

CHAPTER II

LITERATURE SURVEY

2.1 Cellulose: structure features and properties

2.1.1 Source of cellulose

Cellulose is found in plants as microfibrils (2-20 nm diameter and 100 - 40000 nm long). These form the structurally strong framework in the cell walls. Cellulose is mostly prepared from wood pulp. Commercial cellulose production concentrates on easily harvested sources such as wood or on the highly pure sources such as cotton (Table 2.1). As a naturally occurring material, cellulose may contain by-products, i.e. application problems and difficulties in chemical modifications are possible. However, up to date cellulose isolation and purification yield materials of high purity and variability. [1]

2.1.2 Structure features

Cellulose is a polydisperse linear homopolymer consisting of regio- and enantioselective β -1, 4- glycosidic linked D-glucose unit (so-called anhydroglucose units, AGU, Figure 2.1). The polymer contains three reactive hydroxyl groups at the C-2, C-3, and C-6 atoms, which are, in general, accessible to the typical conversions of primary and secondary alcoholic OH groups. [2, 3]

2.1.2.1 Crystalline structure

Solid cellulose shows a highly ordered microcrystalline structure alternating with regions of distinctly lower (amorphous regions). The crystalline nature of cellulose originates from intermolecular forces between neighbouring cellulose chains over long lengths. All native cellulose shows the same crystal lattice structure, called cellulose I. However, various modification of native cellulose can alter the lattice structure to yield other types of crystals [1, 4]. The intermolecular forces in the crystalline domains are mainly hydrogen bonds between adjacent cellulose chains in the same lattice plane, which results in a sheet-like structure of packed cellulose chains. In addition, the sheets are probably connected to one another by hydrogen bonds and/or van der Waal's forces. The organization of

cellulose molecules into parallel arrangements is responsible for the formation of crystallites. The length of an elementary crystallite range from 12 to 20 nm and the width from 2.5 to 4 nm.

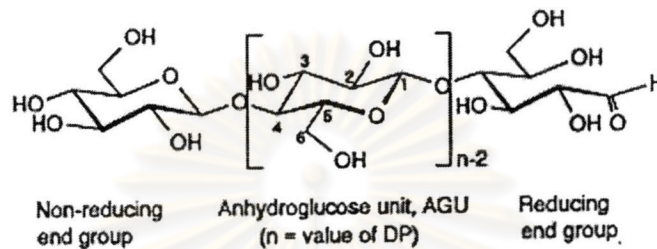


Figure 2.1 Molecular structure of cellulose [3]

2.1.2.2 Supermolecular structure

The tendency of hydroxyl groups to form intermolecular hydrogen bonds between neighbouring cellulose chains, in combination with the stiff, straight nature of cellulose molecules, results in the formation of crystallite strands. Such a strand of several crystals linked together by segments of long cellulose molecules constitutes the so-called elementary fibril, which is the basic structural component of the cellulose fibre. The interlinking regions between the crystalline areas in the strands have a distinctly less pronounced organization and thus constitute the amorphous cellulose. The elementary fibrils are packed together to form larger aggregates called micro- and macrofibrils, these aggregations are then further organized in a typical manner in the cell wall. [1, 4]

Table 2.1 Chemical composition of some cellulose source (according to Horn [5])

Source	Composition (%)			
	Cellulose	Hemicellulose	Lignin	Extract
Wheat straw	30	50	15	5
Begasse	40	30	20	10
Soft wood	40-44	25-29	25-31	1-5
Hard wood	43-47	25-35	16-24	2-8
Flax	71.5	20.6	2.2	6.0
Jute	71.2	13.6	13.1	1.8
Henequen	77.6	4.8	13.1	3.6
Ramie	76.2	16.7	0.7	6.4
Cotton	95	2	0.9	0.4

In this context, it is worth mentioning that the vicinal secondary hydroxyl groups may undergo typical glycol reactions. Based on this molecular structure, i.e. the tacticity and uniform distribution of the hydroxyl groups, ordered hydrogen bond systems form various types of supra- molecular semicrystalline structure. The signification of the accessibility factor in affecting the cellulose reactivity is generally accepted today. Not only the crystallinity but also hydrogen bonding pattern have a strong influence on the whole chemical behavior of cellulose. A further consequence of supra- molecular structure is the insolubility of the macromolecular in the water as well as in common organic liquids, which stimulated and still stimulates the search for solvents appropriate for homogenous phase reactions which are still unconventional synthesis [6].

Cellulose is an insoluble molecule consisting of between 2000 - 14000 residues with some preparations being somewhat shorter. It forms crystals where intra-molecular (O3-H with O5 and O6 with H-O2) and intra-strand (O6-H with O3) hydrogen bonds holds the network flat allowing the more hydrophobic ribbon faces to stack. Each residue is oriented 180° to the next with the chain synthesized two residues at a time. Although individual strand of cellulose are intrinsically no less hydrophilic, or no more hydrophobic, than some other soluble polysaccharides (such as amylose) this tendency to form crystals utilizing extensive intra- and intermolecular hydrogen bonding makes it completely insoluble in normal aqueous solutions.

2.1.3 Application of cellulose

Cellulose has many uses as an anticake agent, emulsifier, stabilizer, dispersing agent, thickener, and gelling agent. Novel cellulose derivatives are beginning to play an important role in the "design for the environment" concept being adopted for materials in general and packaging materials in specific. Derivative of cellulose affords materials that are processible into various useful forms, such as three dimensional objects fibers, and solutions to be used for coating or casting (of films or membranes). Secondly, the physical properties of cellulose can be greatly modified by derivatization. Cellulose derivatives were used into wide range of application such as coating, control release, plastics, biodegradable, optical films, membrane structure, composites and laminates [4]. Examples of some type of cellulose and applications are given in Table 2.2. The modified properties of these cellulose derivatives give

entry into a range of applications greatly expanded from those available to the parent polysaccharide. It is important to gain a fundamental understanding of how structural changes are effected by cellulose esterification, the ability to predict how those changes will impact properties and an understanding of how those property changes translate into performance vs. application requirements, in some cases in cooperation with other materials or ingredients.

Table 2.2 some types of cellulose and their applications [4]

Type of cellulose	Applications
Cellulose acetate	Extruded tape, packaging film, blister packs, skins, containers, premium toys, electrical appliances housings and electrical insulation
Cellulose acetate butyrate (CAB) and cellulose propionate	Tooth brush handles, safety goggles, blister packs
Ethyl cellulose	Flashlight cases, fire extinguisher components and electrical appliance parts
Cellulose triacetate	Photographic albums, electrical insulation applications and photographic films base
Cellulose nitrate	Toilet articles and industrial items fabricated from sheet, rod and tube

2.2 Media for cellulose functionalization

A major stimulation for the investigation of alternative paths for polysaccharide functionalization was the discovery of a variety of new solvents for polyglucans especially for cellulose with its extended supra-molecular structure. Of course, the main driving force looking for new ways to dissolve cellulose is the need to develop alternative paths for fiber spinning and related processes excluding well documented problems of the viscose process. In addition, the use of cellulose solvents for characterization of cellulosic materials has grown in significance over the last years as well. A detailed discussion about all cellulose solvents known and the mechanism of dissolution is well beyond scope of this part. Several good, comprehensive reviews have been appeared.

Dissolution of cellulose destroys the highly organized hydrogen-bonding system surrounding the single polyglucan chain. It needs to be mentioned that not only the physical dissolution of the polysaccharide (non-derivatization) is capable for alternative synthesis paths but also the functionalization after partial derivation, i.e. after dissolving the polymer in so-called derivatizing solvent [8-11]. In the latter case cellulose intermediates are formed in situ by introducing new functional group via covalent bonds especially ester moieties of rather low hydrolytic stability. Furthermore, it is possible to isolate these intermediates or to synthesize similar compounds and to conduct subsequently the homogeneous modification starting from the polymers dissolved in an inert simple organic solvent. A clear line between these cellulose intermediates and true cellulose derivatives can not be drawn. But it seems reasonable to define cellulose intermediates as hydrolytically unstable cellulose derivatives that can be either obtained by isolation from solutions of derivatizing solvents or as specifically synthesized cellulose derivatives with substituents which are easily cleaved off during a common work-up procedure, e.g. in aqueous media. A nice example is that of cellulose trifluoroacetates where the reaction of trifluoroacetic acid/trifluoroacetic anhydride with the polymer produces the soluble product, which can be even isolated and redissolved in common organic solvents. On the other hand, formation of cellulose acetate followed by a separate dissolution in acetone would not be classified as a cellulose solution [12].

Non-derivatizing solvents include both single and multi-component systems. Although a wide variety of these solvents were developed and investigated in recent

years only a few have shown a potential for a controlled and homogeneous functionalization of polysaccharides. Limitations are high toxicity, high reactivity of the solvents leading to undesired side reactions, and the loss of solubility during reactions yielding inhomogeneous conditions by formation of gels and pastes which can be hardly mixed and even by formation of deswollen particles of low reactivity which set down in the reaction medium.

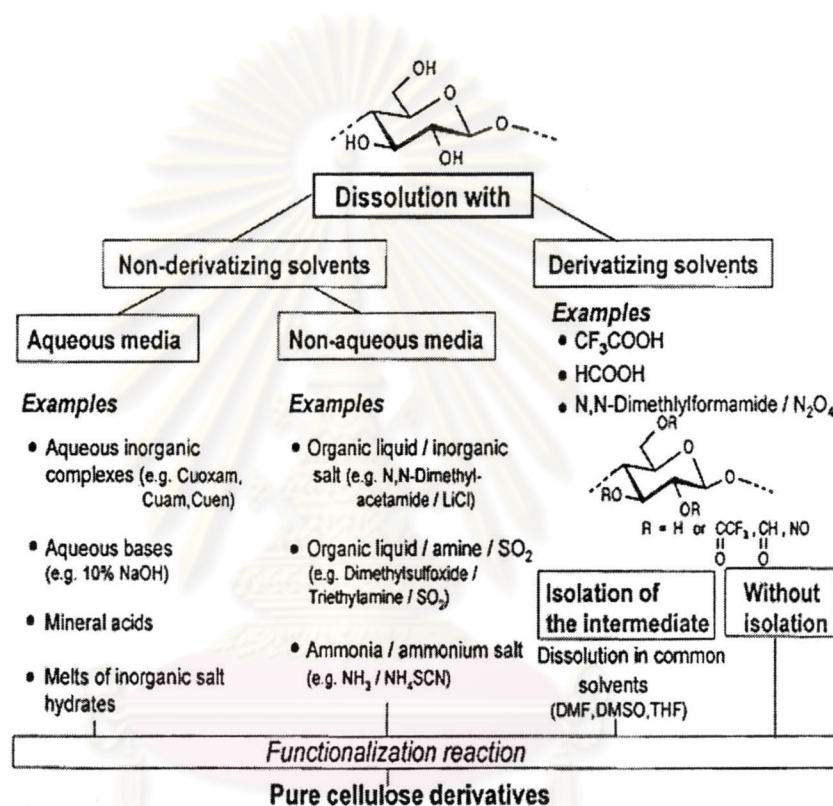


Figure 2.2 Classification of cellulose solvents suitable as medium for chemical functionalization reaction

A suitable, though approximate classification of cellulose solvents which will be used in this paper is given in Figure 2.2 and identifies three types of systems, namely non-derivatizing and derivatizing ones subdividing in aqueous and non-aqueous systems. The main idea of this part is to discuss cellulose solvents which may be used as reaction medium for chemical functionalization of cellulose.

2.2.1. Aqueous non-derivatizing solvents

Aqueous solvents for cellulose, e.g. solutions of inorganic salts and complex compounds, were widely used for cellulose regeneration. The best known solvents of this group are cuprammonium hydroxide (Cuam) and cupriethylenediamine hydroxide (Cuen). Regeneration of membranes from Cuam solution provides high quality products for hemodialysis [13]. It is even possible to dissolve the polymer in about 10 % aqueous NaOH solution, however the solubility is limited to cellulose of comparably low degree of polymerization (DP) of up to 200. Recent results were published by Isogai and Atalla [14]. The application as medium for completely homogeneous functionalization reactions is just of limited interest. This is due to the high tendency of these media towards hydrolysis of reagents applied for modification, problems concerning the purification of the derivatives obtained, and their tendency to become inhomogeneous during the reaction. Thus, cellulose is already regenerated from solvent complexes by changing the pH value of the medium. Typical aqueous solvents are summarized in Table 2.3.

Nevertheless, a number of modern aqueous solvents, e.g. the aqueous solution of Ni(tren)(OH)₂ [tris(2-aminoethyl)amine], were studied in terms of the mechanism of dissolution and for their potential as medium for homogeneous etherification reactions. It has been shown that the new metal complexes (Ni-tren and Cd-tren) completely dissolve cellulose by deprotonating and coordinative binding of the hydroxyl groups in the 2 and 3 positions within the anhydroglucose units (AGU). It is possible to convert cellulose dissolved in Ni-tren (concentration of up to 10% (w/v)) in a fully homogeneous process to carboxymethyl cellulose (CMC) [15]. Structure investigations by means of ¹H-NMR analysis after chain degradation and HPLC analysis after complete depolymerization revealed that these products show a statistic content of the different repeating units and a distribution of the carboxymethyl functions on the level of the AGU in the order C-2 ≥ C-6 > C-3, i.e. they possess the same functionalization pattern as ethers prepared in a highly swollen state as applied for commercial production of CMC [16]. This result clearly shows that both simple activation of cellulose with aqueous NaOH and the complete dissolution of the polysaccharide lead to reactive sites with an almost even accessibility and hence there is no particular advantage of a conversion of the dissolved polymer [17].

Table 2.3 Example of aqueous cellulose solvents

Type of compound	Solvent abbreviation	Active species
Transition metal complexes with amines or NH ₃	Cadoxen Cdtren Cooxen Cupren Cuam Cuem Nioxam Nioxen Nitren Pden Zincoxen	$[\text{Cd}(\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2)_3](\text{OH})_2$ $[\text{Cd}(\text{H}_2\text{NCH}_2\text{CH}_2)_3\text{N}](\text{OH})_2$ $[\text{Co}(\text{NH}_2-(\text{CH}_2)_2-\text{NH}_2)_3](\text{OH})_2$ $[\text{Cu}(\text{H}_2\text{N}-(\text{CH}_2)_3-\text{NH}_2)_2](\text{OH})_2$ $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ $[\text{Cu}(\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2)_2](\text{OH})_2$ $[\text{Ni}(\text{NH}_3)_6](\text{OH})_2$ $[\text{Ni}(\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2)_3](\text{OH})_2$ $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2)_3\text{N}](\text{OH})_2$ $[\text{Pd}(\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2)](\text{OH})_2$ $[\text{Zn}(\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}_2)_2](\text{OH})_2$
Transition metal complex with tartaric acid Ammonium hydroxide	FeTNa Triton B TEOH Triton F GuOH	$\text{Na}_6[\text{Fe}(\text{C}_4\text{H}_3\text{O}_6)_3]$ Trimethylbenzyl ammonium hydroxide Tetraethylammonium hydroxide Dimethyldibenzyl ammonium hydroxide Guanidinium hydroxide
Alkali hydroxides		NaOH LiOH

Besides aqueous solvent complexes, molten inorganic salt hydrates have gained attention as new solvents and media for cellulose modification. Thus, molten compounds of the general formula $\text{LiX}\cdot\text{H}$ ($\text{X}^- = \text{I}^- , \text{NO}_3^- , \text{CH}_3\text{OO}^- , \text{ClO}_4^-$) were found to dissolve cellulose with DP values as high as 1500 (Table 4) [18-20]. Very effective is $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ yielding transparent cellulose solutions within a few minutes. Furthermore, mixture of $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ with $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ or the eutectic mixture of $\text{NaSCN}/\text{KSCN}/\text{H}_2\text{O}$ with different amount of $\text{LiSCN}\cdot 2\text{H}_2\text{O}$ were proved to dissolve cellulose. In case of $\text{LiI}\cdot 2\text{H}_2\text{O}$ the dissolution is explained on the basis of the salt composition consisting of a soft polarizing anion and polarizing cation. In this regard it was surprising that $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ gave the best results. The reason should be strong interaction of cellulose with the hydrated Li^+ -ions and the structure of the molten $\text{LiClO}_4\cdot 3\text{H}_2\text{O}$ as revealed by X-ray scattering. The formation of an addition compound as stated for the interaction between cellulose and perchloride acid was excluded. Furthermore, it is possible to acquire NMR-spectra in these systems and to regenerate cellulose II from them.



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Table 2.4 Example of molten salt hydrates as swelling media and solvents for cellulose

Type	Swelling of cellulose	Dissolution of cellulose
Pure cellulose	$\text{LiCl} \cdot \text{H}_2\text{O} (2 \leq x \leq 5)$	$\text{ZnCl}_2 \cdot \text{H}_2\text{O}$
	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$
	$\text{NaClO}_4 / \text{H}_2\text{O}$	$\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O} (x < 6)$
	$\text{Mg}(\text{ClO}_4)_2 / \text{H}_2\text{O}$	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$
Salt Mixture		$\text{LiSCN} \cdot 2\text{H}_2\text{O}$
	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O} / \text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O} / \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
	$\text{NaSCN} / \text{KSCN} / \text{H}_2\text{O}$	$\text{LiClO}_4 \cdot 3\text{H}_2\text{O} / \text{Mg}(\text{ClO}_4)_2 / \text{H}_2\text{O}$
		$\text{LiClO}_4 \cdot 3\text{H}_2\text{O} / \text{NaClO}_4 / \text{H}_2\text{O}$
		$\text{LiCl} / \text{ZnCl}_2 / \text{H}_2\text{O}$
		$\text{NaSCN} / \text{KSCN} / \text{LiSCN} / \text{H}_2\text{O}$
	$\text{NaSCN} / \text{KSCN} / \text{Ca}(\text{SCN})_2 / \text{H}_2\text{O}$	

2.2.2. Non-aqueous non-derivatizing solvents

Various solvents of this group were found in the last two decades [18-20]. Important examples with regard to cellulose functionalization are summarized in table 2.5. A more detailed description of non-aqueous, non-derivatizing solvents is published elsewhere.

The system N,N-dimethylacetamide (DMAc)/LiCl shows an enormous for the analysis of cellulose and for the preparation of wide variety of derivatives.

Table 2.5 Typical non-aqueous cellulose solvents (in most a preactivation of the cellulose is required)

Number of components	Substance group	Examples
Unicomponent	<i>N</i> -Alkylpyridinium halogenides Oxides of tertiary amines	Ethylpyridinium chloride <i>N</i> -Methylmorpholine- <i>N</i> -oxide Triethylamine- <i>N</i> -oxide
Biocomponent	Dimethyl sulfoxide/solvent Liquid ammoniacal/sodium Dipolar aprotic solvents/LiCl Pyridine or Quinoline containing system Liquid SO ₃ /Secondary or Tertiary amines	DMSO/methylamine DMSO/CaCl ₂ NH ₃ /NaI(NH ₄ I) (DMAc)/LiCl Pyridine/resorcinol SO ₃ /triethyl amine
Tricomponent	NH ₃ or amine/salt /polar solvent NH ₃ or amine/SO ₂ or SOCl ₂ /polar solvent	NH ₃ /NaCl/DMSO Ethylenediamine/NaI/ <i>N,N</i> -Dimethylformamide Diethylamine/SO ₂ /DMSO

Its usefulness in analysis is due to the fact that the solvent is colorless and dissolution succeeds without or at least with negligible degradation even in case of high molecular weight polysaccharides, e.g. cotton linters or bacterial cellulose. Thus, it was possible to investigate the dissolved cellulose by means of ¹³C-NMR spectroscopy, electro spray mass spectroscopy (EMI-MS), size exclusion chromatography and light scattering technique. Although it is the solvent of choice for

these applications. A dissolution mechanism for cellulose in this solvent has still not been clearly postulated. Different solvent-polymer structures were proposed [21-25].

A number of modified compositions were investigated. DMAc can be substituted in the solvent mixture with N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), DMSO, N-methylpyridine or hexamethylphosphoric triamide but only NMP, the cyclic analog of DMA, was found to dissolve the polysaccharide without major degradation. In case of the preparation of bromodeoxycellulose it was useful to apply LiBr instead of LiCl as salt. Besides the synthesis of ester, sulfonates and deoxyderivatives, the preparation of lactones and carbamates succeeds in high yields, at moderate temperatures and moderate reagent concentrations in DMA/LiCl [26-27]. Thus, homogeneous phase carbanilation with phenylisocyanate produces a completely functionalized derivative which has been widely adopted for the determination of molecular weights in non-aqueous solvents by means of gel permeation chromatography (GPC). Furthermore, cellulose was homogeneously derivatized with pesticides using the isocyanate derivatives of, e.g. 4-amino-(1,1-dimethylethyl)-3-(methylthio)-(1,2,4)-triazine-5(4H)-one (metribuzin) to obtain products with a controlled release of bioactive compound [28-29].

The mixture 1,3-dimethyl-2-imidazolidinone (DMI) and LiCl was found to be suitable for dissolving cellulose [30-31]. The advantages of the nowadays commercially available DMI consist in its thermal stability and low toxicity. DMI/LiCl is able to dissolve cellulose samples with DP values as high as 1200 and concentrations of 2-10% (w/w) applying the same procedure as used for DMA/LiCl, i.e. an activation of the polymer by a heat treatment or a step-wise solvent exchange is absolutely necessary. ^{13}C -NMR spectra of cellulose acquired both in DMI and DMA in combination with LiCl exhibit the same chemical shift, i.e. a comparable solvent structure may be assumed with regard to functionalization. DMA/LiCl is suitable both for esterification and etherification. The reactivity of the OH functions is in the order $C-6 > C-2 > C-3$ as found in other non-aqueous cellulose solvents, too. It is worth mentioning that even the etherification proceeds with a remarkable efficiency as shown in preliminary studies. Thus, the methylation of cellulose to Tris-*O*-methyl cellulose in one step procedure.

Other non-aqueous, non-derivatizing solvents suitable for homogeneous modification are mixtures with general composition: polar organic liquid/SO₂/primary,

secondary or tertiary aliphatic or secondary alicyclic amine. From the wide variety of possible mixtures dimethyl sulfoxide (DMSO)/ SO₂/dithylamine is most versatile. Whereas reaction succeed just to a limited extend, etherification with a great number of different reagents was very efficient. It was show that the degradation occurring during dissolution and modification reaction can be dramatically diminished by utilization of protective gas atmosphere. Investigations concerning the solvent structure, i.e. the specific interaction between the polysaccharide and the components of the mixture showed that it is basically a donor acceptor interaction. It was state that this solvent is an non-derivatizing one [32-33].

In case of single component solvents, N-alkylpyridinium halides and N-oxides of tertiary amines are worth mentioning. Typical structures are shown in Figure 2.3. The most powerful solvents in this regard are N-ethyl-pyridinium chloride and N-methylmorpholine-N-oxide (NMNO). The advantage of an easy work up procedure after modification of polysaccharides in these solvents is ruled out by the fact that most of these substances are solid at room temperature and need to be applied as melts and, on the other hand, they are highly explosive. Thus, these compounds are often diluted with common organic liquids to give appropriate reaction media. Among these additives for N-ethyl-pyridinium chloride (m.p. 118°C) are DMF, DMSO, sulfolane pyridine and N-methyl pyrrolidone [34]. In this way it was possible to decrease the melting point to 75°C and to apply the solvent for homogeneous acylation of cellulose [35,36].

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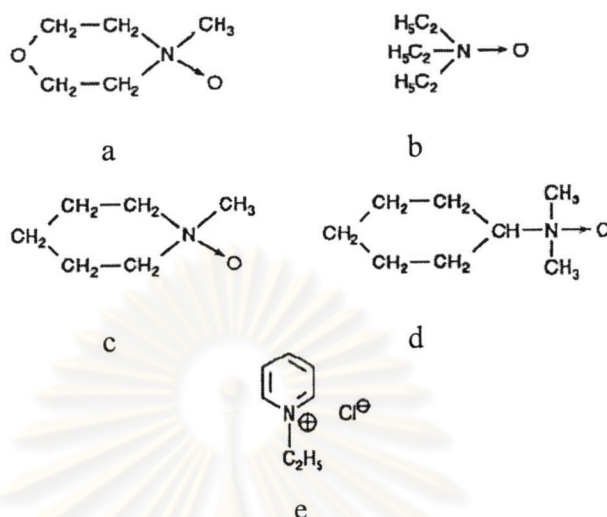


Figure 2.3 Structure of typical single component solvents of cellulose (a) N-methyl-morpholine-N-oxide(NMNO), (b) triethylamine-N-oxide , (c) N-methyl-piperidine-N-oxide, (d) N,N-dimethylcyclohexylamine-N-oxide, (e) N-ethylpyridium chloride

NMNO dissolves cellulose typically as the monohydrate (about 13% water) at about 100°C. It has gained quite an enormous attention for cellulose regeneration and a new fiber spinning process based on NMNO as solvent is already industrially realized forming the so-called Lyocell fibers. Recent results were published dealing with the investigation of the interaction of cellulose with the solvent by means of ¹³C CPMAS NMR and microscopy. In contrast to *N*-ethylmorpholine-*N*-oxide, that converts cellulose I into cellulose III but does not dissolve the polymer, NMNO is able to break hydrogen bonds. Particularly to *O*-6, sufficiently to liberate individual chains and, thereby, to dissolve the polysaccharide sheets. Interestingly, by carboxymethylation of cellulose in NMNO/DMSO mixtures, the solvent behaves as a non-aqueous one although the reaction started with the NMNO monohydrate[15,35].

A novel and powerful new solvent for cellulose consists in the mixture DMSO/tetrabutylammonium fluoride trihydrate (TBAF). The advantage of DMSO/TBAF is that cellulose with a degree of polymerization as high as 650

dissolves without any pretreatment within 15 mm. A remarkable finding was that only the fluoride is able to give clear solutions. If the halide is changed, no dissolution occurs. Highly resolved ^{13}C -NMR spectra of cellulose can be obtained showing all the ring carbons of the AGU and giving no hints for a derivatization during the dissolution process. It should be mentioned that the solutions contain a certain amount of water because TBAF is used as commercially available tri-hydrate and the cellulose is air-dried only [36].

2.2.3. Aprotic derivatizing solvents and soluble intermediates

All the solvents previously discussed show physical dissolution of polysaccharide without derivatization of any hydroxyl group. An acceptable alternative to this route is the application of so-called derivatizing solvents or the utilization of hydrolytically unstable, organo-soluble cellulose intermediates. A representative summary of such solvents and the derivative formed in situ is given in Figure 2.4.

The major disadvantage of the derivatizing solvents is the occurrence of side reaction during dissolution and formation of undefined structures. In turn, this leads to products hardly reproducible. Nevertheless, the N,N-dimethylformamide (DMF/ N_2O_4) solvent, yielding cellulose nitrite as intermediate, has found considerable interest in the synthesis of inorganic cellulose esters, e.g. cellulose sulfates despite its highly toxic nature [37-40]. Although long known as solvent, the dissolution mechanism was a long lasting controversy. Golova et al. favored compound of cellulose and N_2O_4 , solvated by complex formation with dipolar aprotic medium [41]. But today it is well-accepted fact that dissolution under strictly anhydrous condition succeeds by formation of the cellulose trinitrite [38]. In this process the first step is a heterolytic cleavage of the N_2O_4 molecule which initiates the esterification to the nitrite. If small amounts of water are present in the solvent system, the cellulose molecule is only partially derivatized in this step with a preferred conversion of the primary hydroxyl groups. Variation of the solvent components is possible. Instead of DMF, DMSO may be applied and N_2O_4 can be substituted with NO nitrosyl sulfuric acid, nitrosyl hexachloroantimonate or nitrosyl tetra fluoroborate yielding solutions within the same time [42].

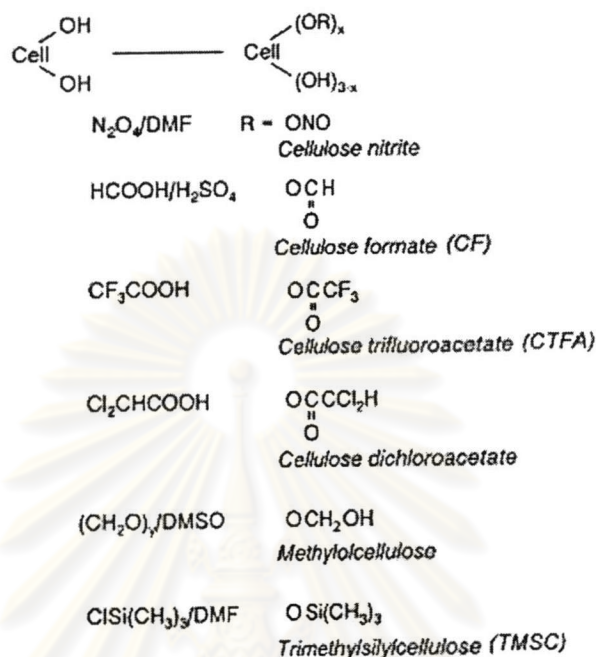


Figure 2.4 Representative example of aprotic derivatizing solvents of cellulose and intermediates formed

A rather interesting derivatizing solvent utilized for esterification is the mixture DMSO/paraformaldehyde. The major advantage of this system is that it dissolves cellulose rapidly and almost without degradation even in case of high molecular weight polymers. Cellulose is here dissolved by formation of the hemiacetal, i.e. so-called methylol cellulose is obtained. ^{13}C -NMR spectroscopy revealed that the acetalization occurs preferentially at the 6 position of the AGU. This methylol structure remains intact during subsequent functionalization in non-aqueous media resulting in derivatives with a pronounced substitution of the secondary OH groups as can be determined by means of GLC after complete hydrolysis of a subsequently etherified cellulose. In contrast, the methylol functions can be easily removed by a treatment with water. Noteworthy is the fact that during the dissolution a growth of oligoxy methyleneoxide chains may occur. The free terminal hydroxyl

groups of these chains may also be derivatized in a subsequent step. Nevertheless, the solvent was exploited for the preparation of a whole number of ethers yielding almost completely functionalized non-ionic cellulose derivatives and for the synthesis of ester via homogeneous conversion with anhydrides [43-45].

A much higher predictability compared with the application of the derivatizing solvents can be realized if the intermediates formed during the dissolution of the polysaccharide are isolated prior to the conversion into the final derivative (Figure 2.4).The increasing reproducibility is due to the fact that structure analysis of the intermediates is possible, on one hand. On the other, these intermediates can be dissolved in a wide variety of common organic solvents which decreases the tendency towards side reactions drastically (especially degradation). Therefore, reactive intermediates can be the starting material for a variety of highly engineered derivatives. Besides the investigation of trialkylsilyl derivative and subsequent functionalization of the rather reactive cellulose xanthogenate, which was only of limited interest in the context of reactive intermediate compare with its wide its utilization for cellulose regeneration, cellulose formates (CF) and halogenoacetic acid esters of cellulose are the most studied intermediates within new strategy of functionalization.

The interaction of cellulose with formic acid was applied to determine the degree of disorder of the cellulose structure and the chemical accessibility of hydroxyl groups. Moreover, solutions of cellulose in formic acid and CF were in terms of their potential for cellulose fiber preparation by regeneration. These CFs are obtained by treating cellulose in surplus of formic acid without catalyst over periods of 4-15 days or with sulfuric acid as catalyst yields fairly degraded polymer with *DS* values of about 2.5. CF can be isolated from mixtures of cellulose, formic acid, phosphoric acid and water. They are soluble in DMF and *DS* values of up to 1.2 are reached. The formulation takes place in the order $C-6 > C-2 > C-3$ as revealed by ^{13}C -NMR spectroscopy. If sulfuric acid is applied as catalyst, the reaction is complete within 15 min. The CF preparation has a DP of about 200 (DP of the starting cellulose was 600). In case of the application of partially hydrolyzed POCl_3 as swelling and dehydrating agent it is possible to increase the *DS* of up to 2.2 yielding formates soluble in DMSO, DMF and pyridine with DP values of 280 (starting from spruce sulfite pulp, DP = 680) within 4 h reaction time [46-49]. These products were

thermally stable of up to 280°C under anhydrous conditions. Another interesting path for the preparation of CF samples was published by Vigo et al. [50]. It was shown that cellulose can be converted with a reagent obtained from thionyl chloride and DMF. Thereby, the formiminium compound is formed as reactive intermediate during this reaction. An appropriate work up procedure gives CF.

Solutions of cellulose as well as of chitosan in trifluoroacetic acid (TFA) were extensively studied by means of NMR spectroscopy showing that the primary OH groups are almost completely functionalized [51]. The interaction of cellulose and TFA was investigated in terms of its kinetics. The dissolution of cellulose in mixtures of TFA with different organic liquids strongly depends on the electron acceptor behavior of the liquid. Furthermore, during dissolution of cellulose in mixtures containing TFA/C₂Cl₂ trifluoroacetylation occurs only to a limited extent and the polysaccharide is rather slowly degraded. Interestingly, the solutions show the formation of mesophases at cellulose concentrations as low as 4% (w/w) which can be used to regenerate strong fibers. Attempts were made to use cellulose dissolved in TFA directly for the preparation of cellulose esters (C₂-C₁₀) by conversion with the corresponding carbonic acid anhydrides. It was stated that esters with DS values between 2.9 and 3 were accessible [52]. Furthermore, the preparation of mixed esters was achieved by acylation of cellulose in TFA with mixtures of various carbonic acid anhydrides and acetic anhydride.

Pure cellulose trifluoroacetates (CTFA) soluble in DMSO, pyridine, and DMF can be easily prepared by treating cellulose with mixtures of TEA and an anhydride [53]. These intermediates had DS values of 1.5 and were completely substituted at the C-6 position as can be concluded both from ¹³C-NMR spectroscopy and from HPLC after methylation, saponification and complete depolymerization. Thereby, the inverse pattern of functionalization of the methylether functions is determined. If the trifluoroacetylation is carried out in the presence of chlorinated hydrocarbons as co-solvents (e.g. chloroform), the DS can be increased up to 2.2 yielding products that are soluble in THF. The CTFA are thermostable of up to 250°C and can be saponified completely within 6 min.

Dichloroacetic acid represents a rather new solvent for cellulose. Cellulose dichloroacetates can be isolated from a mixture of the acid and its anhydride after reaction times of up to 12 days or by conversion of cellulose with partially

hydrolyzed POCl_3 [54]. Product obtained possess *DS* values in the range from 1.6 to 1.9 which are soluble in DMSO, DMF, pyridine, and THF as wet crude product) with DP values of up to 270. All the dichloroacetates obtained are thermostable of up to 280°C but become insoluble after treatment of temperatures higher than 150°C . They exhibit an almost complete functionalization at the 6 position as concluded from ^{13}C -NMR experiments and from the HPLC method developed for the analysis of CTFA.

All intermediates described can be applied in subsequent functionalization reactions in homogeneous phase. Thus, a wide variety of organic esters, inorganic esters, carbamates, and ethers with a specific distribution of functional groups were prepared. In case of the application of modern organic reagents e.g. N,N-carbonyldiimidazole and under aprotic conditions, these reactions yield final products with inverse patterns of functionalization with negligible side reactions, i.e. the primary substituent acts as protective group and usually simple cleaved off during the work up procedure. Especially the CTFA is a promising intermediate because of its easy preparation combined with the highest degree of polymerization accessible (CTFA with DP values of up to 820 were obtained), its solubility in a wide variety of common organic solvents, its fast cleavage under aqueous conditions, and its stability under aprotic conditions. Thus, a mixed 6-mono-O-trifluoroacetyl-1,2,3-di-O-methyl cellulose show neither transesterification nor migration under typical acetylation conditions, conditions, i.e. by a treatment with acetic acid anhydride in the presence of pyridine at 80°C for several hours. ^1H - ^1H -COSY-NMR experiments performed before and after that treatment gave no hints for any structural changes [55].

2.3 Unconventional synthesis paths for and types of carbonic acid esters of Cellulose

Esters of cellulose especially the acetate are long known derivatives of the polysaccharide. Thus, cellulose acetate (CA) was first synthesized by Schuetzenberger in 1865 and was industrially produced as early as 1900 [83]. Conventionally CAs are prepared by conversion of cellulose with an excess of acetic anhydride in the presence of sulfuric acid or perchloric acid as catalyst. Two different methods are applied today to obtain the cellulose ester. The majority of the CAs is produced using a route which includes the dissolution of products formed. On the other hand, it is possible to carry out the acetylation on the intact fiber. The products obtained in the first step are fully esterified. Usually they are partially deacetylated in an one-pot hydrolysis to give the widely applied acetone soluble 2.5 acetate (acetyl content Ca. 40%; DS_{AC} 2.4-2.6). This synthetic detour is necessary because CA samples with same DS synthesized directly from cellulose are not soluble in acetone [84-86]. Structure analyses to elucidate the reasons for this behavior and the search for new synthesis tools for a more effective acetylation are still among the major stimulants for the work in this field.

2.3.1 Homogenous esterification of cellulose

2.3.1.1 Acylation in non-derivatizing solvents and new activation procedures

From the various non-derivatizing solvents discussed above *N,N*-dimethylacetamide (DMAc) or *N*-methylpyrrolidone in combination with LiCl have gained special importance. Moreover, DMi/LiCl and DMSO/TBAF are of interest from our point of view.

The esterification of cellulose in DMAc/LiCl using carbonic acid anhydrides and the -chlorides was among the first attempts of chemical modification of the polysaccharide under totally homogeneous conditions [57]. It was observed that cellulose solutions in DMAc/LiCl with polymer concentrations higher than 10% (w/w) form mesophases. In this case, the conversion of the polysaccharide may be combined with a number of unreproducible effects because in the region of useable solutions of up to 15% (w/w) these anisotropic systems are not fully stable

[58]. Nevertheless, the advantages of acylation in homogeneous phase in DMA/LiCl are an excellent control of the *DS* values and an uniform distribution of the functional groups along the polymer chains. Moreover, a selectivity of the functionalization reaction within the AGUs may appear. Thus, the reaction of cellulose with acetyl chloride in the presence of pyridine as base gives a CA with complete functionalization of the primary hydroxyl groups at *DS* values starting from 1.6 [60].

Especially in case of esters with aromatic functions, the use of the acyl chlorides is still a convenient and effective path. 4-Phenylbenzoyl cellulose was obtained from the homogeneous esterification yielding polymers with *DS* values as high as 2.4. Phenylacetoxycellulose, 4-methoxyphenylacetoxycellulose, and *p*-toloylacetoxycellulose with *DS* values of 1.8-1.9 could be prepared according to this procedure [61].

In terms of its usefulness as protective group for polysaccharides, the adamantoyl moiety was investigated recently. The remarkable finding was that the introduction of the adamantoyl ester is most effective and selective if the carbonic acid chloride is used. Alternative methods, e.g. the application of *p*-toluenesulfonyl chloride (Tos-Cl) or *N,N*-carbonyldiimidazole in combination with the free acid, which are still under investigation, yield comparable results [62].

The preparation of esters with long chains using the acyl chlorides, e.g. *n*-octanoic to octadecanoic was investigated. Besides the acyl chlorides for the synthesis of the simple fatty triester, mixed triesters were obtained by conversion of cellulose in DMA/LiCl with the fatty acid and acetic acid anhydride in the presence of HClO₄. Comparable results were published for the reaction of cellulose with acyl chloride, e.g. stearyl chloride in combination with triethylamine (TEA) [63]. The advantage of TEA in comparison with pyridine as base is the lower acidity of the hydrochloride formed resulting in a decreased tendency towards chain degradation and split-off of the ester functions introduced. Comparable homogeneous esterification reactions with long chain acid chlorides were performed using hemicelluloses from poplar chips dissolved in DMA/LiCl. *DS* values between 0.32 and 1.51 were accessible. It is possible to stearylate over 75% of the hydroxyl groups in native hemicelluloses via this route. Anhydrides of dicarbonic acid were applied for the synthesis of water-soluble carbonic acid half esters of cellulose. A reactivity in the order phthalic anhydride > maleic anhydride > succinic anhydride was observed [64].

New and effective procedures for homogeneous acylation were studied which could be employed in large scale as well. Acetates, propionates, butyrates and mixed acetates/propionates with a stoichiometric control of the acetyl content can be obtained by reacting dissolved cellulose with acid anhydrides, without catalyst, at 110°C for 4 h. It was shown that the acylation of the polysaccharide occurs without degradation of the polymer [65].

A highly efficient and sophisticated method is the conversion of cellulose dissolved in DMAc/LiCl with diketene (FIGURE 2.5) or with a mixture of diketene/carbonyl acid anhydrides [66]. Via this route it is possible to prepare both pure acetoacetates or mixed acetoacetate/carbonyl acid esters of cellulose (especially with acetyl and propionyl moieties). The reaction with diketene is a very useful alternative to the conversion of cellulose with *tert*-butyl acetoacetate [67-68]. Which is not able to yield products with high DS values in predictable processes. The reactive intermediate in both cases is acetylketene. The reaction can as well be carried out in NMP/LiCl. Acetoacetylation with diketene occurs very rapidly at temperatures of 100-110 °C. Thus, a complete derivatization was observed within 30 min.

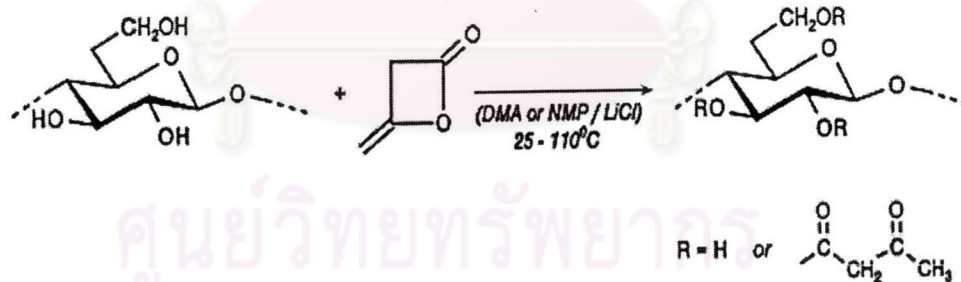


Figure 2.5 Reaction scheme illustrating the acylation of cellulose with diketene yielding cellulose acetoacetate in one-step under homogenous conditions[63]

Besides the application of carbonyl acid chlorides and anhydrides for acylation, a number of very efficient reagents for the in situ activation of the carbonyl acids were applied which can be used without degrading the

polysaccharide backbone during the reaction. Starting from the free acid overcomes a number of disadvantages connected to the acylation with the derivatives discussed above. Whereas acid chlorides are most reactive, they are collectively insoluble (except acetyl chloride) in the solvent system when TEA is present as base. In case of carbonic acid anhydrides which permit a homogeneous conversion, problems arise from their limited commercial availability and the inherent inefficiency because only half of the reagent becomes incorporated into the product. This makes the use of the free acid combined with suitable activation a desirable tool.

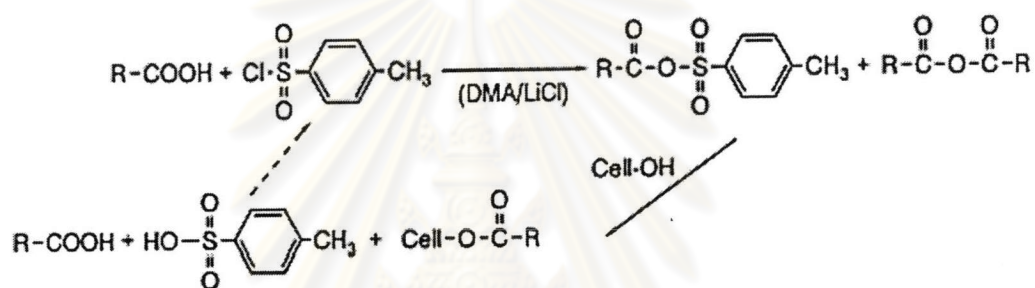


Figure 2.6 Acylation of cellulose dissolve in DMAc/LiCl using in situ activative of the carbonic acid by forming the mixed carbonic/p-toluenesulfonic acid anhydride

In situ activation of the carbonic acids is possible with Tos-Cl. It was first applied for the preparation of cellulose acetates [69]. During the reaction the mixed p-toluenesulfonic/carbonic acid anhydride is formed which represents the reactive species (Figure 2.6). The extension of this path on the homogeneous derivatization of cellulose with waxy carbonic acids was studied. It was shown that cellulose esters, having alkyl substituents in the range from C₁₂ (laurylic acid) to C₂₀ (eicosanoic acid), can be obtained with almost complete functionalization of the accessible OH groups (DS values 2.8-2.9) [70]. The esters were examined in terms of their thermal characteristics by means of differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) leading to the result that the ester moiety transition temperature is increased by 10°C per C-atom of the ester moieties.

Another interesting cellulose derivative accessible via this path is the cellulose anthracene-9-carboxylate [71]. This bulky ester can be prepared with DS values as high as 1.0. The ester moiety is fluorescence active. The amazing result was that the fluorescence spectra of the ester and the free acid are identical. Recently, we have investigated the derivatization of cellulose with oxacarboxylic acids in DMA/LiCl [72]. It was shown that the conversion with 3,6,9-trioxydecanoic acid (TODA) or 3,6-dioxahexanoic acid yields non-ionic cellulose esters with DS values in the range from 0.4 to 3.0. These celluloses start to dissolve in water at a DS as low as 0.4. In addition they are soluble in common organic solvents like acetone or ethanol and resist a thermal treatment of up to 325°C.

A very powerful condensation agent is *N,N*-dicyclohexylcarbodiimide (DCC). It is well known in peptide and protein chemistry as agent for the coupling of amino functions and carboxylic groups. In combination with 4-pyrrolidinopyridine (PP) it was first exploited by Samaranayake and Glasser for the synthesis of cellulose esters starting from the free carboxylic acids. This approach can be used to prepare derivatives with low DS efficiently [73-75]. Among the advantages of the method are the high reactivity of the intermediately formed mixed anhydride with PP and a completely homogeneous reaction in DMA/LiCl. If the reaction is carried out with the anhydrides of the carbonic acids, the by-product acid is recycled by forming the mixed anhydride with PP which is applied only in catalytic amounts. The highly toxic DCC can be recycled from the reaction mixture (Figure 2.7). Only a modest excess of the reagent is necessary because of the high efficiency of the reaction. DCC/PP was a suitable reagent for the preparation of a number of bulky esters (larger than butyrate). Thus, long chain fatty acid esters of up to eicosan acid ester were obtained with a wide range of DS values and even with complete functionalization of all hydroxyl groups. These polymers were prepared as thermoplastic bone-component compounds. Their thermal and rheological behavior was studied [76-77].

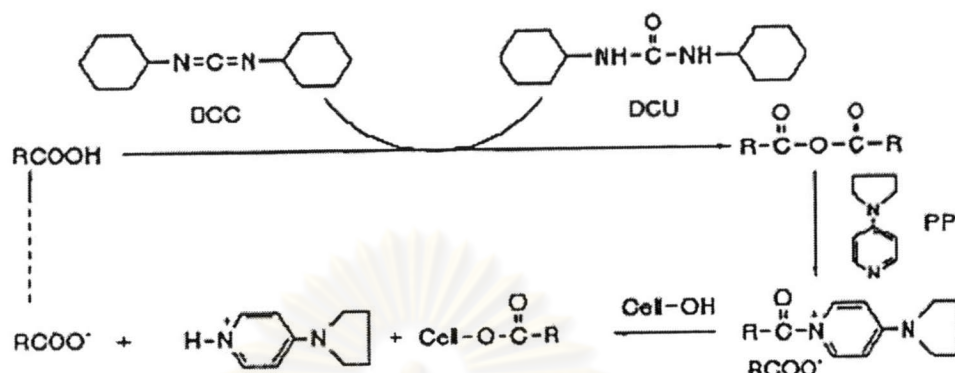


Figure 2.7 Synthesis of cellulose esters with carbonic acid activated in situ with N,N-dicyclohexylcarbodiimide [78]

Moreover, unsaturated esters (e.g. methacrylic-, cinnamic- and vinyl acetic acid ester) and esters of aromatic carbonic acids including p-N,N-dimethylamino)benzoate were synthesized using N,N-dimethylaminopyridine (DMAP) as catalyst. The amino group containing ester was synthesized because it provides a site for the conversion to a quaternary ammonium derivative which imparts water solubility.

A method, which have gained limited interest up to now, is the acylation of cellulose with the free carbonic acid using N,N-carbonyldiimidazole as activating reagent. The derivative has DS value of up to 1.4 . The reagent is also very efficient for the subsequent homogeneous esterification of cellulose inter-mediate in pyridine or DMF [78].

Very recently the conversion of cellulose in DMI/LiCl was studied and the results were compared with those of the homogeneous acetylation of the polymer in DMA/LiCl. The reaction was carried out with acetic anhydride and pyridine as a base. CA with a DS value of 1.4 was accessible showing a same distribution of substituents as products obtained in DMA/LiCl (reactivity: C-6> C-2> C-3). The solvent is especially for etherification reaction [32] .

Another solvent for cellulose recently found is the mixture DMSO/TBAF. The system studied in terms of its usefulness for homogeneous acylation reactions contained 2.9% cellulose and 16.6% TBAF. An alternative to the esterification with an acid anhydride is the transesterification with carbonic acid esters which is an uncommon method in cellulose chemistry in contrast to starch modification. Especially the use of vinyl acetates and its higher homologues is a very interesting path because the formation of the acetic aldehyde during the reaction shifts the equilibrium towards the product side. Thus, it is possible to obtain cellulose acetates with DS values of 2.7 by applying 10 mol reagent per mol AGU over 70 h at 40°C. Moreover, the DS_{Acetate} can be directly controlled by the amount of reagent. Even long chain alkyl esters can be synthesized via this route. The one-step synthesis of cellulose butyrates, laurates and in addition the preparation of benzoates was carried out showing that fatty acid esters of cellulose with DS values as high as 2.6 (in case of the laureate) are accessible [36].

2.3.1.2 Acylation of cellulose in derivatizing solvents

The solvents DMSO/paraformaldehyde (PF), chloral/DMF/pyridine, TFA, and DMF/N₂O₄ were investigated as reaction medium for the homogeneous conversion of cellulose.

A variety of methods were studied for the homogeneous esterification of polysaccharide dissolved in DMSO/PF. The polymer can be converted with a number of carbonic acid anhydrides in the presence of pyridine at low temperatures [78-80]. Among the acylating reagents are aliphatic compounds, e.g. acetic and butyric anhydride, aromatic acid derivatives like phthalic anhydride and even unsaturated species like methacrylic and maleinic anhydrides. The DS values reached are usually in the range from 0.2 to 2.0, except acetylation where DS values of up to 2.5 were realized. By means of ¹H- and ¹³C-NMR spectroscopy it was shown that the hydroxyl groups of the methylol chains are preferentially acetylated with the carbonic acid anhydrides. Acylation with acetyl chloride or with the free acid succeeded just to a limited extent. Furthermore, introduction of acetyl groups by transesterification has been achieved with methylene diacetate and ethylene diacetate yielding polymers with high DS values (acetyl content 22%). For this purpose, the cellulose dissolved in DMSO/PF is treated with the reagents in the presence of

sodium acetate at 90°C. Moreover, the reaction of cellulose with acetic anhydride in the presence of potassium acetate was investigated. An interesting observation was that the DMSO in the solvent system can be substituted with DMF or DMA [81]. Quite recently this solvent has found some interest again. Homogeneous esterification with trimethylacetic anhydride (TMAA), trimellitic anhydride (TMA) and phthalic anhydride (PA) in DMSO/PF using high α -cellulose pulps of fast growing plant species was described. The corresponding esters are prepared by treating the solutions of cellulose with TMA and PA in the presence of pyridine for 8 h at 80-100°C. DS values between 2.4 and 2.6 are accessible. The esters were studied in terms of their thermal behavior. They are versatile compounds because of their elastomeric and thermoplastic properties and can be used for the preparation of films, membranes and enteric film coatings of medical tablets.

Although highly toxic, the cellulose solvent DMF/ N₂O₄ was widely used for the preparation of cellulose esters. Noteworthy is its extensive exploitation for the synthesis of inorganic esters, e.g. phosphates and sulfates[82]. Esters of carbonic acids can be obtained both with anhydrides and chlorides of carbonic acids in the presence of an appropriate base, e.g. pyridine. A variety of acid chlorides was applied for the esterification including capryonyl-, caproyl-, lauryl-, palmitoyl-, and stearyl chloride . The reaction succeeds via transesterification of the cellulose nitrite formed during dissolution of the polymer. The conversion with acetic anhydride yields cellulose acetates with DS values of up to 2. In case of the preparation of derivatives with DS values of about 0.5, the transesterification is rather selective at position 2 of the AGU as can be concluded from ¹³C-NMR spectra. Comparable results were obtained for acetylation of cellulose in the derivatizing solvent chloral/DMF/pyridine [81]. Treatment of the dissolved cellulose with acetyl chloride or acetic anhydride yields polymers with DS values of up to 2.5.

A suitable alternative to esterification reaction in the multicomponent systems discussed is the subsequent acylation of cellulose dissolved in TFA. Cellulose is partially trifluoroacetylated in the dissolved state (DS_{CTFA} about 1 -1.5). Solutions of CTFA in a surplus of TFA were used for subsequent esterification in a number of studies. Thus, Emelyanov et al. investigated the acylation after treatment of cellulose for 24 h with TFA Anhydrides of acetic-, propionic-, 3-nitrophthalic acid and a variety of aliphatic, aromatic and unsaturated acid chlorides,

e.g. acetyl-, acryl-, cinnamoyl-, benzoyl-, and 4-nitrobenzyl chloride, as well as free acids like benzoic acid in combination with TFAA were applied as acylation reagents. The course of reaction was followed by IR spectroscopy leading to the conclusion that partial transesterification occurs during acylation. Isolation in aprotic media yields mixed esters with almost complete functionalization. After reaction for several hours at 50°C the DS of trifluoroacetyl function is usually at about 1.4 and the amount of the second acyl component ranges from DS 0.5 to 1.6. Comparable results were obtained by Salin et al. [52]. In this study cellulose esters with DS values in the range from 2.9 to 3.0 were prepared by reacting cellulose in TFA with carbonic acid anhydrides (C₂-C₁₀) at 60°C. These esters were studied in terms of their viscosity in solution and T_g dependent on the acyl moiety. Furthermore, the preparation of mixed esters of cellulose in TEA was investigated using mixtures of acetic anhydride and aliphatic acids. It was stated that the method yields polymers with DS higher than 2.8 with DS_{acetayl} between 1.3 and 1.7.

2.3.1.3 Esterification of organo-soluble cellulose intermediates

A rather new way of homogeneous esterification of polysaccharides is the application of soluble, regenerable intermediates. An important advantage compared to the functionalization reactions in derivatizing solvents is that acylation with highly reactive reagents can be performed in inert common organic solvents avoiding side reactions. Important intermediates are the trifluoroacetates, formates, and dichloroacetates as well as trialkylsilyl derivatives of cellulose of various *DS* values. These compounds can be subsequently esterified in homogeneous phase with carbonic acid chlorides and anhydrides or with the free acid after in situ activation. Usually the substituent introduced in the first step remains at the polymer backbone during the subsequent functionalization and is cleaved off during the work up procedure in protic media eventually catalyzed by changing the pH values to acidic or basic conditions. In case of the trialkylsilyl cellulose derivatives the application of fluoride ions for deprotection is a suitable method as well [83]. Typical examples of homogeneous esterification reactions carried out via intermediates are given in Table 2.6. As already discussed in detail above, the intermediates show a fairly defined distribution of substituents within the AGU. Thus, the CTFA is completely functionalized at the C-6 position at a total DS_{CTFA} of 1.5. Consequently, the partial

derivatization does not only impart solubility but in addition causes a selectivity in the subsequent modification.

Besides the preparation of inorganic esters and carbamates via cellulose intermediates (CTFA, CF and cellulose dichloroacetates), the synthesis of carbonic acid esters was extensively studied. In addition to the conversion with aromatic acids e.g. 4-nitrobenzoic acid, 4-nitrocinnamic acid, and long chain fatty acids (palmitic acid), the synthesis of spacer modified unsaturated esters (e.g. N-cinnamoyl-11-aminoundecanoic acid) was investigated [84]. The acid chlorides and Tos-Cl for the in situ activation of the free carbonic acids were applied. For the first time it was shown that N,N-carbonyldiimidazole and chloromethylene-dimethyliminium chloride (CDIC) can be used for the in situ activation of the carbonic acids which is a new tool for cellulose derivatization (Figure 2.8).



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Table 2.6 Example of subsequent reaction on cellulose intermediates isolate under aprotic condition with different degree of Substitution

Cellulose intermediate/DS	Reagents	Cellulosic products (after work-up)
Cellulose trifluoroacetate /1.5	pyridine/SO ₃ N,N-carbonyldiimidazole/ 4-nitrobenzoic acid 4-Nitrobenzoic acid / tosyl chloride Plamitoyl chloride/tosyl chloride NaOH/Sodium Monochloroacetate(SMCA) Phenyl isocyanate pyridine/SO ₃ DMF/SO ₃ NaOH/(SMCA) Pyridine/SO ₃	Cellulose sulfate Cellulose-4-nitrobenzoate Cellulose-4-nitrobenzoate Cellulose palmitate CMC Cellulose phenylcarbamate Cellulose sulfate Cellulose sulfate CMC Cellulosesulfate
Cellulose dichloroacetate/1.6	3, 4-Dinitrobenzoyl chloride	Cellulose-3,4-dinitrobenzoate
Trimethylsilyl cellulose/1.6	4-Bromobenzoyl chloride	Cellulose-4-bromobenzoate
Trimethylsilyl cellulose/2.0	4-Nitrobenzoyl chloride	Cellulose-4-nitrobenzoate ^b
Trimethylsilyl cellulose/2.5	NaOH/(SMCA)	Carboxymethyl
Trimethylsilyl cellulose/1.1		

The rather uncommon activation with CDIC was exploited for the synthesis of cellulose-4-nitrobenzoates starting from CTFA (DS_{CTFA} of 1.5) dissolved in DMF and yields polymers with $DS_{Nitrobenzoate}$ of 0.5 soluble in DMSO. The reaction with *N,N*-carbonyldiimidazole is an efficient and mild process [85]. Thus, the activation of the carbonic acid is carried out at room temperature in DMF. The esterification succeeds at 60°C. Products with DS values of up to 0.9 can be obtained from cellulose trifluoroacetate (DS_{CTFA} of 1.5). The trifluoroacetyl function is usually removed during the work up procedure in aqueous media.

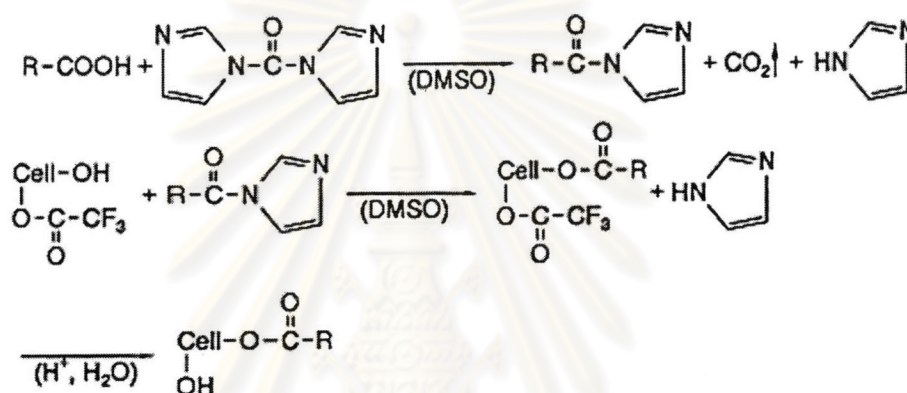


Figure 2.8 Acylation of organo-soluble cellulose trifluoroacetate with carbonic acids activated in situ with *N,N*-carbonyldiimidazole.

Trimethylsilyl cellulose (TMSC) was applied for the esterification with nitro- and bromo substituted benzoyl chlorides. It was stated that in dependence on the reaction conditions it is possible to obtain subsequent derivatives with inverse distribution of the substituents or to replace the silyl functions. Thus, treatment of TMSC with acid chlorides, especially 3,4-dinitrobenzoyl chloride and 4-bromobenzoyl chloride in the presence of tertiary amines leads to an acylation of the remaining OH functions [86]. On the other hand, during the reaction with acid chlorides at elevated temperature, e.g. in nitrobenzene at 160°C, without catalyst, trimethylsiloxy groups are found to react selectively while the OH groups are unaffected. Recently, the acylation of partially silylated TMS-polyvinylalcohol was studied. An acylation in nitrobenzene at 160°C in the absence of catalysts and proton acceptors resulted however in an unselective conversion of both hydroxy- and trimethylsiloxy groups [87]. For the reaction of TMSC with sulfating reagents a

replacement reagents was concluded where the SO_3 attacks the Si-bond yielding polymers with the same substitution pattern as the starting intermediate

2.3.2 Methods for heterogeneous esterification

Besides the homogeneous esterification, new paths were developed for heterogeneous processes. For this topic is just very briefly discussed because it pointed out the scope of this thesis.

A very efficient method for cellulose esterification under heterogeneous reaction conditions is the so called impeller method. The carbonic acids used are converted to reactive mixed anhydrides during these reactions. Chloroacetyl-, methoxyacetyl- and most important trifluoroacetyl moieties are used as impellers [88]. Tri-O-propionates and tri-O-butyrate of cellulose can be obtained in this way. On the other hand, new catalysts were developed, e.g. titanium-(IV)-alkoxid compounds like titanium-(IV)-isopropoxide (Table7) [89]. It was shown that the catalyst can be applied for the preparation of partially esterified cellulose derivatives if an appropriate solvent is used. Furthermore, the esterification of cellulose with acetyl chloride at elevated temperatures and in vacuum using 1,4-dioxan/pyridine as reaction medium is known. Vacuum is applied to remove the liberated HCl during the reaction [90].

Acylation of the polymer is also possible by conversion of cellulose suspended in pyridine or DMF using sulfonic acid chlorides as activating agent. Thus, it was demonstrated that CA can be obtained in a wide range of DS values by treatment of the polysaccharide with acetic acid in the presence of Tos-Cl or methanesulfonyl chloride [69]. Highly efficient is the reaction with the alkali or alkaline earth salt of acetic acids in combination with Tos-Cl [91-92]. These methods were extended for the preparation of aromatic cellulose esters, e.g. nitro-, chloro-, methyl-, methoxy-benzoyl esters and 4-azido-benzoyl esters. On the other hand, it is possible to carry out transesterification reactions. For this procedure it was shown that a certain combination of reagent and solvent leads to a modified distribution of the ester functions within the AGU.

The classical method to prepare cellulose esters, i.e. converting the polymer suspended in pyridine with carbonic acid chlorides, is still an important

procedure even to synthesize cellulose with unconventional functional groups and hence with new properties. For example, products containing photo reactive moieties like stilbene-4-carboxylate- , cinnamoyl- , 2-methylstilbene-5-carboxylate, and p-phenylazobenzoate functions were synthesized recently.



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2.4. Energy for chemistry

Pressure and temperature are important parameters in reaction processes in chemical systems. In order to minimize energy and control reactions with a view to green chemistry, attempts are being made to make the energy input in chemical systems as efficient as possible. Approaches are being taken and possibilities investigated to use until now scarcely used forms of energy, so-called non-classical energy forms, in order to optimize the duration. In classical processes energy is added to the system by heat transfer, electromagnetic radiation in the ultraviolet (UV), visible or infrared (IR) range or in the form of electrical energy. On the other hand, microwave radiation, ultrasound and the direct application of mechanical energy are among the non-classical forms [93]. In this fields of esterification, the energy that useful are conventional and microwave heating.

2.4.1 Conventional Heating Methods

In all conventional means for heating reaction mixtures, heating proceeds from a surface, usually the inside surface of the reaction vessel. Whether one uses a heating mantle, oil bath, steam bath, or even an immersion heater, the mixture must be in physical contact with a surface that is at a higher temperature than the rest of the mixture.

In conventional heating, energy is transferred from a surface, to the bulk mixture, and eventually to the reacting species. The energy can either make the reaction thermodynamically allowed or it can increase the reaction kinetics.

In conventional heating, spontaneous mixing of the reaction mixture may occur through convection, or mechanical means (stirring) can be employed to homogeneously distribute the reactants and temperature throughout the reaction vessel. Equilibrium temperature conditions can be established and maintained.

Although it is an obvious point, it should be noted here that in all conventional heating of open reaction vessels, the highest temperature that can be achieved is limited by the boiling point of the particular mixture. In order to reach a higher temperature in the open vessel, a higher-boiling solvent must be used.

2.4.2 Microwave Heating

Microwave heating occurs somewhat differently from conventional heating. First, the reaction vessel must be substantially transparent to the passage of microwaves. The selection of vessel materials is limited to fluoropolymers and only a few other engineering plastics such as polypropylene, or glass fiber filled PEEK (poly ether-ether-ketone). Heating of the reaction mixture does not proceed from the surface of the vessel; the vessel wall is almost always at a lower temperature than the reaction mixture. In fact, the vessel wall can be an effective route for heat loss from the reaction mixture.

Second, for microwave heating to occur, there must be some component of the reaction mixture that absorbs the penetrating microwaves. Microwaves will penetrate the reaction mixture, and if they are absorbed, the energy will be converted into heat. Just as with conventional heating, mixing of the reaction mixture may occur through convection, or mechanical means (stirring) can be employed to homogeneously distribute the reactants and temperature throughout the reaction vessel [93].

2.4.2.1 Source of microwave

Electromagnetic radiation is energy which is discharged from mobile, electric charges and spreads out as a wave. The wavelength of this radiation decreases with increasing energy. If the wavelength of microwave is in the range 1 mm to 1 m which correspond to frequency of 300 MHz to 300 GHz. Household microwave ovens produce radiation with a fixed frequency of 2.45 GHz. In the electromagnetic spectrum microwaves lie between radio waves (1 m to 104 m) and infrared waves (760 nm to 0.5 mm).

Microwave radiation is produced by electrical discharge. Humans and animals also emit measurable quantities of microwaves in addition to thermal radiation [94]. Technically microwaves can be produced using a magnetron. This is a transmitter known as a real-time tube, in which electrons are emitted from a cylindrical hot cathode and accelerated towards the sheath-like anode which surrounds it. During their trajectory the electrons are diverted by a vertical magnetic field as a result of the Lorentz force which occurs. This causes the electrons to be deflected tangentially onto the specially constructed anode surface, so that they cause resonance vibrations there.

The microwave radiation is finally emitted from an antenna of the magnetron in a complicated oscillator, travels through a waveguid into microwave chamber where heating occurs. Microwaves are propagated in a vacuum at the speed of light, like any other form of electromagnetic radiation. If the penetration depth of materials is less than samples size, it is considered as a “surface heating”. On the other hand, a volumetric heating will occur in a bulk material when the penetrate depth is larger than a sample size. however they are reflected by metal surfaces. As a result of this property, microwaves can be screened effectively using metal sheets and even close-meshed wire nets. The metal casing and the perforated sheet at the front of household microwave ovens screen the microwaves.

2.4.2.2 Mechanisms of microwave

One can broadly characterize how bulk materials behave in a microwave field [95]. Materials can absorb the energy(e.g. water, carbon), they can reflect the energy(e.g. metal), or they can simply pass the energy(PP, glass, silica, alumina). It should be noted that few materials are either pure absorbers, pure reflectors, or completely transparent to microwaves. The chemical composition of the material, as well as the physical size and shape, will affect how it behaves in a microwave field.

Microwave interaction with matter is characterized by a penetration depth. That is, microwaves can penetrate only a certain distance into a bulk material. Not only is the penetration depth a function of the material composition, it is a function of the frequency of the microwaves. There are two specific mechanisms of interaction between materials and microwaves:

(1) Dipole interactions

(2) Ionic conduction

Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves.

Dipole interactions occur with polar molecules. The polar ends of a molecule tend to align themselves and oscillate in step with the oscillating electrical field of the microwaves. Collisions and friction between the moving molecules result in heating. Broadly, the more polar a molecule, the more effectively it will couple with (and be influenced by) the microwave field.

Ionic conduction is only minimally different from dipole interactions. Obviously, ions in solution do not have a dipole moment. They are charged species that are distributed and can couple with the oscillating electrical field of the microwaves. The effectiveness or rate of microwave heating of an ionic solution is a function of the concentration of ions in solution.

Materials have physical properties that can be measured and used to predict their behavior in a microwave field. One calculated parameter is the dissipation factor, often called the loss tangent. The dissipation factor is a ratio of the dielectric loss (loss factor) to the dielectric constant. Taken one more step, the dielectric loss is a measure of how well a material absorbs the electromagnetic energy to which it is exposed, while the dielectric constant is a measure of the polarizability of a material, essentially how strongly it resists the movement of either polar molecules or ionic species in the material. Both the dielectric loss and the dielectric constant are measurable properties.

2.4.2.3 The effect of microwave

To understand how microwave heating can have effects that are different from conventional heating techniques, one must focus on what in the reaction mixture is actually absorbing the microwave energy. One must recognize the simple fact that materials or components of a reaction mixture can differ in their ability to absorb microwaves. Differential absorption of microwaves will lead to differential heating and localized thermal inhomogeneities that cannot be duplicated by conventional heating techniques.

To illustrate the consequences, several examples are presented wherein we consider microwave absorption by a bulk solvent and/or by the minor concentration of reactants in the solvent[95].

Example 1: Solvent and reactants absorb microwaves equally

If the bulk solvent and reactants absorb microwaves equally, then energy transfer and heating will occur to the allowed depth of penetration into the bulk mixture. Homogeneous reaction conditions can be established with thorough mixing, and at equilibrium (chemical and thermal), the temperature of the reactants will be the same as that of the bulk solvent.

In this case, reaction rates can be increased by increasing the temperature of the reaction mixture. This can easily be achieved using closed-vessel microwave

techniques, using the same reaction chemistry and solvent. Alternatively, using conventional heating techniques, higher reaction temperatures can be achieved in a closed reactor system, or by using a higher-boiling solvent in an open vessel.

Example 2: Solvent absorbs microwaves, reactants much less so

If the bulk solvent absorbs microwaves, but the reactants do not absorb (or absorb to a lesser extent than the solvent), then energy transfer and heating of the solvent will occur to the allowed depth of penetration. The bulk solvent will, in turn, heat the reactants by conduction. Homogeneous reaction conditions can be established with thorough mixing, and at equilibrium the temperature of the reactants will be the same as that of the bulk solvent.

This case is little different from conventional heating techniques. Reaction rates can be increased by increasing the temperature of the reaction mixture. Using closed-vessel microwave techniques previously mentioned. In conventional heating techniques, higher reaction temperatures can be achieved in a closed-vessel reactor system, or by using a higher-boiling solvent in an open vessel.

Example 3: Reactants absorb microwaves, solvent much less so

If the bulk solvent does not absorb microwaves, but the reactants do, then direct energy transfer and heating of the reactant molecules will occur to the allowed depth of penetration. The bulk solvent will, in turn, be heated by conduction from the reactants. Although homogeneous reaction conditions can be established with thorough mixing, the temperature of the reactants will always be higher than that of the solvent, as long as the solvent continues to lose heat to the environment through the vessel wall.

This case is significantly different from conventional heating techniques. Reaction rates can be increased by increasing the temperature of the reactants, Heat transfer from reactant to bulk solvent must be fast enough to overcome the heat loss from the reaction mixture to the environment. For this effect to be sustainable, careful attention must be paid to vessel design and vessel cooling. This effect can be achieved using microwave reflux techniques. It must be recognized that only the bulk temperature can be measured by direct insertion of a monitoring probe, so there really isn't any practical way of measuring a temperature differential between the reactants

and the solvent. Multimode cavities, with their higher output power (1,000 watts or more), are best suited to creating the necessary conditions for obtaining this unique microwave effect.

Example 4: Catalysts on microwave absorbing supports

Some unusual reaction conditions can be created in a microwave field when catalysts are present in the mixture, particularly when the catalyst is deposited on a microwave-absorbing material. Palladium on carbon is a common catalyst in some reaction mechanisms. Carbon or graphite is an excellent absorber of microwave energy, with a dissipation factor significantly higher than most solvents.

An unexpected effect of the microwave field is that it can directly heat some catalyst supports, and create a condition where the catalyst is at a substantially higher temperature than the rest of the bulk mixture. The catalyst support will transfer heat to the bulk mixture by conduction. There really isn't any practical way to measure the temperature at the surface of the catalyst support. The enhanced reactivity, however, can be quite dramatic, as evidenced by the reaction products. This superheating of the catalyst cannot be duplicated by conventional means. Multimode cavities, with their higher output power (1,000 watts or more), are better suited to creating the necessary conditions for obtaining this unique microwave effect.

The use of microwave radiation in processing of polymers offers a number of distinct benefits over conventional processing alternatives. In the microwave field the heating process often occurs more homogeneously and thus more rapidly than with the conventional heating. The microwave heating presents some advantages, such as remarkable decrease in reaction time and in some cases, cleaner reactions and better yields have been reported. For example, C. stage and et.al. [8] found that the esterification of cellulose with long chain acyl chloride in homogenous media induced by microwave irradiation. The system used was cellulose/lauroyl chloride/N,N-dimethyl acetamide/LiCl and N,N-dimethylaminopyridine as catalyst. The use of microwave result in dramatic drop in reaction time 1 min irradiation was sufficient, compared with 30 min to 2 days, when conventional used.

In addition, G. Antova and P. Vasvaova [95] found that the possibility for obtain cellulose stearate by direct esterification and tranesterification under

microwave heating. The system used was toluene sulphonic acid as catalyst and stearic acid/methyl stearate as modify agent. Research is made upon the influence of different parameters such as molar proportion of the initial substances, quantity of catalyst and duration of reaction upon the degree of esterification.

P. Krausz and et. al.[97] found that the method for esterification of microcrystalline cellulose with dodecanoyl chloride as modify agent. This methodology used microwave irradiation under solvent-free condition in presence of basic catalyst.

2.5. BIODEGRADABLE POLYMER

There has been much awareness regarding the harmful effects of polymer materials on the environment. Conventional non-degradable polymer systems (e.g. polyethylene, polypropylene etc.) are used for high volume, short-term applications such as packaging, medical, automobile and agricultural areas. This leads to the quest for new as well as modified degradable polymers, which can replace existing synthetic polymers. Replacement of these polymer systems requires that the degradable polymers have properties that are sufficiently comparable to those of the conventional polymers. These desirable properties can be achieved by creating new environmentally friendly polymers or modifying existing degradable polymers.

The biodegradation of polymers proceeds by hydrolysis and oxidation. The presence of hydrolysable and/or oxidizable linkages in the polymer main chain, the presence of suitable substituents, correct stereoconfiguration, balance of hydrophobicity and hydrophilicity, and conformational flexibility contribute to the biodegradability of the polymer. Biodegradable polymers may be divided into three classes :

- (a) natural polymers originating from plant or animal resources
(e.g. cellulose, starch, protein, collagen, etc.)
- (b) biosynthetic polymers produced by fermentation processes by micro-organisms (e.g. poly-hydroxy alkanates)
- (c) certain synthetic polymers possessing the biodegradable properties explained earlier (e.g. polycaprolactone and poly-lactic acid)

Natural polymers like cellulose and starch are not thermally processable unless modified. Cellulose has a degradation temperature below its melting temperature and hence cannot be processed in the melt. Moreover, because of its complex morphology of crystalline regions and hydrogen bonding, cellulose is difficult to dissolve in common solvents. Processing with the help of a suitable solvent has been possible with N-methylmorpholine-N-oxide (N-MMNO) and water or dimethylacetamide (DMAc)/lithium chloride (LiCl). Hence cellulose can be spun into lyotropic liquid crystalline fiber, but the process is complicated and dangerous due to rigorous solvent handling protocols. However, modified cellulose, such as cellulose esters, can be melt processed as a thermoplastic polymer, since their melting temperature can be significantly reduced below their degradation point. Similarly, modified starch has been incorporated into polymer blend systems to provide biodegradability.

Conversion of cellulose to fibre and film using regeneration processes does not significantly affect the biodegradability. In essence, however, refining of cellulose and its derivatization means a change in the molecular structure and thus the biodegradability. Cellulose products have a long industrial history. For example, cellulose nitrate has been produced since 1878. Celluloid was the first thermoplastic polymer material and has developed a number of other applications. Consumer trends and packaging technology were later revolutionised by Cellophane, the first transparent packaging materials. The rigid chain structure of cellulose has been utilized since 1920 to produce this dimensionally stable, water vapour permeable, biodegradable regenerated cellulose with the requisite rigidity.

5. Syringe, Needle and Septum
6. Cooling system
7. 50 ml-Volumetric flask
8. 250 ml-Three-neck round bottom flask
9. Buchner funnel and Suction flask
10. Microwave Oven

The esterification of cellulose was performed under microwave energy using a 2.4 GHz , household-microwave oven (LG intellowave, LG Ltd.).



Figure 3.1 LG-Microwave Oven

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3.2.2 Sample Preparation

Glass Mold

Cellulosic film was prepared by pouring the cellulose ester solution directly onto a glass mold. The mold was made from 0.3 mm thick glass sheet. The square removable eadge with its outer and inner size of 25 cm x 25 cm and 19 cm x 19 cm ,respectively, was glued on the top of the glass sheet (25 cm²) so that the total area of the glass mold was 0.3 cm (thick) x 19 cm (width) x 19 cm (length).



Figure 3.2 Glass mold

3.2.3 Physical Property Testing

1. Micrometer

A micrometer (Peacock, Model G, Japan) was used to measure thickness of the film samples. Figure 3.3 displays the micrometer used in this research.



Figure 3.3 Micrometer

2. Gloss Meter

Micro-gloss 60° with standard holder of BYK-Gardner GmbH, Germany presented in figure 3.4 was employed to measure specular gloss of the film samples according to the ASTM D 523 standard method.

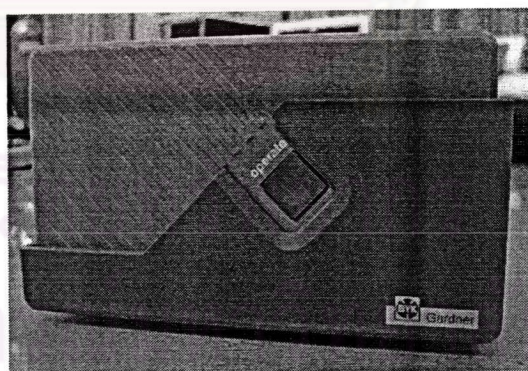


Figure 3.4 BYK-Gardner Micro-gloss 60°

3. Contact Angle Meter

A contact angle meter (CAM-PLUS MICRO Tantec Inc., USA, as shown in figure 3.5) was used to determine the wettability of the film samples.

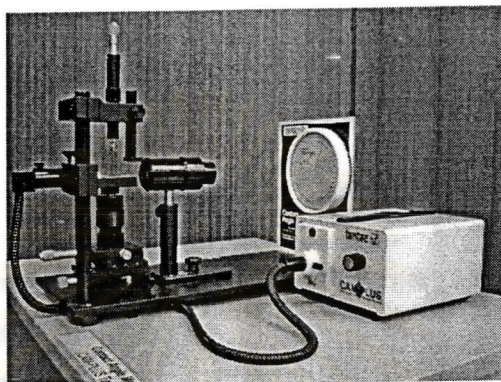


Figure 3.5 Tantec CAM-PLUS MICRO contact angle meter

4. Scanning Electron Microscope

The surface morphology of unmodified, esterified cellulose powder, and cellulosic film samples was analyzed using a scanning electron microscope.



Figure 3.6 SEM:JEOL:JSM-6400

5. Fourier Transform Infrared Spectrometer

Fourier Transform Infrared spectrometer (Nicolet Impact 400D) presented in figure 3.7 was used to determine the functional groups of cellulose ester powder.



Figure 3.7 Nicolet impact 400d - FTIR

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3.3 Mechanical Property Testing

Tensile Testing Machine

Tensile properties of the film samples were tested by universal testing machine LLOYD LR 100K (figure 3.8) according to the ASTM D 882.

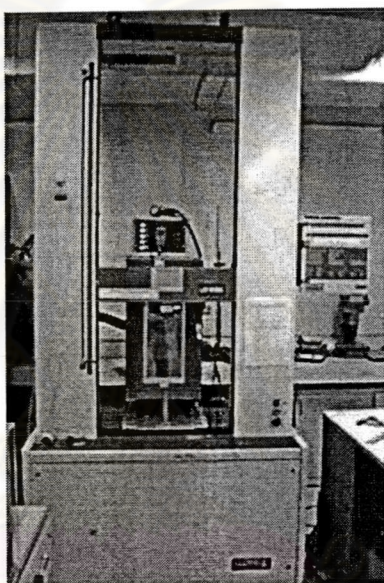


Figure 3.8 Universal Testing Machine LLOYD LR 100K

3.4 Thermal Property Characterization

3.4.1 Thermogravimetric Analyzer (TGA)

Thermogravimetric analysis of the sample were obtained by Mettler Toldo TGA/SDTA851e/LS/1600 (figure 3.9). The heating rate was set at 10^0 C/min. Samples were carried out under nitrogen atmosphere.

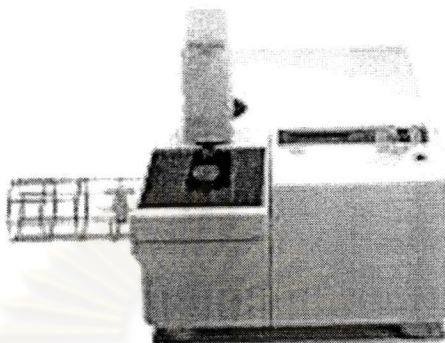


Figure 3.9 Mettler Toldo TGA/SDTA851e/LS/1600

3.4.2 Differential Scanning Calorimeter (DSC)

DSC822-e/400w (Figure 3.10) was used to characterize thermal properties regarding the transition temperature of the film sample. The heating rate was set at 20 °C/min. Measurement on range of weight 5-10 mg was carried out under nitrogen atmosphere.

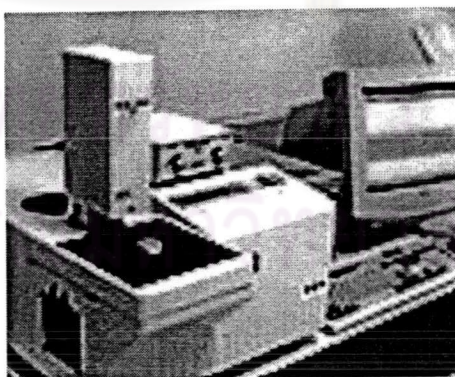


Figure 3.10 Mettler Toldo DSC822-e/400w

3.5 Chemical analysis

X-ray Fluorescence (XRF) Analysis was used to measure the elemental composition of cellulose powder product.

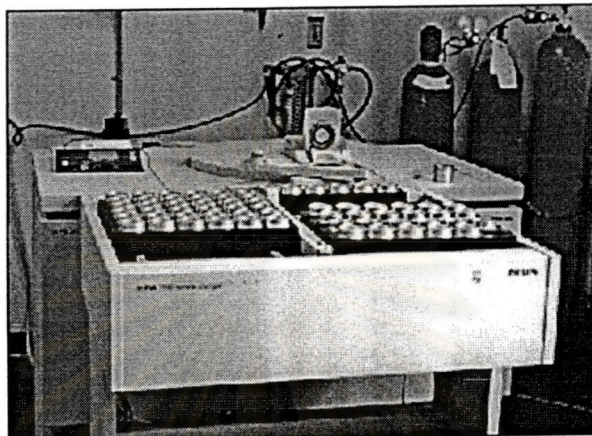


Figure 3.11 X-ray Fluorescence Analysis Machine

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