outstanding accessibility of cellulose in homogeneous systems.

In contrast, pronounced heterogeneous conditions were beneficially used in esterifications of cellulose nanocrystals as a prerequisite for retaining their original supramolecular arrangement. Esterification with highly reactive **chloroacetyl chloride** was employed as an intermediate reaction in modifications of cellulose nanocrystals with betaine esters. Studies of these procedures revealed the importance of adjusting the reagent amount in order to ensure appropriate heterogeneous conditions and thus preserve the structure and geometry of the nanocrystals. For the same reason controlling (or restricting) bulk modification is of great relevance and should be included in future work on these reactions.

Betaine ester modified cellulose nanocrystals displayed a remarkably strong tendency to aggregate in spite of a high cationic surface charge. Strong interactions (hydrophobic and/or electrostatic) between created betaine esters most likely contribute to the observed behaviour and are of interest for further studies.

In the view of existing large-scale modifications, feasible only with heterogeneous, preferably aqueous procedures, a special emphasis in this work was placed on heterogeneous modifications in aqueous media. Studies of oxirane mediated etherifications under aqueous alkaline conditions illustrate specificity of aqueous systems, where the presence of water inevitably imposes competing reactions. This was reflected in relatively low degrees of modification as compared to the non-aqueous systems. Apart from the commonly used **N-oxiranylmethyltrimethylammonium chloride**, two new compounds, **N-oxiranylmethyl-N-methylmorpholinium chloride** and **2-oxiranylpyridine**, emerged as efficient agents for obtaining cationic cellulose ethers under these conditions. Increased cellulose accessibility and low water content are crucial in suppressing competing water reactions. Nevertheless, in spite of the presumably low reactivity of crystalline surfaces and thus substantial competing reactions with water, this type of chemistry was successfully applied on the surface cationization of cellulose nanocrystals. Treatment with **N-oxiranylmethyltrimethylammonium chloride** yielded sufficient surface cationization to ensure electrostatic stabilization in aqueous suspensions and remarkably altered self-ordering properties.

Moreover, providing cellulose with reactive pyridine groups in the case of **2-oxiranylpyridine** etherification and good leaving groups (**N-methylmorpholine**) in the case of etherification with **N-oxiranylmethyl-N-methylmorpholinium chloride** opens up for further modifications. Here the quaternization of pyridine containing cellulose and self-crosslinking of so called N-methylmorpholine cellulose have been studied. Studies of self-crosslinking demonstrated the remarkable impact of this modification on cellulose properties evident even at low crosslinking levels. Adjusting reaction conditions in order to facilitate inter- or intra-fibre crosslinking is of great relevance for material properties.

Indispensable in further studies of all modifications studied in this work is a more comprehensive characterization in terms of substitution profiles at different hierarchical levels, as well as quantification of possible tandem reactions and their consequences for obtained properties in the case of oxirane reactions. It is the main prerequisite for understanding the course of chemical conversions and thus the basis for their future optimization.

From the reactivity point of view, optimization is often a matter of cellulose accessibility, especially in heterogeneous modifications, where it usually acts as the main limiting factor. Besides, in systems associated with competing side reactions (aqueous media) increasing cellulose reactivity, not only in terms of accessibility, but also in terms of the appropriate chemical activation of cellulose hydroxyls is crucial in order to ensure efficient conversion. Hence, future efforts on optimization and further development of studied reactions should primarily focus on methods for cellulose activation, supported by improved product characterization.

Finally, as a step towards broader utilization of the studied reagents, their environmental impact should be taken into account and possibilities for environmentally friendly utilization investigated, including recycling, employment of water as the reaction media, minimizing waste generation, etc.

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Paper I

New coupling reagents for homogeneous esterification of cellulose

Hasani M, Westman G

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Paper II

Cationization of cellulose by employing N-oxiranylmethyl-N-methylmorpholinium chloride and 2-oxiranylpyridine as etherification agents

Hasani M, Westman G, Potthast A, Rosenau T

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Paper III

**Self-crosslinking of 2-hydroxypropyl-N-methylmorpholinium
chloride cellulose fibres**

Hasani M, Westman G

Submitted to Cellulose

Paper IV

Cationic surface functionalization of cellulose nanocrystals

Hasani M, Cranston ED, Westman G, Gray DG

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Paper V

Cationization of cellulose nanocrystals through introduction of betaine esters

Hasani M, Westman G

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