Cellulose derived Diels-Alder covalent adaptable networks: a route towards recyclable thermosets

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Abstract

Plastic materials have grown to become essential in our everyday lives but the usage of plastics is connected to two significant issues; the major part is produced from fossil-based resources and only a fraction of the materials is recycled. Thermosets are especially difficult to recycle due to their permanent crosslinks, which is suboptimal. An alternative approach for crosslinking emerging in the last decades, is to utilise dynamic covalent bonds that can be formed and broken reversibly under certain stimuli. This gives rise to covalent adaptable networks (CANs) which can be recycled more easily compared to traditional thermosets. The goal of this work was to functionalize microcrystalline cellulose (MCC) with furan moieties to enable reversible crosslinking via the Diels-Alder (DA) reaction. A material of this kind solves both issues of renewability of the raw material and recyclability, and therefore could contribute towards more sustainable plastics.

In order to find an effective way to graft furan moieties onto MCC, thorough exploratory work was conducted, testing out numerous pathways experimentally. Eventually, an efficient route was successfully developed, synthesising a novel, fully bio-based cellulose ester with an estimated degree of substitution ranging between 0.5 and 2.5. This was done by first reacting furfuryl alcohol with succinic anhydride to form the corresponding acid ester. The carboxylic acid was then activated in-situ with 1,1'-carbonyldiimidazole before being reacted with cellulose homogeneously in DMAc/LiCl. The products were characterised with FTIR and solution-state NMR spectroscopy, as well as thermogravimetric analysis which showed a slightly lower thermal stability of the products compared to pristine MCC, but more importantly still high enough to handle temperatures where the reverse DA-reaction occurs. Initial testing of synthesising a CAN by combining the chemically modified cellulose with a flexible bismaleimide, showed that the DA reaction took place as desired. To complete the work in the future, the CAN synthesis will have to be developed further in order to make the material on larger scales, to then study the recyclability and characterise the final material properties.

Sammanfattning

Plastmaterial utgör idag en fundamental del av vår vardag men användningen av plast är kopplad till två stora problem; den största delen produceras av fossilbaserade resurser och endast en bråkdel av materialen återvinns. Härdplaster är särskilt svåra att återvinna på grund av deras permanenta tvärbindningar vilket är suboptimalt. Ett alternativt tillvägagångssätt för att skapa tvärbundna material som har växt fram under de senaste decennierna är att använda dynamiska kovalenta bindningar som kan bildas och brytas reversibelt under särskilda stimuli. Detta ger upphov till dynamiska kovalenta nätverk som kan återvinnas lättare jämfört med traditionella härdplaster. Målet med detta arbete var att funktionalisera mikrokristallin cellulosa med furan-substituenter för att möjliggöra reversibla tvärbindningar via Diels-Alder-reaktionen (DA-reaktionen). Ett material av den här typen löser både problemen kring förnybarheten av råmaterialet och återvinningsbarheten, och skulle därmed kunna bidra till mer hållbara plaster.

För att hitta ett effektivt sätt att modifiera cellulosa utfördes extensivt experimentellt arbete där flertalet syntesvägar testades. Till slut utvecklades en välfungerande metod, där en ny, helt biobaserad cellulosaester med en uppskattad substitutionsgrad mellan 0,5 och 2,5, syntetiserades. Detta gjordes genom att först reagera furfurylalkohol med bärnstenssyraanhydrid för att bilda den korresponderande syraestern. Karboxylsyran aktiverades sedan in-situ med 1,1'-karbonyldiimidazol innan den fick reagera med cellulosa under homogena förhållanden i DMAc/LiCl. Produkterna karakteriserades genom FTIR- och lösnings-NMR-spektroskopi, samt termogravimetrisk analys som visade en något lägre termisk stabilitet för produkterna jämfört med den ursprungliga cellulosan, men desto viktigare fortfarande tillräckligt hög för att hantera temperaturer där den omvända DA-reaktionen kan förväntas ske. Initial testning av att syntetisera ett DA-nätverk genom att kombinera den kemiskt modifierade cellulosan med en flexibel bismaleimid, visade att DA-reaktionen skedde som förväntat. För att färdigställa arbetet i framtiden kommer nätverkssyntesen att behöva utvecklas vidare för att tillverka materialet i större skala och sedan studera återvinningsbarheten samt karakterisera de slutliga materialegenskaperna.

Popular Scientific Summary

Development of a bio-based and recyclable thermoset plastic material from cellulose

In order to get away from today's current dependence on fossil-based plastic materials that are recycled at exceedingly low rates, significant efforts will be required. This is especially evident for thermoset plastics which inherently are more difficult to recycle. During this project, a new type of more sustainable thermoset material was developed starting from cellulose, which is the most abundant polymer in nature. The synthesised material solves both issues of renewability of the raw material and recyclability, and therefore could contribute towards more sustainable plastics.

Plastic materials have grown to become essential in our everyday lives and can be found practically everywhere, from e.g. food packaging and cosmetics to automotive parts and high-tech electronics. This is partly because of the versatile and tuneable properties these materials have, like low weight, good barrier properties and insulating capabilities. Plastics consist of long molecular chains, which are called polymers. These are in turn composed of many smaller repeating units, called monomers. The materials are often divided into thermoplastics and thermosets. Thermoplastics consist of linear or branched polymers that are bound together by entanglements and intermolecular forces which generally can be melted, whereas thermosets consist of networks where the polymeric chains are also covalently bonded to each other via crosslinks. The crosslinks tend to give many improved material properties such as an increased mechanical strength and thermal stability, but the materials instead suffer from worse recyclability due to the permanent covalent crosslinks, prohibiting melting.

Two highly concerning issues connected to the usage of plastics today is that the major part is produced from fossil-based resources and that only a fraction of the materials is recycled. In order to enhance the poor recyclability of thermosets, an alternative approach for crosslinking has emerged in the last decades, utilising covalent bonds that can be formed and broken reversibly under certain stimuli. This gives rise to so called covalent adaptable networks and in this way many of the desired material properties of traditional thermosets can be maintained while enabling a significantly improved recyclability. Various dynamic bonds have been explored so far for this purpose, and one common type is using the Diels-Alder reaction. This is a well-known reaction from organic chemistry, occurring between a diene and a dienophile, resulting in a six-membered ring with one double bond. Since the reaction can be reversed by heating above certain temperatures, a thermoset material with Diels-Alder links incorporated into its structure can be thermally reprocessed similar to thermoplastics.

Cellulose is a linear polysaccharide consisting of repeating glucose units and is the most abundant polymer in nature, providing plants and trees with their strength. The goal of this work was to chemically modify microcrystalline cellulose, which is a widely available and pure form of cellulose, with furan moieties to enable reversible crosslinking via the Diels-Alder reaction. This was successfully done after exploring numerous unsuccessful synthetic

pathways experimentally. By then combining the furan-functionalized cellulose with a bismaleimide crosslinker, the crosslinking reaction could be monitored as desired in initial tests on lab scale. To complete the work in the future, the synthesis of the covalent adaptable network will have to be developed further in order to make the material on larger scales, to lastly study the recyclability and the final material properties.

Populärvetenskaplig sammanfattning

Utveckling av ett biobaserat och återvinningsbart härdplastmaterial från cellulosa

För att bli kvitt dagens beroende av fossilbaserade plastmaterial som återvinns till ytterst låga nivåer kommer betydande insatser att krävas. Detta är särskilt tydligt för härdplaster som i sig är extra svåra att återvinna. Under det här projektet utvecklades en ny typ av mer miljövänligt härdplastmaterial med utgångspunkt från cellulosa, som är den mest förekommande polymeren i naturen. Det syntetiserade materialet löser både problemen kring förnyelse av råvaran och återvinningsbarheten, och skulle därmed kunna bidra till mer hållbara plaster.

Plastmaterial har vuxit till att utgöra en fundamental av vår vardag och kan hittas praktiskt taget överallt, inom alltifrån t.ex. livsmedelsförpackningar och kosmetika till bildelar och avancerad elektronik. Detta beror delvis på de mångsidiga och anpassningsbara egenskaperna som dessa material har, så som låg vikt, utmärkta barriäregenskaper och isoleringsförmåga. Plast består av långa molekylkedjor som kallas polymerer och dessa är i sin tur sammansatta av många mindre repeterande byggstenar, så kallade monomerer. Materialen delas ofta in i termoplaster och härdplaster. Termoplaster består av linjära eller förgrenade polymerer som är bundna till varandra genom intermolekylära krafter och intrassling på molekylär nivå, och kan i allmänhet smältas, medan härdplaster består av nätverk där de polymera kedjorna också är kovalent bundna till varandra via tvärbindningar. Tvärbindningarna tenderar att ge många förbättrade materialegenskaper såsom ökad mekanisk hållfasthet och termisk stabilitet, men materialen är istället mycket svårare att återvinna på grund av de permanenta kovalenta tvärbindningarna som förhindrar smältning.

Två stora problem kopplade till plastanvändningen idag är att den största delen framställs av fossilbaserade resurser och att endast en bråkdel av materialen återvinns. För att förbättra den dåliga återvinningsbarheten hos härdplaster har ett alternativt tillvägagångssätt för tvärbindning växt fram under de senaste decennierna, där kovalenta bindningar som kan bildas och brytas reversibelt under vissa stimuli används. Detta ger upphov till dynamiska kovalenta nätverk och på så sätt kan många av de önskvärda materialegenskaperna hos traditionella härdplaster bibehållas samtidigt som det möjliggör en väsentligt förbättrad återvinningsbarhet. Flertalet dynamiska bindningar har hittills undersökts för detta ändamål, och en vanlig typ är att utnyttja Diels-Alder-reaktionen. Detta är en välkänd reaktion från den organiska kemin, som sker mellan en dien och en dienofil, vilket resulterar i en ring med sex kolatomer och en dubbelbindning. Eftersom reaktionen kan reverseras genom uppvärmning över särskilda temperaturer, kan ett härdplastmaterial med Diels-Alder-länkar inbyggda i sin struktur bearbetas på ett liknande vis som termoplaster.

Cellulosa är en linjär polysackarid som består av repeterande glukosenheter och är den mest förekommande polymeren i naturen, som bidrar till styrkan hos växter och träd. Målet med detta arbete var att kemiskt modifiera mikrokristallin cellulosa, som är en rikligt tillgänglig och

ren form av cellulosa, med furansubstituenter för att möjliggöra reversibla tvärbindningar via Diels-Alder-reaktionen. Detta kunde åstadkommas framgångsrikt efter att ha utforskat ett flertal misslyckade syntesvägar experimentellt. Genom att sedan kombinera den furan-funktionaliserade cellulosan med en bismaleimid-tvärbindare kunde tvärbindningsreaktionen observeras som förväntat i initiala tester på labbskala. För att färdigställa arbetet i framtiden kommer syntesen av det tvärbundna nätverket att behöva utvecklas vidare för att tillverka materialet i större skala, för att sedan studera återvinningsbarheten och de slutliga materialegenskaperna.

List of Abbreviations

AGU	Anhydroglucose Unit
CAN	Covalent Adaptable Network
CDI	1,1'-Carbonyldiimidazole
COSY	Correlation Spectroscopy
DA	Diels-Alder
DCM	Dichloromethane
DMAc	N,N-Dimethylacetamide
DMAP	4-Dimethylaminopyridine
DMSO	Dimethyl Sulfoxide
DOSY	Diffusion-Ordered Spectroscopy
DP	Degree of Polymerisation
DS	Degree of Substitution
FOBA	4-(Furan-2-ylmethoxy)-4-oxobutanoic Acid
FTIR	Fourier Transform Infrared
HMBC	Heteronuclear Multiple Bond Correlation
HOMO	Highest Occupied Molecular Orbital
HSQC	Heteronuclear Single Quantum Coherence
LUMO	Lowest Unoccupied Molecular Orbital
MCC	Microcrystalline Cellulose
NMR	Nuclear Magnetic Resonance
$[P_{4444}][OAc]$	Tetra-n-butylphosphonium Acetate
RBF	Round Bottom Flask
TBAF	Tetra-n-butylammonium Fluoride
TGA	Thermogravimetric Analysis
TLC	Thin Layer Chromatography

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1. Introduction

Plastic materials have become ubiquitous in our everyday lives and their production and consumption are increasing at a steady rate in today's rapidly developing world. Fossil-based, non-recycled plastics constitute the major part and in 2022 over 400 million tons of plastics were produced globally with less than 10% being made from recycled or renewable resources in a circular manner (*1*). The plastics industry faces a number of critical challenges in order to transform it into a more sustainable path, including turning towards bio-based feedstocks while designing materials that can be recycled efficiently (*2*). To successfully deal with these issues, there is no doubt that significant research efforts will be required.

Thermosets, which are polymeric materials that are crosslinked chemically by covalent bonds, offer several advantageous material properties like excellent mechanical properties, dimensional stability and chemical resistance (*3*). The main drawback is however that these materials are especially difficult to recycle due to their permanent crosslinks. An alternative approach for crosslinking that has emerged in the past decades, is to utilise dynamic covalent bonds that can be formed and broken reversibly under certain conditions. This gives rise to covalent adaptable networks (CANs) that can be reprocessed and recycled much more easily compared to conventional thermosets, while still maintaining many of the sought-after material properties.

The idea for this master's thesis is to utilise cellulose, which is an abundant, renewable biopolymer, as a sustainable alternative to conventional fossil resources to synthesise a recyclable thermoset. The cellulose chains can be modified with functionalities to enable reversible crosslinks between them to give a CAN material, as displayed in Figure 1.1. In this case the reversible Diels-Alder (DA) reaction between furan and maleimide is utilised by grafting furan moieties onto the cellulose and combining with a bismaleimide crosslinker. A material of this kind solves both issues of renewability of the raw material and recyclability, and therefore could contribute towards more sustainable plastics.

The disposition of this report is as follows: first a background is presented in Section 2, covering the basic theory on CANs, the DA reaction and cellulose. Then an experimental part is provided under Section 3, where procedures for a developed functionalization route of cellulose, the used materials and characterisation techniques are described. In Section 4, the main results of the work are presented, where the first part covers the exploratory work that led to developing the final modification pathway, and the remainder focuses on more detailed results and discussions on the final route. Section 5 gives a summary of how this work will be developed further in the future and lastly in Section 6, the main conclusions of the thesis are presented.

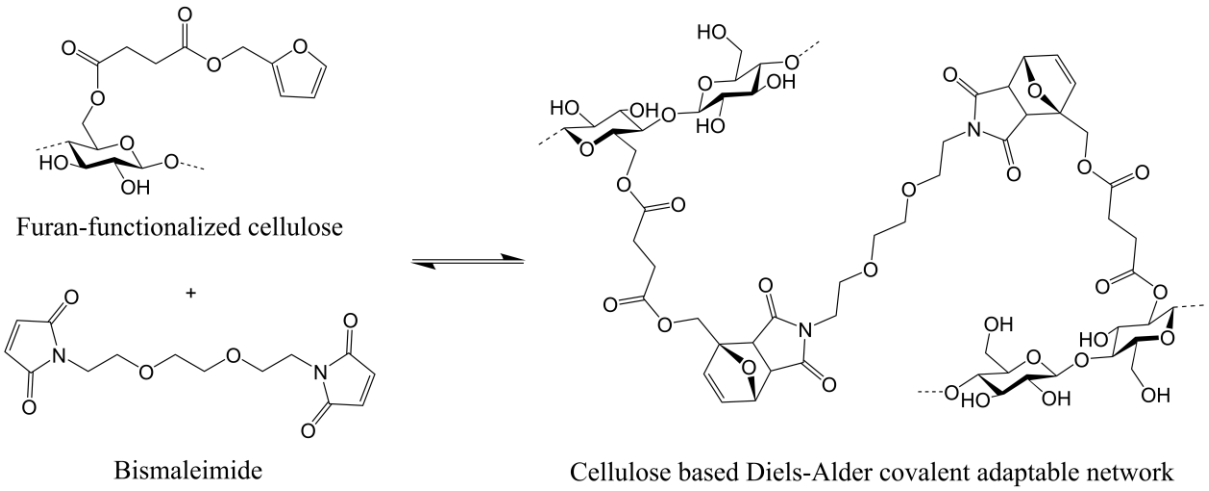

Figure 1.1. Synthesis of a Diels-Alder covalent adaptable network based on cellulose functionalized with furan moieties and a bismaleimide crosslinker.

1.1 Aim

The aim of this work is to synthesise a novel recyclable thermoset from cellulose that meets the demand for more sustainable and circular plastic materials. This will be achieved by developing a pathway to functionalize microcrystalline cellulose with furan moieties and synthesising a bismaleimide crosslinker, in order to combine these to make a cellulose derived Diels-Alder covalent adaptable network.

2. Background

Since large-scale production began around 1950, plastics have grown to become an integral part in practically all aspects of our lives thanks to their versatile properties. In 2017, researchers estimated that a total of 8.3 billion tons of virgin plastics had been produced, with a compound annual growth rate of 8.4% since 1950 (*4*). As of 2022, over 400 million tons of plastics were produced on a yearly rate, with less than 10% originating from renewable or recycled resources (*1*). If we were to continue on the same track, an estimated 12 billion tons of plastic waste will have accumulated in landfills and nature by 2050, showcasing the urgency to deal with the global plastic challenges (*4*).

Commonly, plastic materials are classified as either thermoplastics or thermosets, which is based on their processing characteristics (*3*). Thermoplastics consist of linear or branched structures where the polymer chains are entangled and interact via intermolecular forces. These materials can generally be melted, flow freely and be reprocessed relatively easily. Thermosets on the other hand are three-dimensional networks that contain covalent crosslinks between chains. They exhibit several superior material properties like better strength, creep resistance, thermal stability, dimensional stability and chemical resistance, but instead suffer from significantly worse recyclability as these materials cannot be melted and reprocessed easily due the permanent crosslinks. Thermosets are generally used in slightly more demanding, high-performance, non-single-use applications and contribute to around 10-15% of the global plastic production volume (*5*). The majority of the used thermoset materials today are based on non-renewable feedstocks and these are generally difficult to reuse, degrade and recycle, and toxicity related to the materials and their constituents is another common drawback (*3*).

2.1 Covalent adaptable networks

To deal with the issues connected to traditional thermosets, efforts have been put towards developing more sustainable alternatives (*3*). This includes turning towards renewable resources, extending the service life and making them more easily degradable. From this the development of covalent adaptable networks (CANs) have emerged in the past decades, which solves many of the sustainability issues of thermosets. These materials behave like normal thermosets while being used, but the crosslinks can be reversed upon certain stimuli, like heating or UV-light. The materials can therefore still be reprocessed and recycled similar to thermoplastics, while maintaining many of the desired material properties of thermosets like excellent strength and dimensional stability. Additionally, this type of structure can give rise to other desirable functions such as self-healing, weldability and programmability.

The bond energy of a dynamic covalent bond is between that of intermolecular forces and covalent bonds and the dynamic nature depends on the external stimuli (*3*). The bonds behave like normal covalent bonds without the stimuli but become dynamic with the appropriate stimuli. Generally, CANs are divided into two main groups depending if the bond exchange is dominated by associative or dissociative characteristics. In associative networks, bond breaking occurs at the same time as bond forming which gives a constant crosslink density, maintaining the network integrity. This resembles an S_N2 reaction and the type of CAN

materials following this behaviour are called vitrimers (*6*). In dissociative networks on the other hand, bond breaking occurs first in one separate step before new bonds can form, analogous to an S_N1 reaction, which results in loss of network integrity. These types of exchange mechanisms are depicted in Figure 2.1. In several cases the exchange may occur through more than mechanism though and can depend on the specific conditions.

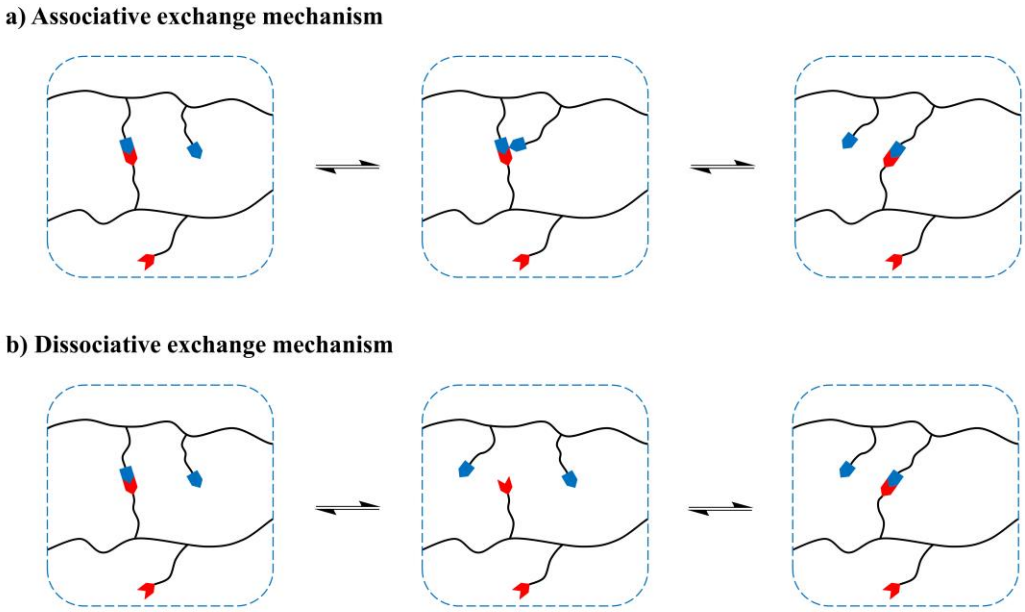

Figure 2.1. a) Illustration of an associative network with a constant crosslink density upon bond exchange, which are referred to as vitrimers and **b)** a dissociative network where bond breakage occurs before new bonds can form.

A wide number of dynamic bonds have been explored so far, including e.g. ester bonds exchanging through transesterification, imine bonds and bonds exchanging through the Diels-Alder (DA) reaction (*3*). Usage of DA links is expected to lead to a dissociative behaviour, since the reverse DA reaction has to occur first before a new forward reaction can take place. This type of network behaviour that can lead to a decrease in crosslinks has sometimes been viewed as a disadvantage compared to vitrimers which maintains the network integrity. It has however been shown that the difference is often very small and that the reprocessing behaviour is nearly identical over a broad range of temperatures (*6*).

In order to engineer the properties of dynamic CAN materials, it is important to understand the nature of the dynamic behaviour of the applied bonds and the structure-property relationships (*7*). This includes how molecular motifs and the network topology relates to the obtained macroscopic properties at different timescales. A practical example relating to these aspects can be given from researchers who made a polymethacrylate based DA network, comparing rigid and flexible bismaleimide crosslinkers (*8*). It was shown that the glass transition temperature decreased when using the flexible bismaleimide crosslinker, as it contained multiple ethylene glycol links which increased the mobility. This in turn also led to better self-healing properties and shows the importance of the crosslinker and how the material is designed on the molecular level.

2.2 The Diels-Alder reaction

The Diels-Alder (DA) reaction is a cycloaddition reaction between a conjugated diene and a dienophile and was first described by Otto Diels and Kurt Alder in 1928 (*9*). It is denoted as [4+2] where 4 and 2 refers to both the number of π-electrons involved in the electronic rearrangement as well as the number of atoms forming the six-membered ring. The simplest reaction is shown in Figure 2.2a, leading to the unsaturated cyclohexene. Since its discovery, the reaction has been employed at an increasing rate in organic synthesis and has proved to be very useful for making more complex organic molecules. In more recent years, utilisation of the reversibility of the reaction has been of growing interest in polymer research, as it can enable e.g. self-healing and improved recyclability (*10*). This reaction is therefore a promising candidate in the design of novel CANs.

The substituents and their electronic effects on the diene and dienophile strongly influence the reaction rate (*9*). With the help of frontier molecular orbital theory, this can be explained in more detail, including how regio- and stereochemical control can be achieved for different starting materials. In the majority of DA reactions, a diene with electron donating substituents and dienophile with electron withdrawing substituents are used. In this case the highest occupied molecular orbital (HOMO) of the diene matches the lowest unoccupied molecular orbital (LUMO) of the dienophile quite well, leading to an accelerated reaction due to the lowered energy gap, ΔE. This is referred to as a normal electron-demand reaction. Since the HOMO and LUMO of the reagents are relatively close to each other, the reaction can also be run in inverse demand. This instead requires electron withdrawing substituents on the diene and electron donating substituents on the dienophile. A visual representation of these two modes are displayed in Figure 2.2b. For typical DA reactions, the enthalpy and entropy change have both negative values, which means that the reverse reaction becomes favoured at higher temperatures (*11*).

Furan and maleimide is one of the most well studied reagent pairs for the DA reaction (*10*). This reaction proceeds under normal electron demand and can occur already at room temperature depending on the specific furan and maleimide derivatives used. The reverse reaction can start occurring around 100 °C, allowing reversal under quite mild conditions (although this can also limit the operating temperature of the resulting network material). In this case of reagents, two diastereomers are formed during the reaction; endo, which is the kinetically preferred product, and exo, which is the thermodynamically most stable product. The two variants are displayed in Figure 2.2c and the specific reaction conditions that are applied will affect the ratio of these (*12*). The exo adduct is preferred thermodynamically due to less steric repulsion in the product, while the endo adduct often is kinetically preferred due to secondary orbital interactions which have a stabilising effect in the transition state (*9*). Because of this, the major product is often the slightly less stable endo product, which is sometimes referred to as the “endo rule”. The ratio may change over time though, gradually increasing the amount of exo adduct. During the reverse reaction, the endo compound disintegrates back to the starting materials at lower temperatures. This may be an advantage in certain cases so controlling the diastereoselectivity is therefore generally of interest if possible.

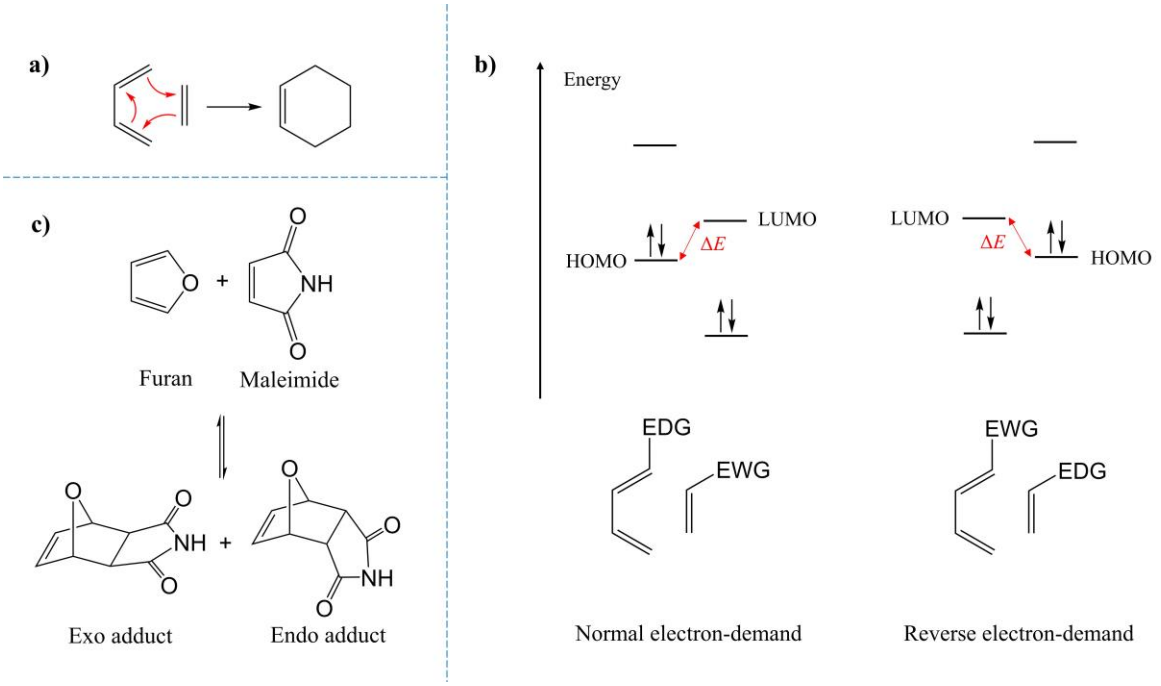

Figure 2.2. a) The simplest DA reaction between 1,3-butadiene and ethylene, forming cyclohexene. **b)** HOMO and LUMO energies of the diene and dienophile pair depending on their substituents with either electron donating groups (EDGs) or electron withdrawing groups (EWGs). **c)** DA reaction between furan and maleimide, leading to two diastereomers which are called exo and endo respectively.

As mentioned previously, using the DA reaction leads to CANs with dissociative exchange mechanisms. Thanks to the high reversibility of this reaction under relatively mild conditions, it allows for designing crosslinked materials that are recyclable and reprocessable. In one article, researchers developed an epoxy thermoset with Diels-Alder links embedded into its structure (*13*). It was shown that the thermoset could be recycled at room temperature utilising sonochemistry, in other words under very mild conditions, which shows the usefulness and potential of implementing the dynamic Diels-Alder bonds to construct recyclable materials.

2.3 Cellulose – an abundant, renewable resource

Cellulose is a non-toxic, biodegradable and naturally occurring polysaccharide, known as the most abundant polymer in nature with about 1.5 trillion tons being produced annually as biomass (*14*). The research work discovering cellulose began in 1837 by the French chemist Anselme Payen, who managed to obtain a fibrous solid after treating plant mass with acid and ammonia, followed by extraction with water, ethanol and ether. Through elemental analysis, he determined the molecular formula of the substance to be $C_6H_{10}O_5$, which was termed cellulose in 1839 (*15*). Today cellulose is widely used on commercial scale in e.g. the food, pharmaceutical, paper and composite material industries, and a variety of isolation processes exist, utilising different chemical processes combined with mechanical and thermal treatments (*14*). Due to its abundance and renewable character, cellulose has attracted significant attention within the research community towards more novel applications.

The polymeric cellulose chains have a linear structure without branches, consisting of D-glucopyranose units linked by β-1,4-glycosidic bonds, where two glucopyranose units are

connected via an oxygen atom connected to C-1 of one unit and C-4 of the other, as shown in Figure 2.3 (*14*). The molecular formula is $(C_6H_{10}O_5)_n$, where n denotes the degree of polymerisation (DP). Each monomeric glucose unit in a chain is referred to as an anhydroglucose unit (AGU) and contains three hydroxyl groups, with two secondary alcohol groups at C-2 and C-3 positions and one primary at the C-6 position. The chain ends are chemically different, with one nonreducing end containing a free hydroxyl group at C-4 and one reducing end with the glucopyranose unit in equilibrium with its aldehyde function. The DP of native cellulose from different origins in nature is around 1 000 - 30 000 and is polydisperse, meaning that the DP of different chains varies according to a distribution of different molecular weights.

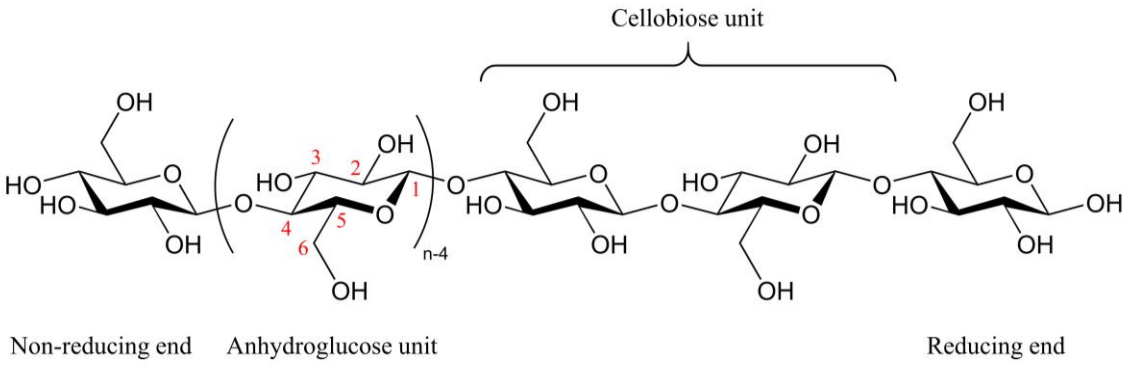

Figure 2.3. The structure of cellulose, consisting of repeating D-glucopyranose units in a linear arrangement. The carbon atoms in each AGU are numbered as shown in the figure. Two AGUs give the cellobiose unit.

Various systems of hydrogen bonds strongly influence the properties of the cellulose such as the hydroxyl group reactivity and crystallinity, and lead to a limited solubility in most solvents (*14*). The hydroxyl groups can interact with each other both intramolecularly within a chain, as well as intermolecularly between different chains. Together with the glycosidic linkage, the intramolecular interactions are responsible for the stiffness and rigidity of the cellulose chains, and gives a high tendency for crystallisation and forming fibrillar structures. Intermolecular hydrogen bonds give rise to strong interaction between chains and as the bonding pattern can vary, which leads to different variations of the crystalline arrangement of the chains, four polymorphs of cellulose are known. Cellulose I is the structure of native cellulose which is the most commonly found type in nature. Cellulose II consists of a more densely packed structure due to a different, more interbonded hydrogen bonding pattern, and is more thermodynamically stable. Cellulose I can be irreversibly converted to II by mercerisation with alkali treatment or precipitation from the dissolved state. Treatment of either cellulose I or II with ammonia or amines can transform it reversibly to cellulose III, and this structure can in turn be transformed to cellulose IV in glycerol at high temperatures. When it comes to the usage and modification of cellulose, cellulose I and II are the only ones with practical significance. Apart from the crystalline domains, there are also amorphous regions. These influences both the physical and chemical properties, and e.g. reactions usually occur first in these less ordered regions.

In nature, cellulose is found broadly and is present in wood, plants, animals (tunicate), algae, bacteria, fungi and minerals, with the major source being wood and plant fibres (*14*). These cellulosic materials generally are composed of hierarchical structures, starting from arrangements at the nanoscale, going all the way up to macroscopic fibres. The cellulose can occur in pure form but is usually present together with hemicellulose and lignin, with small amounts of other compounds. The content varies between different plants, e.g. wood contains about 40 - 50% cellulose whereas cotton contains more than 90% making it a quite pure source. Bacterial cellulose is produced directly as a fibre network which is very pure and has a high DP and crystallinity.

Natural cellulose can be processed into different micro- and nanoscale structures which can be classified into cellulose fibres, micro/nanofibrils, filaments, and crystals (*16*). These forms differ in morphology and have varying sizes, aspect ratios, crystallinity and physicochemical properties. In wood and plants, cellulose is synthesised as microfibrils that assemble to fibres, with lengths ranging from millimetres to metres depending on type. Microfibrils, which is also called microfibrillated cellulose, and nanofibrils can be obtained by mechanically disintegrating cellulose fibres, and filaments can in turn be made from cellulose nanofibres. By subjecting cellulose microfibrils to a combination of chemical and mechanical treatments, the crystalline regions of the fibrils can be extracted, giving microcrystalline cellulose (MCC) with a particle diameter in the micrometre scale, or cellulose nanocrystals with a diameter in the nanoscale. These are stiff, rod-like particles composed of nearly perfect crystalline structures of cellulose chains.

MCC is a fine, white, odourless powder (*14*) that was commercialised in 1962, under the name Avicel (*15*). It is produced commercially by treating biomass with sodium hydroxide to remove other constituents yielding alpha-cellulose, followed by acid hydrolysis which takes place in the more amorphous regions, giving a crystalline, water-insoluble product. During the hydrolysis, the DP decreases until it levels off, reaching a plateau ranging between 25 to 300 depending on the cellulose source (*14*). The degree of crystallinity of MCC is typically around 55 - 80 % (*15*). MCC has found applications in e.g. food, cosmetic, pharmaceutical and polymer composite industries and is commonly used in cellulose modification research.

Due to the strong hydrogen bonding between chains, cellulose cannot be melted easily and special solvent systems are required to dissolve cellulose (*14*). The available solvents are divided into derivatizing solvents which form covalent bonds with cellulose, and non-derivatizing solvents which only interact physically with the chains. One class of the latter type is polar aprotic solvents containing electrolytes, where the introduced ions' purpose is to efficiently interact with both the hydrogen bonds of cellulose and the liquid to allow solvation to occur. Two common examples are N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) and dimethyl sulfoxide/tetra-n-butylammonium fluoride (DMSO/TBAF). In the case of DMAc/LiCl, the cellulose has to be activated by heating whereas DMSO/TBAF can be used without any pretreatment (*17*). Detailed studies of the dissolution mechanism in DMAc/LiCl shows that the chloride ions form strong hydrogen bonds with the hydroxyl protons, breaking up the internal cellulose hydrogen bonds, and that the lithium ions are solvated by DMAc molecules (*18*). Two other common solvent classes are ionic liquids, which is a group of ionic

compounds with low melting points, and aqueous basic solvents, which have a dissolution zone at specific concentrations and temperatures (*14*). The majority of the known solvents are only used at a lab scale.

Functionalization of cellulose can be achieved utilising the reactive hydroxyl groups on the chains to improve the properties such as giving better solubility or thermoplastic properties (*16*). Since the hydroxyl groups are relatively poor nucleophiles, achieving reactions is not always very straightforward and generally require relatively harsh conditions. An important parameter in the chemical modification is the degree of substitution (DS) of the cellulose. This describes how many of the hydroxyl groups per AGU that have been replaced after a chemical reaction, and can range from 0 to 3. Currently, commercial cellulose derivatives are produced under heterogeneous reaction conditions and some examples of widely used products are cellulose acetate, carboxymethyl cellulose, methyl cellulose and hydroxyalkyl ethers (*14*). The dissolution of cellulose does however enable broader possibilities to modify cellulose chemically in order to synthesise novel derivatives.

One important type of transformation of cellulose is acylation which can be carried out homogeneously to make novel cellulose esters (*14*). By using mild in-situ activation of various carboxylic acids, a broad variety of esters have been synthesised. N,N′-carbonyldiimidazole (CDI) is regarded as a promising option with enormous potential in this area, which was first used in 1962. It transforms the carboxylic acid into the more reactive imidazolide with CO_2 and imidazole as the only by-products. Another type of transformation that can be achieved by using homogeneous conditions is making tosylated cellulose from tosyl chloride, which in turn can be reacted with amines to make a variety of amine containing products through nucleophilic substitutions.

The kind of branching in the modified cellulose is critical in terms of the obtained material properties. Although pure cellulose is relatively stable thermally it cannot be processed easily in the melt state due to its strong hydrogen bonds and lacking thermoplasticity. It is therefore generally of interest to enable proper processability of modified products at temperatures before degradation starts occurring, in order to allow melt processing with a practically useful processing window. In one article, researchers modified cellulose with substituents containing both flexible and rigid units via esterification and peracetylation (*19*). This led to relatively low glass transition temperatures between 80 and 160 °C and products that could be processed in the melt state into various shapes.

While the area of CANs is an emerging research topic, only a limited amount of research has been conducted in the area of cellulose derived CANs utilising the reversible DA reaction. In one article, a cellulose furoate derivative was synthesised from hydroxyethyl cellulose, and combined with a bismaleimide crosslinker (*20*). Due to the specific furoate structure, the network formation was very slow though. Hydrogels have also been reported, using furfuryl amine modified nanocellulose combined with a similar bismaleimide (*21*). In this case the reverse DA reaction could be achieved at 95°C. Chitosan is another example of a starting material that has been used to construct a similar DA-based CAN material, which showed the occurrence of the retro DA reaction around 110 - 130 °C (*22*). These examples showcase the potential for the development of novel cellulose derived DA CANs.

3. Experimental

3.1 Materials

Succinic anhydride (≥ 99%, Sigma-Aldrich), furfuryl alcohol (≥ 98%, Sigma-Aldrich), 4-(dimethylamino)pyridine (DMAP, 99%, Sigma-Aldrich), triethylamine (99%, Thermo Scientific), dichloromethane (DCM, ≥ 98% stabilised with 0.2% ethanol, VWR Chemicals), hydrochloric acid (37%, Sigma-Aldrich), magnesium sulfate (99%, VWR Chemicals), N,N-dimethylacetamide (DMAc, 99.5%, Thermo Scientific), lithium chloride (99%, Thermo Scientific), 1,1'-carbonyldiimidazole (CDI, ≥ 97%, Sigma-Aldrich), ethanol (99.97%, VWR), maleic anhydride (≥ 99%, Fluka), 1,8-diamino-3,6-dioxaoctane (≥ 98%, Sigma-Aldrich), sodium acetate (100%, VWR Chemicals), acetic anhydride (≥ 99%, Sigma-Aldrich), acetone (≥ 99%, VWR Chemicals), methanol (≥ 98.5%, VWR Chemicals), ethyl acetate (≥ 99%, VWR Chemicals), heptane (99.8%, VWR Chemicals), silica gel 60 (40 - 63 μm, VWR Chemicals), chloroform-*d* (99.8 atom% D, VWR Chemicals) and DMSO-d_6 (99.9 atom% D, Thermo Scientific) were all used as received.

Microcrystalline cellulose (MCC, average particle size 50 μm, Thermo Scientific) was dried at 60 °C under vacuum for at least 48 h and was then stored under vacuum at room temperature prior to use. Tetra-n-butylphosphonium acetate ([P_{4444}][OAc]) was synthesised previously by Lukas Marcos Celada and Celine Aarsen, according to option A described in a published article (*23*). A 1:4 w/w mixture of [P_{4444}][OAc] and DMSO-d_6 was kindly supplied for the NMR analysis of the functionalized cellulose products.

3.2 Synthesis of 4-(furan-2-ylmethoxy)-4-oxobutanoic acid

Ring-opening of succinic anhydride with furfuryl alcohol was done under basic conditions to yield the corresponding ester carboxylate, adapting a previously reported method which used the 3-substituted regioisomer of furfuryl alcohol (*24*). 10 mL of furfuryl alcohol (115.2 mmol, 1 eq.) and 50 mL of DCM were added to a 250 mL RBF equipped with a stirring bar. 16.06 mL of triethylamine (115.2 mmol, 1 eq.), 1.407 g of 4-dimethylaminopyridine (DMAP, 11.5 mmol, 0.1 eq.) and 14.985 g of succinic anhydride (149.7 mmol, 1.3 eq.) were added to the RBF. The reaction was allowed to proceed for 1 h at room temperature under a nitrogen atmosphere. The reaction mixture was transferred to a 500 mL separatory funnel along with 200 mL of additional DCM. The organic layer was washed two times with 200 mL of 1 M aqueous HCl (prepared by dilution of concentrated HCl with deionised water), then once with 200 mL of water and finally dried over magnesium sulphate. The solvent was removed by rotary evaporation at 40 °C down to vacuum to obtain the product as a slightly brown, viscous oil.

3.3 Esterification of microcrystalline cellulose with CDI activated FOBA

The following method was based on an established procedure for cellulose esterification using CDI activated carboxylic acids and the solvent system DMAc/LiCl (*25*). For a typical run, 0.5 g of dried microcrystalline cellulose (3.08 mmol AGUs, 1 eq.) was suspended in 20 mL of DMAc in a 50 mL RBF under magnetic stirring. The mixture was heated to 130 °C and kept stirring for 1.5 h under a nitrogen atmosphere. The slurry was cooled down to 100 °C and 1.5 g of anhydrous LiCl (8 wt% w.r.t. DMAc) was added. The mixture was cooled down to room temperature and stirred overnight to allow full dissolution.

3.00 g of CDI (18.5 mmol, 6 eq.) was added to a solution of 3.667 g of FOBA (18.5 mmol, 6 eq.) in 10 mL of DMAc. The clear solution was stirred for 24 h at 40 °C under a nitrogen atmosphere. The prepared FOBA/CDI solution was added to the cellulose solution. The homogeneous solution was then heated to 70 °C and stirred for 24 h under a nitrogen atmosphere. Afterwards, the reaction mixture was poured into 100 mL of ethanol to precipitate the product which was then collected by filtration. The product was crushed in a mortar to turn it into a finer powder, washed three times with 50 mL of ethanol and finally dried under vacuum at 60 °C over a weekend.

3.4 Synthesis of 1,8-bismaleimido-3,6-dioxaoctane

The procedure was followed based on the literature with some slight modifications (*26*,*27*). 6.18 g of maleic anhydride (64 mmol, 2 eq.) was dissolved in 30 mL of acetone in a 100 mL RBF equipped with a condenser. The solution was cooled down to 2 - 4 °C with an ice bath. 4.70 mL of 1,8-diamino-3,6-dioxaoctane (32 mmol, 1 eq.) in 5 mL of acetone was added slowly dropwise using a dropping funnel, under vigorous stirring and a nitrogen atmosphere. The mixture was removed from cooling and stirred for 2 h at room temperature. 1.53 mL of triethylamine (11 mmol, 0.3 eq.) and 1.07 g of sodium acetate (13 mmol, 0.4 eq.) was added to the reaction mixture. 10.21 mL of acetic anhydride (108 mmol, 3.4 eq.) was then added slowly under stirring using a dropping funnel. The reaction mixture was heated to 50 °C for 2.5 h. Afterwards, the reaction mixture which had a dark black colour, was concentrated in a rotary evaporator at 40 °C down to vacuum.

The concentrate was purified using silica gel chromatography. Gradient elution was applied starting from pure DCM, adding increasing amounts of methanol. The concentrated reaction mixture was re-dissolved in 15 mL of DCM. The product was added carefully on the top of the column (diameter = 5 cm, height = 15 cm, volume = 80 mL). The column was washed with about two column volumes of DCM making sure that the solution coming out was not coloured. 160 mL of 1 vol% methanol in DCM was applied. Then 160 mL of 2 vol% methanol in DCM was applied. The eluate fractions were collected in 25 mL glass tubes and were analysed with TLC using 2:1 ethyl acetate and heptane eluent, giving a retardation factor (R_f) of 0.306 for the product. The fractions with product were combined and concentrated using rotary evaporation. The formed white crystals were redissolved in a 1:1 v/v mixture of acetone and ethanol (about

10 mL/g product) under heating and then recrystallised by allowing the solution to cool down slowly, first at room temperature, then in a fridge and lastly in a freezer.

3.5 Characterisation

3.5.1 Nuclear magnetic resonance spectroscopy

NMR spectroscopy was applied for structural analysis on a Bruker Avance III HD 400 MHz spectrometer, with a BBFO probe equipped with a Z-gradient coil. All spectra except for the FOBA-cellulose samples were recorded at room temperature. The chemical shifts are referenced to the residual solvent signals ($CDCl_3$: $\delta = 7.26$ ppm for ^1H, $\delta = 77.16$ ppm for ^{13}C and DMSO-d_6: $\delta = 2.50$ ppm for ^1H). Unless stated otherwise, ^1H spectra were acquired using a 30° flip angle, 2 dummy scans, 32 scans and 1 s relaxation delay. ^{13}C spectra were acquired using a 30° flip angle, 4 dummy scans, 1024 scans and 2 s relaxation delay. COSY (Correlation Spectroscopy) spectra were recorded using the standard Bruker pulse sequence cosygpqf and COSYGPSW parameter set with 8 dummy scans, 4 scans and 2 s relaxation delay. HSQC (Heteronuclear Single Quantum Coherence) spectra were recorded using the standard Bruker pulse sequence hsqcetgpsi with 16 dummy scans, 4 scans and 1.5 s relaxation delay. HMBC (Heteronuclear Multiple Bond Correlation) spectra were recorded using the standard Bruker pulse sequence hmbcgplpndqf and HMBCGP parameter set with 16 dummy scans, 16 scans and 1.5 s relaxation delay. All recorded spectra were processed and analysed with MestReNova.

In order to prepare samples of FOBA-cellulose, about 50 mg of product was suspended in 950 mg of 1:4 [P_{4444}][OAc]:DMSO-d_6 solution in a glass vial equipped with a magnetic stirring bar. The glass vials were heated to 65 °C and stirred for 6 h until the solutions appeared to be homogeneous. The solutions were then transferred to 5 mm NMR tubes and analysed in the NMR spectrometer at 65 °C. Diffusion-edited ^1H experiments were conducted using a Bruker ledbpgp2s1d pulse sequence, applying a 1D bipolar-pulse pair with stimulated echo and a diffusion-ordered spectroscopy (DOSY) pulse sequence with 3 s relaxation delay, 0.5 s acquisition time, 16 dummy scans, 512 number of scans, a spectral width of 20 ppm with the transmitter offset on 6.1 ppm, 200 ms diffusion time, 0.2 ms gradient recovery delay, 5 ms eddy current delay, 2.5 ms diffusion gradient pulse duration and 80% z-gradient strength with a 50 G/cm probe z-gradient strength.

3.5.2 Fourier transform infrared spectroscopy

FTIR spectroscopy was conducted on a PerkinElmer Spectrum 100 spectrometer in attenuated total reflection mode, equipped with a diamond crystal and a temperature control unit (Specac, Heated Golden Gate Controller). The spectra were recorded using 16 scans, between 4000 and 600 cm^{-1} and a 2 cm^{-1} resolution.

3.5.3 Thermogravimetric analysis

The thermal stability was investigated with TGA using a Mettler Toledo TGA/DSC 1 instrument. About 5 mg of sample were placed in 70 µL alumina crucibles and analysed from

30 to 700 °C with a 10 °C/min heating rate, under a nitrogen atmosphere with 20 ml/min nitrogen flow.

4. Results and Discussion

4.1 Cellulose functionalization

Throughout this project, a wide range of reactions and pathways for modifying cellulose was considered and tested experimentally. Achieving the desired result, i.e. grafting a furan moiety onto the cellulose chains, was quite challenging and the major part of the work therefore went for doing this. A summary of the routes that were investigated are presented briefly in the following section, then the results of the final route that was successfully employed are presented in the remaining subsections under section 4.1.

4.1.1 Explored routes

The different synthetic pathways for functionalizing MCC with a furan moiety that were investigated are summarised in Figure 4.1. Some supplementary information about the used conditions and outcomes for the first unsuccessful routes is given in Appendix A in Table A.1, as well as all acquired FTIR spectra in Figure A.1. Initially, the strategy was to react the cellulose with furfuryl glycidyl ether in one step. The idea here was that this potentially could be a relatively simple reaction with cellulose, only requiring one step which would be advantageous. The side chain would ideally give an increased solubility of the cellulose while also enabling better processability compared to the pure cellulose by adding some flexibility.

In order to achieve this reaction, the cheaper compound allyl glycidyl ether was primarily used to first try to model the optimal conditions. The established combination of DMAc and LiCl was chosen as a solvent system to perform the reaction homogeneously and the conditions that were used were partially based on other similar reported reactions (*28-31*). The two different basic catalysts 1,8-diazabicyclo[5.4.0]undec-7-ene, also known as DBU, and potassium hydroxide were tested. In both cases these conditions led to full gelation of the reaction mixture quickly though, inhibiting any magnetic stirring. This is possibly due to a cascade reaction occurring on the formed hydroxyl group of the epoxide, which can react further with other epoxides leading to the formation of extended side chains, as shown in Figure 4.2a. It was possible to isolate the product as a powder by stirring the reaction mixtures in acetone and filtering off the product a few times.

Due to the possibility of the unwanted cascade reaction, analysis of the product becomes trickier as the degree of substitution is not enough to fully characterise the substitution. The concept of molar substitution also becomes an important parameter, which considers all grafted epoxide molecules and can be higher than three which is the limit for the DS of cellulose. Running FTIR spectroscopy on the products did not provide any clear conclusions on the reaction outcomes. Even though this type of reaction may be achievable with a sufficiently low level of cascade reaction, it will likely require a significant amount of investigative work both in terms of the synthesis and characterisation. Therefore, other options were tested instead.

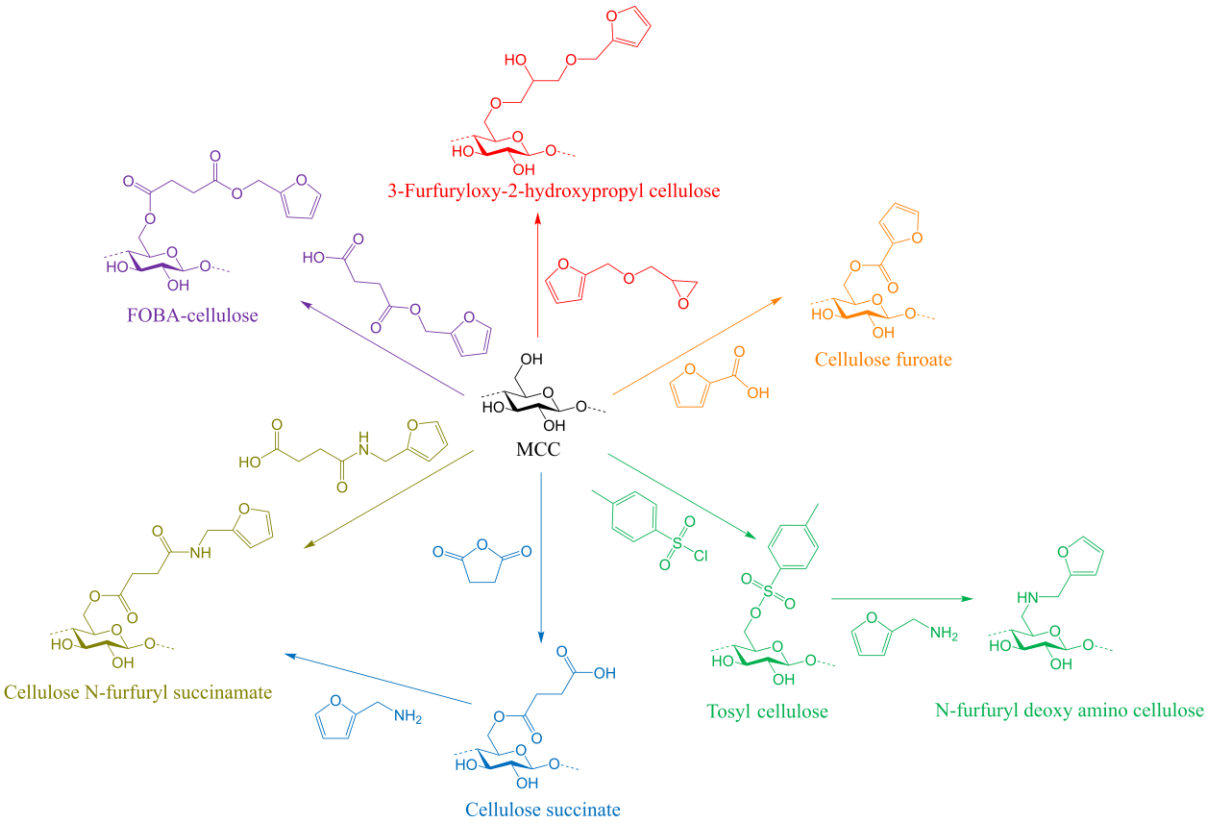

Figure 4.1. An overview of the different pathways that were tested experimentally to modify cellulose. It should be noted that the reactions are not necessarily expected to lead to full regioselectivity towards the primary alcohol as drawn here, but would in most cases be more random in practice with varying degrees of substitution. Forming cellulose N-furfuryl succinamate from cellulose succinate was never tested experimentally.

As an alternative route, employing furoic acid was tested in the same DMAc/LiCl solvent, with 1,1'-carbonyldiimidazole (CDI) to first activate the carboxylic acid in-situ, to then form the corresponding ester, cellulose furoate. This was done simply by replicating a previously reported method, which seemed to work as expected yielding the desired product (*25*). Forming this product can also be done using the more reactive furoyl chloride species, but using CDI is a milder approach leading to only CO_2 and imidazole as by-products and a relatively unchanged pH throughout the reaction, but still with rather high efficiency in terms of affording high DS-values. After performing the reaction, it was however found that the reactivity of this kind of cellulose derivative in DA reactions probably is quite low as compared to a similar DA network (*20*). This is attributed to the electron withdrawing effect of the ester group next to the furan ring, lowering the HOMO energy level, which in turn lowers the reactivity due to the increased orbital energy gaps of the reagents. Therefore, this product was not used any further and instead other routes were considered.

A different approach to perform reactions on cellulose, is to transform the cellulose hydroxyl groups into better leaving groups using tosyl chloride, to then react the formed tosyl cellulose further in substitution reactions with nucleophiles. Tosylation was therefore carried out in DMAc/LiCl in the presence of triethylamine for 24 h at 8 °C, based on a similar reported procedure (*32*). It appeared that the reaction yielded tosylated cellulose, although with an

unknown DS. The product was soluble in DMSO so it was tested to be reacted further with furfuryl amine at 100 °C without any catalyst, applying the conditions reported for similar reactions (*33*). The reaction was only tested once and led to difficulties obtaining the product by precipitation and filtration, so no product could actually be isolated and analysed. Although performing a substitution reaction of this kind on the cellulose should be possible, it may be a bit difficult to reach high substitution efficiencies to afford decently high DS-values. In terms of practical applicability, performing consecutive reactions on the cellulose is not ideal either and would make production more complex and expensive. Toxic reagents are another drawback of the route.

In parallel to the tosylation, succinylation of the cellulose was also investigated. Cellulose succinate is already a well-known cellulose derivative that can be made from succinic anhydride (*34-36*). Since succinic anhydride can be made from bio-based resources in the furfural platform (*37*) and was available to use within this project, it seemed like a reasonable pathway to explore. The idea was that the succinylated cellulose then could be reacted further with furfuryl amine in an amidation reaction, to give a furan-functionalized cellulose ester product. The succinylation reaction was tested in DMAc/LiCl with triethylamine using a previously reported method (*36*). After adding all reagents, the reaction mixture solidified which was not expected. To fully break up the solid into a powder, a mortar was required. The reaction was also tested heterogeneously in DMSO with a small amount of pyridine. This did however seem to lead to a quite low, and possibly uneven degree of substitution, according to FTIR analysis. Generally, the thermal stability of cellulose succinate is quite low which is a clear drawback (*34*). Therefore, it would probably be necessary to fully convert the formed carboxyl groups to amides in the last step. Since the final amidation step may be tricky as well, it appeared to be better to use a different, more simple yet robust approach. As mentioned earlier, avoiding consecutive reactions on cellulose is strongly preferable unless it really is necessary.

Considering the efficiency of using CDI activated carboxylic acids to form cellulose esters, the same product was tried to be obtained in a different order by first reacting the furfuryl amine with succinic anhydride to give the corresponding succinamic acid and then combining it with CDI for esterification of the cellulose. This is a comparatively simple approach, only reacting the cellulose once and under mild conditions, which is advantageous. Reacting furfuryl amine with succinic anhydride was very straightforward based on a previously reported reaction, yielding fully pure N-furfuryl succinamic acid, at room temperature without any catalyst (*38*). This was then used further with CDI to try and form the final product with cellulose in DMAc/LiCl, based on similar conditions used for various other carboxylic acids (*25*). According to FTIR spectroscopy, the cellulose product did however seem to have almost no side groups grafted onto its backbone. This is likely due to a ring closing reaction occurring after the CDI activation, forming N-furfuryl succinimide as shown in Figure 4.2b. If any molecules were grafted onto the cellulose, there would also be a risk that cleavage of the introduced branches occurs in a similar ring closing reaction. This therefore rendered the pathway unusable and also severely limits the usefulness of this type of product, regardless of the synthesis pathway.

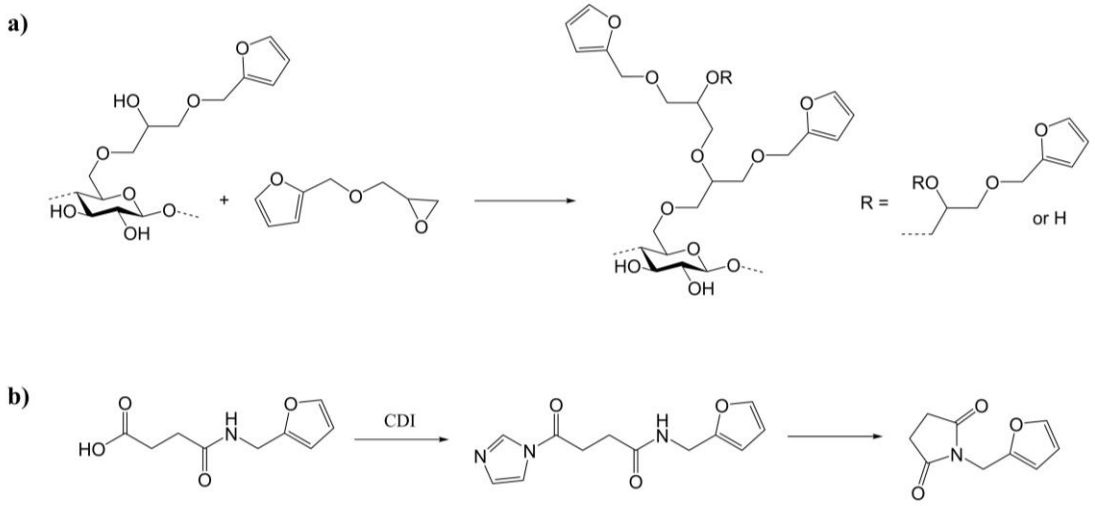

Figure 4.2. a) Proposed cascade reaction in the epoxy route due to the formed hydroxyl groups reacting further with furfuryl glycidyl ether, forming long branches. **b)** Unwanted formation of N-furfuryl succinimide, hindering the desired esterification of cellulose.

To avoid the issues with N-furfuryl succinamic acid while still obtaining a relatively similar product, furfuryl alcohol was used instead of furfuryl amine. Furfuryl alcohol can be combined with succinic anhydride to yield the corresponding ester carboxylate. This can in turn be activated with CDI in-situ before finally being reacted with cellulose in one step. The good thing is that furfuryl alcohol is even more readily available from the furfural platform (*37*), while avoiding the major problem related to the amine. This route therefore gives the possibility to use a simple, efficient and robust method to obtain a fully bio-based cellulose derivative functionalized with furan moieties in only one reaction with cellulose. While it required both a lot of reading and experimental testing to develop an effective modification pathway, the exploratory work provided plenty of valuable insights on all the intricacies related to working with cellulose, which has been very enriching. The results for this final pathway are presented in the remaining sections in more detail.

4.1.2 Synthesis of 4-(furan-2-ylmethoxy)-4-oxobutanoic acid

The first step in order to make the functionalized cellulose was to synthesise 4-(furan-2-ylmethoxy)-4-oxobutanoic acid (FOBA) from furfuryl alcohol and succinic anhydride. This is a quite simple reaction, proceeding as shown in Figure 4.3a, although relatively limited data and usage of this compound is available. The method was adapted from a very similar reaction (*24*) and the reaction worked as desired, yielding FOBA as viscous oil in 92% yield. A fully pure product was not obtained though, as can be seen in the ^{1}H NMR spectrum in Figure 4.3c, with some impurities visible in the spectrum as well as a small amount of unreacted succinic anhydride remaining. The product should be a colourless oil if fully pure (*39*), but in this case it was slightly brown. This means that a more thorough washing procedure and possibly chromatography may be required to obtain a fully pure product. Since the amount of impurities was still quite low, the product was used as it was for further reactions with cellulose.

After the synthesis, the product was stored refrigerated and away from light to prevent any potential decomposition. The lower temperature led to solidification of the product, but it was easily melted again by gentle heating. The product was analysed with FTIR and NMR spectroscopy and the recorded spectra are presented in Figure 4.3b-d. To gain further structural evidence and to do a complete spectral assignment, 2D NMR experiments were conducted using COSY, HSQC and HMBC experiments. The obtained 2D spectra are presented in Appendix B in figures B.1-3.

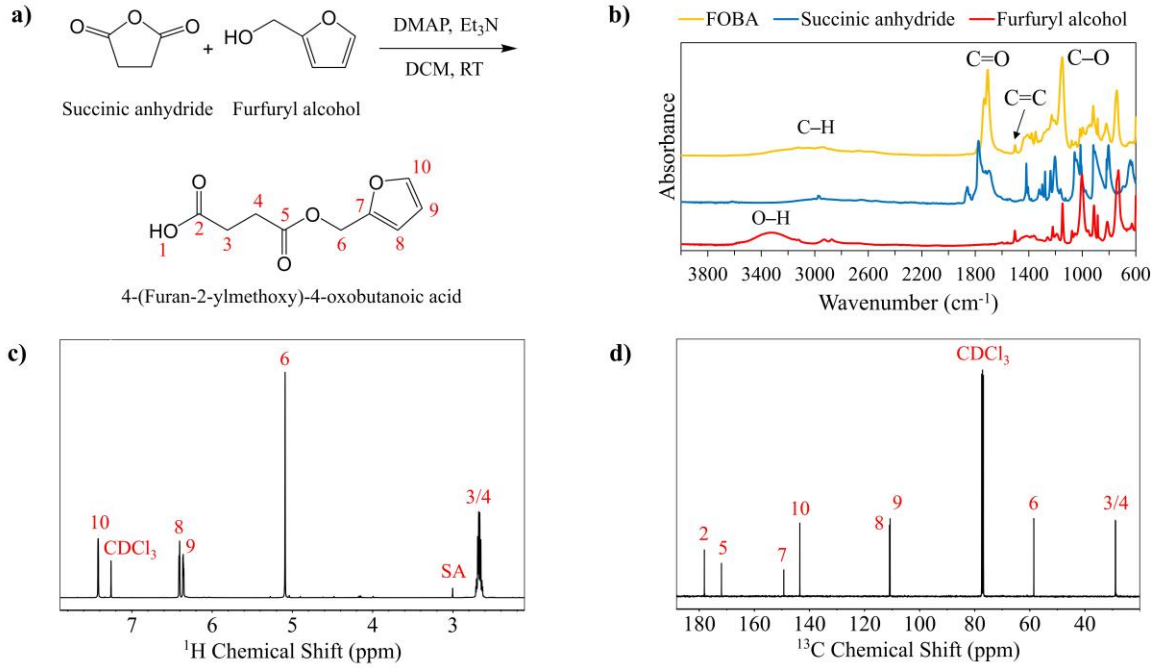

Figure 4.3. a) Synthesis of FOBA, **b)** FTIR spectrum as well as **c)** ^{1}H and **d)** ^{13}C NMR spectra in $CDCl_3$ of the obtained product. An extended relaxation delay of 10 s was required to give accurate integrations in the ^{1}H NMR spectrum. A very broad peak at around 10 - 11.5 ppm could be observed for the carboxylic proton and a small amount of succinic anhydride (SA) and other impurities are visible in the spectrum.

The usage of bio-based chemicals here is a strong plus. Furfuryl alcohol is the chemical produced in the largest volumes from the platform chemical furfural and succinic anhydride is also derived from furfural (*37*), meaning that the synthesised FOBA can be made fully bio-based. Using toxic chemicals is a clear drawback though, with several of the chemicals being highly toxic in the procedure. This synthesis could therefore be developed further according to the principles of green chemistry to make it both greener and more efficient. Ideally it would be possible to obtain a purer and more colourless product without using chromatography as it requires a large amount of solvent. Due to time constraints, it was not possible to put more effort into this synthetic step though.

4.1.3 Synthesis of FOBA-cellulose

After FOBA had been synthesised, it was used for cellulose esterification via in-situ activation with CDI. To the best of my knowledge this is the first time employing this kind of route and synthesising this cellulose ester. The reaction proceeds by first separately activating FOBA

with CDI, transforming the carboxylic OH into the imidazole group, making it a much better leaving group. This process is driven by the release of CO_2 gas (*25*), as shown in Figure 4.4. The activated FOBA solution is then added to a dissolved cellulose solution to allow esterification to proceed. By varying the amount of used acid and catalyst, the degree of substitution generally can be tuned. The reaction was performed at three different molar ratios of FOBA, CDI and cellulose, and the conditions and outcomes of the reactions are presented in Table 4.1. In all three cases, a pale beige product was obtained as a powder. By considering the amount of product that was obtained in each run and that the increased weight compared to the starting material is due to the introduced FOBA side groups, an estimation of the DS can be made. The main uncertainties in this type of calculation are the yield with regard to cellulose and the amount of water and impurities present in the products. Since these are unknown, an estimated span for the DS values is given in Table 4.1, with a more detailed description of the calculations and assumptions in Appendix C.

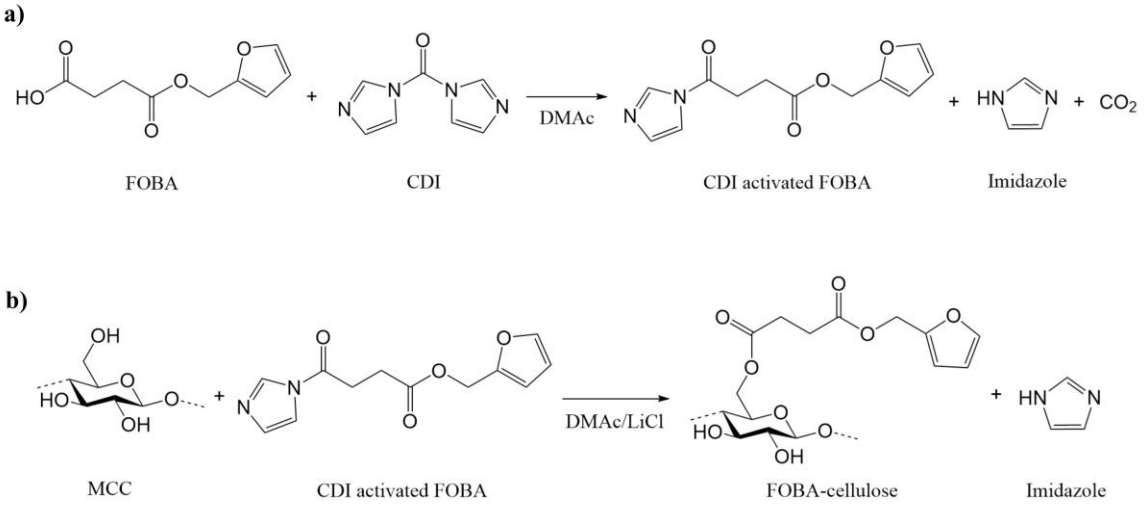

Figure 4.4. a) CDI activation of FOBA and **b)** the consequent reaction with cellulose, yielding the corresponding ester.

The obtained products were added to DMSO in glass vials (about 10 mg to 1 mL DMSO) to investigate their solubilities. The mixtures were vigorously shaken and heated with a heating gun. By visually inspecting the mixtures it could be deducted that all products were practically insoluble as the added powder appeared to have remained unchanged. Slight swelling appeared to occur though so samples from the two last runs (6x and 10x) were analysed with ^{1}H NMR in DMSO-d_6, shown in Appendix C in Figure C.1. It showed very weak peaks for the expected FOBA protons, a clear water peak but no cellulose protons, which further supported the observed swelling behaviour and poor solubility. No significant amount of impurities was seen in the spectra which is positive. The solubilities were also assessed in DMAc. For the first two products (4x and 6x), 20 mg was added to 2 mL of DMAc. The mixtures were heated to 100 °C under vigorous stirring but in neither case, this led to a clear solution. After adding 150 mg of LiCl, clear solutions were obtained. For FOBA-cellulose 10x it was possible to dissolve 50 mg in 2 mL of DMAc simply by heating to 100 °C under stirring, which gave a transparent solution.

Table 4.1. Reaction conditions and results for the three synthesis runs of FOBA-cellulose. In all three runs 0.5 g of MCC was dissolved in 20 mL of DMAc with 1.5 g of LiCl. FOBA was activated with CDI in an additional 10 mL of DMAc.

Name of run	Molar ratio[a]	Amount of product (g)	Estimated DS[b]	Solubility
FOBA-cellulose 4x	1:4:4	0.89	0.5 - 1.1	DMAc/LiCl
FOBA-cellulose 6x	1:6:6	1.11	0.9 - 1.6	DMAc/LiCl
FOBA-cellulose 10x	1:10:10	1.51	1.5 - 2.5	DMAc

[a] Molar ratio of cellulose AGUs/FOBA/CDI.
[b] Estimated based on calculations presented in Appendix C.

FTIR spectra were recorded to do initial characterisation of the product, which are shown in Figure 4.5. These show that the reaction appeared to work well and with good reproducibility as all three runs gave similar results. All the characteristic peaks from FOBA are seen in the spectrum, with the aromatic C–H absorption around 3140 cm^{-1}, C=O absorption at 1730 cm^{-1}, C=C absorption at 1500 cm^{-1} and C–O absorption at 1150 cm^{-1}, with the characteristic cellulose peaks remaining. For the three different runs, a decreasing signal from the cellulose hydroxyl absorption with an increased excess of FOBA during the reaction can be seen, which is expected as the DS should become higher. The results thus provide good evidence that the desired product was formed. One side note is that the KBr pellet method for FTIR is commonly used to make the analysis more standardised and accurate. It would probably be advantageous to use this method, but nonetheless the spectra still give good qualitative information. To obtain more detailed structural information, NMR spectroscopy was used instead which is described in more detail in the next section.

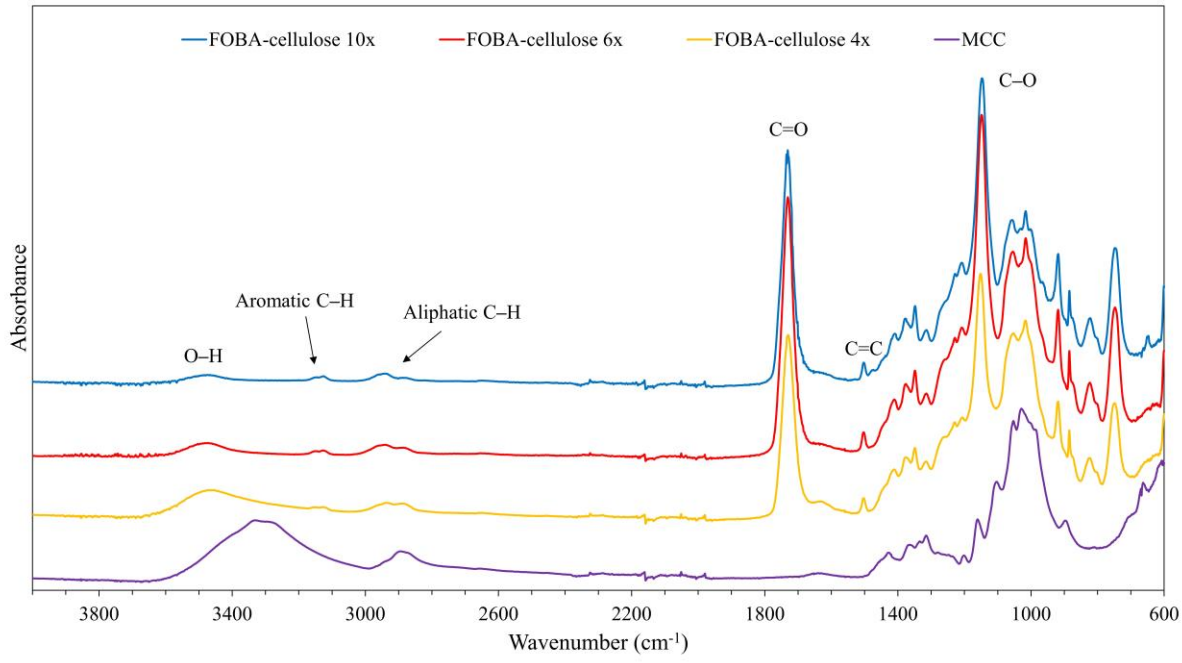

Figure 4.5. FTIR spectra of the MCC starting material and the three FOBA-cellulose products.

There are many advantages using the herein applied conditions to functionalize cellulose. Only one reaction with cellulose is a strong plus, minimising potential degradation and side reactions on the cellulose, as well as enabling an easier synthetic procedure with less solvent-demanding washing steps required. Since the reaction is performed homogeneously, a relatively even distribution of the introduced substituents can be expected. The fact that FOBA is bio-based means that the final cellulose product is fully bio-based which is another major advantage. Utilising CDI for esterification can be done under mild conditions while still enabling a high reaction efficiency. The pH does not change considerably during the reaction, giving negligible chain degradation (*40*). The only by-products that are formed are CO_2 and imidazole which both can be removed easily. Generally, this kind of procedure therefore gives white, non-coloured products, compared to many other procedures that give slight discoloration of the cellulose. The reason that a slightly discoloured product was obtained anyways in this case, is assumed to originate from the impurities in the synthesised FOBA, which already during the CDI activation step gave a dark black colour to the solution after full activation.

CDI is not strictly speaking a catalyst, as it is used in stoichiometric ratio and is consumed in the reaction. This is not ideal in terms of keeping the conditions fully green with no by-products. Optimising the specific reaction steps has not been the main purpose of this project though, but rather to just manage to synthesise functionalized cellulose. Making the entire process greener could therefore be a matter of further investigation, for example trying to find the ideal solvent that can be recovered efficiently, while also making use of the formed imidazole and CO_2, as well as making the washing of the product efficient. One positive aspect with regard to making cellulose esters is that several synthetic routes can be used to form the same product. Using CDI is not necessarily the best option, and for example transforming FOBA to its corresponding vinyl ester is another mild approach that could be investigated. Using the acyl chloride is a common and powerful option thanks to its highly electrophilic character, although it is not as green and might cause hydrolysis of the ester group in FOBA due to the formed HCl upon esterification, which therefore probably would want to be avoided. Other similar alternatives to CDI, also based on in-situ activation, are using tosyl chloride or N,N′-dicyclohexylcarbodiimide, but both of these options require harsher conditions, are less green and generally not as efficient as CDI (*40*).

The reaction temperature of 70 °C was somewhat arbitrarily chosen based on similar previously reported reactions. A reasonable temperature range is 60 - 80 °C, but the optimal temperature and reaction time will have to be investigated through further experiments. Using DMAc/LiCl for homogeneous cellulose modification is commonly utilised on a lab scale and was selected for this reason, but is not utilised on larger scales due to not being feasible economically (*14,41*). This would require efficient recycling of the valuable lithium salt, and the toxicity of DMAc is not ideal either in terms of keeping it green. A reasonable alternative solvent system to test and compare the reaction efficiency with would be DMSO/TBAF. In several cases this leads to a significantly higher grafting efficiency of the activated imidazolide under comparable conditions (*17*). The dissolution process in this case is also much simpler which is advantageous. In case upscaling would become interesting in the future, using more novel bio-based ionic liquids could be interesting to make the process fully sustainable, such as a recently developed betaine based ionic liquid derived from sugar beets (*35*).

The dissolution process of the cellulose is important in terms of undesirable degradation of the cellulose leading to a lowered degree of polymerisation (DP). Ideally the average DP both of the starting material and the obtained products would have been analysed by size exclusion chromatography. Due to not having any access to a suitable instrument for this analysis, it could not be done though. By dissolving the cellulose in DMAc/LiCl, some degradation most likely occurs (*42*) but it should not be a significant problem in terms of making crosslinked materials. One note in this regard is that the obtained cellulose solutions after the dissolution procedure, always had a yellow colour.

The CDI activation process could also be investigated in more detail, following how long it takes until all CDI has been consumed forming the imidazolide, to optimise the process. Various conditions have been reported for the activation, such as 30 min at 80 °C (*43*), 3 h at 60 °C (*41*) and 24 h at 40 °C (*25*). Too long activation times may lead to a detrimental effect, as indicated in one paper (*43*). This could probably be monitored most easily with ^{13}C NMR by looking at the carbonyl carbon signal of the carboxylic acid. This signal should change chemical shift and disappear upon full activation (*41*).

4.1.4 NMR analysis of FOBA-cellulose

While performing reactions on cellulose generally is quite challenging on its own, analysing and characterising the obtained product is often just as difficult. Even though FTIR spectroscopy can be a quite helpful analytical tool, the level of structural details is still limited in the obtained data. One common issue in terms of analysing cellulose products is that they are not easily soluble in conventional NMR solvents, which limits the capabilities of using solution-state NMR experiments. Solid-state NMR can be a good alternative, but instead suffers from poor resolution and requires slightly more specialised equipment and experiments. There are ways to circumvent the solubility challenges though, and in the case of cellulose esters like FOBA-cellulose, peracetylation and perpropionylation of the unreacted cellulose hydroxyl groups is commonly done to increase the solubility (*25*,*43*,*44*).

Perpropionylation of the FOBA-cellulose 6x product was therefore tested by applying a well-established procedure that has been reported for a wide variety of cellulose esters (*25*). This transforms the unreacted hydroxyl groups of the cellulose product into the propionate group in a relatively simple procedure and generally enhances the solubility in e.g. DMSO and chloroform. The increased solubility can then be utilised for conventional NMR analysis in the solution state to do more thorough structural characterisation and to estimate the degree of substitution. The main reason for choosing perpropionylation here is that the introduced methyl protons of the propionate groups are quite shielded and therefore should be well resolved from the remaining peaks in the ^{1}H spectrum, around 1 ppm.

The procedure was applied by allowing 0.25 g of product to react with 5 mL of propionic anhydride, in 5 mL of pyridine in the presence of 50 mg of DMAP as catalyst, at 80 °C for 24 h. The product was then washed in ethanol and dried under vacuum before being analysed with FTIR. The obtained FTIR spectrum, presented in Appendix C in Figure C.2, indicated that the procedure appeared to work as desired, with no peak in the hydroxyl region but with an otherwise relatively unchanged spectrum. Unfortunately, the product was however still

insoluble in both DMSO and chloroform, meaning that the method was not useful for analysis of this kind of product. It may be possible that there will be some solubility for a perpropionylated sample in certain DS-ranges, but obviously it still cannot be used for all samples. Peracetylation could potentially be tested instead, to examine if that gives better solubility.

An alternative method that does not require any further chemical modification of the product, is to use a more powerful NMR-appropriate solvent that can dissolve the product directly. A versatile example is using a 1:4 w/w mixture of $[P_{4444}][OAc]$:DMSO-d_6 which is capable of dissolving even pure microcrystalline cellulose (*23*). The synthesis of $[P_{4444}][OAc]$ is a bit tedious, but thankfully this solvent system was supplied for analysing the FOBA-cellulose products. This ionic liquid has no signals overlapping with the cellulose backbone nor the furfuryl group which makes it rather useful here. The obtained ^{1}H NMR spectra displayed in Figure 4.6a, further confirmed the formation of the desired product with peaks from the furfuryl moiety being clearly visible. Since the protons on the succinyl part have a similar chemical shift as DMSO, this peak cannot be distinguished in these spectra.

By comparing the relative peak areas in NMR spectra, it can often be used for quantitative estimations. Applying quantitative ^{1}H NMR could therefore in theory be done in this case to estimate the DS of the synthesised FOBA-cellulose by comparing the ratio of furfuryl protons and cellulose backbone protons. In order to obtain accurate information however, it is important that the protons are allowed to return back to equilibrium completely between pulses. The spin-lattice relaxation time for the cellulose backbone protons is around 1 - 2.25 s which means that extended relaxation delays become important (*23*). For grafted side groups that have a higher conformational freedom, protons may have even longer relaxation times. As FOBA requires an extended relaxation delay on its own, this could probably be the case and for a 30° flip angle, at least 10 s delay would likely be necessary. Since only normal ^{1}H NMR experiments could be performed with a 1 s relaxation delay between scans, the spectra unfortunately cannot be used for quantitative purposes. Ensuring accurate integration would be a bit challenging here though due to sometimes slightly overlapping peaks and should preferably be done after a more complete spectral evaluation with additional 2D NMR experiments. Since the succinyl protons overlap with the DMSO peak, no quantitative information can be obtained with regard to that part. In the ideal case, quantitative ^{13}C spectra would also be recorded to get additional data. The resolution in the carbon spectrum is normally higher which is a strong advantage, although the experiment times are very long.

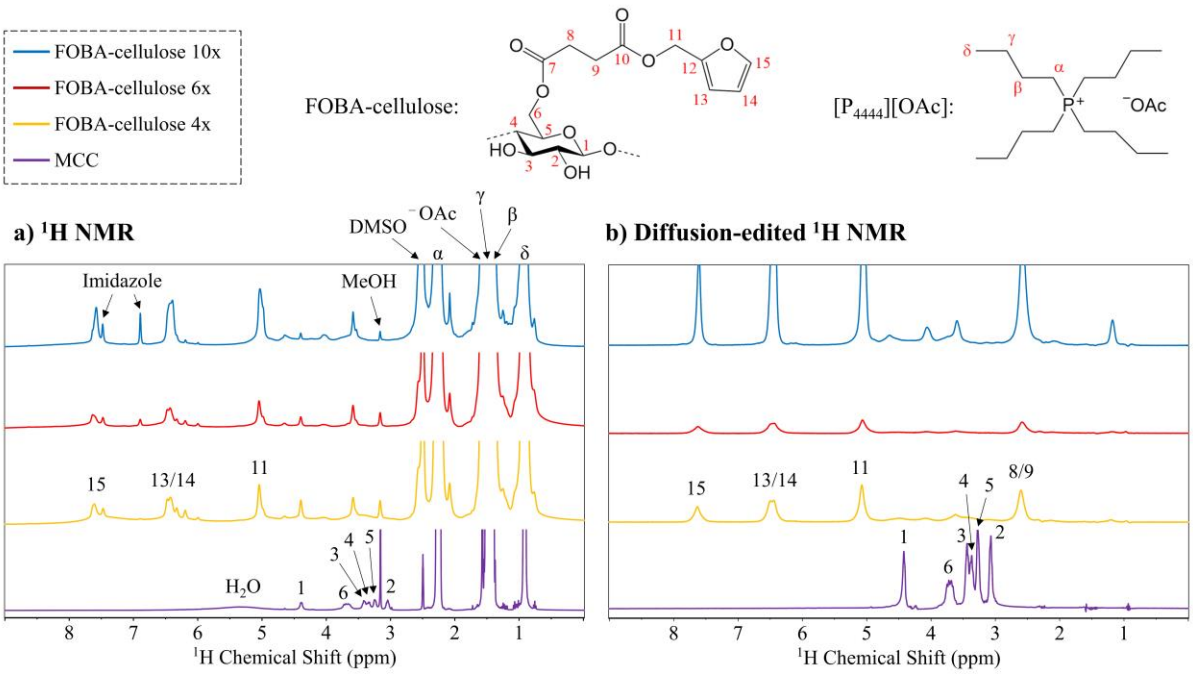

Figure 4.6. a) ^{1}H NMR spectra of the three FOBA-cellulose products and the dried MCC starting material (recorded using 256 scans) and **b)** diffusion-edited ^{1}H NMR spectra where low molecular weight compounds have been edited out via a DOSY-type of experiment. Some water is visible in the MCC even after drying, and a methanol peak can be seen in all spectra which is assumed to originate from the ionic liquid solvent preparation. A small amount of imidazole and impurities appears to be present in the products. The resonances of both cellulose and $[P_{4444}][OAc]$ are assigned based on previously reported NMR data (*23*).

To confirm the covalent attachment of the furfuryl groups onto the cellulose chains, diffusion-edited ^{1}H NMR spectra were recorded, presented in Figure 4.6b. This technique uses a diffusion-ordered spectroscopy (DOSY) sequence, where low molecular weight species are edited out and only polymeric signals remain. It works by applying magnetic field gradient pulses to spatially encode the positions of nuclei during the analysis. The signals from faster diffusing species will be reduced due to their longer average movement after a certain applied diffusion delay, allowing separation of the signals. In this case, the obtained spectra verify the attachment of the furfuryl protons to cellulose and also show the peak of the succinyl protons as the DMSO peak is removed. Due to different nuclei having different relaxation times, the spectrum is not quantitative. One observation that can be made is that the signal intensities between the three samples vary noticeably. A reasonable explanation for this, apart from varying DS-values and sample amounts, is the difference in viscosity of the prepared samples. FOBA-cellulose 10x was notably more viscous than the others, and a higher viscosity gives a lower diffusivity which in turn leads to stronger signals in the given DOSY-NMR experiment, as described earlier. FOBA-cellulose 6x was on the other hand the least viscous sample, and here gave the weakest signals.

In all six spectra of the FOBA-cellulose products, the resolution of the cellulose proton peaks is much lower compared to the pure MCC. A partial explanation for this is the functionalization that has occurred, which is expected to slightly change the chemical shifts of the cellulose protons who are situated next to the introduced side groups. This therefore gives rise to

additional signals at only marginally different chemical shifts. To be able to resolve the peaks more efficiently, ^{13}C NMR would likely be particularly helpful. Depending on the obtained resolution, it may then also be possible to estimate the partial DS on each of the three hydroxyl groups of the AGU. Another observation that can be made is that there is a small unknown peak present in the diffusion-edited spectra around 1 ppm, which is especially evident in the FOBA-cellulose 10x spectrum with the stronger signals, and could correspond to some kind of shielded alkyl protons. It is a bit unclear where this signal comes from, and could possibly be because of a side reaction, potentially caused by impurities. Since this peak was also present in the ^{1}H NMR spectra in pure DMSO-d_6 solvent, shown in Appendix C, these protons are most likely located on some kind of side group. To get more complete structural information here, additional 2D experiments will be required.

A more complete set of 1D and 2D experiments will have to be conducted in the future to do a proper spectral assignment and structural characterisation of the products. This includes starting with quantitative ^{1}H and ^{13}C NMR and multiplicity-edited HSQC experiments, and then potentially doing additional 2D experiments that probably would aid the resonance assignment significantly, like HMBC and HSQC-TOCSY (Heteronuclear Single Quantum Coherence-Total Correlation Spectroscopy). While using this kind of ionic liquid solvent gives higher resolution than analysis in the solid-state, solid-state NMR could still serve as a nice alternative to further verify and complement the results. During this thesis work, no solid-state spectrometer was accessible though.

4.1.5 Thermal analysis of FOBA-cellulose

To further characterise the products, TGA curves were acquired which are presented in Figure 4.7. Values for the temperature where a sample has lost 5% weight ($T_{d5\%}$), the temperature where a sample has lost 10% weight ($T_{d10\%}$) and the percentage of sample left at 700 °C (CY_{700}) are all presented in Table 4.2. It can be observed that the functionalized cellulose products exhibit a lower thermal stability compared to the pure MCC. Both $T_{d5\%}$ and $T_{d10\%}$ are lower for all the products compared to MCC, whereas CY_{700} is higher for the products. It should be noted that some water appears to still be present in the MCC, which also was visible in the ^{1}H NMR spectrum shown in Figure 4.6. This is likely the reason why the weight starts decreasing quite early in the initial part of the TGA curve, but then stabilises at slightly higher temperatures. This means that the real $T_{d5\%}$ and $T_{d10\%}$-values may be even higher for the MCC. Some variability is seen between the different curves of the three FOBA-cellulose products. With the limited data here, it is difficult to identify any clear trends.

One of the more important aspects of the results is that the products are stable until the temperature where the reverse DA reaction takes place (around 100 - 150 °C). This means that it should be fully possible to accomplish the reverse reaction for recycling purposes without causing undesired degradation. Since the TGA analysis was done under a nitrogen atmosphere, further experiments could be done under air instead to obtain additional data that may be of higher practical relevance. Although a network material made from FOBA-cellulose may be reprocessable below its degradation temperature, the low thermal stability observed here

obviously is expected to limit the operating temperature of the material, which needs to be kept in mind.

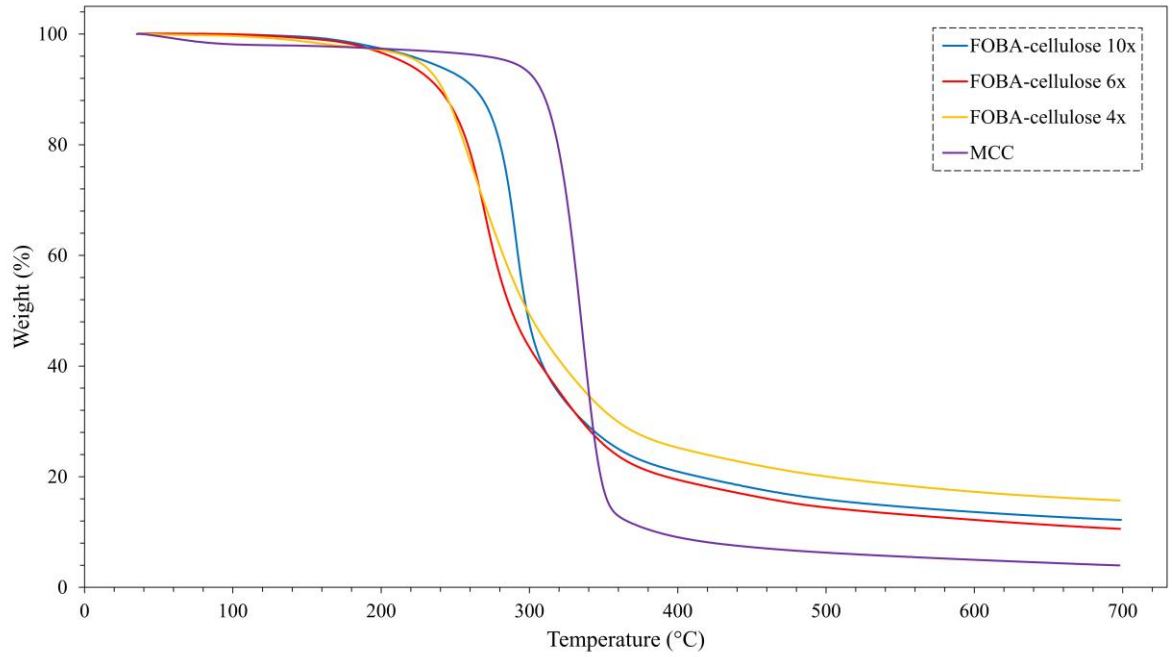

Figure 4.7. Acquired TGA curves of the starting MCC material and of the three FOBA-cellulose products.

Table 4.2. $T_{d5\%}$, $T_{d10\%}$ and CY_{700} for the MCC starting material and the three FOBA-cellulose products.

	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	CY_{700}
MCC	287	308	3.97
FOBA-cellulose 4x	225	242	15.7
FOBA-cellulose 6x	215	239	10.6
FOBA-cellulose 10x	231	263	12.2

To obtain further information on the thermal properties of the products, differential scanning calorimetry was conducted. It did however not provide any useful curves, and instead dynamic mechanical analysis may be a better option to assess e.g. the glass transition temperature. The introduced flexible side group should help provide a better mobility to the stiff cellulose chains, which should give a lower glass transition point. While a lower stability of the products is not ideal in all cases, it could potentially mean that the material will have a better biodegradability. Since this definitely could be something that is of interest, it could be a subject for further investigations in the future.

4.2 Bismaleimide crosslinker synthesis

Once the furan-functionalized cellulose was obtained, the bismaleimide crosslinker could be synthesised. This bismaleimide compound was first patented back in 1989 by Alexander (*46*) and various synthetic procedures have been reported in the literature. It was a bit more difficult to obtain this product than expected, which required testing a number of procedures and eventually using silica gel chromatography. This reaction occurs in two steps as shown in Figure 4.8a. First an uncatalyzed ring-opening reaction of maleic anhydride occurs reacting with the diamine. Then ring-closing of this intermediate is achieved by using sodium acetate to deprotonate the carboxylic OH to make it a stronger nucleophile, acetic anhydride to turn the carboxylic OH/O^- into a better leaving group and triethylamine to make the amide nitrogen more nucleophilic, to form the desired bismaleimide product.

The desired product was obtained only after purifying the crude reaction mixture over silica gel, followed by recrystallisation. Pure, white crystals were obtained at a rather low yield of 20%. The product was characterised with FTIR and NMR spectroscopy and the obtained spectra are presented in Figure 4.8b-d. To gain further structural evidence and to do a complete spectral assignment, 2D NMR experiments were conducted using COSY, HSQC and HMBC experiments. The obtained 2D spectra are presented in Appendix D in figures D.1-3.

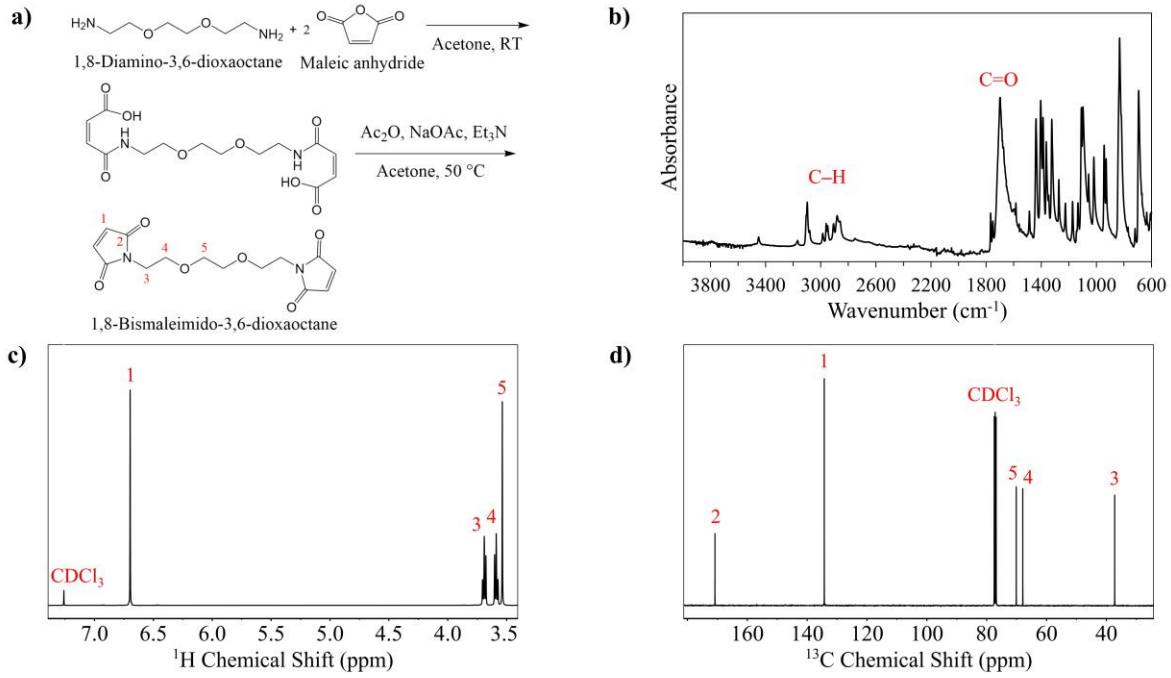

Figure 4.8. a) Synthesis of the bismaleimide, **b)** FTIR spectrum as well as **c)** ^{1}H and **d)** ^{13}C NMR spectra of the obtained product in $CDCl_3$.

The synthetic procedure can most likely be improved to increase the yield. The synthesis was done twice and the second time a slightly less pure product was obtained after the column which also shows that there may be room for improving the reproducibility. During the second run, the crude reaction mixture also solidified after evaporation, once it cooled down to room temperature and was left overnight. It probably therefore is possible to obtain the product through precipitation, which has been reported (*26*). Even though this maybe would not give a

fully pure product, it would probably make the chromatographic purification easier and more effective. If chromatography could be avoided altogether, that would of course be advantageous.

4.3 Synthesis of Diels-Alder covalent adaptable network

Initial testing of network formation was done using the FOBA-cellulose 10x product. Due to the short timeframe of the project, only rather limited work could be done on this part towards the end, meaning that more thorough testing will have to be done in the future instead. Nonetheless, the initial tests indicate that it is possible to perform the DA reaction with the functionalized cellulose and the synthesised bismaleimide crosslinker. Since the used FOBA-cellulose was soluble in DMAc, the reaction was performed in this solvent. The reaction temperature of 60 °C was chosen as similar network reactions have been conducted around this temperature (*21*,*22*). Finding an optimal temperature will require further experiments though, as the forward DA reaction is speeded up at higher temperatures, but the equilibrium is shifted towards favouring the starting materials.

One network experiment was conducted with an approximate ratio of 1:1 furan and maleimide units. This was done by adding 50 mg of FOBA-cellulose 10x (approximately 0.096 mmol AGUs and 0.191 mmol furan functionalities, assuming DS = 2 which gives a molar mass 523.384 g/mol AGUs) to 2 mL of DMAc in a 5 mL RBF equipped with a magnetic stirring bar. The mixture was heated to 100 °C under vigorous stirring and a nitrogen atmosphere which led to obtaining a homogeneous solution of FOBA-cellulose. The solution was then cooled down to 60 °C and 29.5 mg of bismaleimide (0.096 mmol) was added to the solution. The network formation was allowed to proceed at 60 °C for 3 days. The product was precipitated in 50 mL ethanol and filtered off, washed with more ethanol and finally dried under vacuum. It should be noted that the dissolved FOBA-cellulose solution was quite dark brown and that it was difficult to see whether any precipitate was formed throughout the run due to crosslinking. The small scale also made it more difficult to visually inspect the reaction mixture accurately.

The obtained product was analysed with FTIR spectroscopy and the recorded spectrum is shown in Figure 4.9. The results suggest the successful formation of the DA adduct, as the characteristic peaks originating from the furfuryl moiety are less intense, while some of the bismaleimide peaks instead are visible. When compared to the starting materials FOBA-cellulose and bismaleimide, two distinctive carbonyl signals of the product can be observed between 1700 and 1800 cm^{-1}, which are indicative of the ester carbonyl group in FOBA-cellulose and the maleimide carbonyl group in the bismaleimide crosslinker. Moreover, C–H stretching characteristic for alkenes are observed in the bismaleimide spectrum around 3100 cm^{-1}. This signal is no longer observed in the spectrum of the product, which is also a direct result of the reaction between FOBA-cellulose and bismaleimide, forming the DA adduct. Since no clear precipitate could be observed crushing out during the reaction, it remains unclear to what extent crosslinking was achieved and whether the bismaleimide reacted on both functional ends, so further experiments are necessary.

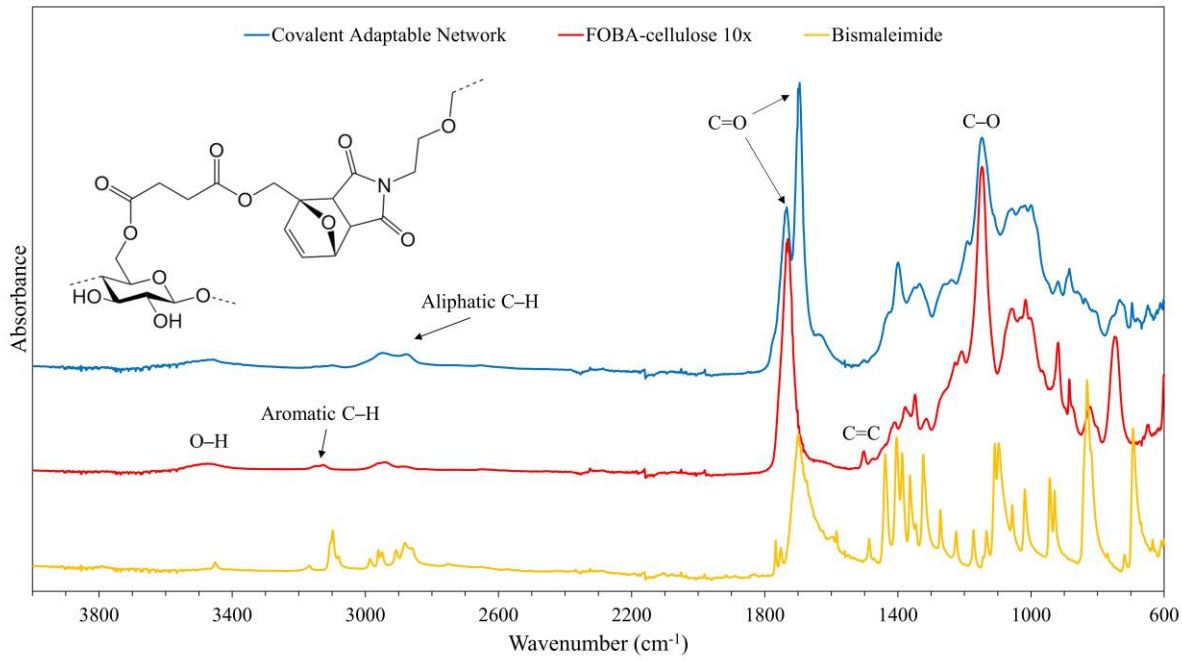

Figure 4.9. FTIR spectra of FOBA-cellulose 10x, bismaleimide and the obtained CAN product.

It is likely possible to monitor the reaction directly through solution NMR in $[P_{4444}][OAc]$:DMSO-d_6 at temperatures relevant for the DA reaction, which could be done to study the kinetics of the reaction while following the reaction in more detail. This would probably be a good first thing to do next in terms of developing a procedure for synthesising the network material. Using UV spectroscopy is an additional option to follow the reaction, potentially by monitoring the decay of a furan band upon DA adduct formation. Another important parameter will be in which molar ratio the bismaleimide should be added in. Once different CAN materials are obtained, these will have to be characterised to evaluate their properties.

Different cellulose substitution degrees and spacer lengths in the bismaleimide crosslinker could be tested to investigate the relationships between network structure and material properties. Exploring different functionalities, shapes and lengths in the grafted side groups of the modified cellulose, utilising the same CDI activated esterification procedure using different carboxylic acids, could probably also be done relatively easily to obtain additional data on how the material properties vary. MCC was chosen here as it is commonly used in cellulose-based materials research and is cheap, widely available and pure. Other types of cellulose feedstocks could be investigated as well though, to widen the applicability of the material.

As mentioned previously, the furan-functionalized FOBA-cellulose is fully bio-based. Maleic anhydride is another example of a compound derived from furfural (*37*). Considering that 1,8-diamino-3,6-dioxaoctane potentially could be derived from biological resources as well, this means that the bismaleimide and in turn the synthesised CAN, can be made completely bio-based. This has a high significance as it allows to lower the burden of using finite, fossil-based resources, and instead only use renewable resources. In order to design an industrially feasible process, a range of other parameters will be of high importance too. It has to be kept in mind

that e.g. solvents and various additional chemicals are used which gives room for optimisation of the entire synthesis pathway to make it as green as possible.

While it is difficult at this point to say which specific applications this kind of material likely would be suitable for, there should be a relatively wide range of possibilities. This will depend on all of the different material properties obtained in the end, like the mechanical properties and thermal stability, which needs further investigation. First off all it could probably be used in applications where the use of furan-functionalized cellulose derivatives has already been reported, e.g. in hydrogel applications (*21*). To name one more potential application, cellulose foams is an area where this type of material could prove to be very useful. One of the main challenges for these materials is obtaining desirable mechanical properties with good strength after the lowered density from foaming (*47*). This kind of crosslinked network structure made here could provide better sturdiness while still giving the option to break the crosslinks relatively easily to give good recyclability.

Using water soluble bismaleimides should be ideal in order to utilise existing foam forming processes, where the foam material is prepared by suspending cellulose fibres in an aqueous foam stabilised by surfactants. This type of material may require longer bismaleimide compounds though to still enable some flexibility of the final foam, for example with an increased number of ethylene oxide units between the maleimide ends, which therefore could be synthesised and tested as well. Drying of the wet foam occurs at temperatures right where the DA reaction takes place so it should be possible to achieve crosslinking during the drying stage, allowing simultaneous drying and curing. Ideally commercially available pulp like softwood kraft pulp could be used and functionalized through an efficient process to allow better scalability of the material. One critical aspect in this regard is that the cellulose foams are made of fibres and therefore differ significantly from other polymeric foams which generally consist of networks of the individual polymeric molecules. The fibre network is instead bonded through the surfaces of the fibres, so the type of modification process, if the reaction mostly is limited to the fibre surface and how this affects the fibre structure and morphology would need to be explored. An additional challenge is often improving the water resistance of the material, and in case of the application for thermal insulation in building materials, fire retardancy is important and would need to be considered (*47*).

5. Future Work

According to initial experimental testing, a novel cellulose-based Diels-Alder CAN material was successfully synthesised during this thesis work. There are however a number of things that still need to be done in order to complete the work. Firstly, more thorough synthesis and characterisation of the final material will have to be carried out in the future. This includes developing a protocol for the CAN synthesis, producing the material on slightly larger scales, studying the processing characteristics of the synthesised material, as well as testing the recyclability and how all of this affects the final material properties. Due to the lack of time this was not possible to do, but these are fundamental aspects in understanding the capabilities and limitations of the material and would have been prioritised as the next step if more time was available. Experimental testing, including tensile testing, dynamic mechanical analysis, TGA and possibly more specialised tests to study e.g. the self-healing properties will have to be conducted.

Secondly, more detailed structural analysis of the FOBA-cellulose products will have to be carried out. This includes doing additional 2D NMR experiments in $[P_{4444}][OAc]$:DMSO-d_6, trying to estimate the degree of substitution with higher accuracy as well as potentially doing complementary solid-state NMR analysis. It would be preferable to obtain FOBA as a fully pure, transparent liquid to make sure that impurities do not interfere with the esterification reaction in any way. To get more comprehensive data on the functionalization, it would be of interest to compare the solvent system DMAc/LiCl with DMSO/TBAF under comparable conditions to assess which option gives the highest reaction efficiency. In case DMSO/TBAF is more efficient it could be used further for synthesising products with a varying degree of substitution. It would also be ideal to analyse the average DP after the functionalization to check how it is affected by the reaction procedure and whether this has a significant effect on the processing and final properties of the network materials. This could probably be done most easily by using size exclusion chromatography with an appropriate solvent system.

While the aim of this thesis project was focused on solely achieving the overall synthesis of a cellulose derived CAN, making each individual process more efficient and greener, maximising the environmental friendliness of the material and following the principles of green chemistry would be of great interest. This includes trying to change the rather toxic and expensive solvent system DMAc/LiCl to a greener alternative, which should be fully possible using existing alternatives. The biodegradability of the material is something that could be studied as well. In this aspect the ester bond might be broken relatively easily enabling better degradability in natural environments. Finally, life cycle assessments combined with studying the material's practical applicability, scaling possibilities and industrial feasibility could be done to get a more complete picture of the material's future potential as a sustainable, bio-based, reprocessable thermoset.

6. Conclusion

In this thesis work, thorough experimental testing was conducted in order to explore novel routes to functionalize microcrystalline cellulose with furan-moieties, aimed for making a cellulose derived Diels-Alder CAN. First furfuryl glycidyl ether was tested using the solvent system DMAc/LiCl which led to problems with fast gelation, presumably due to a cascade reaction on the formed side groups leading to long branches. Then converting cellulose to tosyl cellulose and cellulose succinate was tested, with the goal to react the obtained products further with furfuryl amine. Neither of these routes seemed ideal though and suffered from several issues. Since applying CDI is an efficient option to make cellulose esters from a wide variety of carboxylic acids, this was investigated by first converting furfuryl amine and succinic anhydride to the corresponding succinamic acid. It was found that this specific acid is problematic however, likely related to the amine group causing an undesired ring-closing reaction. By instead using furfuryl alcohol, this problem was eliminated and was found to work very well in order to graft furan groups onto the cellulose chains.

In the developed pathway, furfuryl alcohol and succinic anhydride were first reacted forming FOBA, which then was activated with CDI before finally being reacted with cellulose in DMAc/LiCl at 70 °C for 24 h. The fully bio-based products had estimated DS-values ranging between 0.5 and 2.5 depending on the molar ratio of reagents and were characterised by FTIR and solution-state NMR spectroscopy in the mixed solvent $[P_{4444}][OAc]$ and DMSO-d_6. The thermal stability, assessed by TGA, was somewhat lower compared to the pristine cellulose, but was most importantly higher than the temperature where the reverse DA reaction occurs, providing the option for recycling of such a crosslinked DA network material. A bismaleimide crosslinker containing a polar and flexible spacer was synthesised, by testing and modifying a number of previously reported methods. Initial testing of forming a covalent adaptable network by combining the synthesised FOBA-cellulose with the bismaleimide showed according to FTIR that the DA reaction took place as desired. In the future, more thorough methodology development will have to be done on the network synthesis in order to make a CAN material on slightly larger scales, study the recyclability and characterise the material properties. Once all of this is done it will be possible to assess the developed material's potential as a sustainable, recyclable thermoset.

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Appendix A – Additional information on the explored cellulose modification pathways

Table A.1. The conditions used for all cellulose modification experiments and comments on the outcomes, except for the FOBA-cellulose pathway. The chemical 1,8-diazabicyclo[5.4.0]undec-7-ene is referred to as DBU in the reagents column.

Sample name	Reagents	Solvent	Conditions	Comments
AHP_cell_01	Cellulose (4.15 g), allyl glycidyl ether (3.65 g), NaOH (0.1 g) and Na_2SO_4 (1.76 g)	Deionised water (100 mL)	20 h at 44 °C	No reaction occurred, with an unchanged MCC product according to FTIR
AHP_cell_02	Cellulose (1 g), allyl glycidyl ether (1.06 g), tetrabutylammonium bromide (0.1 g) and DBU (0.05 g)	DMAc (40 mL) and LiCl (3 g)	20 h at 80 °C	Gelation occurred shortly after adding all reagents
FGE_cell_01	Cellulose (1 g), furfuryl glycidyl ether (1.43 g), tetrabutylammonium bromide (0.1 g) and DBU (0.05 g)	DMAc (40 mL) and LiCl (3 g)	20 h at 80 °C	Gelation occurred shortly after adding all reagents
AHP_cell_03	Cellulose (1 g), allyl glycidyl ether (0.7 g) and DBU (two drops)	DMAc (40 mL) and LiCl (3 g)	RT	Gelation occurred shortly after adding all reagents
AHP_cell_04	Cellulose (0.5 g), allyl glycidyl ether (0.7 g) and KOH (0.69 g)	DMAc (20 mL) and LiCl (1.5 g)	22 h at 50 °C	Gelation occurred shortly after adding all reagents
Cell_furoate_01	Cellulose (0.5 g), furoic acid (1.728 g) and CDI (2.5 g)	DMAc (20 mL) and LiCl (1.5 g)	24 h at 60 °C	The reaction appeared to work, replicating a reported method (*25*)

Tosyl_cell_01	Cellulose (0.5 g), tosyl chloride (2.94 g) and Et_3N (3.12 g)	DMAc (20 mL) and LiCl (1.5 g)	24 h at 8 °C	The reaction appeared to work, but with an unknown DS
Furf_am_cell_01	Tosyl cellulose (0.5 g) and furfuryl amine (3.399 g)	DMSO (10 mL)	24 h at 100 °C	No product was isolated due to difficulties with precipitation
Succinyl_cell_01	Cellulose (1 g) and succinic anhydride (1 g)	DMSO (9 mL) and pyridine (1 mL)	18 h at 90 °C	A product was obtained with a relatively low DS according to FTIR
Succinyl_cell_02	Cellulose (1 g), succinic anhydride (0.93 g) and Et_3N (0.94 g)	DMAc (20 mL) and LiCl (1.5 g)	1 h at 30 °C	Solidification of the reaction mixture occurred relatively quickly after starting the reaction
NFSA_cell_01	Cellulose (0.5 g), N-furfuryl succinamic acid (1.824 g) and CDI (1.5 g)	DMAc (20 mL) and LiCl (1.5 g)	24 h at 60 °C	A product was obtained but with very low DS according to FTIR
NFSA_cell_02	Cellulose (0.5 g), N-furfuryl succinamic acid (3.648 g) and CDI (3 g)	DMAc (20 mL) and LiCl (1.5 g)	24 h at 70 °C	A product was obtained but with very low DS according to FTIR
NFSA_cell_03	Cellulose (0.5 g), N-furfuryl succinamic acid (6.927 g) and CDI (5.696 g)	DMAc (20 mL) and LiCl (1.5 g)	24 h at 80 °C	A product was obtained but with very low DS according to FTIR

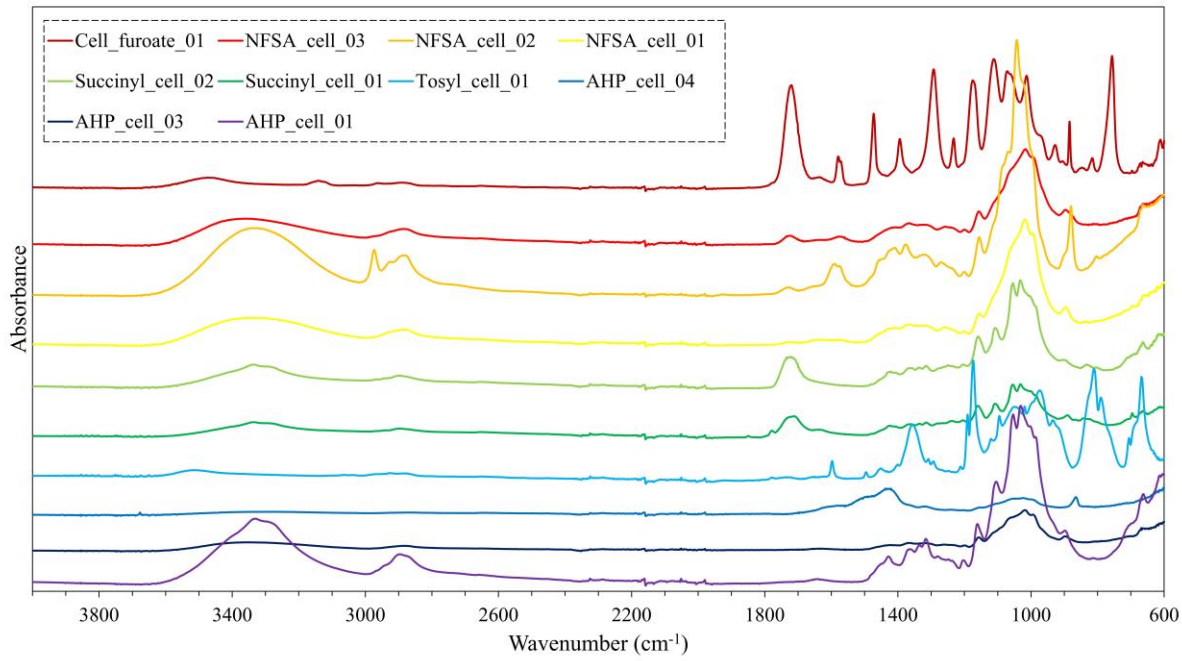

Figure A.1. FTIR spectra of the majority of the products that were obtained with the routes that were considered unsuccessful, with sample names according to the described runs in Table A.1.

Appendix B – Additional information on the FOBA synthesis

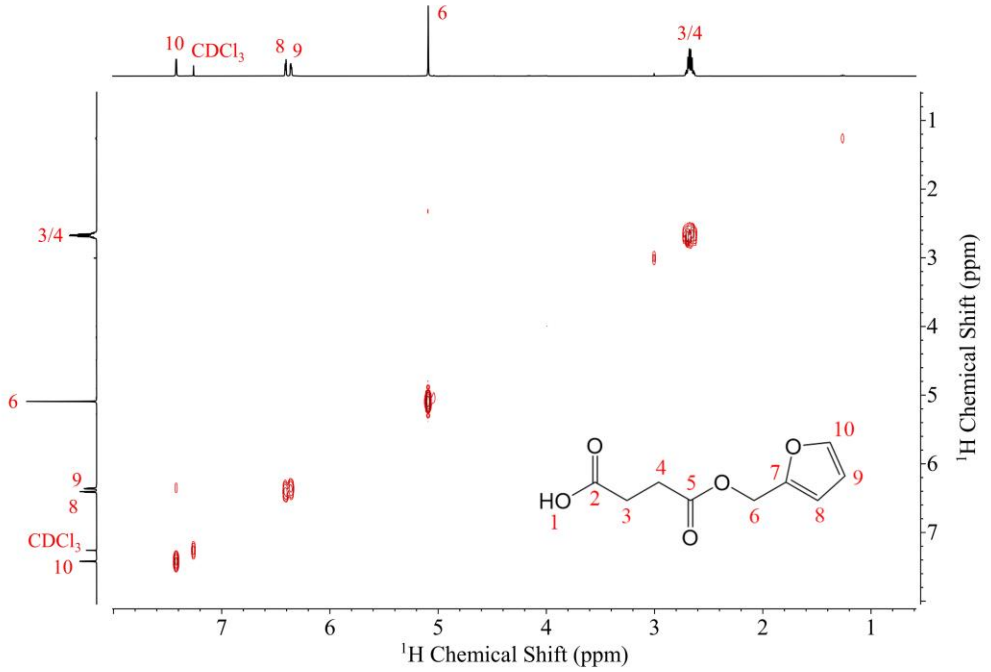

Figure B.1. COSY NMR spectrum of FOBA in $CDCl_3$.

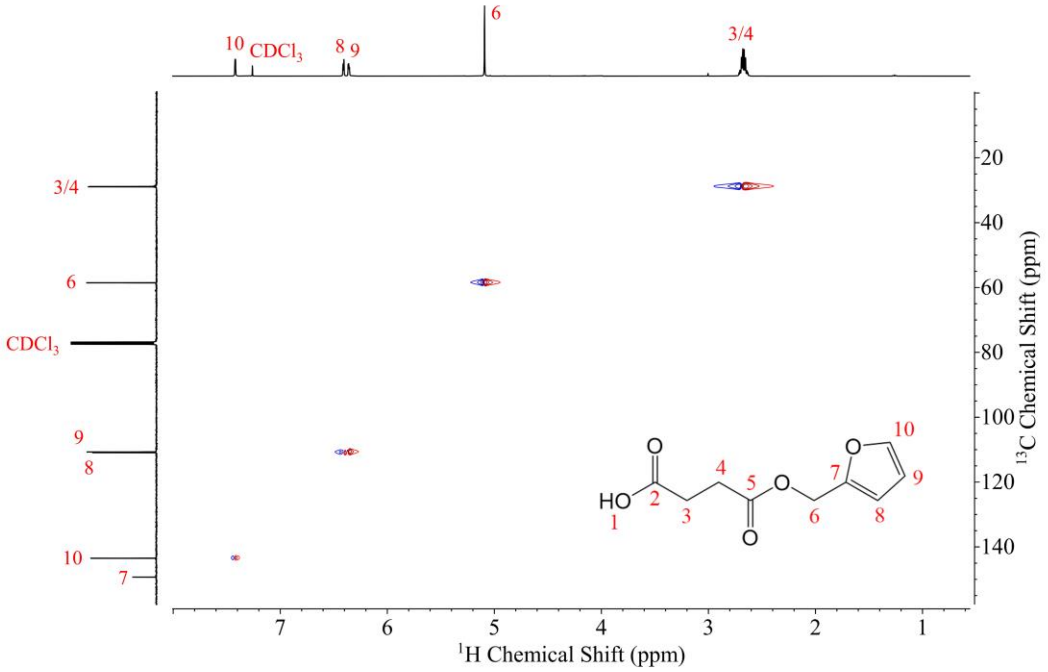

Figure B.2. HSQC NMR spectrum of FOBA in $CDCl_3$.

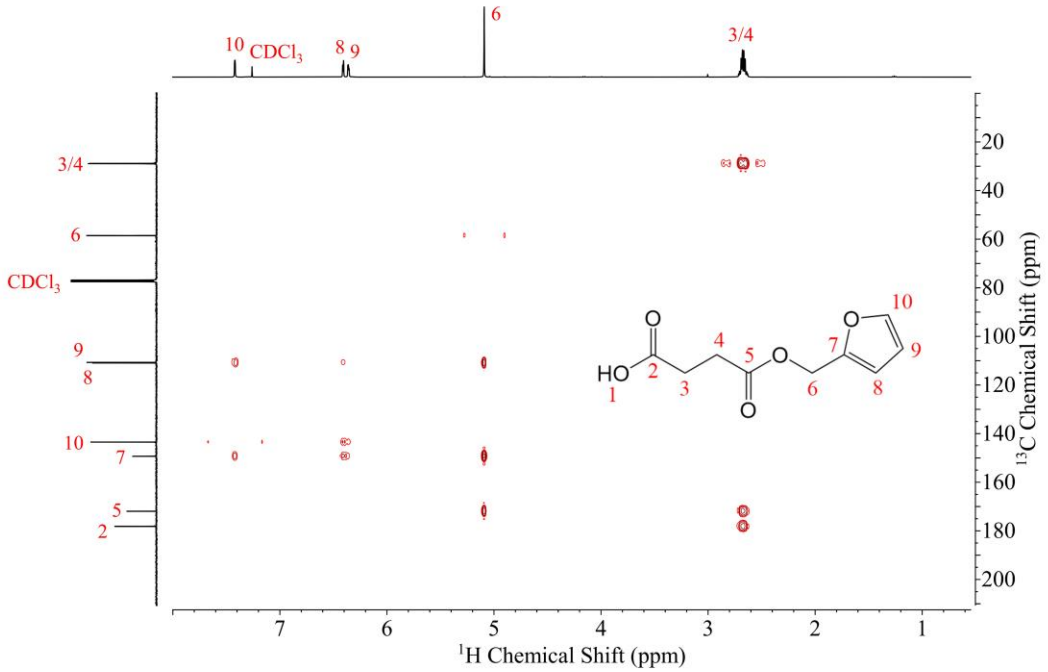

Figure B.3. HMBC NMR spectrum of FOBA in $CDCl_3$.

Appendix C – Additional information on the FOBA-cellulose synthesis

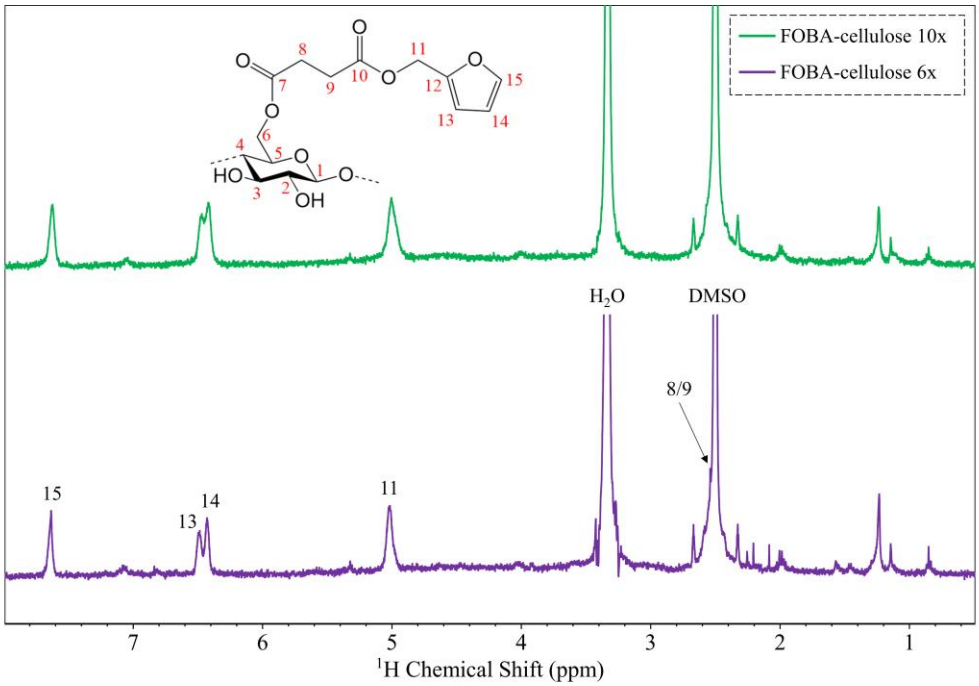

Figure C.1. ^{1}H NMR spectra of the FOBA-cellulose 6x and 10x products in DMSO-d_6.

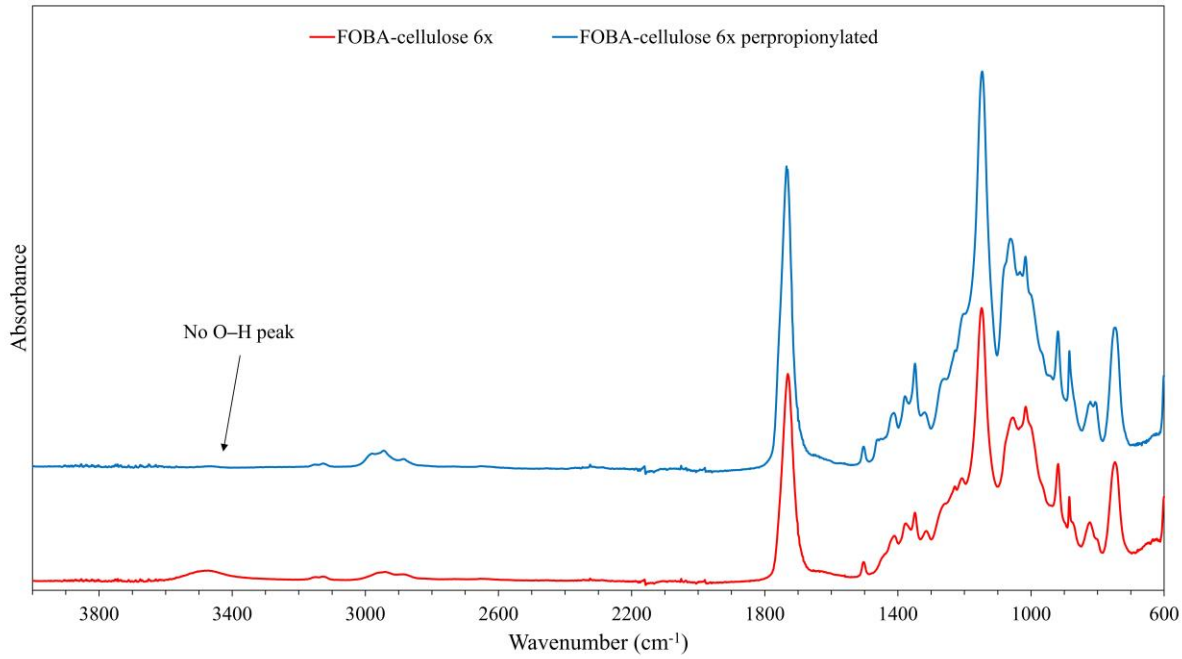

Figure C.2. FTIR spectrum of the FOBA-cellulose 6x product and a perpropionylated sample.

Calculations for DS estimation

In order to estimate the DS of the three FOBA-cellulose products, calculations were done based on the weight of the obtained products, considering that the increased mass compared to the initial amount of cellulose is due to the intended functionalization. Some assumptions are required and since the validity of these are hard to accurately control or justify, one lower estimate is given based on rather conservative assumptions and one more optimistic value is given, in order to give an idea of what the real DS-values are. The actual values are expected to lie somewhere in the range, which can be considered as rough estimates until more accurate experimental data is obtained.

In order to calculate the DS, a simple equation based on the molar mass of the functionalized AGU can be utilised, constructing a basic mass balance according to Equation 1. 0.5 g of cellulose were used in all reactions which equals 3.08 mmol of AGUs based on their molar mass of 162.14 g/mol. The FOBA side groups have a molar mass of 180.155 g/mol, taking into account the loss of a water molecule upon esterification. The equation uses an estimated yield in percent to give how many AGUs that are present. The moles of AGUs multiplicated with the molar mass, which depends on the DS, should then equal the amount of product, m_{product}, adjusted by the weight fraction of actual product, x_{product}.

$$yield \cdot 3.08 \cdot 10^{-3} \cdot (162.14 + DS \cdot 180.155) = x_{product} \cdot m_{product} \qquad (1)$$

The two main uncertainties in the calculations are the yield w.r.t. cellulose and the amount of water and impurities in the product. A more conservative estimate (DS_{low}) can be given by first assuming a 100% yield w.r.t. cellulose. This will always be lower in practice, which leads to an underestimation of the actual DS-value. Secondly, the weight fraction of impurities is assumed to be 10%. The products likely still contained a small amount of mainly water and possibly other impurities, but since the products were dried under vacuum and did not contain significant amounts of impurities according to NMR, the actual fraction of the product should be higher than 90%, which further underestimates the DS. A more optimistic value (DS_{high}) can instead be obtained by assuming a yield of 80% and only 1% of impurities. Side reactions are not directly taken into consideration in either case, but could be viewed as part of the impurity factor. The obtained DS-estimates based on Equation 1 are presented in Table C.1.

Table C.1. Estimated DS-values, assuming a 100% yield w.r.t. cellulose and 10 wt% of impurities in the product for DS_{low} and an 80% yield and 1 wt% of impurities for DS_{high}.

Product	**DS_{low}**	**DS_{high}**
FOBA-cellulose 4x	0.5	1.1
FOBA-cellulose 6x	0.9	1.6
FOBA-cellulose 10x	1.5	2.5

Appendix D – Additional information on the bismaleimide synthesis

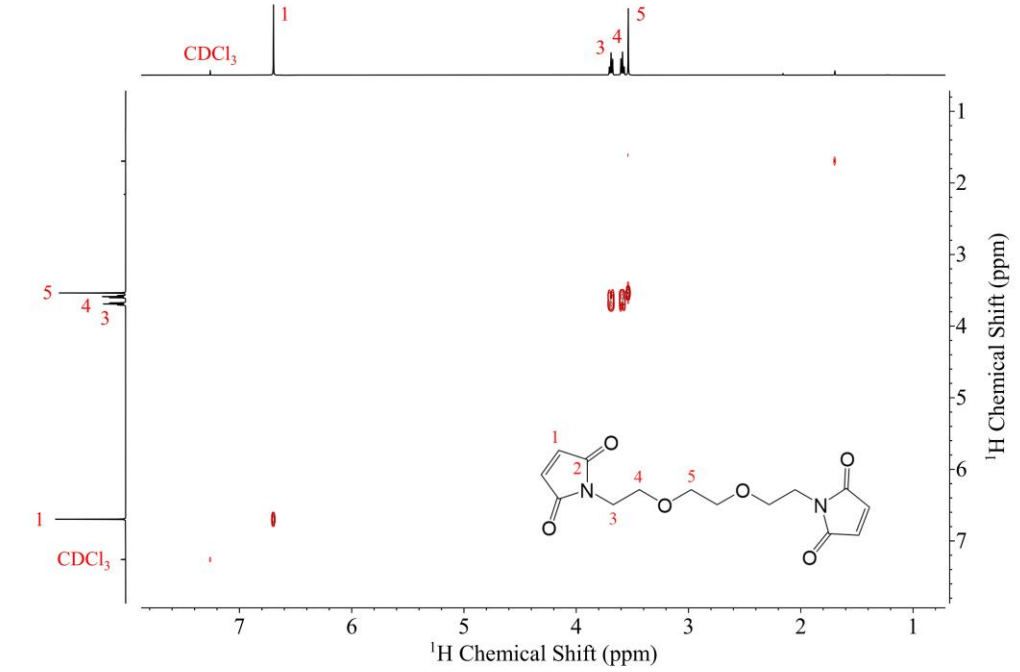

Figure D.1. COSY NMR spectrum of the bismaleimide in $CDCl_3$.

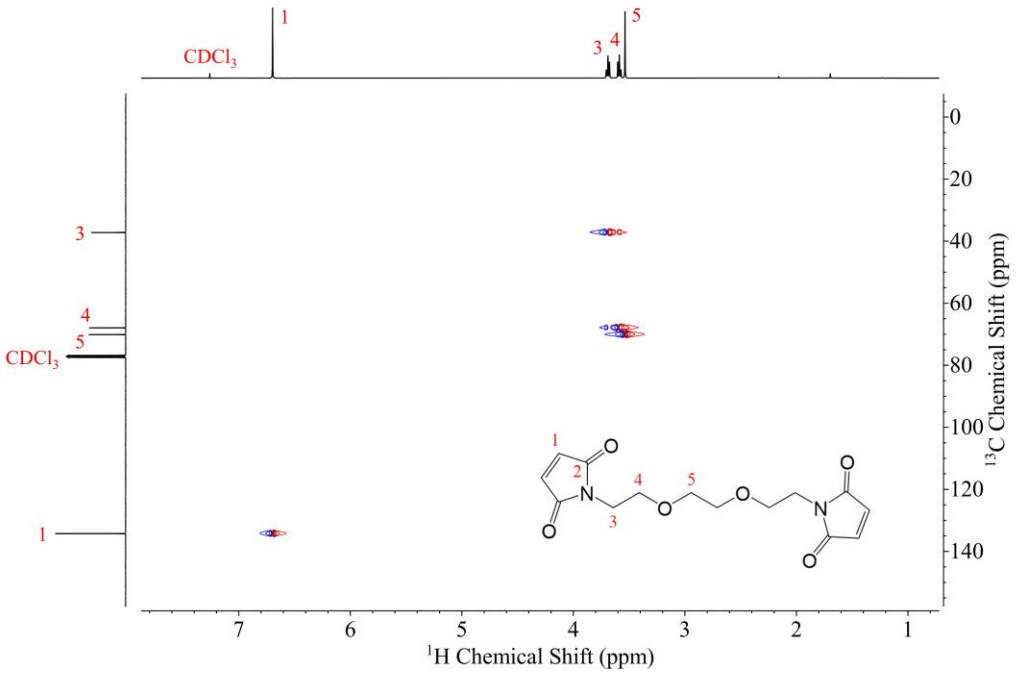

Figure D.2. HSQC NMR spectrum of the bismaleimide in $CDCl_3$.

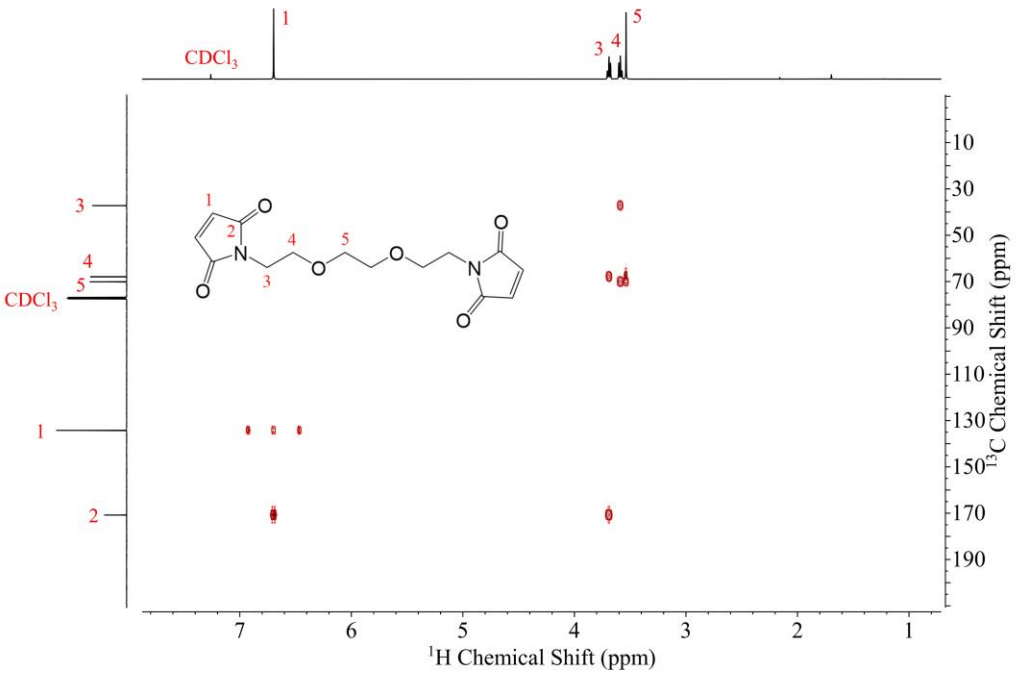

Figure D.3. HMBC NMR spectrum of the bismaleimide in $CDCl_3$.