Cellulose Derivatives: Synthesis, Properties and Applications

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ACADEMIC DISSERTATION

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ABSTRACT

Cellulose is the most abundant polymer on Earth and hence can be regarded as a very important raw material for several purposes. Recently, cellulose has been in the public eye due to its possible use in the production of biofuels. Cellulose is extensively used as a raw material in the paper industry in the production of paper and cardboard products. However, this is not its only use: cellulose has shown its versatility in numerous applications. Moreover, it can be chemically modified to yield cellulose derivatives. These are widely used in various industrial sectors in addition to being used as a source for commodity goods. Efficient utilisation of cellulose as a material source has been challenging, especially in chemical industry, due to poor solubility.

In this study, the aim was to investigate and explore the versatility of cellulose as a starting material for the synthesis of cellulose-based materials, to introduce new synthetic methods for cellulose modification, and to widen the already existing synthetic approaches. Due to the insolubility of cellulose in organic solvents and water, ionic liquids were applied extensively as the media in the modification reactions.

The first specific goal in this study was to explore the reactivity of cellulose in ionic liquids to yield number of cellulose derivatives (**I**). This could be achieved by optimising several different reaction types in ionic liquid media. This 'toolbox' involves the synthesis of useful and soluble cellulose intermediates that can be used for subsequent modification, in addition to synthesis routes for novel cellulose derivatives.

Ionic liquids are good solvents for cellulose that provide a media for wide variety of reactions. They can also increase the efficiency of reactions (**II**). This increased reactivity gave rise to a new protection group strategy for cellulose in which two reaction sites (C-2 and C-6) were simultaneously and selectively protected by *p*-methoxytrityl chloride (**II**). Ionic liquids are generally regarded as inert solvents, though they may also take part in the reaction. An ionic liquid was used as a solvent in Buchwald-Hartwig cross-coupling as a new synthetic approach to yield cellulose aryl ethers. The ionic liquid took part in the reaction by functioning as a ligand for this palladium catalysed reaction. Furthermore, ionic liquids were also applied as electrolyte solution in the electrochemical preparation of (polyaniline)cellulose.

Cellulose derivatives were designed and fine-tuned to obtain certain desired properties. This was done by altering the inherent hydrogen bond network and by introducing different substituents. These substituents either prevented spontaneous formation of hydrogen bonding completely or created new interactions between the cellulose chains. This enabled spontaneous self-assembly leading to supramolecular structures (**III**). It was also demonstrated that the material properties of cellulose can be modified even those molecules with low DS values when highly hydrophobic films and aerogels were prepared from fatty acid derivatives of nanocellulose (**V**). Here, the low DS values preserved the formation of the hydrogen bond network, whereas the long alkyl tails drastically increased the hydrophobic property of the material. Chlorophyll and fullerene cellulose derivatives for bio-based photocurrent generation systems were designed and synthesised. Thus showing their potential in such systems. (Chlorophyll-fullerene)cellulose in particular showed very interesting self-assembly behaviour.

Cellulose derivatives with liquid crystalline substituents were synthesised and were highly orientated and crystalline in nature. They also functioned as UV-absorbent for paper (**IV**). Furthermore, liquid crystallinity of cellulose solutions in ionic liquids was investigated directly in the liquid state by SEM.

This work provides an alternative insight into how the well-known but underused cellulose can be utilised for developing advanced materials and products by using novel approaches.

PREFACE

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II   M. Granström, A. Olszewska, V. Mäkelä, S. Heikkinen, I. Kilpeläinen: A new protection group strategy for cellulose in an ionic liquid: simultaneous protection of two sites to yield 2,6-di-*O*-substituted mono-*p*-methoxytrityl cellulose, *Tetrahedron Letters*, **2009**, 50, 1744-1747.

III   M. Granström, J. Majoinen, J. Kavakka, M. Heikkilä, M. Kemell, I. Kilpeläinen: Effect of self-assembly via π-stacking to morphology and crystallinity on tritylated cellulose, *Materials Letters*, **2009**, 63, 473-476.

IV   M. Granström, M. Havimo, M. Heikkilä, I. Kilpeläinen: Synthesis, characterisation and application of novel self-assembled comb-like liquid crystalline biphenyl-cellulose as UV absorber for paper, *Journal of Materials Chemistry*, **2009**, 19, 639-644.

V   M. Granström, M. Pääkkö, H. Jin, E. Kolehmainen, I. Kilpeläinen, O. Ikkala: Sustainable approach as an alternative preparation method for purely bio-based highly water repellent cellulose materials, **2009**, submitted.

ABBREVIATIONS

AGU	anhydroglucopyranose unit
APS	ammoniumperoxosulphate
[Admim]Br	1-allyl-2,3-dimethylimidazolium bromide
[Amim]Cl	1-allyl-3-methylimidazolium chloride
[Amim]OAc	1-allyl-3-methylimidazolium acetate
BC	bacterial cellulose
B-H	Buchwald-Hartwig cross-coupling
[Bdmim]Cl	1-butyl-2,3-dimethylimidazolium chloride
[Bmim]Br	1-butyl-3-methylimidazolium bromide
[Bmim]Cl	1-butyl-3-methylimidazolium chloride
[Bmim]OAc	1-butyl-3-methylimidazolium acetate
[Bmim]PF$_4$	1-butyl-3-methylimidazolium tetrafluorophosphate
[Bmim]PF$_6$	1-butyl-3-methylimidazolium hexafluorophosphate
[Bmim]SCN	1-butyl-3-methylimidazolium thioisocyanate
CCOA	carbazole carbonyl oxyamine
CDI	*N,N′*-carbonyldiimidazole
Cd-tren	cadmium-tris(2-aminoethyl)amine
CF	cellulose formiate
CMC	carboxymethyl cellulose
[C$_6$mim]Cl	1-hexyl-3-methylimidazolium chloride
[C$_8$mim]Cl	1-octyl-3-methylimidazolium chloride
ClSO$_3$H	chloro sulphonic acid
CNT	carbon nanotube
CP-MAS NMR	cross-polarisation magic angle spinning solid state nuclear magnetic resonance spectroscopy
CS$_2$	carbon disulphide
Cuam	cuprammoniumhydroxide
Cuem	cupriethylenediamine
CV	cyclic voltammetry
DA	donor-acceptor pair
DCC	*N,N*-dicyclohexylcarbodiimide
DEA	diethylamine
DIPEA	*N,N′*-diisopropylethylamine
DMA/LiCl	*N,N*-dimethylacetamide/lithium chloride
DMI/LiCl	1,3-dimethyl-2-imidazolidinone/lithium chloride
DMF-SO$_3$	dimethylformamide sulphurtrioxide complex
DMSO/TBAF	dimethylsulfoxide/tetra-*n*-butylammonium fluoride
DP	degree of polymerisation
DS	degree of substitution
EDA	ethylenediamine
EDCI	1-ethyl-3-(3′-dimethylaminopropyl)carbodiimide
[Emim]AlCl$_4$	1-ethyl-3-methylimidazolium aluminiumtetrachloride
[Emim]BF$_4$	1-ethyl-3-methylimidazolium tetrafluoroborate
[Emim]CF$_3$CO$_2$	1-ethyl-3-methylimidazolium trifluoromethanecarbondioxide
[Emim]CF$_3$SO$_3$	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
[Emim]Cl	1-ethyl-3-methylimidazolium chloride
[Emim]NO$_2$	1-ethyl-3-methylimidazolium nitrite
[Emim]NO$_3$	1-ethyl-3-methylimidazolium nitrate

[Emim]OAc	1-ethyl-3-methylimidazolium acetate
Et$_3$N	triethylamine
FeTNa	ferric sodium tartrate
H$_3$PO$_4$	phosphoric acid
HPC	(hydroxylpropyl)cellulose
HSQC	heteronuclear single quantum coherence
IL	ionic liquid
IR	infrared spectroscopy
ITO	indium tin oxide
KO^{t}Bu	potassium tert-butoxide
LB	Langmuir-Blodgett
LC	liquid crystal
MALDI-TOF	matrix assisted laser desorption/ionisation-time of flight mass spectrometry
MCC	microcrystalline cellulose
[Mmim]Me$_2$PO$_4$	1,3-dimethylimidazolium dimethylphosphate
MOMCl	methoxymethyl chloride
MPLC	medium pressure liquid chromatography
[Napmim]OAc	1-naphtyl-3-methylimidazolium acetate
NC	nanocellulose
Ni-tren	nickel-tris(2-aminoethyl)amine
NMMO	*N*-methylmorpholine-*N*-oxide
NMR	nuclear magnetic resonance
NPM/LiCl	1-methyl-2-pyrrolidinone/lithium chloride
PANI	polyaniline
PF	paraformaldehyde
POM	polarising optical microscopy
RTIL	room temperature ionic liquid
SAM	self-assembled monolayer
SCB	sugarcane bagasse
SEC	size exclusion chromatography
SEM	scanning electron microscopy
TBAF	tetra-*n*-butylammonium fluoride
TEM	transmission electron microscopy
TFA	trifluoroacetic acid
TGA	thermogravimetric analysis
TLC	thin layer chromatography
TrCl	trityl chloride
UV-Vis	ultraviolet-visible spectroscopy
WAXS	wide-angle X-ray scattering
XRD	powder X-ray diffractometer
ZnCl$_2$	zinc chloride

- Imagination is more important than knowledge -

Albert Einstein (1879-1955)

1. Introduction

Cellulose is the most abundant polymer on Earth, which makes it also the most common organic compound. Annual cellulose synthesis by plants is close to 10^{12} tons.[1] Plants contain approximately 33% cellulose whereas wood contains around 50 per cent and cotton contains 90%. Most of the cellulose is utilised as a raw material in paper production. This equates to approximately 10^8 tons of pulp produced annually.[2] From this, only 4 million tons are used for further chemical processing annually.[3] It is quite clear from these values that only a very small fraction of cellulose is used for the production of commodity materials and chemicals. This fact was the starting point of our research into understanding, designing, synthesising and finding new alternative applications for this well known but underused biomaterial.

1.1 Structure and reactivity of cellulose

The chemical and physical properties of cellulose can only be properly understood by acquiring knowledge of the chemical nature of the cellulose molecule in addition to its structure and morphology in the solid state.[4] A profound understanding of the structural properties of native cellulose is a requirement to understand the effects of different substituents on the chemical and physical properties of cellulose and its derivatives.[4] When considering macromolecules of any kind, three structural levels must be distinguished:

1) *The molecular level*

On this level the cellulose is treated as a single macromolecule. At the molecular level the following concepts are considered: chemical constitution, molecular mass, molecular mass distribution, the presence of reactive sites and potential intramolecular interactions.

2) *The supramolecular level*

This is one step further up from the molecular level and considers cellulose molecules as interacting with other cellulose chains in the form of packing and mutual ordering of the macromolecules to form larger structures. At the supramolecular level the following concepts are of importance: aggregation of the molecular chains to form elementary crystals and fibrils, the degree of order within and around the fibrils and fibrillar orientation with respect to the fibre axis.

3) *The morphological level*

This level covers structural entities formed by cellulose molecules. As the structures get larger, they may become very complex. On the morphological level, the existence of distinct cell wall layers in native cellulose fibres or in skin-core structures in man-made cellulosic fibres are investigated. Presence of voids or interfibrillar interstices is also studied.

In this study, the focus is on those levels that emphasise the molecular and the supramolecular level, with considerations about the morphology of the compounds.

1.1.1 Cellulose molecule at the molecular level

Payen was the first to determine the elemental composition of cellulose as early as in 1838.[5] He found that cellulose contains 44 to 45% carbon, 6 to 6.5% hydrogen and the rest consisting of oxygen. Based on these data, the empirical formula was deduced to be $C_6H_{10}O_5$. However, the actual macromolecular structure of cellulose was still unclear. Haworth proposed a chain-like macromolecular structure in the late 1920s, whereas Staudinger delivered the final proof of the highly polymer nature of the cellulose molecule.[6,7,8]

Cellulose is a linear and fairly rigid homopolymer consisting of D-anhydroglucopyranose units (AGU). These units are linked together by β-(1→4) glycosidic bonds formed between C-1 and C-4 of adjacent glucose moieties (Figure 1).[1] In the solid state, AGU units are rotated by 180° with respect to each other due to the constraints of β-linkage. Each of the AGU units has three hydroxyl (OH) groups at C-2, C-3 and C-6 positions. Terminal groups at the either end of the cellulose molecule are quite different in nature from each other. The C-1 OH at one end of the molecule is an aldehyde group with reducing activity. Aldehyde groups form a

pyranose ring through an intramolecular hemiacetal form. In contrast, the C-4 OH on the other end of the chain is an alcoholborne OH constituent and thus is called the non-reducing end. It has been known from the infrared spectroscopy (IR), X-ray crystallography and nuclear magnetic resonance (NMR) investigations, that the AGU ring exists in the pyranose ring form and that this adopts the $^4C_1$-chair formation which constitutes the lowest energy conformation for D-glucopyranose.[9,10,11,12,13,14,15,16]
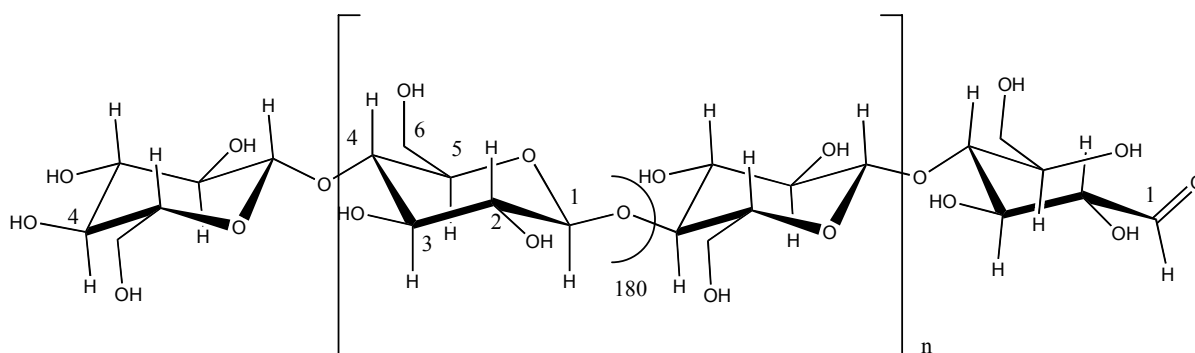
Figure 1. Molecular structure of cellulose representing the cellobiose unit as a repeating unit showing reducing (right) and non-reducing (left) end-groups. When considering only one of these glucopyranose structures, repeated anhydroglucopyranose units (AGU) are rotated 180° with respect to each other.[7]

The chain length of the cellulose polymer varies depending on the cellulose source.[4] For example, naturally occurring vascular plant cellulose has a degree of polymerisation (*DP*) higher than 10 000.[4] The value of *DP* is greatly dependent on the method of isolation and therefore, the cellulose used in practise has an average *DP* of between 800-3000.[4] Microcrystalline cellulose (MCC) used in the present study is pure and highly crystalline cellulose that has been produced by acid hydrolysis and has *DP* values in a range of 300-600. In its commonly used form, isolated cellulose is always polydisperse. It is like nearly all polymers, a mixture of molecules that has the same basic composition but differs in the chain length. Therefore, the molecular mass and the *DP* of cellulose can only be considered as average values.

The chemical character and reactivity of cellulose is determined by the presence of three equatorially positioned OH groups in the AGU, one primary and two secondary groups.[1] In addition, the β-glycosidic linkages of cellulose are susceptible to hydrolytic attack.[1] The

hydroxyl groups do not only play a role in the typical reactions of primary and secondary alcohols that are carried out on cellulose, but also play an important role in the solubility of cellulose.[1] Cellulose is insoluble in common organic solvents and in water.[1] This is due to the fact that the hydroxyl groups are responsible for the extensive hydrogen bonding network forming both, intra- and intermolecular hydrogen bonding as shown in figure 2.[4] In order to dissolve cellulose, the prevailing hydrogen bonding network must be broken.

There are two possible mechanisms by which the OH groups in the cellulose molecule form hydrogen bonds. One is by the interaction between suitably positioned OH groups in the same molecule (intramolecular). These are located between C2-OH and C6-OH groups and C3-OH with endocyclic oxygen (Figure 2a, i and ii). The other mechanism occurs when neighbouring cellulose chains (intermolecular) interact via their C3-OH and C6-OH groups (Figure 2, iii). Intramolecular hydrogen bonds between the hydroxyl group at the C-3 and oxygen of the pyranose ring were first described in the 1960s by Liang and Marchessault, and Blackwell *et al.* who claimed the existence of a second 'pair' of intramolecular hydrogen bonds between the C-6 and C-2 of the neighbouring AGUs.[17,18]

a)
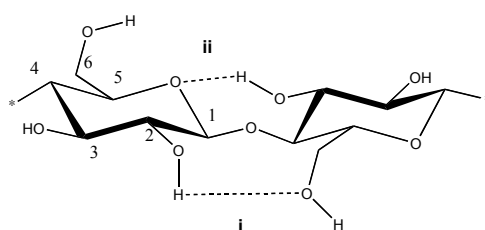
b)
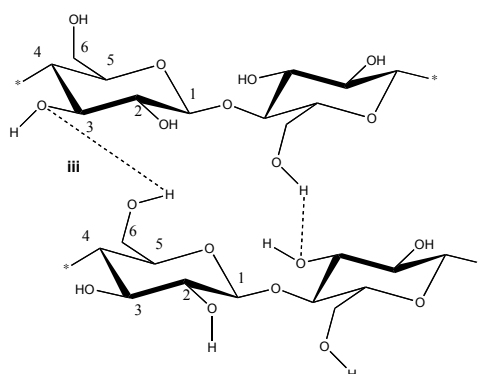
Figure 2. Cellulose structures showing a) the intramolecular hydrogen bonding between C2-OH and C6-OH (i), and C3-OH with endocyclic oxygen (ii); and b) the intermolecular hydrogen bonding between C3-OH and C6-OH (iii) (supramolecular structure).

Cellulose is regarded as a semi-flexible polymer. The relative stiffness and rigidity of the cellulose molecule is mainly due to the intramolecular hydrogen bonding. This property is reflected in its high viscosity in solution, a high tendency to crystallise, and its ability to form fibrillar strands. The chain stiffness property is further favoured by the β-glucosidic linkage that bestows the linear form of the chain. The chair conformation of the pyranose ring also contributes to chain stiffness. This is in contrast to the α-glucosidic bonds of starch.

1.1.2 Supramolecular structure of cellulose

Cellulose chains have a strong tendency to aggregate and to form highly ordered structures and structural entities. The highly regular constitution of the cellulose molecule, the stiffness of the molecular chain and the extensive hydrogen bonding capacity favour molecular alignment and aggregation. Despite this knowledge, the detailed structure of this hydrogen-bond network is still an ongoing subject for discussion.

The history of the supramolecular structure of cellulose, started as early as 1913 when Nishikawa and Ono discovered the structure of fibrous cellulose by the well-defined X-ray diffraction patterns.[19,20] This finding led to the conclusion that individual cellulose molecules tend to arrange themselves in a highly organised manner leading to a 'paracrystalline' state. In the first decades of the past century, chemists believed that cellulose was an oligomeric, possibly ring-like glucane of up to approximately 100 glucose units. Therefore, it was assumed that the micelles consisted of crystalline aggregates of such oligomers.[4] This was first proposed in 1865 by the biologists Naegeli and Schwendener for natural reticulum substrates, such as cellulose.[4] Based on these findings, and the theories of Staudinger on the macromolecular structure, scientists developed the 'fringed fibrillar' model of the structure, which is still the prevailing accepted theory of the supramolecular structure (Figure 3).[21]
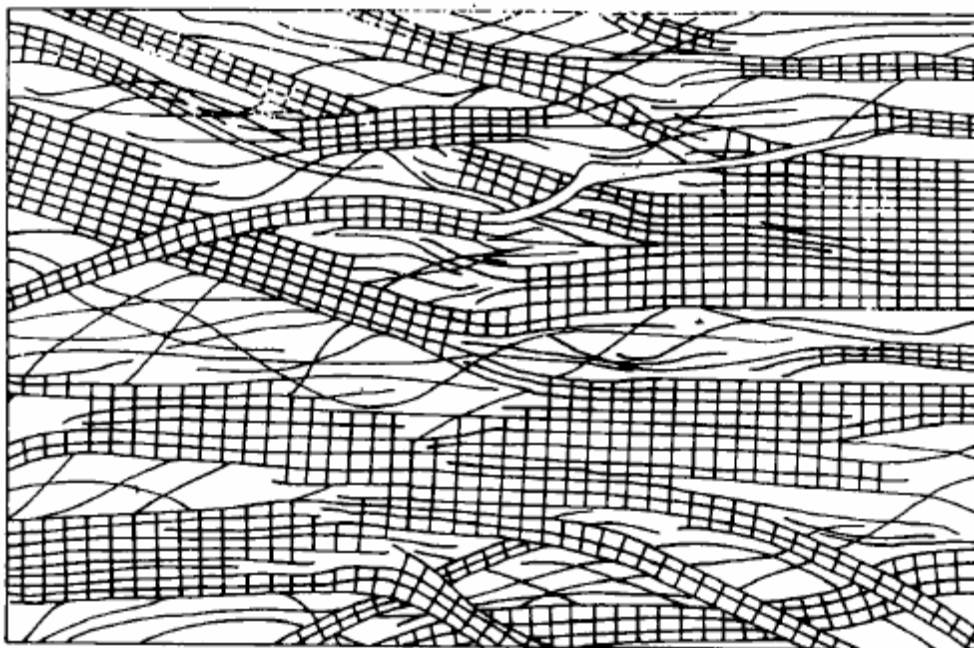
Figure 3. Fringed fibril model of the supramolecular structure of cellulose.[21] The latticework represents the highly ordered (crystalline) region whereas elongated lines represent the low ordered (amorphous) regions.

The supramolecular model of cellulose is based on the organisation of cellulose chains into a parallel arrangements of crystallites and crystallite strands, which are the basic elements of the fibres.[4] The intermolecular hydrogen bonding between C6-OH and C3-OH of adjacent chains are considered to be the major contributors to the structure of cellulose, and is regarded as the predominant factor responsible for uniformal packing.[22] In turn, the consistency of the interchain interactions is governed by the high spatial regularity and availability of the hydroxyl groups. The order of molecules in a cellulose fibre is far from uniform throughout the whole structure, and so it can be assumed that there exists regions within the structure, that have varying amounts of order. Today experimental evidence describes a two-phase model, which clearly divides the supramolecular structure into two regions: low ordered (amorphous) and highly ordered (crystalline) excluding the medium ordered regions completely.[21] In the present study, this fringed fibril model is used as a basic concept to describe the hierarchy of cellulose derivatives formed by self-assembly, and in the context of their crystallinity.

The degree of crystallinity of cellulose and its derivatives can be measured by different X-ray techniques such as by wide-angle X-ray scattering (WAXS) and by powder X-ray diffractometry (XRD).[23] Moreover, solid state NMR methods have proved to be a valuable tools in the determination of the crystallinity of cellulose.[24,25]

Cellulose exists in several polymorph (classes I, II, III, IV) that differ in their unit cell dimensions (Table 1).[4] The combination of X-ray diffraction with model building and also with conformational analyses in the 1970s provided the current model for the structures of cellulose polymorphs, in particular those for cellulose I (native cellulose) and cellulose II (recrystallised cellulose).[22,26,27,28,29]

Table 1. Unit cell dimensions of cellulose polymorphs I, II, III and IV.[1,4]

a-axis (Å)	b-axis (Å)	c-axis (Å)	γ (deg)[a]	Polymorph
7.85	8.17	10.34	96.4	Cellulose I
9.08	7.92	10.34	117.3	Cellulose II
9.9	7.74	10.3	122	Cellulose III
7.9	8.11	10.3	90	Cellulose IV

[a] γ = lattice angle

Native cellulose has a polymorph structure of cellulose I that exists in two crystalline forms: I_α (in algae and bacteria) and I_β (in higher plants).[30,31,32] In cellulose I, a sheetlike structure is stabilised by intermolecular hydrogen bonds. These bonds are parallel to the pyranose rings and the staggered stacking of the sheets by distances equivalent to half-glucose rings along the cellulose chain axis is common in both crystalline forms. The difference between the two allomorphs in native cellulose lies in the mode of staggering: continuous staggering occurs in cellulose I_α, and alternating staggering occurs in cellulose I_β.[33,34,35]

When cellulose I is treated with a strongly alkaline solution or regenerated from a suitable solvent, such as ionic liquid (IL) in the present study, it adopts the different crystal structure polymorph of cellulose II. The X-ray structure of cellulose II reveals that its unit cell consists of two antiparallel chains (Figure 4).[36]
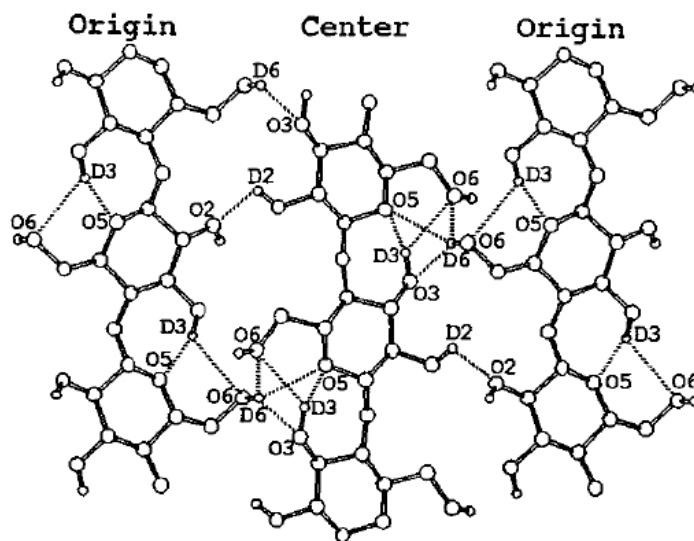
Figure 4. Schematic presentation of the 3D network of hydrogen bonds between origin ('up') and center ('down') chains.[36]

In the cellulose II polymorph, the backbones of these two chains have the same conformation, but they differ in the conformation of their hydroxylmethyl groups (Figure 5).[28] These groups are near the *gt* conformation for the glycosyl residues located at the origin ('up' chain) of the cell.[36] In contrast, the center chain hydroxylmethyl moieties adopt the *tg* conformation ('down' chain).[36] The letter combinations (*gt* and *tg*) are defined as follows: the first letter indicates the torsion angle χ (O5-C5-C6-O6), whereas the second letter indicates the torsion angle χ (C4-C5-C6-O6) as described by Langan *et al*.[36]
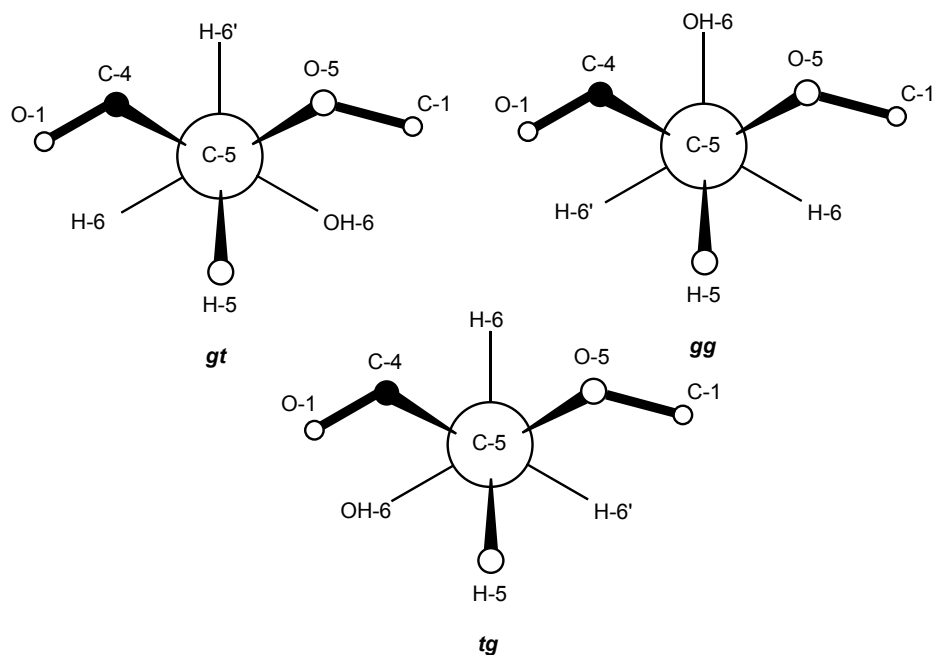
Figure 5. Schematic presentation of the hydroxylmethyl conformations showing the orientation of the C6-O6 bond as *gauche-trans* (*gt*), *gauche-gauche* (*gg*) and *trans-gauche* (*tg*).[37]

The studies of Gessler *et al.* and Raymond *et al.* on the determination of the crystal structure of *β*-cellotetraose and methyl *β*-cellotrioside shows similarities with cellulose II structure.[38,39,40] These findings inspired Langan *et al.* to conclude that a 3D network of hydrogen bonds exists between origin and center chains in crystalline fibres of cellulose II (Figure 5).[36]

Cellulose I fibrils expand when immersed in ammonia or amine solutions by the penetration of these small molecules into the fibrillar structure to form a complex structure. After washing and evaporation of the guest molecules, cellulose fibrils shrink and convert into another crystalline form called cellulose III.[41,42,43,44,45,46,47,48] In the crystal structure of cellulose III, the parallel packed cellulose chains stack without staggering of the C6-OH in the chain direction *i.e.* similar lattice structure to that of cellulose II.[49,50] Due to its capability to from complex structures with guest molecules such as ethylenediamine (EDA) and then release these molecules in the presence of polar solvent, cellulose can be used as a kind of molecular sieve in an aprotic or nonpolar environment.[35]

Cellulose IV is obtained by treating regenerated cellulose (*i.e.* cellulose II) fibres in hot baths under stretch.[4] The lattice structure of this polymorph resembles to that of cellulose I.[4]

1.1.3 Morphological structure of cellulose

The morphological structure of cellulose comprises a well-organised architecture of fibrillar elements. An elementary fibril is considered to be the smallest morphological unit with variable size between 3-20 nm depending on the source of cellulose. In native cellulose, the hierarchy of the fibrillar entities are organised in layers with differing fibrillar textures. However, the arrangement into distinct layers does not exist in regenerated cellulose fibres. These man-made fibres consist of elementary fibrils, which are positioned quite randomly in the structure. A skin-core structure is typical morphology for these regenerated cellulose products.[51] Morphology of the cellulose derivatives can be studied by electron microscopy techniques such as scanning (SEM) or transmission (TEM) electron microscopy.[1] In the current study, SEM was widely used in the investigations of the morphological structures of the synthesised cellulose derivatives.

1.2 Dissolution of cellulose

In this chapter the dissolution of cellulose is explored by covering solvent systems that lead to a homogeneous solution but excludes the heterogeneous (swelling) systems completely. In the current study, all reactions were carried out under homogeneous conditions. Two main classes of solvents are introduced, namely, derivatising and non-derivatising solvent systems. The present chapter concentrates on the 'modern' world of the cellulose solvents, ionic liquids. In this study, they had the essential role of providing the homogeneous media and were regarded as non-derivatising solvents.

In order to dissolve cellulose, one has to find a suitable solvent to break down the prevailing hydrogen bond network, *i.e.* the initial supramolecular structure of cellulose should be destroyed in order to obtain a homogeneous (one-phase) solution. The accessibility of the C6-OH groups in the cellulose structure is the limiting factor for the solubility of cellulose, as it is the main site for the formation of intermolecular hydrogen bonds.[52] Furthermore, cellulose derivatives with unsubstituted C6-OH groups have a tendency to form gels upon dissolving.[53] The solubility of cellulose can be analysed, even though it is not that straightforward and the

results have to be interpreted with caution. In general, the analysis is based on monitoring the changes in chemical structures and physical properties.[1] This can be done by light scattering or by rheological measurements.[1] On the molecular level, the possible derivatisation by the solvent can be investigated by NMR or other spectroscopic techniques.[54]

1.2.1 Historical remarks

Cellulose dissolution and modification has a long history even though it has only attracted greater attention recently in connection with new and 'biofriendly' solvent systems such as ILs. The use of concentrated sodium hydroxide (NaOH) solution in the treatment of the cotton fabric commenced as early as in 1850 when Mercer filed a patent for such process.[55] In the early days, the mechanism of NaOH interactions interested researchers due to numerous applications of cellulose treatments with NaOH solution in fibre modification, dissolution and regeneration. The use of highly concentrated NaOH solutions developed with time to 'modern' NaOH-urea solvent systems, which have greater dissolving power than NaOH alone.[56,57,58] Besides the extensive use of NaOH based solvent systems, there were other solvent systems, from which the most widely used until the 1950s was cuprammonium hydroxide (Cuam) solution.[1] In addition, it has been reported that aqueous solutions of cupriethylene diamine (Cuem) complex and some tetraalkylammonium hydroxides were used as solvents for analytical purposes in those days.[1] In the 1960s, the discovery of numerous metal-complex solvents brought in more variations of cellulose solvents from which the most important were ferric sodium tartrate (FeTNa) and Cadoxen solvent systems.[59] In the following decades, a giant leap towards development of organic solvent systems for cellulose was taken that opened new opportunities for homogeneous cellulose modification. Recently, ILs belonging to this group of organic solvent systems have attracted great attention due to their chemical nature and structural versatility as biofriendly ('green') options for cellulose modification.

1.2.2 Derivatising solvent systems

Derivatising solvent systems dissolve cellulose via covalent modification to yield unstable ethers, esters and acetals.[1] Chemical interactions between cellulose and the solvent are, on the molecular level, fairly well defined and understood.[1] However, the interference of the hydrogen bond system along and between the cellulose chains during the simultaneous dissolution and derivatisation is not completely understood. Moreover, the differences in

solubility of unsubstituted and substituted sites on the AGU into surrounded solvent is yet a matter to be explored. The functional groups introduced during the dissolution should be readily removable prior to the regeneration step. For example, removed by hydrolysis after further derivatisation.[60] Dissolution with derivatising solvents systems lacks reproducibility due to the side reactions and unidentified structures.[60] Even so, a few of these solvents work very efficiently. For example, the N_2O_4 – DMF- system has been used to produce cellulose sulphates (Scheme 1).[61,62]

N_2O_4-DMF

The dissolution mechanism involves the heterolytic cleavage of N_2O_4, followed by the formation of cellulose nitrite (Scheme 1). Selectivity of the reaction is improved by the presence of water resulting in the nitrite formation preferentially occuring at the C-6 position.[63]
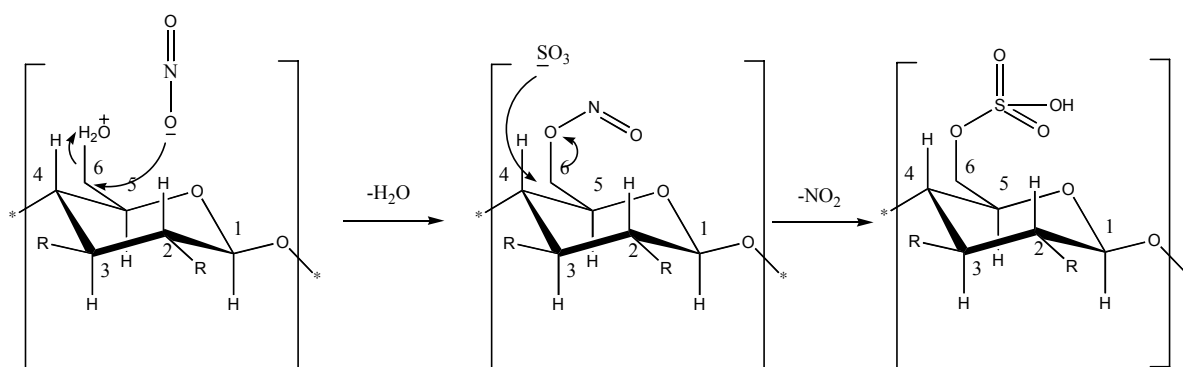
Scheme 1. Mechanism of the formation of the cellulose sulphate via cellulose nitrite intermediate.[63]

H_3PO_4 (>85%)-H_2O

Concentrated phosphoric acid (H_3PO_4) is a well-known solvent for cellulose that forms a phosphate derivative with a selectivity for the C-6 position with the degree of substitution (DS) of approximately 0.2 (Figure 6). Moreover, phosphoric acid promotes lyotropic liquid crystalline behaviour of cellulose at certain concentrations.[64] This concept will be covered in more detail in chapter 1.4.
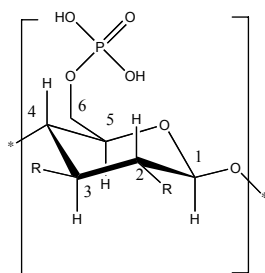
Figure 6. Structure of cellulose phosphate.

(CH₂O)₃-DMSO

The dissolution of cellulose in DMSO-paraformaldehyde (PF) takes place at fairly low temperatures (65-70°C) via hemiacetal formation to yield methyolcellulose (Figure 7).[65,66,67,68,69] The methyol adduct can be removed by the hydrolysis either with water or with protic solvent to yield unsubstituted cellulose.[69]
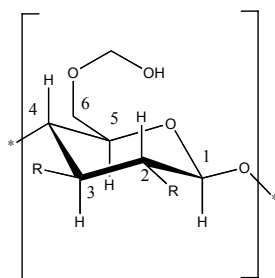
Figure 7. Structure of methyolcellulose.

HCOOH-ZnCl₂

Formic acid is also a good solvent for cellulose forming cellulose formiate (CF) during dissolution (Figure 8). Dissolution is driven by catalysts such as zinc chloride ($ZnCl_2$) or sulphuric acid.[70] When the DS exceeds the value of 2, the formed CF derivative is soluble in formic acid, DMSO and pyridine. It is also possible to isolate the CF derivative from H_3PO_4/formic acid/water mixture.[71] The reactivity of the hydroxyl group in this solvent system was reported to decrease in the order of C-6>C-2>C-3.[71]
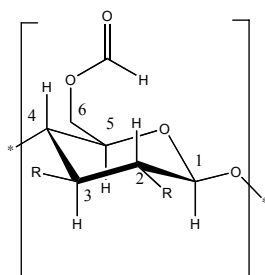
Figure 8. Structure of cellulose formiate.

CS₂-NaOH-H₂O

Cellulose xanthogenate obtained by CS_2-NaOH-H_2O treatment is an important intermediate in the viscose process (Figure 9). The reaction takes place predominantly at the C-2 position up to a DS of 0.5 on alkali cellulose treated with gaseous CS_2, whereas substitution of the C-6 position prevails under 'wet' conditions by reacting slurried alkali cellulose with liquid CS_2.[72]
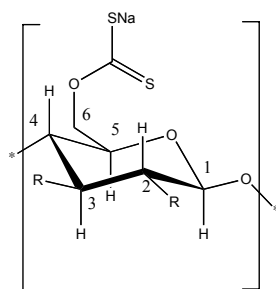
Figure 9. Structure of cellulose xanthogenate.

CF₃COOH-CF₃(CO)₂O

A widely investigated acidic solvent for cellulose is trifluoroacetic acid (TFA), which forms trifluoroacetyl cellulose (Figure 10). The dissolution proceeds at room temperature and it is reported to dissolve even cellulose samples with high *DP* values.[73] However, the dissolution is often accompanied by severe hydrolysis of the cellulose chain and thereby, it is used simultaneously in dissolving and hydrolysing cellulose.[1] Nevertheless, there are few studies in which the substitution has been achieved with a DS value of 1.5.[74]
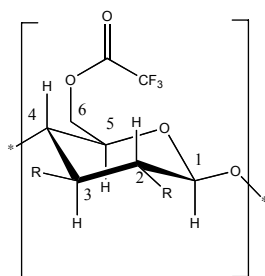
Figure 10. Structure of trifluoroacetyl cellulose.

1.2.3 Non-derivatising solvent systems

In contrast to the derivatising solvent systems, the non-derivatising solvent systems dissolve cellulose without any chemical modification to form a homogeneous phase. These systems

consist of one or more component(s).[75] There has been a great deal of research focusing on the non-derivatising solvent systems. However, only a few solvent systems are suitable for controllable and homogeneous media required for the chemical modification of cellulose. In some cases, restrictions of use include the high reactivity of the solvents, which may lead to side reactions and also toxicity. In addition, the solution may lose its homogeneousity during the reaction as, in some cases, the partially reacted cellulose aggregates. Such aggregates may precipitate out of the solution or form gels. This hinders the reaction from running to completion. It can also result in practical problems such as the stirring of the solution becomes difficult due excessive viscosity.

1.2.3.1 Conventional solvents

Aqueous solvent systems

Cellulose can be dissolved in aqueous solvent systems containing metals such as copper in Cuam and Cuen solutions.[1] The dissolution mechanism involves deprotonation of C2-OH and C3-OH during the metal complex formation as shown in figure 11.[76]
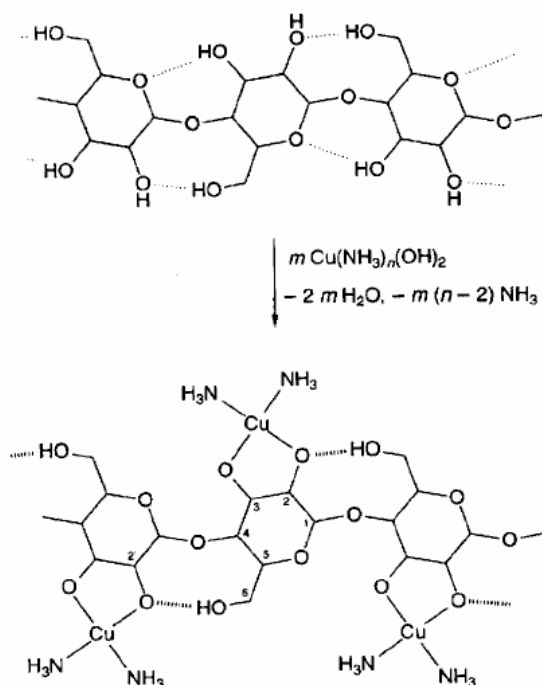
Figure 11. The formation of Cuam-cellulose complex.[76]

There are also other metal containing solvents consisting of nickel (Ni-tren) or cadmium (Cd-tren) in metal-tris(2-aminoethyl)amine.[75,76] The binding site and the dissolution mechanism for these complexes is similar to Cuam and Cuen solutions (C2-OH and C3-OH).[75,76] Colours of these solutions vary as Cuam and Ni-tren have an intensive dark blue colour whereas Cd-tren solution is almost colourless.

MCC can be dissolved without any pretreatment or activation in a 10% NaOH solution and in molten salt hydrates such as magnesium chloridehexahydrate ($MgCl_2 \cdot 6H_2O$), lithium chloridepentahydrate ($LiCl \cdot 5H_2O$), lithium perchlorotrihydrate ($LiClO_4 \cdot 3H_2O$) and zinc chloridetetrahydrate ($ZnCl_2 \cdot 4H_2O$).[77,78] Moreover, the morphology of regenerated cellulose could be altered by varying the composition of the molten salt hydrates.[78]

Organic solvent systems

Organic water-free solvent systems consist of from one to three component(s). A preactivation (swelling) of cellulose to a more soluble form is often a required step. Solvent systems of this kind include the frequently used two-component systems such as *N,N*-dimethylacetamide/lithium chloride (DMA/LiCl) and 1,3-dimethyl-2-imidazolidinone/lithium chloride (DMI/LiCl).[79,80]

Monohydrated *N*-methylmorpholine-*N*-oxide (NMMO) is probably the most used non-derivatising solvent for cellulose in industry, and it is used in the manufacturing of man-made fibres.[81] NMMO belongs to the group of one-component tertiary amineoxide solvents for which the first reports on dissolution of cellulose appeared as early as in 1939 (Figure 12). It may however, be misleading to consider tertiary amineoxide solvents as true one-component solvent systems as they usually have to be dissolved either in water or organic solvent (DMF or DMSO) due to their solid and/or explosive nature at room temperature.[82] On the other hand, NMMO loses its capability to dissolve cellulose upon hydration by two or more water molecules.[83]
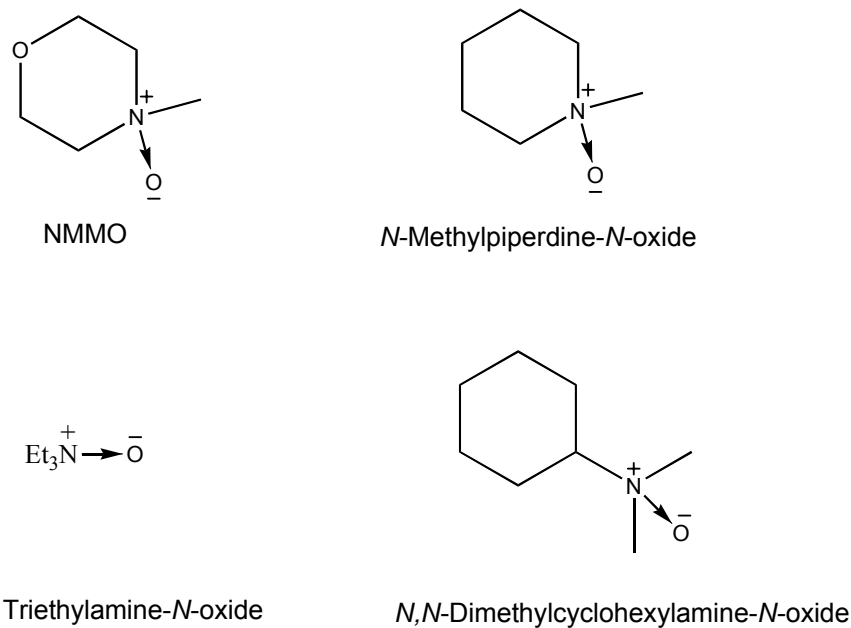
Figure 12. Structures of one-component tertiary amineoxide solvents for dissolution of cellulose.

The mechanism of cellulose dissolution in this family of solvents is accompanied by the strong intermolecular interaction between cellulose and a strong N→O dipole. The interaction may be interpreted as the formation of a hydrogen bond complex with a superimposed ionic interaction as shown in figure 13.[51]
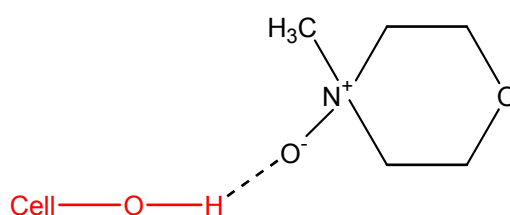
Figure 13. A hydrogen bond complex between cellulose and NMMO during the dissolution.[1]

The two-component DMA/LiCl solvent system is perhaps the most used for homogeneous cellulose modification.[79] The dissolution process can be achieved in two ways: by altering the ratio between the solvent and cellulose.[84] Both of these approaches require an activation step.

Two pathways for the activation step depending on the cellulose concentration exist. The mixture of DMA containing the 2.5% (w/w) of cellulose is stirred at 130°C for two hours (activation step). When the cellulose concentration is higher 4.3% (w/w) the temperature is increased to 160°C. After the activation step the temperature is decreased to 100°C at which dry LiCl is added in one portion. Both, dried cellulose and cellulose that contains 5% (w/w) of water can be used. Then, the mixture is let to cool to room temperature to obtain a clear solution. In order to remove the remaining water bound to cellulose, the solvent is distilled under a nitrogen atmosphere. In addition, the dissolution process is similar for both DMI/LiCl and 1-methyl-2-pyrrolidinone (NPM)/LiCl solvent systems.[80,85]

The dissolution mechanism with DMA/LiCl follows the same principle as with NMMO which takes advantage of the strong intermolecular interaction between the cellulose and the strong dipole such as in the case of DMA carbonyl group (Figure 14).
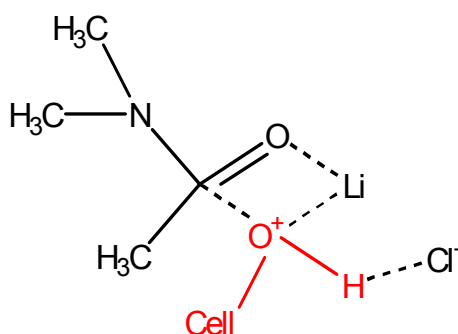
Figure 14. Proposed interactions between cellulose and DMA/LiCl solvent system during the dissolution.[1]

Another important two-component solvent for cellulose is DMSO/tetra-*n*-butylammonium fluoride (TBAF). This dissolution process is simpler than that of DMA/LiCl as a clear solution is obtained after 15 minutes of stirring at room temperature and an activation step is not needed. However, the system lacks flexibility regarding the choice of halide anion.

Dissolution of cellulose was not achieved when fluoride was replaced by either chloride or bromide.[85] A further limitation is the possible Hofmann elimination upon heating in the presence of water (Scheme 2).[86,87] It has also been claimed that Swern oxidation by DMSO is one of the shortcomings of this solvent system.[88] However, Swern oxidation is very unlikely under standard dissolution and reaction conditions as it requires the presence of an 'activator' such as oxalyl chloride.[89]
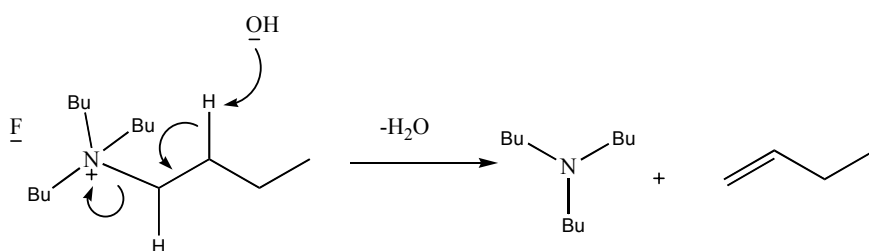
Scheme 2. Reaction mechanism of Hofmann elimination of TBAF.[87]

Although there exists a variety of higher number of component systems such as three-component, only DMSO/SO$_2$/DEA is mentioned here due to its frequent use.[90,91] DEA could be replaced with DMF or DMA to give some variety under practical conditions. The dissolution takes place by the interaction of all of the components of the solvent system with cellulose as is shown in scheme 3.
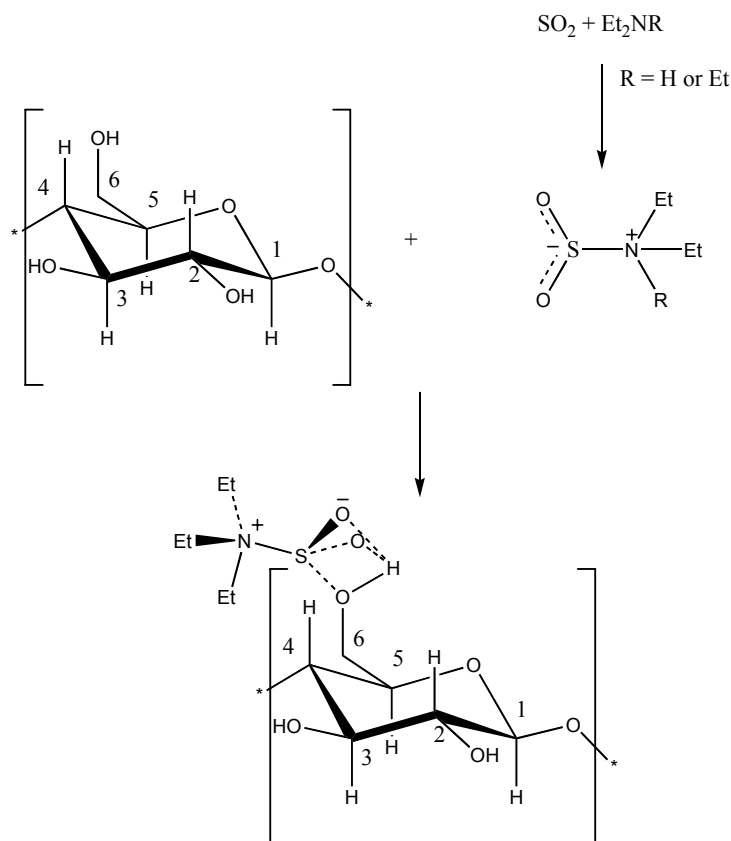
Scheme 3. Proposed interactions between cellulose and DMSO/SO$_2$/DEA solvent system during dissolution.[92]

1.2.3.2 Ionic liquids

Ionic liquids are regarded as low-melting (m.p. < 100°C) salts and hence, they form liquids that consist purely of cations and anions. Some of the ILs are liquids even at room temperature (RTILs). The reason for the low melting point of such salts lies in the symmetry of the respective unit lattice. An asymmetrical cation breaks down the overall symmetry of the molecule (ionic pair) and hence, the packing of the molecules in the lattice becomes irregular and results in low melting points.

Although the first representative of ILs has been known since 1914,[93] they have only comprehensively found their place in research as recently as the 1980s. From the discovery of the first useful IL, ethylammonium nitrate, it took a fairly long time to discover that several tetraalkylammonium salts were air- and moisture-stable with the properties of being useful as solvents for synthesis, spectroscopy and electrochemistry.[94] ILs are often associated with

'green chemistry'. If these solvents are efficiently recycled, the overall waste production of the process is decreased. This is the 'green' aspect. However, ILs are still synthesised using conventional organic solvents, which detracts from their overall green chemistry value. This is an issue that still has to be addressed in research.

In carbohydrate research, it took a long time for the discovery of ILs as efficient media for chemical modifications. The first suggestion of using molten *N*-ethylpyridinium chloride in the presence of nitrogen containing bases to dissolve cellulose, was made in 1934 (Figure 12).[95] However, little practical use was seen at the time since the melting point of this IL is relatively high (118°C). The study by Swatloski *et al.* can be seen as a cornerstone in the dissolution of cellulose by ILs.[96] They demonstrated that now cellulose can be dissolved at high concentrations 25% (w/w) in imidazolium-based ILs (Figure 15).[96] These authors also discussed the nature of the anion and the alkyl substituent (R) of the cation on the dissolution capacity for cellulose (Table 2).[96]

X^-	R
Cl^-	Methyl (Mmim)
Br^-	Ethyl (Emim)
BF_4^-	Butyl (Bmim)
PF_6^-	Allyl (Amim)
$AlCl_4^-$	Hexyl (Hmim)
$Me_2PO_4^-$	
SCN^-	
OAc^-	
$HCOO^-$	
$NCNCN^-$	
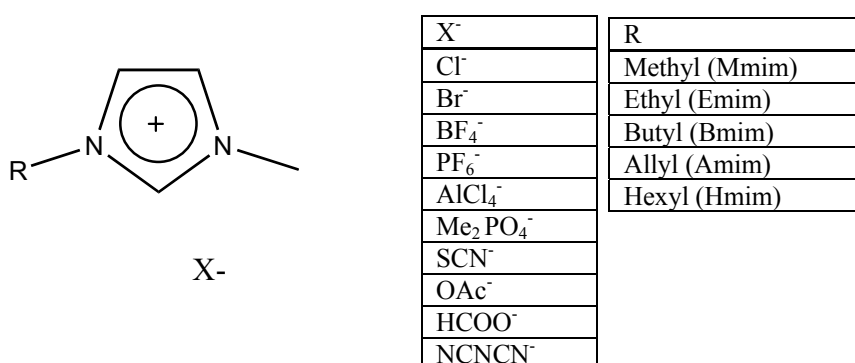
Figure 15. A collection and general structure of 1-alkyl-3-methyl-imidazolium-based ionic liquid used for cellulose dissolution.

Table 2. Solubility of cellulose in different ILs using conventional heating or microwave irradiation.[96]

IL	Heating Method	Solubility % (w/w)
[Bmim]Cl	Heating at 100°C	10%
[Bmim]Cl	Heating at 70°C	3%
[Bmim]Cl	Heating at 80°C and sonication	5%
[C$_6$mim]Cl	Heating at 100°C	5%
[C$_8$mim]Cl	Heating at 100°C	Poor
[Bmim]Cl	Microwave irradiation with pulsing 3-5 sec	25%
[Bmim]Br	Microwave irradiation	5-7%
[Bmim]SCN	Microwave irradiation	5-7%
[Bmim]PF$_4$	Microwave irradiation	None
[Bmim]PF$_6$	Microwave irradiation	None

Swatloski *et al.* suggested that the major contributor for the solubility of cellulose in [Bmim]Cl over conventional solvents is the high chloride concentration that allows rapid and efficient dissolution by breaking the prevailing hydrogen bond network (Scheme 4).[96] When the length of the alkyl chain was increased from C$_4$ to C$_6$ or C$_8$ as in [C$_6$mim]Cl and [C$_8$mim]Cl, the solubility of cellulose decreased. Ionic liquids incorporating anions that are strong hydrogen bond acceptors were the most effective solvents, whereas ILs containing non-co-ordinating anions, including BF$_4^-$ and PF$_6^-$, were non-solvents.[96]
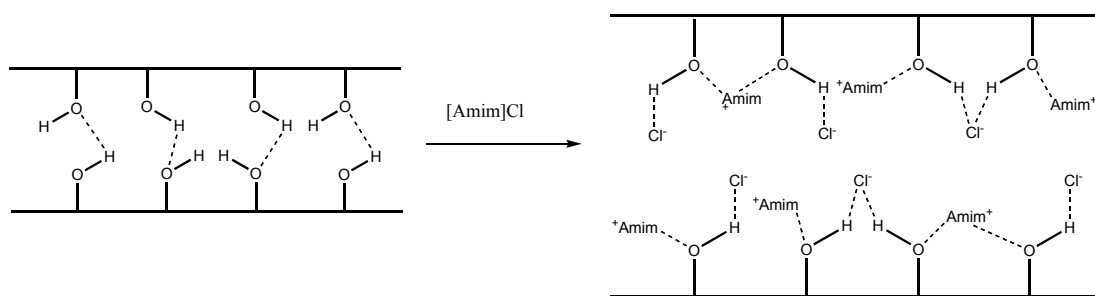
Scheme 4. Dissolution mechanism of cellulose in ILs. [Amim]Cl is shown here as an example.[103]

The presence of water in imidazolium-based ILs significantly decreases the solubility of cellulose.[96] This is due to the competitive hydrogen bonding of water to the cellulose microfibrils, which inhibits solubilisation.[96] When the water concentration is approximately 1% (w/w), dissolution of cellulose no longer occurs.[96] A newcomer in the family of imidazolium-based ILs for cellulose dissolution is 1,3-dimethylimidazolium dimethylphosphate ([Mmim]Me$_2$PO$_4$) that has the lowest viscosity of the ILs mentioned above. Nevertheless, it does not tolerate water, even at trace amounts.[97] However, there are contradictory reports stating the opposite effect of water on the solubility.

The value of ILs lies in the wide variation of their structures and hence, the name 'designer' solvent frequently appears in the literature.[98] ILs can be designed to meet the certain requirements such as viscosity or melting point by varying the cation and anion as desired.[98] The effect of the anion on the melting point of 1-ethyl-3-methylimidazolium-based ([Emim]) is shown in table 3.[99] As the size of the anion is increased, the melting point decreases, which is a common phenomena in all imidazolium-based ILs. This is due to the increased distance between the cation and anion, which makes the ionic interaction weaker.

Table 3. The effect of anion on melting point in [Emim]-based ILs.[99]

IL	Melting point (°C)
[Emim]Cl	87
[Emim]NO$_2$	55
[Emim]NO$_3$	38
[Emim]AlCl$_4$	7
[Emim]BF$_4$	6 (T_g)
[Emim]CF$_3$SO$_3$	-9
[Emim]CF$_3$CO$_2$	-14

Ionic liquids have seemingly simple structures consisting of anions and cations. However, it has been shown that their physical properties cannot be explained by electrostatic interactions alone.[100] The viscosity properties of ILs are dependent on the length of the alkyl group on the cation - when the alkyl chain length increases, the viscosity also increases.[96] This may be considered somewhat surprising. Generally, when the size of the alkyl groups is increased, the decrease in overall electrostatic interactions and hydrogen bonding are expected to decrease the viscosity.[100] X-ray diffraction studies have shown that solid IL consists of ions connected together by hydrogen bonds (Figure 16).[101,102] It has been suggested that this network is maintained in the liquid state and thus also exists in solutions of ILs in organic solvents.[100] Due to this kind of behaviour, it has been stated that ILs and their solutions in organic solvents can be considered as heterogeneous at the nanoscale.[100]
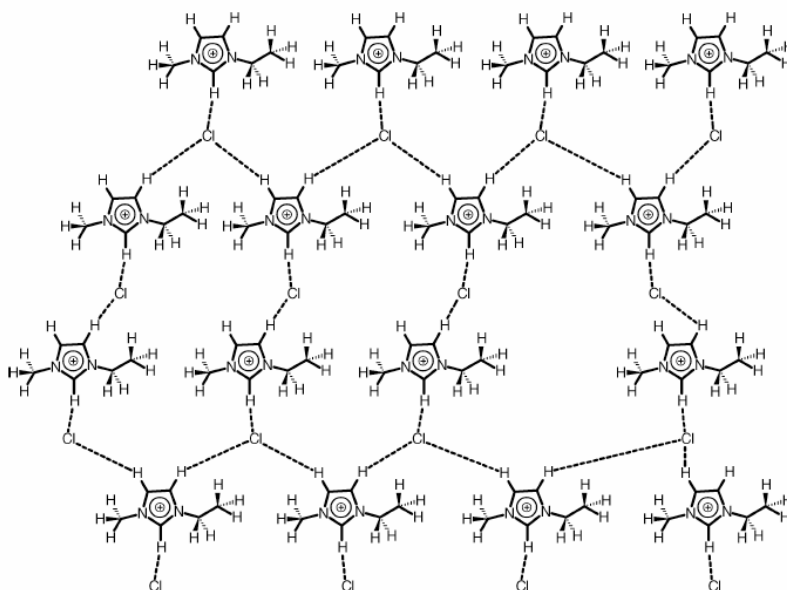
Figure 16. Diagram of the hydrogen bond network in [Emim]Cl ionic liquid.[101]

The physical properties of ILs are dependent on several interactions and structural features. When the alkyl group is short, the equilibrium distance between the cations is determined by the head group Coulombic interactions. These have less influence when the alkyl group is long and the structure of the IL is affected by dispersion interactions between the tails. The dominant interactions in ILs between the cation and anion are shown in figure 17 using [Amim]Cl as an example.
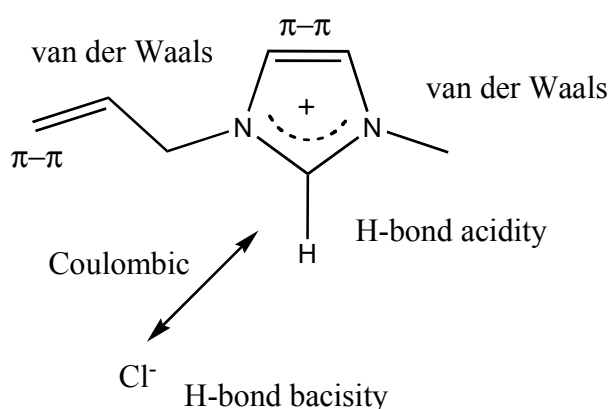
Figure 17. Structure of [Amim]Cl showing the dominant interactions.

The choice of IL is often a compromise between solubilising power and its rheological properties. For example, [Bmim]Cl is solid at room temperature. On the other hand, [C$_6$mim]Cl, [C$_8$mim]Cl and [Amim]Cl are viscous liquids, though [Amim]Cl can crystallise at room temperature (**I**).[96] In addition to melting point, viscosity is another important factor when it comes to the synthesis of cellulose derivatives, particularly as the viscosity should be as low as possible. A detailed study on the dissolution in [Amim]Cl of different types of cellulose including MCC, dissolved pulp and cotton linters, was carried out by Zhang *et al*.[103] The dissolution of cellulose was monitored using a polarizing optical microscope on a 5% (w/w) pulp sample that had a *DP* of 650 at 80°C (Figure 18).[103] Dissolution of cellulose into [Amim]Cl differed from that of NMMO solvent as the swelling of fibres prior to dissolution was not observed. In the beginning, the dissolution occurred rapidly, then the rate declined with time which may be due to the more perfect crystalline structure in residual cellulose fibrils. It was demonstrated that [Amim]Cl was able to dissolve even high *DP* cellulose completely in 30 min. An 8% (w/w) sample of cotton linters was also completely dissolved at 80°C.[103] The ^{13}C NMR spectrum of MCC dissolved in [Amim]Cl gave well-resolved signals for C-1 and C-6. Therefore, [Amim]Cl can be considered as a true solvent for cellulose dispersing at the molecular level.[103] Overall, [Amim]Cl has been shown to have great solubilising power at low viscosity and will be further discussed in context of the present study (**I, II, III, IV, V**).
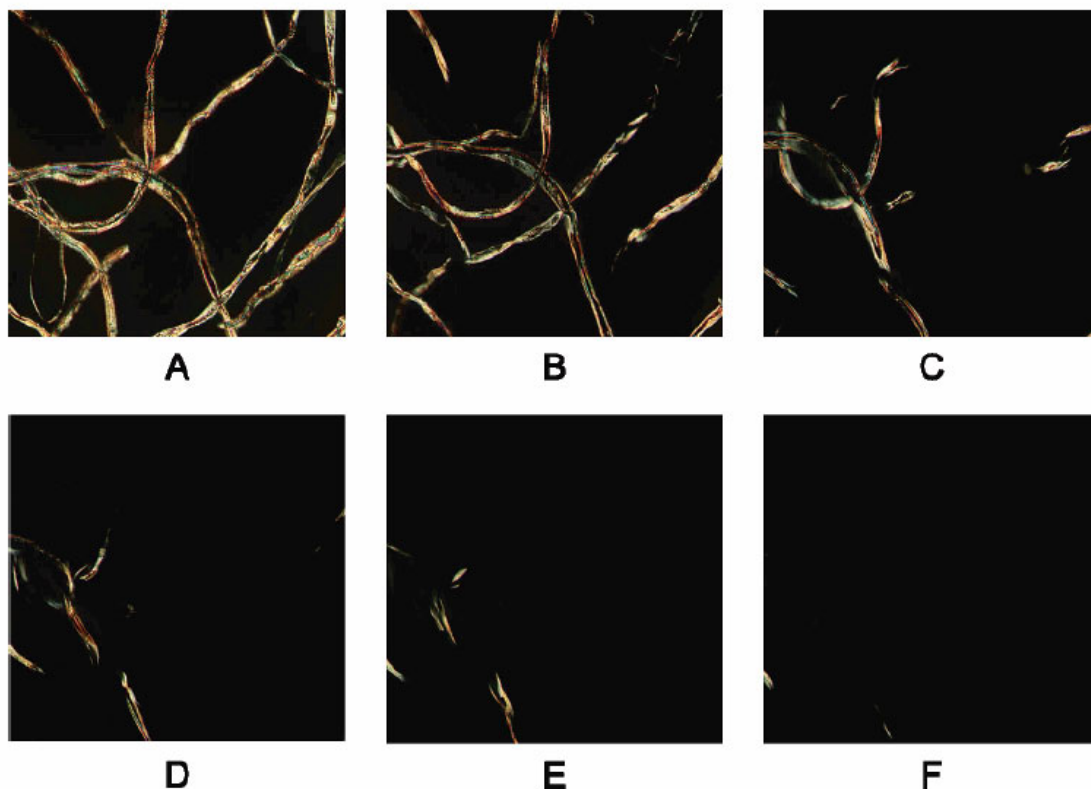
Figure 18. Polarising optical microscopy images of pulp dissolution in [Amim]Cl at different times: a) 0 b) 10 c) 15 d) 17.5 e) 25 f) 30 min.[103]

1.3 Synthesis of cellulose derivatives

In this chapter, the literature on the synthesis of cellulose derivatives in ILs is covered as it is directly related to the current study. The reactions described in published studies are collated on the basis of reaction types (*i.e.* acylation etc.). Most of the research has concentrated purely on the synthesis of cellulose derivatives. However, the material properties of the obtained derivatives have been overlooked. The research has centered on the determination of DS values of the derivatives which is, of course, a very important factor. Nevertheless, the field of new synthetic approaches applied to cellulose in IL reaction media lacks empirical data. In some cases, ILs may provide more reactive or stable environment for certain reactions (**II**). This issue will be discussed in more detail in relation with the current work.

Cellulose is a versatile starting material for several applications. It is directly linked to the paper industry in which cellulose is used in a conventional way, as a structural material for paper and cardboard products. However, even though this is the current major use of cellulose, only the imagination is the limit for the utilisation of this extremely versatile and

adaptable material. Cellulose can be chemically modified to yield derivatives which are used widely in different industrial sectors in addition to conventional applications. As an example, in 2003, 3.2 million tons of cellulose was used as a raw material in the production of regenerated fibres and films in addition to cellulose derivatives.[104] Derivatives are further used as coatings, laminations, optical films and absorbents. Additionally, cellulose derivatives can be found as additives in building materials and also in pharmaceutical, food and cosmetic products. Table 4 summarises industrially and commercially important cellulose derivatives and their application sectors.[105]

Table 4. Commercially important cellulose esters and ethers.[105]

Product	Global Production (t/a)	FG	DS	Solubility	Application
Cellulose acetate	900 000	-OAc	0.6–0.9	Water	Coatings and membranes
			1.2–1.8	2-methoxy ethanol	
			2.2-2.7	Acetone	
			2.8-3.0	Chloroform	
Cellulose nitrate	200 000	-NO$_2$	1.8–2.0	Ethanol	Membranes and explosives
			2.0-2.3	Methanol, Acetone	
			2.2-2.8	Acetone	
Cellulose xanthate	32 000000	-C(S)SNa	0.5-0.6	NaOH/water	Textiles
Carboxymethyl cellulose	300 000	-CH$_2$COONa	0.5-2.9	Water	Coatings, paints, adhesives and pharmaceuticals
Methyl cellulose	150 000	-CH$_3$	0.4-0.6	4% aq. NaOH	Films, textiles, food- and tobacco industry
			1.3-2.6	Cold water	
			2.5-3.0	Organic solvents	
Ethyl cellulose	4000	-CH$_2$CH$_3$	0.5-0.7	4% aq. NaOH	Pharmaceutical industry
			0.8-1.7	Cold water	
			2.3-2.6	Organic solvents	
Hydroxylethyl cellulose	50 000	-CH$_2$CH$_2$OH	0.1-0.5	4% aq. NaOH	Paints, coatings, films and cosmetics
			0.6-1.5	Water	

Commercial cellulose esters and ethers are produced under heterogeneous reaction conditions by using acids and acid anhydrides as reagents. On the other hand, the main synthetic route for ethers is Williamson ether synthesis.[1] Major drawbacks of heterogeneous phase reactions are the limited reaction rates and lack of regioselectivity in certain reactions. The ramification of these drawbacks are that the accessibility of free hydroxyl groups of cellulose is the determining factor for selectivity and for the DS. In contrast, when carrying out reactions in homogeneous solutions, the regioselectivity of the reaction is determined by the reactivity differences among the free hydroxyl groups on the cellulose molecules, not by their accessibility. In addition to controllable selectivity of the reaction, the DS values can be tuned varying from low DS derivatives to highly substituted compounds. Therefore, the material properties of the obtained cellulose derivative may also be adjusted in the desired way (**III**, **IV** and **V**).

1.3.1 Esterification of cellulose

The first IL used in the esterification of cellulose were *N*-alkylpyridinium halides, especially *N*-ethylpyridinium chloride and *N*-benzylpyridinium chloride.[95] These solvents had high melting points and were therefore diluted with organic solvents, such as DMSO, DMF or pyridine.[95] Such mixtures provided a homogeneous reaction media and several derivatives were synthesised using carboxylic acid anhydrides or chlorides and pyridine as a base. These derivatives include acetates (**1**), butyrates (**2**), benzoates (**3**), phthalates (**4**) and anthranilic (**5**) acid esters of cellulose (Figure 19).[95] However, the DS values have not been reported for these derivatives and thereby, the efficiencies of these reactions are difficult to judge.
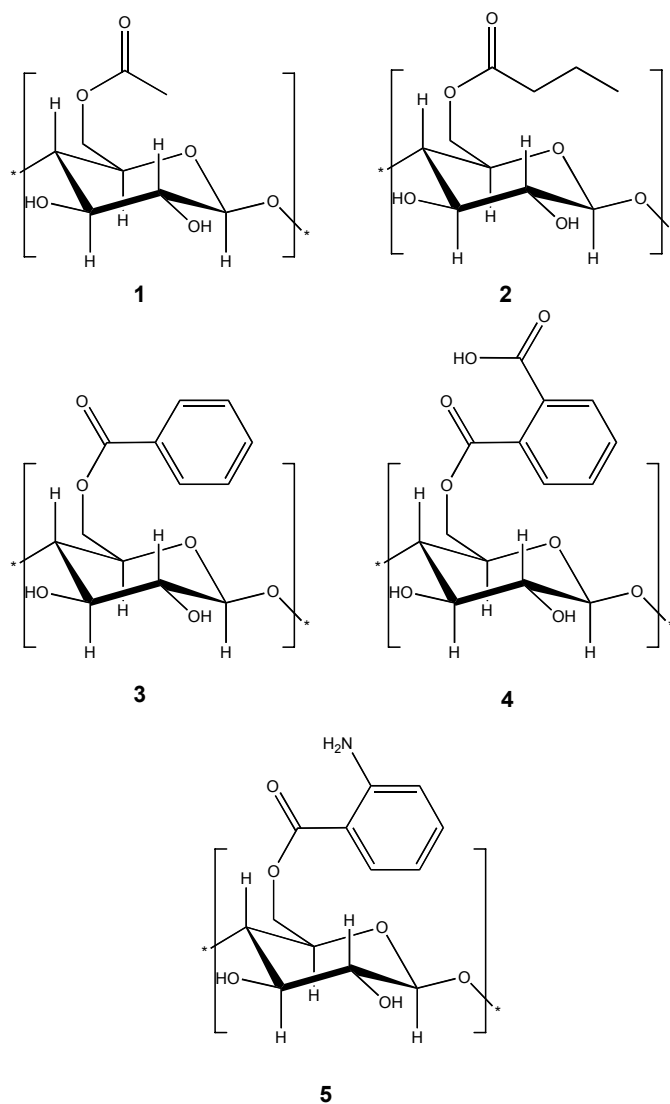
Figure 19. Schematic structures of cellulose acid esters synthesised in *N*-benzylpyridinium chloride/pyridine used as early IL: acetate (**1**), butyrate (**2**), benzoate (**3**), phthalate (**4**) and anthranilic (**5**) acid esters of cellulose.[95]

1.3.1.1 Acetylation of cellulose

Acetylation of cellulose has been comprehensively studied in different ILs. Reactions have been carried out either in the presence of a base or without and using acetic anhydride or acetic chloride as reagents. Ionic liquids have been found to function not just as solvents but also as active base catalysts for the acetylation reactions.[106]

Commercially, cellulose acetates are produced by the reaction of cellulose with an excess of acetic anhydride in the presence of sulphuric acid or perchloric acid as the catalyst.[107] Due to the heterogeneous nature of the reaction, it is impossible to produce partially acetylated cellulose directly.[107] In contrast, acetylation of cellulose in IL can be controlled to yield derivatives with various DS values.[106] Furthermore, when ILs are used as the reaction media, the amounts of reagents can be reduced as catalyst is not needed for the reaction. This also makes the recyclability of the solvent easier and achievable.[88]

Several publications report acetylation of cellulose without a catalyst in different ILs. These include chlorozincate (**6**), 1-allyl-2,3-dimethylimidazolium bromide, [Admim]Br (**7**), 1-butyl-2,3-dimethylimidazolium chloride, [Bdmim]Cl (**8**), 3-methyl-*N*-butylpyridinium chloride (**9**), benzyldimethyl(tetradecyl)ammonium chloride (**10**), [Bmim]Cl and [Emim]Cl among others (Figure 15 and 20).[106,108,109,110,111,112] Wu *et al.* studied the acetylation with acetic anhydride in [Amim]Cl in the absence of a catalyst and obtained cellulose acetate with DS values between 0.94 to 2.74.[106] In contrast, an uncatalysed acetylation of cellulose with acetic anhydride in DMA/LiCl often yields derivatives with low DS values.[113] It has been reported that in all acetylation reactions, the DS values were increased with increasing equivalence of the acetylation reagent. However, Wu *et al.* claimed a decline of DS with higher (> 6.5) equivalents of acetic anhydride in [Amim]Cl.[106,108] This behaviour was explained by a weakened capacity of [Amim]Cl towards acetylation resulting from an excess of acetic anhydride.[106] However, variations in solubility could be regarded as a more likely explanation for the decline in DS value. It has also been shown that the addition of pyridine into the IL reaction mixture can increase the DS value, if acetic anhydride is used.[109] In this context, the reaction mechanism should be considered in order to understand the role of the IL in the reaction (Scheme 5b).[114]
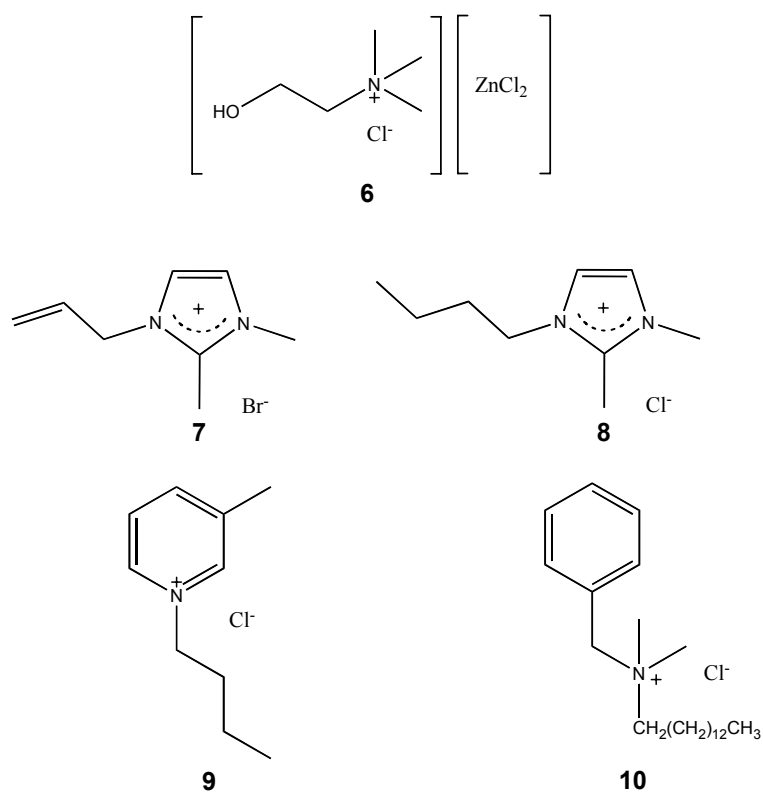
Figure 20. Structures of different ILs used in the acetylation reactions: chlorozincate (**6**), 1-allyl-2,3-dimethylimidazolium bromide (**7**), [Admim]Br, 1-butyl-2,3-dimethylimidazolium chloride (**8**), [Bdmim]Cl, 3-methyl-*N*-butylpyridinium chloride (**9**), benzyldimethyl(tetradecyl)ammonium chloride (**10**).

The reaction mechanism of the acetylation of alcohols in a conventional organic solvent in the presence of pyridine is presented in scheme 5a.[115] Pyridine functions as a catalyst initiating the reaction by attacking the carbonyl group of acetic anhydride and thus produces a highly reactive intermediate which the alcohol can then attack producing the *O*-acetoyl derivative along with acetic acid. Pyridine is then released back to the catalytic cycle by deprotonation by acetic anion.
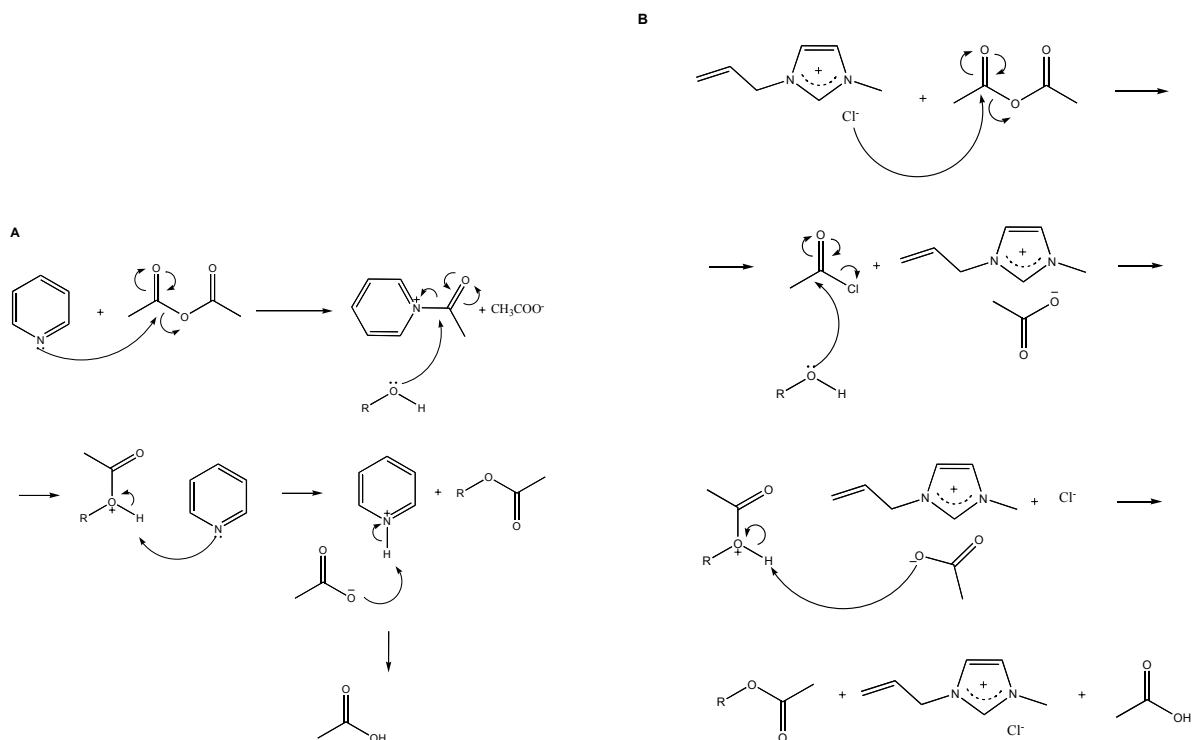
Scheme 5. Reaction mechanisms of acetylation of an alcohol a) in the presence of a pyridine catalyst in conventional organic solvent[115] and b) in the ionic liquid ([Amim]Cl) without the base catalyst.[114]

The catalytic activity of ILs can be explained by following (Scheme 5b). The IL functions as a catalyst initiating the reaction. The chloride anion as a nucleophile attacks the acetic anhydride. This produces more reactive acetic acid chloride, while releasing the acetic anion. This, in turn, co-ordinates with the imidazolium cation to form another IL structure namely, [Amim]OAc. Alcohol attacks the acetic acid chloride releasing the chloride anion back to the 'catalytic cycle'. Then the alcohol derivative is deprotonated by the acetic anion to yield acetic acid. It should be noted that in contrast to pyridine, IL does not function as an acid scavenger.

1.3.1.2 Acylation of cellulose with carboxylic acid derivatives

1.3.1.2.1   Long chain aliphatic carboxylic acids

Only a few publications on the acylation of cellulose with long chain aliphatic carboxylic acids (*i.e.* fatty acids) in IL reaction media have been published (**I**).[88] This may be partially due to the low solubility of long chain aliphatic acid derivatives in some ILs forming

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heterogeneous solutions, which occur either right at the beginning or in the course of the reaction.[88] Obviously, this is an undesired phenomenon that hinders the reaction to yield fully substituted derivatives.[88] Such behaviour was observed in a study in which cellulose was reacted with lauroyl chloride in different ILs.[88]

The reactions yielded a fairly low DS (0.12-1.54) and the choice of IL did not improve the reaction remarkably.[88] These authors stated that additional studies were necessary in order to explore the poor solubility of long chain carboxylic acids as acylating reagents in ILs in order to be able to conduct reactions under homogeneous conditions.[88] The reaction with fatty acids as acylating reagents has serious drawbacks in ILs when compared to the DMA/LiCl system. In DMA/LiCl solvent system the derivatives can be synthesised with controllable DS values ranging from less substituted to fully substituted derivatives.[116]

1.3.1.2.2   Other carboxylic acids

Pentanoyl, hexanoyl and benzoyl chloride

Successful acylation of cellulose in ILs with high DS values has been achieved with the following acid chlorides: pentanoyl chloride, hexanoyl chloride and benzoyl chloride.[117] Derivatives with DS values ranging from 0.8 to 3.0 were obtained after reaction at 80°C in [Bmim]Cl for 2 h.[117] From these three reagents, pentanoyl chloride and benzoyl chloride exhibited the highest reactivity in [Bmim]Cl, whereas the reaction with hexanoyl chloride required an increase in the amount of the acylating reagent in order to yield high DS derivatives.[117] Contrary to that found for acetylation, these reactions required a base (pyridine) for the efficient acylation.[106,117] A relationship between the length of the alkyl chain of the acylating reagent with that of the imidazolium cation in IL molecule was observed when the DS values of acylated cellulose derivatives synthesised in [Bmim]Cl were investigated. These preliminary results showed that similar length of the alkyl chain in acylating reagent and in imidazolium cation yield derivatives with low substitution degrees.[117] This phenomenon is, however not yet fully understood.

Phthalic and succinic anhydride

Phthalated cellulose (**4**, Figure 19) is a potential biodegradable material for absorbing heavy metals from industrial waste waters due to its metal chelating properties. Cellulose aceto

phthalate is already used in the pharmaceutical industry as an enteric coating for tablets and capsules.[118]

Liu *et al.* studied the phthalation of cellulose by phthalic anhydride in the absence of base in [Amim]Cl or [Bmim]Cl. This yielded phthalated cellulose with DS values ranging from 0.1 to 0.73 for [Amim]Cl and 0.12 to 2.54 for [Bmim]Cl.[119,120] Cellulose concentration (2.5% w/w) was kept constant in all reactions.[119] These authors claimed that the degradation of cellulose took place in both ILs, but was less severe in [Amim]Cl.[119] Dissolution was carried out at 80°C for 10 hours and a decrease in intrinsic viscosity, *DP* and molecular weight was observed.[119]

In theory, phthalated cellulose could provide a reaction site for further modification reactions.[119] However, this carboxylic acid group can be considered to be fairly sterically hindered as it is *ortho* to the ester linkage site on the phenyl ring. Moreover, there are no examples of subsequently modified phthalated cellulose derivatives reported in the literature.

Succinoylation of cellulose in [Amim]Cl yielded very low DS values ranging from 0.071 to 0.22.[121] The low DS values were thought to be caused by the low reactivity of succinic anhydride. It was also stated that the low DS would prevent the cross-linking reaction from occuring. However, the situation may just be the reverse, in that the low DS values may be due to the cross-linking reactions. Further, the solubility of the product may be limited, which would inhibit the progress of the reaction.
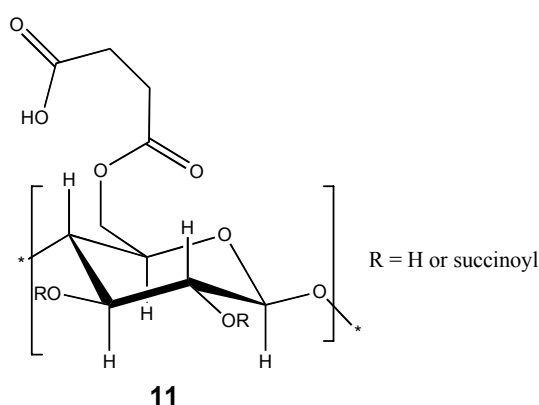
Figure 21. Structure of succinoyl (**11**) cellulose.

Cellulose fuoroates have been synthesised in [Bmim]Cl (Figure 22a).[122,86] Cellulose 2-furan carboxylic acid esters (fuoroate) are interesting materials due to their capability to form rot resistance membranes (Figure 22b).[123,124,125] Reactions were carried out using two routes in [Bmim]Cl. In the first route, cellulose was reacted with 2-furoyl chloride in the presence of pyridine, whereas in the second route 2-furan carboxylic acid was activated by N,N'-carbonyldiimidazole (CDI).[122]
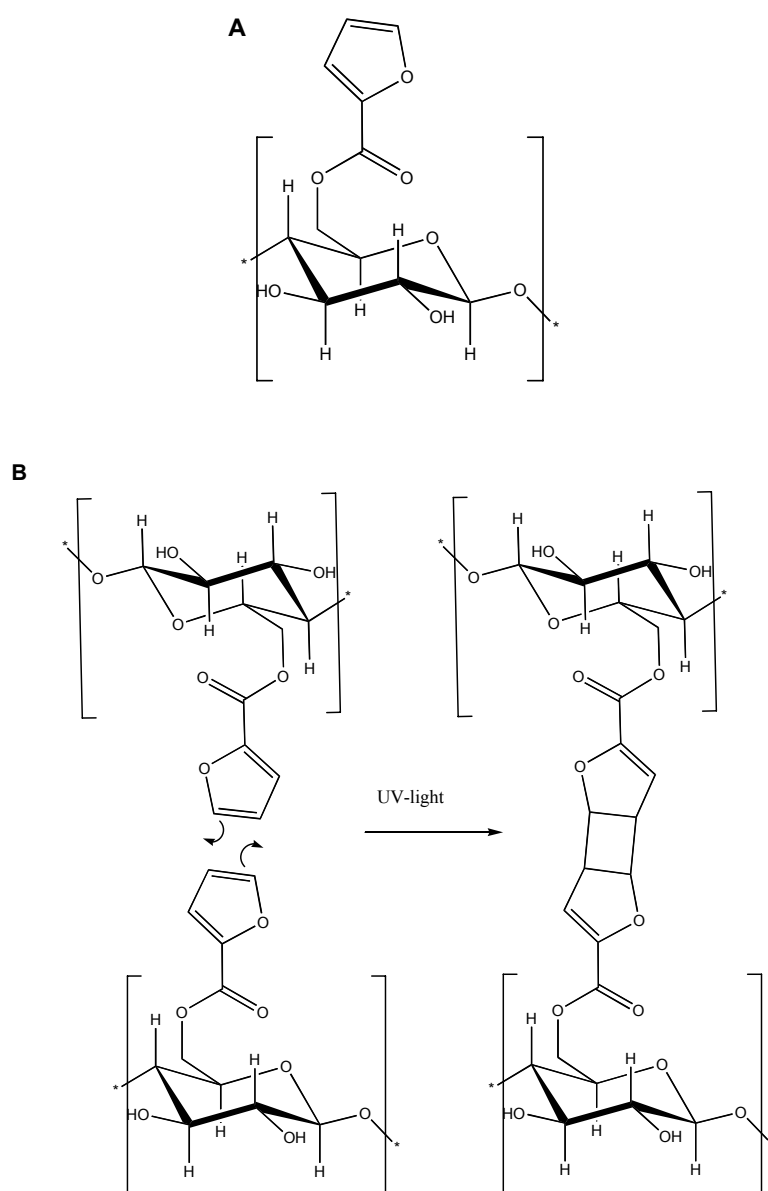
Figure 22. a) Structure of cellulose fuoroate having DS of 1 and b) photo-cross-linking of cellulose fuoroates to obtain membranes.

Furoylations yielded DS values of between 0.5 and 3.0 at 65°C within 3 h.[122] A substantial difference in DS values between the products obtained from different reaction routes was observed. The acid chloride/pyridine route gave higher DS values (DS of 3), whereas the activation route yielded a maximum DS value of 1.33. The *DP* of the starting material affected the reactivity of cellulose with furoyl chloride by a great deal. When cotton linters of a high *DP* (*DP*=1800) were used, a DS value of 0.67 was obtained.[122] Pyridine was required for the successful reaction as severe hydrolysis of the cellulose chain was observed in the absence of base.[122] Reactions in DMA/LiCl system yielded fully substituted derivatives (DS of 3) after 22 h reaction.[126,127] On a laboratory scale, it seems that there is no practical value in using ILs over conventional solvents systems, except for high *DP* cellulose.

It would have been interesting to see if the solvent used in the reaction had affected the material properties, but the authors did not asses these properties. It is known that the cellulose fibres spun from ILs have different properties to those obtained from the conventional viscous process.[128]

1.3.1.3 Sulphation of cellulose

Homogeneous sulphation of bagasse cellulose was studied in [Bmim]Cl in order to obtain anticoagulation active cellulose sulphates.[129] These materials are potential candidates for replacing heparin as anticoagulant agents.[129] The activity of heparin as an effective anticoagulant is mainly due to the functional sulphate groups that have high poly-anionic density.[130] In addition, concerns about the animal origin of heparin have increased interest in finding new low-cost and biosourced non-animal analogues.[129] Cellulose sulphates have β-1,4-glucan sulphate structures very similar to sulphated glycan structure of heparin and therefore, could be regarded as a potential source of heparin analogues.[129]

Previous studies on the sulphation of cellulose have been carried out either in a heterogeneous system starting with an activated cellulose suspension, or in homogeneous systems starting with a partially substituted cellulose derivative in aqueous solution.[131,132] Problems associated with heterogeneous systems have been described earlier in chapter 1.3. In contrast, DS values in homogeneous reactions are limited to the available hydroxyl groups as the reaction starts with substituted derivatives.[129]

Sulphation of cellulose in [Bmim]Cl was carried out using dimethylformamide-sulphurtrioxide complex (DMF-SO$_3$) as a sulphation agent generated from chlorosulphonic acid (1 eq.) (ClSO$_3$H) and DMF (9 eq.).[129] The complex was reacted with cellulose in [Bmim]Cl solution at 30°C for 1 to 2 hours. It yielded DS values of between 0.52 and 2.95 and product yields of between 47 to 92%.[129] The increased reaction time resulted in a considerable increase in DS, but decreased yields. This is probably due to the degradation of cellulose under highly acidic conditions. The reaction times were shorter than those in the heterogeneous synthesis (5 h or longer) and had similar DS and yields.[133] It was seen that in all cases, independent of the DS or reaction conditions, the hydroxyl group at C-6 was the most reactive followed by C-2, with the least reactive being C-3.[129]

1.3.2 Carbanilation of cellulose

Cellulose tricarbanilates with various functional groups on their aromatic rings are reported to form lyotropic liquid crystalline phases, and can be used to separate enantiomers.[134,135,136]
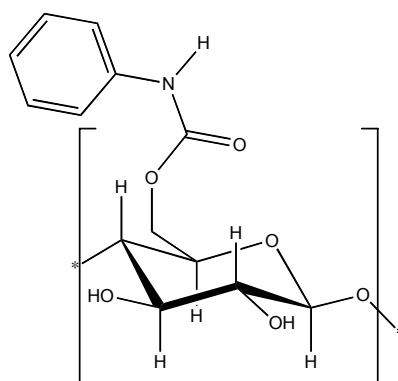
Figure 23. Structure of cellulose carbanilate.

Carbanilation of cellulose using either low and high *DP* cellulose sources including: MCC, cotton linters, pulp and bacterial cellulose (BC), have been conducted in [Bmim]Cl.[88,110] This reaction has also been studied earlier under homogeneous conditions using DMA/LiCl.[137] In [Bmim]Cl solution the reaction yielded cellulose carbanitrile with a DS range of between 0.26 and 3.0, independent of the *DP* and source of cellulose.[110] However, the high *DP* cellulose containing hemicelluloses had a low reactivity and hence, required longer reaction times with increased amounts of reagents. The difference in reactivity between the cellulose

sources was explained by the presence of hemicellulose in the pulp. The solubility of the products was dependent on the DS values of the products; DS > 2.4 were completely soluble in DMSO, DMF and THF.

It is known that carbanilation liberates CO_2 under normal reaction conditions. However, with ILs, it was observed that CO_2 was indeed being liberated but additionally, the formation of aniline was evident and verified by ^{13}C NMR.[110] This side-reaction originates from the presence of water. The formation of aniline by the reaction of phenyl isocyanate and water is plausible by considering the following putative reaction mechanism (Scheme 6).
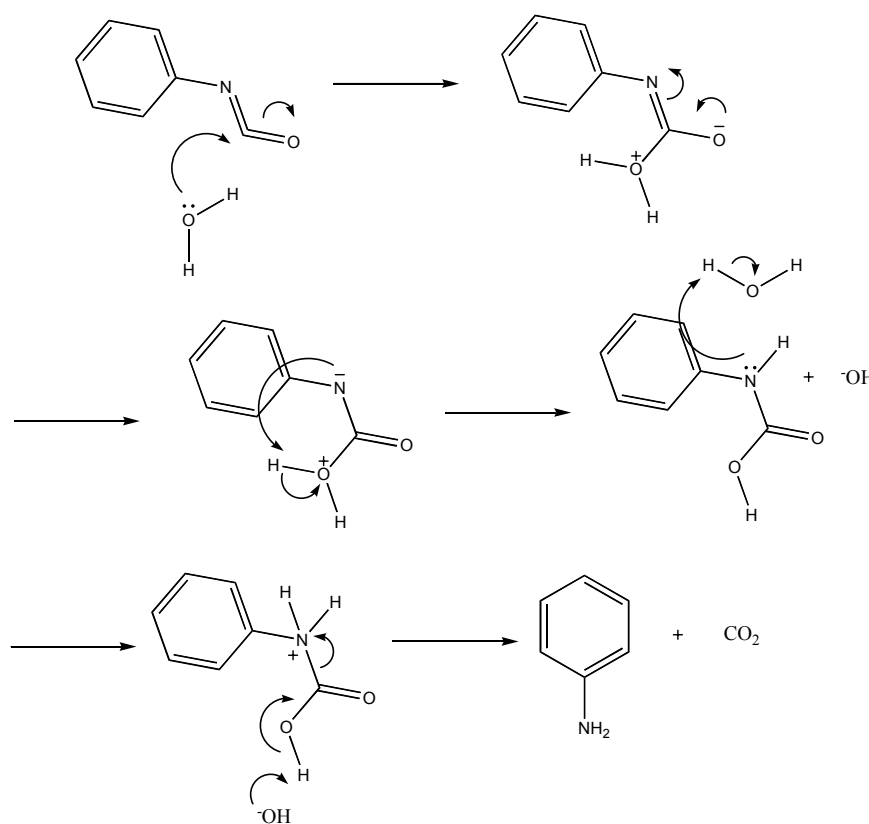
Scheme 6. Proposed reaction mechanism of the side reaction forming aniline and CO_2.

1.3.3   Etherification of cellulose

1.3.3.1 Carboxymethylation, -ethylation and -propylation

Carboxymethylation of cellulose in a wide variety of ILs was first described by Myllymäki and Aksela in a related patent.[138] Carboxymethylation of cellulose in [Bmim]Cl was achieved by diluting the cellulose-IL solution with DMSO to effect suitable mixing.[109] A solution of NaOH and sodium mono-chloroacetate dissolved in DMSO was added into the cellulose-IL-DMSO solution, which formed a gel-like mixture. Carboxymethyl cellulose (CMC) was obtained with a DS of 0.49 when an equivalency of 1:1 was used (Figure 24). In spite of the increased equivalency of reagents to 1 (AGU):3, the DS did not increase. The authors did not discuss this point further and the spectral data was not interpreted in enough detail to explore the possible side products from the reaction. Nonetheless, they later reported a lack of reproducibility of the reaction due to the reaction between the base and IL.[139] Moreover, the reaction is not homogeneous as NaOH is not soluble in IL and the cellulose precipitates from the solution during the course of the reaction.[139] It is generally perceived that strong bases such as NaOH cannot be used with imidazolium-based ILs that have C-2 protons as this results in side-reactions. The C-2 proton is fairly acidic with a dissociation constant (pK_a) of 24 in DMSO[140] and is deprotonated by strong bases to form carbene (Scheme 7). The presence of carbene in the reaction mixture inhibits the reaction from proceeding further due to its reaction with the monochloroacetate (Scheme 7).
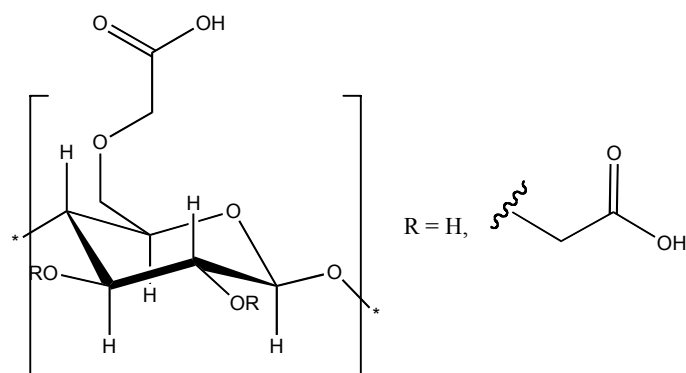
Figure 24. Schematic structure of carboxymethyl cellulose (CMC).
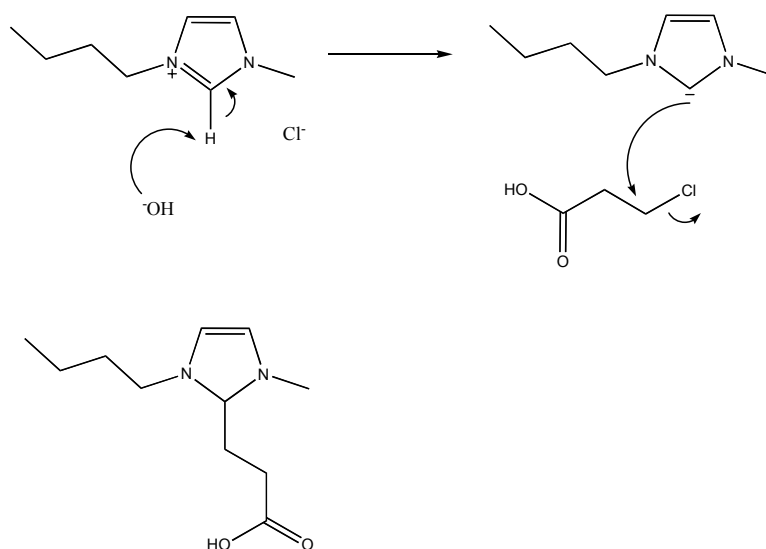
Scheme 7. Formation of carbene in the presence of a strong base such as NaOH. The carbene reacts further with monochloroacetate.

In contrast to reaction in ILs, the carboxymethylation of cellulose under homogeneous conditions in conventional solvent systems, namely Ni(tren)OH$_2$, NMMO and melt of LiClO$_4$·3H$_2$O proceeds fairly well resulting in higher DS values.[141] For MCC in Ni(tren)OH$_2$ solvent a DS of 0.54 was obtained with a large excess of reagents (1:20 NaOH:10 monochloroacetate). The DS could be increased to 0.71 by a stepwise addition of reagents. Spruce pulp was used as a cellulose source for the reaction in NMMO with same amount of reagents that yielded a DS of 1.26, whereas the reaction carried out in a melt of LiClO$_4$·3H$_2$O gave a DS of only 0.69.

Carboxyethylation and propylation of cellulose has also been studied in [Bmim]Cl and in [Amim]Cl, but the reactions yielded relatively low DS values that ranged from 0.01 to 1.53.[142]

The carbene side-reaction is the limiting factor for many reactions carried out in imidazolium-based reaction media in the presence of a strong base. Therefore, the choice of base is crucial to prevent the formation of the carbene species. This will be discussed in more detail in a chapter, '1.3.4 Side reactions in imidazolium-based ionic liquids'.

1.3.3.2 Tritylation

Tritylation of cellulose is a well-known reaction that produces regioselectively of C-6 substituted cellulose derivatives leaving positions C-2 and C-3 available for subsequent modifications (Figure 25).[143,144,145,146,147,148,149] Regioselectively substituted cellulose derivatives are of increasing interest due to their unique properties as compared to those of statistically substituted analogues.
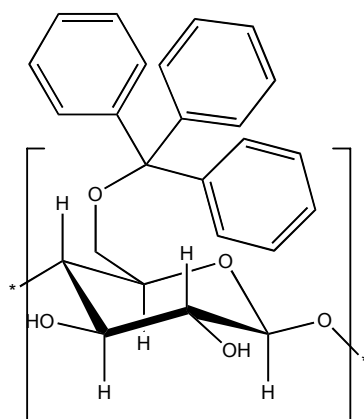
Figure 25. Structure of trityl cellulose.

Reactions involving the use of ILs in tritylation were carried out in molten salts using pyridine as a solvent and/or inorganic base.[95,138] These reactions were reported in the quite apart years, in 1934 and then much later in 2005.[95,138] Tritylation of cellulose in a 'real' IL was investigated using [Bmim]Cl as a reaction medium with triphenylmethyl chloride (trityl chloride, TrCl) in the presence of pyridine.[150] The presence of base in this reaction was crucial as otherwise the reaction would have resulted in the substantial hydrolysis of cellulose. It was also observed that even when pyridine was used, a long reaction time (*i.e.* 24h) caused extensive hydrolysis of cellulose at 100°C.[150] This problem was avoided by decreasing the reaction time to 14 h, though the impact of the reaction temperature was not studied.[150] It was observed that shorter reaction times (*i.e.* 1 or 3h) were sufficient to yield DS of almost 1. This result demonstrates an advantage over the traditional DMA/LiCl solvent system in which comparable DS values were obtained during 24 h reaction time.[145] Tritylation was also explored by using triethylamine as a base.[150] This resulted in DS of 0.98 in 1.5 h.[150]

The recycling of [Bmim]Cl was not achieved when pyridine was used. This was because the formed pyridinium hydrochloride could not be separated by extraction.[150] Triethylamine is not fully miscible in [Bmim]Cl and hence, it was easier to extract it from the IL.[150] In this case, [Bmim]Cl could be recycled successfully.[150]

An attempt to tritylate cellulose in [Emim]OAc with trityl chloride yielded cellulose acetate with a DS of 0.75. This will be described in great detail in a later chapter, '1.3.4 Side Reactions in Imidazolium-based Ionic Liquids'.

1.3.3.3 Cationic functionalisation

Cationic cellulose derivatives are industrially very important compounds and have many applications in: the paper industry, cosmetics, and textiles, in flotation and flocculation and in drilling fluids.[151] These substances are also utilised in the removal of acidic dyes from aqueous effluent produced by the textile industry thereby reducing the environmental impact of the processes.[152]

Previously, cationic cellulose derivatives have been prepared by the etherification of cellulose using glycidyl ammonium salts or alkylene epoxides in the presence of suitable alkaline catalyst, usually NaOH.[153] Cationic substitution values of between 0.034 and 0.5 moles per quaternary nitrogen per mole of glucose unit have been reported in these reactions.[154] However, these reactions give low yields and require large amounts of organic solvents.[151] Other approaches such as the coupling of oligo-ionomers to cellulose fibres and grafting on cationic polymer chains have been reported, though these also give poor yields.[153]

An attractive approach has been described by Abbott *et al.* in which an IL analogue was used as a solvent and also a reagent.[153] This alternative IL analogue, eutetic mixture of choline chloride and urea, was used for heterogeneous cationic functionalisation of cellulose (Scheme 8).[153] Moreover, this has the advantages of being non-toxic, biodegradable and has no Lewis acidity, though it has a poor solubilising capacity for cellulose.[153] In the reaction with cellulose, it functions as both reagent and a solvent. However, it does not provide homogeneous reaction conditions as it is not capable of dissolving cellulose and therefore, the reaction may be regarded as heterogeneous.
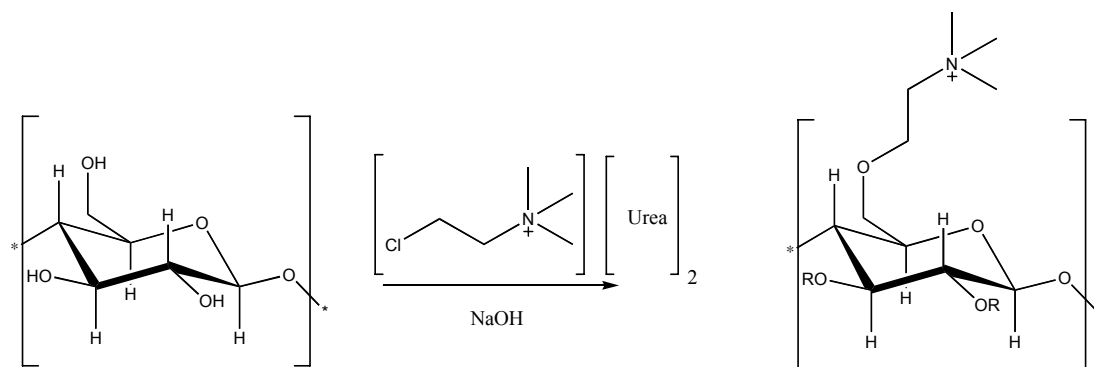
Scheme 8. Cationic functionalisation of cellulose with a choline derivative and urea in the presence of NaOH. R represents the cationic substitutent.[153]

Maximum DS of 0.19% was obtained in this heterogeneous cationic functionalisation.[153] The authors indicated, that all the hydroxyl groups on the fibre surface were substituted due to the ease of accessibility for the reagents.[153] The effects on fibre morphology were studied by SEM, which clearly indicated that fibres were wetted upon contact with this solvent.[153] The authors claimed that the wetting of the fibres was sufficient for the complete derivatisation of the accessible hydroxyl groups.

1.3.4 Side reactions in imidazolium-based ionic liquids

Baylis-Hillman reaction

It was soon realised that these new solvents have some disadvantages under certain reaction conditions, especially in context with the chemical modification of cellulose. The very first report on the side-reactions caused by imidazolium-based ILs was observed when [Bmim]Cl was used as a solvent in Baylis-Hillman reaction (Scheme 9).[155] This reaction resulted in low yields due to the direct addition of the deprotonated imidazolium salt to the aldehyde (Scheme 10).[155]
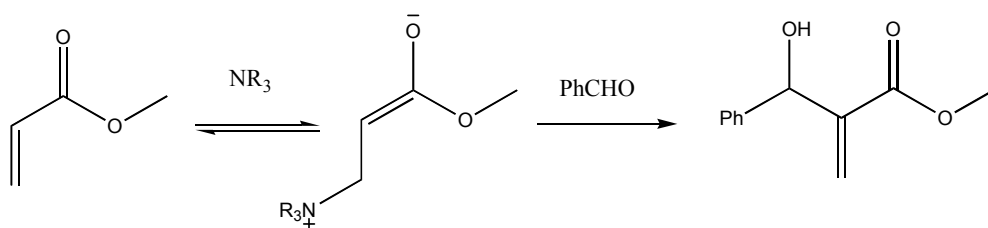
Scheme 9. Baylis-Hillman reaction.[155]
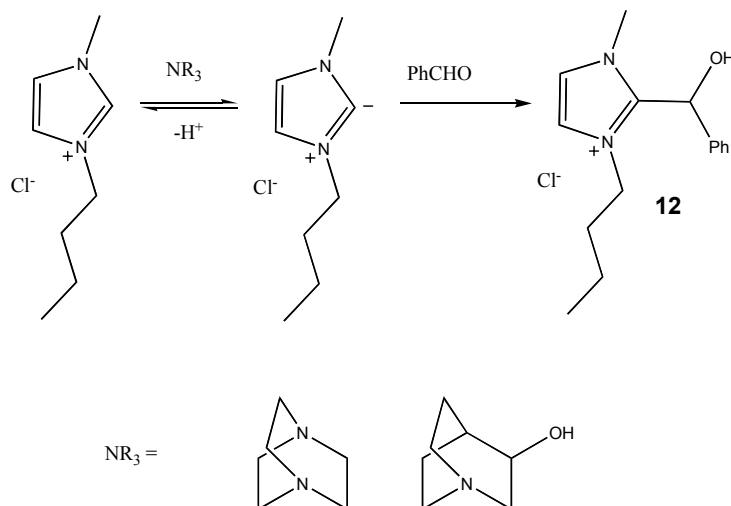
Scheme 10. A side reaction of [Bmim]Cl with aldehyde in Baylis-Hillman reaction.[155]

Contradictory results were reported by Rosa *et al.* who stated the opposite effect of ILs on the yields in Baylis-Hillman reaction.[156] It was claimed that the presence of imidazolium-based ILs has beneficial properties on the reaction and that the IL could be recycled four times in the same reaction thus increasing the yields in every cycle.[156] This recycling is understandable as more of the IL is converted in every cycle into a compound **(12)** leaving more and more benzaldehyde available for the actual reaction (Scheme 10).[155]

As the C-2 proton of imidazolium salts is weakly acidic, strong bases such as KO^{t}Bu have been reported to deprotonate it to form carbene.[157,158] However, it has been found that even mild bases with a pK_a as low as 8-9 are powerful enough to generate the corresponding carbene. This is quite surprising considering the pK_a of imidazolium salts (*i.e.* 24).[140,155] In some Pd-catalysed cross-coupling reactions, such as in Suzuki and Heck reactions, the imidazolium adduct may be regarded as a stabilising intermediate that forms complexes with

the palladium catalyst.[159,160,161,162,163] This will be discussed further in the context of Buchwald-Hartwig reaction in chapter 3.5, 'Buchwald-Hartwig cross-coupling'.

Reducing-end substitution of cellulose

It was recently observed after the dissolution of cellulose in imidazolium-based ILs and subsequent regeneration, that it exhibited less fluorescence with carbonyl-selective fluorescence label (Carbazole carbonyl oxyamine, CCOA) than the native directly labelled starting cellulose.[164,165] This was thought to indicate a reaction between the IL and carbonyl groups of cellulose.[164] As discussed earlier, these carbonyl groups are present in the form of: a hemiacetal at the reducing end of the cellulose molecule, as the keto form at C-2 and C-3 or the aldehyde form at C-6 along the cellulose chain.[164] These groups are the result of random oxidation during cellulose processing and aging.[164]

Ebner *et al.* suggested that this was caused by the reaction between the reducing end of cellulose and IL (Scheme 11).[164] However, it seems that the suggested structure of the product is not correct as the C-1 lacks the hydroxyl group (Scheme 11).
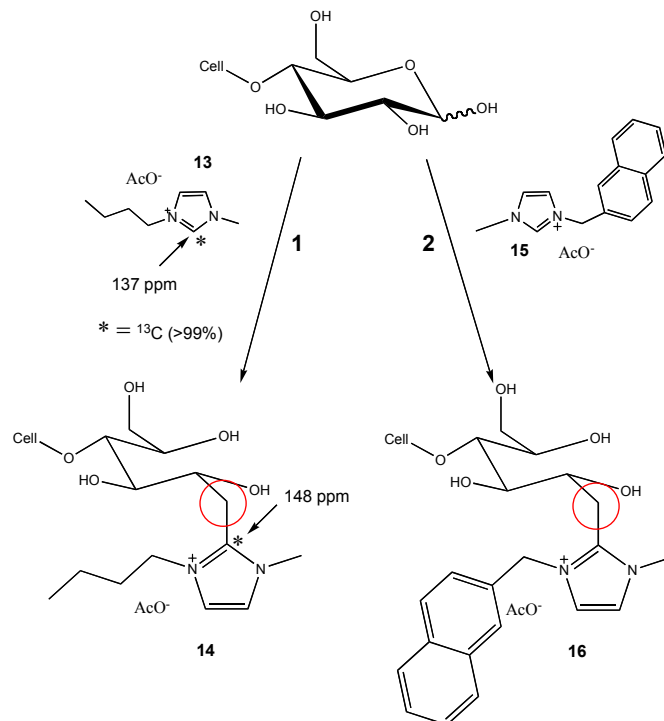
Scheme 11. Reaction scheme showing the reducing-end substitution of cellulose 1) with labelled [Bmim]OAc (**13**) to yield compound (**14**) 2) with [Napmim]OAc (**15**) to yield compound (**16**).[164] The missing hydroxyl groups are indicated by the red circles.

The product from the reaction could not be determined by NMR when cellulose with a *DP* of 500 was used due to the very low amount of IL bound to the reducing end. Hence, isotopically labelled IL (**13**), [Bmim]OAc, was used (Scheme 12). A weak signal at 147.8 ppm corresponding to C-2 of the imidazolium moieties at the endwise-derivatised cellulose (**14**) was observed in the ^{13}C NMR spectrum. In order to have more evidence for this derivatisation, the same reaction was carried out using unlabeled [Napmim]OAc (**15**), which yielded a strongly fluorescent [Napmim]-cellulose derivative (**16**).

Reducing-end substitution of cellooligomers (average *DP* of 6) by [Emim]OAc was also observed by Liebert *et al.*[166] The authors presented the correct structure of the substituted product.

When considering the production of cellulose derivatives, this side-reaction obviously has to be taken under consideration. Luckily this can be avoided by choosing the correct reaction conditions and work-up procedures. This again highlights the detrimental effect of a strong base on the reaction.

Acetylation as a side reaction

An attempt to carry out acylation, tritylation and tosylation of cellulose in [Emim]OAc resulted in cellulose acetate with maximum DS of 1.86 (Scheme 12).[167] This behaviour is to be expected as anhydrides are generally produced in related reactions.
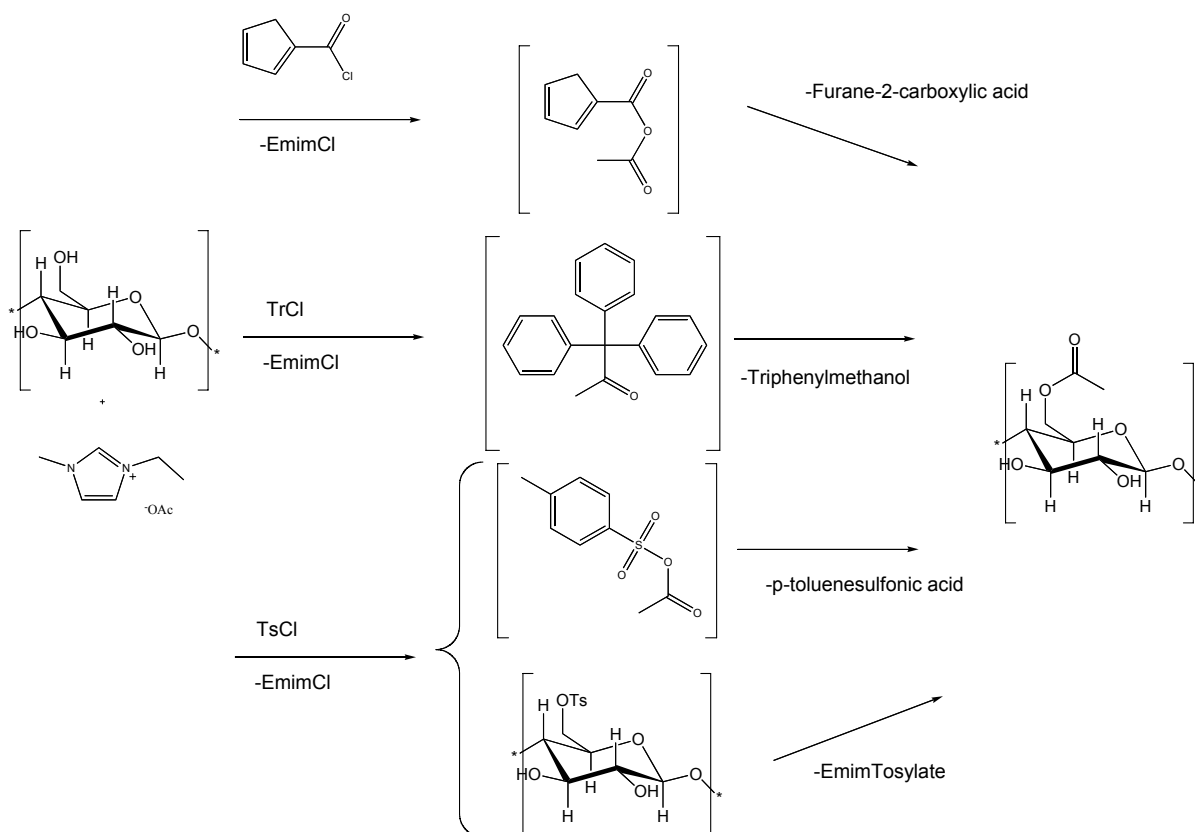
Scheme 12. Synthetic scheme of reactions yielding cellulose acetate in [Emim]OAc.[167]

Tosylation of cellulose also yielded acetylated derivative that had a DS value of 0.55.[167] Two different reaction pathways via different intermediates were proposed for the acetylation.[167] The first pathway proceeds via the formation of tosyl cellulose intermediate, whereas the second involves a mixed anhydride.[167] In order to find out which of these pathways dominates, tosyl cellulose with a DS of 1.33 was dissolved in [Emim]OAc at temperature of 70°C. The reaction was followed by taking samples for IR analyses at time intervals.[167] It was observed that the formation of the acetylated derivative took place and the DS of tosyl groups decreased over time. However, the DS values for the acetyl groups exceeded the values of the tosyl group.[167] This behaviour was not explained. In summary, the authors concluded that it is likely that the reaction takes place via both pathways.[167]

One may argue that the mixed anhydride route seems to be the dominant pathway as it is quite unlikely that the tosylation of cellulose first takes place under such competitive conditions. If the tosyl cellulose were the intermediate, this would suggest that the cellulose has a higher tendency to react with tosyl chloride than the mixed anhydride, which seems fairly implausible. When interpreting data from the reaction with tosyl cellulose as a starting

material, it can be seen that the acetylation of cellulose continues even after complete displacement of the tosyl groups. Therefore, it can be stated that the presence of tosyl cellulose may aid the reaction but it is not a prerequisite for it to proceed.

All of these examples highlight the fact that ILs are not completely inert. Furthermore, they do not only function as solvents but may also participate in the reaction as reagents that form active intermediates. As the knowledge about their possible side-reactions and chemical behaviour increases, the side-reactions may be prevented. Alternatively, they can be used advantageously in certain reactions. As long as the chemical behaviour is known, there are ways to overcome these reactivity issues by choosing suitable ILs and reaction conditions.

1.4 Liquid crystalline cellulose and derivatives

As discussed earlier, cellulose has a unique structure that enables the formation of materials with widely varying properties. These properties can be fine-tuned by: the dissolution and regeneration of cellulose in different solvents, by chemical modification or by affecting these properties in the solution phase by varying concentrations and solvents. One of the most fascinating properties is liquid crystallinity. The liquid crystalline state of cellulose is of great interest due to its unusual flow behaviour and the preferential orientation of the polymer chains to the flow direction, which leads to uniaxially orientated fibres and films of excellent tensile modulus and strength.[168]

1.4.1 Liquid crystal phase as a state of matter

In a solid material, molecules have both positional and orientational order in a lattice.[169] When solid melts to a liquid, both types of order are lost completely allowing the free movement of molecules, which subsequently forms an isotropic solution. The liquid crystalline (LC) phase is an intermediate state of matter between solid and liquid states in which the molecules are free to move about in much the same fashion as in a liquid. However, as the molecules move they tend to remain orientated in a certain direction (Figure 26).[169] The preferred direction of the orientation of the molecules is determined by the director vector.[169]
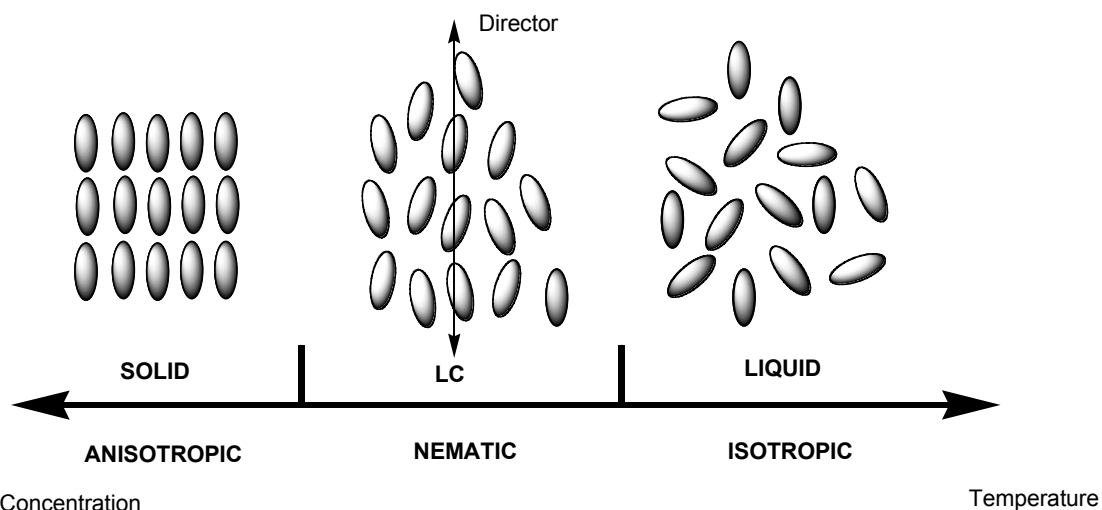
Figure 26. Schematic diagram showing the orientation of molecules in different states; in solid, liquid crystal (LC) and liquid. Concentration is increased to the left whereas temperature is increased to the right.[169]

The liquid crystalline phase may be introduced either by an increase in temperature (thermotropic liquid crystals) or by an increase in concentration/solvent (lyotropic liquid crystals).[169] Cellulose and its derivatives have the ability to behave as both thermotropic and as lyotropic liquid crystals. In general, there are several different known liquid crystal phases depending on the structure or combination of the molecules. In this study, we will concentrate only on the liquid crystalline phases, which are important for cellulose and its derivatives. These LC phases are called nematic, chiral nematic (*i.e.* cholesteric) and smectic. In the nematic phase, molecules have only orientational order making it the least ordered LC phase, whereas in smectic phase, they have both orientational and positional order (Figure 27).[169]
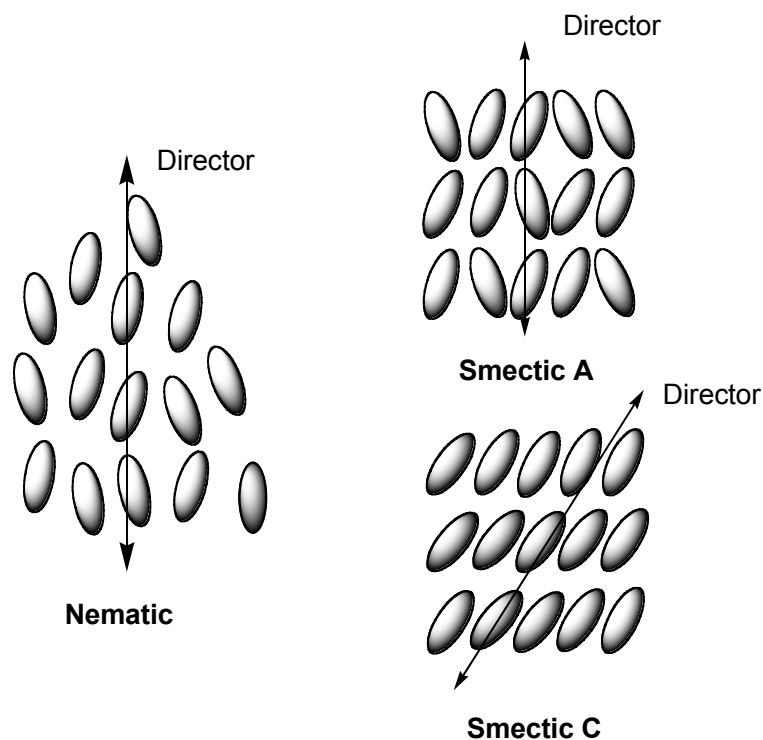
Figure 27. Different liquid crystalline phases showing the orientation of the molecules in the phase; nematic, smectic A and smectic C.[169]

In addition, optically active molecules can form a chiral nematic phase (*i.e* cholesteric phase) (Figure 28).[169] In the chiral nematic phase, the molecules are orientated in a helix that turns their individual directors in one full turn, which is called the pitch.[169] This twist produces some spectacular optical properties.[169]
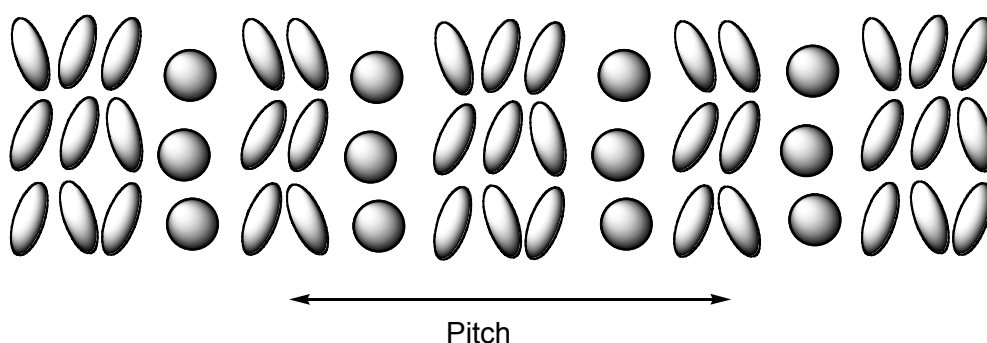
Figure 28. Orientation of the molecules in chiral nematic phase indicating the pitch length.[169]

1.4.2 Cellulose and its derivatives as liquid crystalline polymers

In 1956, Flory predicted that polymers with stiff linear chains would form ordered phases in their respective melt and in concentrated solutions.[170,171] In 1980, this behaviour was reported for cellulose derivatives, such as (hydroxylpropyl)cellulose (HPC) in water, which at high concentrations can reflect visible light due to its chiral nematic structure.[172] HPC was also the first cellulosic derivative reported to form spontaneous anisotropic solutions when dissolved in aqueous and organic solvents.[173] Since that discovery, other cellulose derivatives including: acetoxypropyl cellulose, cellulose acetate, (acetyl)(ethyl)cellulose and ethyl-cyanoethyl cellulose) and cellulose itself have also been reported to form ordered solutions (Figure 29).[174,175,176,177,178,179,180] Gray *et al.* have shown that the use of polar or acidic solvents promotes the formation of the mesophase for cellulose solutions.[181] Highly substituted cellulose with large substituents preferentially forms nematic phases in many solvents.[181] Cellulose with low DS values or smaller substituents needs specific solvent interaction in order to form such mesophases. A critical concentration at which the mesophase is formed, lies in the range of 30 to 60% (w/w) for cellulose derivatives in a variety of solvents.[182] Cellulose itself has been reported to have critical concentrations as low as 7.5% (w/w) in phosphoric acid.[178]

Suspensions of cellulose crystallites are also capable of forming chiral nematic phases spontaneously.[183] The mesophase forming ability of cellulose crystallites suspension differs between cellulose types. It is in turn, affected by the mineral acid chosen for the initial hydrolysis to obtain these crystallites.[184] The use of either sulphuric or phosphoric acid yields a chiral nematic phase, whereas the use of HCl hydrolysis gives a viscous suspension that forms a birefringent glassy phase after post-sulphation treatment.[184,185] These chiral nematic phases are able to self-assemble, and hence separate from the isotropic solution to provide a material with unique properties. Cellulose films with the optical properties of chiral nematic liquid crystals can be prepared by simply casting from these suspensions.[184] Such films can be tailored to reflect different colours of light by altering the salt concentration of the suspension for a given source of cellulose and set of hydrolysis conditions.[184] Moreover, aqueous suspensions of cellulose microfibrils are reported to form chiral nematic phases above the critical concentration and can be aligned with a magnetic field.[186]
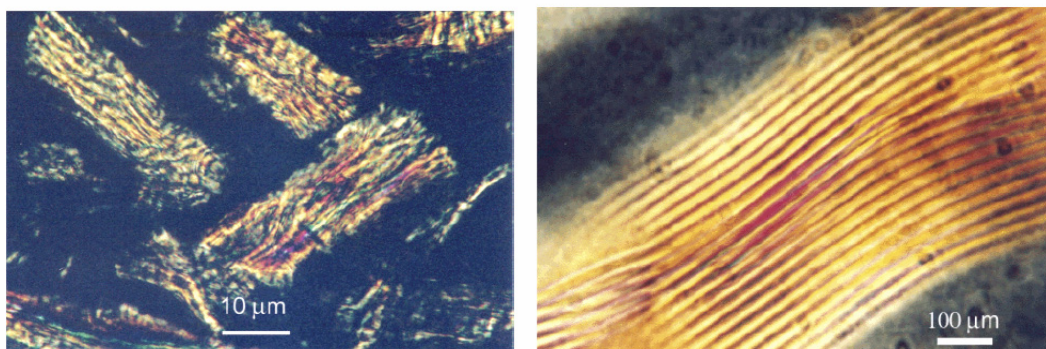
Figure 29. Optical micrographs of 16% (w/w) microcrystalline cellulose aqueous suspension showing nematic domains after 10 min. (left hand side image) and typical chiral nematic phase with fingerprint texture after 1 day from the suspension preparation (right hand side image).[187]

Although cellulose is not a rigid molecule, it appears to have backbone stiff enough to form ordered phases. Cellulose derivatives have also been shown to form thermotropic liquid crystals as acetoxypropyl cellulose and HPC display cholesteric colours on heating.[174,188] In addition, the propanoate ester of HPC behaves as a thermotropic LC, which is able to reflect visible light at ambient temperature.[189] Numerous other HPC acid esters have been reported to form chiral nematic phase upon heating.[188] Furthermore, tri-*O*-(β-methoxyethoxy)ethyl cellulose exhibits a chiral nematic phase over wide temperatures ranging from room temperaure to 180°C.[190] Benzoylated bacterial cellulose has been prepared showing smectic LC phases.[191] From a series of alkyl substituted cellulose derivatives, only those with alkyl chains longer than 8 carbons exhibited a columnar LC phase.[192] This novel liquid crystalline phase for cellulose-based materials was reported to have high viscosity when compared with cholesteric ether type cellulose derivatives.[192]

2. Aims of the Study

In the modern world, the consumption of disposable materials has increased and hence, the load on the environment has increased dramatically. Consequently, the demand for bio-based materials with renewable, low-cost and sustainable properties has increased. Cellulose-based materials can potentially provide products to meet this demand. In addition, the chemical modification of cellulose-based materials could be developed to meet the requirements set for environmental legislation, by for example, applying ionic liquid technology. Cellulose as a raw material has several useful attributes; it is abundant, bio-based and renewable just to mention a few. Furthermore, cellulose has proved to be a versatile material due to its unique chemical structure, which provides a superior platform for several new biomaterials. However, the efficient use of this versatile material has been hampered by its insolubility in organic solvents and in water. Ionic liquids have opened up more possibilities for direct and homogeneous modification by aiding the competent use of cellulose.

General aim of this thesis was to focus on the developing advanced materials and products from cellulose by novel approaches. Our research strategy in this study was based on the following concepts:

i)   To understand the behaviour of cellulose in ionic liquids (**I**).

ii)   To carry out and optimise several reaction types on cellulose in ionic liquids (**I**, **II**).

iii) To explore new synthetic strategies and yield novel cellulose derivatives (See Results and Discussion, pages 66 to 102, **I**, **IV**).

iv)   To investigate the structure-property relationship regarding the nature of the substituent and DS (**III**, **IV**, **V**).

v)   To produce and characterise cellulose-based materials (**IV**, **V**).

Results and methods for obtaining these aims are reported in the following chapters (unpublished) and in publications **I-V**.

3. Results and Discussion

In this chapter, the results achieved in this study will be discussed in detail. First, the starting material, microcrystalline cellulose, MCC, will be discussed along with some aspects of another cellulose starting material, nanocellulose (NC), which was used in this study to obtain hydrophobic cellulose aerogels and films. The discussion will then move onto synthetic methods used and to investigations on the properties of those obtained derivatives with morphological and liquid crystalline interiors.

3.1 Microcrystalline cellulose and nanocellulose

Microcrystalline cellulose

The production of colloidal suspensions of cellulose by sulphuric acid hydrolysis of cellulose fibres was first reported by Rånby almost 50 years ago.[193] Then it was found that the residual crystalline material had the same crystal structure as the original fibres. Acid degradation of cellulose was further developed by Battista leading to to the commercialisation of MCC.[194] MCC is used in the pharmaceutical industry as a tablet excipient due to its beneficial properties such as zero toxicity, hygroscopicity, chemical inactivity and reversible adsorbency.[195] Most grades of MCC are made by hydrolysis of cellulose by HCl as the hydrolysis agent. Hydrolysis of MCC by H_2SO_4 may result in the formation of sulphated cellulose.

Nanocellulose

The smallest building block of cellulose I is a bundle of parallel glucan chains, namely cellulose fibrils, which are aggregated further to form fibres.[196] In order to preserve this highly entangled structure of fibrils with high strength, new preparation methods have been reported that utilise a combination of high-pressure shear forces and mild enzymatic hydrolysis to yield high aspect ratio nanocellulose NC.[196] NC forms strongly entangled and disordered networks and in this respect, the structure differs greatly from that of MCC.[196]

3.2 Solution properties of cellulose in [Amim]Cl

The very first step in this study was to investigate the solubility properties of cellulose in several ILs. Based on those results, the next step was to select a few ILs to be used in cellulose modification reactions. The constraints for dissolution procedure were that it has to be achieved with temperatures below 100°C to prevent the hydrolysis of cellulose during the dissolution, which ruled out all high-melting ILs such as 2-halide-3-alkyl-1-methylimidazolium chlorides. It was also clear from the literature that imidazolium-based ILs would be an obvious choice with chloride anions as they exhibit the strongest solubilising power for cellulose. After screening out numerous ILs based on the above criteria, we were left with three imidazolium-based ILs, namely [Amim]Cl, [Bmim]Cl and [Mmim]Me$_2$PO$_4$ from which [Amim]Cl was the most extensively used in this study. This is due to the fact that [Bmim]Cl is a solid (m.p. 65°C) at room temperature, which reduces its practicality. In contrast, [Mmim]Me$_2$PO$_4$ dissolves cellulose very quickly, but it was soon realised that this IL was a relatively poor medium for modification reactions. [Amim]Cl proved to be a superior solvent possessing a high solubilisation capacity for cellulose solutions with concentrations up to 40% (w/w) could be prepared. In addition, it seemed to be a feasible reaction medium because it has an intermediate viscosity suitable for stirring and mixing in addition to being quite inert.

The rheological behaviour of MCC-[Amim]Cl solutions at varying concentrations were measured in order to obtain more evidence of the solubilisation state, *i.e.* whether true solutions or gels were obtained. It was determined that solutions with concentrations of 5, 10, 15, 20, 22, and 35% (w/w) were true solutions as the loss modulus (G$^{''}$) was greater than that of storage modulus (G$^{'}$). However, the solution with 40% (w/w) concentration exhibited gel-like behaviour with storage modulus values ranging from 9 kPa to 104 kPa.

Viscosities of the solutions were also measured for the same set of concentrations at 100°C (**I**) (Figure 30). As reported in Paper **I**, the viscosity of the solutions with concentrations of 10 and 15% (w/w) showed Newtonian behaviour as the viscosities were not affected by the shear rate. However, shear thinning behaviour was observed as the viscosity decreased with increased applied shearing stress for those concentrations above 15% (w/w). This behaviour is called pseudoplastic behaviour. Such behaviour is typical of high molecular weight macromolecules. From these data, it can be concluded that cellulose modification reactions in

[Amim]Cl have to be performed at low concentrations, below 10% (w/w) to ensure reproducibility of the modification reactions.
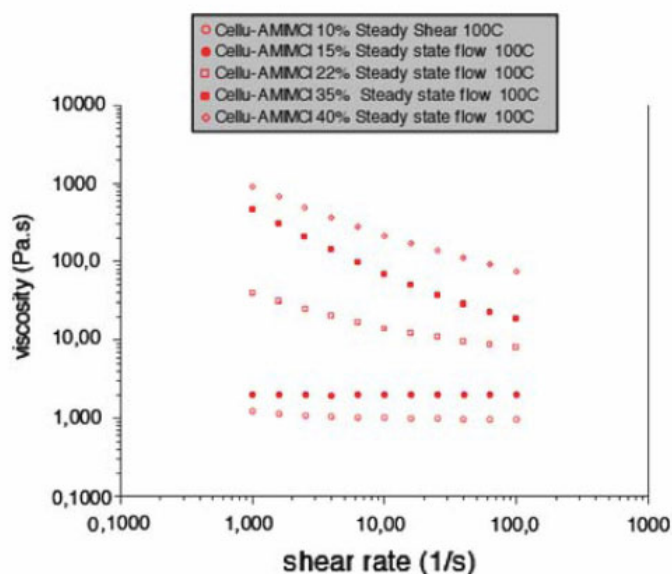
Figure 30. Flow curves of the cellulose solutions in [Amim]Cl with concentrations with 10, 15, 22, 35, 40% (w/w) (**I**).

3.3 Liquid crystalline cellulose

3.3.1 MCC-[Amim]Cl solutions

Liquid crystalline properties of MCC in the IL, [Amim]Cl, were investigated. Solutions of cellulose in [Amim]Cl at variable concentrations of 5, 10, 15, 20, 22, 25, 35 and 40% (w/w) were prepared by heating the solutions at 80°C and by mechanical stirring for the time required for the complete dissolution. This was subsequently confirmed by polarising optical microscopy (POM). It was realised that cellulose solutions with concentrations higher than the critical concentration of 22% (w/w) exhibited liquid crystalline phases under POM and SEM. These solutions exhibited iridescent colours with nematic domains under POM and also had interesting textures in SEM images (Figure 31).
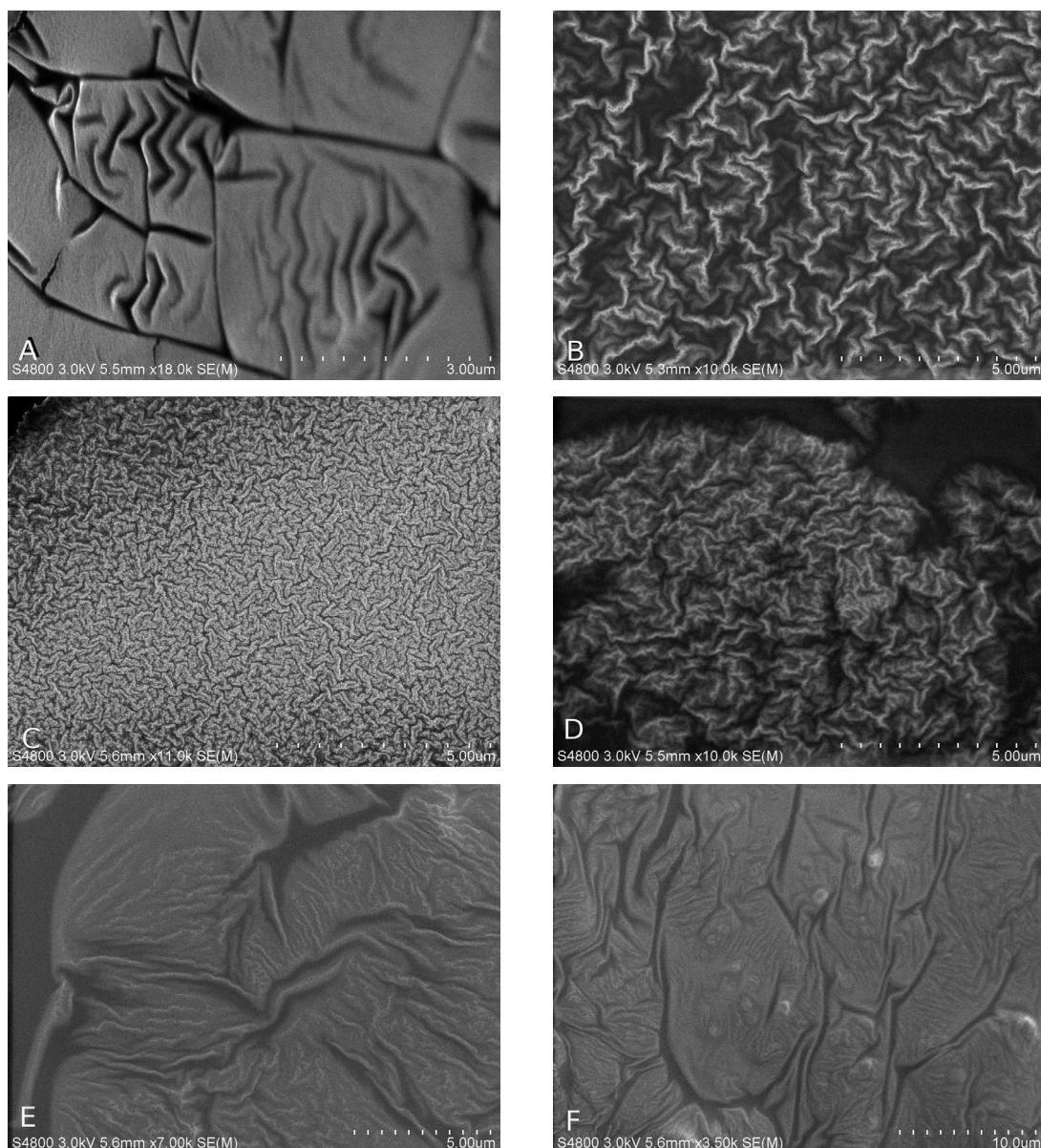
Figure 31. SEM images of MCC-[Amim]Cl solutions with a) 20% b) 22% c) 25% d) 35% e) 40% (higher magnification) f) 40% (lower magnification) (w/w).

SEM images were acquired directly from solutions and revealed changes in morphology with concentration. As seen in Figure 31a, the 20% (w/w) solution did not exhibit any continuous textures even under higher magnification, whereas a solution with 22% (w/w) concentration shows a repeated texture of wrinkles (Figure 31b). This same texture was also seen for 25% and 35% (w/w) solutions (Images 31c and d). However, more elongated morphology was observed with very high concentration of 40% (w/w) showing fingerprint-like textures (Figure 31e and f). It appears that the [Amim]Cl (imidazolium cation) is orientated along with cellulose and hence, exhibits different textures. This conclusion is based on the

previously published work on morphologies of polypyrrole films.[197] It has been reported that polypyrrole films exhibit similar wrinkled morphology in films that resulted from polymerisation at high temperatures.[197] High temperatures in polymerisation reactions yielded polypyrrole with nonlinear α-β (Figure 32a) and β-β (Figure 32b) bonding rather than the usual α-α bonding which results in linear polymer.[197]
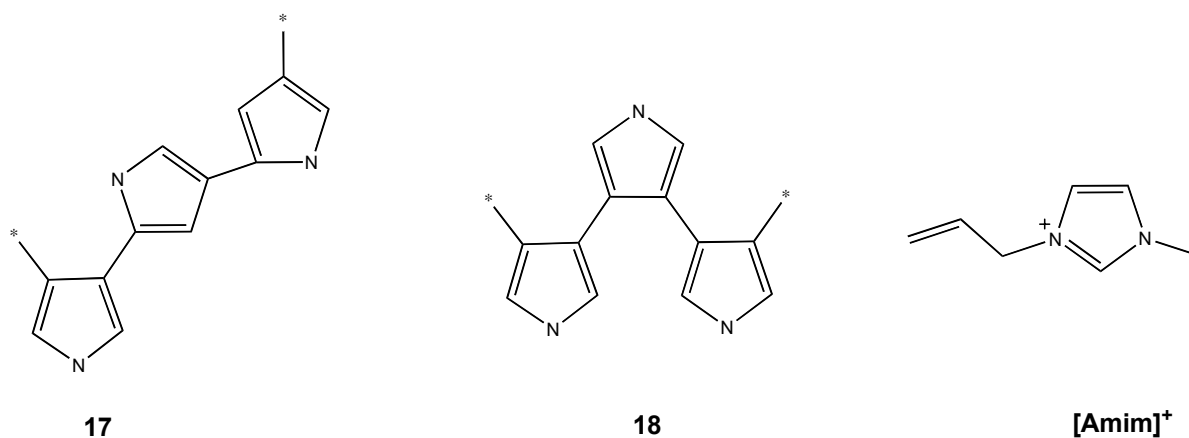
Figure 32. Structure of α-β (**17**), β-β (**18**) bonding in polypyrrole and [Amim]+.

[Amim]+ has quite a similar structure than pyrrole and hence, it seems possible that it behaves similarly in cellulose solutions to that of pyrrole in polypyrrole films. As discussed before (p. 35, Figure 16), imidazolium-based ILs maintain hydrogen bond network in the liquid phase. The upshot of this is that it actually has a structure, which can be orientated further along the cellulose orientation.

In the nematic phase, the molecules are orientated in one direction without any positional order as depicted in figure 27. We assume that concentrations of the 22-35% (w/w) range exhibit the nematic phase as POM images showed the presence of nematic domains without any apparent chiral nematic textures (Figure 31b-c). In the SEM images, the appearance of wrinkled texture is caused by the nematic ordering of cellulose molecules into the nematic domains, which orientated the [Amim]+ cations in a nonlinear fashion. A closer dissection of image 31c at 25% (w/w) solution shows that the wrinkles have a repeated orientation. This may be inferred to be due to further orientation of nematic domains with each other. The change of this texture to a more elongated one at 40% (w/w) concentration, indicated the phase change from nematic to chiral nematic, which is a more ordered phase (Figure 31e). At

this concentration, the [Amim]$^+$ cations again have a different orientation that indicates the fingerprint-like texture typical to that of chiral nematic phase.

To conclude, the high viscosities of ILs enabled direct investigation of solution morphologies by SEM and hence, provide vital information on the liquid crystalline textures of the solution samples of cellulose. In our case, [Amim]Cl functioned not just as a solvent, but also as an indicator for the LC phase identification by changing its orientation with the orientation of cellulose.

3.3.2 (4-Biphenylcarbonitrile)-6-*O*-cellulose

Thermotropic LC properties of (4-biphenylcarbonitrile)-6-*O*-cellulose were investigated. Synthesis of this derivative to yield a DS value of 0.78 was carried out in Paper **IV** (Figure 33)**.** The resulting compound (**19**) was further tested as UV absorbent for paper (**IV**). Here, some additional POM images (Figure 34) of this compound will be shown to accompany the short discussion.

19

Figure 33. Structure of (4-biphenylcarbonitrile)-6-*O*-cellulose (**19**).
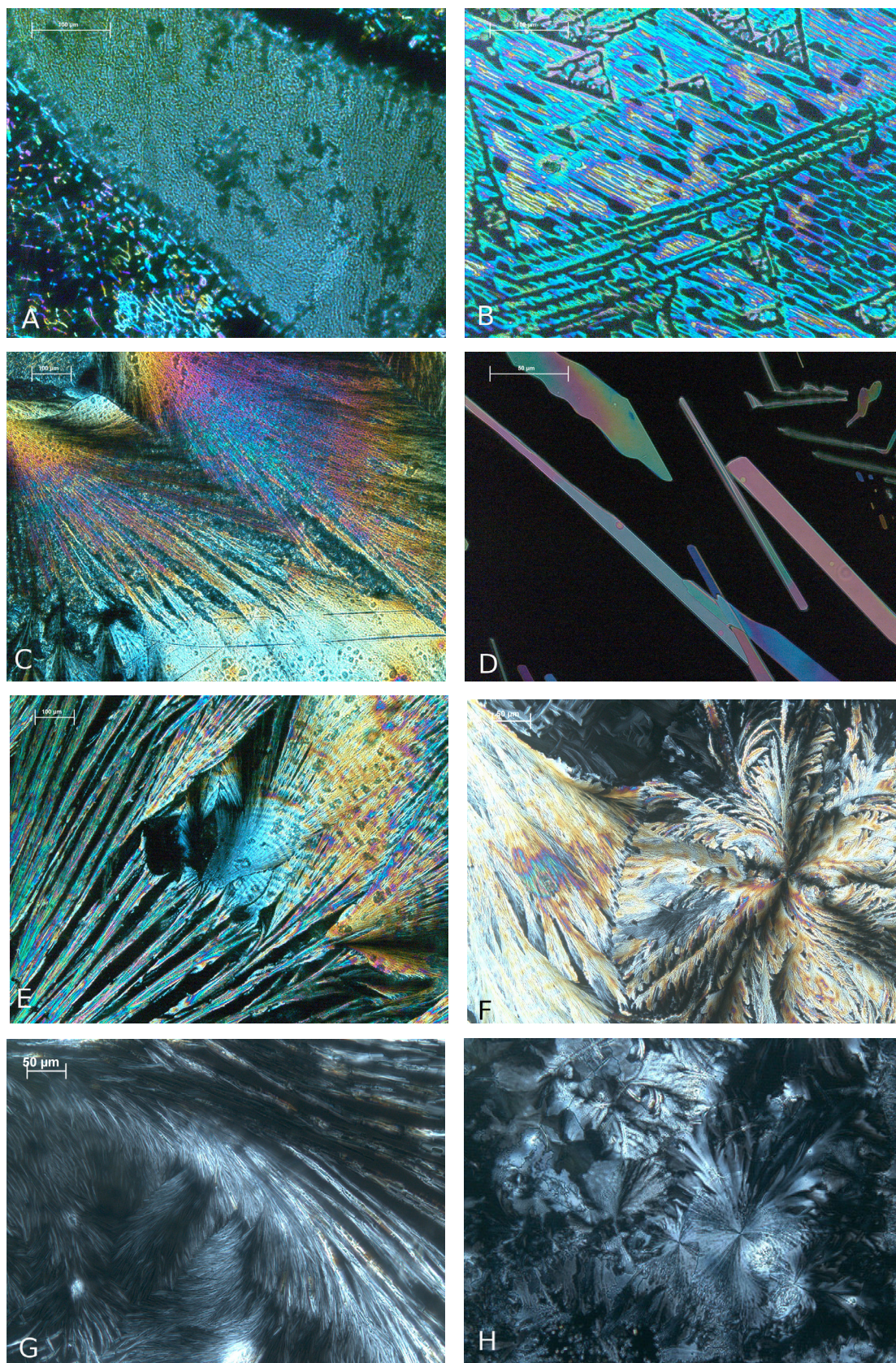
Figure 34. POM images of (4-biphenylcarbonitrile)-6-*O*-cellulose a) at 190°C b) at 180°C c) cooled rapidly from 180°C to RT d) cooled slowly from 180°C to RT e) and f) films at RT by slow evaporation of DMSO g) and h) films produced by shearing.

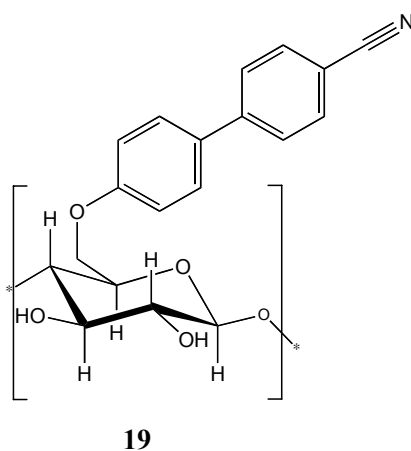Compound (**19**) exhibited birefringent areas at room temperature when examined by polarizing light microscopy (Figure 34c-h). Thin layers of (4-biphenylcarbonitrile)-6-*O*-cellulose from samples dissolved in DMSO were prepared by casting the film and allowing the slow evaporation of the solvent between two glass slides. Different textures were obtained depending on the film preparation technique used. If the films were allowed to form slowly upon standing, the textures were either fan-like or spherulite-like and exhibited strong iridescent colours (Figure 34e-f). Shearing of the films produced two types of texture: longitudinal orientation (Figure 34g) and spherulite texture (Figure 34h). Both of these films resulted in fan-like texture by rapid cooling from 180°C at RT as in Figure 34c, whereas a slow cooling resulted in rod-like domains with iridescent colours as in Figure 34d. A fingerprint domain was observed at 190°C (Figure 34a) and strongly birefringent smectic like texture at 180°C.

3.4 Synthesis of chlorophyllcellulose derivative towards photocurrent applications and nanofibres

One interesting property of cellulose is its relatively stiff backbone, which inspired us to study whether this feature could be utilised to allow the introduction of spatial arrangements to side chain substituents, *i.e.* chlorophylls. If successful, this substitution could yield organised systems with precise repeating distances of substituents. Cellulose was coupled with chlorophyll (*i.e. pyro*-pheophorbide *a*) to investigate its feasibility as a photocurrent generation system as a means of developing novel and advanced bio-based materials. It has been shown before that cellulose can function in such system by Sakakibara *et al*. in which porphyrin-cellulose with stearoyl substituents was used.[198]

The driving force for aiming for a regioselectively chlorophyll substituted cellulose with a DS of 1 is based on the simplified molecular model (Figure 35). The model shows an interesting phenomena *i.e.* all the chlorophyll substituents on the cellulose backbone are on the same side of the chain at C-6 position. This would mean that if a DS of 1 is achieved, the chlorophylls could interact with each other via π-π interactions. This conformation could lead to potentially new photocurrent properties in Langmuir-Blodgett (LB) films and could increase a chlorophyll substituted cellulose's efficiency in such system.
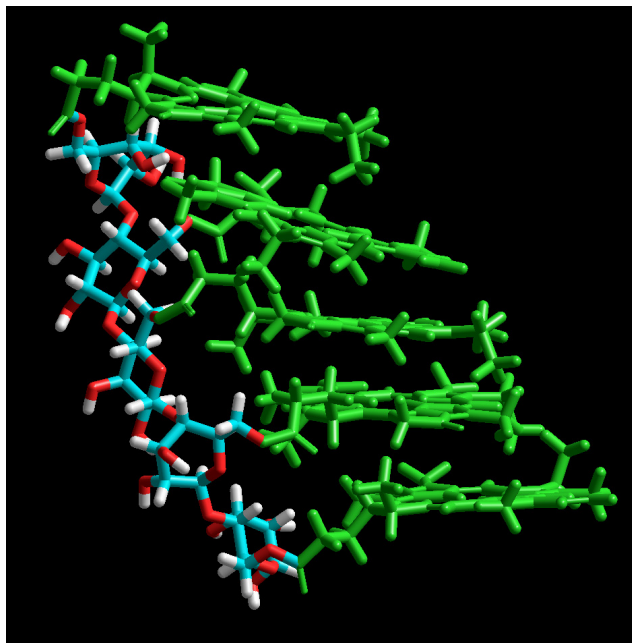
Figure 35. A simplified model of chlorophyllcellulose with DS of 1. Chlorophyll moieties are shown in green and the cellulose backbone in blue, white and red.

In nature, a photo induced electron transfer of high quantum efficiency of almost 100% takes place in highly organised pigment assemblies with the aid of membrane proteins.[198] Protein scaffolds hold pigments at certain intermolecular distances to optimise the electronic coupling, photon capture and energy transfer.[198] This highlights the importance of a precise arrangement of photofunctional molecules on a molecular scale. Therefore, in artificial photocurrent systems it is important to have regioselectively substituted derivatives regularly punctuating the distances between the photoactive substituents.[199] Molecular organised layers of photofunctional molecules are well known. These include LB films, self-assembled monolayers (SAMs) and layer-by-layer assemblies.[200,201] It has been reported that conventional LB films for constructing molecular assemblies have certain disadvantages such as instability in addition to regular molecular ordering in a plane of monolayer films or subtrates.[198,202] Cellulose may solve these problems by controlling the spacing and the assemblies of these functions acting as a carrier.[198] Furthermore, chlorophylls are also known to have excellent abilities to form orientated assemblies as they do this in nature.
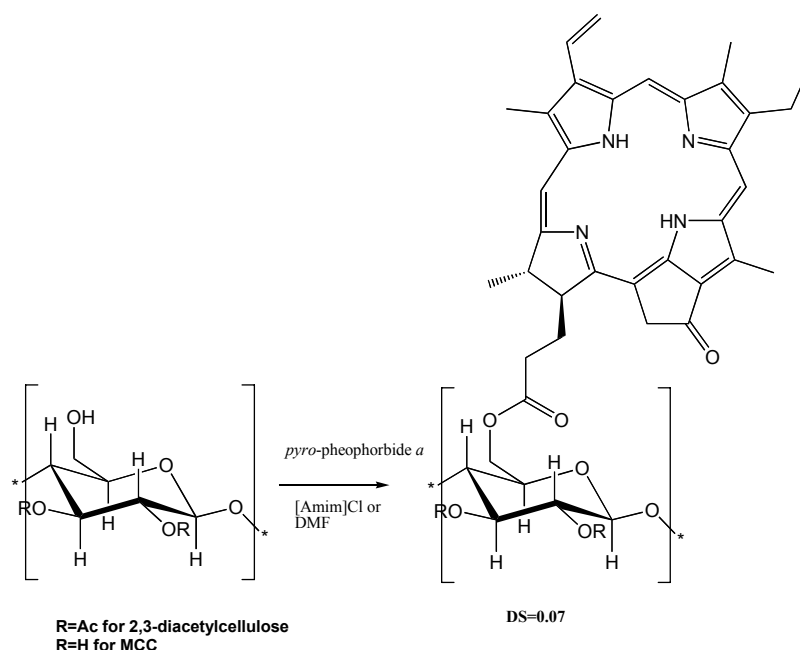
Scheme 13. General reaction scheme for chlorophyll cellulose starting from MCC in [Amim]Cl or 2,3-diacetylcellulose in DMF.

Synthesis of chlorophyllcellulose derivative was somewhat challenging due to the large size of the chlorophyll moiety, which increased the steric hindrance during the course of the reaction. Reactions were carried out in either [Amim]Cl when MCC was used as a starting material, or in DMF when the reaction was performed on 2,3-diacetyl cellulose (Scheme 13). In [Amim]Cl, a maximum DS value of 0.07 was obtained under optimised reaction conditions. In these conditions cellulose (1 eq.) was reacted with chlorophyll (*i.e. pyro*-pheophorbide *a*) (3.2 eq.) through a condensation reaction with *N,N'*-carbonyldiimidazole (CDI) (6.6 eq.) as described in Paper **I**. Several attempts at increasing the DS values to a target DS of close to one were made. The following synthetic strategies were investigated:

i) A mixed anhydride approach was attempted by preparing two different chlorophyll mixed anhydrides. A chlorophyll-dimethylphosphate mixed anhydride preparation was attempted by reacting chlorophyll (*pyro*-pheophorbide *a*) (1 eq.) with dimethylphosphate chloride (1.1 eq.) in the presence of triethylamine (1.1 eq.) in DMF. This reaction resulted in an unidentified chlorophyll compound and hence, could not be used in further studies. The other mixed anhydride candidate, chlorophyll-pivaloyl mixed anhydride was prepared by reacting the chlorophyll (*i.e. pyro*-pheophorbide *a*) (1 eq.) with pivaloyl chloride (1 eq.) in the presence of

pyridine (1.2 eq.). This anhydride was reacted with cellulose and yielded a derivative with DS value of 0.05.

ii) The activation approach seemed to be a key route to a successful reaction even though only a low DS value was obtained. It was decided to investigate this activation approach further still by using auxiliary nucleophiles with the following activation reagents: CDI and *N,N'*-dicyclohexylcarbodiimide (DCC) and 1-ethyl-3-(3'-dimethylaminopropyl)carbodiimide (EDCI). In general, during the activation step of carboxylic acid with the activating agent, the formation of the reactive intermediate, *O*-acyl urea, takes place for DCC. This intermediate can decompose, if the nucleophile does not react at a sufficient rate. This 'deactivation' step must be prevented when a poor nucleophile is to be acylated. However, it can be done by utilising auxiliary nucleophiles. The auxiliary nucleophile forms a new acylating agent; an active ester that has better stability than *O*-acyl urea. This allows the acylation of a poor nucleophile. In this work, pentafluoro phenol (0.5-2 eq.) was used as an auxiliary nucleophile with CDI, DCC and EDCI, which resulted in DS values ranging from 0.05 to 0.07. These results clearly indicate that the problem with the low DS values in cellulose chlorophyll reactions are not due to the poor nucleophilicity of cellulose, but is more likely to be due to steric hindrance associated with chlorophyll.

iii) In order the test the synthesis of chlorophyll cellulose derivatives obtained in conventional organic solvents, (2,3-diacetyl-chlorophyll)cellulose was prepared. Synthesis of this target molecule started from regioselectively protecting the C-6 hydroxyl with the trityl moiety in the reaction between MCC (1 eq.) and trityl chloride (3.2 eq.) in the presence of pyridine (14.5 eq.) as described in Paper **III** (Scheme 14). [Amim]Cl was the IL used and the reaction yielded a DS value of 0.9 with a 98% yield. Trityl cellulose was acetylated by the common procedure with acetic anhydride with pyridine in [Amim]Cl as described in Paper **I**. The overall DS value obtained for 2,3-diacetyl-6-*O*-trityl cellulose was 2.92 and an yield was 83% (**II**). Deprotection of the trityl group was performed on (2,3-diacetyl-6-*O*-trityl)cellulose with HCl in THF to yield 2,3-diacetyl cellulose in 96% yield with a DS value of 2.0. 2,3-Diacetylcellulose (1 eq.) was finally reacted with chlorophyll (*i.e. pyro*-pheophorbide *a*) (1.4 eq.) using the activation approach by DCC (1.4 eq.) and DMAP (1.4 eq.) to give the (2,3-diacetyl-chlorophyll)cellulose of DS of 0.07 for chlorophyll substituents and a 79% yield. This derivative was fully soluble in chloroform and therefore, was used in the preparation of LB films and photocurrent measurements.
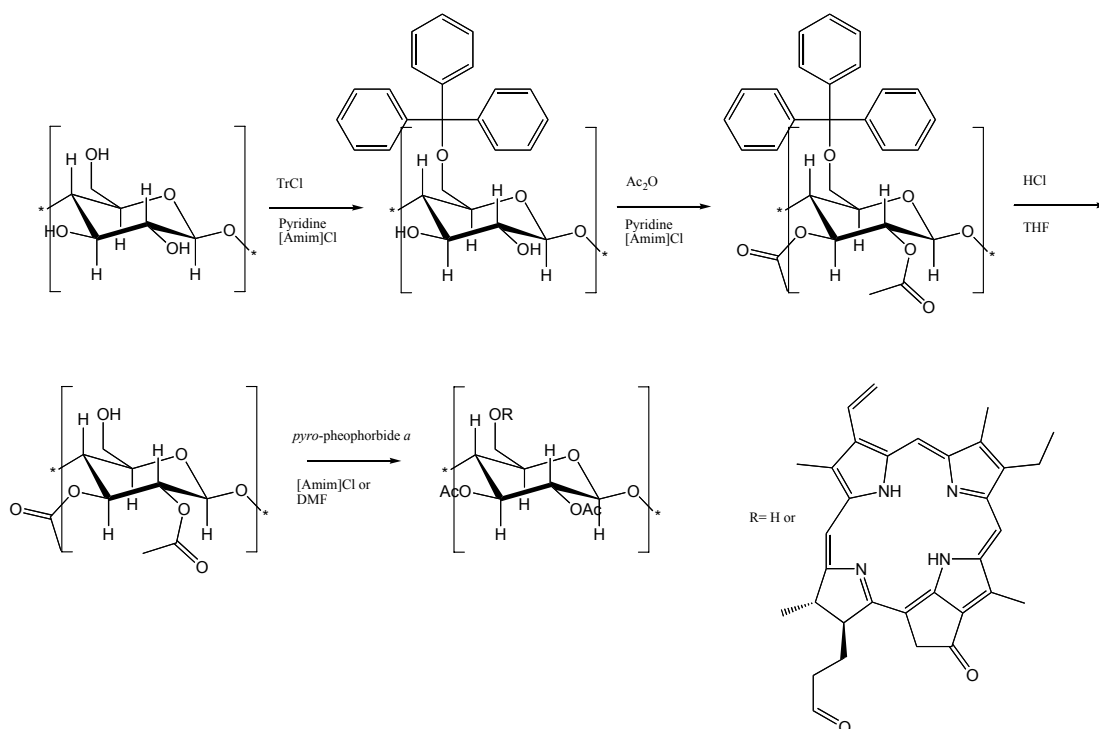
Scheme 14. General synthesis route to (2,3-diacetyl-chlorophyll)cellulose.

Photocurrent properties of a Langmuir-Blodgett film of (2,3-diacetyl-chlorophyll)cellulose

An LB film of (2,3-diacetatyl-chlorophyll)cellulose was prepared and photocurrent measurements were conducted by Dr Sakakibara (Kyoto University) (see Experimental for details).

The existence of a stable monolayer of (2,3-diacetyl-chlorophyll)cellulose on the water surface was confirmed by surface pressure (π)-area (A) isotherm measurements shown in figure 36. The isotherm exhibits a steep rise of surface pressure and a high collapse pressure at 50 mN m^{-1}. The limiting molecular area was ca. 0.5 nm^2 per AGU calculated by the extrapolating the steepest part of the isotherm to zero surface pressure. The limiting molecular area of porphyrin cellulose was reported to be 0.7 nm^2, indicating that the orientation of porphyrin rings is almost perpendicular to the water surface.[198] For (2,3-diacetyl-chlorophyll)cellulose, the limiting molecular area was smaller. Thus it may have a nearly perpendicular orientation with the water surface as the limiting molecular area is close to the that reported to glucopyranose ring (0.55-0.6 nm^2).[198]
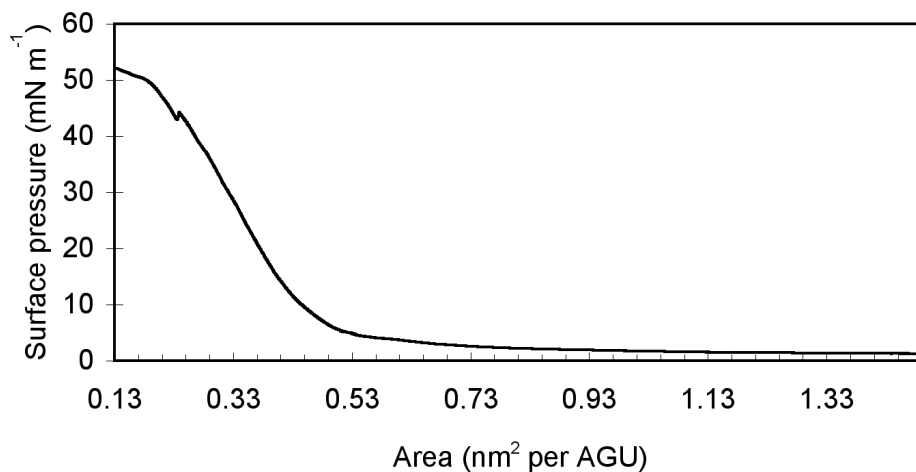
Figure 36. Surface pressure (π)-area (A) isotherm of (2,3-diacetyl-chlorophyll)cellulose derivative.
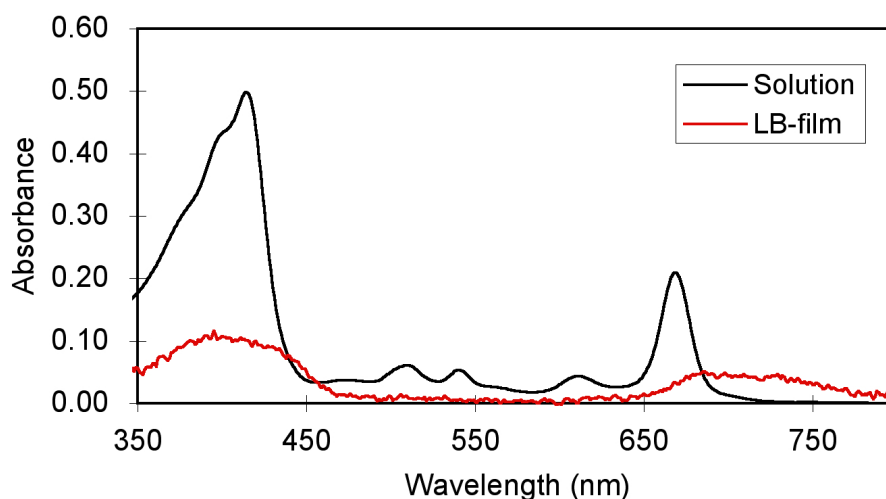
Figure 37. UV-Vis absorption spectra of (2,3-diacetyl-chlorophyll)cellulose in solution (black) and in the monolayer LB film (red).

Figure 37 shows UV-vis absorption spectra of the (2,3-diacetyl-chlorophyll)cellulose derivative in the LB monolayer film and also in the solution. As can be seen, the Soret and Q bands were broader and these bands were shifted in the LB films compared to the shifts in the solution. This indicates the assemblies of (2,3-diacetyl-chlorophyll)cellulose molecules in the film and is characteristic of a densely packed structure.
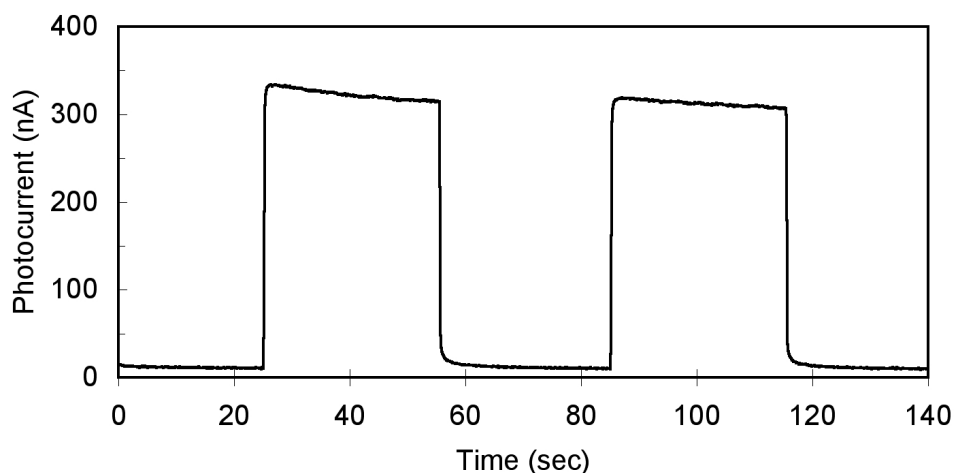
Figure 38. Photoelectrochemical response of LB monolayer film irradiated with visible light.

Figure 38 shows the photocurrent generation by on-and-off illumination of the LB monolayer film irradiated by visible light with a power density of 1.5 mW cm^{-2}. A steady-state anodic photocurrent appeared during light illumination.
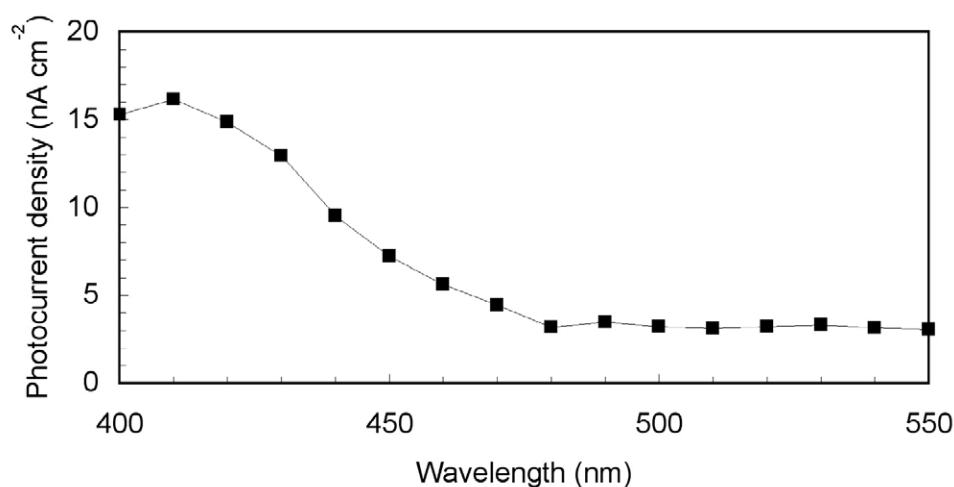
Figure 39. Plot of photocurrent density of the LB monolayer films of (2,3-diacetyl-chlorophyll)cellulose as a function of the irradiation wavelength, *i.e.* action spectra.

Figure 39 shows the plots of the photocurrent density of the LB monolayer films as a function of their irradiation wavelengths, that is, action spectra. The photocurrent density reaches a maximum of 16 nA cm^{-2} at 410 nm. Quantum yield (Φ) of 0.14% and an IPCE value of 0.0033% were obtained under the experimental conditions (applied potential = 0 V vs SCE,

light intensity = 1.5 mW cm^{-2}, λ = 410 nm). A quantum yield of 1.6% was reported with DS value of 0.6 for porphyrin-cellulose.[198] The DS value also affects quantum yields and hence the efficiency of the system. However, the quantum yield obtained for (2,3-diacetyl-chlorophyll)cellulose in this study is considerably higher than that of low molecular weight chlorophyll *a* molecules, which have been reported to have values in a range of 0.01-0.03%.[203]

Chlorophyllcellulose nanofibres

In order to investigate material properties of chlorophyllcellulose (DS of 0.07) further, a preparation of nanofibres by electrospinning was attempted (collaboration with Marjo Pääkkö, TKK). This fibre preparation method is very sensitive to the structural entities and to solvents, in addition to concentration and viscosity of the spinned solution. The structure of MCC is not ideal for the spinning experiments (*i.e.* rod-like, fairly low DP). Moreover, MCC is also substituted with a large moiety. However, this method worked, but was irreproducible. Formation of nanofibres was achieved with a 25% (w/w) chlorophyllcellulose solution in DMSO (Figure 40). Lower concentrations of 10, 15 and 20% (w/w) or higher concentrations of 30, 35 and 40% (w/w) failed to produce fibrillar material, and resulted in the formation of drops.

Figure 40. SEM image of chlorophyllcellulose fibres prepared by electrospinning from 25% (w/w) DMSO solution.

Electrospun chlorophyllcellulose fibres obtained were straight, rod-like fibres without any entanglements (Figure 40). The structure of chlorophyll cellulose fibres was fairly stiff and caused by the large chlorophyll substituents. The substituents are capable of π-stacking between the rings, to stiffen the structure even more. As can be seen from the image, the fibres 'dive' inside the matrix and hence cannot be visualised properly. This is due to the platinum coating used to prepare these SEM samples. Furthermore, the fibres are quite closely packed together in a parallel fashion and junctions at which the fibres are connected can be observed.

3.5 Synthesis of cellulose-based precursors for noncovalent and covalent interactions with carbon nanotubes and fullerenes

Carbon nanotubes (CNTs) have good electronic (*i.e.* good electron acceptors) and mechanical properties and are ideal starting materials for fabricating functional CNT-polymer composites, which have many potential applications, such as being fillers in polymer systems.[204] Moreover, CNT-polysaccharide composites have recently attracted attention due to their potential applications as biosensors.[205,206,207] CNT composites are formed either through physical adsorption or π-π stacking interactions between the polymer and CNT. Furthermore, many of the artificial bio-inspired light absorbing molecular systems mimic the donor-acceptor (DA) pairs.[208,209] These pairs are found in photosynthetic reaction centres, which initiate the charge separation process in photosynthesis.[208] Kavakka *et al.* successfully showed the feasibility of such a pair using a chlorophyll derivative as an electron donor and CNT as an electron acceptor.[208]

This study had two working hypotheses. The first hypothesis was to use a noncovalent approach to prepare a DA pair with chlorophyll-pyrene substituted cellulose that could be mixed with CNTs in organic solvent (Figure 41). The second hypothesis was to attach an acceptor, in this case fullerene, to chlorophyllcellulose covalently (Figure 42).

20

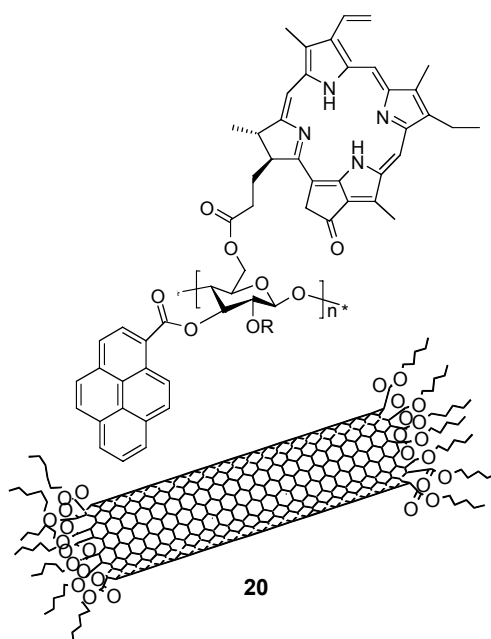**Figure 41.** Schematic presentation of the structure of (chlorophyll-pyrene)cellulose (**20**) mixed with carbon nanotubes. Note: This figure is only schematic and does not represent the outcome of the reaction.

21
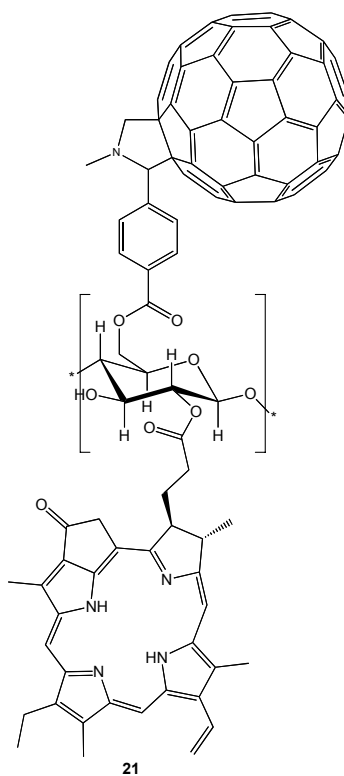
Figure 42. Schematic presentation of the structure of (chlorophyll-fullerene)cellulose (**21**). Note: This figure is only schematic and does not represent the outcome of the reaction.

Synthesis of (chlorophyll-pyrene)cellulose

Inspired by the work of Kavakka *et al.*, it was decided to test whether chlorophyllcellulose could be further substituted with pyrene to enable interactions with CNTs (**20**). It is known that pyrene has an affinity for CNTs.[210] A further modification of chlorophyllcellulose with pyrene would induce affinity towards CNTs and allow the construction of a bio-based DA. The reason for starting the synthesis of chlorophyll-pyrene substituted cellulose from the synthesis of chlorophyll derivative is the large size of the chlorophyll moiety. This moiety is expected to react only at C-6 position and leave C-2 and C-3 as free hydroxyls. Alternatively, the pyrenecellulose could be synthesised first, followed by the insertion of a chlorophyll substituent. However, steric hindrance would restrain the latter reaction yielding even lower DS values. As can be seen from DS of the chlorophyll substitution (0.07), the reaction has not taken place at every C-6 leaving sufficient space for the pyrene substitution preferentially to take place at the C-6 position.

In order to determine the optimal reaction conditions for cellulose derivatisation with pyrene, the reaction was first optimised for unmodified cellulose. The synthesis of pyrene substituted cellulose followed the same protocol as that for chlorophyllcellulose synthesis. Pyrenecellulose was obtained at 66% yield with the low DS value of 0.04. Increasing the equivalency of the reagents from 2 eq. (pyrene carboxylic acid) to 2.5, 3, 5, 8 eq. did not have any affect on the DS value. Similar behaviour has been reported earlier for the reaction between pyrene and HPC using the condensation reaction with DCC, which yielded a maximum DS value of only 0.08.[211] This was thought to be caused by the steric hindrance created by the attached pyrene substituents on cellulose.[211] We believe that there are several factors affecting the low reactivity, one of them being steric hinderence. However, we also suggest that IL reaction medium may be a factor in this phenomenon as imidazolium cations may interact with pyrene in a π-π stacking manner that also hinders the reaction.

The final step in the synthesis of the DA pair was to react chlorophyllcellulose (1 eq.) with pyrene carboxylic acid (2 eq.) under the optimised conditions described above with EDCI (2.5 eq.) and Et₃N (2.5 eq.) (Scheme 15). The purification was carried out by continuous extraction with methanol. This resulted in a (**22**) 25% yield with DS values of 0.07 for chlorophyll and 0.04 for pyrene substituent giving total DS of 0.11. The product was poorly soluble in common organic solvents.
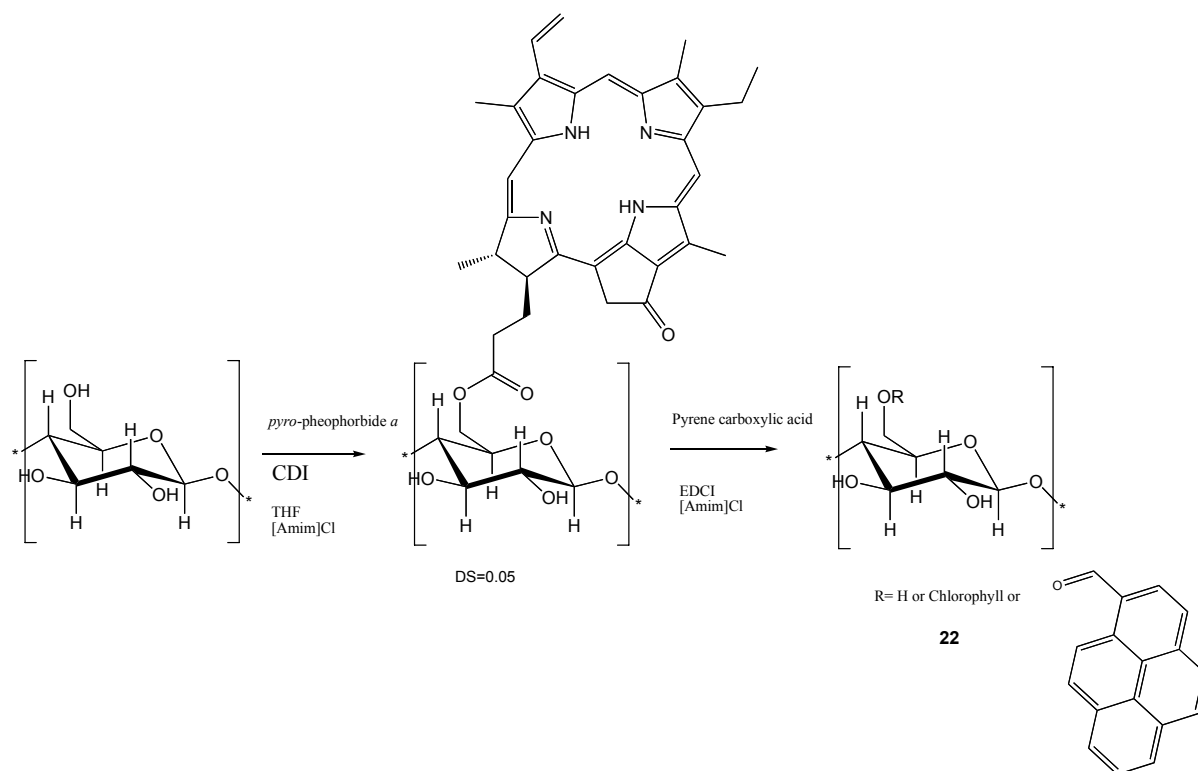
Scheme 15. General synthesis route to (chlorophyll-pyrene)cellulose (**22**).

(Chlorophyll-pyrene)cellulose (**22**) was mixed with CNTs in chloroform to investigate the possible complex formation between (chlorophyll-pyrene)cellulose and CNTs by UV-Vis spectroscopy (Figure 43). The first UV spectrum was recorded 10 mins after mixing these species and the second spectrum at 24 hours after mixing. The spectrum of (chlorophyll-pyrene)cellulose was almost identical to that which was obtained for mixed with CNTs. The only difference occurred at the pyrene and CNT region (250-300 nm, Figure 43) without the expected shifts in the Soret band and the Q band as previously reported for chlorophyll-pyrene/CNT complex.[208] In this case, it may be suggested that the cellulose backbone prevents the close proximity of chlorophylls with the CNTs when the overall DS is low and the derivative is not regioselectively substituted. This inference may be pieced together by the following consideration. When pyrene rings interact with CNTs, the cellulose should adopt a suitable conformation to enable the interaction. Therefore, if there is no chlorophyll on next or near the AGU, then the chlorophyll will not be in close proximity with CNT. Due to the very low DS values of both pyrene and chlorophyll substituents, it seems very unlikely that cellulose would wrap around CNTs. The cellulose backbone itself does not contain any structural elements to drive this kind of interaction.
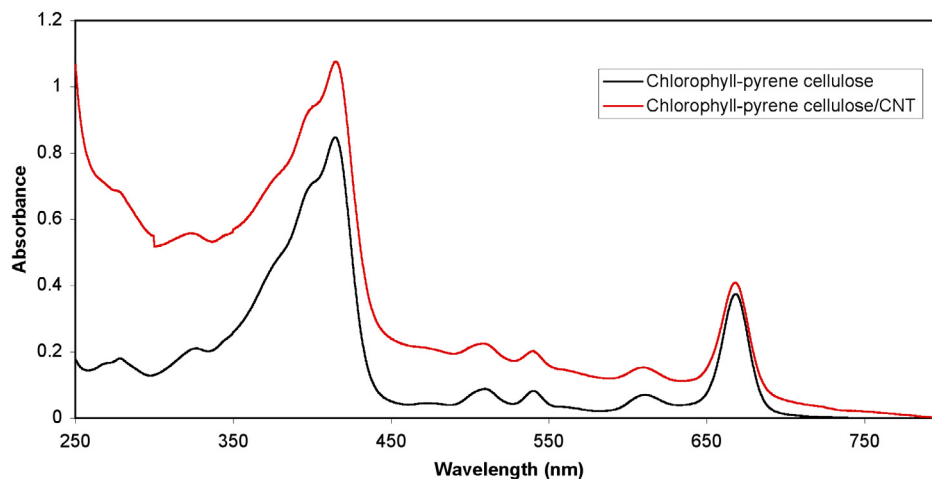
Figure 43. UV-Vis absorption spectra of (chlorophyll-pyrene)cellulose (**22**, black) and (chlorophyll-pyrene)cellulose mixed with CNTs in CHCl$_3$ (**20**, red).

Synthesis of (chlorophyll-fullerene)cellulose

A second approach to generate cellulose based photomimetic systems was to attach an acceptor (in this case, fullerene) covalently to cellulose with the same electron donor as earlier (*i.e.* chlorophyll) (**21**).

First, fullerene with a suitable linker that allows the subsequent reaction with cellulose was synthesised as shown in scheme 16. The synthesis was started by protecting carboxybenzaldehyde (1 eq.) with methoxymethyl chloride (MOMCl) (2 eq.) in the presence of *N,N'*-diisopropylethylamine (DIPEA) (3 eq.) in THF. This gave methoxymethoyl carboxybenzaldehyde (**23**) in a 72% yield. Compound (**24**) was prepared by a modified Prato's method by reacting compound (**23**) with *N*-methylglycine (*i.e.* sarcosine) (5 eq.) and fullerene (2 eq.).[212] Deprotection of the MOM group was achieved under mild conditions by the 'push and pull'[213] method with thioanisole in TFA to afford the final product (**25**) with a 21% overall yield.
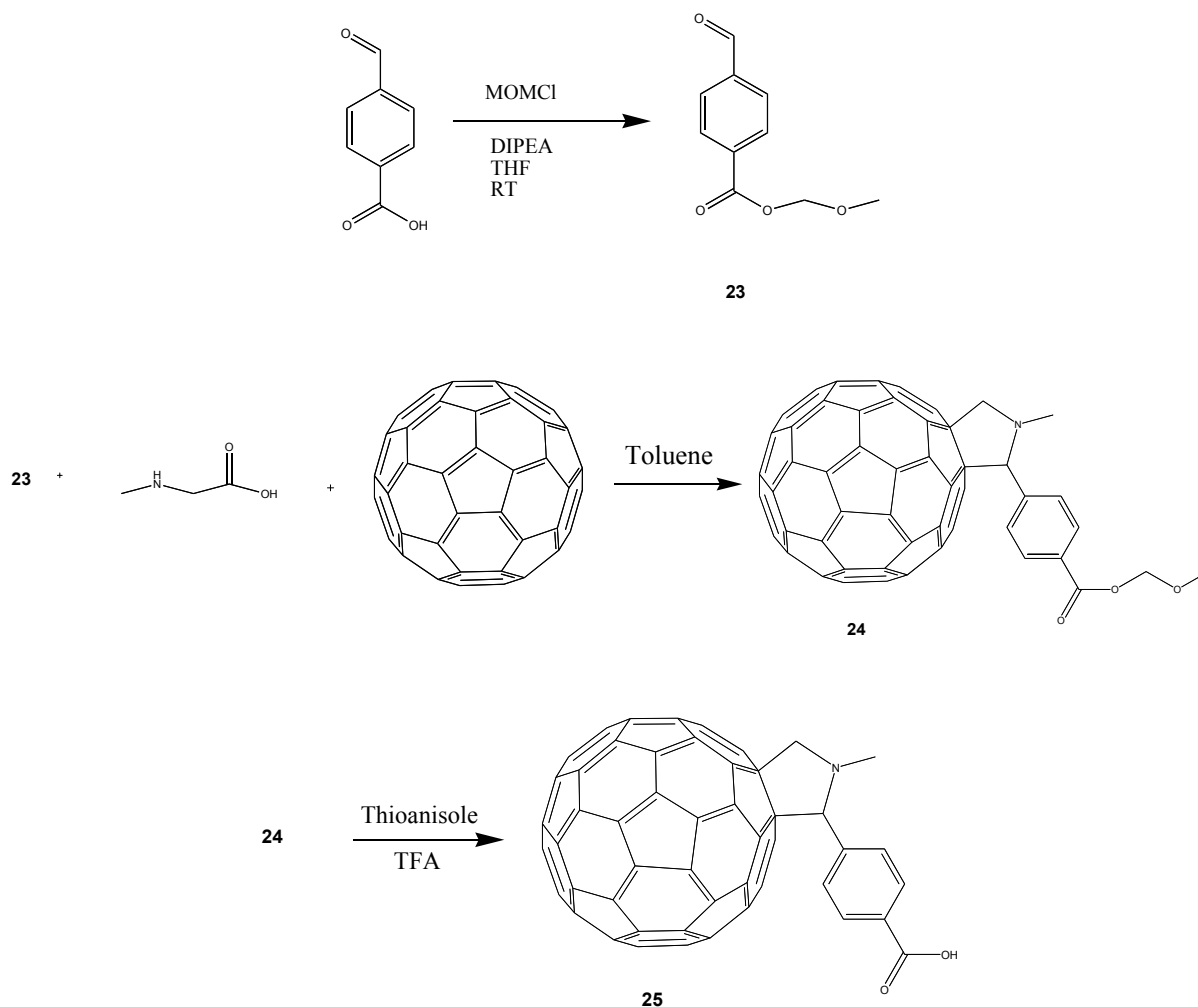
Scheme 16. General synthesis route to fullerene derivative with linker (**25**).

If reaction conditions were not carefully optimised, the reaction yielded di- and trisubstituted fullerenes as side products. MALDI-TOF was an invaluable analytical tool for detecting di-(m/z 1167 (M)) and trisubstituted (m/z 1385 (M)) fullerenes. Other spectroscopical methods such as NMR failed to detect these side products due to the overlap of signals. The formation of these highly substituted fullerenes is not surprising as the reactivity of fullerene is increased upon breaking its aromaticity and symmetry by substitution. Attempts to purify the mixture of mono-, di- and trisubstituted fullerenes by medium pressure liquid chromatography (MPLC) were found to be difficult. This highlights the importance of the optimal reaction conditions as the isolation of these analogues is almost impossible.

Monosubstituted fullerene (**25**) was reacted with chlorophyll cellulose as follows: The compound (**25**) (2.5 eq.) was reacted with CDI (3 eq.) in the presence of Et$_3$N (3 eq.) after which chlorophyll cellulose (1 eq.) in chloroform was added. This reaction yielded product

(21) with a 20% yield. In the UV-Vis spectrum of (**21**), shifts in the Soret band (blue shift, from 460 to 410 nm) and the Q band (blue shift, from 669 to 659 nm) were observed (Figure 44). These shifts are caused by the close proximity of the chlorophyll ring with the surface of fullerene from adjacent cellulose chains (Figure 45). Further characterisation of the product (**21**) is yet to be carried out.
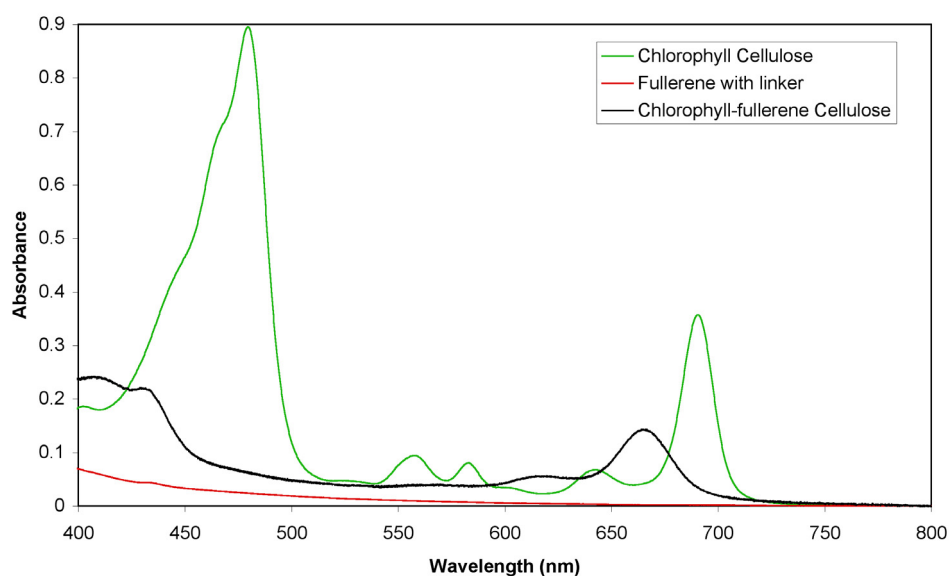
Figure 44. UV-Vis absorption spectra of chlorophyllcellulose (green), fullerene with linker (Scheme 17, **25**, red) and (chlorophyll-fullerene)cellulose (**21**, black).
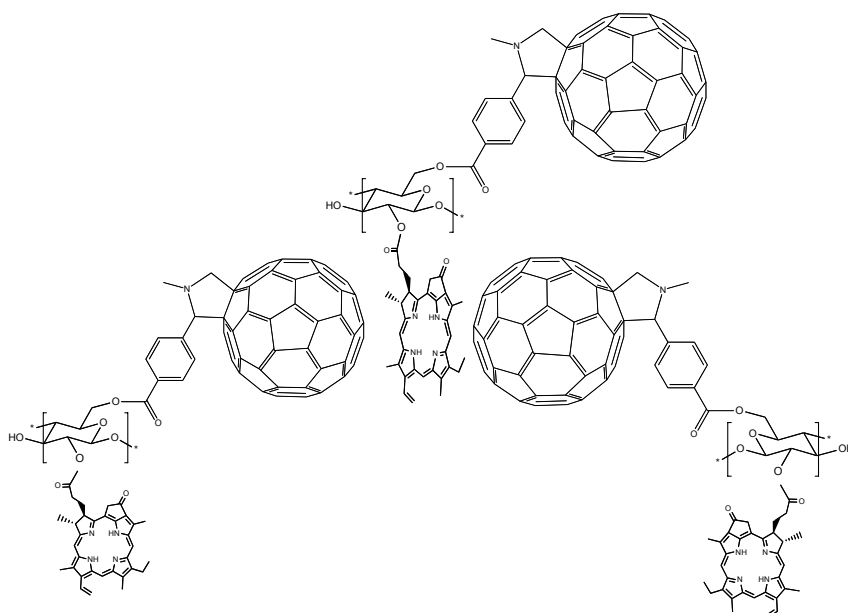
Figure 45. Schematic picture showing the close proximity of chlorophyll ring with the surface of fullerene from adjacent cellulose chain causing the shifts in Soret and Q bands.

3.6 Buchwald-Hartwig cross-coupling

Palladium-catalysed amination of aryl halides and sulphonates (Buchwald-Hartwig cross-coupling (B-H)) has emerged as a valuable method for the preparation of aromatic amines.[214] Recently, the first example of palladium-catalysed aromatic carbon-oxygen (C-O) bond formation was reported. The reaction is the intramolecular Pd-catalysed *ipso* substitution of an aryl halide with an alcohol to provide oxygen heterocycles.[215,216] This method with a related catalyst system was further used for intermolecular coupling of alcohols to aryl bromides (Scheme 17).[217]

Mechanism

Although only preliminary studies on the mechanism of intermolecular C-O bond formation have been carried out, the reaction is assumed to proceed via a similar mechanism as intramolecular C-O formation and related aryl amination (Scheme 17).[217] The oxidative addition of the $Pd(0)L_n$ complex to aryl halide yields the compound (**26**). Next, the corresponding alcohol is combined with the Pd forming complex (**27**). Substitution of the halide by the alcohol in the presence of base gives palladium aryl alkoxide (**28**) followed by a reductive elimination to yield aryl ether (**29**) accompanied by the regeneration of the active catalyst. A common reason for low yields in B-H is the β-hydride elimination, which produces an arene side product.[217] This is a competitive reaction with reductive elimination.[217]
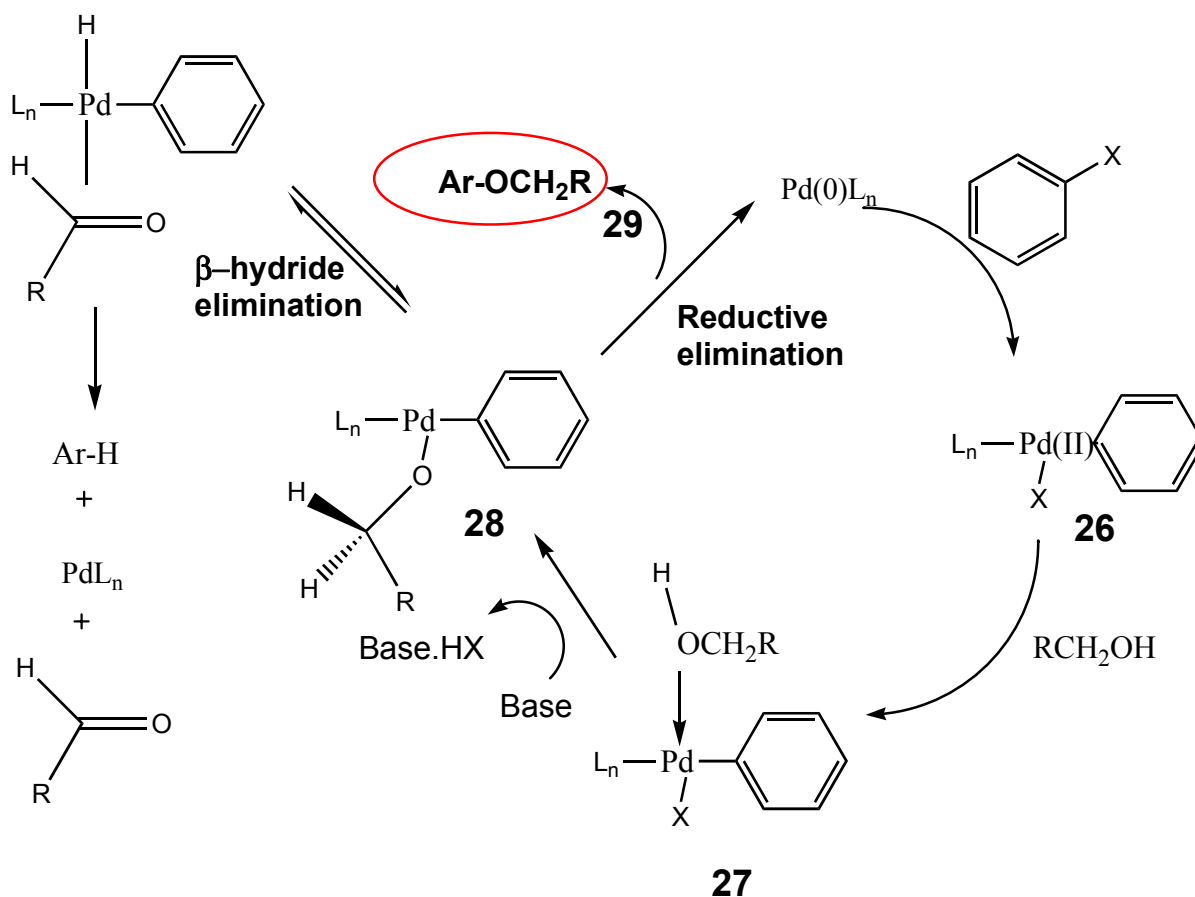
Scheme 17. General reaction mechanism for arylation of alcohols by Buchwald-Hartwig cross-coupling in traditional organic solvent showing the β-hydride elimination side reaction.[217]

As the B-H arylation is selective for primary alcohols, it seems an ideal method to prepare regioselectively arylated cellulose in one reaction step. This kind of cross-coupling reaction has not previously been reported for cellulose. Cellulose in the form of MCC was selectively arylated by *p*-halideanisoles with an *o*-methyl substituent in the presence of Pd catalyst with or without a ligand in [Amim]Cl and [Mmim]Me$_2$PO$_4$. This yielded *o*-methyl anisole cellulose (Figure 46).
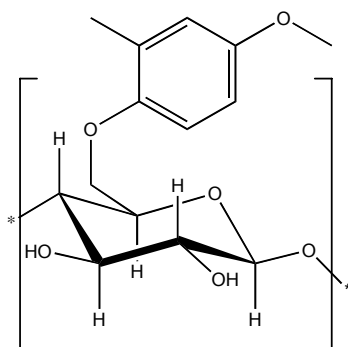
Figure 46. Schematic structure of *o*-methyl anisole cellulose.

Ligands

It has been observed that the structure of the ligand in aryl amination has the major role in determining the reaction pathway between the desired reductive elimination and β-hydride elimination side reaction.[218] Although they still chelate, sterically bulky and less electron-donating ligands favour the reductive elimination step.[218,219] Obviously, alcohols that lack β-hydrogens would only result in the desired product. In this study, two different phosphine-based ligands were tested in order to determine their efficiency and suitability when coupled with cellulose in IL reaction media. These ligands were 2-(di-*tert*-butylphosphino)biphenyl (**30**) and 2-(dicyclohexylphosphino)biphenyl (**31**) (Figure 47).[220] These ligands were, however, not soluble in the ILs used in our reactions, [Amim]Cl and [Mmim]Me$_2$PO$_4$. Moreover, when the reaction was carried out without ligands the yield and the outcome was the same and therefore, additional ligands were not necessary. Thus, there has to be another species that functions as a ligand during the reaction.

30   **31**
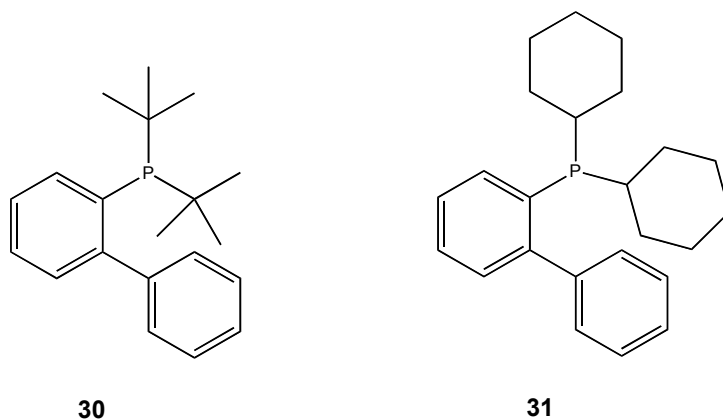
Figure 47. Structures of phosphine-based ligands; 2-(di-*tert*-butylphosphino)biphenyl (**30**) and 2-(dicyclohexylphosphino)biphenyl (**31**) used in Buchwald-Hartwig reaction.

Choice of base

Different bases were also tested for the efficiency in B-H reaction of cellulose. It has been reported that fairly strong bases such as sodium hydride (NaH) are required for the deprotonation step in the cycle. Nevertheless, an inorganic base, caesium carbonate (Cs_2CO_3) has been successfully used.[217] However, with cellulose, the reaction did not proceed even in the presence of a ligand with Cs_2CO_3. Therefore, it was decided to use a stronger base namely, potassium *tert*-butoxide (KO^{t}Bu) instead. As discussed earlier in this text, the utilisation of a strong base such as KO^{t}Bu with imidazolium-based ILs results in the formation of carbene. When KO^{t}Bu was used as the base the formation of carbene or the carbene-Pd complex was manifested as an intensive red colour of the reaction solution. In spite of the formation of the carbene, the reaction was successful and yielded arylated cellulose derivative with a DS of 0.74. As the B-H coupling did not require an additional ligand, it can be suggested the IL took part in the reaction between carbene and palladium catalyst and hence, formed a stable palladium adduct. This hypothesis is supported by reports in the literature in which the use of imidazolium-based ILs resulted in the imidazolium-based palladium catalyst promoting the reaction further in Suzuki cross-coupling.[221]

Palladium catalysts

The B-H reaction was carried out using various palladium catalysts without additional ligands. The palladium catalysts included tetrakis(triphenylphosphine) palladium(0), palladium (II)acetate and palladium(II)dichloride. All the Pd-catalysts were fully soluble in the ILs used and the precipitation of the elemental Pd was not observed. Additionally, the nature of the active palladium catalysts was not crucial as the reactions worked with all of these Pd catalysts. It seems possible that instead of having a typical Pd complex in the reaction cycle, the imidazolylidene-Cl$_2$-Pd(II) complex is formed by the reaction between Pd catalyst and carbene (Figure 48). This complex looses its chloride ligands to form imidazolylidene-Pd(0) complex, which takes part in the reaction cycle (Scheme 18).
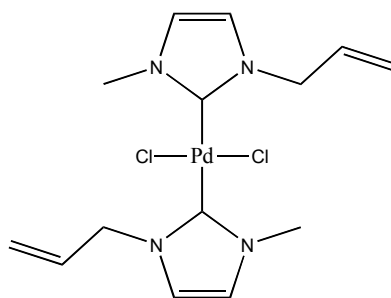
Figure 48. Presupposed structure of imidazolylidene-Cl$_2$-Pd(II) complex formed by the reaction between Pd catalyst and carbene.
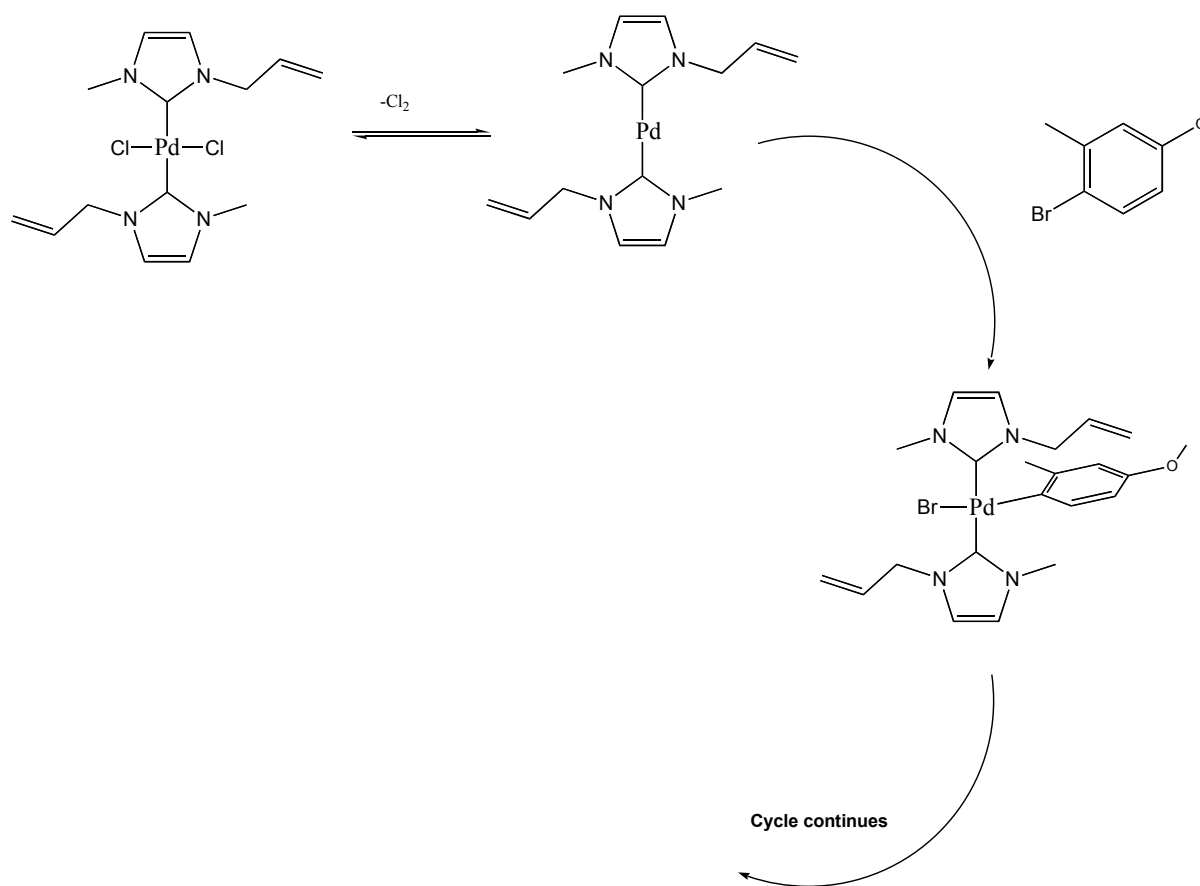
Scheme 18. Reaction cycle showing the formation of imidazolylidene-Pd(0) complex from imidazolylidene-Cl$_2$-Pd(II) complex and the oxidative addition step.

Ligand exchange mechanism

It had been reported that nucleophilic 'co-ordinating' counteranions are detrimental to the success of the amination reaction in B-H amination. Usually, weakly or 'non-co-ordinating' anions, particularly bistriflimide and saccharide derivatives are superior.[222] It also appears that the weakly nucleophilic nature of the arylamine derivative inhibits its participation in the Pd-mediated catalytic cycle when co-ordinating anions and/or solvents are used.[222] This is in

contrast to Suzuki coupling where the reaction is enhanced by chloride anions.[223] The dichotomy between these reactions has been thought to rest upon the nature of the ligand exchange mechanism (Scheme 19).[222]

In B-H amination, the presence of excess halide or other co-ordinating anions in the reaction taking place in IL is expected to hinder the ionisation step (Path C). Thus, this hinders the cross-coupling with weak nucleophiles (Scheme 19).[222] In contrast, a strong nucleophile could allow ligand exchange (or transmetallation) by a nucleophilically assisted process through either: an association to form anionic Pd-intermediate (Path A), or directly through an interchange path (Path B).[222]

Identification of a ligand exchange pathway seems too ambitious at the current stage of the study. However, this mechanism would explain some of the observations. First of all, the IL reaction media are well understood as the formation of carbene-palladium complex are assumed to take part in the reaction. On the other hand, the extent that cellulose acted as a nucleophile is not clear in the reaction cycle. The nucleophilicity of cellulose varies in the cycle according to the stage of deprotonation. It is unknown whether deprotonation takes place before the co-ordination of cellulose with Pd or after. In the general reaction scheme 18, it was shown that the hydroxyl group co-ordinates to Pd before the deprotonation step. If the deprotonation takes place before co-ordination, cellulose can be indeed considered as a strong nucleophile. Then we could assume that ligand exchange would proceed either via association or by direct interchange. As the use of caesium carbonate as a base resulted in an unsuccessful reaction, it can be postulated that co-ordination of the hydroxyl group to Pd before deprotonation step seems unlikely. This may be due to the ease of deprotonation of co-ordinated hydroxyl group species as a consequence of electronic effects. In addition, the pKa of 6-OH group of cellulose is around 15-16, whereas for imidazolium the pKa is 24 and *tert*-butoxide anion has pKa of 18. Obviously, KO^{t}Bu is a strong enough base to deprotonate cellulose and it can also deprotonate the imidazolium cation although its pKa is lower than that for the imidazolium cation.
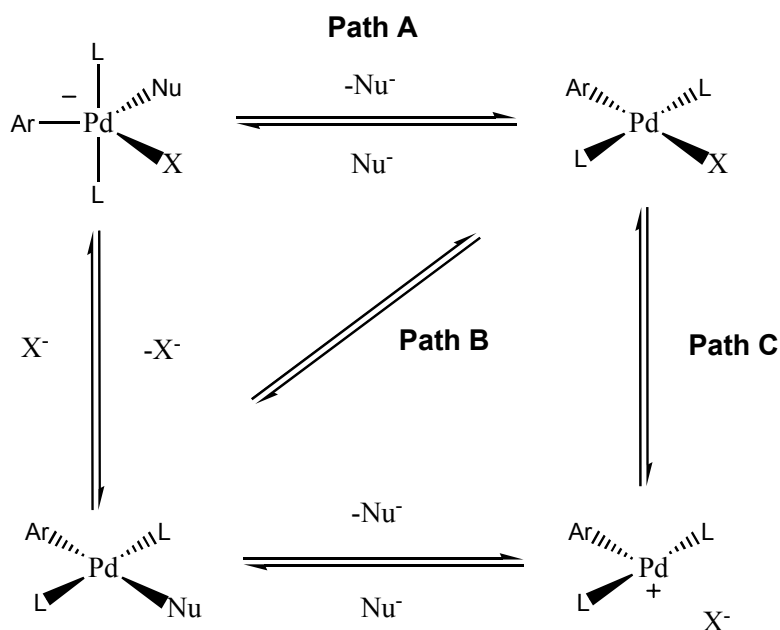
Scheme 19. Proposed ligand exchange pathways in Buchwald-Hartwig amination.[222]

The role of substrate

It has been previously reported that *o*-bromoanisoles are poor substrates, whereas the *ortho* substitution was beneficial for coupling efficiency.[224] Furthermore, it was also shown that the addition of the *ortho* alkyl group increased the selectivity of ether formation dramatically.[224] There was little difference in changing the alkyl group from methyl to ethyl or to isopropanol.[224] However, the length of the alkyl group (*i.e* methyl vs. *n*Pr) had a negative effect on the reaction yield and resulted in a 10% decrease.[224] By introducing the methyl group *ortho* to bromide, the product:arene ratio was increased from 0.24:1 to 2:1 with 2-*tert*-butyl-4-bromoanisole as the reagent.[224] Therefore, *p*-halideanisoles with the *o*-methyl substituent were selected as aryl halides due to the electron-deficient nature associated with an *ortho* alkyl (*i.e.* methyl) substituent.

Optimised reaction conditions

Optimised reaction conditions were obtained by preparing two different solutions. Cellulose (1 mmol) was first dissolved in IL. Another solution was prepared by dissolving the Pd catalyst (10 μmol) in IL in the presence of KO^{t}Bu (2.5 eq.) in a separate flask and heating to 80°C upon which the colour of the solution changed from yellow to red. After complete dissolution, these two solutions were mixed together and the aryl halide (1 eq.) was added. The reaction mixture was stirred at 80°C for two days. DS of 0.74-0.85 were obtained with

yields ranging from 60 to 64%. The product was moderately soluble in DMSO, but enabled characterisation with 2D ^{1}H-^{13}C HSQC. The product was further characterised by ^{31}P NMR and IR.

Side reaction in acetylation of cellulose aryl ether

Since the arylated derivatives were only moderately soluble in chloroform, DMSO, DMA, DMF or THF. We attempted to acetylate the samples to enhance the solubility for detailed NMR characterisation. Acetylation was carried out a using general procedure with an excess of both acetic acid anhydride and pyridine in [Amim]Cl at room temperature (**I**). Unexpectedly, the colour of the reaction mixture changed from pale yellow to red. Initially, it was believed that this was due to the traces of the Pd catalyst or complex in the system even after several purification steps. However, the presence of the catalyst could not be ascertained.

After the work-up and drying procedures, the acetylated and arylated derivative was dissolved in d_6-DMSO and was determined by 2D ^{1}H-^{13}C HSQC along with ^{1}H NMR. In the 2D HSQC spectrum, the presence of only acetylated cellulose was evident. With careful investigation of the spectrum, it was seen that the structure of the obtained acetylated derivative was not uniform and gave several shifts for anomeric C-1 in addition to C-6. It was concluded that side reaction cleavage of the aryl substituent took place. Because pyridine was used as a base in the acetylation in [Amim]Cl, pyridinium hydrochloride was formed (see Scheme 5 for the formation mechanisms). This reagent is known for its 'deprotection' activity, especially for the demethylation of methyl aryl ethers.[225]

The chloride anion of pyridinium hydrochloride can act as a nucleophile (Scheme 20). The chloride attacks on the C-6 of arylated cellulose and cleave the aryl ether: thereby, producing chlorinated and acetylated cellulose. Chlorinated cellulose is reported to have a chemical shift in ^{13}C spectrum at around 59 ppm (**I**). However, this signal was not observed. Thus it can be concluded that the chlorinated and acetylated cellulose is further hydrolysed to yield partly acetylated cellulose.
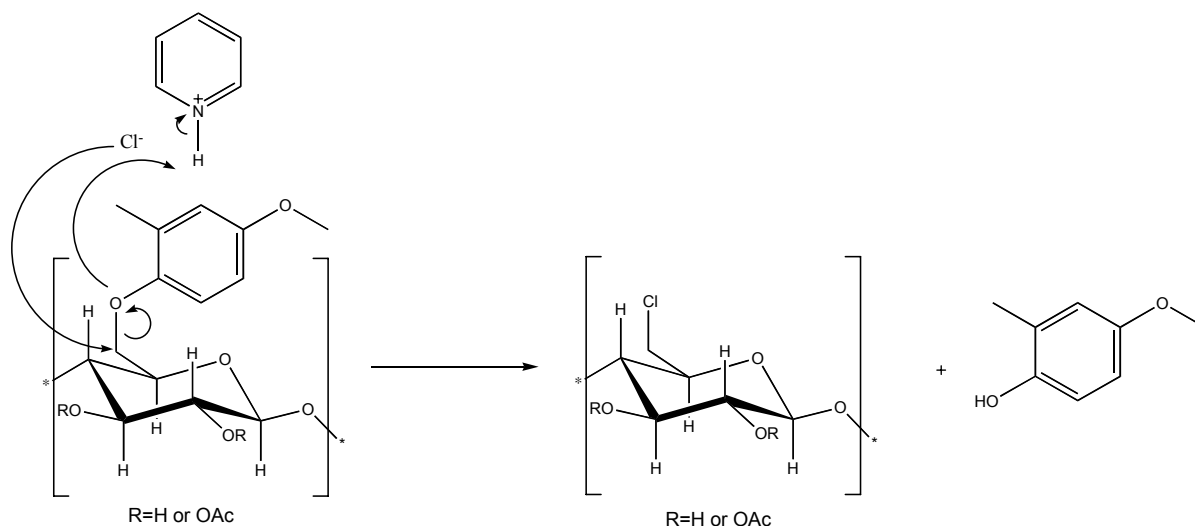
Scheme 20. Proposed reaction mechanism for cleavage of aryl ethers during the acetylation reaction in [Amim]Cl.

As demonstrated here, the Buchwald-Hartwig cross-coupling is an effective method to produce cellulose aryl ethers. This approach allows the regioselective arylation in one reaction step, whereas conventionally, it required protecting group chemistry involving several reaction steps.

3.7 Synthesis of 6-(4-aminophenyl)aminocellulose as a precursor for (polyaniline)cellulose

Cellulose and wood fibres with conductive polymers have been utilised as composites to reinforce mechanical properties.[226] These composite materials with their unique properties open up new applications in the packaging and in areas where specific electrical conductivity, anti-static or electromagnetic shielding properties are required.[226] Usually polymers such as plastics and rubber used in the preparation of polyaniline (PANI) composites have been synthetic polymers that originate from petroleum feedstock. Hence, these are non-biodegradable.[227] In contrast, cellulose as a natural polymer may be seen as an ideal polymer to be coupled with PANI to form new hybrid materials that meet the criteria for renewable resources. Such polyaniline-cellulose composites are prepared heterogeneously by activating (*i.e.* swelling) the cellulose fibres first with acids and then by adding the aniline monomer into the cellulose slurry. This is followed by the addition of an initiator for

polymerisation.[226,228] This results in a composite structure in which the PANI molecules are incorporated inside the cellulose network structure.[228]

Another possible method to obtain these novel materials is based on the covalent and homogeneous approach. Herein, the aim was to synthesise the of 6-(4-aminophenyl)aminocellulose precursor as a monomer in the polymerisation of PANI chains on the cellulose backbone.

6-(4-Aminophenyl)aminocellulose was synthesised via tosylcellulose (DS of 0.84) as described in Paper **I** (Scheme 21). Tosylcellulose (1 eq.) was reacted with 4-phenylenediamine (5 eq.) in the presence of Et₃N (5 eq.) in DMF to yield of 6-(4-aminophenyl)aminocellulose with DS of 0.8 and 81% yield.
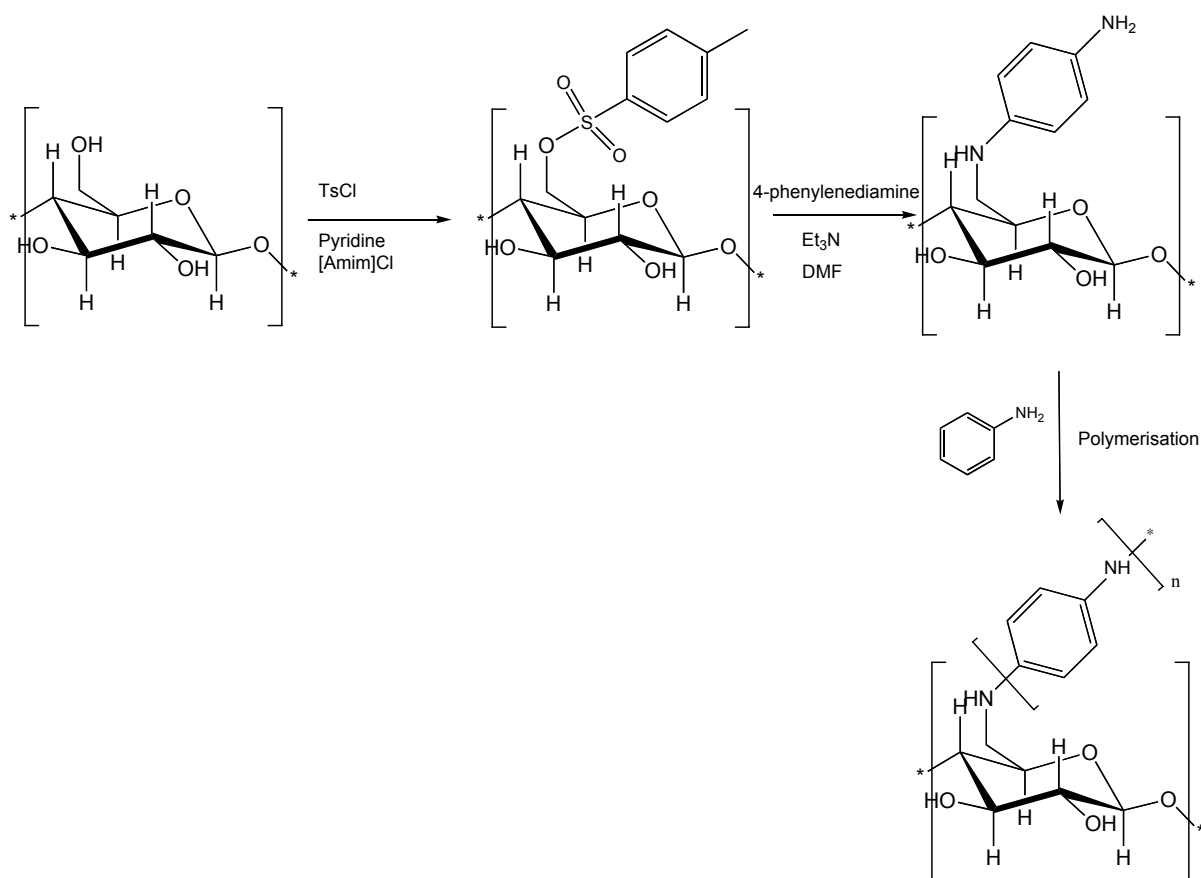
Scheme 21. General synthetic route to (polyaniline)cellulose via of 6-(4-aminophenyl)aminocellulose.

Polymerisation of 6-(4-aminophenyl)aminocellulose

PANI can be switched between its three oxidation states, which are leucoemeraldine, emeraldine and pernigraniline.[229,230] The fully reduced leucoemeraldine form can be oxidised to the half oxidised emeraldine form. This can be oxidised further to the fully oxidised pernigraniline state (Figure 49).[231] These steps are achieved by chemical or electrochemical oxidation. The three bases can be used as insulating materials, whereas emeraldine salt derived by protonation of the half oxidised emeraldine form has conductive properties (Figure 49).[231]
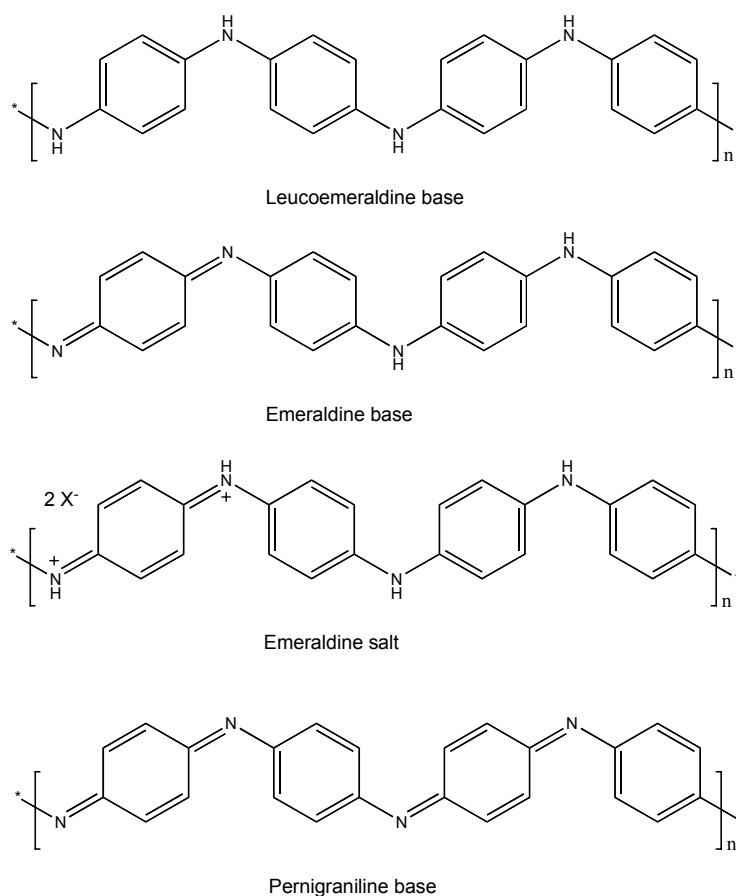
Figure 49. Oxidation states of PANI.[231]

Polymerisation of 6-(4-aminophenyl)aminocellulose with aniline monomer was investigated to obtain PANI-cellulose derivative with PANI chains covalently attached to cellulose as branches (Scheme 21).

The polymerisation of aniline to yield PANI by chemical and electrochemical means in [Amim]Cl-water system was tested to determine the efficiency of IL media in this type of reaction. Both reactions worked efficiently producing PANI although the yield obtained for the electrochemical polymerisation approach was poor and the PANI film produced at the ITO electrode was too brittle to handle. The reaction was also attempted on the 6-(4-aminophenyl)aminocellulose molecule by chemical means as follows. 6-(4-Aminophenyl)aminocellulose (1 eq.) was dissolved in [Amim]Cl after which an aqueous solution of aniline hydrochloride (1.25-10 eq.) was added with vigorous stirring. After the complete mixing of the reagents, ammoniumperoxosulphate (APS) (1.5-12 eq.) was added and the mixture was stirred at room temperature for 48 hours. Cellulose derivative was regenerated from water as a red/brown precipitate. This colour indicated the presence of non-conductive leucoemeraldine form of PANI. This was further confirmed by UV-Vis. CP-MAS NMR and IR showed bands for cellulose and PANI. However, the obtained product was insoluble in common organic solvents and poorly soluble in *m*-cresol. When doped with TFA, the expected green colour of the conductive form, emeraldine salt, was not obtained. Hence, it was concluded that it is not possible to obtain the emeraldine base from the current form of this preparate by doping. The same reaction was carried out using DMA instead of [Amim]Cl to see if the IL caused this behaviour, but the outcome was still the same.

Results from the electrochemical polymerisation were more promising as the solubility of the obtained precipitate was moderate. This showed a greenish colour, which indicated the formation of the emeraldine base form. The electrochemical polymerisation was carried out by cyclic voltammetry (CV) using [Amim]Cl as the electrolyte solution with varying concentrations (0.05-0.1M) of 6-(4-aminophenyl)aminocellulose. Aniline (0.05-0.1M) was added into the solution just before the measurement. The potential was cycled between 0-1.7 V with the rate of 10 mV/s. Cyclic voltagram of 14 cycles are plotted in figure 50. Letters A, B, C and D indicate different stages in the process. Point A indicates the starting potential at which the polymer has not been formed at the ITO electrode and the potential is swept to the so called negative direction. At point B, the potential is negative enough for the cathodic current generation and polymer starts to accumulate at the ITO electrode. At point C, the major amount of monomer deposited at the ITO electrode has reduced (probably only aniline monomer has deposited on ITO and reduced). At Point D the negative sweep is changed to the positive direction and from this point onwards, the cathodic current gets weaker. From the plot in figure 50, it can be concluded that polymerisation had taken place and the formed

polymer was conductive. However, the maximum currents do not appear at the same potential for every cycle as they should appear in an ideal system. It seems that the values are shifted at smaller potentials of increasing frequency. This may be an indication that the redox reaction did not reach an equilibrium. Usually, when the reaction is not in equilibrium, the maximum currents are shifted to higher potentials. Nevertheless, as the polymerisation was proceeding, the maximum currents shifted to closer values with each other. This is probably due to the decreasing aniline concentration in the electrolyte solution.
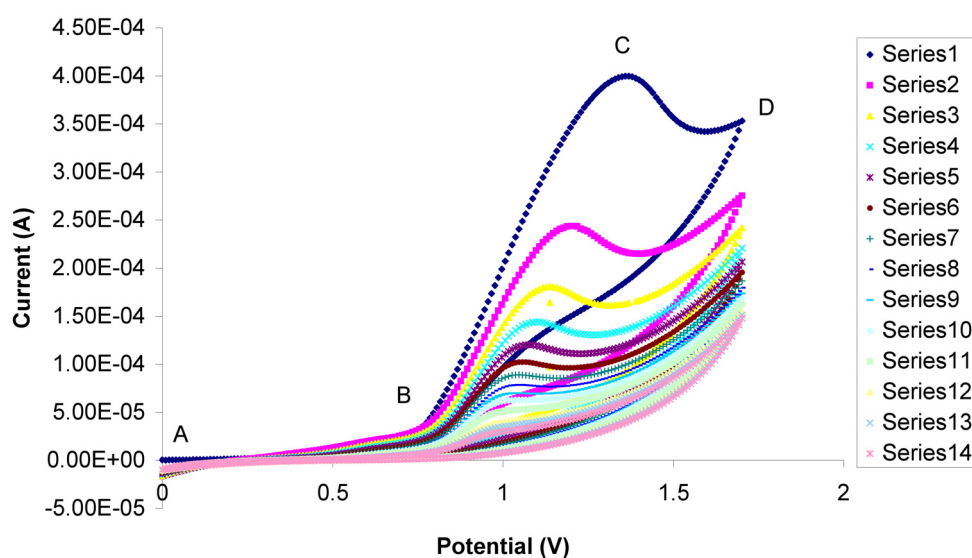
Figure 50. Cyclic voltagram of polymerisation of 6-(4-aminophenyl)aminocellulose with aniline in [Amim]Cl showing 14 cycles.

The electrochemical polymerisation resulted in a poorly formed black film on the ITO glass. The resulting polymer had more of a deposit property than a film. The product was insoluble in any organic solvents. However, when the [Amim]Cl as an the electrolyte solution was poured into water in order to see if the possible product was soluble in [Amim]Cl, a dark green precipitate was obtained. This product was soluble in chloroform and according to the ^{1}H NMR, contained cellulose. A film with interesting textures was obtained, which showed an ordered structure under polarising optical microscopy (POM) and SEM (Figure 51). The POM image indicated the presence of repeated band-like texture whereas SEM revealed the fine structure of this band as spherulite-like repeating units. Interestingly, similar band textures have been obtained for acetoxypropylcellulose and HPC films.[232,233] These periodic structures are formed after the evaporation of solvents.[233]
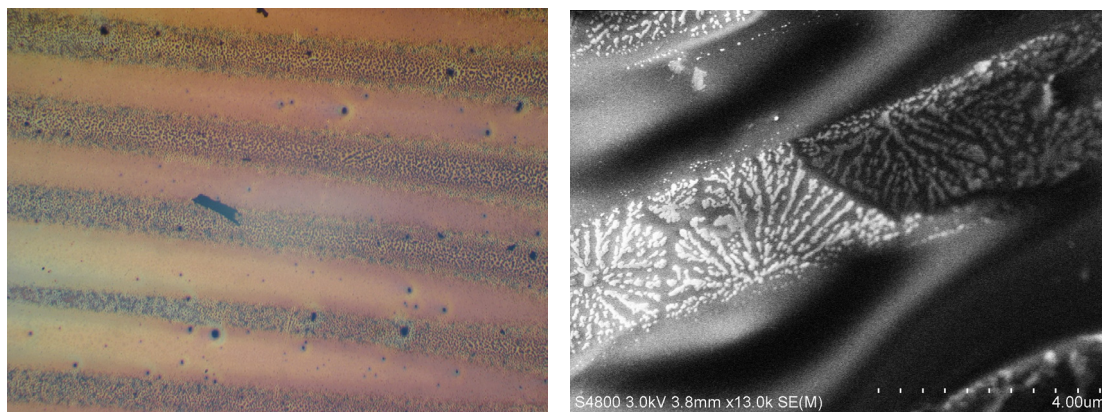
Figure 51. Microscopy images of (polyaniline)cellulose film: POM image (left) and SEM image (right) showing orientated nature of the film.

At this stage, it could be concluded that the electrochemical polymerisation seemed a more feasible and promising method for the preparation of (polyaniline)cellulose than the chemical approach. Moreover, it seemed to form the conducting form of the PANI on cellulose. However, the nature of such a reaction that uses a polymer (6-(4-aminophenyl)aminocellulose) as a monomer is not that straightforward and only preliminary results from these experiments are reported.

4. Experimental

4.1 Synthesis of (2,3-*O*-diacetyl-6-*O*-chlorophyll)cellulose

4.1.1   Synthesis of (2,3-*O*-diacetyl-6-*O*-trityl)cellulose

The synthesis of regioselectively substituted trityl cellulose gave a DS of 0.9 with a 98% yield (**III**). Trityl cellulose (2.0g, 5.3 mmol) was dissolved in [Amim]Cl and acetic acid anhydride (2 ml, excess) and pyridine (2 ml, excess) were added and the reaction mixture was stirred at room temperature for 24 hours. The mixture was poured into water and the formed precipitate was filtered off and washed with plenty of water. The precipitate was dissolved in DMSO from which it was regenerated with water to give (2,3-diacetyl-6-*O*-trityl)cellulose (2.1g, 83%, DS_{Total} = 2.92). ^{13}C NMR (250 MHz, DMSO-d_6): δ = 21.5 (Ac), 62.5 (C-6), 70-73 (C-2,3,5), 76.4 (C-4), 86.2 (C-7), 101.1 (C-1), 112.7 (C-12), 126.4 (C-10), 127.3 (C-11), 134.2 (C-9), 138.4 (C-8), 159.6 (C-13), 171.3 (C=O) CP-MAS NMR (300 MHz): δ = 21.2 (Ac), 62.1 (C-6), 73 (C-2,3,5), 83.2 (C-4), 101.4 (C-1), 127.5 (Tr), 148.3 (Tr), 170.3 (C=O).

4.1.2   Synthesis of 2,3-*O*-diacetylcellulose

(2,3-Diacetyl-6-*O*-trityl)cellulose (1.0g, 2.1 mmol) was dissolved in THF (50 ml) and conc. HCl (1.5 ml) was added. The reaction was stirred at room temperature for 3 days, after which the product was regenerated from water to give 2,3-diacetylcellulose (0.5g, 96%, DS = 2). ^{13}C NMR (250 MHz, DMSO-d_6): δ = 17 (Ac), 59 (C-6), 69 (C-2), 70 (C-3), 72 (C-5), 78 (C-4), 99 (C-1), 171 (C=O).

4.1.3   Synthesis of (2,3-*O*-diacetyl-6-*O*-chlorophyll)cellulose

Chlorophyll (*i.e. pyro*-pheophorbide *a*) (30mg, 0.05 mmol) was dissolved in DMF (10 ml). Then DCC (7mg, 0.05 mmol) with DMAP (10 mg, 0.05 mmol) were added and the reaction was stirred at room temperature for 2 hours and added to the solution of 2,3-diacetylcellulose (10mg, 0.04 mmol) in DMF (5 ml). The reaction was stirred at room temperature for 24 hours. A product was regenerated with water and washed with methanol to give (2,3-diacetyl-6-*O*-chlorophyll)cellulose (9mg, 79%, $DS_{Chlorophyll}$ = 0.07)

^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.4 (H- 8^2), 1.8 (H-18^1), 2.0 (OAc), 2.8/2.9 (H-17^1), 3.3 (H-7^1), 3.4 (H- 5'), 3.7 (H-12^1), 3.9 (H-8^1), 4.1 (H-6), 4.2 (H-6^1), 4.5 (H-1), 4.6 (H-2), 5.3 (H-13^2), 5.4 (H-3), 6.2 (H-3^2), 8.0 (H-3^1), 8.6 (H-20), 9.4 (H-5), 9.6 (H-10).

IR (cm^{-1}): 3422 (OH), 3110 (aromatic), 1690 (C=O), 1466 (C–O), 650 (aromatic).

UV–VIS (λ_{max}, nm): 416, 669.

[Amim]Cl was used as a solvent when unmodified MCC was used as a starting material, and following reagents were used as in the above procedure: activation reagents: CDI (**I**), EDCI and DCC, bases: pyridine, Et$_3$N and DMAP and/or auxiliary nucleophile: pentafluorophenol (0.5-2 eq.)

4.2 Synthesis of (chlorophyll-pyrene)cellulose

Pyrene carboxylic acid (0.3g, 1.2 mmol), EDCI (0.2g, 1.2 mmol) Et$_3$N (0.1g, 1.2 mmol) in dry THF were stirred for 24 hours, after which the THF was removed *in vacuo*. Then chlorophyll cellulose (0.1g, 0.6 mmol) in DMF was added. The mixture was heated at 50°C for 48 hours, after which it was cooled to room temperature. Chlorophyll-pyrenecellulose was regenerated from the mixture of water and methanol (1:1). The precipitate was filtered off and stirred with ethyl acetate to remove the excess of pyrene carboxylic acid and washed further with water and methanol to give (chlorophyll-pyrene)cellulose (**22**) (0.31g, 25%, DS$_{Pyrene}$ = 0.04). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 1.3 (H- 8^2), 1.7 (H-18^1), 2.8/2.9 (H-17^1), 3.2 (H-7^1), 3.3 (H- 5'), 3.6 (H-12^1), 3.8 (H-8^1), 4.0 (H-6), 4.1 (H-6^1), 4.4 (H-1), 4.5 (H-2), 5.2 (H-13^2), 5.3 (H-3), 6.1 (H-3^2), 7.9 (H-3^1), 8.19 (Pyrene, H-2), 8.21 (Pyrene, H-4), 8.3 (Pyrene, H-1), 8.5 (H-20), 9.3 (H-5), 9.6 (H-10). IR (cm^{-1}): 3335 (OH), 2919 (aromatic), 1667-1750 (broad, C=O).

4.3 Synthesis of (chlorophyll-fullerene)cellulose

4.3.1   Protection of carboxybenzaldehyde by methoxymethyl chloride

Carboxybenzaldehyde (1.5g, 0.01 mol) was dissolved in THF (20 ml). *N,N'*-diisopropylethylamine (4.31g, 0.03 mol) and methoxymethyl chloride (1.5 ml, 0.02 mol) were added and the reaction was stirred at RT for 8 hours. The reaction mixture was poured into ice/water and extracted with CH$_2$Cl$_2$ (3 x 20 ml). The resulting combined organic layer

was washed with water and dried with MgSO$_4$ and the solvent was removed *in vacuo* to give methoxymethoylbenzaldehyde (**23**) as a white solid (1.4g, 72%). m/z = 194 (M), ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.5 (s, 3H), 5.5 (s, 2H), 7.9 (d, 2H), 8.2 (d, 2H), 10.1 (s, 1H).

4.3.2 Synthesis of fullerene linker

Methoxymethoylbenzaldehyde (**23**) (0.2g, 0.001 mol), sarcosine (0.5g, 0.005 mol) and fullerene (1.44g, 0.002 mol) were refluxed in toluene for 12 hours. The solvent was removed *in vacuo* and the crude product was purified by column chromatogarphy first by eluting with toluene to obtain the fullerenes and then by eluting with hexane/EtOAc (2:1) to give a product (**24**) (0.2g, 21%). MALDI-TOF: 897 [M-45]$^-$, ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.8 (s, N-CH$_3$), 3.5 (s, CH$_3$), 4.1 (q, 1H), 4.3/5.0 (d,d, 2H), 5.4 (s, 2H), 7.9 (d, 2H), 8.1 (d, 2H).

4.3.3 Deprotection of methoxymethoyl group

Fullerene with linker MOM protection (**24**) (0.2g, 0.21 mmol) was dissolved in TFA (5 ml). Then thioanisole (0.03g, 0.25 mmol) was added and the reaction was stirred at room temperature for 4 hours to give fullerene linker with free acid (**25**) (0.18g, 96%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.7 (s, N-CH$_3$), 3.3 (q, 1H), 4.2/4.9 (dd, 2H), 7.8 (d, 2H), 8.0 (d, 2H), 12.4 (s, broad, OH).

4.3.4 Synthesis of (chlorophyll-fullerene)cellulose

Compound (**3**) (1.2g, 1.3 mmol) was dissolved in chloroform and reacted with CDI (24mg, 0.15 mmol) in the presence of Et$_3$N (0.02g, 0.15 mmol) overnight after which chlorophyll cellulose (0.1g, 0.5 mmol) in chloroform was added. The reaction was stirred at room temperature for 24 hours, after which the solvent was removed *in vacuo* and the product was washed using sodium carbonate, EtOAc and water to yield product (**21**) with 20% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.3 (H- 8^2), 1.7 (H-18^1), 2.3 (N-CH$_3$), 2.8/2.9 (H-17^1), 3.2 (H-7^1), 3.3 (H- 5'), 3.6 (H-12^1), 3.8 (H-8^1), 4.1 (H-6^1), 4.6/4.7 (cellulose, H-6) 5.2 (H-13^2), 3.6-5.3 (cellulose, H-1-5), 6.1 (H-3^2), 7.8 (aromatic ring), 7.9 (H-3^1), 8.0 (aromatic ring), 8.5 (H-20), 9.3 (H-5), 9.6 (H-10).

4.4 Synthesis of pyrenecellulose

Pyrene (0.9g, 3.7 mmol) was reacted with EDCI (0.7g, 3.7 mmol) and Et_3N (0.4g, 3.7 mmol) in dry THF for 24 hours, after which the solvent was removed *in vacuo*. Activated Pyrene was added to the solution of cellulose (0.3g, 1.85 mmol) in [Amim]Cl and the reaction was stirred at 80°C for 48 hours. The reaction mixture was poured into the mixture of water and methanol (1:1) and the precipitate was filtered off and washed with EtOAc, methanol and water to give pyrenecellulose (0.21g, 66%, DS = 0.04). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.8-4.7 (cellulose, H-1-6), 8.19 (pyrene, H-2), 8.21 (pyrene, H-4), 8.3 (pyrene, H-1).

4.5 Buchwald-Hartwig cross-coupling of cellulose with 4-bromo-3-methylanisole

General method 1:

(The corresponding) Pd catalyst (10 µmol) and KO^{t}Bu (2.5 eq.) were stirred at 80°C in the (corresponding) IL until a colour change from yellow to red was observed. Cellulose (2 eq.) dissolved in IL was combined with the catalyst solution, after which 4-bromo-3-methylanisole (1 eq.) was added. Reaction mixture was stirred at 80°C for time ranging from 24 to 48 hours. The reaction mixture was poured into the mixture of water and methanol (1:1) and precipitate was collected by filtration and washed with methanol and water to give a pale yellow solid as a product.

General method 2:

(The corresponding) Pd catalyst (10 µmol), KO^{t}Bu (2.5 eq.), 4-bromo-3-methylanisole (1 eq.) and cellulose (2 eq.) were stirred at 80°C in the (corresponding) IL for between 24 to 48 hours. The reaction mixture was poured into the mixture of water and methanol (1:1) and the resulting precipitate was collected by filtration, then washed with methanol and water to give pale yellow solid as a product.

Corresponding Pd catalysts were: $Pd(OAc)_2$, $PdCl_2$ and $Pd(PPh_3)_4$
Corresponding ionic liquids were: [Amim]Cl and [Mmim]Me$_2$PO$_4$

General outcome and characterisation:

General yields from 60 to 64%, DS = 0.74 to 0.85. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.4 (CH$_3$), 3.9 (OCH$_3$), 3.6 (cellulose, H-5), 3.7 (cellulose, H-4), 4.0/4.2 (cellulose, H-6), 4.5 (cellulose, H-2), 4.6 (cellulose, H-1), 5.1 (cellulose, H-3), 6.5 (aromatic), 6.58 (aromatic), 6.6 (aromatic).

4.6 Synthesis of 6-(4-aminophenyl)aminocellulose

Tosylcellulose (synthesised according the method described in Paper **I**) (0.2g, 0.6 mmol) was dissolved in DMF. Then 4-phenyldiamine (0.34g, 3.2 mmol) and Et$_3$N (0.4 ml, 3.2 mmol) were added and the reaction mixture was stirred for 24 hours. After this the product was regenerated from the mixture of water and methanol (1:1) then washed with ethanol, methanol and water. The purification carried out by regeneration from DMF by the addition of water to give a dark red product (0.12g, 81%, DS = 0.8). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 61.2 (cellulose, C-6), 73.6 (cellulose, C-2), 75.4/76 (cellulose, C-3, C-5), 81.1 (cellulose, C-4), 103.5 (cellulose, C-1), 114 (aromatic), 120 (aromatic).

4.7 Preparation of Langmuir-Blodgett films of chlorophyllcellulose and photocurrent measurements

Langmuir-Blodgett films and photocurrent measurements were prepared by Dr Keita Sakakibara (Kyoto University).

Preparation of Langmuir-Blodgett films:

A diluted solution of the chlorophyllcellulose derivative (0.05 wt-%) in CHCl$_3$ was spread onto a water subphase in a Teflon-coated trough (100x250x5 mm, FSD-300, USI-system). The ultrapure water at a normal resistance of 18.2 Ohm cm (Simpli Lab, Millipore) was used for the subphase. The subphase temperature was kept at 20°C by circulating thermostated water. The surface pressure was measured using a film balance of a Wilhelmy type. After 30 min were allowed for the solvent to evaporate off, the π-A isotherms were measured at a constant compression rate of 6 mm/min. The horizontal lifting method was used to deposit the surface monolayer onto a substrate (quartz and ITO electrode). During the deposition, the surface pressure was kept at 10 mN/m to prepare the LB films.

Photocurrent measurements:

The photocurrent measurements were carried out at a constant bias potential using an electrochemical analyzer (ALS650B, BAS) at room temperature (approximately 25°C) on light irradiation. A 500 W xenon arc short lamp (UXL-500SX, Ushio, Japan) was used as a light source, equipped with a UV and IR cut-off filter (SCF, Ushio, Japan). The monochromatic light was obtained from a xenon lamp filtered with metal interference filters MIF-W type (400-550 nm wavelength, 10 nm fwhm, Vacuum Optics Corporation of Japan). The light intensity at the irradiation substrate surface was measured with a thermopile (MIR-100C, TAZMO, Japan). The LB film on an ITO electrode as a working electrode was contacted with an aqueous solution containing 0.1 M Na_2SO_4 as an electrolyte and 50 mM hydroquinone (H2Q) as a sacrifice electron donor. An electrode area of 1.54 cm^2 was exposed to the electrolyte solution. A saturated calomel electrode (SCE) as a reference electrode and a platinum wire electrode as a counter electrode were used. The electrolyte solution was initially purged with nitrogen for 15 min and then maintained under a flow of nitrogen.

The photocurrent quantum yield (F) based on the number of photons adsorbed by the chlorophyll moiety in the LB film was calculated according to the following equation:

$$F = 100 \times (i/e) / [I(1-10-A)], \qquad I = (Wl) / (hc) \qquad \text{(Equation 1)}$$

where i is the observed photocurrent density, e is the charge of the electron, I is the number of photons per unit area and unit time, A is the absorbance of the monolayer at l nm, l is the wavelength of light illumination, W is light power irradiation at l nm, h is the Planck constant, and c is the light velocity. At the same time, the incident photon-to-current conversion efficiency (IPCE) value was also determined as the following equation:

$$IPCE (\%) = 100 \times 1240 \times i / (Wl) \qquad \text{(Equation 2)}$$

5. Conclusions

The general approach of this thesis was to show the versatility of cellulose as a raw material for novel and advanced cellulose-based materials. A more specific aim was to to introduce new synthetic methods to widen and simplify the existing synthetic methodologies for cellulose modification and to yield novel derivatives. Moreover, ordered supramolecular structures achieved via the self-assembly of cellulose derivatives were explored (**III**). In general, self-assembly of derivatives brought more variation to cellulose utilisation in the form of spontaneous ordering and yielded ordered structures.

In this study, ILs were extensively used as a reaction media. It was shown that imidazolium-based ILs provide homogeneous reaction media for the synthesis of cellulose derivatives (**I**, **II**, **III**, **V**). A toolbox of reactions was developed in order to enable the synthesis of variety of cellulose derivatives in [Amim]Cl (**I**). Ionic liquids are fairly inert, but under certain reaction conditions they may take part in the reaction as a reagent or as a catalyst. In some reactions they may actually enhance the reaction and reactivity as demonstrated here, in Buchwald-Hartwig cross-coupling and tritylation (**II**).

Cellulose has numerous fascinating physical properties such as, liquid crystallinity. By combining the structural features of cellulose with certain substituents, one can prepare cellulose derivatives with interesting and novel properties. For example, highly crystalline and well ordered cellulose derivatives (**IV**) and new supramolecular structural entities (**III**). Moreover, it was shown in this study that nanocellulose can also be modified in ILs to enable the preparation of cellulosic materials with increased hydrophobicity (**V**). Highly hydrophobic cellulose based materials are of great interest when considering biodegradable packaging and coatings. Chlorophyllcellulose derivatives for photocurrent generation systems were designed and synthesised. These derivatives had increased efficiency in photocurrent generation and highlighted the potential of cellulose-based materials in advanced applications.

[Amim]Cl is a powerful solvent for MCC that is capable of dissolving cellulose; even at very high concentrations (40%). Liquid crystallinity of these solutions was investigated directly from the solutions by SEM and showed ordered textures at high cellulose concentrations of between 22 and 40% (w/w). The unique textures of the solutions observed may be due to the

orientation of [Amim]Cl molecules along with those of the cellulose molecules. Therefore, it can be inferred that [Amim]Cl molecules can function as 'indicators' for phase behaviour. This is a straightforward way to examine cellulose solutions directly at solution phase as it enables the detection of the liquid crystalline textures. This approach may be generally useful in liquid crystalline polymers research in which the identification of the LC phases may be difficult using conventional POM approach.

There is an increasing interest in using ILs in industrial processes.[98] The commercial company BASF has licensed the exclusive use of various intellectual property rights for cellulose dissolution and regeneration.[98,234,235] Moreover, Kemira Oyj has patented a method for the dissolution of lignocellulosic materials in ILs.[236] In addition to applications for lignocellulosic materials, perhaps the most successful application of ILs at the industrial scale is the BASIL process.[237]

Due to the versatility of cellulose, cellulose-based materials are potential candidates for replacing non-biodegradable materials originating from petroleum feedstock, and candidates for advanced materials. Biomaterials of this kind meet environmental prerequisites for renewable resources. Furthermore, combining the bio-based cellulose with ecological production methods of cellulose derivatives by utilising ILs, makes the numbers of the end-products huge, imagination being the limit.

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