Sustainable and efficient functionalization methods for carbohydrate polymers

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von
M.Sc. Zafer Söyler
aus
İzmir, Türkei

Dekan: Prof. Dr. R. Fischer
Referent: Prof. Dr. M. A. R. Meier
Korreferent: Prof. Dr. C. Barner-Kowollik
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To my Parents...

Mehmet and Nimet Söyler

Abstract

The ever increasing dependence of mankind on crude oil in combination with its finite availability and along with its environmental impact demonstrates many concerns associated with our current way of life. Economic and environmental considerations underline the need of comprehensive approaches towards a sustainable development, not only in the plastics industry. Indeed, as the annual plastic production erupted to 311 million tons in 2014 and is expected to double by 2035, plastics, which are mainly derived from fossil resources, are excellent candidates to implement more sustainable production strategies. Shifting the current depletive system to a more circular model in production as well as in consumption will not only improve the after-use infrastructures, but also provide benefits to our society in terms of prosperity. Biomass constitutes a very promising and advantageous alternative and renewable resource, offering a broad range of suitable organic structures. The focus of our efforts was to develop new methods and procedures that convert renewable resources to useful products in an as sustainable fashion as possible. We thus established several sustainable methods for efficient carbohydrate modification, especially employing cellulose and starch due to the their high abundance along with their distinctive properties.

Kurzzusammenfassung

Die ständig wachsende Abhängigkeit der Menschheit von Rohöl in Verbindung mit seinem begrenzten Vorkommen und seinem Einfluss auf die Umwelt stellt eine große Herausforderung dar, welche in Folge unseres heutigen Lebensstils aufgetreten ist. Daher müssen in Bezug auf nachhaltiger Wiederverwertung wirtschaftliche und umweltbezogene Aspekte berücksichtigt werden, nicht nur in der Plastik-herstellenden Industrie. Die weltweite jährliche Plastikproduktion stieg im Jahre 2014 auf 311 Millionen Tonnen und wird bis 2035 voraussichtlich auf das Doppelte anwachsen. Tatsächlich bietet Plastik, welches aus fossilem Material gewonnen wird, hervorragendes Potential in der Implementierung von Prozeduren, die nachhaltig verwertbares Material erzeugen. Indem das vorherrschende, unnachhaltige System zu einem verwertbaren und effizienten Prozess umfunktioniert wird, können enorme Verbesserungen für die Wirtschaft und unser Umwelt erreicht werden. Biomasse stellt somit eine sehr vielversprechende und vorteilhafte, alternative und erneuerbare Energiequelle dar, welche auf vielfältige Weise organisch modifiziert werden kann. Das Ziel unserer Arbeit bestand darin neuartige Methoden und Prozeduren bereitzustellen, um erneuerbare Resourcen zu nützlichen Produkten zu entwickeln, und zwar unter Beachtung der Wiederverwertbarkeit und Nachhaltigkeit. Dazu haben wir effiziente und nachhaltige Techniken zur Kohlenhydrat-Modifikation etabliert, insbesondere in Bezug auf Cellulose und Stärke, welche in der Natur reichlich vorkommen und charakteristische Eigenschaften besitzen.

Contents

1. Introduction: The need of sustainability in chemical industry

Crude oil, along with being a major source of energy, is found in every level of modern life of our society influencing economy and technology as well as politics. This once revolutionary liquid material is composed of hydrocarbons with various molecular weights and other complex organic compounds[1]. Its importance arises from the invention of the internal combustion engine, commercial aviation and, of course, application of petroleum based raw materials in the synthesis of plastics, fertilizers, solvents, adhesives, pesticides and many more[2–4].

Indeed, the story, regarding the current thread risking the future of our society, dates back over 5000 years. Oil takes the leading role in this story. It had been used for waterproofing boats, paints as well as medication thousand years a go. As an example to its early utilization, according to Herodotus and Diodorus Siculus, asphalt, more than 4000 years ago, was used in the construction of the walls and towers of Babylon[5]. Many other civilizatizatons utilized this vital source for respective applications. However, the thread arising from its consumption was not obvious in the earlier history until the industrial revolution in the 1800s which could be regarded as the beginning of the curse[2].

Scottish chemist James Young distilled light thin oil from petroleum for use as lamp oil and eventually set up a small business in this regard in 1848. His invention

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with his further endeavours gave rise to developments and advancements on the oil refining technology[6,7].

Refining technology of the crude oil, along with the influence of industrial revolution in the 19th century, had also enormous impact on the chemical industry. Heavy reliance of mankind on fossil fuels indeed started after the World War II, leading for instance to an "explosion" of plastic materials[2]. One of the early example is polystyrene (PS), which was first produced by BASF[8]. Moreover, polyvinyl chloride (PVC) was commercialized in the chemical industry in the late 1920s[8]. Polyethylene (PE) was discovered by Reginald Gibson and Eric Fawcett in 1933[8].

Further development of synthetic polymers in the chemical industry enabled the production of versatile polymeric structures with highly tunable properties with a broad range of applications, including construction materials, light weight engineering plastics, coatings, adhesives, packaging materials and many more. Consequently, today, we are living in a plastic age, since they are currently present in every level of our lives. Therefore, it would not be possible to survive or maintain a life at the current wealth status without them, since they offer high quality of life for our society in many aspects[2–4,8,9].

However, the heavy reliance on fossil-based resources has brought significant environmental challenges, since most of these materials are not degraded in nature. Recent report, called "*Rethinking the future of plastics*", published in the beginning of 2016 by World Economic Forum points to the significance of our current situation[10].

According to the report, the annual plastic production was around 15 million tons in 1964 and erupted to 311 million tons in 2014 and is expected to double by 2035. The major part of these plastics is derived from fossil resources. The growth of the plastic production is very sharp. Moreover, 95% of these materials are not recovered after first use, which also influences the economy badly. Moreover, this report revealed that at least 8 million tons of plastics leak to the ocean each year. In other words, the ratio of plastics to fish in the ocean by weight was 1:5 in 2014 and is expected to be 1:1 in 2050. Plastics can remain in the ocean hundreds of years since they are not degraded in nature. Worse is that they are transformed into microplastics in the ocean and fishes eat these microplastics. These terrifying facts point out that something needs to be done, since this highly effects the ecosystem as well. Shifting the current depletive system to a more circular model in production as well as in consumption will not only improve the after-use infrastructures, but also provide benefits to our society in terms of prosperity[10].

Substitution of non-renewable fossil resources by renewable biomass is regarded as one of the most important building blocks of green chemistry. The switch to renewable resources, for the production of commodity chemicals and bio-based polymers, will significantly help mitigate the carbon footprint of chemicals[9,11].

Regarding the sustainability, the utilization/exploitation of renewable raw materials by avoiding the use of toxic chemicals/reagents, solvents and processes for the manufacture and design of chemical products is highly required to satisfy the twelve principles of *Green Chemistry* which was described by Anastas and Warner in the early 1990s[12,13]. In fact, the term green chemistry was not firstly mentioned in this report. It existed before in the form of clean chemistry in 1980s what initially focussed on the minimization of waste in the production of fine chemicals[14]. However, after the 1990s, it has been realized that excessive consumption of fossil based products have brought deeper investigations on the solution of the problem. Along with the concepts of atom economy[15] and E factor[16] (kgs waste per kg product), the term green chemistry has become a mainstream topic in the early 1990s.

Green chemistry indeed includes three basic elements[17]:

- Minimization of waste by effective utilization of raw materials
- Avoiding the use of toxic chemicals/reagents, solvents and processes for the manufacture and design of chemical products
- Substitution of crude oil based raw materials with renewable biomass.

Interestingly, the so-called established concept of green chemistry does not comprise economical challenges. On the contrary, indeed, sustainable development is mainly framed into three building blocks; social, economic and environmental elements which are illustrated in **Figure 1.1**. So, long term sustainable developments could be established through systematic and comprehensive approaches[17].

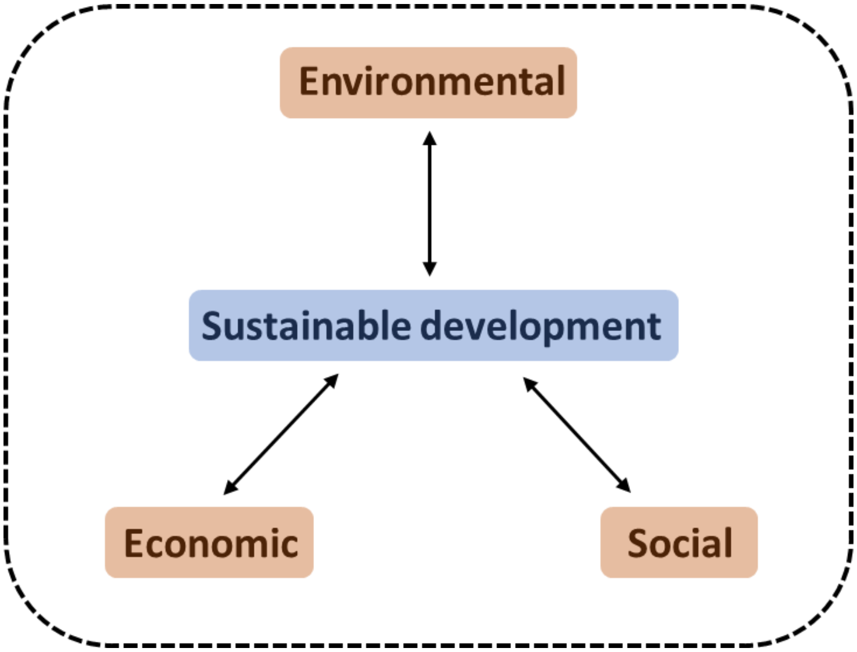


Figure 1.1 Schematic representation of the pillars of sustainable development.

Recently, there is an increasing interest in the synthesis of polymeric materials from renewable resources, mainly driven by the above-mentioned considerations. Biomass, with estimated annual global production of 10^{12} tones[18], constitutes a very promising and advantageous alternative and renewable resource, offering a broad range of suitable organic structures. Thus, intensive research is carried out on the synthesis of novel bio-based monomers and polymers[17,19].

Main components of biomass are depicted in **Figure 1.2**[17] Among them, carbohydrates takes the highest share with 75% of the biomass which can be categorized as storage carbohydrates (starch, inulin and sucrose) and structural polysaccharides (cellulose, hemicelluloses and chitin)[17].

Carbohydrates, including cellulose, starch, hemicellulose, alginate, chitin, *etc*. are the most abundant group of natural polymers on earth and are in the center of interest of various transformations and applications in science and technology, mainly due to their high abundance, biocompatibility, non-toxicity and biodegradability. Carbohydrates possess complex structures composed of different monosaccharides. While cellulose, starch and hemicellulose have only hydroxy functional groups, chitin offers amide groups and alginate has free carboxylic acid moities[20]. Cellulose and starch will be the focus of this thesis and will be explained in details in next chapters.

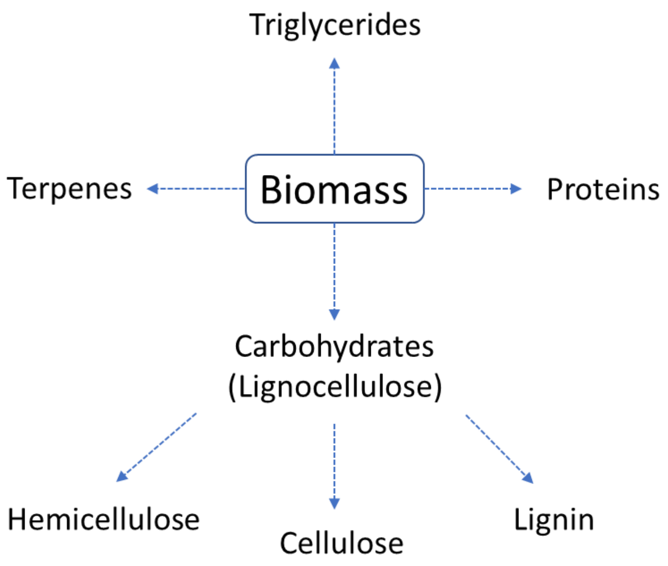


Figure 1.2 Schematic representation of primary components of biomass.

2. Cellulose – A literature review

2.1. Structure and morphology

Cellulose, a naturally occurring biopolymer, is a very important biomass component for the polymer industry, mainly due to its high availability in nature (estimated annual global production of about 1.5 x 10^8 tons) along with its distinctive properties, such as high thermal stability, biodegradability and renewability[21]. This biopolymer can be found in various sources including wood and cotton. Cellulose constitutes the largest single component of wood including hardwoods (43–47 wt%), softwoods (40–44 wt%) and bagasse (ca. 40 wt%)[22] (**see section 2.2, Table 2.2**). Owing to the structural features along with its extraordinary abundance, cellulose has been utilized in various fields of applications including textile fibres[23–30], biofuels[11,31–34], (nano)composites[35–38], or hydrogels[39,40]. Moreover, owing to its non-edible nature, this natural polymer causes no interference with food or feed uses. Indeed, its chemical utilization dates back over 150 years with the discovery of celluloid[41], a nitrocellulose used for several applications, most prominently in the film industry. Since then, tremendous strategies have been developed for the utilization of cellulose in the polymer industry. Yet, due to the recalcitrance of this naturally occurring biopolymer, cellulose still offers significant potential for extensive research and novel applications.

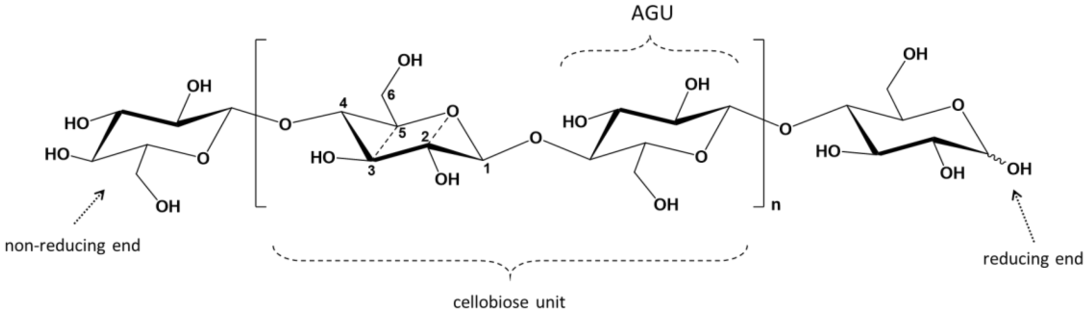
Table 2.1 Summary of DP values of different cellulose samples depending on source and treatment methods.

Type of cellulose	***DP***
Wood pulp	300-1700
Cotton and other plant fibers	800-10000
Bacterial cellulose	800-10000
Regenerated cellulose fibers	250-500
Microcrystalline cellulose	150-300

The structure of cellulose was first described in 1837 by French chemist Anselme Payen[42]. Cellulose is a highly hydrophilic homopolymer of β-1,4 linked anhydroglucose units (AGU). The degree of polymerization (DP) of cellulose is influenced by the source of the cellulose and is in the range of 150-10000, depending on the botanical source and treatment methods of cellulose (**Table 2.1**)[26]. Often cellobiose units are taken into account with a length of 1.3 nm, a disaccharide composed of two anhydroglucose units, owing to the nature of glycosidic bond. β-Configuration at the anomeric carbon of anhydroglucose results in rotation of every second AGU by 180° in order to reach the thermodynamically favored conformation, which is ignored sometimes in the schematic representations of cellulose (**Scheme 2.1**)[43]. From the perspective of a chemist, AGU is considered as repeating unit. It possesses three reactive hydroxyl groups, one primary hydroxyl groups at position C_6 and two secondary hydroxyl groups at C_2 and C_3. AGU units of cellulose exists in $^4C_1$ conformation, where all hydroxyl groups are positioned in the plane of the ring. Thus, a chair conformation of the six membered anhydroglucose ring is favored thermodynamically, where C_2, C_3, C_5, and the oxygen atom are positioned in the same plane, which is indicated by the dashed lines, and C_4 is situated above and C_1 is situated below this plane (**Scheme 2.1**)[43].

One terminus of a cellulose chain is chemically different and called reducing end[44], where a hemiacetal moiety in the *D*-glucopyranose unit is in an equilibrium with the corresponding aldehyde function. This equilibrium leads to the change of the configuration from β- into the α- position in the hemiacetal moiety and the stereochemistry at this anomeric center is thus not fixed. However, the reducing end of cellulose does not affect the overall properties of cellulose. The reducing end of cellulose may be also used for selective modification of cellulose, for instance by reductive amination. The other end of the cellulose chain is referred to as non-reducing end[44].

Each repeating unit possesses three vacant hydroxyl groups that could undergo a chemical reaction. The degree of substitution (DS) is defined as average number of hydroxyl groups per AGU that are substituted. Therefore, the DS can be in the range from 0 (none of the hydroxyl groups are substituted) to 3 (all hydroxyl groups

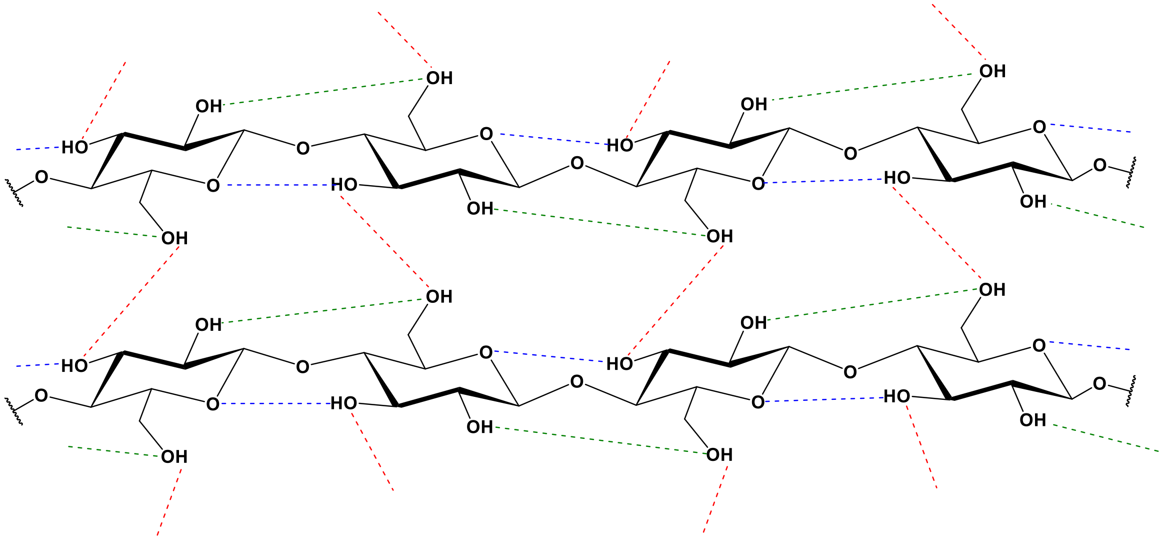


Scheme 2.1 Structural aspects of cellulose.

are substituted). The reactivity of these three vacant hydroxyl groups is different due to the structural features of cellulose. The hydroxyl group positioned at C_6 is a primary hydroxyl group and shows significantly higher reactivity compared to the other two hydroxyl groups positioned at C_2 and C_3, which are secondary hydroxyl groups[21].

The highly ordered and linear structure as well as the very complex intra- and inter- molecular hydrogen bonding network in cellulose are responsible for the insolubility of cellulose in water and common organic solvents. Moreover, cellulose is a semi-crystalline polymer that is composed of crystalline and amorphous domains[21,26]. Dissolution of the amorphous region results in partial degradation of the cellulose backbone, thereby yielding microcrystalline or nanocrystalline cellulose[45].

Cellulose exists in different crystalline allomorphs including cellulose I (I_α and I_β) for native organisms or cellulose II, III_I , III_{II}, IV_I and IV_{II} which could be seen after the treatments of cellulose[26]. I_α and I_β are the most common crystal structures of cellulose. In nature, cellulose I_α is always found together to some degree with cellulose I_β. The proportions of cellulose I_α range from 70% in primitive organisms (e.g., bacteria) to 20% in higher plants. Cellulose II is the thermodynamically most stable crystal structure of cellulose, which is for instance formed upon alkali treatments of cellulose. Chains in cellulose I are arranged in parallel fashion, while chains are arranged antiparallel in cellulose II[21]. Inter- and intra-molecular hydrogen bonds play a crucial role in this manner. Schematic representation of inter-and intramolecular hydrogen bonds in cellulose I are shown in **Scheme 2.2**[43]. The bond angle and bond length of the intermolecular hydrogen bonds between O_3 - O_5 differ in cellulose I and cellulose II[46]. Nuclear magnetic resonance spectroscopy (NMR), particularly solution ^{13}C NMR, is the most reliable technique to analyze the molecular structure of cellulose. Due to the insolubility of cellulose in water and organic solvents, special solvent systems have been developed for this purpose[47]. Dissolution strategies of cellulose will be discussed in the following sections.



Scheme 2.2 Schematic representation of intra- and inter- molecular hydrogen bonds in cellulose I. Intramolecular hydrogen bonds between O_3 - O_5 are marked in blue, intramolecular hydrogen bonds between O_6 - O_2 are marked in green, and intermolecular hydrogen bonds between O_6 - O_3 are marked in red.

2.2 Isolation of cellulose from lignocellulosic biomass: Pulping process

Lignocellulosic biomass, with the annual production of 15 –17 × 10^9 million tonnes, is the most important class of renewable feedstocks and highly promising candidate for the substitution of petroleum-based products due to the high availability along with structural diversity[48–51]. It is composed of three major polymeric components: cellulose (~40%), lignin (~20%) and hemicellulose (~25%). The chemical composition depends on the source of the lignocellulosic biomass, which could be obtained from four major resources: forest residues, agricultural residues, energy crops and cellulosic waste. **Table 2.2** illustrates some of the resources of lignocellulosic biomasses and their chemical compositions[17,52].

Table 2.2 Important sources of lignocellulosic biomasses and their chemical composition.

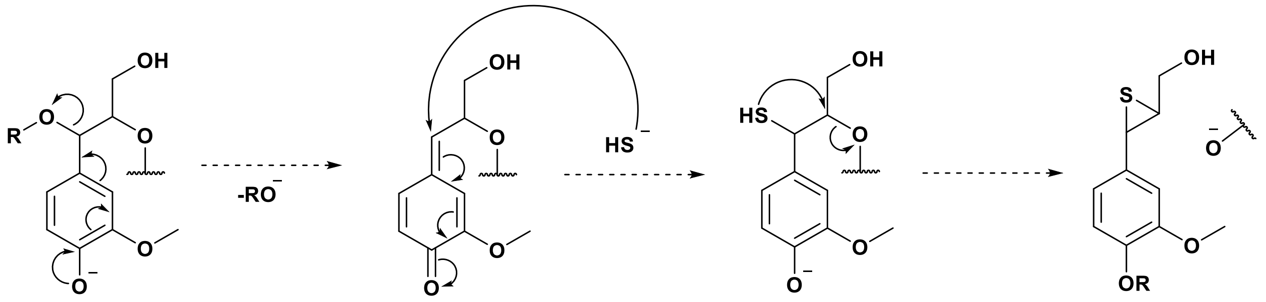
Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Eucalyptus	54.1	18.4	21.5
Pine	42.0-50.0	24.0-27.0	20.0
Wheat straw	35.0-39.0	23.0-30.0	12.0-16.0
Rice straw	29.2-34.7	23.0-25.9	17.0-19.0
Corn Stalks	35.0-39.6	16.8-35.0	7.0-18.4
Sugarcane bagasse	25.0-45.0	28.0-32.0	15.0-25.0
Grasses	25.0-40.0	25.0-50.0	10.0-30.0

Extensive studies revealed that lignocellulosic biomass has a great potential for the sustainable production of biofuels, renewable platform chemicals and various types of functional biopolymers. Thus, it can have a significant impact on the reduction of the carbon foot-print of chemicals as well as the reduction of the use of the crude oil, reducing the environmental pollution caused by fossil-based resources[53–57]. Since lignocellulosic feedstocks do not interfere with food or feed uses, their utilization in the chemical industry is advantageous over other biomass in this manner[58]. Furthermore, huge amounts of lignocellulosic wastes resulting from forestry and agriculture are already available in landfills, which constitute highly affordable renewable feedstocks for the chemical industry[59].

Due to the inherent recalcitrance of the lignocellulosic biomass, conversion of the lignocellulosic biomass into value-added chemicals and polymers still remains a big challenge[51]. Thus, highly complex and crosslinked networks of the polymeric structures have to be processed in advance by employing various pre-treatment methods, depending on the source of the lignocellulosic biomass, for the efficient degradation of the crosslinked networks. Although lignocellulosic biomass is highly available and low-priced, these pre-treatment processes increase the cost of the whole procedure for the production of chemicals[53,60,61]. Thus, extensive studies have been conducted to address this crucial challenge[52]. In this section, isolation methods of cellulose will be mentioned.

There are several strategies to extract cellulose from wood. The process for extracting cellulose from wood is usually called pulping process[21]. The most important part of the pulping process is the separation of cellulose from lignin, which is a three-dimensional crosslinked polyphenolic polymeric network containing mostly carbon-carbon and ether bonds that binds cellulose. This crosslinked network has to be degraded in order to separate cellulose from lignocellulosic biomass[62]. 98% of the wood pulp are used in the paper and cardboard industry, whereas only 2% of the pulp are utilized for the fabrication of fibers, films from regenerated cellulose or are modified *via* esterification/etherification methods to yield commercially important cellulose ester and ether derivatives (**see section 2.3**)[21]. The so-called Kraft process, which constitutes 95% of the overall produced amount among chemical pulping strategies, enables the separation and recovery of wood components in a highly efficient way. Furthermore, the resulting pulp shows a high mechanical strength[62]. Therefore, only the Kraft process will be briefly mentioned in this section.

The wood is debarked and chipped prior to chemical pulping in order to increase the surface area of the material for the efficient process. Afterwards, wood chips are cooked in an aqueous solutions of sodium hydroxide and sodium sulfides as so-called cooking chemicals. Wood chips are cooked at around 140–170 °C for 3–4 h to ensure the breakdown of the lignin network, which occurs at its characteristic aryl ether bonds (**Scheme 2.3**). Upon completion of the cooking process, lignin is degraded to its soluble poly(phenolate) derivatives and hemicelluloses become soluble in the respective aqueous solution. After washing and bleaching the precipitate, cellulose fibers are obtained at the end of the process. Upon drying, cellulose fibers can be used for paper or cardboard or used to manufacture fibers from solutions or used for functionalization[62].



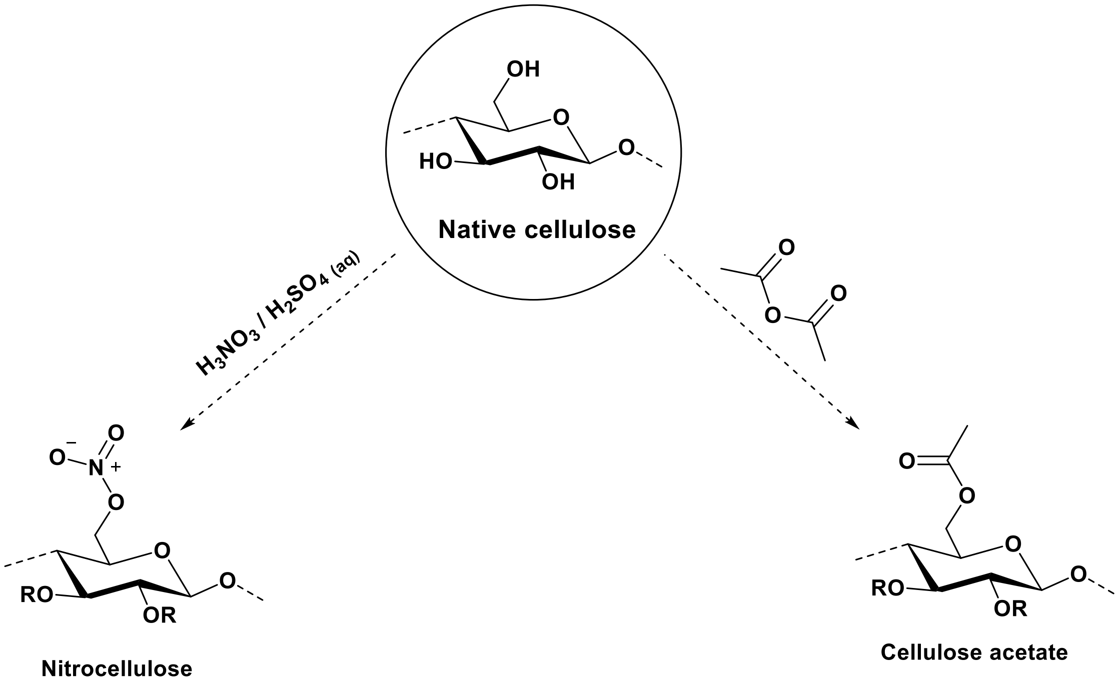
Scheme 2.3 Cleavage of aryl ether bonds during chemical pulping in the Kraft process.

2.3 Commercial cellulose derivatives

Mankind had already used cellulose for thousands of years, not only for generating fire, but also for cloths and papyrus[63]. Since the 18th century, cellulose has a profound influence on our economy, as industrial applications of cellulose started. Today, most of the commercial cellulose derivatives are manufactured *via* esterification and etherification (taking into account the total amount of production with these strategies)[21].

In 1845, the Swiss chemist Christian Friedrich Schönbein discovered cellulose nitrate more or less by coincidence, which constitutes the oldest cellulose ester derivative in the history (**Scheme 2.4**)[64]. According to the story, some amount of a mixture of HNO_3/H_2SO_4 was spilled and he used his wife's cotton apron to clean it, which then gave rise to an explosion as soon as it dried. Afterwards, cellulose nitrate, also called as nitrocellulose, with high nitrogen content was used as important explosive material during the industrial revolution[65]. The first man-made fiber, Chardonnet silk[66] was produced using this cellulose derivative. Moreover, the first man-made plastics, Parkesine[67] and Celluloid[68], were developed on the basis of this modification strategy of cellulose. The nitrogen content has a decisive influence on the application of cellulose nitrate. For example, cellulose nitrate with DS of 2.05 is used in ethanol soluble lacquers, while cellulose nitrate with a DS of 2.70 is used as guncotton, an explosive material[65].

Cellulose acetate, which is the most common commercial cellulose ester derivative, was discovered in 1865 and its commercial use was issued by a patent in 1894, which is currently manufactured on a hundred kiloton scale every year (**Scheme 2.4**)[69]. The annual worldwide production of some important cellulose



Scheme 2.4 Synthetic pathways of the most important commercially available relevant cellulose esters.

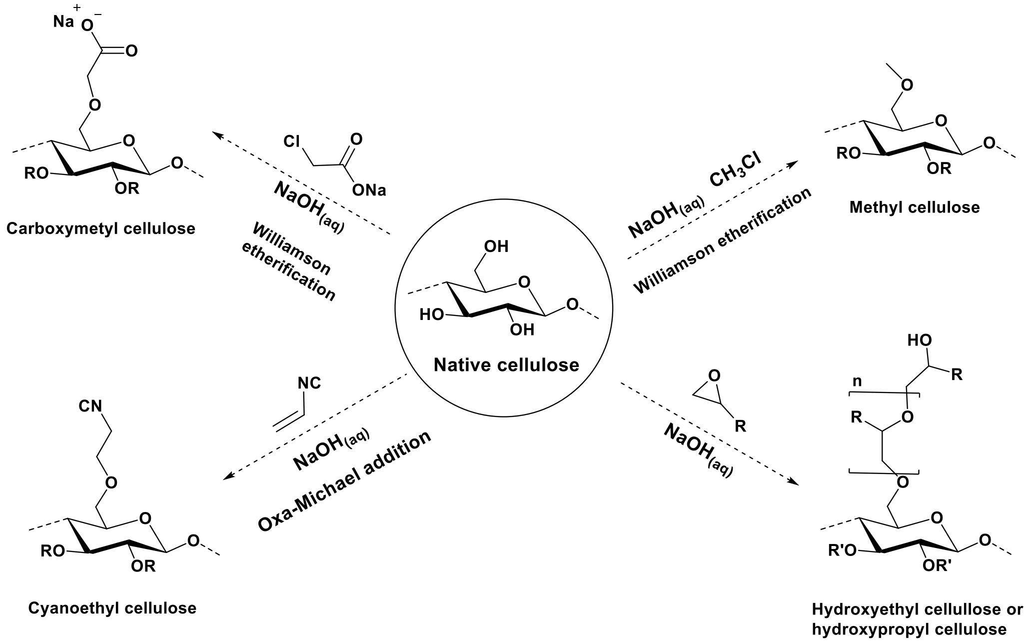
derivatives can be seen in **Table 2.3**[70]**.** The commercial manufacture of cellulose acetate or other cellulose esters is exclusively conducted under heterogenous conditions to avoid high viscosity of cellulose solutions and high costs for solvents. Furthermore, this facilitates the manufacturing process, since it is easier to isolate the product. Acetic anhydride or acyl chloride are the most common reagents for the industrial productions of cellulose acetates. Cellulose acetate is industrially manufactured with a mixture of acetic acid and acetic anhydride in the presence of sulfuric acid as catalyst (15% (w/w) H_2SO_4). The majority of commercial cellulose acetates are produced using additional methylene chloride, which enables better temperature control and helps to reduce the amount of catalyst for the acetylation process (1% (w/w) H_2SO_4)[69,71,72]. The acetylation of cellulose starts heterogeneously and ends up with a homogenous reaction mixture with increasing DS of the cellulose acetate. Acetylated cellulose becomes soluble in common organic solvents, depending on the DS. For instance, cellulose triacetate is soluble in chloroform, whereas cellulose diacetate is soluble in acetone[73]. Cellulose acetate fibers could be produced from acetone solution *via* dry spinning process[73]. Moreover, water soluble cellulose acetate with DS between 0.6 and 0.9 could only be obtained *via* homogenous modification of cellulose[74].

Table 2.3 Representation of the annual worldwide productions of some important commercial cellulose derivatives.

Product	Worldwide production (t/a)	Functional group
Cellulose acetate	900.000	$–C(O)CH_3$
Cellulose nitrate	200.000	$–NO_2$
Cellulose xanthate	3.200.000	$–CS_2Na$
Carboxymethyl cellulose (CMC)	300.000	$–CH_2COONa$
Methyl cellulose	150.000	$–CH_3$
Hydroxyethyl cellulose	50.000	$–CH_2CH_2OH$

The main application of cellulose acetate is in textile industry as textile fibers. They are also used in filters (e.g., cigarette filters) and membranes and in LCD screens[21,65,73]. Moreover, cellulose acetates were used for hydrophobic coatings that enable slow release of active ingredients for medication. They are also applied in agriculture as controlled release systems, for fragrance delivery as well as the release of stabilizers in rubbers[21,75].

Cellulose ethers are also commercially important cellulose derivatives, which are manufactured under homogeneous conditions, contrary to cellulose esters. Cellulose is generally derivatized in an alkali environment upon activation of pulp by an alkali treatment. Most of the cellulose ether derivatives are well soluble in water and not toxic, offering a broad range of application possibilities[76].



Scheme 2.5 Synthetic pathways of most important commercially available relevant cellulose ethers[21,65,73].

Cellulose ethers were first described in 1905[77] and first patents of cellulose ether derivatives were published in 1912[78]. Methyl- ethyl- and benzyl- derivatives of cellulose were already commercially available in 1935, which were mainly utilized as thermoplastics, among other applications[79,80]. There are three main strategies for the manufacture of commercially important cellulose ether derivatives, which are Williamson ether synthesis to yield methyl- or carboxymethyl- cellulose, ring opening polymerization of epoxide derivatives to yield hydroxyethyl- or hydroxypropyl- cellulose and oxa-Michael addition reactions to yield cyanoethyl cellulose. These strategies are based on a nucleophilic attack of (deprotonated) hydroxyl groups of cellulose to the mentioned reagents under alkaline conditions ($NaOH_{aq}$) (**Scheme 2.5**)[21,65,73]

Carboxyl methyl cellulose, which was first reported in 1918 and was already commercially available in the early 1920s, is the most common ionic cellulose ether with largest sales volumes[81–83]. It is used as a thickener in foodstuffs to adjust the desired consistency and texture. Carboxylmethyl cellulose is also utilized in pharmaceuticals as a fat-free ointment base[76]. Furthermore, methyl- and hydroxylalkylmethyl- cellulose ether derivatives play a crucial role in construction as additives in plasters. Hydroxyethyl cellulose is used as a thickener in paints[76]. Compared to the other cellulose ethers, cyanoethyl cellulose is used in the textile industry due to its resistance against mold and microbes[65].

2.4 Dissolution and functionalization of cellulose

Due to the presence of intensive hydrogen bond network, cellulose does not possess solubility in water and common organic solvents which hinders the efficient utilization of this most abundant organic material on earth. Thus, various types of solvent systems have been developed, for decades, for the homogenous utilization of cellulose after the first attempt which was described 150 years ago[84,85]. Endeavors on the cellulose dissolution had a considerable impact to the development of polymer chemistry as well. First man-made fiber Chardonnet silk[66] and first man-made plastics Parkesine[67], and Celluloid[68] could be shown as examples to the fruitful results of the reactive cellulose dissolution studies. Cellulose solvents also shed light to the structural features of macromolecules which was then honored with the Nobel prize for Herman Staudinger in 1953[86]. Today, increasing demands on new methods for the homogenous utilization of cellulose gave rise to the extensive investigations on new solvents for effective cellulose dissolution.

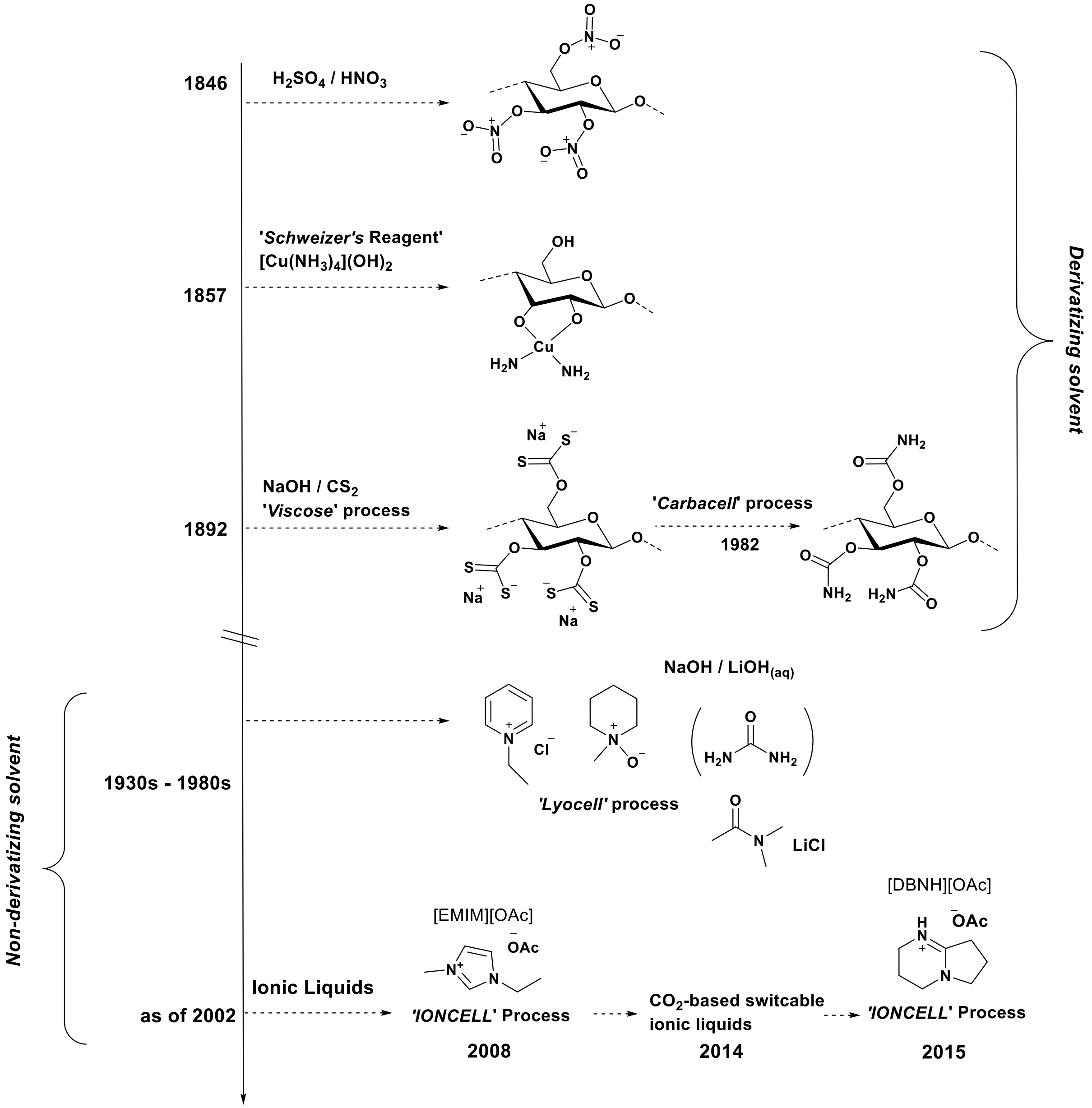
There are possible mechanisms on the disruption of hydrogen bonds system for the solvation of cellulose. In 1980, cellulose solvents were classified as four main categories by Turbak[87] which was based on interactions of cellulose with solvents. Afterwards, Philip modified the reported system and classified the cellulose solvents as follows; derivatizing, non-derivatizing, aqueous and non-aqueous solvents[88]. Nitro cellulose, which could be shown as one of the earliest examples to the dissolution studies of cellulose, was reported by Christian in 1846 by reactive dissolution of cellulose which gave rise to organo-soluble cellulose derivatives[64]. (**see section 2.3**) About 10 years later, Eduard Schweizer demonstrated the possibility of aqueous solvent such as Cuoxam to solubilize cellulose as well[89]. In this solvent system, 'Schweizer's reagent' ($[Cu(NH_3)_4](OH)_2$) was utilized which reacts with cellulose to from a complex with copper *via* bidentate interaction of the O_2 and O_3 hydroxyl residues of AGU, enhancing the solubility of cellulose in the applied solvent media. In 1892, British chemists Charles Cross, Edward Bevan, and Clayton Beadle discovered that cellulose could be dissolved by partial derivatization with carbon disulfide leading to treacle-like highly viscose yellow solution of cellulose as cellulose xanthate[90]. Pure cellulose could be regenerated upon exposure of cellulose xanthate to diluted sulfuric acid. The process was issued as patent in the same year. In 1904, scientists used this solvent strategy for the fabrication of cellulose fibers *via* spinning bath containing a mixture of sulfuric acid and a salt, known as Mueller spin bath[91]. This process afterwards called as '*Viscose'* process which is still highly important commercial cellulose derivative with annual production of 3.2 x 10^6 despite its environmental considerations due to the by-products and volatile CS_2 solvent[70]. Viscose process is still a subject of research in terms of the optimization of the process[92]. An alternative derivatizing solvent to the viscose process was developed by Kemira Oy Saeteri[93] in 1982 which involves the reaction of urea with cellulose under alkaline conditions, yielding partial formation of cellulose carbamate[94]. This process was also applied for the fabrication of cellulose fibers which had similar properties with viscose rayon. Different methods have been developed for obtaining cellulose carbamate including activation with ammonia and the use of inert organic solvents[95,96].

In 1934, low melting salts, a new class of solvents give rise to transparent solutions of cellulose without chemical modification, was reported as solvents for cellulose[97]. It did not attain enough attention for cellulose solubilization until the work reported in 2002 by Swatloski[98]. (**see section 2.4.1 for ionic liquids in details**)

In 1969, Dee Lynn Johnson of Eastman Kodak prepared *N*-methyl morpholine-*N*-oxide (NMMO) monohydrate for the dissolution of cellulose by oxidation of *N*-methyl morpholine with hydrogen peroxide which was then applied for the fabrication of cellulose fibers[99]. Its commercial potential was noted in the late 1970s and today is commercially applied methodology in large scales to manufacture cellulose fibers[100–105]. The process, which constitutes the first non-derivatizing dissolution strategy for the production of cellulose fibers from solvent, is called as *Lyocell* process and is most important alternative up to now for obtaining cellulose fibers. However, instability of NMMO solvent cause the consumption of expensive solvent. There is still intensive research to improve the process in terms of sustainability[106].

Another interesting discovery was Lithium (Li) salt based non-aqueous solvent, mixture of *N,N*-dimethyl acetamide/lithium chloride (DMAc/LiCl), discovered in 1979 by McCormick[107]. Wide range of homogenous functionalization of cellulose have been applied using this solvent mixture and is even an important research topic of today[108–111]. The solvent system also enabled the analysis of solubilized cellulose by means of ^{13}C NMR[112,113], electrospray mass spectroscopy (ESI-MS)[114], size exclusion chromatography (SEC)[115], and light-scattering techniques[116]. Various other solvent systems have been studied for the solubilization of cellulose, including mixture of dimethyl sulfoxide–tetrabutylammonium fluoride (DMSO–TBAF)[117–119].

However, most of the reported solvent mixtures lack sustainability as they are toxic and/or not recoverable. Much efforts have been devoted to establishing more sustainable alternative dissolution strategies of cellulose due to the problems associated with solvent toxicity, instability and limited recyclability. Prof. Clough pointed out in his review that high solubility, fast dissolution, easy recovery, minimum toxicity as well as chemical stability should be taken into consideration as the criteria for designing a cellulose solvent[120]. Alternative solvent systems (ionic liquids and CO_2 based solvent system) will be explained in detail in next sections (**see section 2.4.1 and 2.4.2 for details**) in these regards. The general overview of the evolution of cellulose dissolution strategies through the 19th and 20th centuries can be seen in **Scheme 2.6**[120]**.**



Scheme 2.6. Schematic representation of the evolution of cellulose dissolution strategies through the 19th and 20th centuries.

2.4.1 Ionic liquids for cellulose dissolution and derivatization

In the search of new and “greener” alternative solvents for cellulose dissolution, ionic liquids (ILs) have been comprehensively studied for a homogeneous dissolution of cellulose. ILs are described as low melting salts composed entirely of anions and cations[121–125]. The high efficiency of ILs for cellulose solubilization stems from the intermolecular interactions, due to which the hydrogen bonds in cellulose can be sufficiently disrupted by the anions and cations of the ILs. They mainly benefit from their low volatility, high thermal stability (up to 400 °C) and recyclability, along with their structural diversity, enabling them to take part in various types of homogeneous chemical conversions of biomass. Furthermore, the properties of ILs can be tuned by selective combination of cations and anions depending on the application[124–127]. Indeed, ILs were mainly considered as green solvents and electrolytes at the early stages. Nowadays, ILs have become a hot topic in multidisciplinary areas including chemistry, physics, biology and engineering. A wide range of utilizations and applications of ILs in various fields of chemistry have been developed continuously, such as gas adsorbents[128], lubricants[129], catalysts[130] and explosives[131].

Ionic liquids, firstly described by Graenacher[97] in 1934 as molten salts (i.e. *N*-ethyl pyridinium chloride in the presence of nitrogen-containing bases) were introduced as potential solvent for cellulose solubilization. However, it did not gain enough attention presumably due to the very high melting points (118-120 °C) of the pyridinium salts. In 2002, Swatloski *et al*.[98] introduced the possibility of a series of low melting (70-80 °C) imidazolium-based ILs to dissolve cellulose. In this work, they screened 1-butyl-3-methylimidazolium cations ($[BMIM]^+$) with different anions ranging from simple halide anions (Cl^-) to large, non-coordinating anions ($[PF_6]^-$) for the solubilization of cellulose. They tested cellulose-dissolving pulps, fibrous cellulose, and Whatman® cellulose filter papers for their solubilization studies. It was shown that solutions with cellulose content of 10 wt% could be obtained at 100 °C in [BMIM][Cl]. In addition to this, they increased the cellulose content up to 25 wt% by applying microwave heating in [BMIM][Cl], resulting in clear, colorless and viscous solution of cellulose. The authors pointed out that excessive heating under microwave conditions should be avoided not to induce pyrolysis of cellulose. Lower cellulose contents (5-7 wt%) were obtained using [BMIM][Br] and [BMIM][SCN] as solvents and cellulose did not exhibit solubility in $[BMIM][BF_4]$ or $[BMIM][PF_6]$. Overall, these investigations revealed that the presence of hard chloride anions is crucial for the effective disruption of the hydrogen bond network of cellulose. Moreover, the authors studied the regeneration of cellulose upon addition of water as antisolvent. Scanning electron microscopy (SEM) revealed that significant changes in the morphology was observed in regenerated cellulose when compared to the starting cellulose sample. The fibrous structure of cellulose was disturbed and changed after the regeneration. However, size exclusion chromatography (SEC) did not show a significant decrease of the degree of polymerization (DP) of cellulose after the regeneration process. Thermogravimetric analysis (TGA) revealed that regenerated cellulose exhibited lower thermal stability and higher residual mass after the decomposition step when compared to starting cellulose samples. In conclusion, research has shown that cellulose could be readily solubilized up to 10 wt% by heating and 25 wt% by microwave heating, revealing the most efficient IL, [BMIM][CI]. This work was regarded as the first report that resulted in increased interest in ILs as non-derivatizing solvents for cellulose dissolution. Thus, this pioneer research has led to the development of a countless number of ILs with wide variety of applications in carbohydrate chemistry, mainly on cellulose[124,132,133]. Only one year after, Zhang *et al.*[134] tested 1-allyl-3-methylimidazolium chloride [AMIM][Cl] for the dissolution of cellulose as well as its regeneration upon addition of antisolvent. Furthermore, Zhao *et. al.*[135] investigated six chloride and acetate based ionic liquids for the dissolution of cellulose. The most common cations and anions used today in the synthesis of ILs for cellulose dissolution are depicted in **Figure 2.1**. Cations are generally bulky, unsymmetric and organic in nature, such as imidazolium, pyridinium and pyrrolidinium, while anions may range from simple halide to large organic anions in ILs[123,124,136].

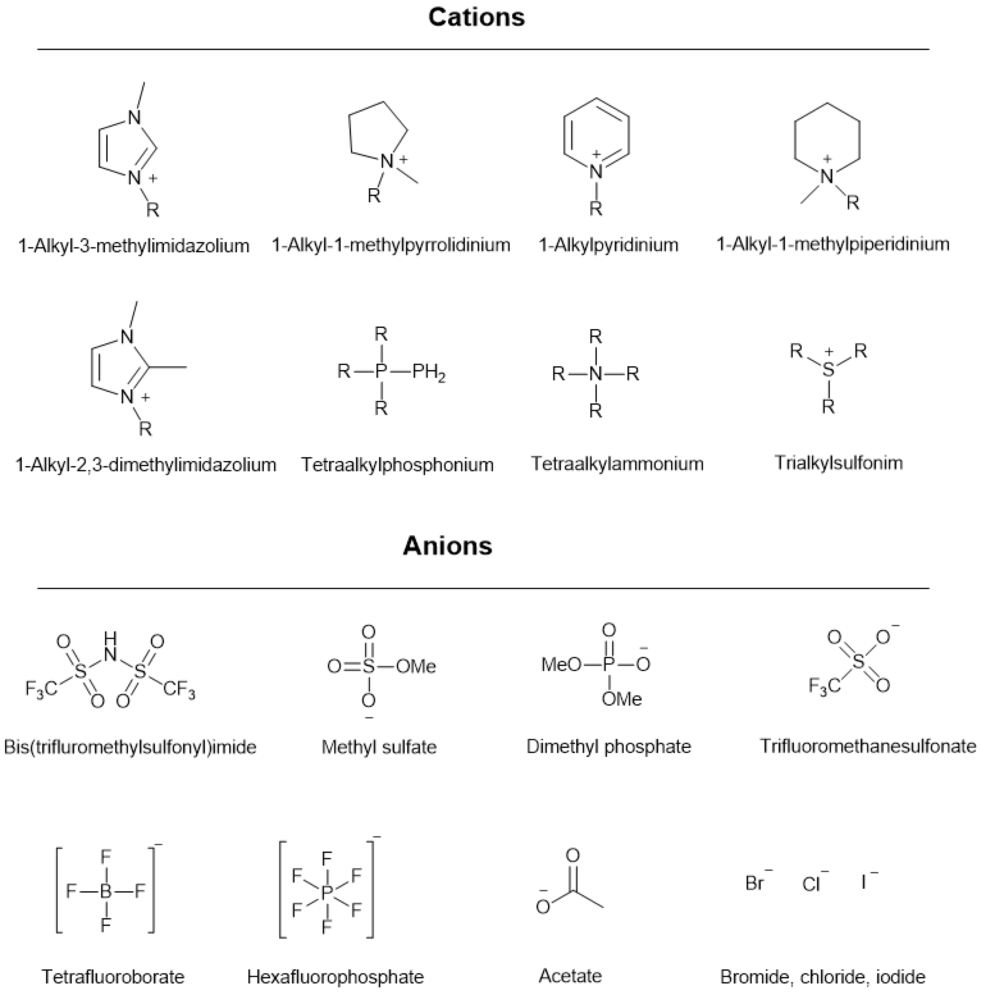
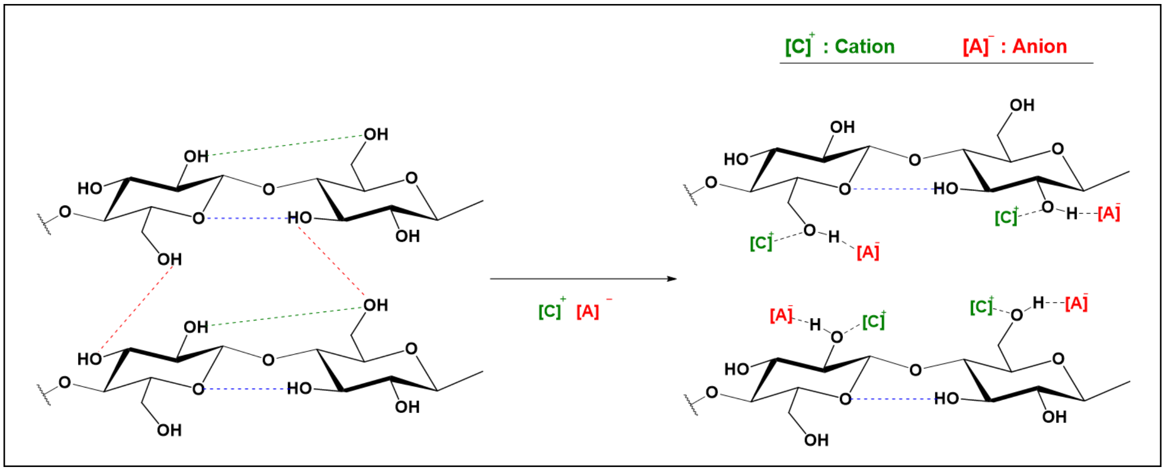


Figure 2.1 Common cations and anions used for the synthesis of ILs[124].

Various methods including nuclear magnetic resonance (NMR) spectroscopy and computer studies have been employed to understand the dissolution mechanism of cellulose in ILs, which is still under debate[136–139]. Contradictory results have been reported, especially regarding the role of cations on cellulose dissolution[136]. It is well-known that interactions between anions of the ILs and hydroxyl groups of cellulose is based on hydrogen bonding, which results in the disruption of inter- and intra- molecular hydrogen bond network of cellulose, providing the efficient solubilization of cellulose. Dissolution of cellulose is highly dependent on the basicity of the ILs. According to the studies, the role of anions is understood, while, not clear yet completely for cations[136]. The proposed dissolution mechanism of cellulose in ILs are shown in **Scheme 2.7.** Lu *et al.*[140] studied the effects of the cationic structure on the dissolution of cellulose in ILs under different conditions. The authors investigated 13 kinds of ILs with fixed anion (CH_3COO^-) but, varied the cationic structures to elucidate the factors effecting the dissolution. It was found that acidic protons of the heterocyclic rings play a crucial role in the dissolution, forming C–H···O hydrogen bonds. They claimed that van der Waals interaction of cations with cellulose are not important. The report concluded that high solubility of cellulose could be achieved by cations comprising acidic protons and cations without high electronegativity of atoms (oxygen and/or nitrogen) as well as large sized groups in the alkyl substituents.

In contrast to this, more recently, Li *et al.*[141] investigated the role of cations on the dissolution of cellulose by applying four kinds of ILs composed of saturated and unsaturated cations. Molecular dynamics simulations were applied to conceive the actual role of the cations. The results revealed that cellulose only dissolved in ILs containing cations with unsaturated heterocyclic rings. This interesting result was explained by authors considering two aspects. One was based on the structure of ILs that delocalization of electrons of the unsaturated imidazolium ring made the ILs more active for better interactions with cellulose and this caused steric hinderance for anions, enabling them to form better hydrogen bond interactions with the hydroxyl groups of cellulose. The authors also observed that steric hindrance was

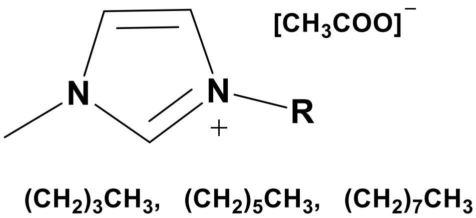


Scheme 2.7 Dissolution of cellulose in ILs[142].

introduced by saturated cations, but this resulted in weaker interactions with cellulose. The second argument is based on dynamic properties, which are highly influenced by the saturation of the heterocyclic ring of the cations. It was found that saturated cations result in a lower diffusion coefficients and higher viscosities, which led to weaker interactions between ions and cellulose. Thus, the dissolution was hindered by saturation of the cations. The authors concluded that cations also play a significant role on the dissolution of cellulose and continued suggesting that the interactions of cations with the cellulose are based on van der Waals forces. However, only heterocyclic cations were taken into account in this work. It should be pointed out that other unsaturated cations need to be investigated and further research is still required to fully understand cellulose dissolution.

More recently, Gehrke *et.al.*[143] further studied the role of carbene formation on the cations of the imidazolium based IL on cellulose dissolution by applying molecular dynamics simulations. [EMIM][OAc], regarded as one of the most powerful ILs for cellulose dissolution, was used as a solvent to understand the effect of carbene formation. Apart from negative effects of carbene formation, which was described in detail in **section 2.4.1.2**, heterocyclic carbene formation was found to have negligible influence on dissolution process. Thus, this interesting finding indicated that it could be possible to design an ionic liquid to dissolve cellulose without degrading it *via* undesired reactions of the solvent's carbene content. The authors concluded that basic anions can be applied with cations other than 1,3-dialkylimidazolium derivatives for the design of new non-derivatizing ILs for cellulose dissolution and fabrication.

Researchers have also shown that there are several other parameters such as effect of co-solvent, of water presence, of the chain length of the substituents of the cation, which significantly alter the dissolving power of ILs[144]. Xu *et. al.*[145] studied the effect of alkyl chain on the dissolving power of the ILs by applying imidazolium based ILs varying the chain length of the cation for cellulose dissolution. (**Scheme 2.8**)



Scheme 2.8 Structures of investigated ILs for cellulose dissolution[145].

The authors found that cellulose solubility increased with increasing chain length of the IL, which was associated with the fact that alkyl chains increased the acidity of hydrogen atoms H_2 and H_4 in imidazolium cation. Increased acidity of the cation facilitates the hydrogen bond formation between acidic hydrogen and hydroxyl oxygen of cellulose, thus improving the cellulose solubility. However, further increase of the chain length resulted in lower solubility of cellulose as hydrophilicity of the ionic liquid decreased, which was against cellulose dissolution.

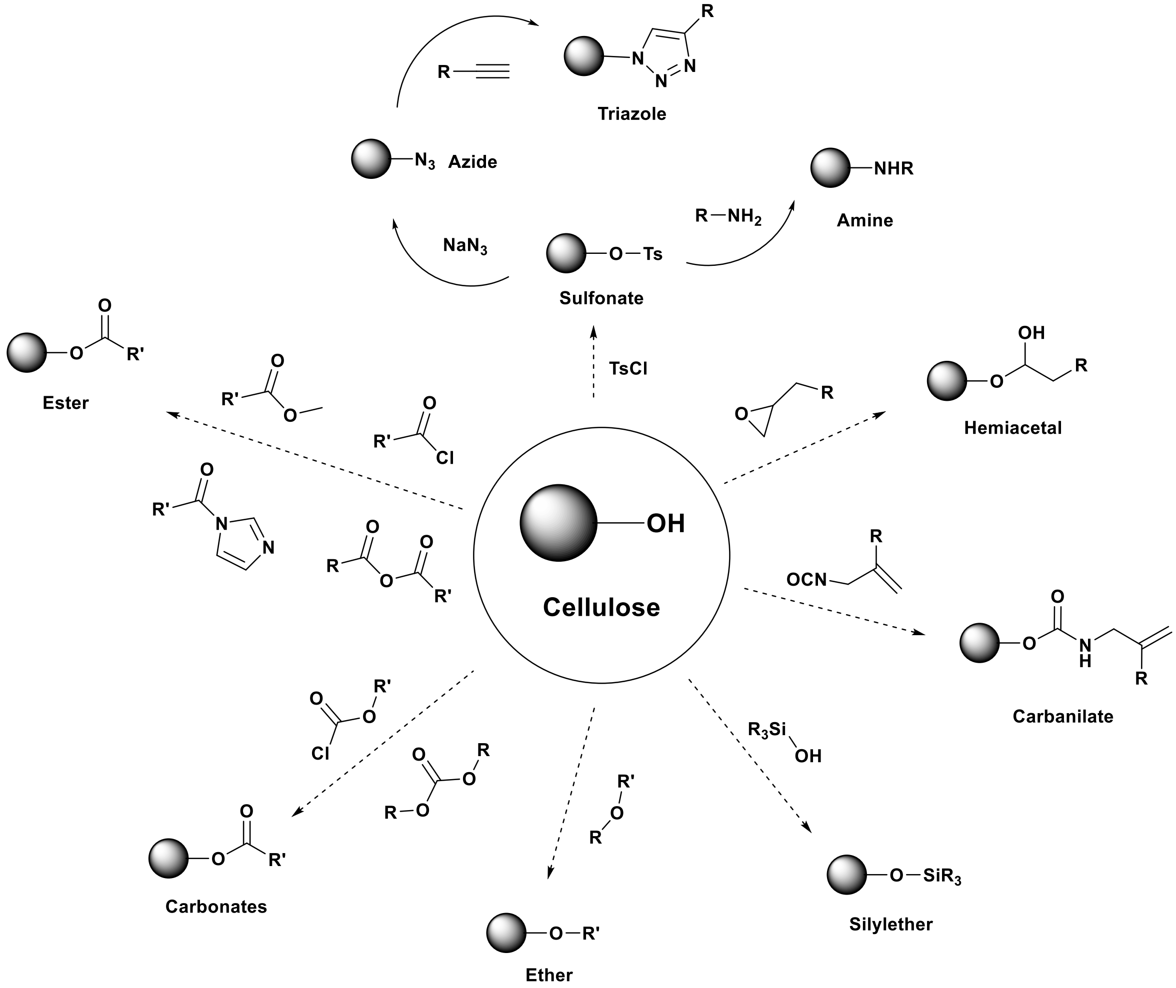
Different research groups systematically investigated the dissolving capability of imidazolium based ILs with carboxylate-based or alkylphosphate-based anions, such as $[HCOO^-]$, $[CH_3(CH_2)_{0-3}COO^-]$, $[PhCOO^-]$, $[HSCH_2COO^-]$ and $[(MeO)(R)PO_2]$, revealing that these ILs were able to solubilize cellulose under milder conditions with higher efficiency. As a result of extensive investigations, imidazolium-based ILs, such as [BMIM][Cl] or 1-ethyl-3-methylimidazolium acetate [EMIM][OAc], were found to be the most efficient, and thus the most frequently used solvents for the homogeneous functionalization of carbohydrate polymers, especially for cellulose[146–153].

Indeed, Heinze *et al.* and Sashina *et al*. reported that a pyridinium-based ionic liquid, 1-butyl-3-methylpyridinium chloride [BmPy][Cl], was more effective than [BMIM][Cl], which succeeded to dissolve 37 wt% of cellulose with a DP of ~600. However, significant pyrolysis of cellulose occurred during dissolution process. Thus, this solvent is mainly used for conversion of cellulose[154–156].

In 2006, another pioneer research has been introduced for the homogenous utilization of cellulose in a new class of distillable acid-base conjugated ILs. These ILs are based on superbases (1,1,3,3-tetramethylguanidine (TMG), 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), etc.) in combination with organic acids. These superbase-based ILs benefit from easy recovery with 99% purity simply by distillation[157–162]. Sixta and coworkers used this strategy, by using [DBNH][OAc] as the solvent, for the fabrication of cellulose fibers resulting in similar properties to Lyocell fibers[159,161,162].

Additionally, several reports have shown that certain ionic liquids display organocatalytic properties during chemical conversions of carbohydrates, depending on the anionic character of the ionic liquid[130].

2.4.1.1 Modification of cellulose using ionic liquids as solvents: selected examples



Scheme 2.9. Overview of the functionalization methods for cellulose[122].

Much effort has been devoted to the functionalization of cellulose applying a wide range of methods so far[122]. The overview of the functionalization methods can be seen in **Scheme 2.9.**

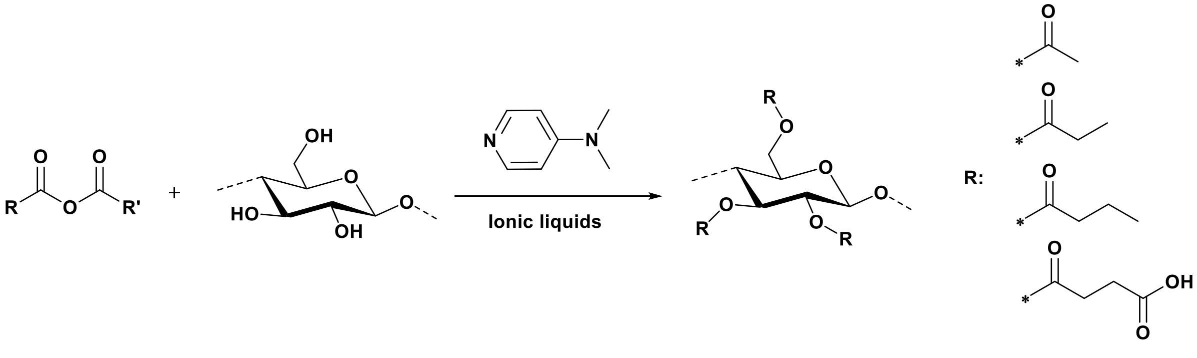
The most common techniques for the functionalization of cellulose remains the esterification and etherification, since vacant hydroxyl groups of cellulose are excellent candidates for transesterification/etherification reactions without prior modification. The obtained products find applications in various fields of chemistry, including coatings, membranes, binders, fillers, composites, explosives, optical films, or medical applications[75,76,122].

There are different pathways reported in the literature for obtaining cellulose esters, such as reactions with carboxylic acid chloride, carboxylic acid anhydride, carboxylic acid imidazolium. Various cellulose esters were synthesized including cellulose acetates, cellulose acetate propionate, cellulose sulfate, cellulose laurate and many others. Some of the cellulose ester derivatives are commercially available with wide range of applications in film, fiber, coating and pharmaceutical industries[122].

Most of the reported synthetic pathways suffer from severe drawbacks, especially in terms of environmental aspects, such as the use of toxic reagents (i.e. allyl bromides to introduce allyl groups *via* etherification, acid chlorides to introduce esters *via* transesterification) and the production of large amounts of waste (side products and stoichiometric amounts of salts), which increase the environmental impact of the procedures. In addition, most of these reagents are dangerous and require extra caution to handle in terms of safety. The focus of this report is thus not only on renewability, but also on developing new synthetic methods within the concept of green chemistry by developing novel procedures producing little to no waste and avoiding toxic chemicals at any stage[13,163]. Thus, herein, we will discuss more sustainable functionalization methods for cellulose in ILs.

2.4.1.1.1 Aliphatic/cyclic anhydrides for modification of cellulose in ILs

Anhydrides are exhaustively employed chemicals for the functionalization of carbohydrate polymers, with or without catalyst (**scheme 2.10**)[164–166]. They are examined under heterogeneous and homogeneous conditions and represent greener alternatives to acyl chlorides since only side product is a corresponding acid which could be recovered and reused for the reproduction of anhydrides[167,168]. Moreover, anhydrides do not need stoichiometric amounts of bases thus waste production is reduced. Last but not least, the synthesis of anhydrides is relative easier and greener when compared to acyl chlorides where highly toxic phosgene is used for the production of acyl chlorides. Commercial cellulose acetates are



Scheme 2.10 Overview of the acylation methods for cellulose in the presence of 4-dimethylaminopyridine (DMAP) as catalyst in ILs.

mainly obtained *via* heterogenous synthesis approach. However, homogenous productions of cellulose acetate are more favorable in terms of adjustable DS values[69]. Although ILs proved to act as transesterification catalysts, additional catalysts were required to obtain higher DS, especially for propionic and butyric anhydride, due to their lower reactivity compared to acetic anhydride. For instance, reactions with catalysts such as 4-dimethylaminopyridine (DMAP) in ILs mostly resulted in higher DS[164]. Acetic anhydride, amongst them, the simplest and most frequently investigated acylation reagent for cellulose modification since cellulose acetates have commercial value[69]. Wu and coworkers[165] used [AMIM][Cl] for the homogenous acetylation of cellulose with acetic anhydride under catalyst free conditions with DS values of 0.94–2.74. It was shown that very high conversions (2.49) were obtained in the first 8 hours at 80 °C. Applying longer reaction times (23 h) could only increase the DS up to 2.74. More recently, Jogunola *et al.*[169] studied acetylation of cellulose using distillable IL, [DBNH][OAc] at 70 °C for 30 minutes obtaining DS values of up to 2.89. The IL could be readily recovered after the modification *via* distillation. Acetylation with acetic anhydride was also used for the deconstruction of wood and fractionation of cellulose as cellulose acetate from wood[170]. In other work, the obtained cellulose acetates were used to fabricate cellulose fibers *via* wet spinning[171]. Moreover, Freitas *et al.*[172] studied the effect of DS on the properties of cellulose acetates. Overall results have shown that ILs are highly efficient media for obtaining high conversions for cellulose acetates without using additional catalysts. However, this does not apply for the synthesis of cellulose propionate and butyrate. Luan *et al.*[164] introduced propionic anhydride and butyric anhydride for homogenous modification of cellulose using [AMIM][Cl] as solvent in the presence of DMAP as catalyst. The authors also studied catalyst free conditions and obtained DS values of 1.24 and 0.46 for cellulose propionate and cellulose butyrate, respectively, due to the lower reactivity compared to acetic anhydride. Applying DMAP as catalyst improved the DS values up to 2.89 and 2.76 for propionate and butyrate, respectively.

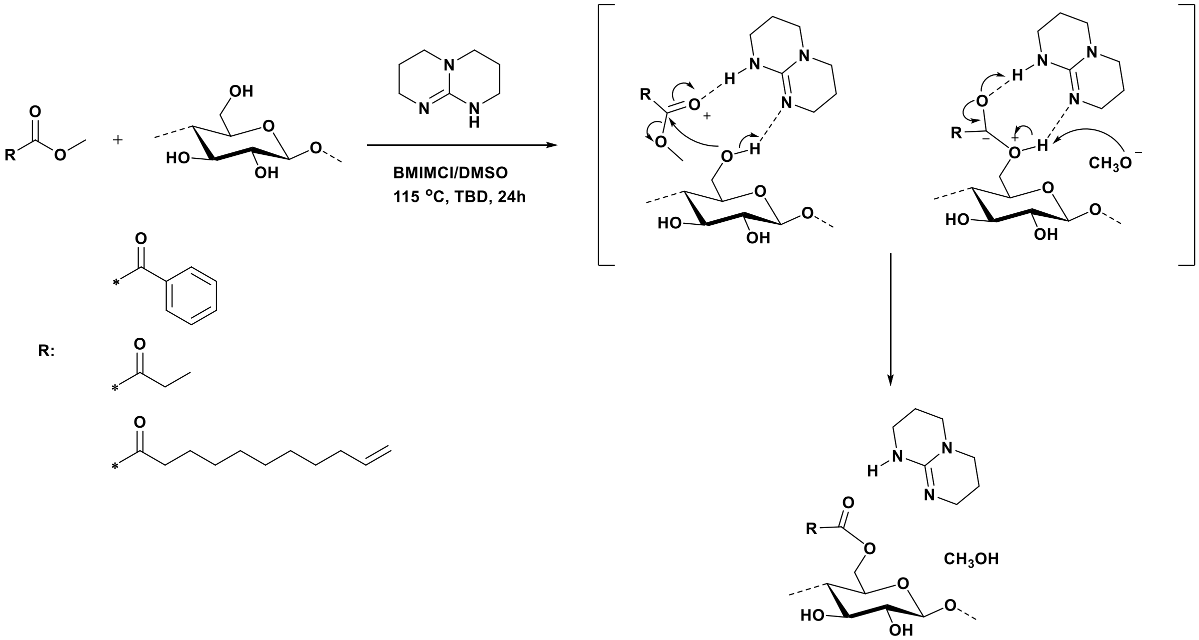
Functionalized anhydrides could also be introduced onto the carbohydrate backbone. For instance, Auzély-Velty *et al.*[173] reported the reaction between 4-pentoneic anhydride and carbohydrates. Alkene functionalized carbohydrates were further functionalized *via* thiol-ene addition employing six different thiols to obtain functional biomaterials.

The acylation of cellulose using succinic anhydride is another approach to introduce carboxylic acid moieties to the cellulose backbone in a sustainable manner. Succinic anhydride can be produced from bio-based raw materials such as sugars[174]. In addition, succinic anhydride does not lead to an undesired by-product, which is yet another contribution to the reduced environmental impact of the procedure. Extensive studies are available on the homogenous succinylation of cellulose using succinic anhydride, leading to various DS values ranging from 0.3 without any catalyst to 2.3 using catalysts such as DMAP, depending also on the reaction conditions[166,175–177]. A variety of solvent systems and catalysts have been studied for this cellulose modification so far. For instance, Yin *et al.*[177] studied a *N,N*-dimethylacetamide/LiCl solvent mixture for the succinylation of cellulose in the presence of triethylamine as catalyst, leading to DS values of up to 1.45. In addition, Li *et. al*.[166] achieved a DS of up to 2.34 in [BMIM][Cl] as solvent in the presence of

DMAP as catalyst at 100 °C. Chen *et. al.*[178] utilized the same catalyst for homogenous succinylation of cellulose in a tetra butylammonium fluoride (TBAF)/dimethyl sulfoxide (DMSO) solvent mixture, leading to a DS up to 2.11. Recently, homogenous succinylation of cellulose was also studied under catalyst free conditions. Liu *et. al.*[179,180] studied a BMIMCl/DMSO solvent mixture as well as [AMIM][Cl] for the succinylation of cellulose without catalyst, obtaining DS values of up to 0.53 and 0.22, respectively. These studies have shown that the presence of a catalyst is essential to obtain high conversions for succinylation of cellulose. Interestingly, none of these reports focused on the recovery of the solvent systems and/or the catalyst, which is of course important regarding the sustainability of the procedure.

2.4.1.1.2 Catalytic transesterification of cellulose in ILs

Recently, Meier and Barner-Kowollik *et al.*[181] developed a sustainable method for the transesterification of cellulose with different methyl esters in the presence of catalytic amounts of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) leading to a DS of up to 0.69, using [BMIM][Cl]/DMSO as solvent mixture (**Scheme 2.11**). Several methyl esters including methyl benzoate, propionate and undecenoate were investigated in the homogeneous transesterification of cellulose as an evidence of the versatility of this novel procedure. This work constitutes several advantages in terms of sustainability when compared to previous transesterification studies conducted with carboxylic acid chlorides and activated carboxylic acids (for instance, CDI coupling).



Scheme 2.11 Mechanism of the transesterification reaction between cellulose and different methyl esters in BMIMCl/DMSO solvent mixture.

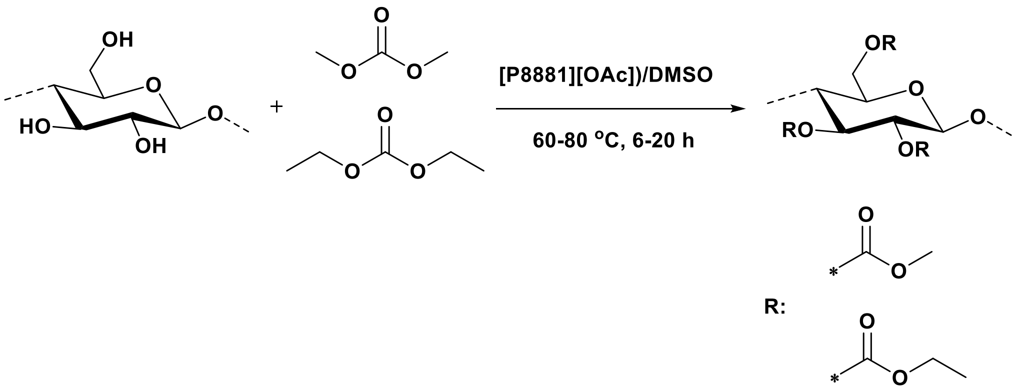
First of all, methyl esters are less reactive and thus less hazardous. Since the only side product of the transesterification is methanol, which could be recovered and reused for the reproduction of methyl esters, at least in theory, also the amount of waste is considerably lower. Stochiometric amounts of bases are furthermore avoided and thus waste formation was significantly reduced. Moreover, [BMIM][Cl]/DMSO solvent mixture could be recovered and reused for further modifications. This work also demonstrated that further modification of cellulose esterified with methyl 10-undecenoate could be accomplished *via* thiol-ene reactions. In conclusion, although it represents the first successful homogeneous catalytic reaction on cellulose, only relatively low DS were reached. More efficient and sustainable utilization of TBD was described in **section 4**

2.4.1.1.3 Environmentally friendly route to cellulose carbonates in ILs

Cellulose carbonates constitute an important class of cellulose derivatives with the possibility to introduce variable side-groups and a wide range of potential applications, such as imaging agents and delivery of therapeutics[182]. Ethyl chloroformate was the first reagent introduced for the synthesis cellulose carbonates in the presence of triethylamine as a catalyst and sacrificial base[183]. Until then, several other studies have been reported on the synthesis of carbonates of cellulose by using varied alkyl- or aryl- chloroformates in the presence of nucleophilic catalysts under different reaction conditions[184–187]. However, these reagents, due to their high reactivity, produce unexpected side products. In addition, they are produced from toxic phosgene, they are not stable under certain conditions, highly toxic themselves and they produce hydrochloric acid in the course of the reaction, which is difficult to recycle, may lead to degradation of the polymeric structure and requires stoichiometric amounts of sacrificial base for their removal *in situ*.

Dialkyl carbonates, which are regarded as halogen-free "green" reagents, were used in various transformations including alkylation, alkoxycarbonylation and transesterification reactions. They are highly promising candidates to substitute their toxic and dangerous classically used counterparts, such as phosgene, methyl halides, or alkyl chloroformates as they are considerably less toxic and limit the production of by-products. Indeed, during the transformations of organic carbonates, mainly CO_2 and alcohols are produced as by-products, which could be reused for the formation organic carbonates, at least in principle. In addition, dialkyl carbonates could be synthesized *via* an environmentally friendly route between dimethyl carbonate (could for instance be prepared from CO_2 and methanol, industrially available from urea and methanol) and alcohols in the presence of catalytic amount of TBD[188–191].

Recently, a more sustainable solution for the synthesis of cellulose carbonates was reported by King and coworkers[192], who employed dimethyl- and diethyl- carbonates for the carbonylation of cellulose in ionic liquids, leading to cellulose alkyl carbonates with moderate degrees of substitution (DS) of ~1. Reactions were performed using ionic liquid-electrolyte trioctylphosphonium acetate ($[P_{8881}]$[OAc])/DMSO or [EMIM][OAc] as solvents without the need of any catalyst (**Scheme 2.12**). Interestingly, applying catalysts such as TBD, tetrabutylammonium bromide (TBAB) or pyridine did not contribute to the alkoxycarbonylation of cellulose. The authors suggested that a thermodynamic equilibrium is already reached without the need of a catalyst under these conditions. A wide range of characterization methods were employed, including heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) NMR for the verification of methyl- and ethyl- carbonates on the cellulose backbone. Moreover, the authors prepared semitransparent and flexible films of cellulose methyl carbonate and tested its mechanical properties with tensile strength measurements exhibiting 35.3 MPa of tensile strength. Thus, this work constitutes the first report to obtain cellulose carbonates using environmentally benign reagents, dimethyl- and diethyl carbonate,



Scheme 2.12 Modification of microcrystalline cellulose with dimethyl- and diethyl-carbonate in ILs.

under catalyst free conditions. Ionic liquid-based drawbacks of the reported procedure were described in **section 2.4.1.2** in more details.

2.4.1.2 Controversial aspects of ionic liquids in cellulose chemistry

In the early years of the discovery of ILs as solvents for cellulose, they were considered as highly efficient, sustainable and non-derivatizing solvents that show sufficient chemical and thermal stability. ILs were described as environmentally benign solvents due to their very low vapor pressure. Initial studies also demonstrated that they could be recycled and regenerated after the reaction, maintaining the ability to solubilize cellulose. However, today, there are countless numbers of ILs reported in the literature as solvents for homogenous utilization of cellulose. Deeper investigations in recent studies have revealed that ILs are not completely innocent solvents for cellulose. Although some of the ionic liquids are still within the concept, considerable amount of ILs are suffering from severe drawbacks, leading to more debate over their benefits[193,194].

To start with, ILs were considered as stable at temperatures higher than 400 °C. With the discovery of new analogous of ILs, some of the EMIM ionic liquids, such as [EMIM][Br], was found to be less stable and degrades below 200 °C. However, ILs are still considered as more stable solvents for cellulose functionalization at elevated temperatures compared to DMAc/LiCl and DMSO/TBAF solvent mixtures[121].

Another deficiency of ILs is the presence of water due to their hygroscopic nature. Water free conditions for cellulose functionalization are difficult to reach in most of the cases. The presence of water creates another problematic situation during the cellulose modification. Degradation of the cellulose takes place, which is promoted by water leading to the hydrolysis of the acetal backbone. The presence of water could also disturb the cellulose functionalization leading to aggregation of the cellulose in ILs[193].

Furthermore, studies have shown that some commercially available ILs, which contain impurities, had influence on the functionalization studies of cellulose. That influence could be positive or negative, depending on the type of the modification. For instance, as one review address the same problem, sillylation of cellulose in [BIMIM][Cl] with lower purity (95 %) resulted in higher efficiency in terms of DS than the one conducted with [BIMIM][Cl] with higher purity (99 %). Thus, it was claimed that 1-methylimidazole as impurities, which is the starting material for the synthesis of dialkyl imidazolium IL, exhibited catalytic activity on the sillylation of cellulose[193,195].

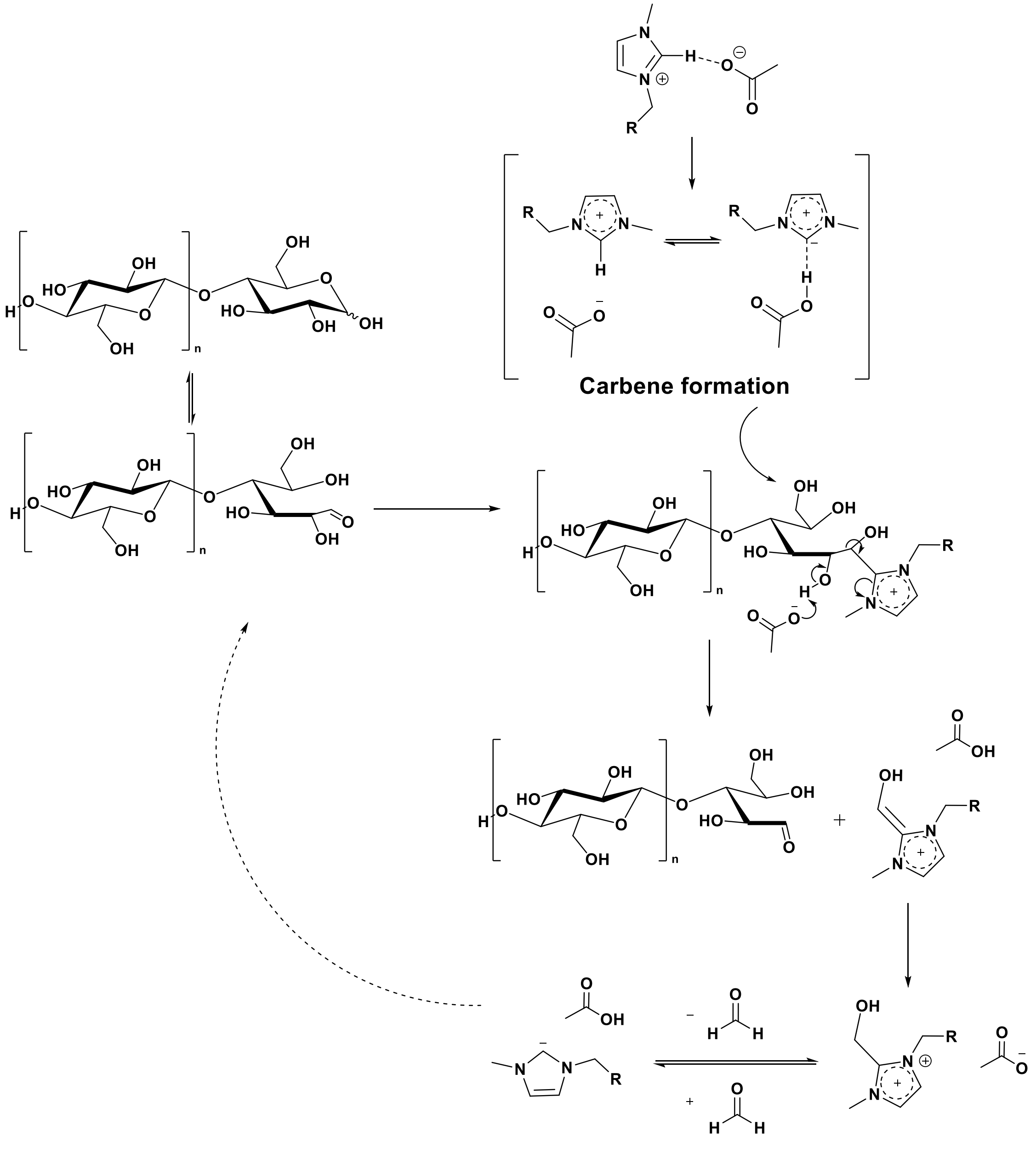
High viscosity of ILs is problematic most of the time to obtain proper and efficient homogenous media for cellulose modification. The used reagents, upon addition to the cellulose solution, should remain a part of the homogenous system to maintain the efficient media for modification, which is almost not possible with high viscosity solution resulting inhomogeneous modification of cellulose. There is often a need of co-solvents to be utilized together with ILs for achieving the efficient homogenous media for cellulose due to the high viscosity of the ILs at low temperatures especially in the case of increased cellulose concentration[193]. Co-solvents, along with decreasing the viscosity of the cellulose solution, were found to have beneficial effects on both dissolution and functionalization of cellulose. For instance, they could help the dissociation of cations and anions of the ILs, facilitating the interaction of ILs with cellulose[196,197]. DMSO is often used as co-solvent for the modification of carbohydrates as it provides a higher conversion and solubility than other suitable solvents, such as DMF and DMAc. DMF and DMAc were shown to be inefficient co-solvents, as they led to low conversions as well as lower solubility of the cellulose[198,199]. In addition to this, DMAc and DMF are more toxic than DMSO, making DMSO a good choice for cellulose modification in terms of sustainability. DMSO can be considered as being environmentally relatively benign due to its high boiling point, low vapor pressure (low volatile organic solvents emission) as well as its relatively low toxicity (LD_{50}-rat-oral (median lethal dose) = 14500 mg/kg; residual solvents limit in pharmaceuticals = 5000 ppm)[200–203]. Simple and even more sustainable solvents (i.e. acetone or alcohols) are not suitable most of the time as co-solvents for cellulose dissolution, because they do not possess the necessary co-solvent dissolving ability and they are chemically not inert in some cases. Another advantage of the usage of co-solvents for ILs is to reduce the high hydrophilicity of the environment by assisting in the proper miscibility of relatively more hydrophobic reagents with the system as well as allowing more efficient homogenous media for cellulose modification[193].

ILs were claimed to be recyclable solvents in the early years after their discovery, which is nowadays a controversial topic as well. Various efforts have been made to solve the recyclability problem of the ILs so far. However, it has not been fully solved yet due to the presence of impurities in ILs, such as amines, acids and non-volatile reagents as well as unfavorable reactivities of certain ionic liquids. Therefore, sustainable and more efficient procedures for IL recovery is still under investigation[193]. Moreover, the toxicity needs to be addressed. Therefore, low biodegradability of some ILs, such as dialkylimidazolium IL, could have bad influence on the environment, especially if the ILs are not recycled after the process. Moreover, ILs need to be synthesized in several steps and are thus quite expensive. Their more economical production are still under investigation as well[193].

Presumably, the biggest drawback of certain ILs is coming from their unfavorable reactivity under certain reaction conditions, which have bad influence both on the efficiency of the reaction and recyclability of the ILs as well as affecting the polymeric structure of cellulose. More recently, there are several studies addressing the corresponding issues in the literature. The structure of ILs are critical in this manner, especially ionic character of the ILs play crucial role according to studies. Wang *et al*.[204] reviewed the chemical stabilities of different types of the imidazolium-based ILs in different reactions and conditions, as these imidazolium-based ILs are the most popular solvents for cellulose functionalization. The authors aimed at providing a guide for a better utilization of ILs. The efficiency and stability of ILs are highly dependent on the type of the reaction and reaction conditions according to the review. Studies have shown that imidazolium ILs have different reaction sites due to their structural features. Since the imidazolium ring is electrophilic, it could undergo reactions with nucleophilic reagents such as sodium benzoate, aniline and thiophenol. Moreover, imidazolium can be deprotonated under moderate basic conditions at the weakly acidic C_2 position, which could then lead to a reaction with aldehydes, alkyl halides, CO_2, and chalcogenides. Under strong basic conditions, imidazolium ILs could decompose by opening of the imidazolium ring. Several studies have also shown that acetate ions are always a drawback due to the relatively high reactivity. Although the acetate ion was found to result in higher conversions and have beneficial effects in some cases, such as in hydroxy alkylation of cellulose[193].

Extensive investigations revealed that the polymeric structure of cellulose was significantly affected by the high reactivity of ILs against cellulose. According to the recent study reported by Gazit *et al.*[205], severe degradation of the cellulose backbone upon solubilization studies with [EMIM][Cl] and [BMIM][Cl] at 85 °C for 5 hours was observed. Degradation of the cellulose backbone was associated with acid hydrolysis, which could be easily avoided by addition of 5 wt% *N*-methylimidazole as a base to the cellulose solution in the course of the solubilization. Interestingly, Gazit *et al.* observed less degradation of the polymeric structure applying [EMIM][OAc] as solvent[205].

However, Cough *et al.*[194] investigated the decomposition pathways of glucose, cellobiose and cellulose dissolved in a variety of ionic liquids in detail using thermal and chromatographic techniques, revealing that carboxylate ionic liquids have a pronounced influence on the degradation of the cellulose and other carbohydrates. Thus, carboxylate ILs [EMIM][OAc], upon formation of *N*-heterocyclic carbenes, undergoes reaction of the C_2 carbon of the imidazolium ring with aldehyde functionality at the reducing end of the carbohydrates, resulting in an imidazolium adduct with a hydroxylated alkyl chain, which subsequently undergoes further degradation by sequential loss of formaldehyde units. (**Scheme 2.13**)[193,194] Cough *et al.* investigated the effect of other anions on the degradation including methylsulfonate, chloride and dimethyl phosphate anions. Substituting carboxylate with dimethyl phosphate anions did not prevent the degradation significantly.



Scheme 2.13 Reaction of reducing end of cellulose with dialkyl imidazolium acetate ILs.

However, no reaction was observed with a model compound (glucose) after 24 hours at 120 °C applying chloride and methanesulfonate ILs. In addition, chloride-based ILs, among these two, showed much higher dissolving power towards cellulose. Moreover, cellulose dissolved in dialkyl imidazolium acetate was found to react with the cation of the IL, which was confirmed applying SEC of regenerated cellulose with fluorescence detector[206].

Indeed, it is worth to mention that comparison of behavior of simple sugars with cellulose in ILs is somehow incorrect completely, since cellulose possesses a much more complex structure compared to simple sugars.

Side reactions constitute another significant problem for ILs. Recent work reported by King *et al.*[192] (described in **section 2.4.1.1.3** in details), who studied alkoxycarbonylation of cellulose under homogenous conditions, observed a side reaction between acetate ILs and dimethyl carbonate, which was employed as carbonylation reagent under their reaction conditions (60-80 °C) and also during the recovery of methanol and dimethyl carbonate. The results have shown that acetate anions react with dimethyl carbonate under certain conditions to give methyl acetate, which was confirmed by ^{1}H and ^{13}C NMR. The authors claimed that this problem could be overcome by applying milder work-up conditions to avoid the cation decomposition in the system.

In conclusion, there is no doubt that ILs are excellent solvents for cellulose. Nevertheless, their chemical stability has to be taken into account. There is thus still room for systematic investigations of ILs in homogenous cellulose utilization, since the chemistry of cellulose in ILs is not completely understood yet. It is obvious that each IL should be considered individually, since different ionic liquids exhibits different behaviors towards cellulose. Moreover, interactions of IL with the reagent for cellulose functionalization should be also considered individually, since one reaction drawback could be an advantage for another reaction. More importantly, properties of ILs such as polarity, reactivity and solubility are readily tunable by permutation of cations and anions, depending on the application. Studies have also indicated that unfavorable reactivity of certain ILs, resulting in corresponding problems, makes their recovery problematic and demanding, which should be addressed in the future as well.

2.4.2 Utilization of CO_2 in homogenous cellulose utilization

Global warming is one of the major problems and is a highly recognized topic in the 21st century. CO_2 is one of the most critical chemicals responsible in this manner, which is a linear molecule with double bonds between carbon and oxygen atoms (O=C=O) and occurs in nature. It is mainly utilized in the photosynthesis of plants as a carbon source. Indeed, CO_2 is an essential chemical for earth's carbon cycle and for the life cycle of animals and plants[207,208]. However, it is a greenhouse gas (GHG) and the increase of its concentration in the atmosphere could lead to severe problems, such as rapid climate changes and constitute a major reason to the global warming[209–211]. Thus, systematic approaches and innovative solutions should be taken into consideration for the control of CO_2.

There are various sources of the CO_2 emission mainly from industries. Apart from applying policy regulations of the goverments on the CO_2 emission reduction, conversion and utilization of CO_2 is essential part of the carbon management. Conversion of CO_2 into valuable chemicals is also important for the sustainable development. Extensive studies have been continuously performed for this purpose. However, there is still a need for the development of CO_2 release in the atmosphore and I believe that this should be considered in a multidisiplinary perspective[212].

It is known that CO_2 is a weak lewis acid and its activation could be performed by inserting it in an organic molecule[213,214]. In the previous studies, the electrochemical reduction was employed in both aqueus and non-aquoues media for the activation of carbondioxide[215,216]. There are many examples describing reactions of CO_2 promoted by bases. Aminidine and guanidine bases are excellent in this context due to thier ability to capture CO_2 efficiently, which arises from their pK_a values (conjugated acids), generally higher than 23. Hindered aminidine and guanidine bases were also utilized as catalyst in reactions involving CO_2. DBU was also used as nucleophilic base in many studies, which is explained in details in previous chapters[213,214,217–219].

Iwatani *et. al.*[220] reported, for the first time, the formation of a zwitterionic adduct between CO_2 and DBU, which gave a white solid. The formation was identified by infrared spectroscopy (IR) and elemental analysis as DBU-CO_2 adduct. Afterwards, Perez *et. al.*[221] reported the fixation and subsequent transfer of CO_2 by using DBU for the synthesis of *N*-alkyl carbamates. Perez *et al.*[214] furthermore investigated some other aminidine bases such as DBU and PMDBD for the complexation studies with CO_2. They demonstrated the formation of the N-CO_2 bond, resulting from corresponding zwitterionic complexes between aminidine bases and CO_2 in the presence of water in acetonitrile (CH_3CN) as solvent, which was confirmed by ^{13}C NMR and supported by theoretical calculations. They detected rapid bicarbonate salt formation during isolation of the product by X-ray crystallography analysis due to the presence of water in the system. Endo *et al.*[222] investigated different aminidines for the same purpose, obtaining similar observation. Furthermore, Heldebrant *et al.*[223] investigated the effect of the water by employing wet and dried DBU for the complexation studies with CO_2. Interestingly, the results revealed that no reaction was observed in the absence of water. Moreover, spectroscopic data demonstrated that the isolated white stable product, which was formed when CO_2 exposed to liquid DBU in the presence of water, corresponded the formation of

$[DBUH^+][HCO_3^-]$ and not DBU:CO_2. This also indicated that there was a need of the source of acidic hydrogen (hydroxyl or amine group) for the formation of the corresponding carbonate complex.

In last decade, Jessop and coworkers[224] reported an exciting and novel solvent system based on the reversible reaction of CO_2 with an alcohol and an aminidine base to convert a non-ionic liquid to an ionic liquid. With this work, a CO_2-based smart solvent system was described for the first time that can be switched reversibly from one property upon exposure to CO_2 atmosphere to another property upon CO_2 release (i.e. by nitrogen or argon flow or aplication of reduced pressure to remove the CO_2). The concept afterwards facilitated many organic synthesis and isolations of the products avoiding the need of solvent removal. This methodology contributed significantly to the reduction of costs and environmental impacts of many organic reactions by eliminating the removal of the solvents at each step.

The reported methodology employed a 1:1 mixture of two non-ionic liquids; DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene) and 1-hexanol in the presence of atmospheric pressure of CO_2 at room temperature, which caused the liquid mixture to become a more viscous ionic liquid (**Figure 2.2a, b**)[224]. This solvent system could be readily converted back to the non-ionic liquid mixture by N_2 or Ar flow at room temperature. The change in the chemical structure was confirmed by ^1H NMR. Furthermore, the conversion process was found to be exothermic and to cause an increase in the viscosity of the liquid. The choice of the source of hydroxyl groups is significant, since the mixture should remain as a liquid in the media after the conversion. In this work, 1-hexyl alcohol was employed, which was then converted to the 1-hexyl carbonate anion and the protonated amidine base, resulting in a viscous liquid at room temperature. However, methanol did not show the same property after the conversion, since the methyl carbonate anion was solid at room temperature. Solvatochromic measurements revealed that the non-ionic mixture was non-polar, similar to chloroform, and miscible with organic solvents. After CO_2 exposure, the liquid became polar, similar to dimethyl formamide, and not miscible

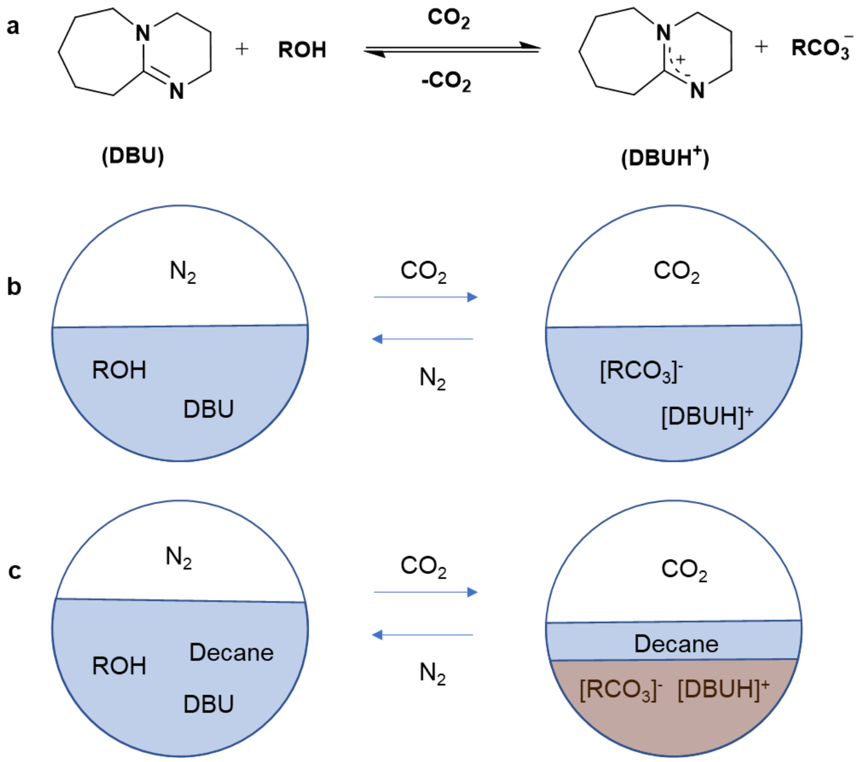
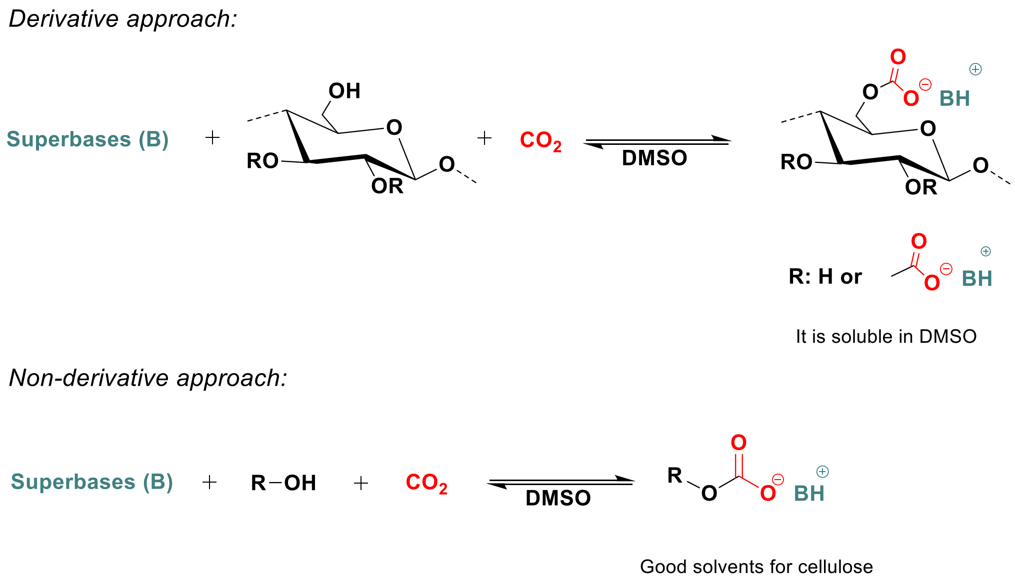


Figure 2.2. **a,** protonation of DBU upon CO_2 exposure in the presence of an alcohol and is deprotonated upon CO_2 release. **b,** polarity changes upon CO_2 exposure on the system resulting in protonated DBU and carbonated alcohol and reversed upon CO_2 release. **c,** changes on the miscibility of decane in two cases; before and after CO_2 exposure.

with chloroform or other organic solvents anymore. The polarity changes was also tested by using decane as organic solvent before and after CO_2 exposure. Decane was miscible with the liquid mixture, which afterwards became immiscible with the liquid mixture upon CO_2 exposure (**Figure 2.2c**). Consequently, atmospheric pressure of CO_2 was utilized for the reversible formation of the carbonate complex in the presence of DBU. The developed methodology is a breakthrough in terms of sustainability, since only atmospheric pressure of CO_2 was utilized under very mild conditions leading to a readily reversible smart solvent system.

More recently, this exciting solvent system found application in carbohydrate dissolution and functionalization. The concept relies on the reversible utilization of CO_2 for the dissolution of cellulose in the presence of a strong base, which was proposed by Xie *et. al.*[225] as well as by Zhang *et. al.*[226] almost simultaneously. This new solvent system succeeded to dissolve up to 8-10 wt% of cellulose. The developed methodology was also patented by Xie *et. al.*[227] This CO_2-based switchable solvent strategy can be considered a breakthrough for the solubilisation of cellulose in terms of efficiency and sustainability. Basically, two distinct strategies were reported on this solvent strategy for cellulose solubilization, a derivative[226] and a non-derivative approach[225] (**Scheme 2.14**)[228]. The derivative approach includes the direct incorporation of CO_2 into the hydroxyl groups of the cellulose in the presence of a superbase, such as DBU, resulting in a reversible carbonate complex on the cellulose backbone, in DMSO as a solvent in the solvent system, while the non-derivative approach employs an additional source of hydroxyl groups, such as ethylene glycol, for the *in situ* solubilization of cellulose. The term '*switchable*' comes from the role of CO_2 in the system as described previously. A carbonate anion is



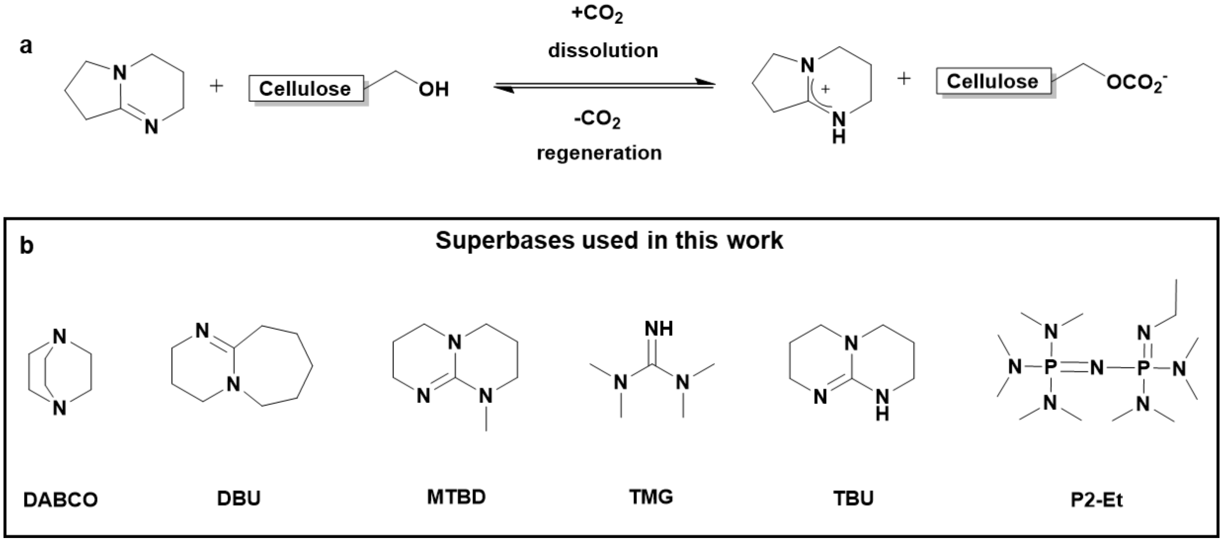
It is soluble in DMSO

Good solvents for cellulose

Scheme 2.14 Derivative and non-derivative approaches for the dissolution of cellulose using CO_2 as a reagent.

formed on the backbone of the cellulose resulting in the solubilisation of native cellulose, which can afterwards readily be regenerated by releasing the CO_2 from the system. A superbase, which is a part of the reversible complexation, could be regenerated as well upon CO_2 release, thus facilitating the recovery of a superbase from the system. Zhang *et. al.*[226] employed the derivative approach for the solubilization of microcrystalline cellulose in the presence of different superbases under different reactions conditions. They achived to dissolve up to 15 wt% of MCC in large amounts by applying 9 wt% of superbase in the presence of 2 bar of CO_2 at 40 °C. They also observed crucial role of the CO_2 in the system by testing the solubilization studies with and without CO_2. The proposed dissolution mechanism and other eligible superbases used for the dissolution are depicted in **Scheme 2.15a, b**[225,226]

They investigated the properties of regenerated cellulose, revealing a decreased crystallinity of MCC as confirmed by X-ray diffraction analysis. Regeneration of cellulose was achieved by addition of ethanol to the liquid mixture, resulting in gel-like precipitation of cellulose. The DMSO/DBN mixture was recovered and used at least thrice for the dissolution of MCC to demonstrate that the solvent system maintained its efficiency after recovery. The authors also claimed that water could also be used for the regeneration of cellulose. However, it would require more energy to recover superbase and DMSO from an aqueous mixture. Analytical methods such as elemental analysis were used to determine the purity of the regenerated cellulose. Authors also investigated other common amines, such as diethyl amine and ethanol amine, as well as natural bases such as guanine and



Scheme 2.15. a, dissolution and regeneration of microcrystalline (MCC) cellulose in the presence of DBN as super base in DMSO as a solvent. **b**, other eligible super bases that could be used for the process.

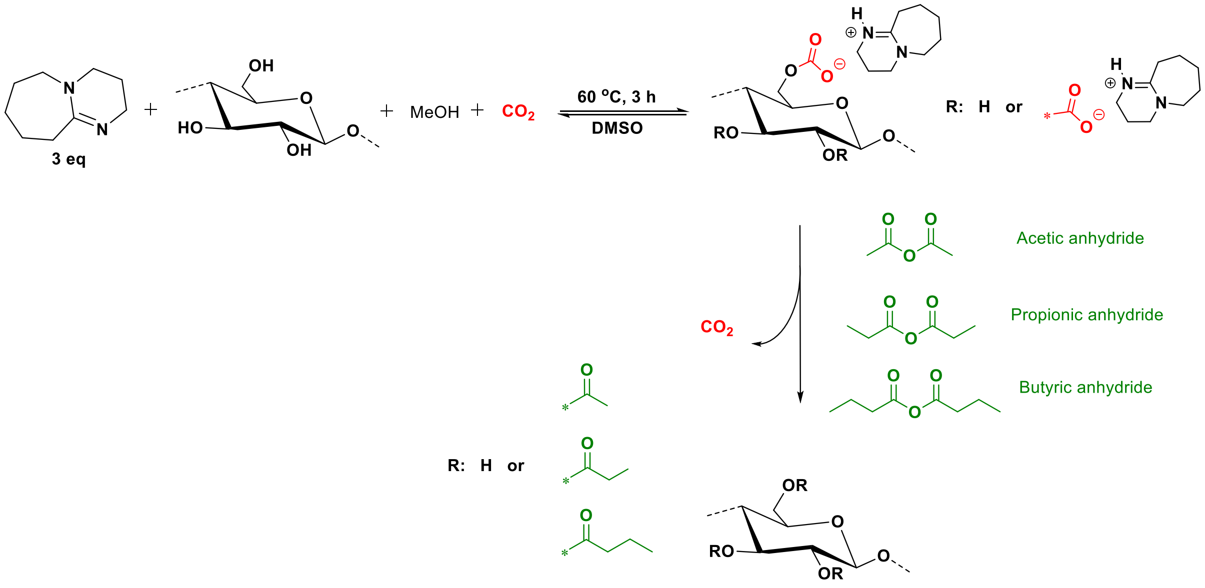
adenosine. However, these weaker bases did not show any solubility of cellulose upon exposure of CO_2, presumably due to the incapability of these bases to activate hydroxyl groups of cellulose. The results also showed that the capability of the bases to activate hydroxyl groups of cellulose is not related to their pK_a values. For instance, DBN showed similar results on dissolution of cellulose although it has a lower pKa value (18) when compared to DBU (pK_a=24), TBD (pK_a=26) or others. This outcome indicated that the structure of a superbases plays an important role in the dissolution process. The authors also claimed that stabilization of the positive charge is more favorable by delocalization on cellulose dissolution, thus P2-Et showed the highest efficiency. Cyclic non-ionic strong bases relatively showed lower reactivity when compared to non-cyclic strong bases such as TMG, suggesting that dissolution of cellulose highly depends on the structure of the base. Similar results were also observed in room temperature ILs. Consequently, a highly efficient and sustainable solvent strategy was reported, which succeeded to dissolve cellulose up to 15 wt%. Although the values are slightly lower than reported in ILs, dissolution of cellulose in this work was conducted much faster under much milder conditons by loading low amounts of superbases.

Compared to classic ionic liquids, this solvent system is more efficient, more sustainable (i.e. no multi-step synthesis is required for IL synthesis and recovery is straightforward), and cheaper, since the only chemical to be synthesized is a superbase. Moreover, solvent recovery is easier. Recently, several studies have been reported on the homogenous modifications of cellulose using this solvent system, including acylation[228] and grafting[229] from approaches. In all cases, milder reaction conditions leading to higher conversions compared to classic ionic liquids were described. Recent studies have shown that the superbase has a dual role in the system, both being part of the solvent system and acting as a catalyst in reactions. Indeed, the superbase is not fully converted into its protonated form in the solvent system according to the equilibrium constant. Therefore, the remaining free superbase maintains its catalytic activity, which explains higher conversions under mild conditions. Morever, substitution of the hydroxyl groups of cellulose upon chemical modification results in CO_2 escape from the system which also leads to the escape of a superbase, increasing the reactivity of the media on the course of the reaction[230,231].

Xie *et. al.*[225] reported the same CO_2-based switchable solvent strategy by employing the non-derivative approach for the dissolution of cellulose. Ethylene glycol was utilized as the source of hydroxyl groups for the synthesis of the ionic liquid mixture in DMSO. The methodology succeeded to dissolve up to 10 wt% of cellulose. Ionic liquid mixture was prepared using TMG as superbase in the presence of 0.5 MPa of CO_2 that was able to solubilise cellulose only in one hour at 60 °C. The authors investigated other simple alcohols including methanol and ethanol. However, they did not show full solubility of cellulose under similar conditions. Wide angle X-ray diffraction analysis of the regenerated cellulose showed that the peaks of raw MCC completely dissapeared and turned to the peaks belonging to cellulose I structure.

Yang *et. al.*[228] used this strategy for the functionalization of cellulose with acetic anhydride, propionic anhydride and butyric anhydride, in the presence of DBU, CO_2 and methanol, leading to high DS between 2.59 and 2.82. (**Scheme 2.16)**

Taking advantage of a similar switchable solvent strategy, Song *et. al.*[229] described the *in situ* grafting of *L*-lactide from cellulose by ring opening polymerization with a molar substitution (MS_{PLLA}) of poly(*L*-lactide) in the range of 0.37–5.32. This recent work demonstrated that ROP grafting was a promising method for the carbohydrate modification and resulted in a thermoplastic material with tunable T_g ranging from 220 to 80 °C, depending on the DS and MS. This strategy represents a promising sustainable approach not only for the acylation of cellulose or other carbohydrates, but also for the production carbohydrate esters in general from aliphatic, cyclic anhydrides or methyl esters with higher DS. The other significant advantage of this concept over ILs is the improved processability in terms of recycling and purification. Further investigations are still required to obtain a better understanding of the proposed mechanism and also the recycling process.



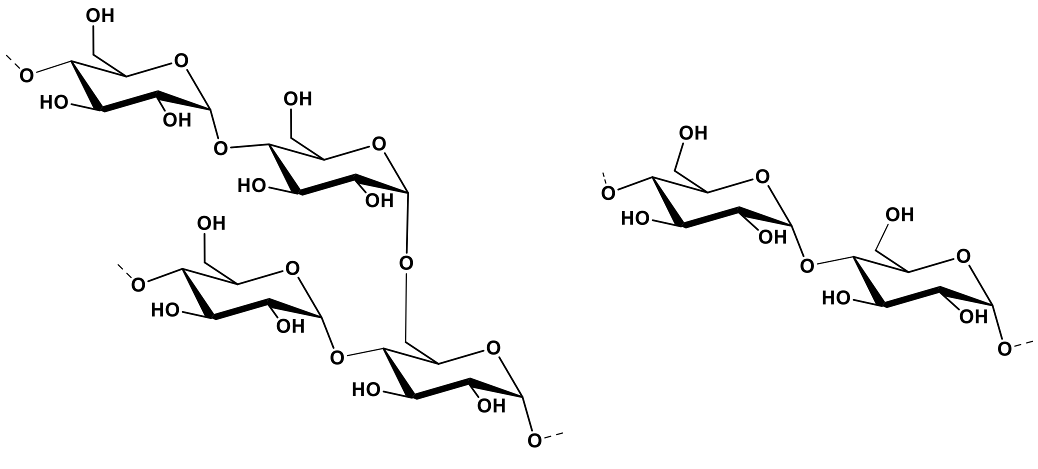
Scheme 2.16 Activation and *in situ* derivatization of cellulose in CO$_2$-based solvent system.

In conclusion, with this solvent strategy;

- The possible degradation of the polymeric structure is minimized since very mild conditions are applied for the solubilization of cellulose (10-15 min., room temperature) which also indicates the dissolving power of the strategy.
- The solvent system is cheaper since the only chemical to be synthesized is a superbase.
- Regeneration of pure cellulose could be performed simply by releasing CO_2 (air or Ar flow) from the system without the need of any anti-solvents.
- Since superbase, which is the part of the solvent system, is partly used in carbonate complex on cellulose backbone, it still maintains catalytic activity on the system which offers manifold organic conversions when the variety of superbase are considered (TBD, DBU, TMG, DBN, DABCO, etc) (this is the case when homogenous modification is on the table)

3. Starch

Starch is an attractive renewable feedstock, since it is available in large amounts and can be isolated from several raw materials including maize, wheat, pea or potato. Maize starch dominates with a share of 82% of the worldwide production[232,233]. Starch is mainly used as a source of carbon and energy in plants[234]. Unlike cellulose, starch exhibits a random-coil conformation owing to the *α*-1,4 link between the glucopyranose units[235,236]. Starch has two main components, amylose and amylopectin, which have been comprehensively studied so far[237,238]. The components of starch, amylose and amylopectin, can be seen in **Scheme 3.1**. The botanical origin of starch influences the ratio of amylose and amylopectin, which is distinctive for the properties of starch[239].



Amylopectin **Amylose**

Scheme 3.1 Structural components of starch; amylopectin and amylose.

Amylose and amylopectin significantly differ in size, structure and properties, since amylose is a linear polymer of α-1,4 linked glucopyranose units, while amylopectin is a polymer of α-1,4 linked glucopyranose units with additional α-1,6 linked glucopyranose units[240,241]. In contrast to the popular belief, amyloses possess few branches (ca. 5%). Amylopectin is the major molecule compared to amylose in most botanical sources. (e.g. 72% in maize starch and 80% in potato starch) The length of the branching units in amylopectin are also influenced by the botanical source of starch. Branch chains are found in double helical, crystalline structure and arranged in clusters. The molecular weight of amylopectin is in the range of 10^7–10^8, while amylose exhibits relatively lower values in the range of 10^5–10^6.[242]

Native starch is found in semi-crystalline granular forms which could be transformed into dispersed and amorphous molecules by heating in water or applying organic solvents such as DMSO or aqueous alkaline solutions. The conversion process of crystalline and granular structure of starch to dispersed and amorphous state is called gelatinization. Solvated starch has tendency to convert back to an aggregated, insoluble state above its glass transition temperature, particularly in amylose due to the linear structure. This is known as retrogradation and enhanced at temperatures between 0-5 °C[242].

Since starch is highly abundant, naturally occurring, non-toxic, cheap and renewable, it is highly desirable to utilize it as a renewable feedstock. Furthermore, this polysaccharide possesses imposing properties including high thermal stability, high strength and durability, as well as biodegradability. However, it has inherently several disadvantages, such as low solubility in organic solvents, brittleness, high hydrophilicity and a lack of thermoplasticity. To overcome these shortcomings, modification of starch is necessary and often achieved by substitution of its free hydroxyl groups. In this way, various functional groups can be introduced to tune its properties. Chemical modifications of starch are widely applied due to the accessible free hydroxyl groups. In this way, various kinds of novel functional groups can be introduced. Esterification[243], etherification[244], grafting[245], and crosslinking methods[246] are some of the most employed methods for the chemical functionalization of starch.

4. Catalytic transesterification of starch with plant oils

4.1 Abstract

In this work, the transesterification of maize starch with olive oil or high oleic (ho) sunflower oil was studied under homogeneous conditions in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst. Most importantly, this method used two renewable resources directly, without any pretreatment or derivatization, for the synthesis of polymeric materials with desirable properties[198]. Moreover, the solvent, oils and catalyst could be recovered with an easy work-up and reused for further modifications. The obtained fatty acid starch esters (FASEs) were highly soluble in common organic solvents and were thoroughly characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, ATR-FTIR, SEC, DSC and TGA. Degrees of substitutions (DS) were calculated using the ^{31}P NMR method and DS values of ~1.3 were obtained. DSC analysis revealed thermal transitions of the modified starches at around 80-90 °C. Films were produced from these FASEs and their hydrophobic surfaces were characterized by contact angle measurements. Furthermore, mechanical properties were examined by tensile strength measurements and showed around 40 and 80%

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elongation at break for modified maize starch and modified amylose from maize, respectively.

4.2 Introduction

As described in **section 3**, chemical modifications of starch are widely applied due to the accessible free hydroxyl groups. In this way, various kinds of novel functional groups can be introduced. Herein, the most common methods for esterification of starch as well as limitations of the current procedures in terms of sustainability will be mentioned briefly.

Fatty acid derived compounds, such as fatty acid chlorides[247], vinyl esters[248], or fatty acid imidazolides[249] were employed before for the chemical functionalization of starch, leading to different degrees of substitutions. Commonly, the film forming capacity of modified starches, especially modified with various fatty acids, is investigated, since a completely bio-based product is obtained that can potentially replace the synthetic films used in food packing[250].

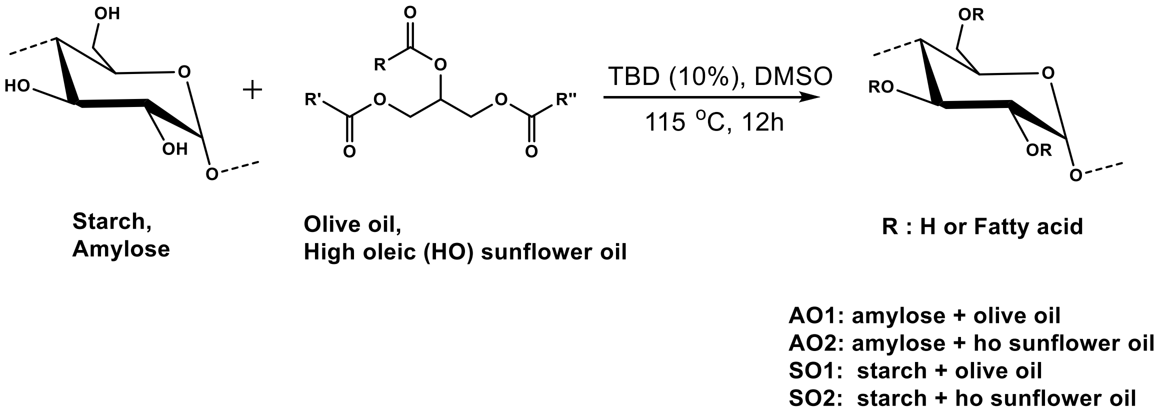
However, in these reported methods, the use of toxic chemicals as well as non-sustainable routes dominate. In order to achieve a more sustainable production, the used reagents should be non-toxic, eco-friendly and recoverable in order to be reused for further reactions. Moreover, the isolation methods should respect the targets of green chemistry and unnecessary derivatizations should be avoided[13].

Besides starch, plant oils also play a crucial role as renewable feedstocks due to the efficient, cost-effective and sustainable access of various high value products such as lubricants[251] and surfactants[252]. The functional groups present in triglycerides offer many possibilities for chemical modification, such as hydrolysis, transesterification, hydrogenation, metathesis, and many others[253–256].

1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD) is a bicyclic guanidine base, known to be an efficient catalyst for the variety of base-mediated organic conversions, such as transesterification reactions[188,257–259]. Recently, our group developed a sustainable method for the transesterification of cellulose with different methyl esters in the presence of catalytic amounts of TBD, leading to a DS (degree of substitution) of up to 0.69, using 1-butyl-3-methylimidazolium chloride/DMSO as solvent mixture[181] (**section 2.4.1.1.2**). This methodology represents the first catalytic homogeneous functionalization of cellulose and was the starting point of the herein reported investigations. Thus, we introduce hereby a highly efficient and sustainable procedure for the transesterification of maize starch. Plant oils (olive oil and high oleic sunflower oil) were directly used as transesterification reagents in the presence of catalytic amounts of TBD in DMSO as solvent. Importantly, we also investigate the recyclability and further reuse of the plant oils and TBD. This work represents a new approach for the modification of carbohydrates in terms of efficiency, renewability, and sustainability.

4.3 Results and discussion

In the light of previous findings, mentioned in the motivation of the work, we investigated TBD as catalyst for the direct transesterification of starch and amylose from maize using plant oils as transesterification reagents. Maize starch was supplied from a local supermarket and directly functionalized with olive oil (**SO1**) or high oleic sunflower oil (**SO2**), resulting in fatty acid starch esters with improved thermal and mechanical properties. Additionally, amylose from maize was also tested for the transesterification with olive oil (**AO1**) and high oleic sunflower oil (**AO2**) to investigate the differences in the resulting properties (**Scheme 4.1**). Thus, two renewable resources are reacted with each other without the need of chemical derivatization or activation. DMSO was selected as the “greenest” possible solvent for this process. Solvents considered as truly green (i.e. water, acetone, some esters or alcohols) are not suitable here, since they are chemically not inert to the



Scheme 4.1. Modification of starch and amylose with plant oil in the presence of catalytic amounts of TBD.

process and/or do not possess the necessary dissolving power and high boiling point. Other chemically suitable solvents, such as dimethylformamide or dimethylacetamide, have much higher concerns and should certainly be replaced according to several solvent selection guides. More generally speaking, DMSO can be considered as environmentally relatively benign due to its boiling point and very low vapor pressure (low volatile organic solvents emission) as well as its considerably low toxicity ($LD_{50\text{-rat-oral}}$ = 14500 mg/kg; residual solvents limit in pharmaceuticals = 5000 ppm). Last but not least, DMSO was found to be a promising candidate for the replacement of the toxic solvents such as DMF and DMAc also in other applications[200–203]. TBD is preferred as a transesterification catalyst, since it is known as highly reactive catalyst for esterification reactions[188]. Starch was dried under vacuum for 24 hours at 100 °C prior to modification since a negative effect (of residual water) on the catalytic activity of TBD was observed otherwise. The fatty acid compositions of the utilized plant oils were determined by ^{1}H NMR and the average molecular weights of the plant oils were thereof determined (**supporting information Fig. 4.S22**). Primary optimization studies of our new catalytic procedure were throughly conducted by using ATR-IR spectroscopy. The effect of concentration with respect to starch, amount of catalyst, type of the catalyst, amount of plant oil, reaction time and the reaction temperature were some of the parameters varied to optimize the reaction conditions. The optimization was performed by monitoring the intensity of the characteristic carbonyl peak of the substituted fatty acids at around 1735 cm^{-1} (**supporting information, Figures 4.S1-S7**). Spectra were normalized to the intensity of the C−O stretching vibrations of glycopyranose at 1018 cm^{-1} to allow a straighforward relative comparisons of the different degrees of modifications obtained, since the pyranose oxygen absorption is not influenced significantly upon transesterification. Absorbances in the fingerprint region at 935, 857 and 578 cm^{-1} represent the anhydro glucose ring. The peak at around 3260 cm^{-1} is attributed to stretching vibrations of the OH groups of starch, which is reduced and shifted to 3413 cm^{-1} after the modification. In addition, new peaks at 3006, 2921 and 2852, 1737 and 1150 cm^{-1} were observed and correspond to =C−H, $-CH_3$, C=O and C−O stretching vibrations of the introduced fatty acid chains, respectively (**Figure 4.1**). A complete overview over the optimization data can be found in the supplementary information. Among the investigated parameters, the effect of concentration showed a very

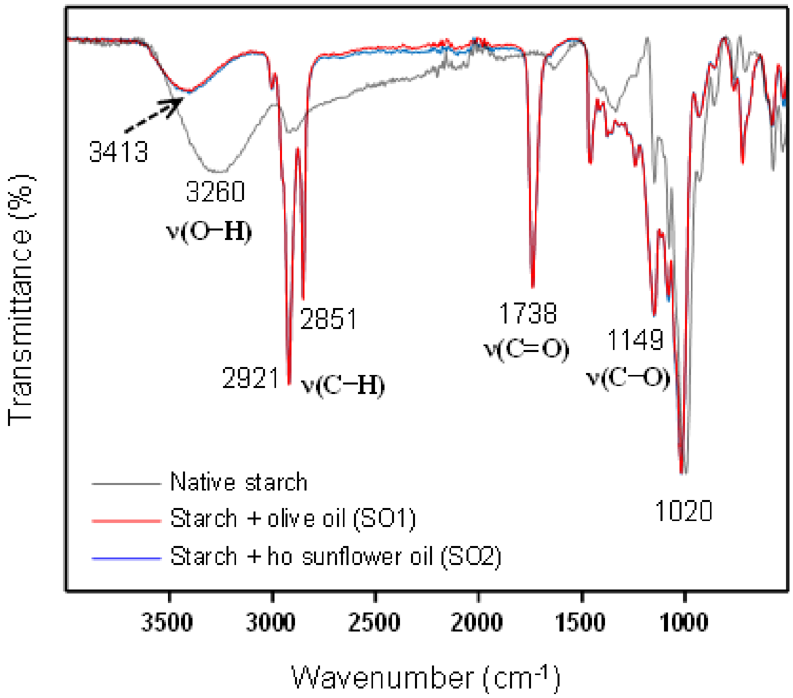


Figure 4.1 ATR-IR of native starch, **SO1** and **SO2**.

pronounced influence on the reaction. The solubility of the transesterified starch significantly changes in the course of the reaction. Indeed, as the hydroxyl groups of the starch are esterified, the modified starch, at some point, becomes insoluble and precipitates during the modification, thus limiting the DS. By taking this into account, different concentrations were tested and the maximum DS values were achived when 4% (w/w) of starch was dissolved in DMSO. Additionally, the reacted oil (diglycerides and monoglycerides) might behave as co-solvent, maintaining a homogeneous phase by acting as amphiphile. To ascertain this hypothesis, methyl oleate was tested as reagent for the transesterification of starch, since oleic acid is the dominant fatty acid in olive oil and high oleic sunflower oil. As expected, precipitation of the product was observed and lower conversions were obtained as compared to the respective reaction with plant oils. This solubility improvement, as demonstrated most likely due to the intermediately formed amphiphilic molecules, constitutes an important advantage of this direct transesterification procedure. Morever, different organocataysts were tested for the transesterification, including 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), but TBD performed best in this screening (**see supporting information**). In addition, more than 10 mol% of TBD (per –OH group) did not improve the DS. A temperature of 115 °C was required in order to obtain a maximum DS within 12 h of reaction time. No further enhancement of the DS was observed applying longer reaction times or higher temperatures. Olive oil and high oleic sunflower oil, with resembling fatty acid compositions, were found to react similarly with both starch and amylose resulting in a comparable DS. Other plant oils, such as sunflower and soybean oil, were also tested as reagents for the modification. Although the isolated products seemed to have the same physical appearance and ATR-IR demonstrated (**Fig. 4.S7**) the same intensity of the carbonyl peak when compared to other products, they did not show solubility in any solvents and thus were not characterized further. Presumably, crosslinking took place when soybean and sunflower oil with higher content of multiple unsaturated fatty acids, such as linoleic acid, were reacted with starch. In order to confirm this hypothesis, methyl linoleate was tested for the modification. The solvent mixture became dark during the reaction and the product was not soluble in any solvent upon isolation, confirming our assumption. NMR spectroscopy was applied in order to further prove the substitution of fatty acid chains onto starch backbone (**supporting information, Figures 4.S8-S15**). Exemplary ^{1}H and ^{13}C NMR spectra are shown in **Figure 4.2**. The peak assignment is provided in the experimental part and confirms the successfull modification. Furthermore, a ^{31}P NMR method was

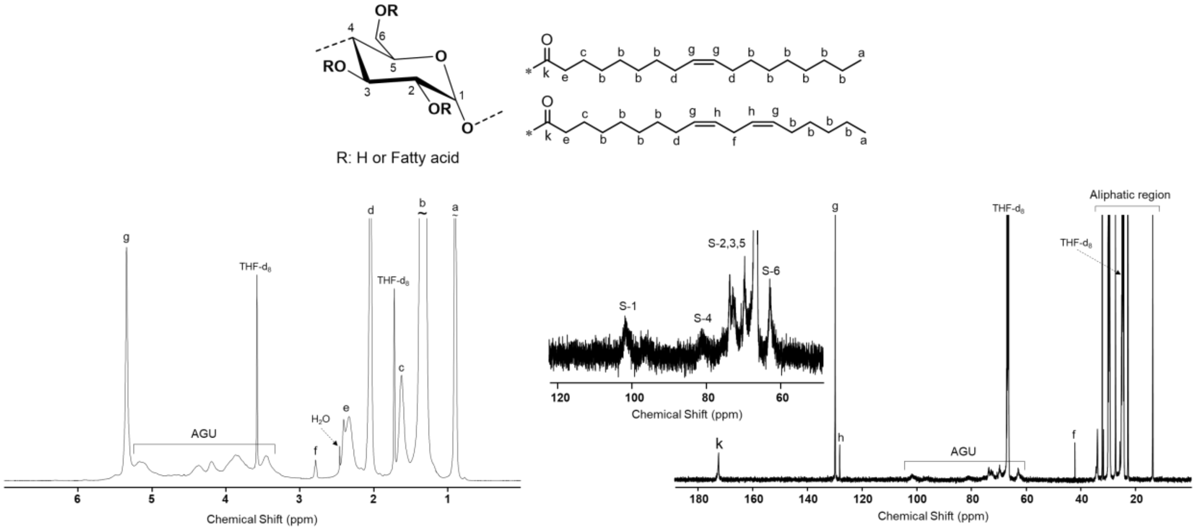


Figure 4.2. ^{1}H (left) and ^{13}C NMR (right) of the modified starch with olive oil (**SO1**).

applied for the determination of the DS (**supporting information, Figures 4.S16-S19**). The free hydroxyl groups were allowed to react with the phosphorylating agent, revealing a broad peak between 144-150 ppm, which is attributed to phosphorylated hydroxyl groups of the starch. Benzoic acid was chosen as a standard, since its peak does not overlap with the peak of free hydroxyl groups of starches. Calculation of the DS was performed according to a reported calculation method[260]. SEC measurements of all products were performed and revealed high molecular weights and molecular weight distributions without shoulders (**Figure 4.3**). Moreover, modified starches exhibited higher average molecular weights (M_n) as well as higher dispersities (*Đ*), compared to modified amylose derivatives (**Figure 4.3 and Table 4.1**).

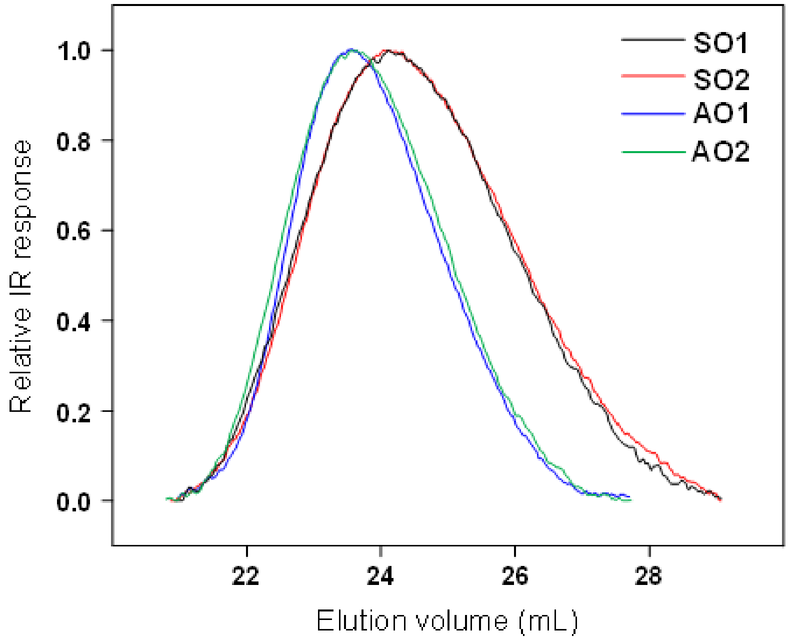


Figure 4.3 SEC traces of starch and amylose esters (**AO1, AO2, SO1, SO2**) in THF after catalytic transesterification. All SEC measurements were carried out relative to polystyrene calibration.

Table 4.1. SEC data of starch and amylose esters.

Product	***M*n (kDa)**	***M*w (kDa)**	***Đ***	**DS[(a)]**	**Yield[(b)] (%)**
SO1	232	397	3.51	1.29	84
SO2	251	404	3.24	1.33	88
AO1	143	276	2.15	1.24	84
AO2	151	294	2.05	1.30	92

[(a)]DS values were calculated by ^{31}P NMR method. [(b)]Yields were calculated based on DS values.

Starches have found promising applications in the packaging industry[250]. Therefore, four types of films were prepared by solubilizing the starch esters in THF or CH_2Cl_2 and casted on teflon plates. The films were allowed to form at room temperature and then dried under vacuum. All resulting films were transparent and flexible. The mechanical behaviour of the starch ester films were examined using a tensile strength instrument. In general, the films did not show high tensile strength due to the long fatty acid chains, similar with previously reported work[261]. In addition, starch films were found to have higher tensile strength compared to amylose films. This could be ascribed to lower molecular weights of the amylose utilized for the modification. On the other hand, modified starch and amylose derivatives displayed approximately 40% and 80% of elongation at break, respectively (**Figure 4.4 and Table 4.2**). Hydrophobic surfaces of casted films of the starch esters were characterized by water contact angle measurements and showed increased hydrophobicity of the surfaces compared to native starch (85 ± 4)° due to the introduced hydrophobic fatty acid chains (**supporting information, Fig. 4.S21**). One of the obtained films is depicted in **Figure 4.5**. Starch and amylose esters were readily soluble in organic solvents, such as THF, $CHCl_3$, CH_2Cl_2 or toluene and swelled in polar solvents such as water and DMSO (**Table 4.3**). DSC of starch esters revealed thermal transitions at around 80-90 ^oC, which are relatively high due to the different fatty acid chains on the backbone of the starch (**see supporting information, Fig. 4.S20**). Thermal gravimetric analysis showed increased thermal stabilities of modified starch and amylose by around 10 ˚C and 25 ˚C, respectively,

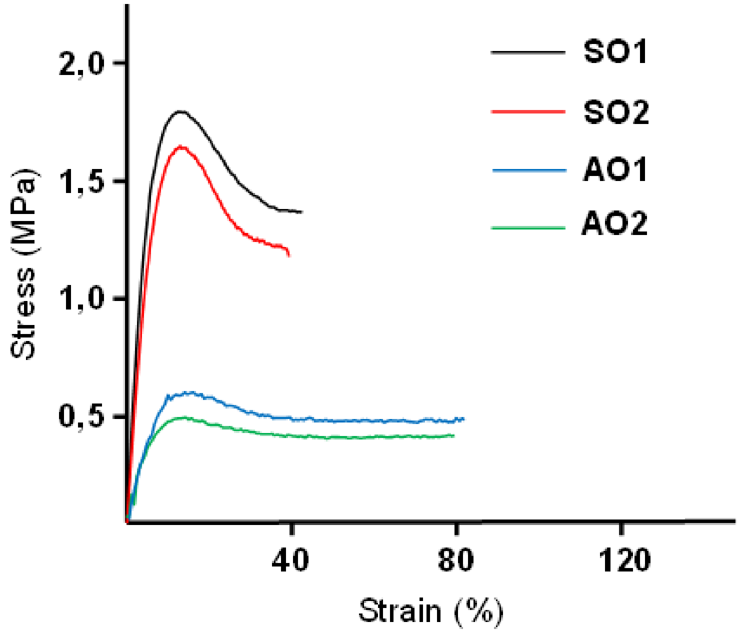


Figure 4.4 Tensile tests of the starch and amylose films.

Table 4.2 Thermal and mechanical properties data of casted starch and amylose ester films.

Product	T_g (ºC)	T_d (ºC)	Elongation at break (%)	Strain (MPa)	Young's modulus[a] (MPa)
SO1	82	274	44	1.85	7.02
SO2	92	275	42	1.63	7.85
AO1	89	287	83	0.60	19.66
AO2	90	288	80	0.50	23.00

(a)The Young's modulus of the films was calculated from the tensile strength graphs (**Figure 4.4**).

compared to native starch. Evaporation of water was observed between 25-175 °C. Amylose esters were found to have higher thermal stability, probably due to their unbranched structure (**Figure 4.6**). The isolation of the products and recovery

Figure 4.5 Photograph of starch olive oil film (**SO1**).

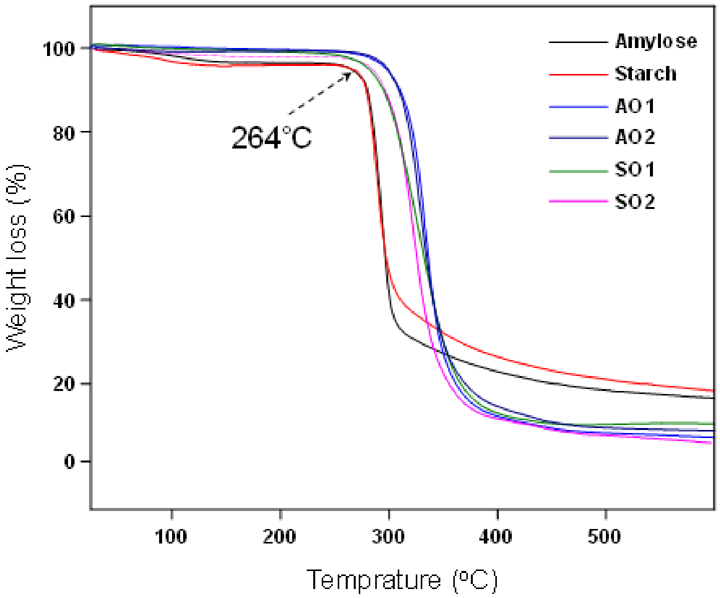


Figure 4.6. TGA curves of the starch and amylose esters.

of the DMSO, oil and the catalyst was perfomed with an easy work-up avoiding extraction and coloumn chromatography. The solvents utilized for the isolation and recovery were distilled and reused. The complete new procedure, including modification, isolation of products and recovery of oil, TBD and DMSO is summarized in a flowchart (**Figure 4.7**), indicating the sustainability and efficiency of the developed methodology. TBD was tested for further modifications after recovery, revealing only a slightly reduced reactivity probably due to water present in the reaction mixture. The recovered oils were also tested for further modifications and showed similar results compared to the starting oils. NMR data of the recovered TBD and olive oil can be found in the supporting information. After a second recovery, the recovered oil should be mixed with fresh plant oil in

Table 4.3 Solubility of transesterified starch esters with plant oils in different organic solvents.[a]

solvent	solubility	solvent	solubility
Tetrahydrofuran	soluble	Pyridine	soluble
Dichloromethane	soluble	Dimethyl sulfoxide	swells
Chloroform	soluble	Dimethylformamide	swells
Xylene	soluble	Acetone	Not soluble
Benzene	soluble	Ethyl acetate	Not soluble
Toluene	soluble	Diethyl ether	cloudy

[a]All solubility studies were performed with the concentration of 50 mg mL^{-1}.

order to achieve sufficient modification (a relatively low conversions was observed after the second modification using only the (two times) recovered oil, which is attributed to the reduced amount of available fatty acids).

4.4 Conclusions

We herein report a highly efficient, relatively cheap and sustainable method for the chemical modification of starch *via* direct transesterification with plant oils under homogeneous conditions. Starch esters with improved thermal and mechanical properties were obtained. The developed method represents a promising alternative to the conventional esterification methods, where over-stoichiometric amounts of activated acid derivatives are employed. This method could be transferred to starches from other biological origin leading to varied potential applications in industry. Additionally, the recovery of plant oils, solvent and catalyst was successful using an easy work-up avoiding toxic solvents and methods such as extraction or column chromatography.

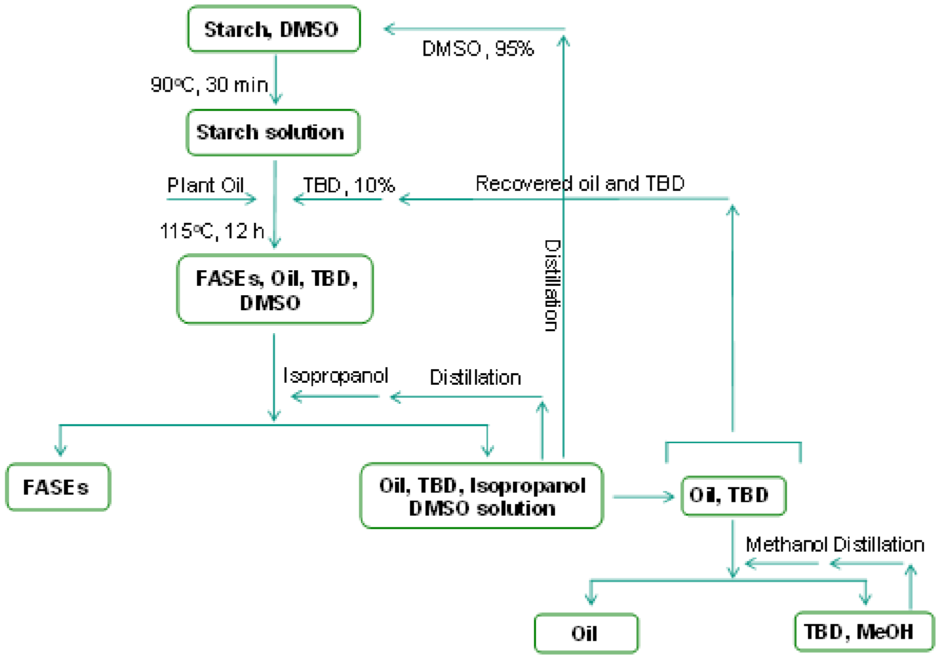


Figure 4.7 Flowchart of the whole procedure including modification, isolation of products and recovery of oil, TBD and DMSO.

4.5 Experimental section

Materials

All chemicals were used without further purification, if not stated otherwise. Maize starch and olive oil were purchased from a local supermarket. Amylose (starch from corn), dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), benzoic acid (ACS reagent, ≥99.5%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), tetrahydrofuran (for SEC, GC-MS, dry, contains 250 ppm BHT as inhibitor, >99.9%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, 95%), chromium (III) acetylacetonate, (99.99% trace metals basis), oleic acid (natural, FCC), linoleic acid (technical, 60-74%, GC), were purchased from Sigma Aldrich. Deuterated chloroform ($CDCl_3$-d) was purchased from Merck. Pyridine (water-free, for analysis) was purchased from Acros Organics. High oleic sunflower oil was kindly provided by Cargill. Starch and amylose were dried prior to use (24 h at 100 °C) in order to reduce the amount of water to a minimum. Methyl oleate and methyl linoleate were synthesized from oleic acid and linoleic acid, respectively, *via* reported transesterification procedure using methanol and sulfuric acid[262]. Other solvents such as methanol and isopropanol were used in technical grade.

General procedure for the synthesis of fatty acid starch esters (FASEs)

Starch (0.50 g, 3.08 mmol) was suspended in 12 mL of DMSO and allowed to stir for 30 min at 90 °C to obtain a clear solution. Afterwards, 1,5,7-

triazabicyclo[4.4.0]dec-5-ene (0.13 g, 0.90 mmol) and the corresponding plant oil (8.00 g, 10.00 mmol) were added to the reaction mixture and stirred for 12 h at 115 °C. The resulting homogeneous mixture was added dropwise to isopropanol (250 mL) to obtain an oily precipitate. The crude product was collected, dissolved in THF (10 mL) and reprecipitated in isopropanol. This washing procedure was repeated three times to remove the unreacted oil and DMSO completely. The pure oily product was dried under vacuum for further analysis. ATR–IR (cm^{-1}): 3260 v(O−H), 3006 v(C=C–H), 2921–2851 v_{as}(CH_2), v_s(CH_2), 1738 v(C=O), 1149 v(C–O), ^{1}H NMR (500 MHz, THF-d_8) δ_H ppm: 5.34 (m, 2H), 3.3–5.5 (m, AGU, 7H) 2.79 (m, 2H), 2.33 (m., 2H), 2.05 (m, 4H), 1.62 (m., 2H), 1.34 (m., 20H), 0.9 (m., 3H). ^{13}C NMR (500 MHz, THF-d_8) δ_C ppm: 173.44, 130.73, 129.06, 102.60, 74.52, 73.67, 73.27, 70.59, 63.90, 34.86, 33.01, 30.89, 30.41, 28.26, 23.68, 14.59.

Recovery of DMSO, TBD and plant oil

After precipitation of the product in isopropanol, the filtrate containing isopropanol, DMSO, plant oil and TBD was evaporated using the rotary evaporator recovering isopropanol. Then, DMSO was distilled using a distillation apparatus. The remaining mixture was poured into methanol. The plant oils were not miscible with methanol and were separated by separatory funnel. Subsequently, methanol was evaporated using a rotary evaporator to obtain TBD.

^{31}P NMR method for DS determination

Degree of substitutions (DS) were determined by ^{31}P NMR using a Bruker Ascend™ 400 MHz spectrometer with 512 scans, a delay time *d*1 of 3 seconds and a spectral width of 80 ppm (180 –100 ppm). Samples were prepared according to the following procedure: an exact amount of 25 mg of a starch ester sample was weighted and dissolved in 400 µL of $CDCl_3$. Pyridine (150 µl) was added upon complete dissolution. Afterwards, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2-Cl-TMDP, 100 µl, 0.63 mmol) was added to the solution and allowed to stir for 5 minutes. 150 µL of a solution of chromium (III) acetylacetonate (3.6 mg mL^{-1}) as relaxation agent and benzoic acid (4.0 mg mL^{-1}) as internal standard in $CDCl_3$/pyridine (1:1.6) were added and the solution was stirred for further 5 minutes. Then, 70 µl of the solution was transferred to an NMR tube. DS values were calculated according to the reported equation[260].

Instrumentation

Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H NMR spectra were recorded using Bruker Avance DRX 500 MHz with 1024 scans and a time delay *d*1 of 5 seconds at 50 °C. Data were reported in ppm relative to THF-d_8 at 1.73 and 3.58 ppm. ^{13}C NMR spectra were recorded using a Bruker Avance DRX 500 with 30.000 scans and a time delay *d*1 of 5 seconds at 50 °C. Data are reported in ppm relative to THF-d_8 at 25.37 and 67.57 ppm. All products were dissolved in THF-d_8 with the concentrations of 50 mg mL^{-1}.

Infrared Spectroscopy (IR)

Infrared spectra of all samples were recorded on a Bruker alpha-p instrument via ATR technology.

Size Exclusion Chromatography

Measurements were performed on a Polymer Laboratories (Varian) PL-SEC 50 Plus Integrated System, containing an autosampler, a PLgel 5 mm bead-size guard column (50 x 7.5 mm), one PLgel 5mm Mixed E column (300 x 7.5 mm), three PLgel 5mm Mixed C columns (300 x 7.5 mm) and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL min^{-1}. The system was calibrated with polystyrene standards with molecular weights ranging from 476 to 2.5 × 106 g mol^{-1}.

Differential scanning calorimetry (DSC)

DSC experiments were carried out with a DSC821e (Mettler Toledo) calorimeter using 100 µL aluminum crucibles under nitrogen atmosphere. An amount of 20-30 mg for each sample was measured in two heating circles of 0-175 °C with heating and cooling rate of 15K/min. The second heating curves were considered for the accurate examination. Samples were measured at least three times for the verification of the results.

Thermal Gravimetric Analysis (TGA)

TGA measurements were conducted with a Netzsch STA 409C instrument applying α-Al_2O_3 as a crucible material and reference sample. The samples were heated from 25 °C up to 600 °C under nitrogen flow with a heating rate of 5 K min^{-1}, with sample mass of ~20 mg. Weight loss of the sample was evaluated for the determination of the thermal degradation.

Film Preparation

All products were dissolved in THF or CH_2Cl_2 and casted on 100 mm × 20 mm teflon plates with a minimum concentration of 10% (w/w). The films were allowed to form at room temperature and dried under vacuum. Films with three different thicknesses were prepared.

Tensile Tests

Tensile strength of cast films were measured using GABO EXPLEXOR 150N instrument. All resulting data were an average of four measurements. The casted films were cut into 16 mm × 2 mm strips and measured with a speed of 0.5 mm/min.

Water Contact Angle Measurements (WCA)

Images of water droplets on the surface of the casted films were taken using UK 1115 digital camera from EHD imaging. Contact angles of the casted films against water droplet were calculated using ImageJ software with a Dropsnake plugin. The reported contact angles were the result of three measurements.

4.6 Supporting information

1) IR-Spectra of optimization studies
2) NMR data of modified starches
3) NMR data of phosphorylated, modified starches
4) DSC data of modified starches
5) Contact angle measurements of prepared films
6) NMR data of used plant oils (for the determination of fatty acid composition)
7) NMR data of recovered TBD

1) IR-Spectra of optimization studies

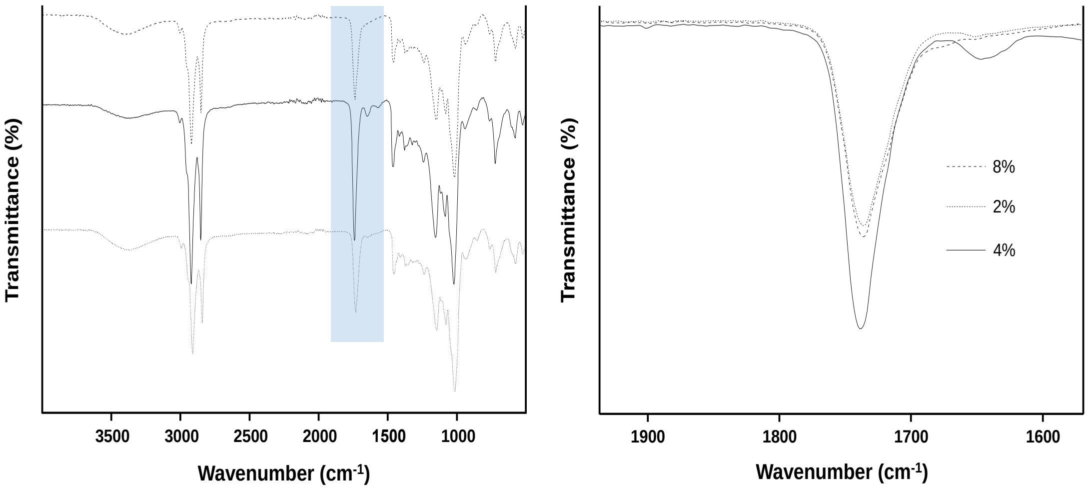


Fig. 4.S1 ATR-IR spectra (left) and carbonyl peak (right) of modified starch with olive oil at different concentrations in DMSO (12 h, 3 eq. olive oil, 10 mol% TBD, 90 ^{o}C). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1018 cm^{-1}.

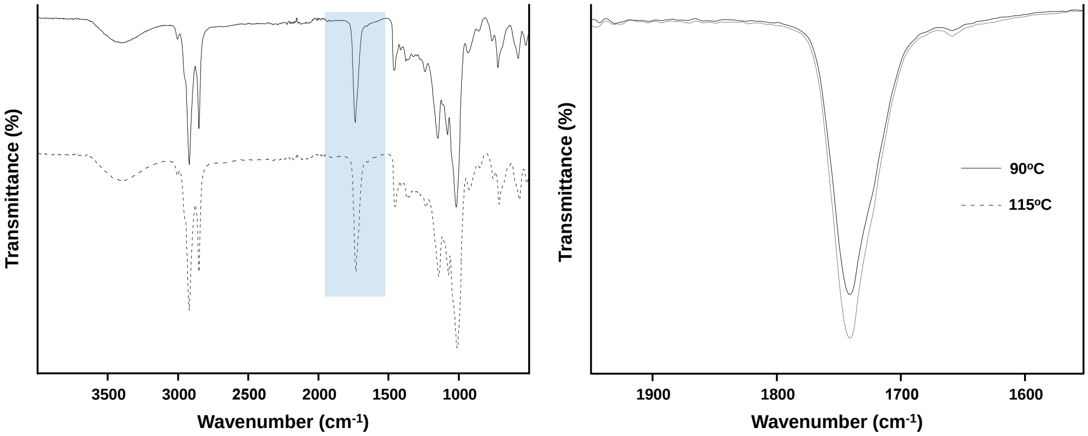


Fig. 4.S2 ATR-IR spectra (left) and carbonyl peak (right) of modified starch with olive oil at different temperatures in DMSO (12 h, 3 eq. olive oil, 10 mol% TBD, 4% starch concentration, (w/w)). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1018 cm^{-1}.

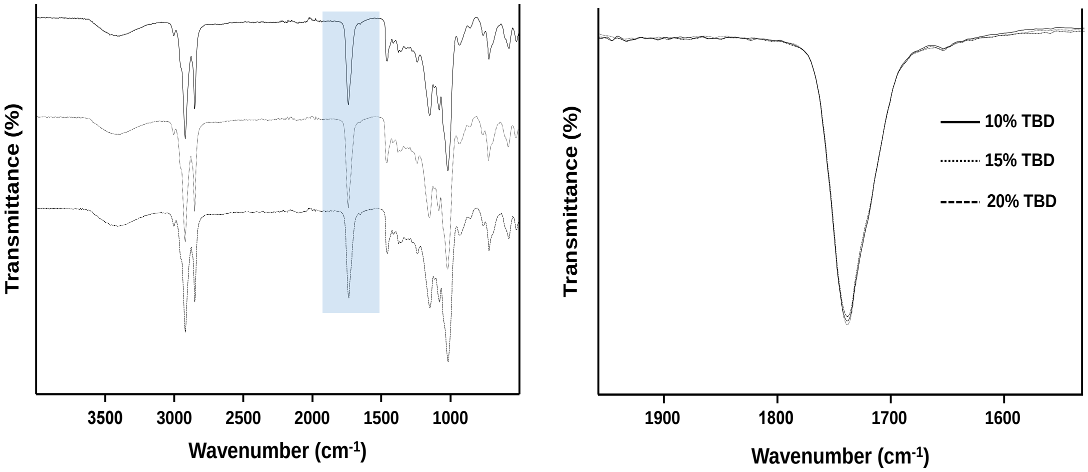


Fig. 4.S3 ATR-IR spectra (left) and carbonyl peak (right) of modified starch with olive oil in the presence of different amounts of TBD in DMSO (12 h, 3 eq. olive oil, 90 °C, 4% starch concentration, (w/w)). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1018 cm^{-1}.

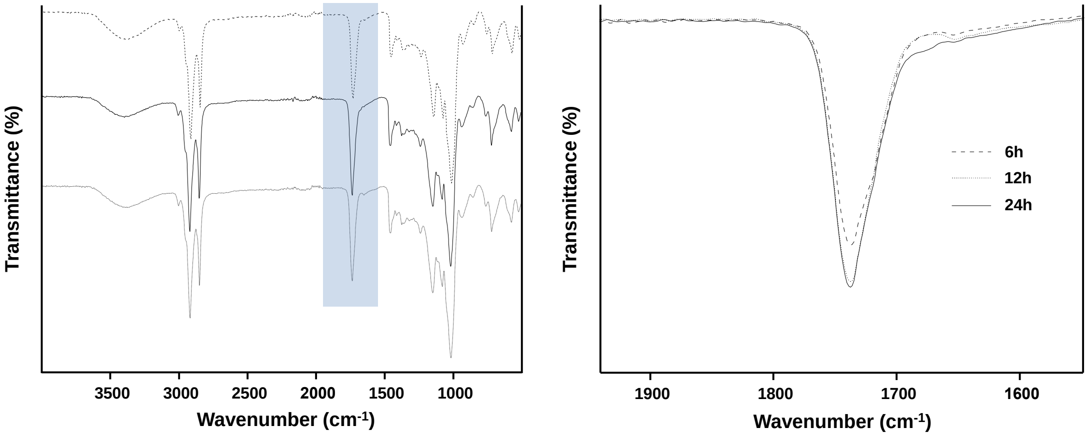


Fig. 4.S4 ATR-IR spectra (left) and carbonyl peak (right) of modified starch with olive oil at different reaction times in DMSO (3 eq. olive oil, 10 mol% TBD, 90 °C, 4% starch concentration, (w/w)). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1018 cm^{-1}.

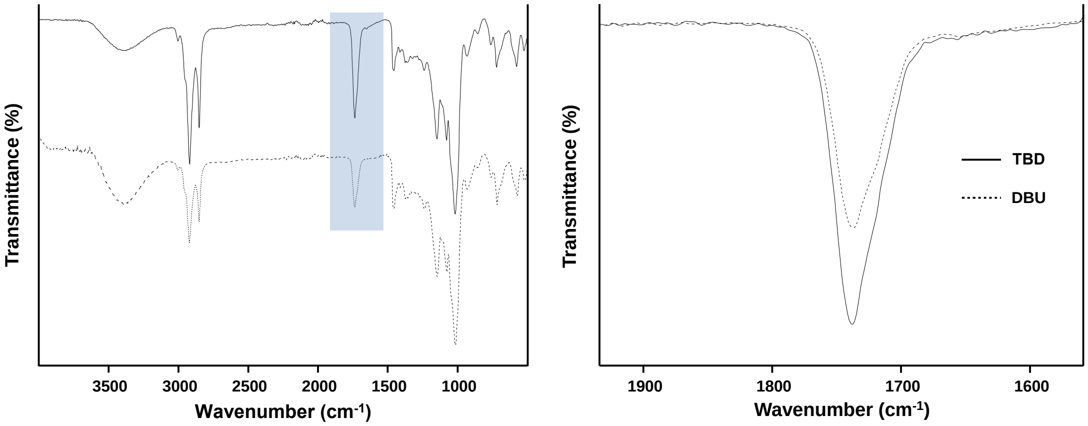


Fig. 4.S5 ATR-IR spectra (left) and carbonyl peak (right) of modified starch with olive oil in the presence of different catalysts in DMSO (12 h, 3 eq. olive oil, 90 °C, 4% starch concentration, (w/w)). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1018 cm^{-1}.

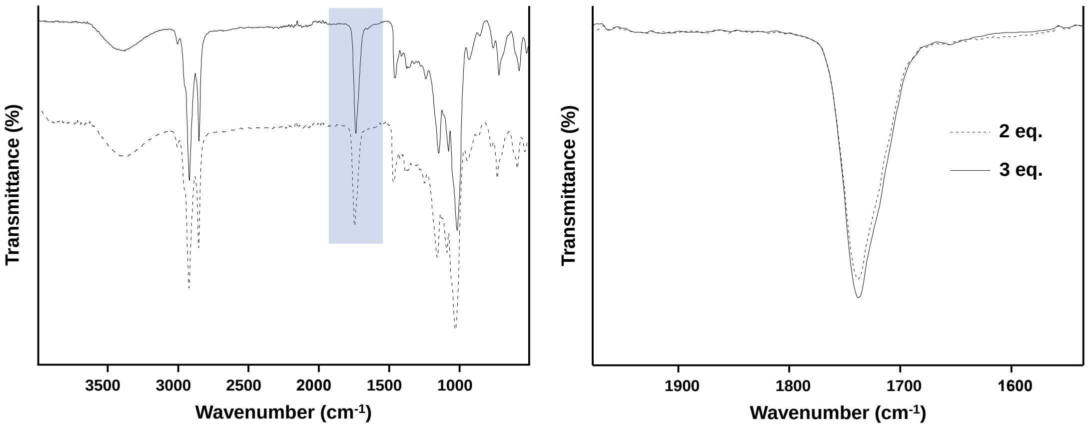


Fig. 4.S6 ATR-IR spectra (left) and carbonyl peak (right) of modified starch with olive oil in different amounts of olive in DMSO (12 h, 10 mol% TBD 90 °C, 4% starch concentration, (w/w)). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1018 cm^{-1}.

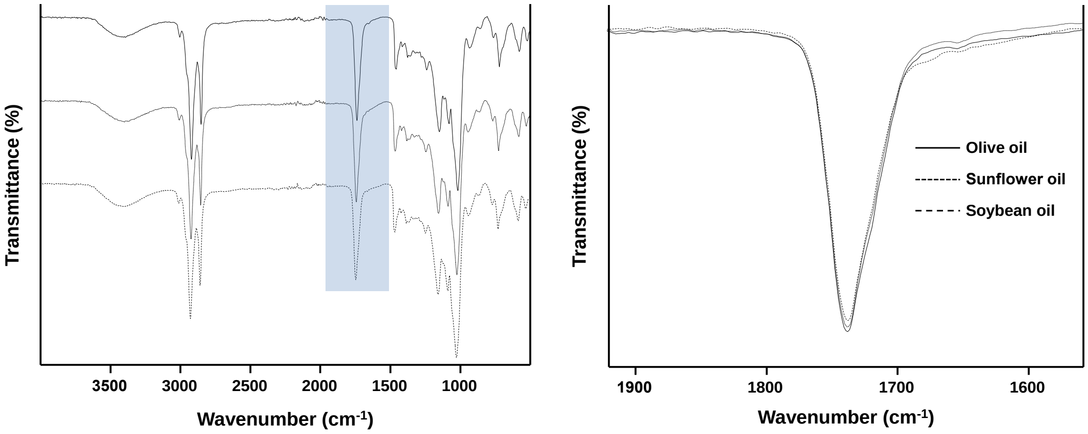


Fig. 4.S7 ATR-IR spectra (left) and carbonyl peak (right) of modified starch with different plant oils in DMSO (12 h, 10 mol% TBD, 90 ^{o}C, 4% starch concentration, (w/w)). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1018 cm^{-1}.

2) NMR data of modified starches

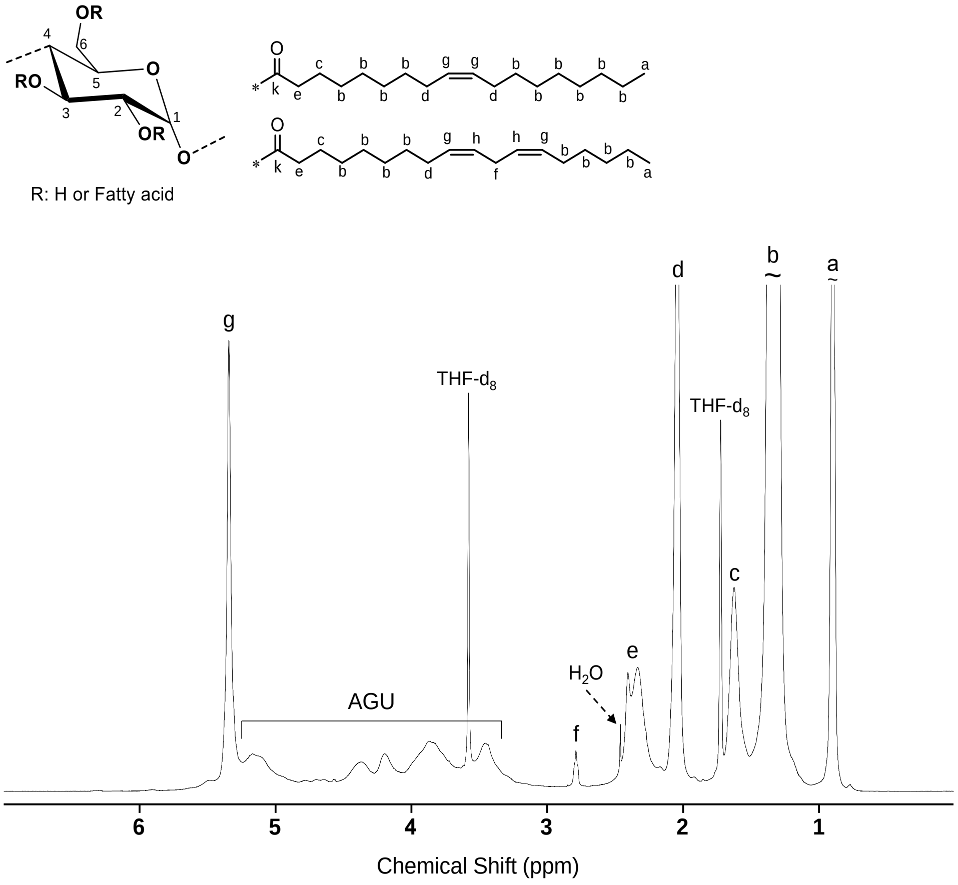


Fig. 4.S8 ^{1}H NMR of modified starch with olive oil (SO1).

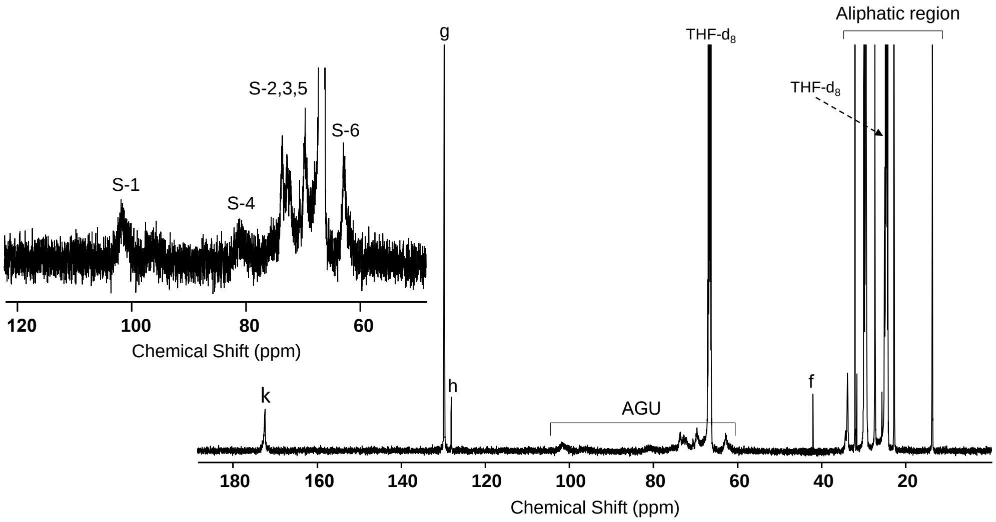


Fig. 4.S9 ^{13}C NMR of modified starch with olive oil (SO1).

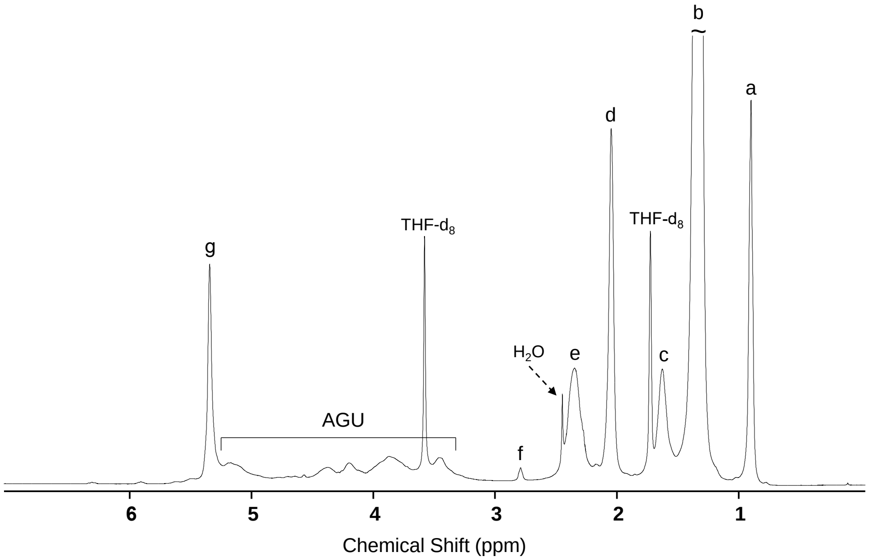


Fig. 4.S10 ^{1}H NMR of modified starch with high oleic sunflower oil (SO2).

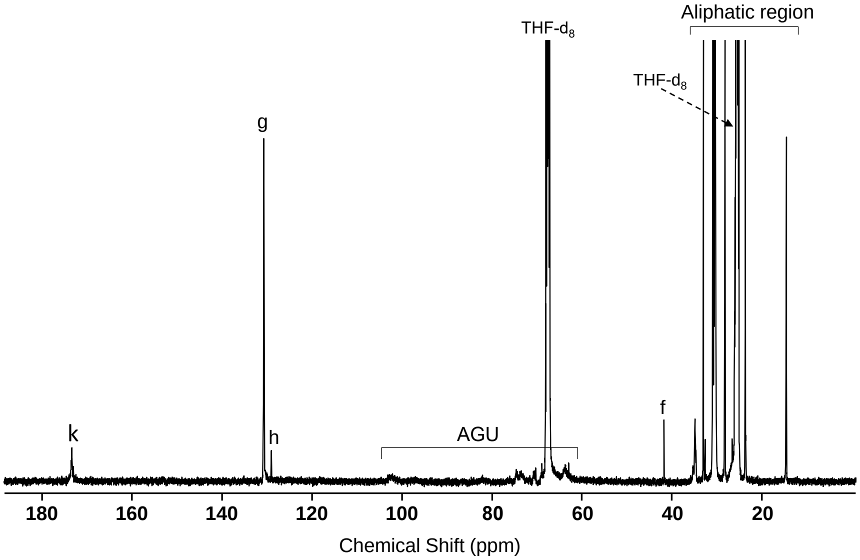


Fig. 4.S11 ^{13}C NMR of modified starch with high oleic sunflower oil (SO2).

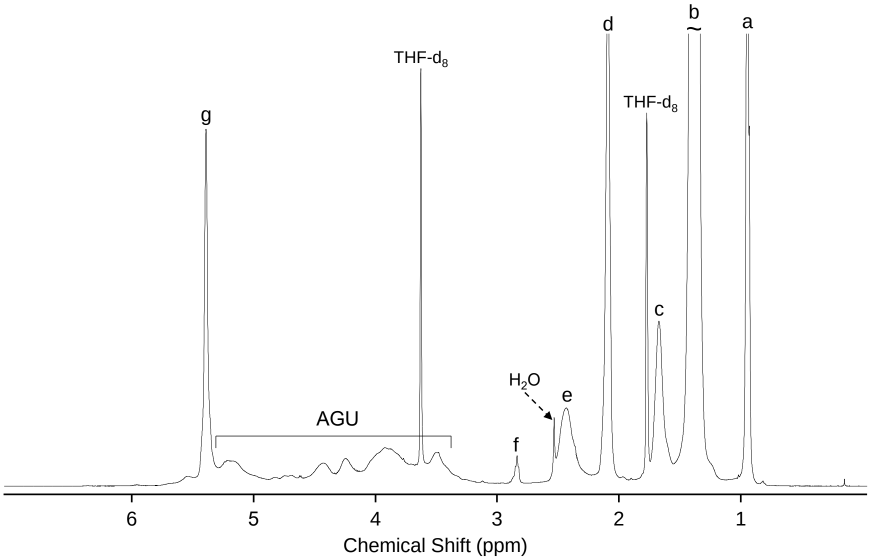


Fig. 4.S12 ^{1}H NMR of modified amylose with olive oil (AO1).

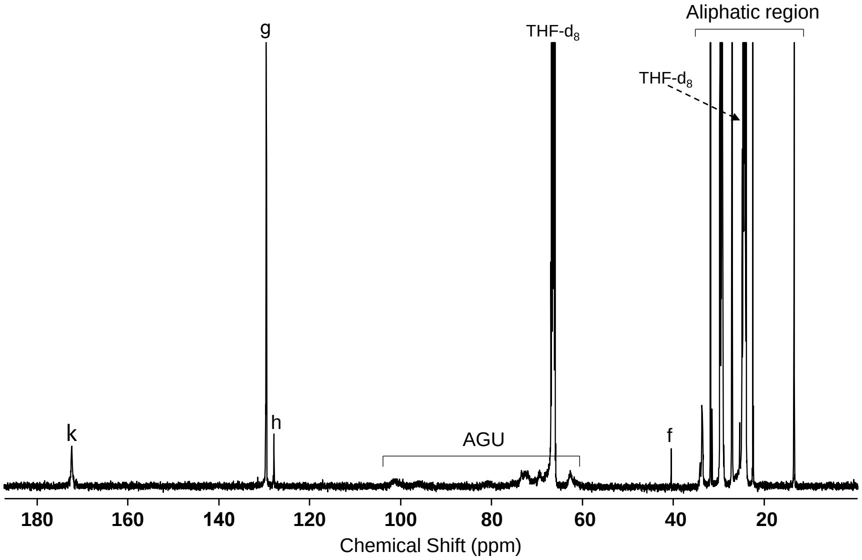


Fig. 4.S13 ^{13}C NMR of modified amylose with olive oil (AO1).

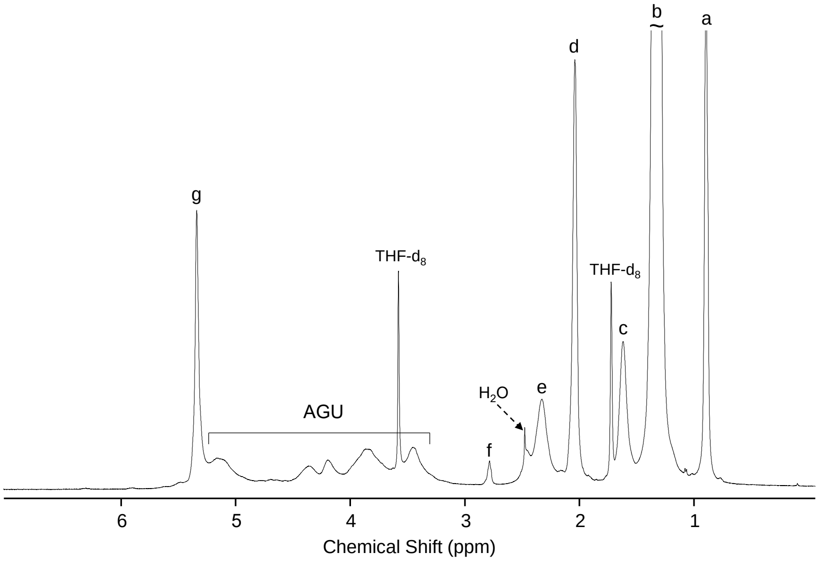


Fig. 4.S14 ^{1}H NMR of modified amylose with high oleic sunflower oil (AO2).

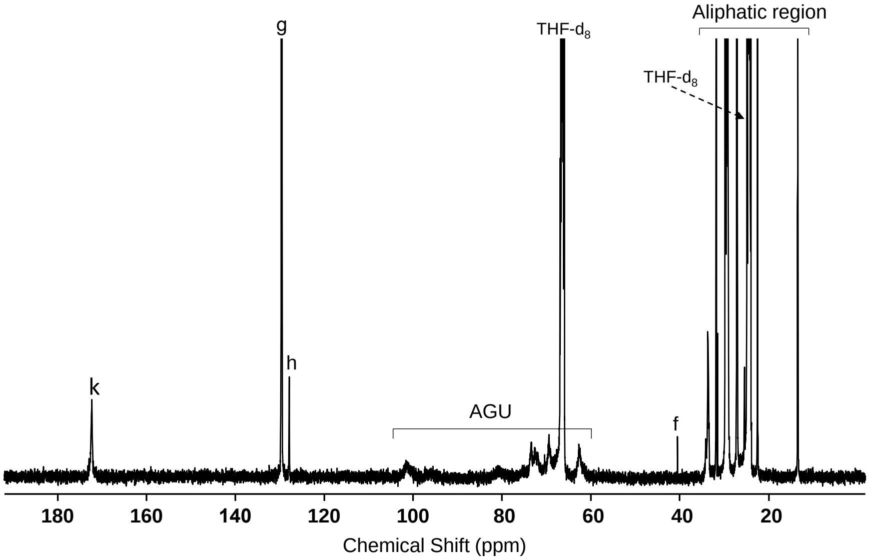


Fig. 4.S15 ^{13}C NMR of modified amylose with high oleic sunflower oil (AO2).

3) NMR data of phosphorylated, modified starches

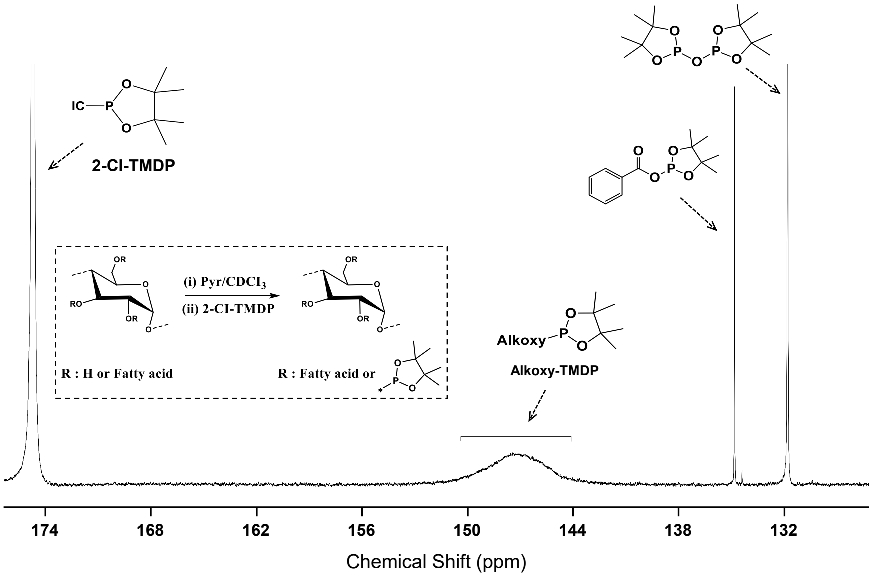


Fig. 4.S16 ^{31}P NMR of modified starch with olive oil (SO1).

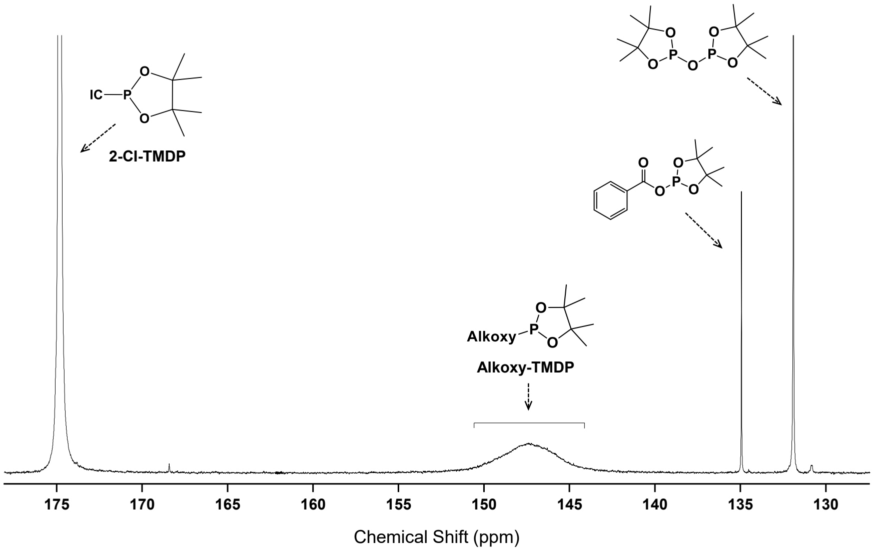


Fig. 4.S17 ^{31}P NMR of modified starch with high oleic sunflower oil (SO2).

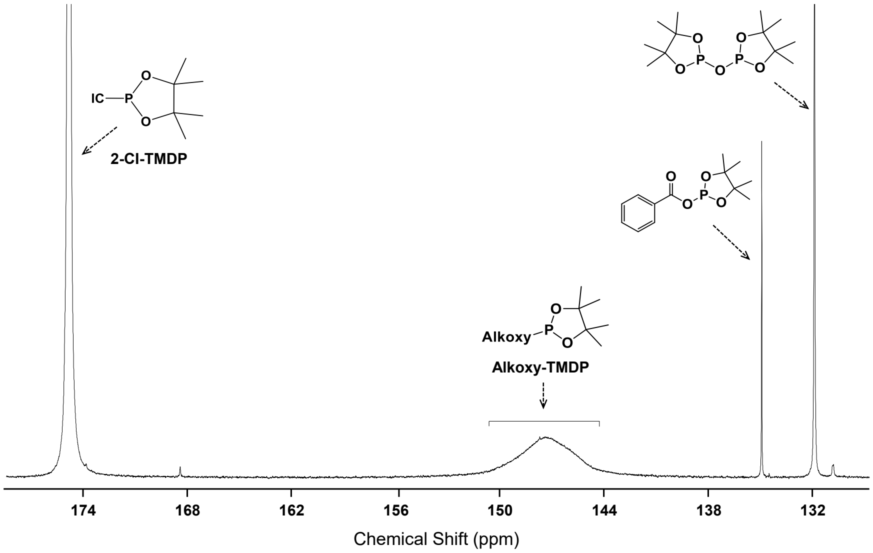


Fig. 4.S18 ^{31}P NMR of modified amylose with olive oil (AO1).

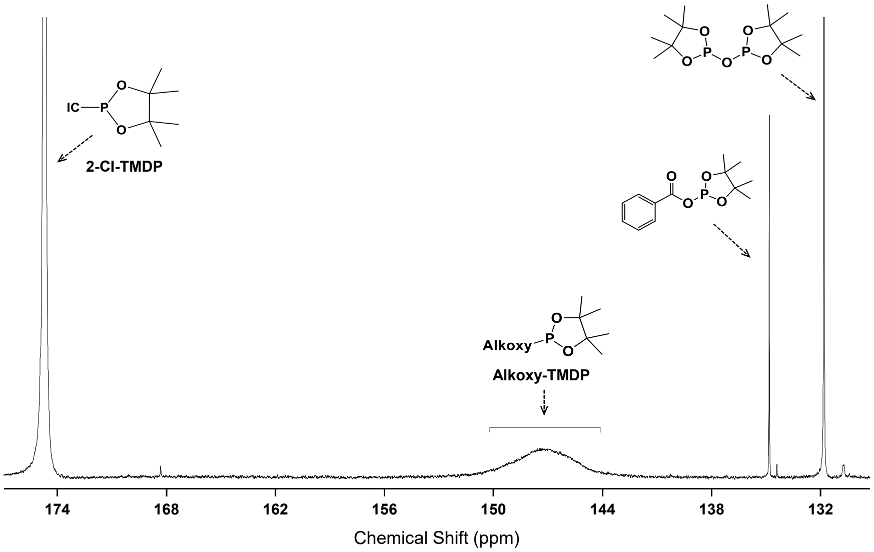


Fig. 4.S19 ^{31}P NMR of modified amylose with high oleic sunlower oil (AO2).

4) DSC data of modified starches

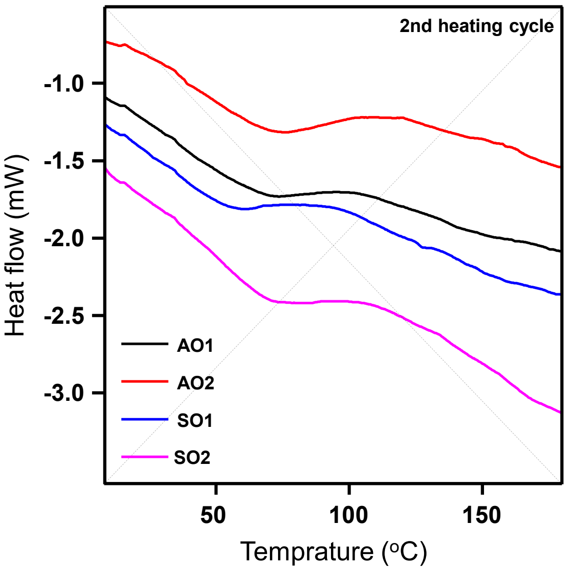


Fig. 4.S20 DSC results of products.

5) Contact angle measurements of prepared films

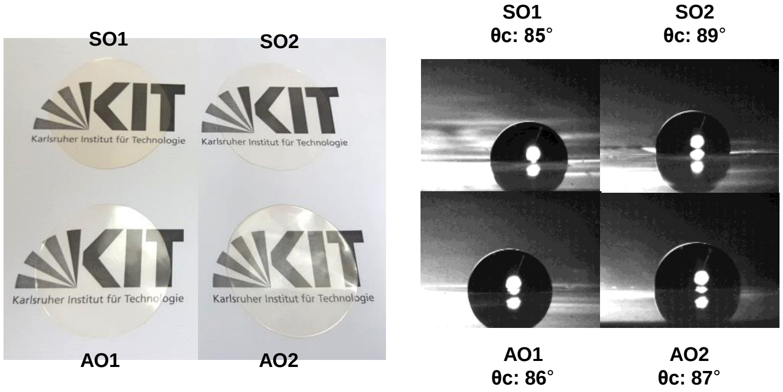
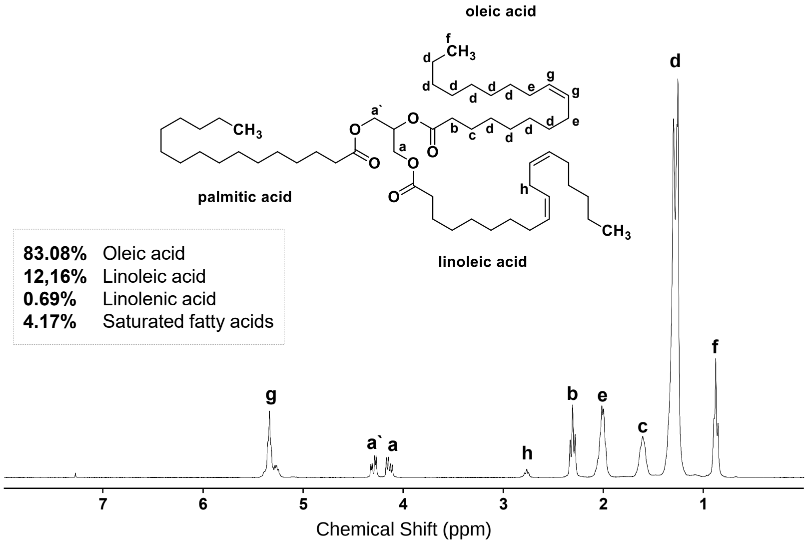


Fig. 4.S21 Casted starch and amylose films (left) and water contact angle pictures of all casted films (right).

6) NMR data of used plant oils (for the determination of fatty acid composition)



83.08%	Oleic acid
12,16%	Linoleic acid
0.69%	Linolenic acid
4.17%	Saturated fatty acids

Fig. 4.S22 ^{1}H NMR of pure olive oil.

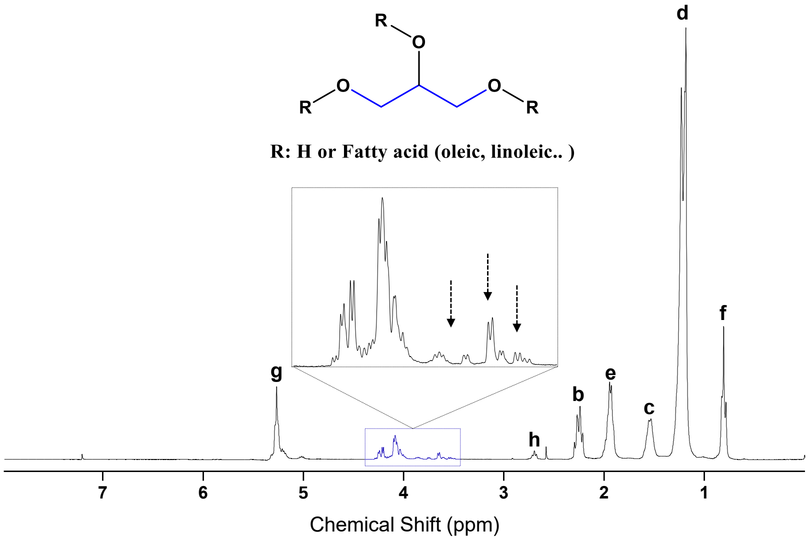


Fig. 4.S23 ^{1}H NMR of the recovered olive oil after modification.

7) NMR data of recovered TBD

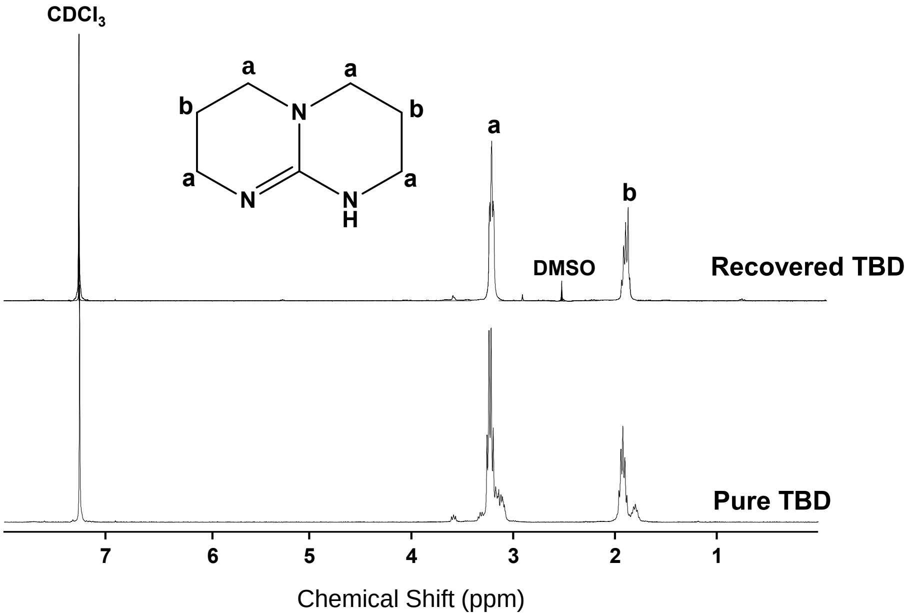


Fig. 4.S24 ^{1}H NMR of pure and recovered TBD.

5. Sustainable functionalization of cellulose with diallyl carbonate

5.1 Abstract

A functional and environmentally benign alkoxycarbonylation reagent, diallyl carbonate (DAC), was employed for the sustainable and catalyst-free allyloxycarbonylation of cellulose under homogenous conditions using 1-butyl-3-methylimidazolium chloride (BMIMCl) as a solvent. As a result of optimization studies of the reaction conditions and molar ratio of DAC, cellulose was successfully converted to cellulose allyl carbonate exhibiting degrees of substitution (DS) of 0.8–1.3. The optimized conditions were also applied to maize starch leading to a DS of 1.2, thus demonstrating the reproducibility and versatility of the established procedure. The obtained cellulose and starch allyl carbonates were thoroughly characterized by ATR-IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as by size exclusion chromatography (GPC). Thermal properties were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). A transparent thin film was produced from cellulose allyl carbonate and mechanical properties were examined by tensile strength measurements, showing 21.6 MPa of tensile strength with 40% elongation at break. Additionally, cellulose allyl carbonate

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This chapter is adapted with permission from reference [**199**], copyright 2017 the Royal Society of Chemistry. Some of the experimental results were partially included in the theses of Felix Poschen and Florian Steegborn. The experimental work and corresponding results in the theses were obtained together with bachelor students. The theses were completely mentored (co-supervision) by me.

was successfully modified *via* thiol-ene chemistry employing 1-butane thiol, resulting in a material with improved thermal properties, showing a thermal transition (T_g) at 84 ^oC. Furthermore, the reported methodology represents a step forward in terms of sustainability for carbohydrate and especially cellulose modification, since non-toxic reagents were used and BMIMCl as well as the excess of DAC could be recycled and reused for further reactions[199].

5.2 Introduction

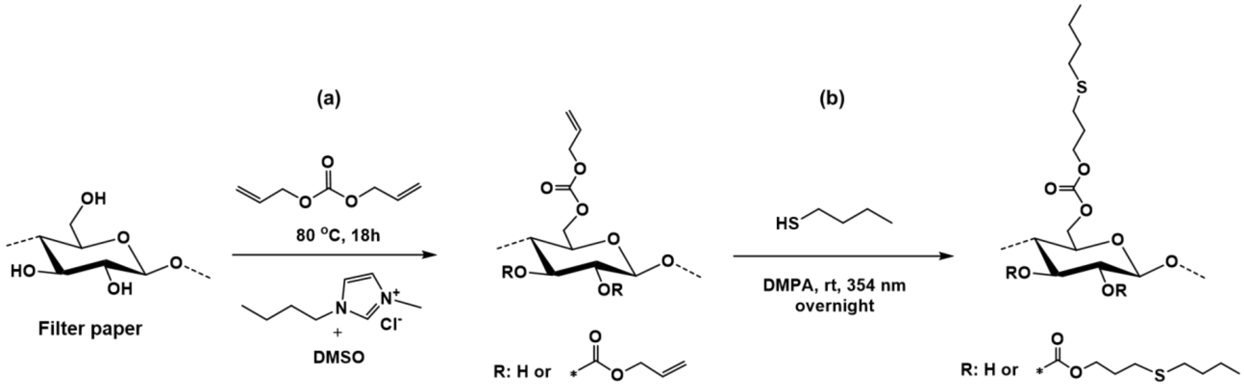
Cellulose carbonates constitute an important class of cellulose derivatives with multifunctional capabilities and a wide range of potential applications, such as imaging agents and for the delivery of therapeutics[182]. Ethyl chloroformate was the first reagent introduced for the synthesis cellulose carbonates in the presence of triethylamine as a catalyst and sacrificial base[183]. Until then, several other studies have been reported on the synthesis of carbonates of cellulose by using varied alkyl or aryl chloroformates in the presence of nucleophilic catalysts under different reaction conditions[184–187]. However, these reagents, due to their high reactivity, produce unexpected side products. In addition, they are produced from toxic phosgene, they are not stable under certain conditions, highly toxic themselves and they produce hydrochloric acid in the course of the reaction, which is difficult to recycle, may lead to degradation of the polymeric structure and requires stoichiometric amounts of sacrificial base for their removal *in situ*.

Recently, a more sustainable solution for the synthesis of cellulose carbonates was reported by King and co-workers[192], who employed dimethyl- and diethyl-carbonates for the carbonylation of cellulose in ionic liquids, leading to cellulose alkyl carbonates with moderate degrees of substitution (DS) of ~1. Dialkylcarbonates, which are regarded as halogen-free "green" reagents, were used in various transformations including alkylation, alkoxycarbonylation and transesterification reactions. They are highly promising candidates to substitute their toxic and dangerous classically used counterparts, such as phosgene, methyl halides, or alkyl chloroformates as they are considerably less toxic and limit the production of by-products. Indeed, during the transformations of organic carbonates, mainly CO_2 and alcohols are produced as by-products, which could be reused for the formation organic carbonates, at least in principle. In addition, dialkyl carbonates could be synthesized *via* an environmentally friendly route between dimethyl carbonate (could for instance be prepared from CO_2 and methanol, industrially available from urea and methanol) and alcohols in the presence of catalytic amount of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)[184,185,188,189,263,264].

Herein, we introduce diallyl carbonate (DAC) for the sustainable production of functional cellulose carbonates in a BMIMCl/DMSO solvent mixture (**CC1-CC6**). The optimized reaction conditions were also applied to maize starch (**SC1**) in order to investigate the reproducibility and versatility of the established procedure. Moreover, the cellulose allyl carbonate prepared with the highest degree of substitution (**CC5**) was further modified by thiol-ene addition (**CC5T**) (**Scheme 5.1**). In this work, we also investigate recyclability and further reuse of the recovered DAC and BMIMCl.

5.3 Results and discussion

Taking into account the recent findings on sustainable cellulose carbonate synthesis (**Section 2.4.1.1.3**), we investigated a new route for the allyloxycarbonylation of cellulose with diallyl carbonate (DAC) under homogenous conditions using 1-butyl-3-methylimidazolium chloride (BMIMCl) as solvent and without any additional catalyst. (**Scheme 5.1**) Cellulose carbonates with degrees of substitutions (DS) between 0.8–1.3 could be obtained by adjusting the reaction conditions and molar ratio of DAC (**Table 5.1**). Diallyl carbonate (DAC), which is employed as a functional group containing alkoxycarbonylation reagent in this work, was synthesized *via* an environmentally friendly route by a reaction between allyl alcohol and dimethyl carbonate in the presence of a catalytic amount of TBD, yielding a colourless liquid[188]. The optimization results for the allyloxycarbonylation of cellulose with DAC are summarized in **Table 5.1**. ^{31}P NMR spectroscopy was applied for the determination of the DS of cellulose and starch allyl carbonates. The free hydroxyl groups were allowed to react with the phosphorylating agent (**see experimental**



Scheme 5.1 (a) Alkoxycarbonylation of cellulose with diallyl carbonate in a BMIMCl/DMSO solvent mixture (18 h, 80 °C, 10% (w/w) DMSO & 2% (w/w) cellulose concentration). **(b)** Thiol-ene addition reaction between cellulose allyl carbonate and 1-butane thiol (rt, overnight, 5 mol% DMPA, 354 nm).

Table 5.1 Summary of degree of substitution (DS) of obtained cellulose (**CC1-CC6**) and starch (**SC1**) allyl carbonates in the BMIMCl/DMSO solvent mixture (10% w/w DMSO & 2% w/w cellulose concentration) under different reaction conditions.

Product	Eq. DAC[a]	*T* (°C)	Time (h)	DS[b]
CC1	3	70	18	0.82
CC2	3	80	12	0.88
CC3	3	80	18	1.04
CC4	4	70	18	0.92
CC5	4	80	18	1.32
CC6	4	80	24	1.30
SC1	4	80	12	1.22

[a] Equivalents of diallyl carbonate with respect to -OH group. [b] DS was calculated from ^{31}P NMR spectroscopy.

section for details), revealing a broad peak between 140–155 ppm, which is attributed to phosphorylated hydroxyl groups of the cellulose and starch. Benzoic acid was chosen as internal standard because the peak of its resulting phosphorylated derivative does not overlap with the peak of the phosphorylated hydroxyl groups of cellulose and starch. The ratio of integration of the free hydroxyl groups relative to the integration of the internal standart was used for the determination of the DS (**supporting info. Fig. 5.S6, S7**) according to a reported method[260].

Filter paper was utilized as a cellulose source and maize starch was supplied from a local supermarket. Cellulose and starch were dried under vacuum for 24 h at 100 °C prior to modification in order to minimize potential negative effects of residual water on the conversion. Primary optimization studies of our procedure were conducted by using ATR-IR spectroscopy. The effects of the concentration of cellulose, of the type of ionic liquid, of the amount of co-solvent, of the catalyst, of the molecular ratio of DAC, of the reaction time and temperature were investigated. The optimization was performed by monitoring the intensity of the carbonyl peak at around 1735 cm^{-1} that is characteristic of the substituted carbonate moiety (**supporting info. Fig. 5.S3, S4**). Spectra were normalized to the intensity of the C−O stretching vibration of glycopyranose at 1050 cm^{-1} and at 1015 cm^{-1} for cellulose and starch, respectively, to have a relative comparison of the different degrees of modifications, since the pyranose oxygen absorption is not influenced significantly upon the allyloxycarbonylation process.

Absorbances in the fingerprint region at 982, 896 and 606 cm^{-1} represent the anhydroglucose unit. The peak at around 3300 cm^{-1} is attributed to stretching vibrations of the OH groups of cellulose, which is reduced and shifted to 3400 cm^{-1} after the modification. In addition, new peaks at 1735 and 1240 cm^{-1} were observed and attributed to the C=O and C−O stretching vibrations of the introduced allyl carbonate moiety, respectively (**Figure 5.1**). A complete overview of the optimization data can be found in the supplementary information. ^{1}H and ^{13}C NMR spectroscopies were used for a further confirmation of the formation of cellulose and starch allyl carbonates. After the modification, the peaks belonging to the backbone of the cellulose and starch and the new peaks introduced by allyloxycarbonylation are clearly observed in ^{1}H and ^{13}C NMR (**Figure 5.2 and supporting info. Fig. 5.S5**). Indeed, the new peaks in the ^{1}H NMR spectra, at around 5.90, 5.30, and 4.61 and

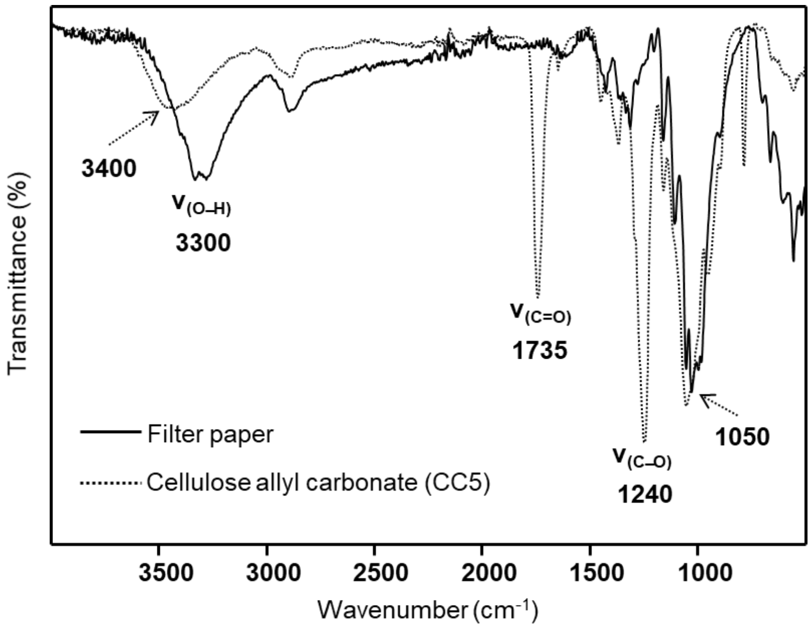


Figure 5.1 ATR-IR data of unmodified filter paper and modified filter paper with DAC. (DS: ~1.3).

on the ^{13}C NMR spectra at 117.79, 131.77 and 153.70 ppm, are attributed to the allyl moiety of the carbonate.

1-Butyl-3-methylimidazolium chloride (BMIMCl), 1-Ethyl-3-methylimidazolium acetate (EMIMOAc) and 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$) were tested as solvents for the homogenous modification of cellulose in order to determine the optimal solvent for this process, since imidazolium based ionic liquids have been shown to be more efficient solvents for the homogenous utilization of cellulose. Analyses by ATR-IR showed that BMIMCl was the most efficient solvent, giving the highest conversion, probably due to its capability to act as organocatalyst for the allyloxycarbonylation of cellulose as well as serving as a good solvent (**supporting info. Fig. 5.S3**).

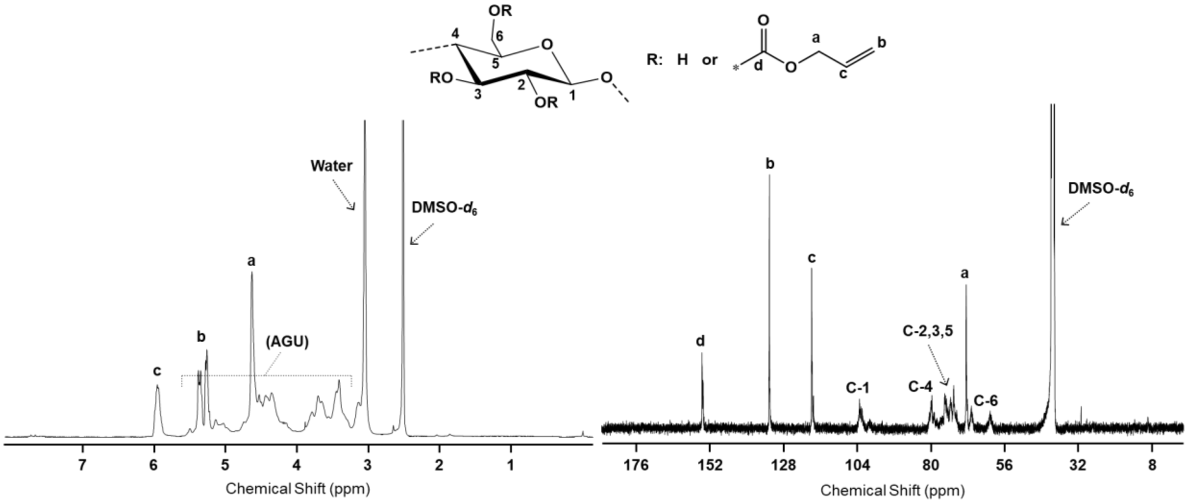


Figure 5.2 Exemplary ^{1}H NMR (left) and ^{13}C NMR (right) of modified filter paper with DAC.

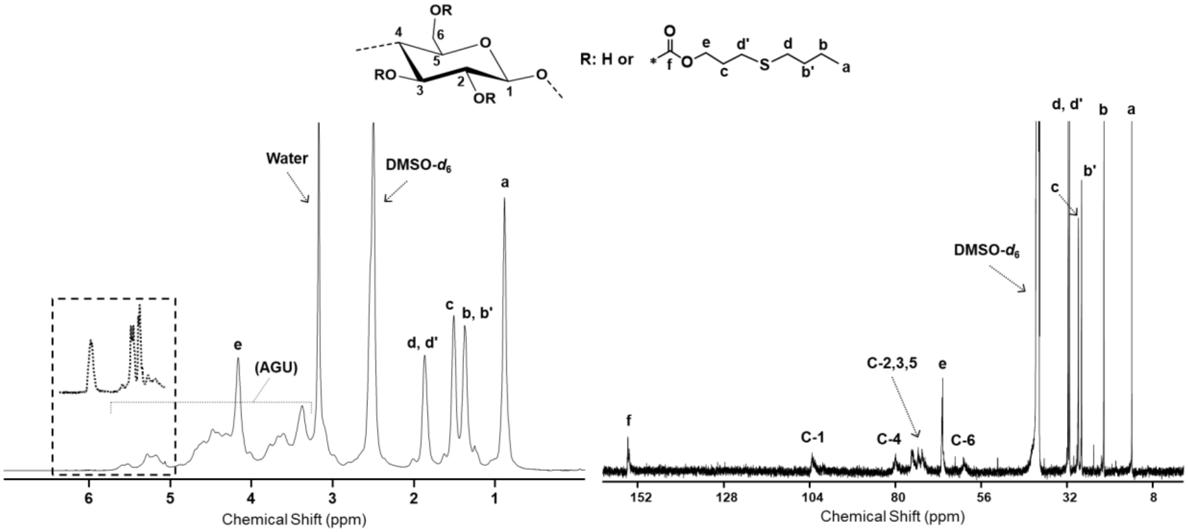


Figure 5.3 ^{1}H NMR (left) and ^{13}C NMR (right) of thiol-ene product of cellulose allyl carbonate.

Since ILs are highly viscous liquids, there is a need of co-solvent to avoid any aggregation as well as to decrease the viscosity of the reaction mixture[138,265]. From our observations, the utilization of co-solvents did not only facilitate the solubilization of cellulose but also proved to have positive effects on the DS. DMSO is often used as solvent for the modification of carbohydrates as it provides a higher conversion and solubility than other suitable solvents, such as DMF and DMAc[198,199]. These three polar aprotic organic solvents were also tested as co-solvents here. DMF and DMAc showed to be inefficient co-solvents, as they led to low conversions as well as lower solubility of the cellulose. In addition to this, DMAc and DMF are more toxic than DMSO, making DMSO a good choice for our modification procedure. DMSO can be considered as being environmentally relatively benign due to its high boiling point, low vapor pressure (low volatile organic solvents emission) as well as its relatively low toxicity ($LD_{50\text{-rat-oral}}$ (median lethal dose) = 14500 mg/kg; residual solvents limit in pharmaceuticals = 5000 ppm)[200–203]. Simple and even more sustainable solvents (i.e. acetone or alcohols) are not suitable for our modification procedure, because they are chemically not inert and do not possess the necessary co-solvent dissolving ability. 10% (w/w) of DMSO as co-solvent with respect to BMIMCl was found to be the most efficient solvent mixture, allowing to obtain a clear solution suitable for efficient modifications. In addition, the overall concentration of cellulose in the solvent mixture plays an important role in terms of achievable conversions. Different concentrations were tested, and the maximum efficiency was achieved if 2% (w/w) of cellulose was dissolved in the BMIMCl/DMSO solvent mixture. Higher concentrations of cellulose caused gelation during the addition of DAC and thus had a negative influence on the conversions.

The optimum reaction temperature and time were investigated for achieving the maximum DS in the synthesis of cellulose allyl carbonate. 80 °C and 18 hours gave the best results. Longer reaction times did not enhance the conversion as observed by ATR-IR. However, lower and higher temperatures than 80 °C resulted in lower conversions (**supporting info. Fig. 5.S4**). In addition, GPC analyses revealed that higher reaction temperatures and longer reaction times accelerated the cellulose backbone degradation (**supporting info. Fig. 5.S8, S9**). From our observations, the resistance against cellulose backbone degradation decreases as the secondary hydroxy groups on the anhydroglucose units (C2 and C3) start taking part in the carbonylation process. Indeed, hydroxyl groups, particularly at the C3 position of the anhydroglucose unit, are responsible for intramolecular hydrogen bonding with the glycosidic linkage, which is an important factor for the resistance against backbone degradation. As intermolecular hydrogen bonds are disrupted by solvation and are reduced with the functionalization of the hydroxy groups in this allyloxycarbonylation process, the resistance against cellulose backbone degradation decreases[266,267].

Different organocatalysts, such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and tetra butylammonium bromide (TBAB) were tested for the allyloxycarbonylation of cellulose. Especially TBD and DBU generally play significant catalytic roles in a wide range of organic conversions including the sustainable synthesis of organic carbonates[188,268,269]. These organocatalysts are also known for modifications of carbohydrate polymers, such as the sustainable esterification of starch with plant oils[198]. However, in our study, no enhancement of DS was observed by adding these catalysts (**supporting info. Fig. 5.S4**). Similar results were obtained by King *et al.*[192] in a recent report, who investigated the synthesis of cellulose methyl carbonate using dimethyl carbonate in a trioctylphosphonium acetate ($P_{8881}OAc$)/DMSO solvent mixture, leading to DS values of ~1. The authors suggested that a thermodynamically stable mixture is already reached without the need of a catalyst under these conditions. Moreover, applying higher amounts of these organocatalysts (1 eq. per–OH group) resulted in insoluble products after precipitation. Higher amounts of catalysts presumably caused crosslinking reactions between free hydroxyl groups and substituted allyl carbonate, since substituted allyl carbonates on the cellulose backbone are also reactive towards inter- and intra- molecular nucleophilic attacks by free hydroxyl groups. This absence of catalyst indicates that the BMIMCI/DMSO mixture plays a catalytic role as well as serves as good solvent for the allyoxycarbonylation of cellulose and starch.

No side reaction was observed during the allyloxycarbonylation process using the BMIMCI/DMSO solvent mixture in this work, in contrary to the recent work[192] reported by King *et al.,* who observed a side reaction between acetate ionic liquids and dimethyl carbonate under their reaction conditions. (60–80 °C) The authors solved this problem by applying milder work-up conditions to avoid the cation decomposition in the system. In our case, a classic work up was possible. Further optimization studies were performed using different molar ratios of DAC for the determination of highest possible conversion of OH-groups of the carbohydrate. 4 equivalents of DAC (with respect to –OH groups) gave the highest conversion, resulting in a DS of 1.3 (**supporting info. Fig. 5.S3**). Applying higher amounts of DAC did not further improve the conversion. After the reaction, BMIMCI and DAC were successfully recovered *via* a facile work-up. Fractional distillation was applied to recover DMSO (90 °C, 50 mbar) and DAC (110 °C, 10 mbar). The remaining solid substance was pure BMIMCI. The recovered BMIMCI and DAC could be reused for the further reactions, maintaining their efficiency. The purity of recovered BMIMCl and DAC could be shown by ^{1}H NMR spectroscopy (**supporting info. Fig. 5.S13, S14**). The complete procedure, including modification, isolation of products, and recovery of BMIMCl, DAC, and DMSO is summarized in a flowchart (**Figure 5.4**), highlighting the sustainability of the developed methodology.

The optimized conditions were also applied to maize starch, leading to a DS of ~1.2, demonstrating the versatility of the established procedure, which could potentially be transferred to other types of polysaccharides targeting various types of potential applications. Moreover, the cellulose allyl carbonate with DS of 1.3 was used for subsequent modification *via* thiol-ene chemistry to evidence its viability for further modification and thus tuning of the thermomechanical properties.

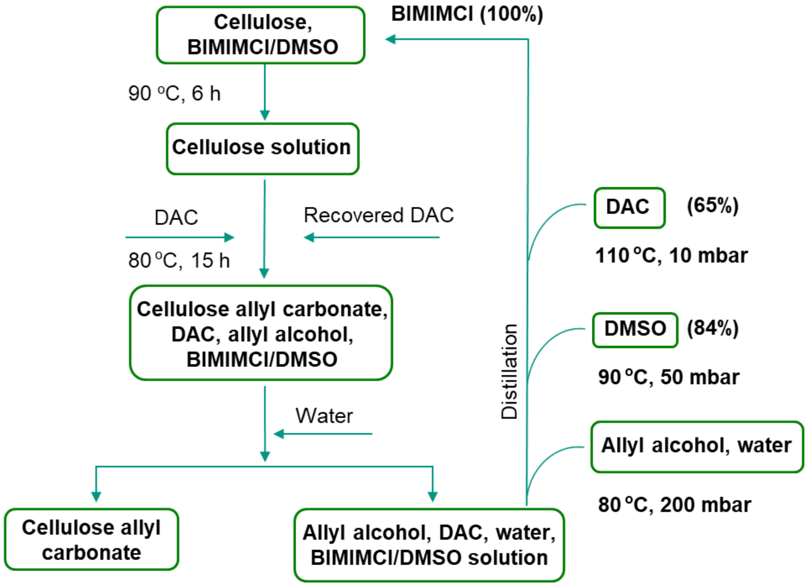


Figure 5.4 Flowchart of the whole procedure including modification, isolation and recovery.

Table 5.2 GPC data of modified cellulose and starch products.

Product	M_n (kDa)	M_w (kDa)	*Đ*	DS[a]	Yield(b) (%)
Filter paper	40	126	3.1	–	–
CC5	82	347	4.2	1.3	86
CC5T	122	576	4.7	1.3	92
SC1	84	523	6.2	1.2	83

[a]calculated from ^{31}P NMR; [b] calculated from DS values

The reaction was performed under homogenous conditions in DMSO as a solvent using 1-butane thiol under 354 nm of ultraviolet light (UV) in the presence of a catalytic amount of 2,2-dimethoxy-2-phenyl acetophenone (5 mol%) (DMPA) as photo initiator. ^{1}H and ^{13}C NMR revealed the quantitative conversion of the allyl groups to thioethers. Indeed, the peaks at 5.90 and 5.30 ppm corresponding to allyl moiety disappeared in the ^{1}H NMR, and the peak at 4.61 ppm corresponding to the methylene of the allyl moiety shifted to 4.16 ppm after the thiol-ene addition. ^{1}H and ^{13}C NMR also confirms the thioether formation, showing the new peaks of the butyl group in the aliphatic region (**Figure 5.3**). Comparison of the relative molecular weights and dispersities of the obtained products was performed by GPC (**Figure 5.5, Table 5.2, supporting info 5.S9**). Since the filter paper is not soluble in the GPC solvent, a solvent exchange procedure was applied in order to solubilize the filter paper in DMAc/LiBr[116,270], which is regarded as the mildest procedure to dissolve cellulose. A relative molecular weight of 40 KDa was observed. GPC analysis revealed higher molecular weights of cellulose and starch allyl carbonates as well as the thiol-ene product of the cellulose, thus further indicating the success of the modifications and the mildness of the procedure.

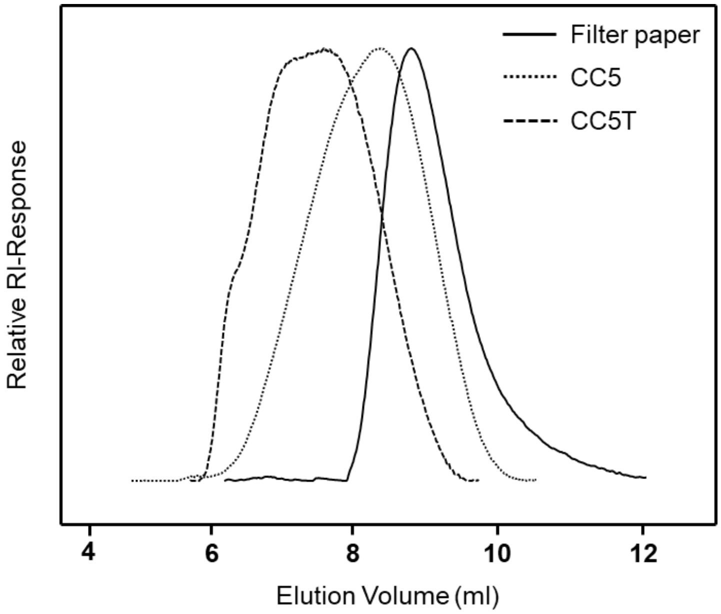


Figure 5.5 GPC graph of unmodified filter paper, modified filter paper with diallyl carbonate (**CC5**) and thiol-ene product of cellulose allyl carbonate (**CC5T**). All GPC measurements were carried out relative to poly(methyl methacrylate) calibration in DMAc/LiBr (1% w/w).

Finally, the obtained cellulose and starch allyl carbonate were well soluble in DMSO and pyridine. A thin film was prepared by solubilizing cellulose allyl carbonate (CC5) in pyridine (other, more sustainable solvents were evaluated, but without success; DMSO is not suitable for film formation) with a concentration of 1% (w/w) and cast on a teflon plate. The film was allowed to form at room temperature and dried under vacuum. The resulting film was transparent and flexible (**Figure 5.7**). The mechanical properties of the film were examined using a tensometer. The film showed 21.6 MPa of strength with 40% elongation at break (**supporting info. 5.S12**). The film formation of starch allyl carbonate was also tested, but the resulting film was extremely brittle and not viable for mechanical tests. Differential scanning

Table 5.3 Thermal behaviour of the unmodified and modified cellulose and starch.

Product	T_g (ºC)	T_d (ºC)
Filter paper	–	305
Maize starch	–	264
CC5	–	155
CC5T	84	170
SC1	–	160

calorimetry was applied to observe the thermal behaviour of the obtained products. Similar to native cellulose and starch, the obtained cellulose and starch allyl carbonates did not show any thermal transition in the range between -50 and 175 °C. However, the thiol-ene product of cellulose allyl carbonate showed a glass transition temperature (T_g) of 84 °C (**Figure 5.6 and Table 5.3**). This indicates that the resulting thiol-ene product of cellulose might be processed thermally. Moreover, in the future, the thermal transitions of the resulting thiol-ene products of the cellulose and starch allyl carbonate could be tuned by adjusting the structure of the employed thiol. Thermal gravimetric analysis revealed that cellulose and starch allyl carbonate exhibit 5% degradation temperatures of 155 °C and 160 °C, respectively and thus degrade much earlier than native cellulose and starch, for which degradation occurs at 305 °C and 264 °C, respectively (**Table 5.3**). This could be ascribed to reactive allyl moiety as well as carbonates attached to the cellulose backbone. Possibly, free hydroxy groups react with substituted allyl carbonates at

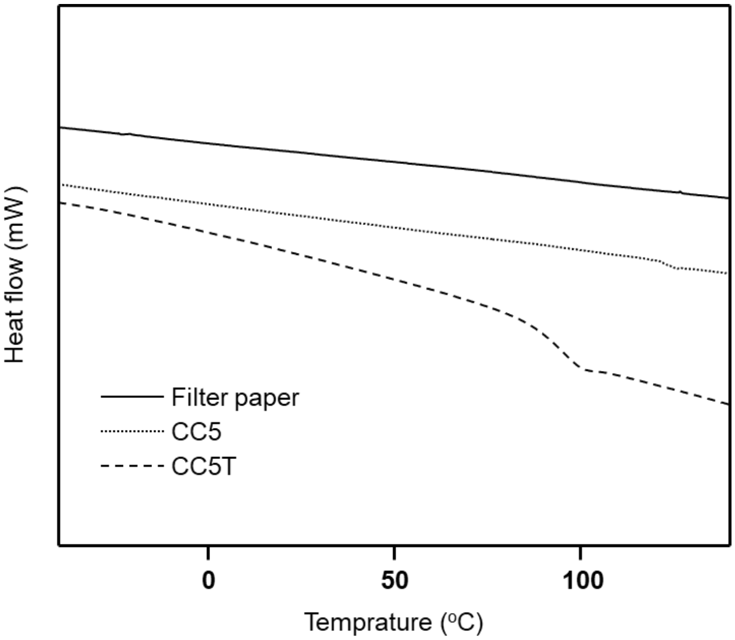


Figure 5.6 DSC graph of filter paper, modified filter paper with DAC (**CC5**) and thiol-ene product of cellulose allyl carbonate (**CC5T**)

elevated temperatures causing the early degradation of the anhydroglucose units of these polysaccharides.

The thiol-ene product of cellulose shows a somewhat higher degradation temperature (5% degradation temperature of 170 °C) than cellulose allyl carbonate, probably due to increased steric hindrance (**Table 5.3 and supporting info. Fig. 5.S10, S11**).

Figure 5.7 Photograph of the cast film of cellulose allyl carbonate (CC5).

5.4 Conclusions

In this work, we demonstrated the sustainable synthesis of cellulose and starch allyl carbonates using the environmentally friendly reagent diallyl carbonate in a BMIMCl/DMSO solvent mixture leading to DS values of 1.3 and 1.2, respectively. The established procedure was conducted without the need of any catalyst, indicating that the BMIMCl/DMSO solvent mixture also played a catalytic role. The absence of an additional catalyst also facilitates the recovery of the BMIMCl/DMSO solvent mixture and of the excess of diallyl carbonate, reducing the environmental impact of the procedure. A transparent cast film of cellulose allyl carbonate (**Figure 5.7**) exhibiting promising mechanical property with a tensile strength of 21.6 MPa and 40% elongation at break was produced. The introduction of the allyl moiety through the allyloxycarbonylation process enables facile further functionalization of cellulose and starch, for instance *via* thiol-ene chemistry resulting in carbohydrate based materials with tunable properties for wide range of potential applications. The developed methodology represents a promising alternative to the conventional synthesis of cellulose carbonates, in which over-stoichiometric amounts of chloroformates are employed. Moreover, this procedure avoids utilization of toxic chemicals and of undesired side products and wastes, such as hydrochloric acid, which significantly reduces the molecular weight of the carbohydrates and has to be removed using stoichiometric amounts of base in conventional approaches. Additionally, the recovery of BMIMCl, DAC, and DMSO was successful using a facile work-up.

5.5 Experimental part

Materials and Instrumentation

All chemicals were used without further purification, if not stated otherwise. Filter paper was purchased from Whatman™ (filter paper, No. 5), maize starch was purchased from a local supermarket. 1-Butyl-3-methylimidazolium acetate (BMIMCl, 95%), 1-ethyl-3-methylimidazolium acetate (EMIMOAc, ≥95%), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$, 97%), dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%), tetrabutylammonium bromide (TBAB, ACS reagent, ≥98.0%), benzoic acid (ACS reagent, ≥99.5%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), 1-butane thiol (99%), dimethyl carbonate (anhydrous, ≥99%), allyl alcohol (≥99%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, 95%), chromium (III) acetylacetonate, (99.99% trace metals basis), were purchased from Sigma Aldrich. Deuterated dimethyl sulfoxide (DMSO-d_6) was purchased from Merck. Pyridine (water-free, for analysis) was purchased from Acros Organics. Filter paper and maize starch were dried prior to use (24 h at 105 °C) in order to reduce the amount of water to a minimum. Diallyl carbonate was synthesized *via* modification of reported procedure using dimethyl carbonate and allyl alcohol in the presence of catalytic amount (5 mol%) of TBD[188]. Other solvents were used in technical grade.

General procedure for the synthesis of cellulose and starch allyl carbonate

Filter paper (0.20 g, 1.23 mmol) was suspended in 10 mL of a BMIMCl/DMSO (10% w/w DMSO) solvent mixture and allowed to stir for 6 hours at 90 °C to obtain a clear homogenous solution. Afterwards, the reaction temperature was brought to 80 °C and diallyl carbonate was added dropwise to the reaction mixture for 6 hours to avoid any gelation during addition. After completion of the addition of DAC, the reaction mixture was stirred for 18 h at 80 °C. The resulting homogeneous mixture was added dropwise to vigorously stirring water (200 mL) to obtain a white precipitate and further washed with water (2 x 200 mL) to remove the unreacted DAC, BMIMCl and DMSO completely. The pure white product was dried under vacuum for further analysis. Yields are shown in **Table 5.2.** ATR–IR (cm^{-1}): 3400 v(O−H), 1735 v(C=O), 1240 v(C–O). ^{1}H NMR (500 MHz, DMSO-d_{6}) δ_{H} ppm: 5.84–6.00 (m, 1H), 5.18–5.44 (m, 2H), 4.61 (m, 2H) 3.20–5.50 (m, AGU, 7H). ^{13}C NMR (500 MHz, DMSO-d_{6}) δ_{C} ppm: 153.70, 131.77, 117.79, 102.32, 79.49, 74.62, 72.85, 71.81, 67.53.

Procedure for the thiol-ene addition reaction

Cellulose allyl carbonate (0.10 g, 0.37 mmol, calculated from DS value) with DS of ~1.3 was dissolved in 2 mL of DMSO. Then, 1-butane thiol (0.05 g, 0.55 mmol) and DMPA (0.006 g, 0.02 mmol) was added to the reaction mixture and allowed to stir overnight at room temperature under UV radiation (354 nm). After completion of the reaction, the resulting homogenous mixture was poured into vigorously stirring water (100 mL) to obtain a precipitate and further washed with water (2 x 100 mL). Then, the resulting white precipitate was further washed with hexane (2 x 50 mL). The pure white product was dried under vacuum for further analysis. ATR–IR (cm^{-1}): 3386 v(O−H), 1738 v(C=O), 1232 v(C–O). ^{1}H NMR (500 MHz, DMSO-d_{6}) δ_{H} ppm: 3.30–5.68 (m, AGU, 7H), 4.16 (m, 2H), 1.87 (m, 2H), 1.51 (m, 2H), 1.38 (m, 2H), 0.89 (m, 2H). ^{13}C NMR (500 MHz, DMSO-d_{6}) δ_{C} ppm: 154.08, 102.53, 79.22, 74.76, 72.90, 71.89, 66.22, 31.00, 30.64, 28.15, 27.24, 21.03, 13.15.

Recovery of DAC, DMSO and BMIMCl

After precipitation of the product in water, the filtrate containing water, DMSO, unreacted DAC, BMIMCl and allyl alcohol was evaporated using the rotary evaporator recovering water and allyl alcohol. Then, DMSO and DAC were distilled via fractional distillation. The remaining solid was pure BMIMCl. See flowchart of the whole procedure including additional details is presented in **Figure 5.4**.

^{31}P NMR method for DS determination

Degrees of substitution (DS) were determined by ^{31}P NMR using a Bruker Ascend™ 400 MHz spectrometer with 512 scans, a delay time d_1 of 3 seconds and a spectral width of 80 ppm (180 –100 ppm). The samples were prepared according to the following procedure: an exact amount of 25 mg of a sample was weighed and dissolved in 400 µL of pyridine and 100 µL of $CDCl_3$. Afterwards, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2-Cl-TMDP, 100 µl, 0.63 mmol) was added to the solution followed by addition of 500 µL of $CDCl_3$. The resulting homogenous mixture was allowed to stir for 5 minutes. Then, 150 µL of a solution of chromium (III) acetylacetonate (3.6 mg mL^{-1}) as relaxation agent and benzoic acid (4.0 mg mL^{-1}) as internal standard in $CDCl_3$/pyridine (1:1.6) were added and the solution was stirred for further 5 minutes. Then, 70 µl of the solution was transferred to an NMR tube. DS values were calculated according to a reported equation[260].

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR spectra were recorded using Bruker Avance DRX 500 MHz with 1024 scans and a time delay d_1 of 5 seconds at 90 °C. Data were reported in ppm relative to DMSO-d_6 at 2.5 ppm. ^{13}C NMR spectra were recorded using a Bruker Avance DRX 500 with 30.000 scans and a time delay d_1 of 5 seconds at 90 °C. Data are reported in ppm relative to DMSO-d_6 at 39.51 ppm. All products were dissolved in DMSO-d_6 with the concentrations of 45-60 mg mL^{-1}.

Infrared Spectroscopy (IR)

Infrared spectra of all samples were recorded on a Bruker alpha-p instrument equipped with an ATR accessory.

Gel Permeation Chromatography (GPC)

GPC was carried out using DMAc (1g L^{-1} LiBr) as eluent with a sample concentration of 3g L^{-1} on a Polymer Laboratories PL-GPC 50 Plus Integrated System containing an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm), followed by three PLgel 5 μm Mixed-C columns (300 × 7.5 mm), and a refractive index detector at 50 °C with a flow rate of 1 mL min^{-1}. The system was calibrated against poly(methyl methacrylate) standards with molecular weights ranging from 700 to 2×10^6 Da. The dissolved samples was filtered through polytetrafluorethylene (PTFE) membranes with a pore size of 0.2 μm prior to injection. GPC of Whatman™ filter paper, No. 5 was achieved by a solvent exchange procedure, which is regarded as mildest procedure to dissolve cellulose in DMAc/LiBr[116,270].

Differential scanning calorimetry (DSC)

DSC experiments were carried out with a DSC821e (Mettler Toledo) calorimeter using 40 µL aluminum crucibles under nitrogen atmosphere. An amount of 10-15 mg for each sample was measured in two heating circles of -50–175 °C with heating and cooling rate of 15K/min. The second heating curves were considered for the accurate examination. Samples were measured at least three times for the verification of the results.

Thermal Gravimetric Analysis (TGA)

TGA measurements were conducted with a Netzsch STA 409C instrument applying α-Al_2O_3 as a crucible material and reference sample. The samples were heated from 25 °C up to 600 °C under nitrogen flow with a heating rate of 5 K min^{-1}, with sample mass of ~20 mg. Weight loss of the sample was evaluated for the determination of the thermal degradation.

Film Preparation

The sample was dissolved in pyridine and cast on 100 mm × 20 mm teflon plates with a minimum concentration of 1% (w/w). The films were allowed to form at room temperature and dried under vacuum.

Tensile Tests

Tensile strength of cast film was measured using GABO EXPLEXOR 150N instrument. All resulting data were an average of three measurements. The cast films were cut into 16 mm × 2 mm strips and measured with a speed of 0.3 mm/min.

5.6 Supporting information

1) IR-Spectra of modified cellulose and starch (including optimization studies)
2) NMR data of modified starch
3) NMR data of phosphorylated, modified cellulose and starch
4) GPC data of modified cellulose and starch
5) TGA data of modified cellulose and starch
6) Tensile strength measurements of modified cellulose
7) NMR data of recovered DAC and BMIMCI

1) IR-Spectra of modified cellulose and starch (including optimization studies)

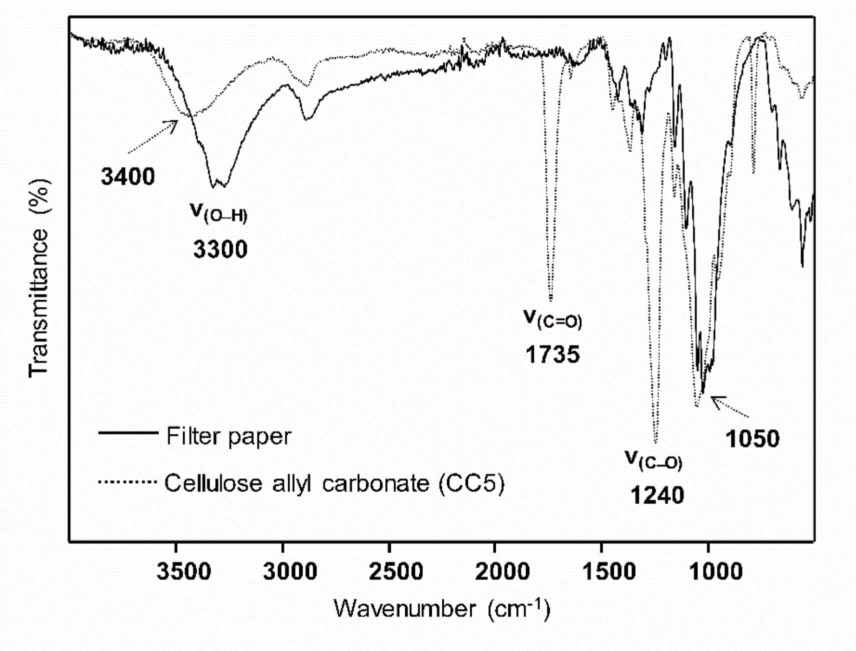


Fig. 5.S1 ATR-IR spectra of filter paper and modified filter paper with diallyl carbonate (DAC) (DS: ~1.3) in BMIMCl/DMSO solvent mixture (18 h, 4 eq. DAC, 80 °C, 10% (w/w) DMSO & 2% (w/w) cellulose concentration). Spectra were normalized to the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

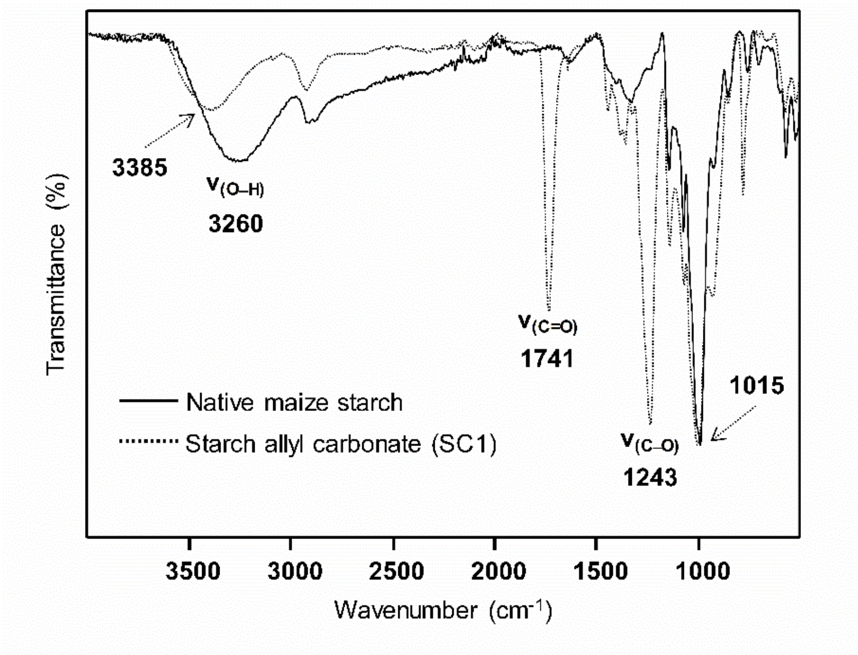


Fig. 5.S2 ATR-IR spectra of maize starch and modified maize starch with DAC (DS: ~1.2) in BMIMCl/DMSO solvent mixture (18 h, 4 eq. DAC, 80 °C, 10% (w/w) DMSO & 2% (w/w) starch concentration). Spectra were normalized to the intensity of the glycopyranose oxygen absorption at around 1015 cm^{-1}.

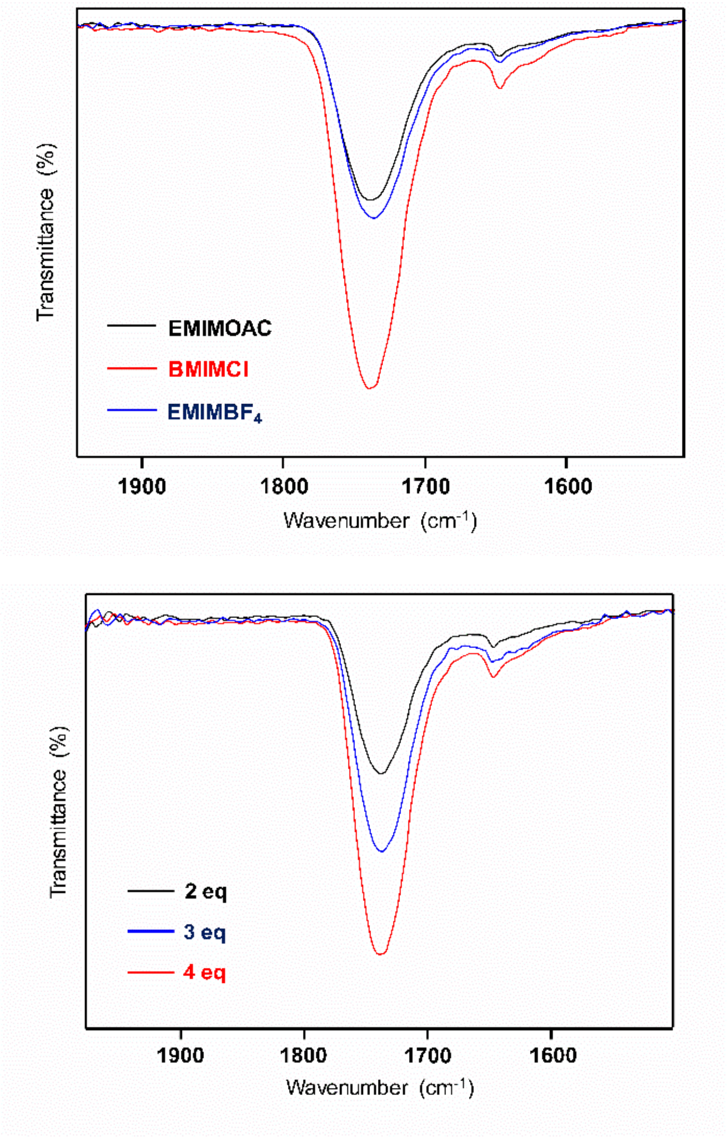
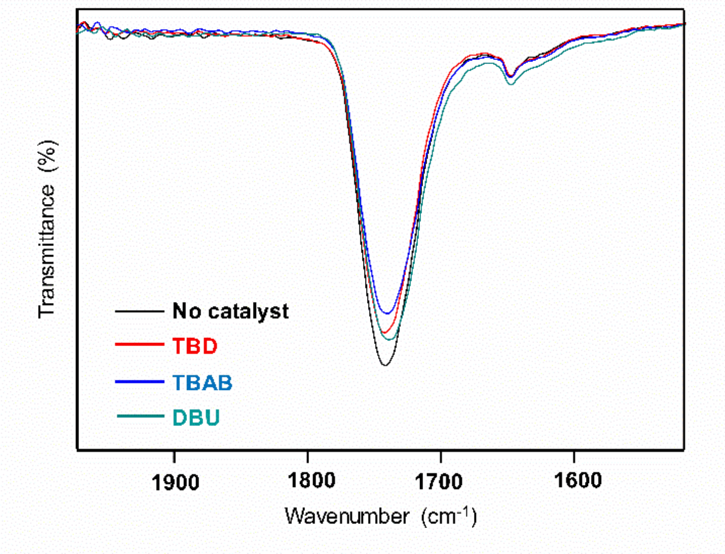


Fig. 5.S3 ATR-IR spectra of carbonyl peak intensities (**up**) of modified filter paper with DAC in different ionic liquids, 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-ethyl-3-methylimidazolium acetate (EMIMOAc) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$) (18 h, 3 eq. DAC, 80 °C, 10% (w/w) DMSO & 2% (w/w) cellulose concentration) and ATR-IR spectra of carbonyl peak intensities (**down**) of modified filter paper with different molar ratios of DAC in BMIMCl/DMSO solvent mixture (18 h, 80 °C, 10% (w/w) DMSO & 2% (w/w) cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.



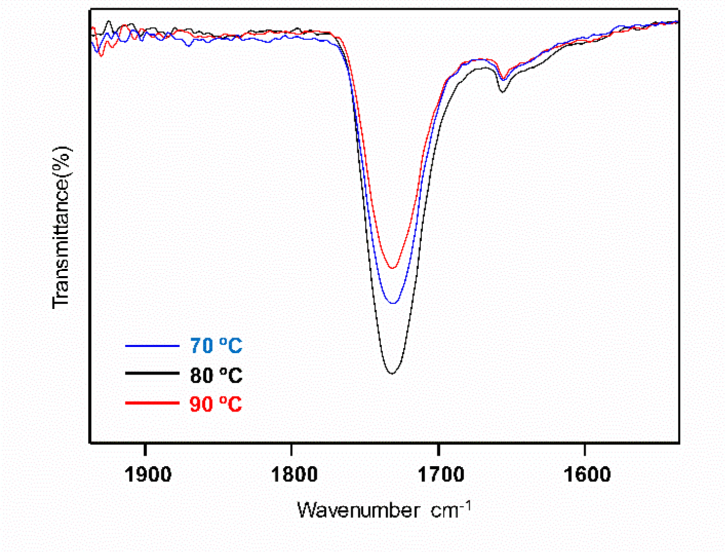


Fig. 5.S4 ATR-IR spectra of carbonyl peak intensities (left) of modified filter paper with DAC in BMIMCl/DMSO solvent mixture using different catalysts (18 h, 4 eq. DAC, 80 °C, 10 mol% of catalyst, 10% (w/w) DMSO & 2% (w/w) cellulose concentration) and ATR-IR spectra of carbonyl peak intensities (right) of modified filter paper with DAC in BMIMCl/DMSO solvent mixture at different reaction temperatures (18 h, 4 eq. DAC, 10% (w/w) DMSO & 2% (w/w) cellulose concentration). Spectra were normalized to the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

2) NMR data of modified starch

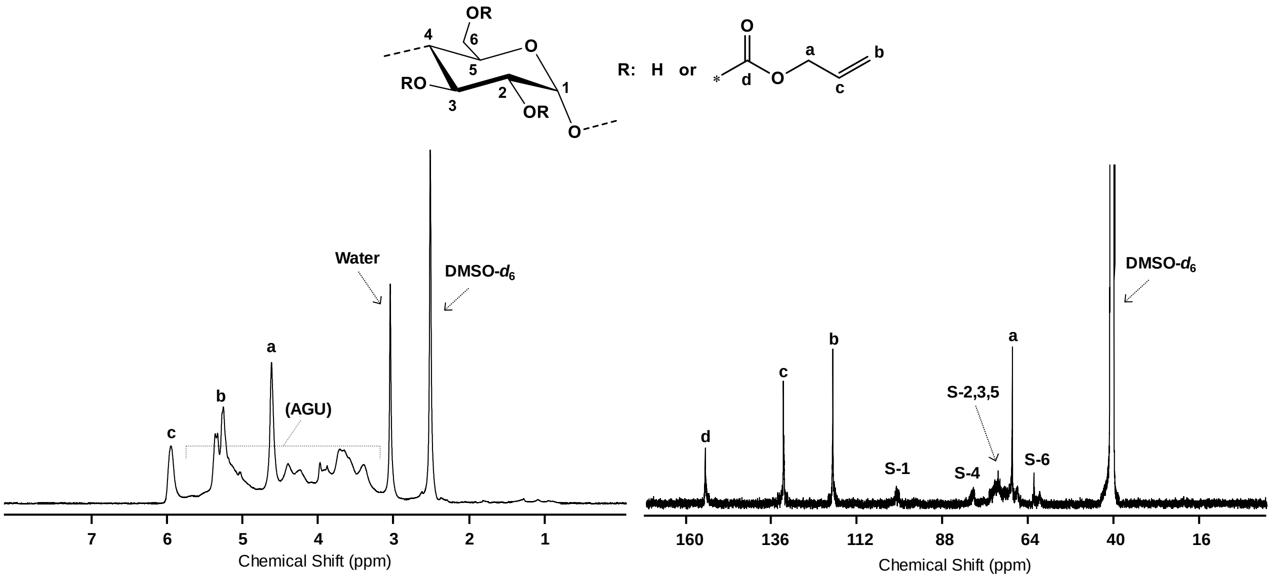


Fig. 5.S5 ^{1}H NMR (left) and ^{13}C NMR (right) of modified starch with DAC.

3) NMR data of phosphorylated, modified cellulose and starch

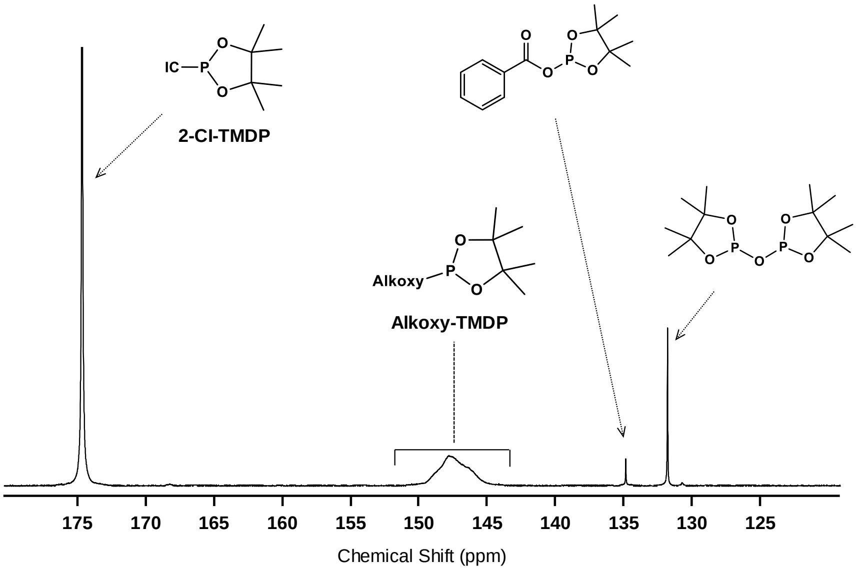


Fig. 5.S6 ^{31}P NMR of modified filter paper with DAC.

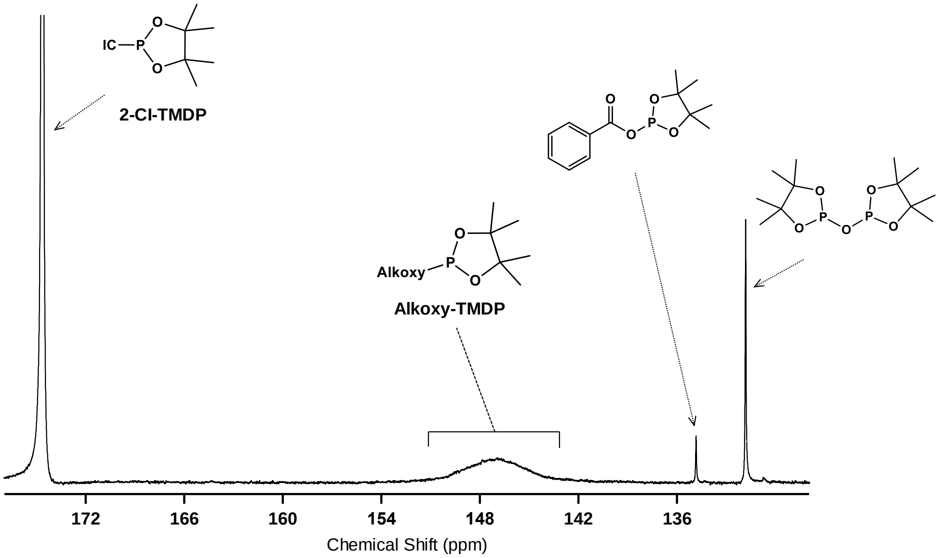
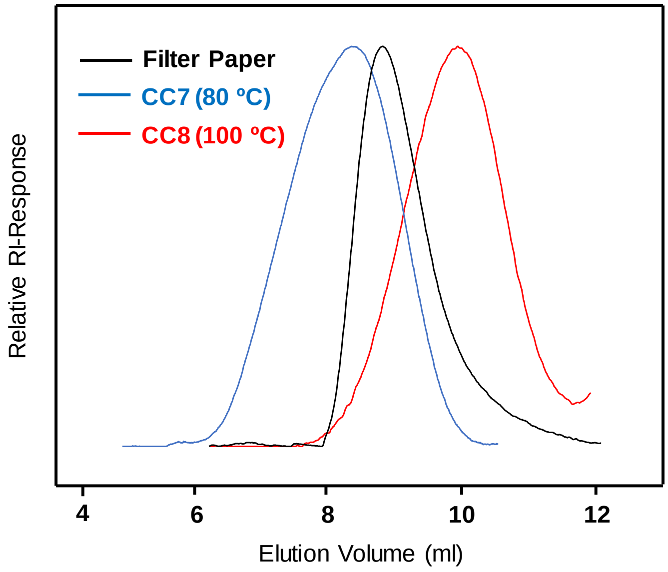


Fig. 5.S7 ^{31}P NMR of modified maize starch with DAC.

4) GPC data of modified cellulose and starch



Product[a]	M_w [kDa]	M_n [kDa][b]	*Đ*
Filter paper	**78**	**40**	**1.93**
CC7	**349**	**82**	**4.20**
CC8	**67**	**15**	**4.32**

[a] Reaction conditions: 18 h, 3eq. DAC, BIMIMCl/DMSO solvent mixture (10% (w/w) DMSO & 2% (w/w) cellulose concentration). [b] All GPC measurements were carried out relative to poly(methyl methacrylate) calibration in DMAc/LiBr (1% w/w)

Fig. 5.S8 GPC data of unmodified filter paper and modified filter paper with DAC at different temperatures.

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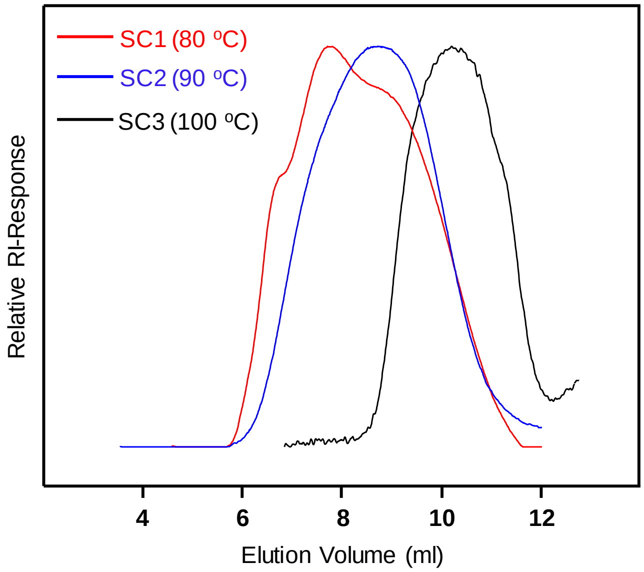

Product[a]	M_n [kDa][b]	M_w [kDa]	*Đ*
SC1	**84**	**523**	**6.21**
SC2	**66**	**256**	**3.88**
SC3	**12**	**27**	**2.19**

[a] Reaction conditions: 18 h, 3eq. DAC, BMIMCl/DMSO solvent mixture (10% (w/w) DMSO & 2% (w/w) starch concentration).
[b] All GPC measurements were carried out relative to poly(methyl methacrylate) calibration in DMAc/LiBr (1% w/w).

Fig. 5.S9 GPC data of modified maize starch with DAC at different temperatures.

5) TGA data of modified cellulose and starch

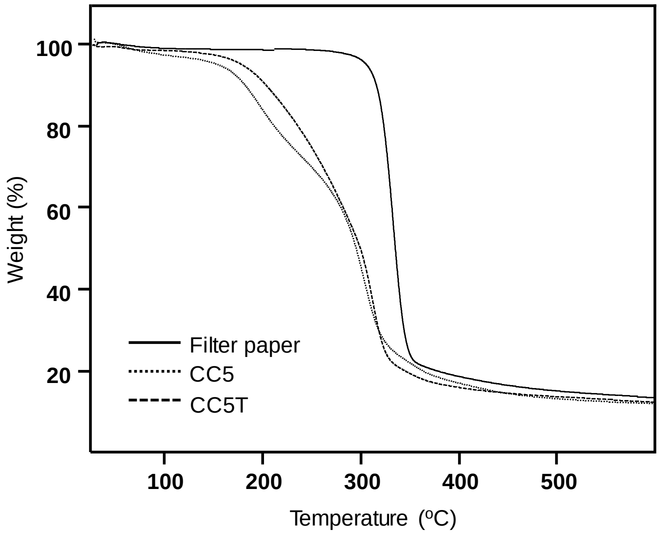

Fig. 5.S10 TGA data of unmodified filter paper, modified filter paper with DAC (CC5) and thiol-ene product of cellulose allyl carbonate (CC5T).

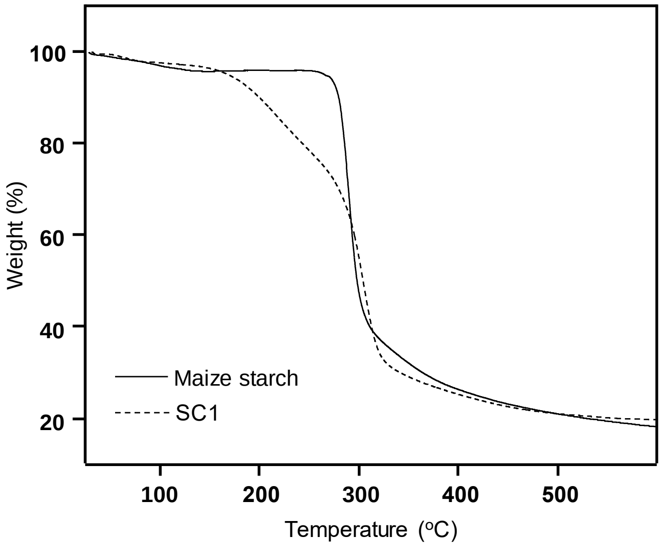

Fig. 5.S11 TGA data of unmodified maize starch and modified maize starch with DAC.

6) Tensile strength measurement of modified cellulose

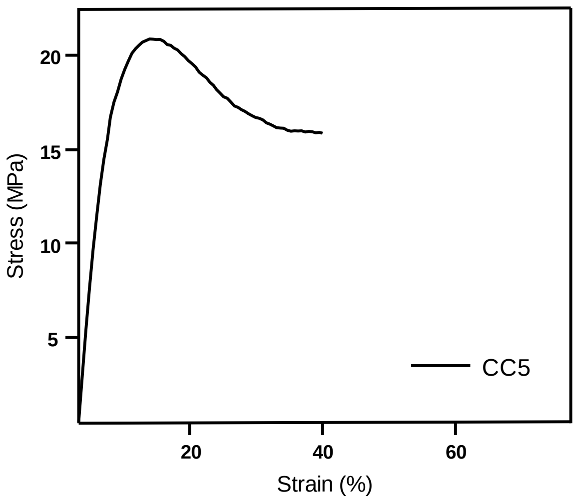

Fig. 5.S12 Tensile strength measurement of modified filter paper with DAC (DS: ~1.3).

7) NMR data of recovered DAC and BMIMCl

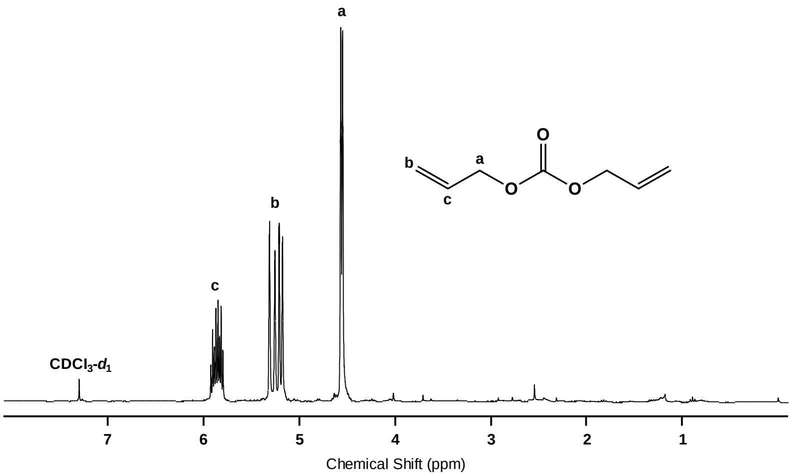

Fig. 5.S13 ^{1}H NMR of recovered DAC.

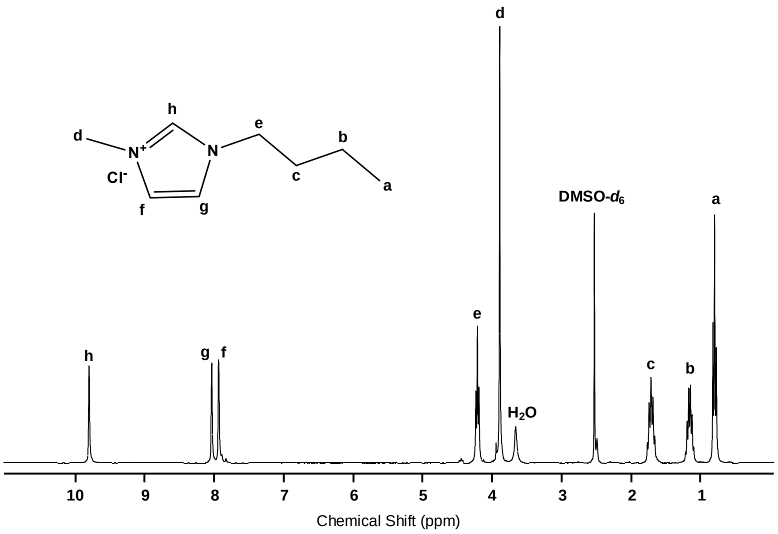

Fig. 5.S14 ^{1}H NMR of recovered BMIMCl.

6. Succinylation of cellulose in a CO_2-based switchable solvent and subsequent Passerini reactions

6.1 Abstract

A rapid and effective dissolution and activation of cellulose was demonstrated by a reversible reaction of CO_2 with the hydroxyl groups of the cellulose backbone in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The dissolved cellulose was subsequently subjected to *in situ* derivatization with succinic anhydride without the need of any additional catalyst under very mild conditions. As a result of optimization studies, cellulose was successfully converted to cellulose succinates with degrees of substitution (DS) ranging from 1.51 to 2.59, depending on the reaction conditions and the molar ratio of succinic anhydride. The optimized reaction conditions were successfully applied to different types of cellulose samples including microcrystalline cellulose (MCC) and organosolv wood pulp (WP), exhibiting similar conversions. Furthermore, the carboxylic acid moiety, introduced by the succinylation, was further converted *via* Passerini three-component reactions (Passerini-3CR). ^{31}P NMR revealed the quantitative conversions of carboxylic acid moieties on the cellulose backbone under mild conditions. All obtained products

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were thoroughly characterized by ATR-IR, ^{1}H,^{13}C, and ^{31}P NMR spectroscopies as well as by size exclusion chromatography (SEC). Thermal properties of the obtained products were investigated by differential scanning calorimetry (DSC) and by thermogravimetric analysis (TGA), revealing glass transitions (T_g) for all the Passerini products at 76 and 91 °C and high thermal stability at 278 and 289 °C, respectively. The reported methodology represents a very mild, highly efficient and sustainable route for the dissolution of cellulose and the synthesis of cellulose succinates. The subsequent modifications of the obtained cellulose succinates *via* Passerini reactions resulted in materials with improved thermal properties and offers a straightforward and versatile modification strategy for cellulose[271].

6.2 Introduction

Recently, a more sustainable CO_2-based switchable solvent system for cellulose solubilisation was proposed by Xie *et al.*[225] as well as by Zhang *et al.*[226] almost simultaneously. This CO_2-based switchable solvent strategy can be considered a breakthrough for the solubilisation of cellulose in terms of efficiency and sustainability. Basically, two distinct strategies were reported concerning this solvent strategy, a derivative[226] and a non-derivative[225] approach (**Section 2.4.2, Scheme 2.14**). The derivative approach includes the direct incorporation of CO_2 to the hydroxyl groups of the cellulose in the presence of a superbase, such as DBU, resulting a reversible carbonate complex on the cellulose backbone, in DMSO as a solvent, while the non-derivative approach employs an additional source of hydroxyl groups, such as ethylene glycol, for the *in situ* solubilization of cellulose. The term 'switchable' comes from the role of CO_2 in the system. A carbonate anion is formed resulting in the solubilisation of native cellulose, which can afterwards readily be regenerated by releasing the CO_2 from the system. A superbase, which is a part of the reversible complexation could be regenerated as well upon CO_2 release, thus, facilitating the recovery of the superbase from the system. Compared to classic ionic liquids (ILs), this solvent system is more efficient, more sustainable (i.e. no multi-step synthesis is required for IL synthesis and recovery is straightforward), and cheaper, since the only chemical to be synthesized is DBU (or another superbase). Moreover, solvent recovery is easier. Recently, several studies have been reported on the homogenous modifications of cellulose using this solvent system, including acylation[228] and grafting[229] from approaches. In all cases, milder reaction conditions leading to higher conversions compared to classic ionic liquids were described. Recent studies have shown that the superbase has a dual role in this system, both being part of the solvent system and acting as a catalyst in reactions. Indeed, the superbase is not fully converted into its protonated form in the solvent system. Therefore, the remaining free superbase maintains its catalytic activity, thus explaining higher conversions under mild conditions[230,231].

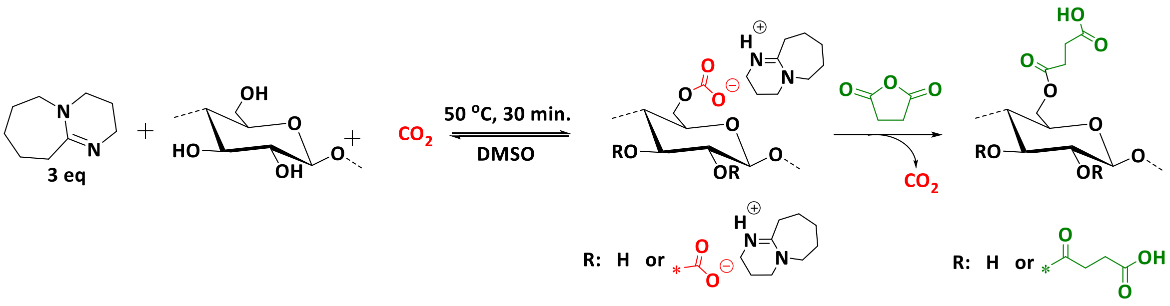
The acylation of cellulose using succinic anhydride is one approach to introduce carboxylic acid moieties to the cellulose backbone in a sustainable manner. Succinic anhydride can be produced from bio-based raw materials such as sugars[174]. In addition, succinic anhydride does not lead to an undesired corresponding by-product, which is yet another contribution to the reduced environmental impact of the procedure. Extensive studies are available on the homogenous succinylation of cellulose using succinic anhydride leading to various DS ranging from 0.3 without any catalyst to 2.3 using catalysts such as 4-(dimethylamino)pyridine (DMAP), depending also on the reaction conditions[166,175,177,179,180]. A variety of solvent systems and catalysts have been studied for this cellulose modification so far. For instance, Yin *et. al.*[177] studied a *N,N*-dimethylacetamide/LiCl solvent mixture for the succinylation of cellulose in the presence of triethylamine as catalyst, leading to DS values of up to 1.45. In addition, Li *et. al.*[166] achieved a DS of up to 2.34 in 1-butyl-3-methylimidazolium chloride (BMIMCl) as solvent in the presence of DMAP as catalyst at 100 °C. Chen *et. al.*[178] utilized the same catalyst for homogenous succinylation of cellulose in a tetra butylammonium fluoride (TBAF)/dimethyl sulfoxide (DMSO) solvent mixture, leading to a DS up to 2.11. Recently, homogenous succinylation of cellulose was also studied under catalyst free conditions. Liu *et. al.*[179,180] studied a BMIMCl/DMSO solvent mixture as well as 1-allyl-3-methylimidazolium chloride (AMIMCl) for the succinylation of cellulose without catalyst, obtaining DS values of up to 0.53 and 0.22, respectively. These previous studies have shown that the presence of a catalyst is essential to obtain high conversions. Interestingly, none of these reports focused on the recovery of the solvent systems and/or the catalyst, which is of course important regarding the sustainability of the procedure.

Along with various potential applications, such as absorbents for soil in agriculture or for the removal of heavy metals from waste water[272,273], the carboxylic acid moieties introduced by succinylation offer unique opportunities for further modification of cellulose, for instance *via* multicomponent reactions (MCRs) such as the Passerini three component (Passerini 3-CR) or the Ugi four component (Ugi 4-CR) reactions. MCRs are well explored and comprehensively studied for a wide range of chemical conversions. The latter reactions are very robust, versatile and offer advantages such as high atom economy, one pot reactions and high yields[274,275]. To the best of our knowledge, the corresponding multicomponent reactions have so far only been used for the crosslinking studies of carbohydrate polymers, including carboxymethyl cellulose and chitosan, to obtain hydrogels[276]. The modification of cellulose *via* Passerini-3CR and/or Ugi-4CR, which has not been reported before, is an innovative and powerful approach for the development of cellulose-based materials with desired tunable properties by selective combination of the different components employed.

Herein, we thus report an efficient and sustainable methodology for the modification of cellulose with succinic anhydride in a CO_2-based switchable solvent system (**Scheme 6.1**). This improved methodology enables higher conversions under milder conditions, if compared to previous studies (see literature discussion above). Moreover, we introduce the use of Passerini-3CR multicomponent reactions as versatile and mild modification strategy for cellulose. Indeed, succinylated cellulose prepared with the highest degree of substitution (**SFP 6**) was further modified *via* Passerini-3CR with excellent conversions and yields (**Scheme 6.2**).

6.3 Results and discussion

In this work, we demonstrate the rapid and efficient dissolution and activation of cellulose for the subsequent derivatization with succinic anhydride. (**Scheme 6.1**) The dissolution of cellulose was achieved at 50 °C in 30 minutes (compared to previously reported 60°C for 3h) by applying 2-5 bar of CO_2 pressure in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1 eq. with respect to -OH groups of cellulose) in DMSO as a solvent. Thus, applying the derivative approach (**see Section 2.4.2, Scheme 2.14**), the hydroxyl groups on the cellulose backbone could react reversibly with CO_2 to yield carbonate anions, resulting in a DMSO soluble polymeric structure. Since very mild conditions were applied for the effective dissolution of cellulose, this solvent system exhibits several advantages in terms of efficiency and sustainable economy over ionic liquids, for which much longer times (6-12 h) and higher temperatures (90-120 °C) are usually required. The activation is reversible and under release of the CO_2 cellulose can easily be regenerated. However, our observations showed that the solvent system could be preserved in a



Scheme 6.1 Dissolution and activation of cellulose for the subsequent derivatization with succinic anhydride using CO_2-based switchable solvent.

closed system under argon atmosphere for a couple of weeks, maintaining its efficiency. DMSO is often used as solvent or co-solvent for the homogenous functionalization of carbohydrates as it provides higher solubility and efficiency than its alternatives, DMAc and DMF[198,199]. Moreover, DMSO is regarded as an environmentally relatively benign solvent due to its high boiling point and low vapor pressure. Consequently, DMSO is selected as 'greenest' possible solvent and is thus widely employed for the functionalization of carbohydrate polymers, especially for cellulose[181,199]. Furthermore, DBU, which is part of the solvent system in this work, is a well-known organocatalyst for various transformations, including esterification and alkylation reactions[268,269]. This organocatalyst, along with being a part of the solvent system, maintained its catalytic activity in the course of the reactions with excellent efficiency in this work.

Filter paper (whatman™ cellulose filter paper, No. 5) was utilized as a cellulose source for the optimization studies of the succinylation reaction. All the cellulose samples were dried under vacuum for 24 h at 100 °C prior to modification in order to minimize potential negative effects of residual water on the conversion. The optimization results for the succinylation of cellulose samples with succinic anhydride are summarized in **Table 6.1**. ^{1}H NMR spectroscopy was used for the determination of the DS of the succinylated cellulose samples. For this, the obtained succinylated cellulose samples were dried under high vacuum at high temperatures to reduce the effect of residual water on DS value calculation. The method used for calculation of the DS values can be found in the supporting information and relies on a large number of scans for each measurement at increased temperature, to ensure well-resolved ^{1}H NMR spectra. The effects of the concentration of cellulose,

Table 6.1 Summary of the degree of substitution (DS) of modified filter paper with succinic anhydride (SA) (4% w/w DMSO concentration) under different reaction conditions.

Products	Eq. SA[a]	*T* (°C)	Time (min)	DS[b]
SFP 1	2.25	RT	30	1.51
SFP 2	2.25	RT	60	1.53
SFP 3	2.25	RT	90	1.51
SFP 4	3	RT	30	1.88
SFP 5	3.75	RT	30	2.16
SFP 6	4.5	RT	30	2.59
SFP 7	6	RT	30	2.62
SFP 8	4.5	60	10	2.22
SFP 9	4.5	60	30	–[c]
SFP 10	4.5	80	10	2.06
SFP 11	4.5	80	30	–[c]

[a] Equivalents of succinic anhydride with respect to anhydroglucose units (AGU). [b] DS was calculated from ^{1}H NMR spectroscopy. [c] Not determined, insoluble material. (RT: room temperature)

of the succinic anhydride molecular ratio as well as of the reaction time and temperature were investigated. The initial screening of the optimization studies was conducted by using ATR-IR spectroscopy. The optimization was performed by monitoring the intensity of the carbonyl peak at around 1703 cm^{-1} that is characteristic of the substituted ester moiety. Spectra were normalized to the intensity of the C−O stretching vibration of glucopyranose as internal reference at around 1050 cm^{-1} to have a relative comparison of the different degrees of modifications, since the pyranose oxygen absorption is not influenced significantly upon the succinylation process.

Absorbances in the fingerprint region around 982, 896 and 606 cm^{-1} are associated with the anhydroglucose unit of native cellulose. The peak at around 3300 cm^{-1} corresponds to stretching vibrations of the OH groups of native cellulose, which is reduced and replaced after the modification by a very broad signal between 2390−3680 cm^{-1} characteristic of the introduced −COOH stretching vibrations. In addition, new peaks at 1704 and 1148 cm^{-1} were observed and attributed to the C=O and C−O stretching vibrations of the introduced carboxyl moiety, respectively

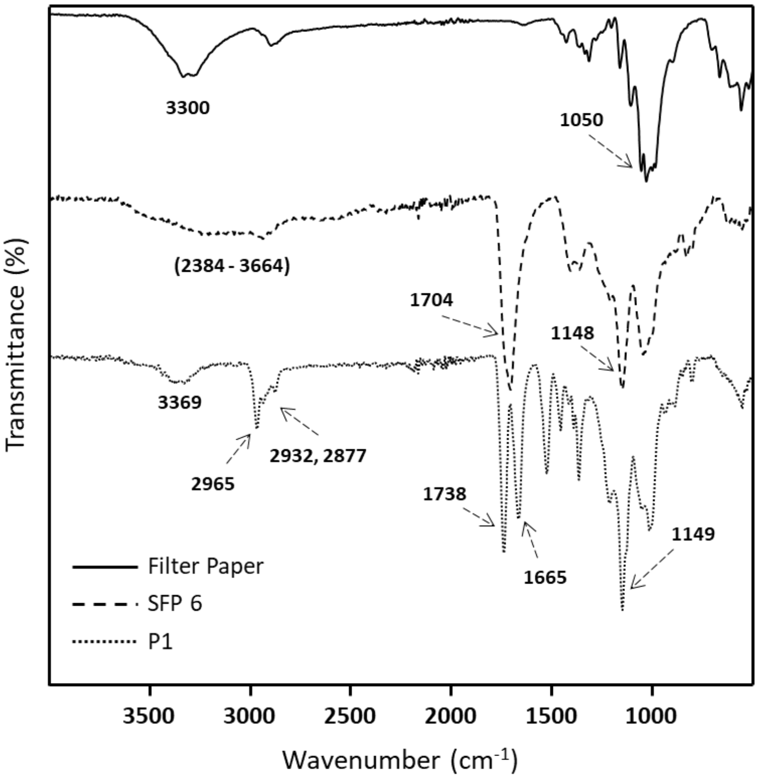


Figure 6.1 ATR-IR data of native filter paper, succinylated filter paper (**SFP 6**), and Passerini (**P1**) product of filter paper.

(**Figure 6.1**). A complete overview of the optimization data can be found in the supplementary information. ^{1}H and ^{13}C NMR spectroscopies were used for a further confirmation of the structure of the succinylated cellulose. After the modification, the peaks belonging to the backbone of the cellulose and the new peaks introduced by succinylation are clearly observed (**Figure 6.2**). The new broad peak at around 11.8 ppm corresponds to the protons of the carboxylic acid moiety. Methylene groups of the introduced succinate at around 2.5 ppm overlap with the NMR solvent DMSO-d_6 and cannot be clearly observed in ^{1}H NMR. However, ^{13}C NMR reveals the presence of the methylene signals at around 28.36 and 28.02 ppm. Moreover, the new peaks at around 172.46 and 170.77 ppm are characteristic of the ester and acid functionalities of the introduced succinates, respectively. Moreover, peaks associated with ester groups attached from positions c_6, c_3 and c_2 could be clearly seen in ^{13}C NMR. (**Figure 6.2**) However, there is still rooms for systematic

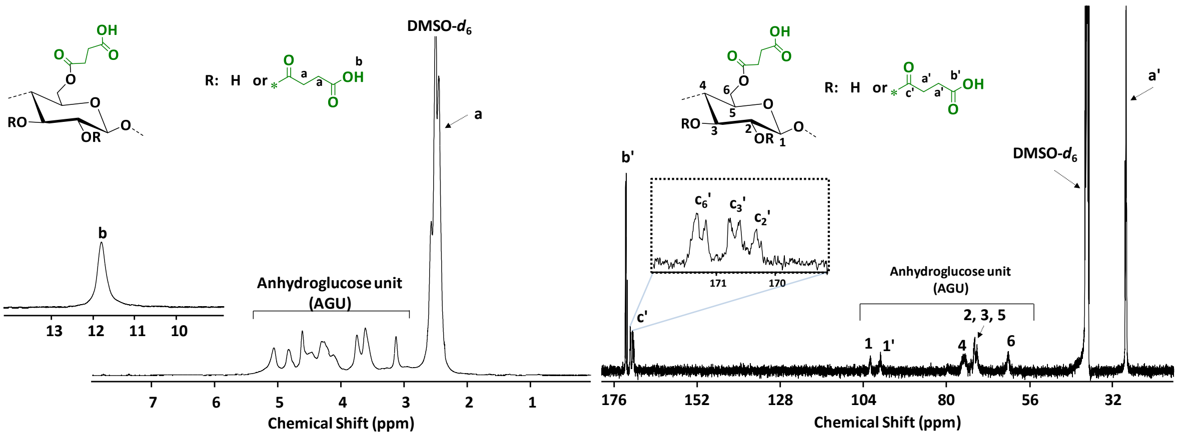


Figure 6.2 ^{1}H (left) and ^{13}C NMR (right) of the succinylated filter paper (**SFP 6**) in DMSO-d_6.

regioselectivity studies of all succinylated cellulose samples since there is no solution NMR studies reported for succinylated cellulose in the literature.

From our observations, the concentration of cellulose constitutes a predominant factor for homogenous reactions of cellulose. Therefore, different concentrations of cellulose were tested to determine the highest possible conversion and 4% (w/w) of cellulose concentration gave the best result in terms of conversion. Lower concentrations of cellulose (i.e. 2% and 3% (w/w)) led to lower conversions. (**Supporting info. Fig. 6.S3**). Higher concentrations, above 4%, resulted in a very viscous reaction mixture during the addition of succinic anhydride. Thus, the magnetic stirring could not be maintained at these higher concentrations.

Furthermore, different reaction temperatures were tested, and the highest conversions were obtained applying room temperature. Higher reaction temperatures, such as 60 and 80 °C, resulted in lower conversions and after 30 min of reaction time, the product isolated by reprecipitation was insoluble in common organic solvents, probably due to crosslinking (**Supporting info. Fig. 6.S2, S4, S5**). Similar results were observed in previous studies at high reaction temperatures (100 °C)[166]. Here, lower reaction temperatures (60-80 °C) resulted in crosslinked materials, presumably due to the higher reactivity of the applied solvent system in comparison to previous studies.

The optimum reaction time for obtaining the highest conversion and yield was also investigated and found to be 30 minutes. Applying longer times did not improve the DS.

Additionally, the molar ratio of succinic anhydride has a pronounced influence on the reaction. The DS could be adjusted (from 1.51 to 2.59, the highest reported in literature yet) by changing the molar ratio of succinic anhydride (from 2.25 to 4.50 eq. per AGU), resulting in different material properties (**Supporting info. Fig. 6.S1)**. The optimized reaction conditions were applied to different types of cellulose samples, including microcrystalline cellulose (MCC) and organosolv wood pulp (WP), exhibiting similar conversions, thus also demonstrating the reproducibility and versatility of the established procedure (**Supporting info. Fig. 6.S6).**

Size exclusion chromatography (SEC, relative calibration) of the succinylated cellulose samples revealed very high molecular weights in the range of 150-270 kDa, depending on the type of the cellulose. As expected, succinylated filter paper (SFP) had the highest molecular weight with 271 kDa. Succinylated microcrystalline cellulose (SMCC) and organosolv wood pulp (SWP) exhibited similar molecular weights with 150 and 160 kDa, respectively (**Table 6.2 and supporting info 6.S14**). Moreover, although the reported values are relative to the PMMA standards used for calibration, reaching very high molecular weights of modified cellulose samples highlights the mildness of the applied procedures and indicates that the possible degradation of the cellulose backbone was minimized. The thermal properties of the succinylated filter paper with the highest DS (**SFP 6**) were further characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). No thermal transition was observed. Moreover, it showed low thermal stability (5% degradation temperature of 202 °C) when compared to unmodified filter paper (305 °C) (**Table 6.2**). This could be ascribed to the high acid content, introduced *via* succinylation, on the cellulose backbone, which presumably

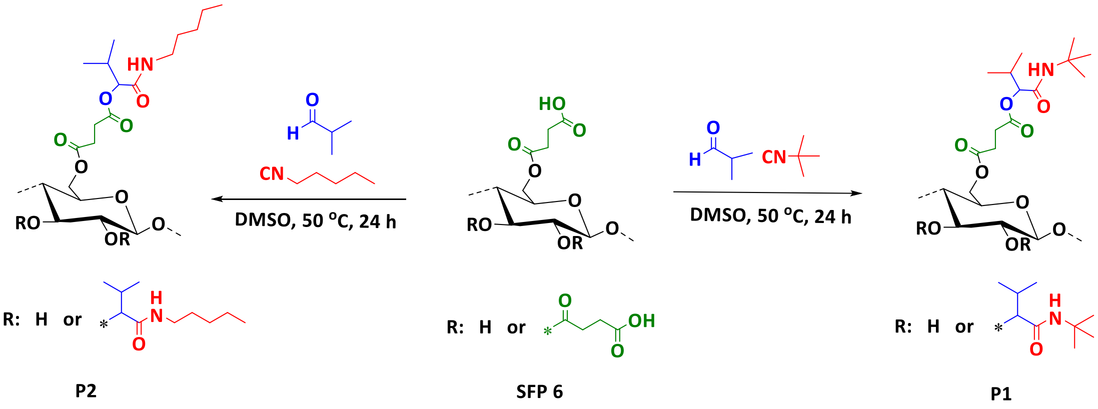
Table 6.2 SEC data, degrees of substitutions, conversions of carboxylic acid moieties, and thermal behaviours of modified cellulose samples.

Product	**M_n (kDa)**	**M_w (kDa)**	**$Đ^a$**	**DS[b]**	**Conversion[d] (%)**	**Yield[e] (%)**	**T_g (°C)**	**T_d (°C)**
Filter paper	–	–	–	–	–	–	–	305
SFP 6	271	714	2.6	2.59	–	86	–	202
SMCC	166	353	2.1	2.51	–	91	–	– [f]
SWP	167	593	3.5	2.57	–	82	–	– [f]
P1	177	587	3.3	2.59/2.64[c]	100	87	91	289
P2	212	690	3.2	2.59/2.64[c]	100	92	76	278

[a] GPC measurements were carried out relative to poly(methyl methacrylate) calibration in DMAc/LiBr (1% w/w). [b] DS was calculated by ^{1}H NMR. [c] DS value was calculated from ^{31}P NMR of Passerini product. [d] Conversion of the carboxylic acid moieties were calculated by ^{31}P NMR. [e] Yields were calculated from DS values (detailed calculations can be found in the supporting information). [f] Not measured

causes the degradation of the polymeric structure at high temperatures. After the reaction, DMSO and DBU were successfully recovered *via* a facile work-up. Fractional distillation was applied to recover the DMSO (90 °C, 25 mbar). The remaining mixture, composed of DBU and succinic anhydride/succinic acid or salts, was transferred into ethyl acetate and washed with a 6 M NaOH (3 × 10 mL) solution to recover DBU (56 %). The high purity of recovered DBU could be shown by ^{1}H and ^{13}C NMR spectroscopy (**Supporting info. Fig. 6.S17, S18**). Indeed, the low recovery yield of the DBU might be improved in the future by applying larger scale reactions by avoiding sample loss. In this work, the recovery of the unreacted succinic anhydride or succinic acid/salt was not attempted, again due to the small reaction scales used for this initial study.

Along with various potential applications, such as absorbents for soil in agriculture or for the removal of heavy metals from waste water[272,273], the carboxylic acid moieties introduced by succinylation offer unique opportunities for further modification of cellulose, for instance *via* multicomponent reactions (MCRs) such as the Passerini three component (Passerini 3-CR) or the Ugi four component (Ugi 4-CR) reactions. MCRs are well explored and comprehensively studied for a wide range of chemical conversions. The latter reactions are very robust, versatile and offer advantages such as high atom economy, one pot reactions and high yields[274,275]. To the best of our knowledge, the corresponding multicomponent reactions have so far only been used for the crosslinking studies of carbohydrate polymers, including carboxymethyl cellulose and chitosan, to obtain hydrogels[276]. The modification of cellulose *via* Passerini-3CR or Ugi-4CR, which has not been reported before, is an innovative and powerful approach for the development of cellulose-based materials with desired tunable properties by selective combination of the different components employed.



Scheme 6.2 Modification of the succinylated filter paper *via* Passerini-3CR reactions.

Thus, the obtained succinylated filter paper with the highest DS (DS: 2.59 from ^{1}H NMR, **SFP 6**) was further derivatized by Passerini three-component (Passerini 3-CR) reactions (**Scheme 2**). Two different reactions (**P1, P2**) for Passerini 3-CR were performed in order to easily tune the properties and the molecular structure of the modified cellulose. All reactions were performed under homogenous conditions using DMSO as a solvent. The concentration of the starting materials in Passerini reactions is a key parameter. Thus, different concentrations of succinylated cellulose were tested and 50 mg/mL was found to be most efficient. Reactions were performed at 50 °C to ensure the homogeneity of the reaction media and also to reduce the viscosity of the reaction mixture, enabling feasible stirring. Passerini reactions were completed within the 24 hours to achieve highest conversions of the carboxylic acid moieties. The conversion of carboxyl moieties was determined by ^{31}P NMR spectroscopy. The possible unreacted carboxylic acid moieties as well as the free hydroxyl groups reacted with the phosphorylating agent, revealing a broad peak between 140–155 ppm and at around 134 ppm, respectively. Results have

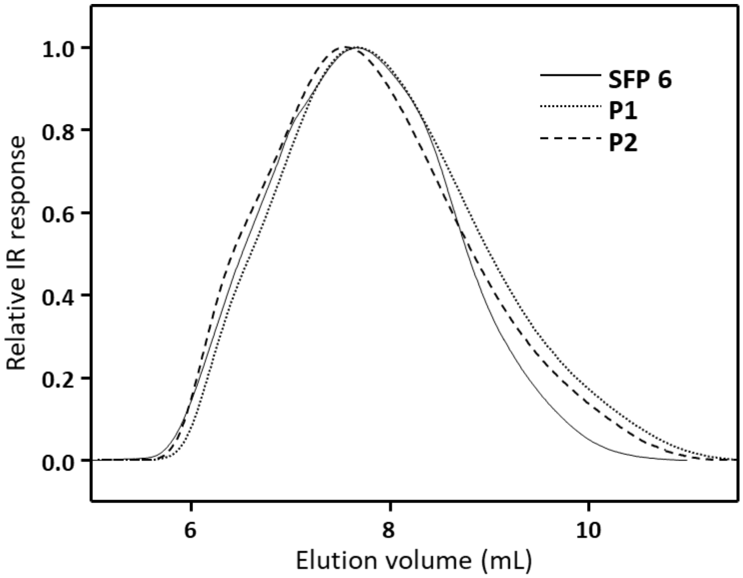


Figure 6.3 GPC traces of succinylated filter paper (**SFP 6**), Passerini products of filter paper (**P1, P2**).

shown that all Passerini reactions on succinylated filter paper resulted in full conversions of carboxyl moieties, since no signal at around 134 ppm was observed in ^{31}P NMR. Thus, the DS value of succinylation obtained from ^{1}H NMR (DS: 2.59) could be confirmed by ^{31}P NMR revealing very similar DS values. (DS: 2.64 from ^{31}P NMR). This consistency also verifies the reliability of our method for the determination of DS values of succinylated cellulose (**Table 6.2 and Supporting info. Fig. 6.S11,S12)**. The details of the calculation of the conversion of the carboxylic acid moieties of the Passerini products by ^{31}P NMR are described in the supporting information. All Passerini products of cellulose were soluble in common organic solvents including tetrahydrofuran, chloroform, dichloromethane, methanol as well as dimethyl sulfoxide and dimethyl formamide, thus significantly simplifying their analysis. The success of the MCRs was also observed by ATR-IR spectroscopy (**Figure 6.1 and supporting info. Fig. 6.S7,S8**). In both cases, the

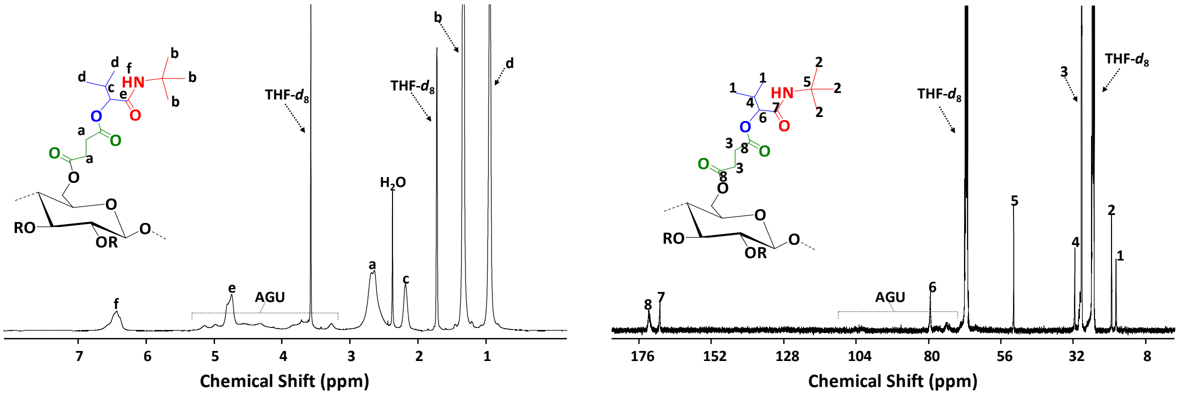


Figure 6.4 ^{1}H (**left**) and ^{13}C (**right**) NMR of the Passerini product of the filter paper (**P1**)

broad signal between 2390−3680 cm^{-1}, which represents the carboxylic acid moiety introduced *via* succinylation, almost completely disappeared and is replaced by less broad peaks between 3150−3700 cm^{-1}, which are attributed to the mixtures of newly introduced v(N−H), *via* MCRs, and unreacted v(O−H) streching vibrations from the cellulose backbone. Regarding the Passerini products, a new peak at around 1660 cm^{-1} corresponding to the introduced amide functionality appeared. Further confirmation of the multicomponent products was obtained using ^{1}H and ^{13}C NMR spectroscopy (**Figure 6.4 and Supporting info. Fig. 6.S9,S10**). ^{1}H NMR of the modified filter papers revealed that the broad peak at around 11.8 ppm, which is associated with hydrogen of carboxyl moiety, disappeared and new corresponding peaks of the components appeared and are clearly seen after the modification.

Moreover, the hydrogen of amide moiety, introduced *via* Passerini reactions, was clearly observed at around 6.5 ppm in ^{1}H NMR. ^{13}C NMR provides further confirmation of the completion of the Passerini reactions. Peaks at around 170 ppm, corresponding to carboxyl moieties of succinylated filter paper, disappeared and

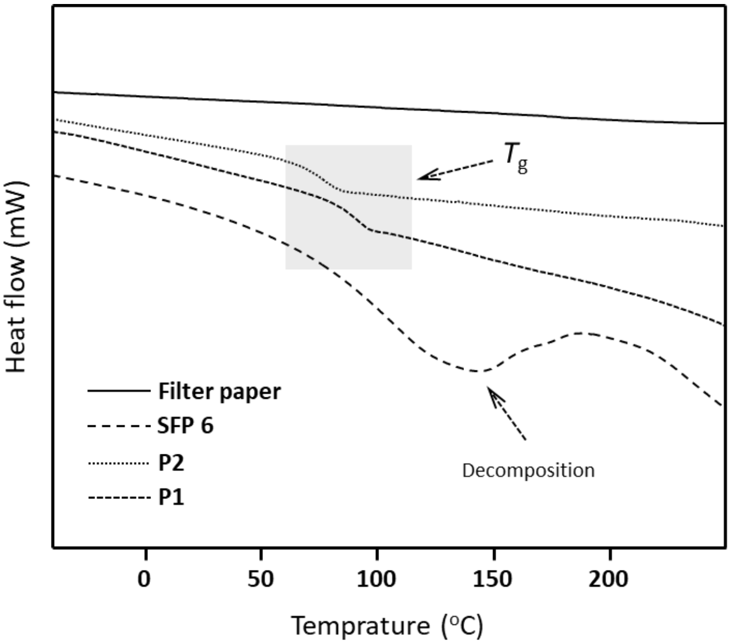


Figure 6.5 DSC data of filter paper, succinylated filter paper (**SFP 6**), and Passerini products of filter paper (**P1, P2**).

were replaced by peaks belonging to carbonyl groups of the amide groups at around 169 ppm for Passerini products. The peaks associated with the cellulose backbone are barely observed by ^{13}C NMR after the modification. The general overview of the peaks and spectra can be seen in the experimental section and supporting information, respectively.

Moreover, SEC traces did not reveal any major change in hydrodynamic volume upon further modification of filter paper, resulting in very high molecular weights, 177 and 225 kDa for P1 and P2, respectively, (**Table 6.2, Figure 6.3**) and thus no significant degradation of the cellulosic backbone. The slight decrease of the molecular weights of the Passerini products compared to succinylated filter paper could be ascribed to a different swelling behavior. However, comparison of the SEC data should remain within the Passerini products, not with succinylated cellulose, due to the highly different solubility (and thus hydrodynamic volume and swelling behavior) of the samples.

The thermal properties of the Passerini products were investigated by DSC and TGA. All Passerini products of the filter paper showed glass transitions (T_g) at 76 and 91 °C for P1 and P2, respectively (**Figure 6.5**). Interestingly, we showed the possibility not only to introduce thermal processability on cellulose, but also the ability to tune the thermal properties by simple variation of components chosen for the MCRs. The TGA measurements showed that all the Passerini products possessed high thermal stability, with degradation at 278 and 289 °C for P1 and P2, respectively. Values were found to be higher than the one of the succinylated cellulose (202 °C) and close to the native cellulose (305 °C) (**Supporting info. Fig. 6.S15).**

6.4 Conclusions

In this work, we report a rapid and efficient dissolution and activation of cellulose for the subsequent derivatization with succinic anhydride in a CO_2 based switchable solvent under very mild conditions. We demonstrated that the degree of substitutions can be adjusted (1.51 to 2.59) by changing the reactions conditions and the molar ratio of succinic anhydride. The reported solvent system is more efficient, more sustainable, and also cheaper compared to other procedures, since the only chemical to be synthesized is DBU, less toxic and easier to recover. Additionally, this solvent system did not employ any additional catalyst, since DBU is the part of the solvent system and also acted as a catalyst. Additionally, the recovery of DMSO and DBU was successful using a facile work-up. This work thus constitutes a valuable contribution towards a more sustainable polymer industry and shows several advantages compared to previous studies on the succinylation of cellulose, where more expensive solvent systems, additional catalysts (such as DMAP), higher equivalents of succinic anhydride (6 eq per AGU) were utilized at elevated temperatures (100-120 °C). Finally, introducing thermal transitions (here T_g) to cellulose remains an important research interest. By utilizing the carboxylic acid moiety introduced in the succinylated cellulose, we successfully carried out Passerini 3-CR post modifications. The procedure presents a straightforward functionalization with a high atom economy leading to cellulose-based materials with adjustable thermal properties. The possibility to tune the properties of the Passerini products by simply utilizing various aldehydes and isocyanides *via* a one pot procedure facilitates the synthesis of a variety of cellulose-based materials that are not accessible *via* etherification, esterification or other commonly applied methods.

6.5 Experimental part

Materials

All chemicals were used without further purification, unless otherwise stated. Filter paper was purchased from Whatman™ (filter paper, No. 5), organosolv wood pulp was kindly provided by our colleague, microcrystalline cellulose (MCC, powder), dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%), 1-pentyl isocyanide (97%), 2-phenylpropionaldehyde (98%), benzoic acid (ACS reagent, ≥99.5%), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, 95%), chromium (III) acetylacetonate, (99.99% trace metals basis) were purchased from Sigma Aldrich. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), succinic anhydride (>95) isobutyraldehyde (≥99%), tertbutyl isocyanide (98%) was purchased from TCI Europe N.V. Deuterated chloroform ($CDCl_3$-*d*), deuterated dimethyl sulfoxide (DMSO−d_6), deuterated tetrahydrofuran (THF−d_8) was purchased from Merck. CO_2 was purchased from air liquide. Native cellulose samples were dried prior to use (24 h at 100 °C) in order to reduce the amount of water to a minimum. Other solvents, such as hexane, were used in technical grade.

General procedure for the solubilization and *in situ* synthesis of cellulose succinate

Cellulose (0.50 g, 3.08 mmol) was suspended in 12.5 mL of DMSO followed by addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (1.41 g, 9.25 mmol) and allowed to stir for 30 minutes at 50 °C in the presence of CO_2 (2-5 bar) to obtain a clear solution. Afterwards, succinic anhydride (1.39 g, 13.8 mmol, 4.5 eq. per AGU) was added to the clear solution of cellulose and stirred for 30 minutes at room temperature. The resulting reaction mixture was poured to vigorously stirring water (200 mL). Then, water was slightly acidified with a diluted (0.05 M) hydrochloric acid solution to obtain white precipitates. The crude product was collected and dissolved in DMSO and reprecipitated in water (200 mL). The white product was further washed with water (200 × 3 mL) to remove DMSO, DBU and unreacted succinic anhydride, completely. The pure white product was dried under vacuum at 70 °C for further analysis. Yield was calculated from DS value. Yield: 86% ATR−IR (cm^{-1}): 2390−3680 mixtures of v(COOH), v(O−H), $v_{as}(CH_2)$, and $v_s(CH_2)$, 1703 v(C=O), 1147 v(C−O) ^{1}H NMR (500 MHz, DMSO−d_6) δ_H ppm: 11.8 (br, 1H), 3.0−5.3 (m, AGU, 7H), 2.46−2.57 (m, 4H). ^{13}C NMR (500 MHz, DMSO−d_6) δ_C ppm: 172.46, 170.77, 101.97, 99.14, 75.27, 72.03, 71.20, 62.22, 28.36, 28.02.

General procedure for the Passerini (3-CR) on succinylated filter paper

Succinylated filter paper (0.1 g, 0.24 mmol, DS: 2.59) was suspended in 2 mL of DMSO and allowed to stir at 50 °C to obtain a clear solution. Afterwards, the (2 eq. with respect to −COOH group, DS: 2.64) corresponding aldehyde (1.26 mmol) and isocyanide (1.26 mmol) were added drop-wise to the reaction mixture and allowed to stir for 24 hours at 50 °C. After the completion of the reaction, the resulting mixture was poured to vigorously stirring water (100 mL) to obtain white precipitates. The crude product was collected and dissolved in THF (3 mL) and reprecipitated in water (100 mL). Then, the precipitates were collected and dissolved in THF (3 mL) and reprecipitated in hexane (100 mL). This washing procedure with hexane was repeated two times to completely remove unreacted Passerini components. The pure white product was filtered and dried under vacuum at 50 °C, 24 h for further analysis. Yields were calculated from theoretical yields of respective Passerini products. **P1:** Yield: 87% ATR−IR (cm^{-1}): 3195−3506 mixtures of v(N−H) and v(O−H), 2965−2877 $v_{as}(CH_2)$, $v_s(CH_2)$, 1737 ester v(C=O), 1665 amide v(C=O), 1149 v(C−O) ^1H NMR (500 MHz, THF−d_8) δ_H ppm: 6.44 (br, 1H), 4.74 (m, 1H), 3.30−5.35 (m, AGU, 7H), 2.69 (m, 4H), 2.19 (br, 1H), 1.3 (s, 9H), 0.95 (s, 6H). ^{13}C NMR (500 MHz, THF−d_8) δ_C ppm: 172.72, 168.94, 79.40, 51.71, 31.47, 29.25, 19.31, 17.83. **P2:** Yield: 92% ATR−IR (cm^{-1}): 3174−3509 mixtures of v(N−H) and v(O−H), 2872−2960 $v_{as}(CH_2)$, $v_s(CH_2)$, 1737 ester v(C=O), 1655 amide v(C=O) 1149 v(C−O) ^1H NMR (500 MHz, THF−d_8) δ_H ppm: 7.09 (br, 1H), 4.87 (m, 1H), 3.40−5.20 (m, AGU, 7H), 3.18 (br, 2H), 2.67 (m, 4H), 2.21 (br, 1H), 1.51 (m, 2H), 1.33 (m, 4H), 0.97 (s, 6H), 0.90 (s, 3H). ^{13}C NMR (500 MHz, THF−d_8) δ_C ppm: 172.92, 169.54, 79.40, 39.98, 31.55, 30.17, 23.28, 19.31, 17.83, 14.45.

Recovery of DMSO and DBU

After precipitation of the product in water, the filtrate containing DMSO and DBU was evaporated using the rotary evaporator recovering water. Then, DMSO was distilled using a distillation apparatus (90 °C, 25 mbar). The remaining mixture was transferred to ethyl acetate (50 mL) and washed with water (3 × 10 mL, 6M, NaOH). The organic phases were collected and dried over $NaSO_4$. Then, the mixture was filtered, and ethyl acetate was evaporated using rotary evaporator to obtain DBU (Recovery yield: 56%).

^{31}P NMR Method for DS determination

Degree of substitutions (DS) were determined by ^{31}P NMR using a Bruker Ascend™ 400 MHz spectrometer with 1024 scans, a delay time *d*1 of 3 seconds and a spectral width of 90 ppm (190−100 ppm). Samples were prepared according to the following procedure: an exact amount of 25 mg of a sample was weighted and dissolved in 500 µL of $CDCl_3$. Pyridine (150 µl) was added upon complete dissolution. Afterwards, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2-Cl-TMDP, 100 µl, 0.63 mmol) was added to the solution and allowed to stir for 5 minutes a solution of chromium (III) acetylacetonate (50 µL, 50 mM in Pyridine : $CDCl_3$ / 3 : 2) as relaxation agent and *endo*-*N*-hydroxy-5-norbornene-2,3-dicarboximide (125 µL, 123.21 mM in Pyridine : $CDCl_3$ / 3 : 2, 0.0154 mmol) as internal standard were added and the solution was stirred for further 5 minutes. Then, 700 µl of the solution was transferred to an NMR tube. DS values and carboxyl moiety conversions of Passerini products were calculated according to the reported equation[260].

Instrumentation

Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H NMR spectra were recorded using Bruker Avance DRX 500 MHz with (for succinylated cellulose samples) 3000 scans and a time delay *d*1 of 5 seconds at 80 °C. Data were reported in ppm relative to DMSO−d_6 at 2.5 ppm and with (for multicomponent products) 1024 scans and a time delay *d*1 of 5 seconds at 50 °C. Data were reported in ppm relative to THF−d_8 at 1.73 and 3.58 ppm. ^{13}C NMR spectra were recorded using a Bruker Avance DRX 500 with 30000 scans and a time delay *d*1 of 5 seconds at 50 °C. Data are reported in ppm relative to THF−d_8 at 25.37 and 67.57 ppm (for multicomponent products) and DMSO−d_6 at 39.51 ppm (for succinylated cellulose samples). All products were dissolved in THF−d_8 and DMSO−d_6 with the concentrations of 30−50 mg mL^{-1}.

Infrared Spectroscopy (IR)

Infrared spectra of all samples were recorded on a Bruker alpha-p instrument using ATR technology.

Size Exclusion Chromatography (SEC)

Measurements were performed using a SEC system with DMAc (1g L^{-1} LiBr) as eluent with a sample concentration of 3g L^{-1} on a Polymer Laboratories PL-GPC 50 Plus Integrated System containing an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm), followed by three PLgel 5 μm Mixed-C columns (300 × 7.5 mm), and a refractive index detector at 50 °C with a flow rate of 1 mL min^{-1}. The system was calibrated against poly(methyl methacrylate) standards with molecular weights ranging from 700 to 2×10^6 Da. The dissolved samples were filtered through polytetrafluorethylene (PTFE) membranes with a pore size of 0.2 μm prior to injection.

Differential scanning calorimetry (DSC)

DSC experiments were carried out with a DSC821e (Mettler Toledo) calorimeter using 100 µL aluminum crucibles . An amount of 30 mg for each sample was measured in two heating cycles of -75−250 °C with heating and cooling rate of 15 K/min. The second heating curves were considered for the accurate examination. Samples were measured at least three times for the verification of the results.

Thermal Gravimetric Analysis (TGA)

TGA measurements were conducted with a Netzsch STA 409C instrument applying α-Al_2O_3 as a crucible material and reference sample. The samples (~ 20 mg) were heated from 25 °C to 500 °C under nitrogen flow with a heating rate of 5 K min^{-1}. Weight loss of the sample was evaluated for the determination of the thermal degradation.

6.6 Supporting Information

1) Calculation methods of the DS and conversion values of modified cellulose samples
2) IR-Spectra of modified cellulose (including optimization studies)
3) NMR data of modified cellulose
4) NMR data of phosphorylated, modified cellulose
5) SEC data of modified cellulose
6) TGA data of modified cellulose
7) DSC data of modified cellulose
8) NMR data of recovered DBU

1) Calculation methods of the DS and conversion values of modified cellulose samples

- **Calculation method of DS values of succinylated cellulose samples**

The DS values of succinylated cellulose samples were calculated by **Eq. (1)**:

$$\mathrm{DS} = \frac{7 \times (\mathrm{I}_{\text{-COOH}})}{1 \times (\mathrm{I}_{\text{H, AGU}})}$$

Where $\mathrm{I}_{\text{-COOH}}$ is the peak integral of carboxylic acid proton and I_{AGU} is the peak integral of anhydroglucose unit.

- **Calculation method of DS of Passerini products of cellulose**

As mentioned in the manuscript, since full conversions were obtained in Passerini products (No peak was detected from phosphorylated carboxylic acid at around 134 ppm in ^{31}P NMR). So, DS could be directly calculated as follows:

^{31}P NMR analysis was carried out as follows:

$\mathrm{MW_S}$: molecular weight (g mol^{-1}) of the substituent without including the oxygen atom between cellulose and the substituent (succinylation + Passerini components);
$\mathrm{IS_{vol}}$: amount of internal standard used in volume, mL;
$\mathrm{IS_{mol}}$: amount of internal standard used in mole, mmol;
$\mathrm{I_R}$: integration ratio of remaining phosphorylated cellulose hydroxyl groups against internal standard;
$\mathrm{W_S}$: sample weight, mg;
$\mathrm{DS_{max}}$: maximum DS value of 3 for unsubstituted cellulose;
$\mathrm{OH_C}$: free hydroxyl groups per weight unit of cellulose = $\mathrm{DS_{max}}/\mathrm{MW_{AGU}}$ = 3/162.16 = 0.01852 mol g^{-1}

The **Eq. (2)** for the calculation of the number of free hydroxyl groups per weight unit of substrate (**$\mathrm{OH_S}$**, mol g^{-1}):

$$\mathrm{OH_S} = \frac{\mathrm{IS_{mol}} \times \mathrm{IS_{vol}} \times \mathrm{I_R}}{1\,000\,000 \times \mathrm{W_S}}$$

The final **Eq. (3)** for the calculation of the DS from ^{31}P NMR analysis (**$\mathrm{DS_{31P}}$**):

$$\mathrm{DS_{31P}} = \mathrm{DS_{max}} = \frac{\frac{1}{\mathrm{OH_S}} - \frac{1}{\mathrm{OH_C}}}{\mathrm{MW_S} + \frac{1}{\mathrm{OH_S}} - 1}$$

2) IR-Spectra of modified cellulose (including optimization studies)

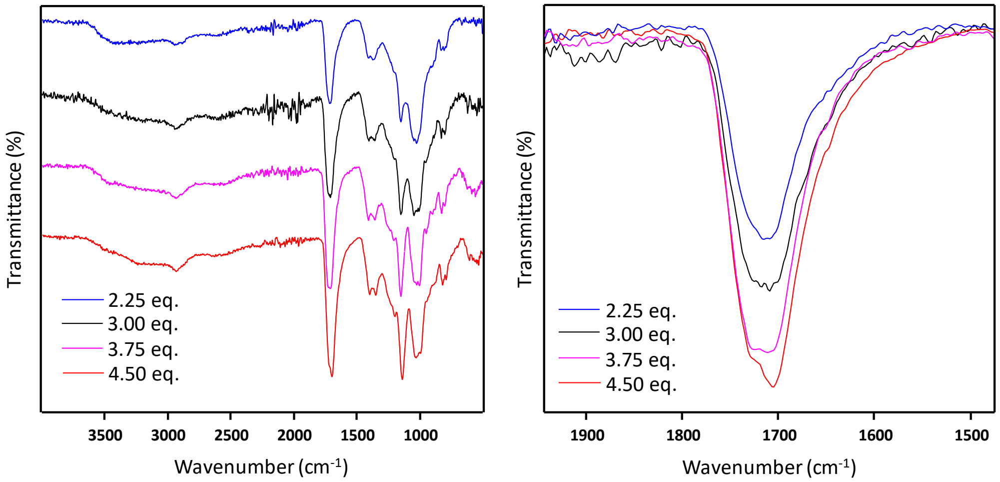


Fig. 6.S1 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with different equivalents (per AGU) of succinic anhydride in CO_2-based switchable solvent (30 min., room temperature, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

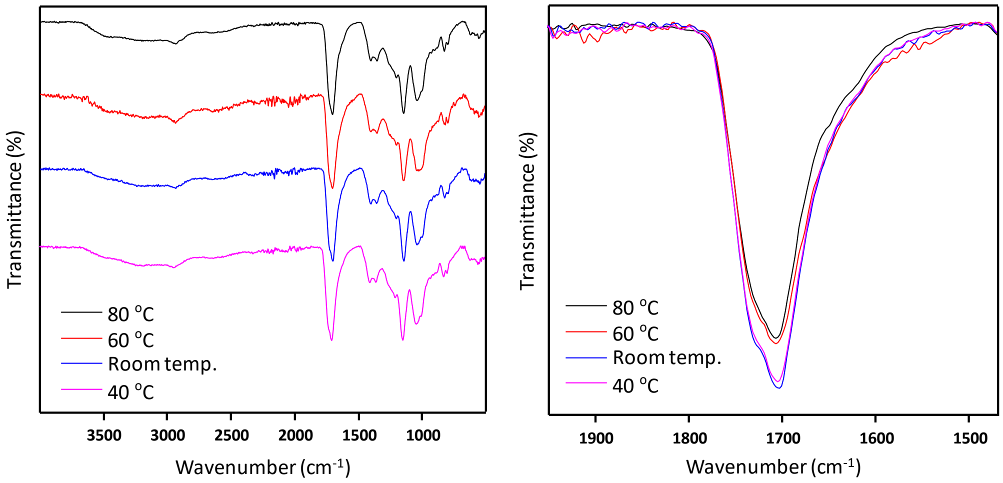


Fig. 6.S2 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at different reaction temperatures in CO_2-based switchable solvent (10 min for. reactions at 60 °C and 80 °C, 30 min for. reaction at room temp), 4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

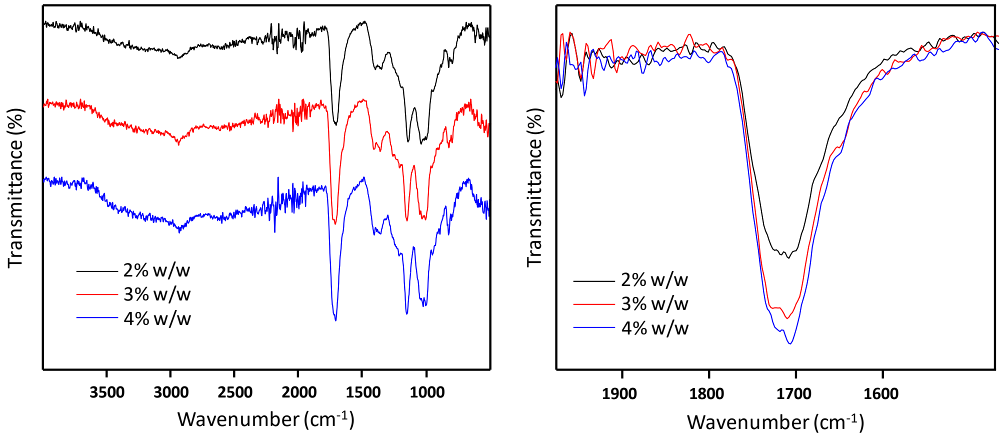


Fig. 6.S3 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at different cellulose concentrations in CO_2-based switchable solvent (30 min., room temperature, 4.5 eq. per AGU succinic anhydride). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

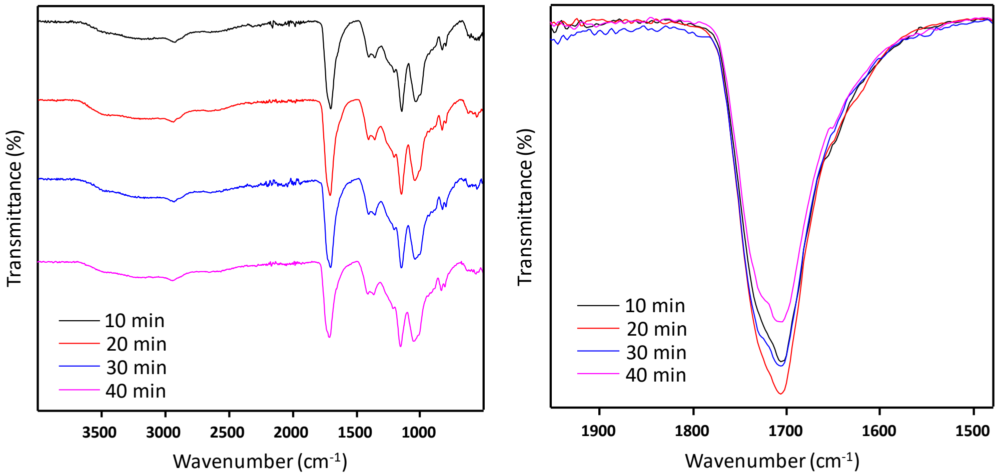


Fig. 6.S4 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at 60 °C in CO_2-based switchable solvent (4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

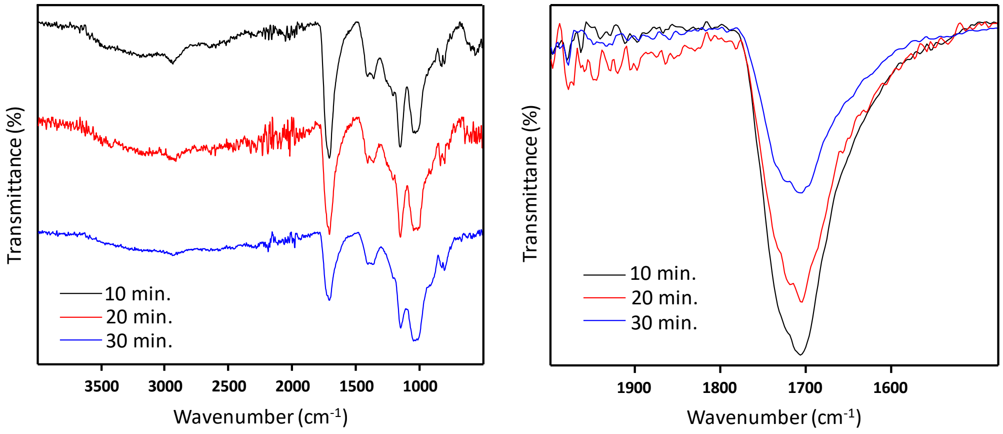


Fig. 6.S5 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper with succinic anhydride at 80 ^{o}C in CO_2-based switchable solvent (4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

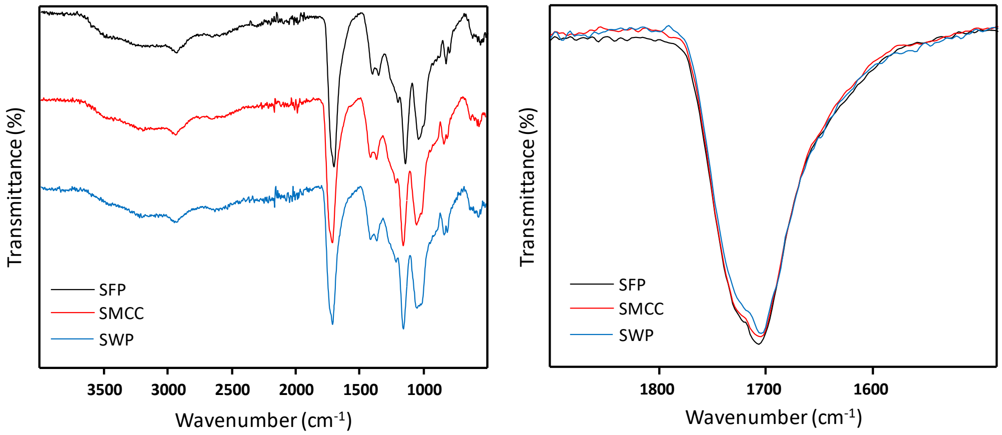


Fig. 6.S6 ATR-IR spectra (left) and carbonyl peak (right) of modified filter paper (SFP), microcrystalline cellulose (SMCC), and organosolv wood pulp (SWP) with succinic anhydride in CO_2-based switchable solvent (30 min, 4.5 eq. per AGU succinic anhydride, DMSO 4% w/w cellulose concentration). Spectra were normalized with the intensity of the glycopyranose oxygen absorption at around 1050 cm^{-1}.

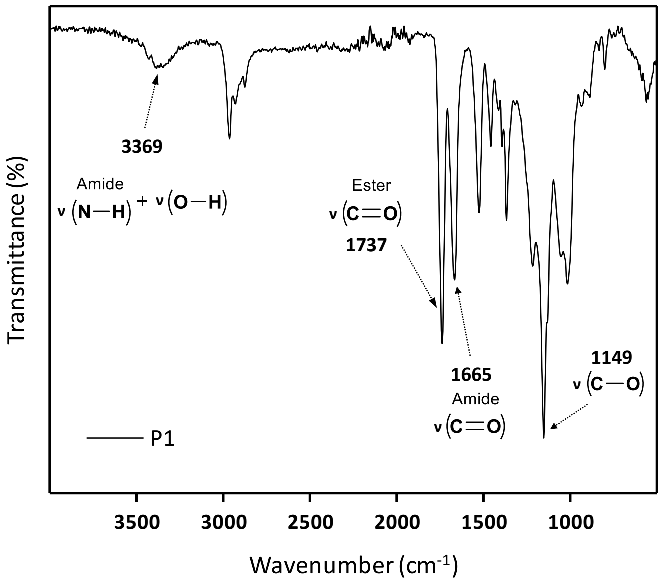


Fig. 6.S7 ATR-IR spectra of Passerini product (**P1**) of succinylated filter paper. (24 h, isobutyraldehyde (2 eq.), tertbutyl isocyanide (2 eq.), 50 °C, DMSO, 50 mg mL^{-1} cellulose concentration.)

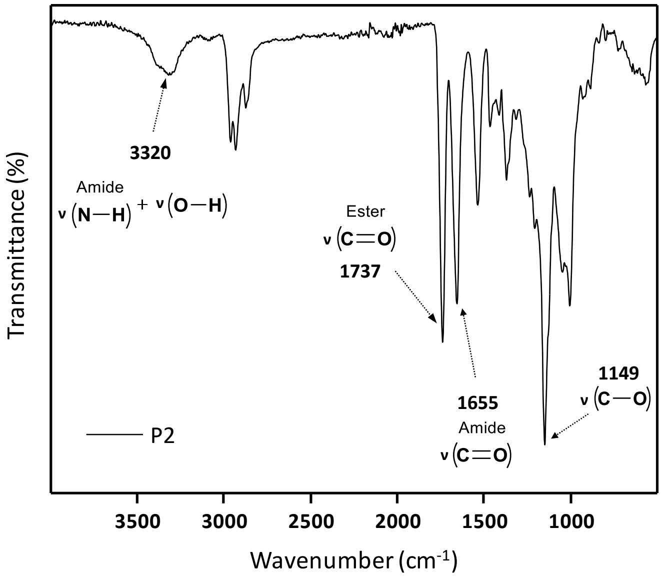


Fig. 6.S8 ATR-IR spectra of Passerini product (**P2**) of succinylated filter paper. (24 h, isobutyraldehyde (2 eq.), 1-pentyl isocyanide (2 eq.), 50 °C, DMSO, 50 mg mL^{-1} cellulose concentration.)

2) NMR data of modified cellulose

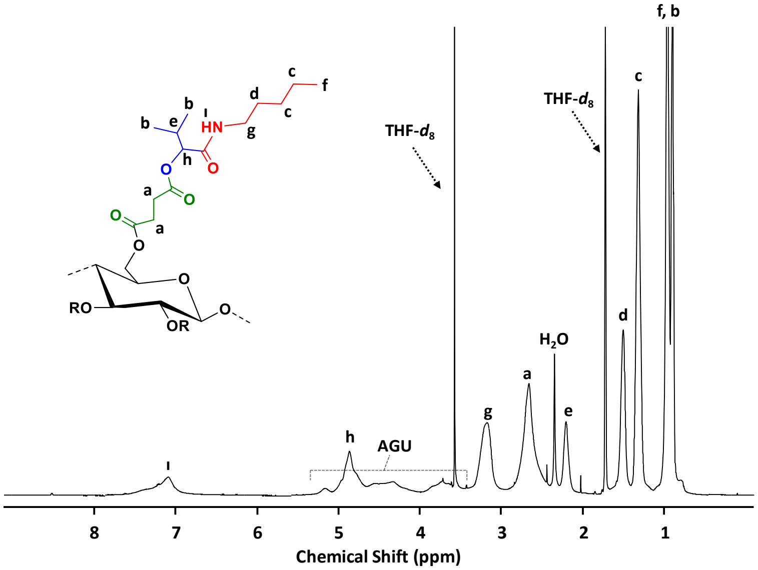


Fig. 6.S9 ^{1}H NMR of Passerini product (**P2**) of succinylated filter paper (DS: 2.64)

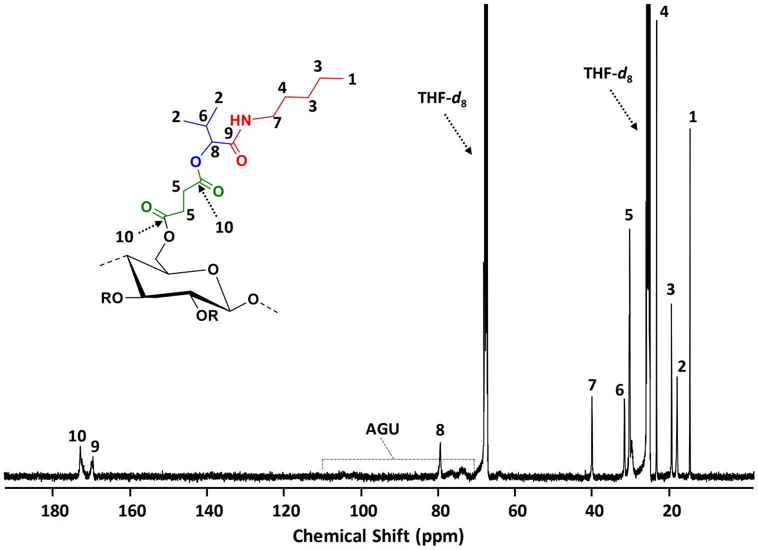


Fig. 6.S10 ^{13}C NMR of Passerini product (**P2**) of succinylated filter paper (DS: 2.64)

2) NMR data of phosphorylated, modified cellulose

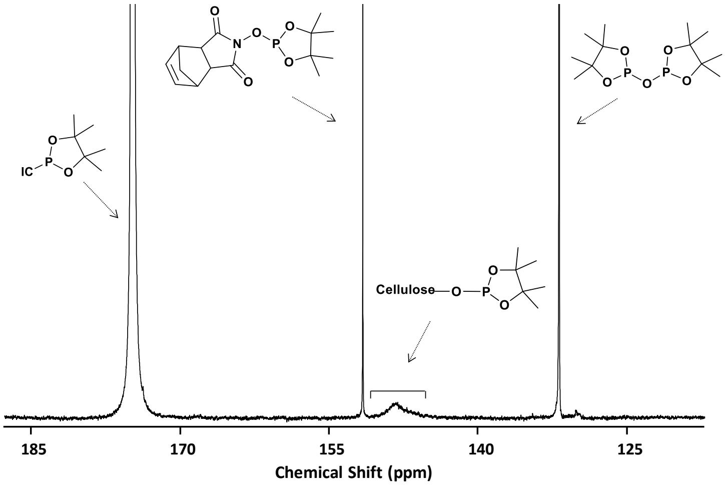


Fig. 6.S11 ^{31}P NMR of Passerini product (**P1**) of succinylated filter paper (conversion: 100%)

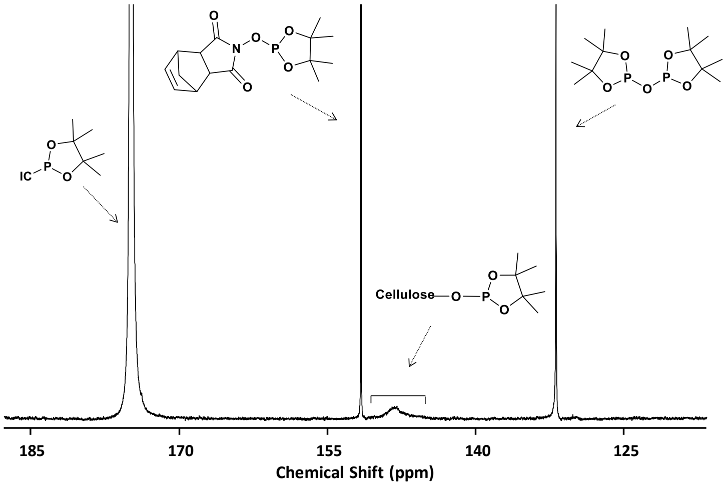
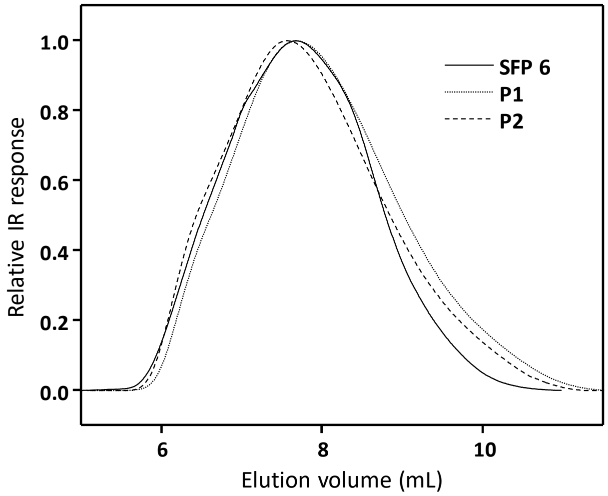


Fig. 6.S12 ^{31}P NMR of Passerini product (**P2**) of succinylated filter paper (conversion: 100%)

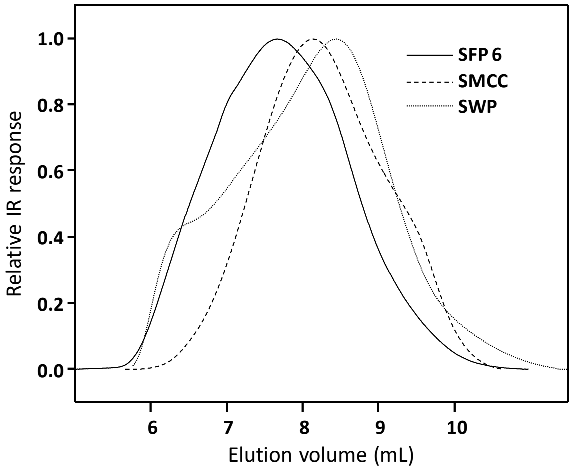
2) SEC data of modified cellulose



Product	M_n [kDa][b]	M_w [kDa][b]	Đ
SFP	271	714	2.6
P1	177	587	3.3
P2	212	690	3.2

[b] Data obtained from the GPC performed in DMAc/LiBr (1%, w/w) relative to PMMA calibration.

Fig. 6.S13 SEC traces of succinylated filter paper (**SFP 6**) and Passerini products of succinylated filter paper (**P1, P2**).

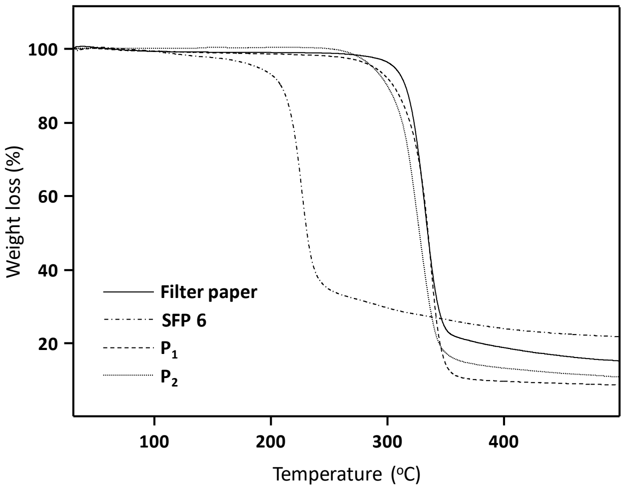


Product	M_n [kDa][a]	M_w [kDa][a]	Đ	DS[b]
SFP	271	714	2.6	2.64
SMCC	166	353	2.1	2.51
SWP	167	593	3.5	2.57

[a] Data obtained from the GPC performed in DMAc/LiBr (1%, w/w) relative to PMMA calibration. [b] Data obtained from ^{1}H NMR.

Fig. 6.S14 SEC traces of succinylated filter paper (**SFP 6**), microcrystalline cellulose (**SMCC**), and organosolv wood pulp (**SWP**).

2) TGA data of modified cellulose



Product	T_d [ºC]
Filter paper	305
SFP 6	202
P_1	289
P_2	278

Fig. 6.S15 TGA data of filter paper, succinylated filter paper (**SFP 6**), and Passerini products of succinylated filter paper (**P1, P2**).

2) DSC data of modified cellulose

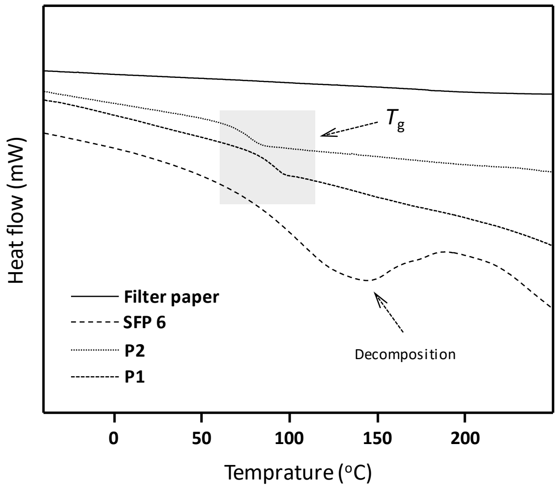


Fig. 6.S16 DSC data of filter paper, succinylated filter paper (**SFP 6**), and Passerini products of succinylated filter paper (**P1, P2**).

2) NMR data of recovered DBU

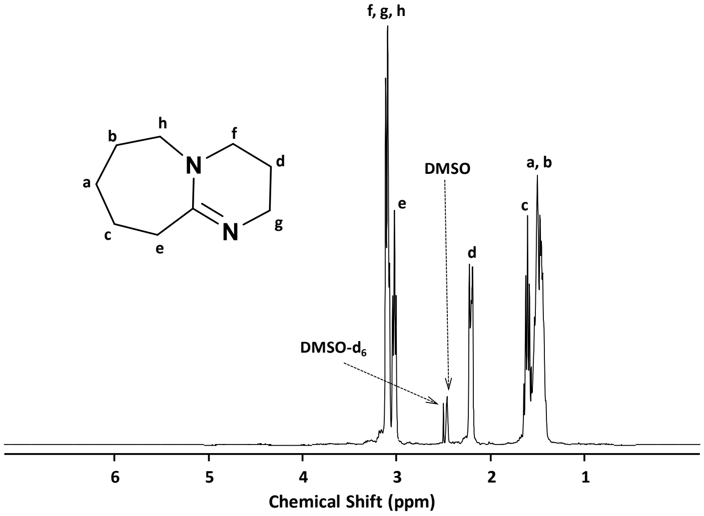


Fig. 6.S17 ^{1}H NMR of recovered 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

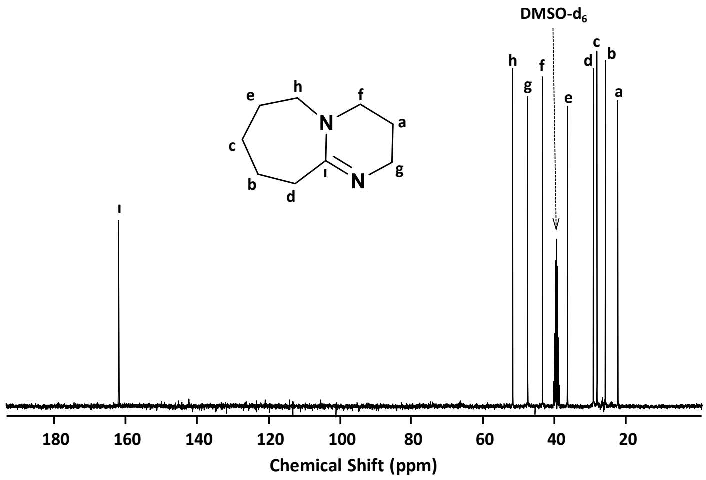


Fig. 6.S18 ^{13}C NMR of recovered 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).

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