Polymer Science

Cellulose: Fascinating Biopolymer and Sustainable Raw Material

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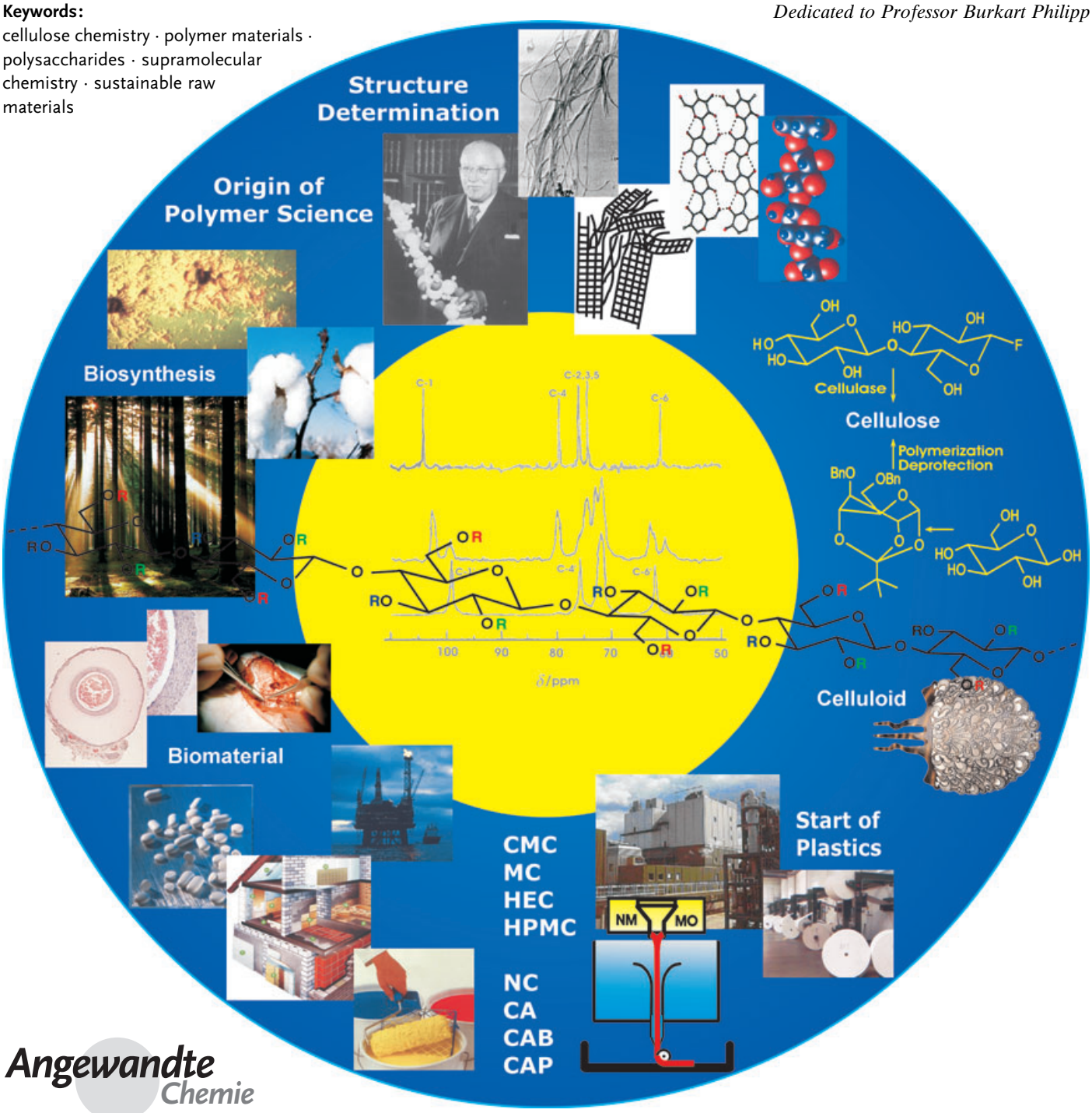
Dedicated to Professor Burkart Philipp



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As the most important skeletal component in plants, the polysaccharide cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties. Formed by the repeated connection of D-glucose building blocks, the highly functionalized, linear stiff-chain homopolymer is characterized by its hydrophilicity, chirality, biodegradability, broad chemical modifying capacity, and its formation of versatile semicrystalline fiber morphologies. In view of the considerable increase in interdisciplinary cellulose research and product development over the past decade worldwide, this paper assembles the current knowledge in the structure and chemistry of cellulose, and in the development of innovative cellulose esters and ethers for coatings, films, membranes, building materials, drilling techniques, pharmaceuticals, and foodstuffs. New frontiers, including environmentally friendly cellulose fiber technologies, bacterial cellulose biomaterials, and in-vitro syntheses of cellulose are highlighted together with future aims, strategies, and perspectives of cellulose research and its applications.

From the Contents

1. Introduction

In 1838 the French chemist Anselme Payen described a resistant fibrous solid that remains behind after treatment of various plant tissues with acids and ammonia, and after subsequent extraction with water, alcohol, and ether.[1] He determined the molecular formula to be $C_6H_{10}O_5$ by elemental analysis, and observed the isomerism with starch. The term "cellulose" for this plant constituent was first used in 1839 in a report of the French academy on the work of Payen.[2]

Thousands of years prior to the discovery of the "sugar of the plant cell wall", cellulose was used in the form of wood, cotton, and other plant fibers as an energy source, for building materials, and for clothing. Since the Egyptian papyri, a considerable part of human culture has been shaped by cellulose materials.

As a chemical raw material, cellulose has been used for about 150 years. The formation of cellulose nitrate by reaction with nitric acid[3] and the corresponding technical synthesis of the first thermoplastic polymer material called celluloid (camphor used as plasticizer) by the Hyatt Manufacturing Company in 1870 demonstrated that new materials could be produced on an industrial scale by the chemical modification of cellulose.[4] With this knowledge came an increased use of synthetic fibers based on wood cellulose, instead of native cellulose fibers, for textiles and technical products. The first example herein is the production of regenerate cellulose filaments by spinning a solution of cellulose in a mixture of copper(II) hydroxide and aqueous ammonia, in which tetraamminecopper(II) hydroxide (cuprammonium hydroxide) $[Cu(NH_3)_4](OH)_2$ is formed,[5] followed by the currently most important large-scale technical process in fiber production, the viscose process.[6] In this process, cellulose is transformed into cellulose xanthogenate (see Scheme 16 and Figure 18) followed by spinning its solution in aqueous sodium hydroxide (viscose).

From the current point of view, cellulose is the most common organic polymer, representing about 1.5×10^{12} tons of the total annual biomass production, and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products.[7] Wood pulp remains the most important raw material source for the processing of cellulose, most of which is used for the production of paper and cardboard. Approximately 2% ($\approx$3.2 million tons in 2003) were used for the production of cellulose regenerate fibers and films, as well as for the synthesis of a large number of cellulose esters and ethers. Such cellulose derivatives produced on an industrial scale (see Schemes 16 and 17 in Section 4) are used for coatings, laminates, optical films and sorption media, as well as for property-determining additives in building materials, pharmaceuticals, foodstuffs, and cosmetics. In the field of synthetic fibers, the Lyocell process made an industrial breakthrough as an environmentally friendly alternative to the viscose process, whereby cellulose is regenerated from

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solution in *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate by spinning (Section 5). Numerous new applications of cellulose take advantage of its biocompatibility and chirality for the immobilization of proteins,[8] antibodies,[9] and heparin,[10] and for the separation of enantiomeric molecules[11] as well as the formation of cellulose composites with synthetic polymers and biopolymers.[12]

The fascination of the cellulose biopolymer is a result of its specific structure, which is described in more detail in the following section. The fusion of both carbohydrate and polymer chemistry in a macromolecule composed of repeating glucose units generates surprising specificity and impressively diverse architectures, reactivities and functions. In contrast to carbohydrates of low molar mass, the reactions and properties of cellulose are determined by intermolecular interactions, cross-linking reactions, chain lengths, chain-length distribution, and by the distribution of functional groups on the repeating units and along the polymer chains. Cellulose differs from synthetic polymers by virtue of its distinct polyfunctionality, its high chain stiffness, and its sensitivity toward the hydrolysis and oxidation of the chain-forming acetal groups, which determine its chemistry and handling.

The elucidation of the polymeric structure of cellulose can be traced back to 1920 with the pioneering work of Hermann Staudinger.[13] Through acetylation and deacetylation of cellulose, he recognized that its structure does not merely consist of an aggregation of D-glucose units. Rather, the glucose units were found to be linked to each other covalently to form long molecular chains. This, along with Staudinger's research with other chain molecules, marked the discovery of the polymeric state of molecules and of the corresponding reactions that are unique to polymers and represents the origin of polymer science.

Figure 1 shows the molecular structure of cellulose as a carbohydrate polymer generated from repeating β-D-glucopyranose molecules that are covalently linked through acetal functions between the equatorial OH group of C4 and the C1 carbon atom (β-1,4-glucan), which is, in principle, the manner in which cellulose is biogenetically formed. As a result, cellulose is an extensive, linear-chain polymer with a large number of hydroxy groups (three per anhydroglucose (AGU) unit) present in the thermodynamically preferred $^4C_1$ conformation. To accommodate the preferred bond angles of the acetal oxygen bridges, every second AGU ring is rotated 180° in the plane. In this manner, two adjacent structural units define the disaccharide cellobiose.

The chain length of cellulose expressed in the number of constituent AGUs (degree of polymerization, DP) varies with the origin and treatment of the raw material. In case of wood

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Brigitte Heublein studied chemistry at the Friedrich Schiller University of Jena and received her master's degree (diploma) in 1969 with her investigations of cationic polymerization of vinyl monomers. She received her PhD in 1974 from research into the control of cationic polymerizations of vinyl monomers with Prof. G. Heublein at the Institute of Organic and Macromolecular Chemistry, and was associated with that research group until 1989. Since 1990 she has been working in organic natural products and polysaccharide chemistry under the direction of Prof. D. Klemm.

Hans-Peter Fink studied physics at Rostock University, where he received his diploma in 1973 and his PhD in 1977 under Prof. G. Becherer on X-ray diffraction analysis of glass ceramics. Between 1975 and 1992 he worked at the Institute for Polymer Chemistry in Teltow–Seehof, conducting structural investigations of cellulose which was also the topic of his habilitation (1991, Rostock University). He has been employed at the Fraunhofer Institute for Applied Polymer Research since its foundation in 1992, and he currently heads the Division of Natural Polymers of the Institute. He has been awarded repeatedly for his contributions to the field of cellulose research, most recently in 2002, with the Jisuke Hayashi Award of the Cellulose Society of Japan.

Andreas Bohn studied mineralogy at the universities of Münster and Berlin, where he graduated in 1994 from the Hahn–Meitner Institute with a diploma thesis on X-ray and neutron scattering investigations of the structure of proton conductors. Since 1995 he has been working in the department of structure characterization at the Fraunhofer Institute for Applied Polymer Research in Teltow and Potsdam (Golm). In 2000 he received his PhD degree with a thesis on X-ray diffraction investigations of the structure and orientation of bacterial cellulose and regenerated cellulose films. He has since headed the group of X-ray structure characterization at the Institute.

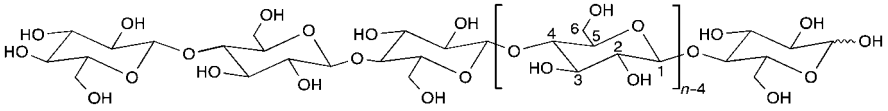


Figure 1. Molecular structure of cellulose (n = DP, degree of polymerization).

pulp, the values are typically 300 and 1700. Cotton and other plant fibers have DP values in the 800–10000 range, depending on treatment; similar DP values are observed in bacterial cellulose. Regenerate fibers from cellulose contain 250–500 repeating units per chain. By acid treatment and cellulase-catalyzed hydrolysis, cellulose can be quantitatively decomposed to D-glucose. Partial chain degradation yields powdery cellulose substrates of the microcrystalline cellulose type[14] (such as Avicel) with DP values between 150 and 300. A β(1→4) linked glucan with 20–30 repeating units offers all properties of cellulose.[15]

The cellulose chain consists at one end of a D-glucose unit with an original C4-OH group (the nonreducing end); the other end is terminated with an original C1-OH group, which is in equilibrium with the aldehyde structure (the reducing end). Technical celluloses, such as bleached wood pulp, contain additional carbonyl and carboxy groups as a result of the isolation and purification processes that play a significant role in the processing of cellulose.[16]

The molecular structure imparts cellulose with its characteristic properties: hydrophilicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of the OH groups (Section 3). It is also the basis for extensive hydrogen bond networks, which give cellulose a multitude of partially crystalline fiber structures and morphologies (Section 2). The properties of cellulose are therefore determined by a defined hierarchical order in supramolecular structure and organization.

Scheme 1 presents the four different pathways by which cellulose is accessed today. As described above, the dominant pathway is the production of cellulose from plants. In the seed hairs of cotton, cellulose is available in almost pure form. In contrast, wood cellulose forms a native composite material with lignin and other polysaccharides (hemicelluloses) from which it is isolated by large-scale chemical pulping, separation, and purification processes.

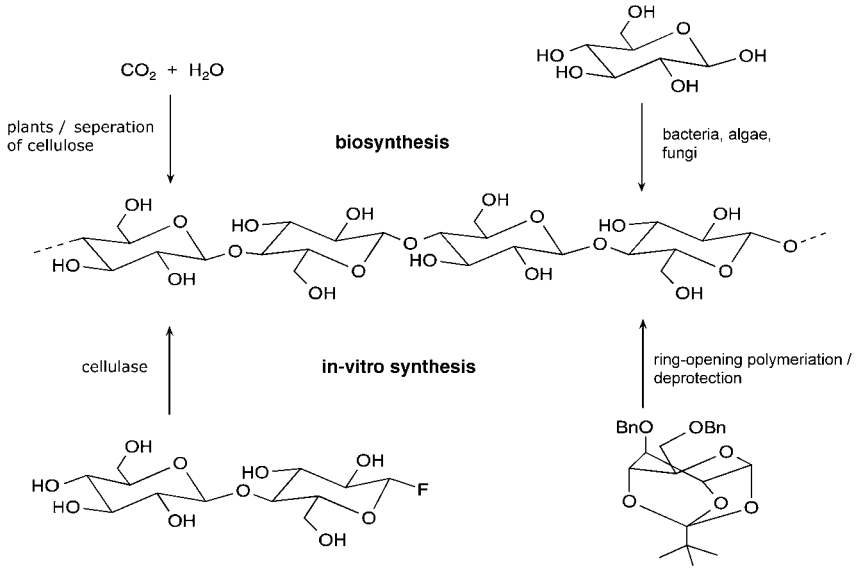
Apart from plants, certain bacteria, algae, and fungi produce cellulose as well. Because of their specific supramolecular structures, these cellulose forms are frequently used as model substances for further research on cellulose structure, crystallinity, and reactivity, as well as for the development of new materials and biomaterials (Section 6). On this basis, the biosynthesis of cellulose has been investigated in detail over the past decades.[17] Therefore, it is known that the biosynthesis of cellulose has been part of the life cycle of cyanobacteria for over 3.5 billion years.[18]

The synthesis of cellulose in vitro should be highlighted as an additional important development in recent years.[15] The first reported cellulase-catalyzed formation of cellulose was based on cellobiosyl fluoride,[19] and the first chemosynthesis was carried out through a ring-opening polymerization of substituted D-glucose pivalate moieties, followed by deprotection (Section 7).[20]

A considerable stimulation of scientific and technological research in the field of cellulose has been triggered over the past 10 years in response to the growing global importance in renewable resources and environmentally compatible materials. With its foundations in the knowledge contained in monographs, books and review articles,[21] this review presents important current developments and discusses the aims, strategies, and perspectives in the field of cellulose. The topics highlighted herein were chosen for their current importance to the field of cellulose research and the nature of the innovative impetus associated with a given development; their selection reflects the experience of the authors. Thus, a collection of current cellulose research and development has been created that combines discussions of structure, synthesis, innovative products, and new frontiers in an updated contribution to the scientific literature.

2. Structure and Properties of Cellulose in the Solid State and in Solution

The hierarchical structure of cellulose, formed by the hydrogen bond network between hydroxy groups, has been the subject of intense research for more than 100 years, marked with frequent controversy over results and a consistent supply of new insight.[22] Directly from the beginning, progress was closely connected with the introduction and continued development of structure-analysis methods, such as X-ray diffraction, electron microscopy, high-resolution ^{13}C solid state NMR spectroscopy, and neutron diffraction



Scheme 1. Principle pathways to cellulose formation.

analysis. A detailed analysis and modeling of the various structural levels of cellulose is essential for synthetic reaction procedures, and for the controlled structure formation and properties of cellulose-based chemical products (man-made cellulosics).

2.1. Solid-State Structures of Native Cellulose

As shown in the molecular structure represented in Figure 1, the hydroxy groups of β-1,4-glucan cellulose are placed at positions C2 and C3 (secondary, equatorial) as well as C6 (primary). The CH_2OH side group is arranged in a *trans-gauche* (*tg*) position relative to the O5–C5 and C4–C5 bonds. As a result of the supramolecular structure of cellulose, the solid state is represented by areas of both high order (crystalline) and low order (amorphous).

2.1.1. Crystal Structure

As a first approximation, the crystal structure of native cellulose (cellulose I) determined by X-ray diffraction can be described by a monoclinic unit cell (space group $P2_1$) which contains two cellulose chains in a parallel orientation with a twofold screw axis.[23] In the 1980s, ^{13}C-CP/MAS NMR spectroscopy was used in the initial discovery that native cellulose is present in two different crystalline cellulose I modifications (I_α and I_β), which can be found alongside each other; the I_α/I_β ratio depends on the origin of the cellulose.[24] Investigations with electron microbeam diffraction[25] and combined X-ray and neutron diffraction[26] recently revealed the corresponding crystalline structures to have triclinic (I_α) and monoclinic (I_β) unit cells. Figure 2 shows a schematic representation of the I_β crystal structure. In the side view (Figure 2b) of the central chains of a unit cell, two intramolecular, chain-stiffening hydrogen bonds are revealed. Notably, one of the most recent reports on the I_β structure[27] describes different conformations for neighboring chains as well as different H-bonding systems inside neighboring molecular layers.

Apart from the thermodynamically less stable cellulose I, cellulose may occur in other crystal structures (cellulose II, III, and IV),[21] of which cellulose II (Figure 2) is the most stable structure of technical relevance. It can be formed from cellulose I by treatment with aqueous sodium hydroxide (mercerization) or by dissolution of the cellulose and

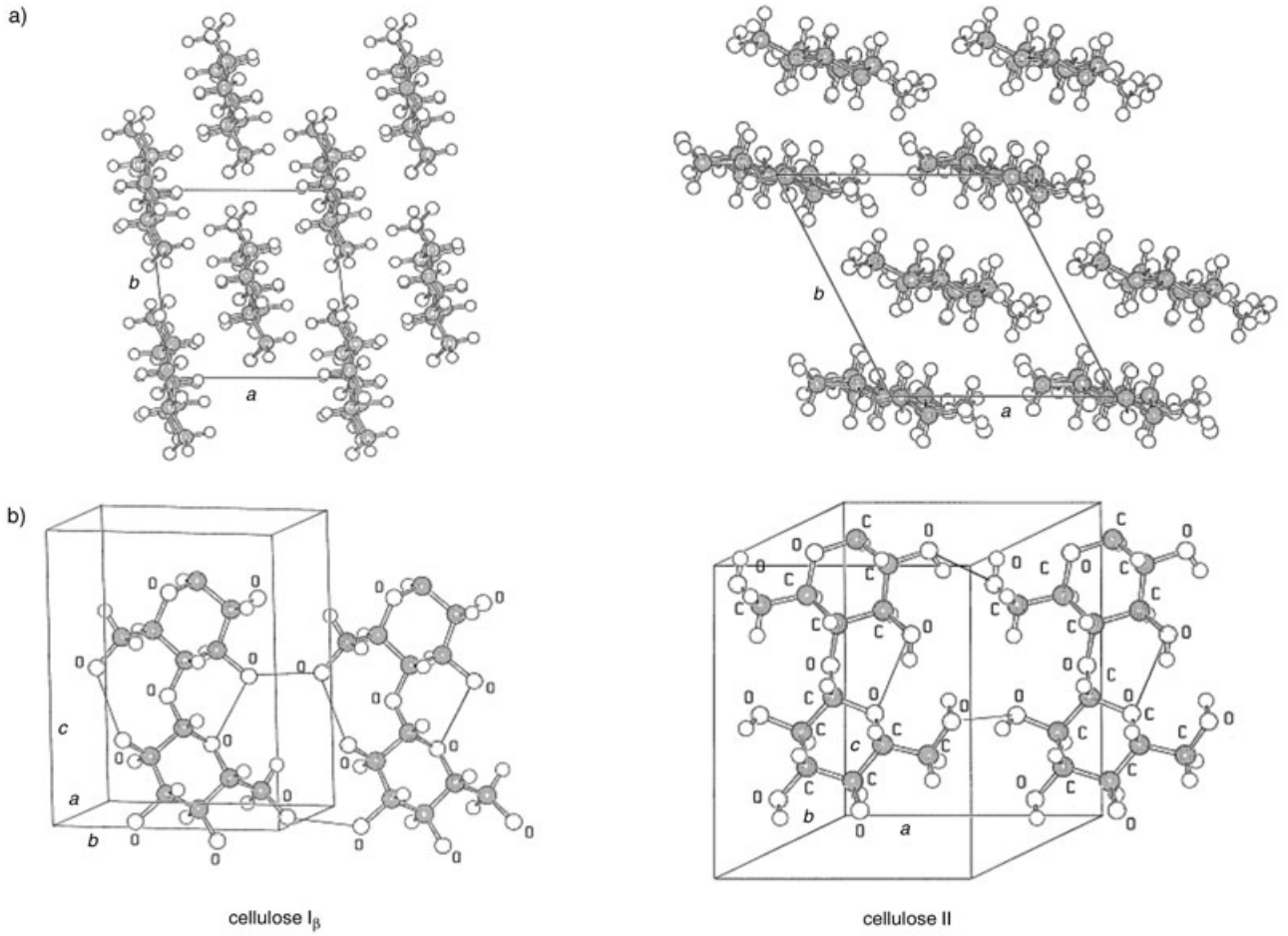


Figure 2. Crystal structures of cellulose I_β and cellulose II: a) projection of the unit cell (UC) along the *a*–*b* plane; b) projection of the UC parallel to the (100) lattice plane (cellulose I) and the (010) lattice plane (cellulose II).[22c]

subsequent precipitation/regeneration, as is done in the formation of fiber and film. This monoclinic crystal structure[28] with two antiparallel chains in the unit cell is characterized by the specific unit cell geometry with a modified H-bonding system. The alkalization of cellulose is of considerable importance to commercial-scale cellulose production as a method for increasing the reactivity (activation) of subsequent reactions as well as for the mercerization of cotton. Depending on the concentration of lye, the temperature, and mechanical load, it is possible to convert cellulose I into various crystalline alkali forms, each with a different crystal structure and variable NaOH and water content.[29] All forms will then convert into crystalline "hydrato cellulose" (water cellulose) during washout, and to cellulose II through drying (Figure 3). It is not yet understood how the parallel chain arrangement of cellulose I undergoes transition into the antiparallel orientation of cellulose II without an intermediate dispersion of cellulose molecules.

There are currently only a few reports on the structure of noncrystalline random cellulose chain segments.[30] More knowledge in this area is required, as these structure elements have a significant influence on the accessibility and reactivity of cellulose, as well as on the properties of man-made cellulose fibers.

2.1.2. *Morphology*

The biological function and numerous applications of cellulose are based on its distinct fiber morphology. The morphological hierarchy is defined by elementary fibrils, microfibrils, and microfibrillar bands.[31] The lateral dimensions of these structural units are between 1.5 and 3.5 nm (elementary fibrils), between 10 and 30 nm (microfibrils), and on the order of 100 nm (microfibrillar bands). The length of the microfibrils is on the order of several hundred nm. Figure 4 shows electron micrographs of the fibrillar structure of samples of varying origin; a structural model of an initially hydrated bacterial cellulose sample is shown in Figure 28 (Section 6.1).

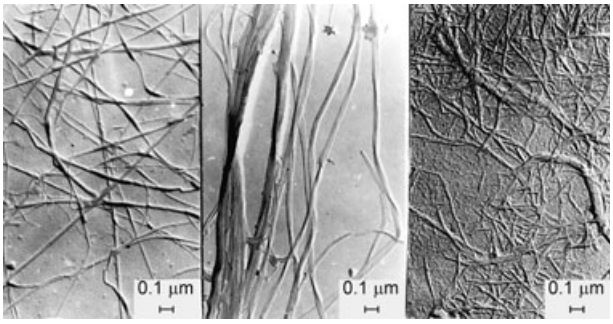


Figure 4. Electron micrographs of cellulosic microfibrils of varying origins:[32] left, *Valonia* spp. (algae) cellulose; center, cotton linters; right, spruce sulfite pulps.

The fringed fibrillar model with crystalline regions of varying dimensions (crystallites) and noncrystalline regions has proven successful for the description of the structure of microfibrils and the partial crystalline structure of cellulose in connection with the reactivity of this polymer[29c] (Figure 5).

The degree of crystallinity of cellulose and the dimensions of the crystallites have been the subject of extensive investigations for many years;[33] some results of X-ray diffraction measurements of native celluloses have been compiled in

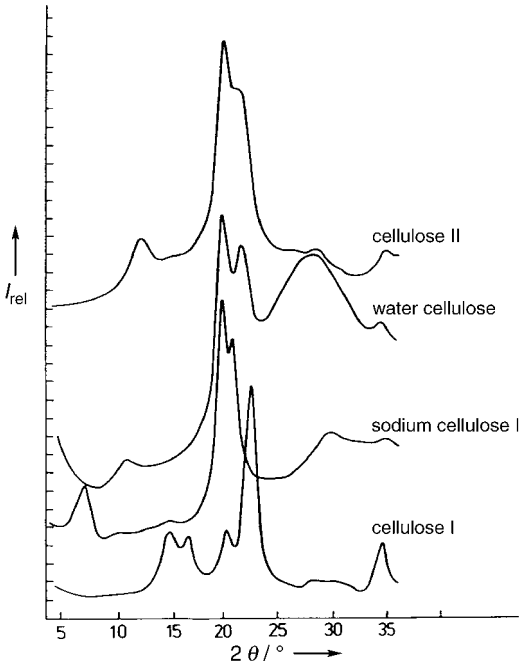


Figure 3. X-ray wide-angle scattering curves of cellulose modifications formed during alkalization and regeneration[29c] (I_{rel} = relative intensity, 2θ = diffraction angle).

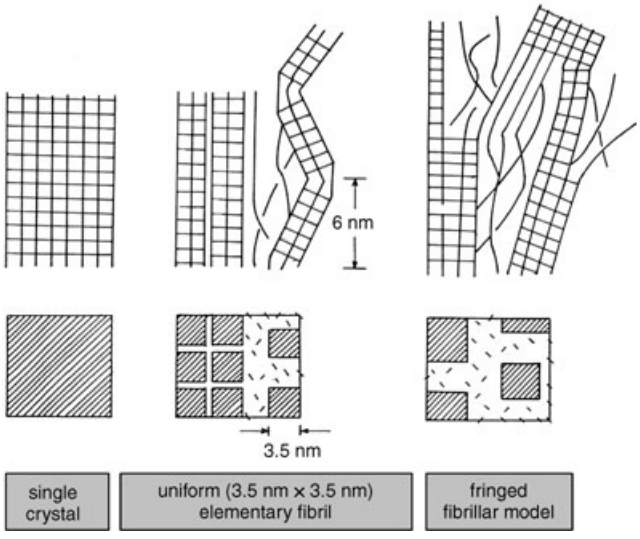


Figure 5. Various models of the supramolecular structure of cellulose microfibrils.[29c]

Table 1: Degrees of crystallinity (x_c), crystallite sizes ($D_{(hkl)}$), and lateral dimensions (d) of microfibrils of native celluloses

Cellulose Source	x_c [%]	crystallite sizes [nm]			d [nm]
		$D_{(1\bar{1}0)}$	$D_{(110)}$	$D_{(020)}$	
algal cellulose	>80%	10.1	9.7	8.9	10–35
bacterial cellulose	65–79	5.3	6.5	5.7	4–7
cotton linters	56–65	4.7	5.4	6.0	7–9
ramie	44–47	4.6		5.0	3–12
flax	44 (56)[a]	4–5	4–5	4–5	3–18
hemp	44 (59)[a]	3–5	3–5	3–5	3–18
dissolving pulp	43–56			4.1–4.7	10–30

[a] Degree of crystallinity relative to cellulose.

Table 1. The corresponding values of regenerated cellulose in the form of filaments and films are given in Table 4 (Section 5.5.1).

Notably, the lateral crystallite dimensions of regenerated cellulose (cellulose II) are in the range of ≈4–5 nm regardless of the production process (Table 4), whereas in native celluloses, values of up to 20 nm have been observed. The reasons for the formation of nearly uniform cross-sectional dimensions of these cellulose II crystallites from different structure-forming processes still have to be clarified.

The pore structure can be considered the counterpart to the fibril morphology of cellulose. It is considerably important for the accessibility in chemical reactions and enzymatic degradation.[34] The controlled variation of pore structures enables cellulose products to meet the needs of a wide range of applications, from highly specialized membrane and carrier materials to consumer goods, such as nonwovens[35] with excellent absorption properties.

2.1.3. *Growth Architectures and Material Design*

As the skeletal component in all plants, cellulose is organized in a cellular hierarchical structure. In combination with the accompanying substances hemicelluloses, lignin, and pectin, this structure leads to the extraordinary properties of native composite materials, such as wood, cotton, flax, and hemp. Figure 6 schematically illustrates the cell walls of cotton and wood with differently structured layers, in which the secondary cell-wall layer S2 contains the main quantity of cellulose.

The cellulose molecules organized in the cell walls in the form of microfibrils have characteristic orientations (helix angles), which differ as a function of the cell wall layer, and according to the plant type as well. Figure 7 shows X-ray fiber diffraction patterns of cotton and bast fibers (flax, hemp, and jute), which reflect the different average orientations of the crystalline spectra of these natural fibers.

The lower orientation of the cellulose microfibrils in cotton fibers (helix angle ≈18°) gives rise to a smaller module of elasticity and a higher elongation at breakage compared with bast fibers, which have a much higher microfibril orientation (helix angle ≈4°–5°) and fiber strength. The adaptation of the mechanical properties of wood to environmental conditions through corresponding helix angles is fascinating, and has yet to be rivaled in technical composite materials.[37] However, it is already possible to adapt the parameters of cellulosic man-made fibers to user requirements through a targeted influence on the orientation (with particular respect to the noncrystalline chain segments). It is therefore possible to develop man-made cellulose fibers similar to cotton with low orientation (high elongation), and technical fibers with high orientation and a high modulus of elasticity, similar to bast fibers.

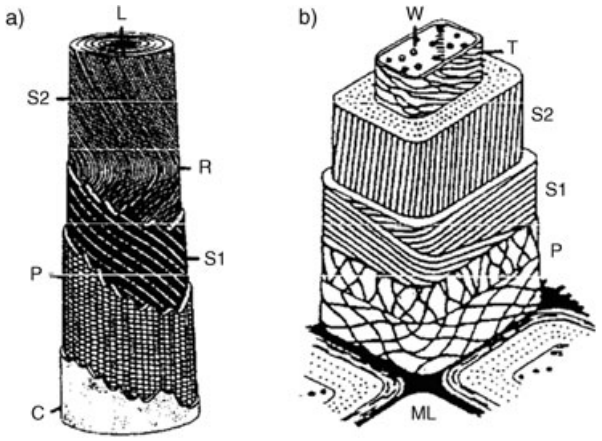


Figure 6. Structural design of plant cell walls exemplified by a) cotton and b) wood fibers:[21b] C = cuticula layer, L = lumen, ML = middle lamella, P = primary cell wall layer, R = reversing point, S1 = secondary cell wall layer 1, S2 = secondary cell wall layer 2, *T* = tertiary cell wall, W = wart layer.

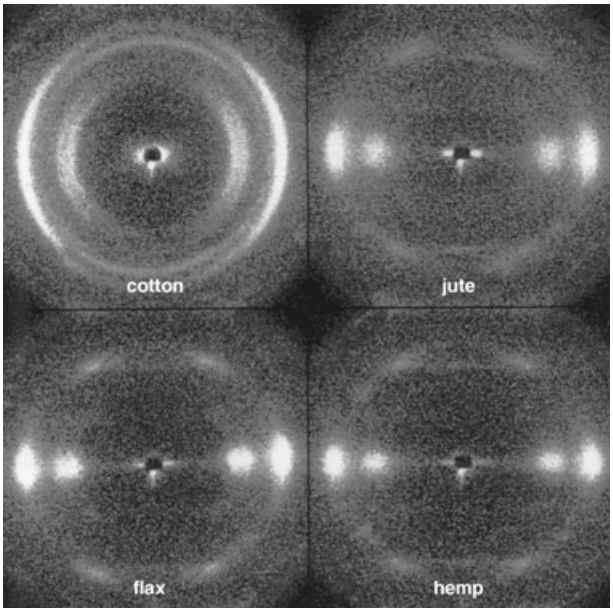


Figure 7. X-ray fiber diagrams of various natural cellulosic fibers.[36]

2.2. *Solution Structures of Cellulose and Cellulose Derivatives*

An understanding of the structure of cellulose and cellulose derivatives in solution is not only a matter of scientific interest, but has great practical importance as well.

Examples include the shaping of cellulose from spinning solutions,[38] modification of the synthesis of cellulose derivatives (Section 3) and the properties of water-soluble cellulose ethers (Section 4), which all are dependent on the solution structure. For this reason, questions regarding the structure of cellulose in solution have been the subject of intense research and discussion over the past decades. According to Schurz,[38a] a differentiation is made initially between molecularly dispersed and network solutions, to which a portion of gel particles may be added. Figure 8 illustrates suggested models of the different solution states of cellulose derivatives, which may depend on the type of solvent, polymer concentration, chain length distribution, and the type, pattern, and degree of cellulose substitution.

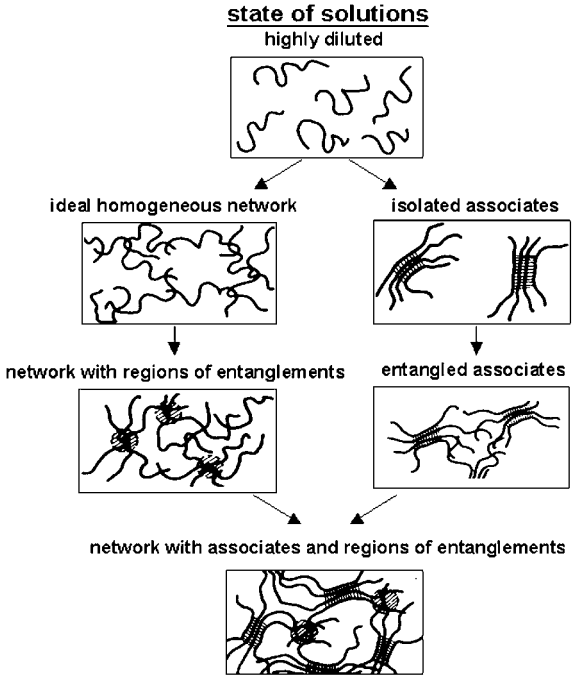


Figure 8. Scheme of the potential dissolution states of cellulose.[38a]

As a rule, cellulose derivatives with free OH groups are not molecularly dispersible. Investigations with partially substituted cellulose carbanilates and benzoates revealed, however, that aggregate-free solutions can occur through specific polymer–solvent (e.g. DMF) interactions.[39] On the other hand, completely substituted products (such as cellulose tricarbanilates) can be molecularly soluble or, owing to strong intermolecular interactions, insoluble as is the case with trimethylsilyl cellulose with DS 3.0.

Whereas highly diluted solutions have been used for fundamental research of solution structures, applied practices, such as the viscous process, employ concentrated systems with polymer concentrations of 8–12%, which are described as network solutions with gel-particle portion in accordance with model assumptions.[38b,c] Apart from rheological examinations, gel-particle characterizations are also normally carried out to determine the quality of a given spinning solution.[38]

Over the past few years the research group of Burchard, in particular, has carried out extensive fundamental research into the structure of cellulose and cellulose derivatives in solution by means of static and dynamic light scattering.[40] With regioselective modified cellulose ethers, new insight was gained into the entropy effect during the dissolution of cellulose derivatives (Section 3.2.3).[39,40]

The initial research results on the solution state of cellulose in *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate as a technically relevant system (Section 5) substantiate the presence of bimodal molecule aggregations with up to 1000 chains, which can be attributed to incomplete dissolution of crystal structures of the starting cellulose material.[41] In the first approximation, the average number of molecules in the smaller aggregates corresponds to that of crystallites (50–100), whereas the average number of molecules in larger aggregates correlates with the number of molecules found in a microfibril (250–1000).[42] In a ternary solvent system composed of NMMO, water, and diethylenetriamine [bis-(2-aminoethyl)-amine], cellulose is molecularly soluble within a temperature range of 25–60 °C. Therefore, the average molar mass and other properties of the dissolved molecules could be determined by means of light scattering.[43]

2.3. Liquid-Crystalline Cellulose Structures

Owing to chain stiffness, cellulose and certain cellulose derivatives in solutions of higher concentration may form cholesteric (chiral-nematic) structures. Since the discovery of the lyotropic liquid-crystalline state of hydroxypropyl cellulose in water,[44] a multitude of cellulose derivatives were found, which produce lyotropic or thermotropic liquid-crystalline phases.[45] Chiral-nematic films and gels are formed from the solutions. The influence of the solvent and of the chain stiffness on the pitch and handedness of the chiral-nematic structures was examined.[46]

Regioselectively substituted (position 2, 3 or 6 of the AGU) cellulose phenylurethanes with F, Cl, or CH_3 groups in the phenyl ring form lyotropic liquid-crystalline mesophases in highly concentrated solutions, the structure and optical properties of which depend strongly on the site of substitution, as well as on the concentration and temperature of the solution.[46] The photo-cross-linking of cellulose-(3-chlorophenyl)-urethanes in mixtures with acrylate monomers produces semi-interpenetrating polymer networks, which can change their selective reflection under compression.[47] Cellulose urethanes with azo-dye substituents and acrylates of hydroxypropyl cellulose are other well-analyzed lyotropic liquid-crystalline cellulose products. The latter form gels in water through photo-cross-linking, and their resulting color is determined by the water content.[47] The optical properties that can be controlled by the pitch of cholesteric phases open up important fields of application, such as color pigments in car paints and as copy protection color for document papers.

Liquid-crystalline states of unsubstituted cellulose are significant with particular respect to new spinning methods and the production of high-performance fibers. Suitable

solvents for this include NMMO, a mixture of trifluoroacetic acid and chlorinated alkanes, DMA/LiCl, ammonium rhodanide in liquid ammonia,[48] and concentrated phosphoric acid. However, any spinning process based in these liquid-crystalline systems has yet to gain industrial acceptance. The cellulose concentrations in NMMO used in the Lyocell process are below the liquid-crystalline phase range (Section 5).

Recently, developments appear to have emerged in conjunction with the possible production of chiral-nematic suspensions from cellulose crystallites or microfibrils.[46a]

3. Cellulose Chemistry: New Syntheses, Products and Supramolecular Architectures

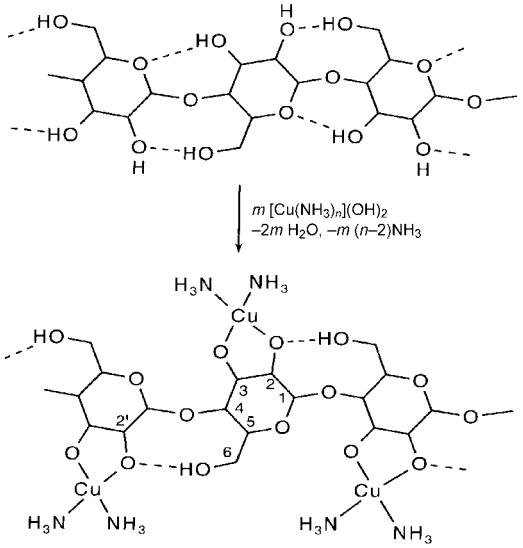
3.1. Specific Features of the Reactions of Cellulose

The insolubility of cellulose in water and in most organic solvents caused by its supramolecular structure is the reason behind the fact that all commercially available products are currently produced through reactions of cellulose in the solid, or more or less swollen state (heterogeneous reactions).[49] Because each repeating unit of cellulose has three hydroxy groups available for reaction, and the stability of the chain-forming acetal groups toward various reagents, oxygen, and mechanical and thermal load is limited, additional questions emerge over substituent distribution in the product and over chain degradation during synthesis.

In case of heterogeneous reactions, the accessibility and reactivity of the OH groups are clearly determined by hydrogen bond-breaking activation steps (through alkaline compounds such as NaOH, Section 2.1.1)[50] and by interaction with the reaction media (e.g. swelling).[51] Thus, the "linear" transfer of the typical reactions of organic chemistry to cellulose is not easily done. However, the control of cellulose activation and of the type of heterogeneous reaction permits effective synthesis of cellulose products with desired degrees of reaction, reproducible substitution patterns, and targeted properties at both the laboratory and production scales. There remain important aspects of the synthesis procedure that are understood only partially. Therefore, a lot of experience and the right "feeling" are still required in cellulose syntheses.

Through the use of specific cellulose solvents,[21a] which disrupt hydrogen bonds and thus dissolve the adducts formed, the influence of the supramolecular structure of cellulose on the reaction procedure is eliminated almost completely. In this context, a solution of LiCl in DMA (DMA/LiCl) is one of the most important solvent systems for cellulose in organic syntheses[52] as well as for analytical purposes.[53] The structure of this binary medium, the mechanism of dissolution, the influence of water on the dissolving activity, and the state of dissolution of cellulose have been investigated in detail.[40,54]

Over the past few years, it was demonstrated that tetrabutylammonium fluoride trihydrate in DMSO (DMSO/TBAF) effectively dissolves cellulose and is very useful for homogeneous syntheses.[55] Fundamental progress has also been made in the classical field of metal-containing cellulose solvents like cuprammonium hydroxide.[56] In doing so, the solution structure of cellulose in this copper-containing medium was elucidated (Scheme 2).[53]

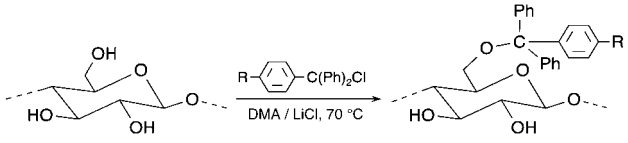


Scheme 2. Complex formation of cellulose in cuprammonium hydroxide.[53]

Extensive preparative work on the laboratory scale has been carried out over the past 20 years with cellulose solvent systems. As a result, new types of cellulose derivatives have been synthesized and the knowledge of reaction mechanisms, reaction control, structure–property relationships (solubility, film formation, stability), and structure analysis has been increased.[57] Until now, it has not been possible to transfer the homogeneous reactions to technical scale, as the handling of aprotic dipolar media and salt components poses an obstacle.

Of course, partially substituted soluble cellulose derivatives are also good substrates for reactions under homogeneous conditions (see Sections 3.2.1 and 3.2.4 as well).[58] Cellulose ethers have proven particularly useful as intermediates and regioselective protecting groups. Typical examples include trityl,[59] methoxy-substituted trityl,[60,61] bulky silyl (Section 3.2.3), as well as allyl and benzyl ethers.[62] Table 2 contains example data for trityl protecting groups.[60]

Table 2: Trityl and methoxytrityl ethers as O6-selective protecting groups.

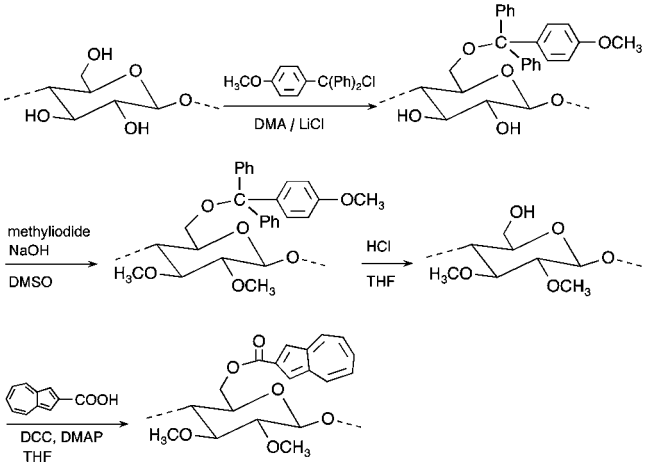


Polymer R	t [h]	DS 6	3	2	Σ
H	48	0.96	0.01	0.13	1.10
OCH_3	4	0.97	0.00	0.06	1.03
OCH_3	48	0.96	0.00	0.10	1.06

Limited chain degradation can be accepted in most reactions of cellulose without loss of the product properties, if chain lengths beyond the convergence range of the material parameters are not obtained. Transformation of cellulose with phenyl isocyanate (carbanilation) and silylation (Section 3.2.3) take place without chain degradation, for example.[58]

3.2. New Cellulose Products and Selective Syntheses

The wide range of preparative and structure-analytical studies over the past 10 years includes characterization of the donor–acceptor properties of cellulose substrates and derivatives by means of solvatochromic EDA complexes[63] and investigations of cellulose thiosulfates and self-assembling derivatives.[64] Part of this work also includes studies of celluloses with reduced functionality (at O2 and O3 as ether-protected substrates for subsequent reactions at C6-OH groups)[61] as well as cellulose products with covalently fixed dyes (e.g. azulene carboxylic acid ester) and their optoelectronic properties[65] (Scheme 3).



Scheme 3. 2,3-Methyl ether as a regioselective control element in the formation of celluloses with optoelectronic properties.

Products of current research include specifically modified cellulose derivatives for applications in enantioselective chromatography[66] and as biomaterials,[67] as are new types of cellulose products produced by acylysis and "retrosynthesis".[68] There are also reports of structure change and modification of cellulose in low-temperature salt melts/ionic solvents,[69] structure analysis of cellulose and substituted cellulose derivatives,[70] and determination of the polymer dynamics of cellulose derivatives in solution by dielectric relaxation spectroscopy.[71] The viscoelastic and rheo-optical properties of water-soluble cellulose derivatives and their ultrasonic degradation to smaller units with well-defined molar masses has also been investigated.[72]

A special challenge for synthetic work are the selective reactions of the OH groups of the repeating cellulose units and along the polymer chains. This problem is, of course, typical in polysaccharide chemistry. Horton and Yalpani have presented pioneering work in this area.[73] Results with the regiochemistry of cellulose are also the subject of review articles.[74]

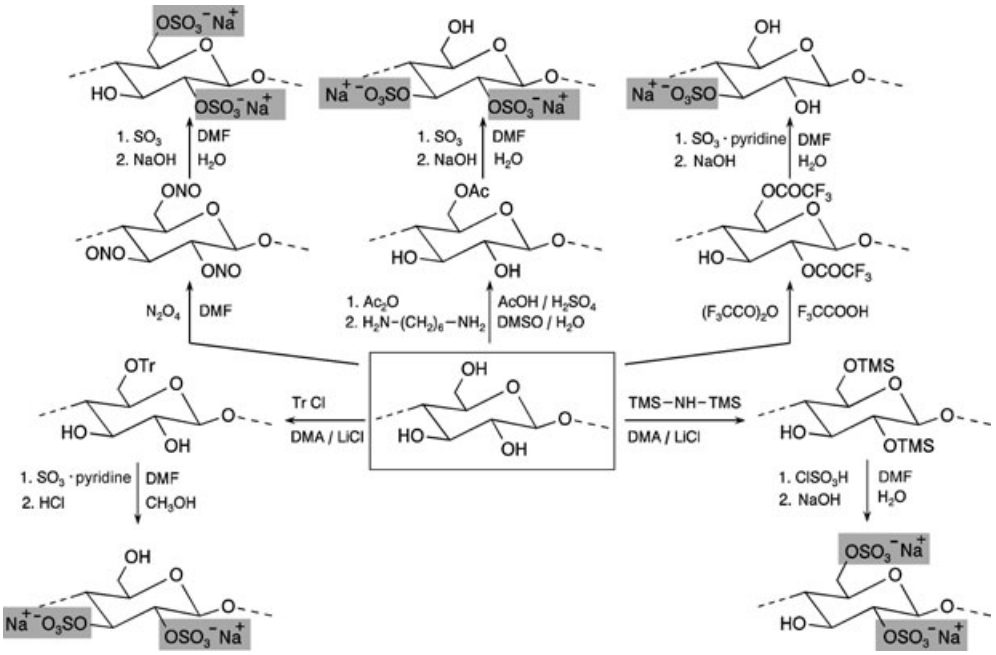
The difference in reactivity between the primary hydroxy group at C6 (highly accessible) and the secondary hydroxy group at C2 (highly acidic and in close proximity to the acetal function) is exploited for selective reactions of cellulose, but is overshadowed by the hydrogen bridge networks described in Section 2. Furthermore, AGUs can be activated along the cellulose chains in a manner to favor reaction preferentially at certain chain segments ("reactive microstructures"). At the laboratory scale, regioselective syntheses of cellulose products are particularly successful with protecting group techniques and the selective involvement of OH groups in discrete solvation and activation states, by specific downstream reactions, by enzymatic transformations of reactive cellulose derivatives, and by chemosynthesis with functionalized glucose as starting material.

Cellulose derivatives with functionalization patterns of high uniformity are important not only for comparison with statistically modified celluloses, but are particularly important as products with new properties and applications. Their importance also lies with respect to questions that remain open about the solution structure of cellulose derivatives and for the design of supramolecular architectures (Section 3.3). Typical examples include 6-*O*- and 2,3-di-*O*-acetyl-6-*O*-triphenylmethylcellulose,[75] 2,6-di-*O*-thexyldimethylsilylcellulose, and 3-*O*-alkylcelluloses,[76] as well as methyl ethers regioselectively modified with fluorescent benzyl ether groups.[77]

3.2.1. Progress in the Synthesis of Cellulose Esters

During the past decade, cellulose sulfates have undergone intense investigation,[21a] as their water-soluble sodium salts offer excellent rheological and gel-forming properties, which has increased their importance as film-forming materials, anionic polyelectrolytes, and biologically active polymers. In view of this application potential, cellulose sulfates are also mentioned in Scheme 16, Section 4, although they have not been used technically to a large extent. One priority with these products has also been the synthesis of cellulose sulfates with a regioselective distribution of substituents, which is possible by sulfation of cellulose ester and cellulose ether intermediates, including the use of protecting groups.[21a,78]

Scheme 4 highlights typical examples of this. For cellulose nitrites and trimethylsilyl ethers, sulfation takes place through the substitution of these functional groups. In the cases of acetate, trifluoroacetate, and trityl ether, sulfation occurs by transformation of the free OH groups. The acetate route proceeds through the selective diamine-catalyzed hydrolysis of cellulose triacetate to the preferentially formed 6-acetate intermediate. The regioselectivities illustrated in Scheme 4 are supported by published DS (degree of substitution) data.[21a] Whereas the reversibility of the direct sulfation of cellulose leads to a statistic distribution along the polymer chain, regioselective sulfations are successful with partially protected precursors, which render inputs irreversible, and

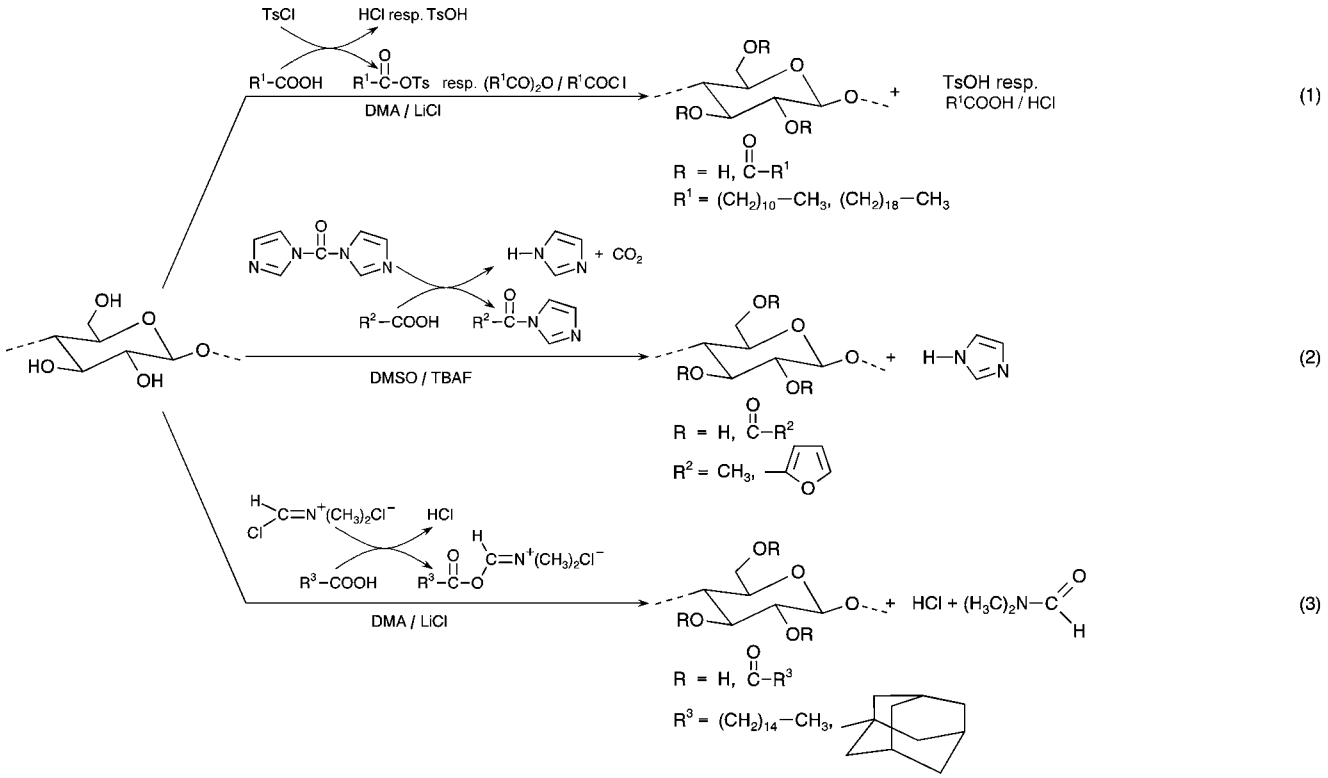


Scheme 4. Synthesis pathways to cellulose sulfates with regioselective distribution of ionic groups.

result from kinetically controlled reactions. A further option toward regioselectivity involves the conversion of reactive intermediates.

In view of their thermoplastic behavior and self-organization, cellulose esters of long-chain carboxylic acids were systematically studied.[79] In this context, composites and nanocomposites of cellulose and its derivatives with lignin as well as supramolecular architectures play an important role as natural composite wood substitute materials.[79] Cellulose esters of aliphatic, aromatic, bulky, and functionalized carboxylic acids are available through the activation of free acids in situ with tosyl chloride, *N*,*N*′-carbonyldiimidazole, and iminium chloride under homogeneous acylation with DMA/LiCl or DMSO/TBAF. From this, a wide range in the degree of substitution, various substituent distributions, and interesting properties (bioactivity, thermal and dissolution behavior) are possible (Scheme 5).[80]

The successful deacetylation of cellulose acetates (CAs) by means of acetyl esterases was recently reported.[81] Regioselectively C6-substituted CAs with a low degree of substitution (DS) can be produced by enzymes of the carbohydrate esterase (CE) family 1. Esterases of the CE 5 family lead to regioselectively 3,6-di-*O*-acetylated CAs, whereas the regioselective modification at position 3 is possible with CE 4 enzymes. Systematic investigations dem-



Scheme 5. Esterification of cellulose by the in-situ activation of the carboxylic acid by (1) tosyl chloride, (2) *N*,*N*′-carbonyldiimidazole, and (3) iminium chloride.

onstrate that the distribution of acetate groups within the AGU and along the cellulose chains of the starting acetates influences the effect of the enzymes. Acetate groups at position 2 are particularly active. The acetylase of *Aspergillus niger* catalyzes preferential deacetylation of cellulose acetate (CA) to form a product that is C6-acetylated along the polymer chain.[81a,82]

3.2.2. Cellulose Ethers with Nonstatistical Substituent Distribution along the Chains

Blocklike carboxymethyl celluloses (CMCs)[83] can be created by using the concept of reactive structure fractions.[84] This term was applied to activated noncrystalline areas of cellulose, which by treatment with low concentrations of aqueous sodium hydroxide, permit a selective attack on the alkylation reagent. This connection exploits the fact that the activation of the cellulose by aqueous sodium hydroxide is dependent on the concentration of base and on the lateral dimensions of the ordered areas. Therefore, with appropriate concentrations of base, noncrystalline chain segments can react in a blocklike manner. Another possible route to CMCs with unconventional substituent distributions is through the derivatization of cellulose in reactive microstructures, which are formed by induced-phase separation.[80a] In this case, NaOH used for activation is added in the form of anhydrous particles to a solution of cellulose in DMA/LiCl, which initiates a phase separation under gel formation. At the solution–particle interface, active cellulose is regenerated (reactive microstructures) in the chain segments with sodium monochloroacetate to give CMCs with DS values up to 2.2 in one reaction step. Structure analysis of these CMC products revealed a distribution of substituents that deviates significantly from statistical prediction.[80a]

The phase-separation principle can also be extended to other solvent systems (DMSO, TBAF, and NMMO), various cellulose intermediates (CA and TMSC; Figure 9), as well as

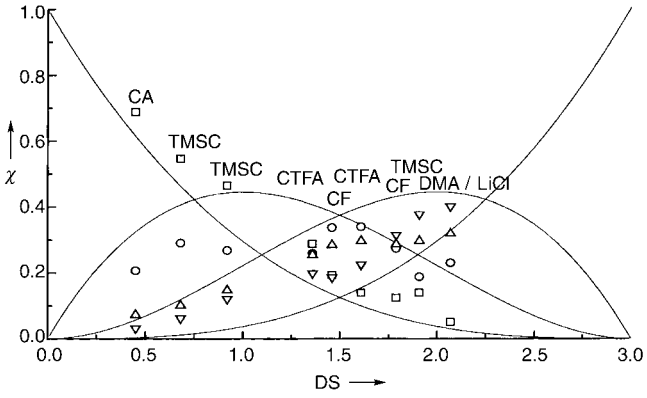


Figure 9. Mole fractions χ of glucose (○), mono-*O*-carboxymethyl glucoses (□), di-*O*-carboxymethyl glucoses (△), and 2,3,6-tri-*O*-carboxymethylglucose (▽) in hydrolyzed carboxymethyl cellulose samples as a function of the degree of substitution (DS) determined by HPLC. Starting from cellulose acetate (CA), trimethylsilyl cellulose (TMSC), cellulose trifluoroacetate (CTFA), cellulose formate (CF), and cellulose dissolved in DMA/LiCl, the polymers were synthesized by induced-phase separation.[80a]

other cellulose ether syntheses (Figure 10). In all cases, blocklike functionalization patterns occur and thus the formation of products with new properties. The curves

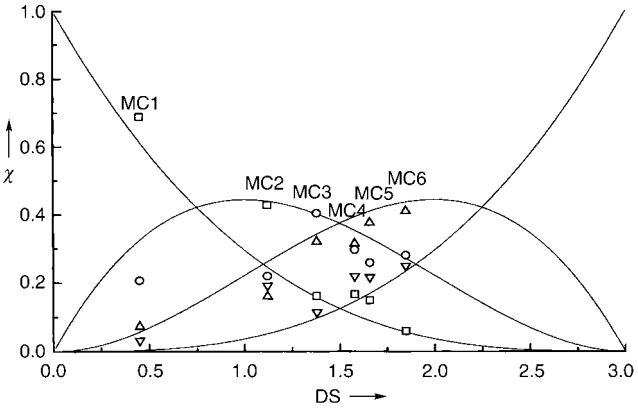


Figure 10. Mole fractions χ of glucose (○), mono-*O*-methyl glucoses (□), di-*O*-methyl glucoses (△), and 2,3,6-tri-*O*-methylglucose (▽) in hydrolyzed methyl cellulose (MC) samples as a function of the degree of substitution (DS) determined by HPLC.[80a]

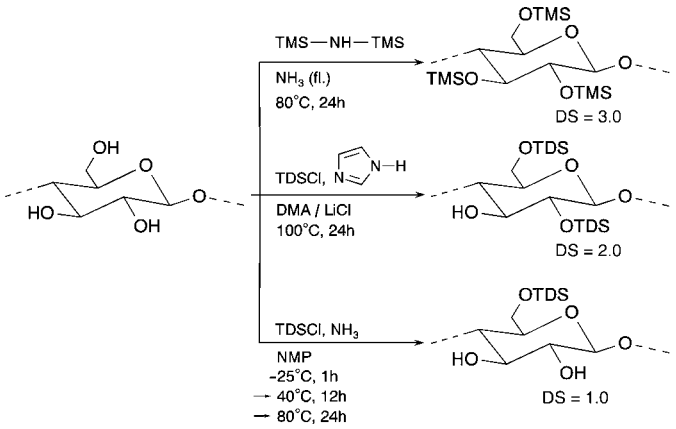
presented in the Figures correspond to the molar fractions, which were calculated by a simplified statistical model by Spurlin.[80e] This model is based on the assumption of uniform reactivity between the OH groups of C2, C3 and C6, independent of the DS value already present. Whereas the mole fractions of heterogeneously synthesized cellulose ethers agree with model calculations,[80f] the mole fractions of samples produced by induced-phase separation deviate from this model. In all cases, the portion of unsubstituted and trisubstituted AGUs is extremely high. The resulting blocklike functionalization pattern is also reflected in the new properties of these products. The partial DS values of positions 2, 3 and 6 of the carboxymethyl celluloses can be calculated from the ^{1}H NMR spectra of the carboxymethyl glucoses obtained by chain degradation.[80f]

3.2.3. Silyl Celluloses

The silylation of polar protic groups (such as OH) with chlorosilanes and silazanes leads to silyl ethers which are characterized by a remarkable increase in thermal stability, lipophilic behavior and a lack of hydrogen bonds. Owing to the simple cleavage of the silyl ethers under acidic conditions, or through nucleophilic attack, they can be used as selective protecting groups in organic synthesis.[85] Therefore, the introduction of silyl groups and the properties of silyl ethers are very attractive in carbohydrate and polysaccharide chemistry.

The silylation of cellulose has been known for about 50 years.[86] During the last decade, it proved to be a suitable way to prepare silyl celluloses for the formation of supramolecular structures (Section 3.3.1) and to differentiate between the three OH groups of the AGU in regioselective syntheses with silicon-containing protecting groups.[87,88]

As shown in Scheme 6, trimethylsilylation with hexamethyldisilazane (HMDS) in liquid ammonia results in a complete conversion of all hydroxy groups to form 2,3,6-tri-*O*-trimethylsilyl cellulose with a DS value of 3.0.[89] The



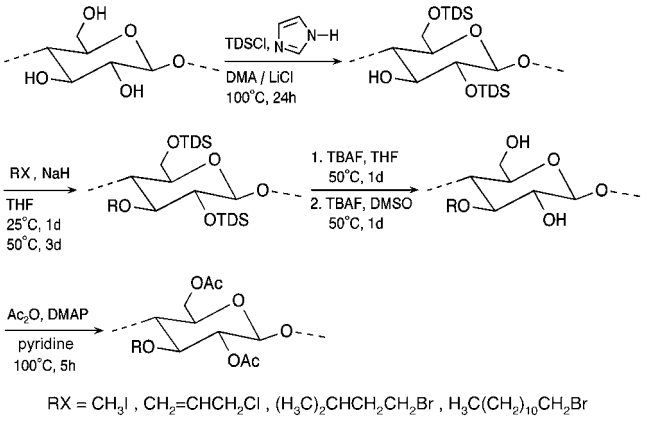
Scheme 6. Various reactivities of the hydroxy groups of cellulose during silylation.

activation of the cellulose with liquid ammonia takes about 30 min. In this process, the accessibility of the OH groups reaches such degree that the rate of silylation (with saccharin as catalyst)[88b,c] follows first-order kinetics up to 50%, although the reaction takes place heterogeneously at the suspended cellulose. During the silylation and desilylation reactions described below, no degradation of the cellulose chain occurs.[88]

If the OH groups are made accessible by dissolving the polymer in DMA/LiCl (homogeneous reaction) and if the synthesis takes place in the presence of imidazole, the bulky silylation reagent thexyldimethylchlorosilane (TDSCl) will lead to complete silylation at O6 and O2 (DS value = 2.0), which means that the primary and the most reactive secondary OH groups are converted.[90] If silyl ether formation starts with the same reagent in cellulose suspension in aprotic dipolar media such as *N*-methylpyrrolidone (NMP), which contain gaseous ammonia, a specific solution state of the silyl cellulose is observed after silylation of all primary C6-OH groups, and after evaporation of the ammonia at about 40 °C. This state does not permit any further reaction of the secondary hydroxy groups, even in cases of large reagent excess, increased temperature, and very long reaction times.[88a]

Structure analysis of the regioselectively substituted silyl celluloses has been particularly successful with 2D NMR spectroscopy after methylation of all free OH groups, complete desilylation, and acetylation of all OH functions created (Scheme 7).[88a] Such analysis is also possible after a simplified analogous process in which acetylation is carried out on the hydroxy groups not converted during the silylation.

Through this complex sample preparation, a remarkable improvement in spectral resolution is observed. In this manner, the structure of 2,6-di-*O*-TDS cellulose could be determined by NMR spectroscopy of 2,6-di-*O*-acetyl-3-*O*-

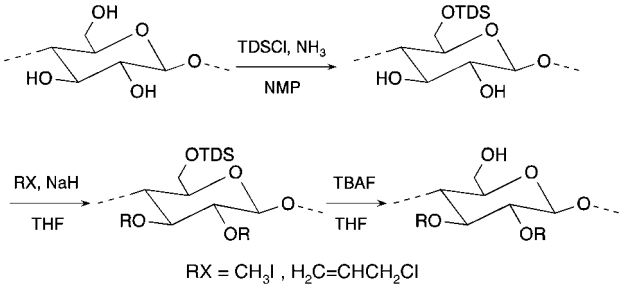


Scheme 7. Synthesis of 3-*O*-ethers of cellulose from 2,6-di-*O*-thexyldimethylsilylcellulose.

methyl cellulose. Likewise, the structure of 6-*O*-TDS cellulose was determined with 2,3-di-*O*-acetyl-6-*O*-TDS cellulose under spectroscopic analysis. An exact correlation between the signals and the protons of the AGU can made with the resultant cross-peaks. The downfield signal shifts of H-2 (4.94 ppm) and H-3 (4.58 ppm) verify the subsequent acetylation of the secondary OH groups. The methylene protons of the AGU reveal a typical high-field shift of H-6a (3.64 ppm) and H-6b (3.14 ppm) as a result of O6 silylation.[88a]

A permethylation analysis was carried out in parallel, with chain degradation of the methylated samples by aqueous trifluoroacetic acid and HPLC analysis of the methyl glucoses.[91] Furthermore, analysis of the silicon content in a classical manner by the elementary analysis of SiO_2 has proven to be very useful and reliable.

The desilylation of cellulose silyl ethers can lead to completely desilylated cellulose regenerates (films, particles, and filaments), to partially silylated celluloses with an alternative distribution of silyl groups,[89b,c] or to regioselectively substituted cellulose derivatives by using the protecting group technique.[90] Typical examples are the syntheses of 3- and 2,3-alkyl ethers of cellulose (Scheme 7 and 8).



Scheme 8. Synthesis of 2,3-di-*O*-alkylcelluloses by the protecting group techniques.

The structure of these regioselectively functionalized celluloses can be determined by ^{13}C NMR spectroscopy (Figure 11), 2D ^{1}H–^{1}H and ^{1}H–^{13}C techniques (Figure 12) and COSY-DQF spectra (Figure 13). ^{1}H NMR spectroscopy requires the acetylation of the free OH groups.

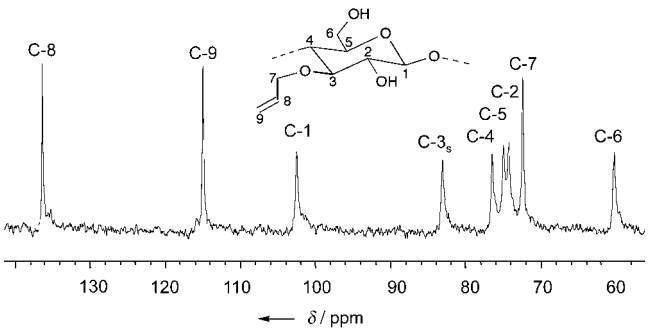


Figure 11. ^{13}C NMR spectrum of 3-*O*-allyl cellulose in [D_6]DMSO at 60 °C.[88a]

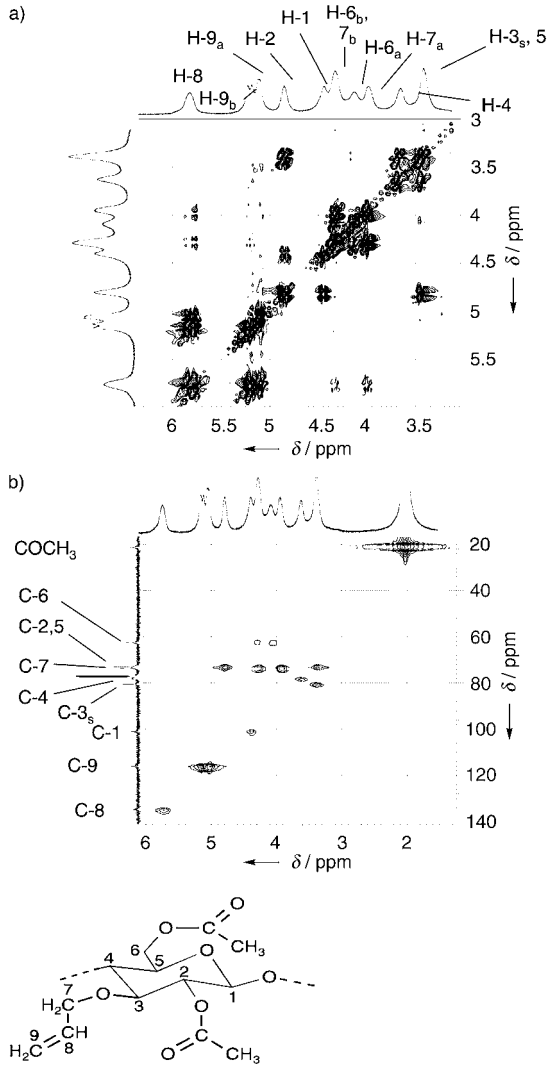


Figure 12. a) ^{1}H–^{1}H NMR spectrum and b) ^{1}H–^{13}C-HMQC measurement of 3-*O*-allyl-2,6-di-*O*-acetylcellulose in $CDCl_3$ at 40 °C.[88a]

Regular selectively functionalized celluloses are important for gaining new insight into the solubility and solution structure of cellulose derivatives. The use of aliphatic O3 cellulose ethers with various alkyl group lengths, it was demonstrated that short alkyl residues (e.g. pentyl) at the stiff cellulose backbone leads to insolubility, whereas long alkyl chains (e.g. dodecyl) result in molecularly soluble products. Together with other facts, these results indicate that entropic effects affect solubility to a much greater extent than enthalpic factors that have been considered in the interpretation of the solvation effects up to this point in time.[39,40,76]

3.2.4. *Cellulose Sulfonates*

The synthesis of organosulfonic acid esters (sulfonates) by simple esterification of the OH groups of cellulose with the corresponding sulfonic acid chlorides or anhydrides is an effective way to attach (in contrast to all cellulose derivatives important up to now) nucleofuge groups to cellulose. The cellulose sulfonates therefore open a wide range of substituted products, which are not available through the conventional methods of "O chemistry" of cellulose (that is, attack of the O atom donor of the OH groups to electrophiles). Moreover, they also have interesting polymeric and material properties, creating new fields of application.[92]

The most frequently synthesized and used cellulose sulfonates are the *p*-toluenesulfonates (tosylates) followed by the methanesulfonates (mesylates), *p*-bromobenzenesulfonates (brosylates), and trifluoromethanesulfonates (triflates). The current knowledge of the synthesis, properties, and subsequent reactions of the cellulose sulfonates is subject of a review.[93]

The synthesis of cellulose sulfonates (Scheme 9) has been previously carried out in suspension (heterogeneous). The homogeneous esterification is successful in solutions of cellulose in DMA/LiCl. In this case, the preparation of cellulose tosylate can be optimized to an extent that permits control of the DS value and the formation of polymers that are free of by-products. At temperatures of +7 °C, for example, cellulose tosylate with a maximum DS value of 2.3 can be synthesized with tosyl chloride in the presence of triethylamine, which can also be controlled by the molar ratio of tosyl chloride/AGU of the cellulose. Scheme 10 demonstrates examples of important downstream reactions of cellulose tosylate.

3.2.5. *Aminocelluloses*

The term aminocellulose refers to aminodeoxy derivatives that bear the nitrogen function directly on the cellulose skeleton, in contrast to the well-known amino acid esters and amino ethers of cellulose.[21a] Corresponding halogen derivatives and sulfonates are typical starting materials for the synthesis of aminodeoxycelluloses.

Cellulose derivatives with amino anchor groups for the immobilization of enzymes and other proteins were obtained through a specific structural design based on cellulose tosylates. In a typical example, cellulose tosylate (DS = 2.3) reacts with 1,4-phenylenediamine (PDA) in DMSO at 100 °C in the presence of TEA[94] (Scheme 11).

To ensure the S_N2 alkylation of only one of the PDA amino groups in homogeneous solution, and to obtain colorless products, a molar ratio of 9:1 PDA/AGU was used. Under these conditions, PDA cellulose is formed with

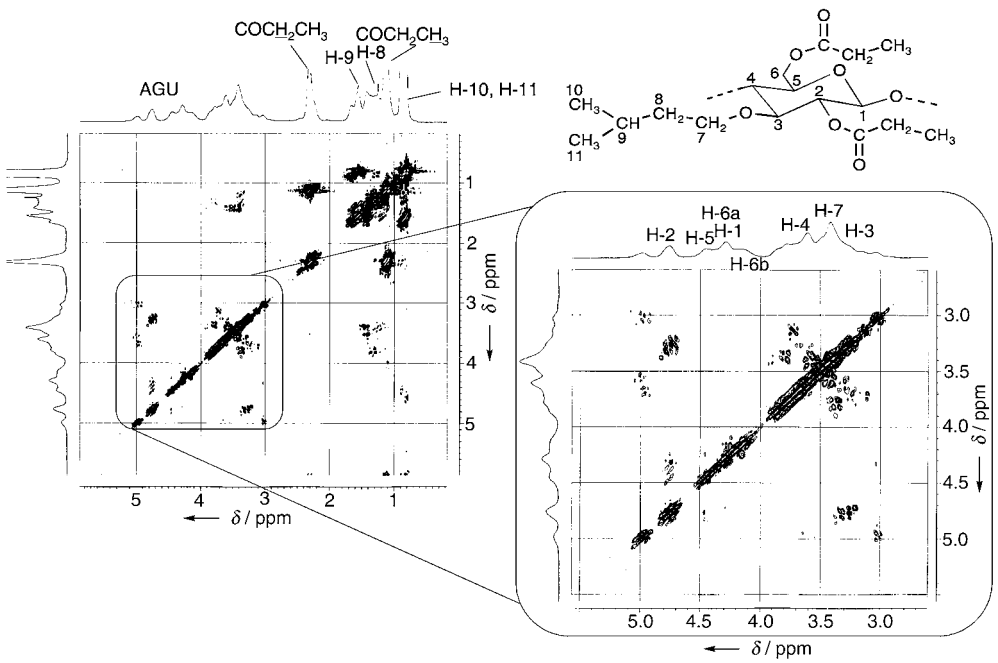
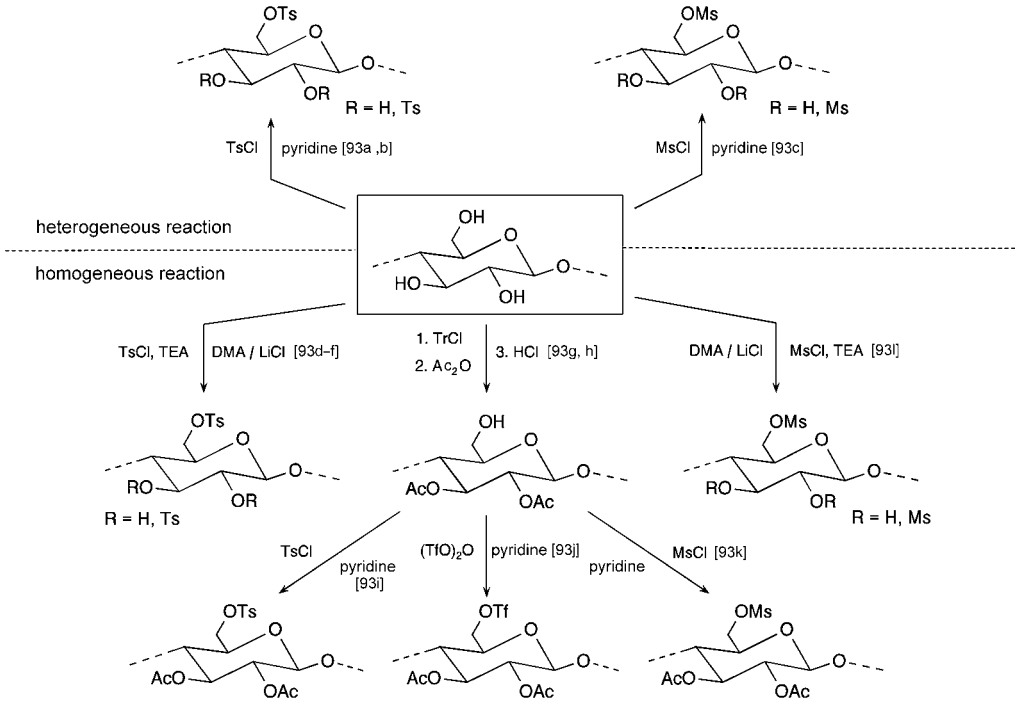


Figure 13. COSY-DQF spectrum of 3-*O*-isopentyl-2,6-di-*O*-propionyl cellulose in $CDCl_3$ at 40 °C.[88a]



Scheme 9. Synthesis routes for cellulose sulfonates.[93]

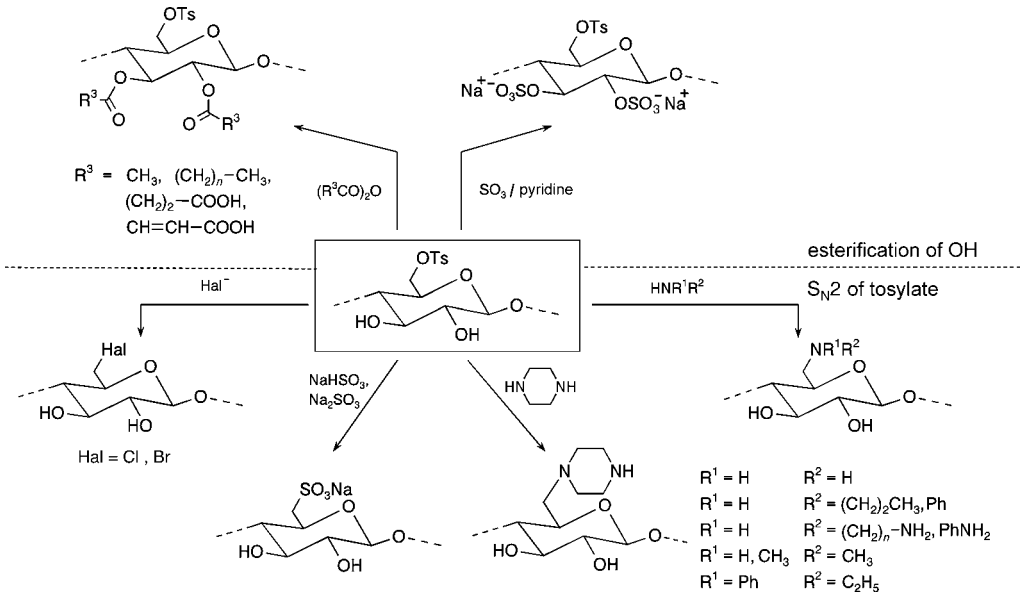
$DS_{PDA} = 0.75$ and $DS_{tosylate} = 1.30$. The ^{13}C NMR spectroscopic data reveal that the transformation occurs at the 6-tosylate group of the starting polymer. The remaining secondary tosylate groups assist in the solubility and film formation of the product.

The PDA celluloses are suitable polymer carriers for the immobilization of enzymes with, for example, glutaraldehyde, diazo coupling, or ascorbic acid, and for the combined fixation of redox-active dyes by oxidative coupling (Figure 14). The potential of PDA cellulose films was investigated by the immobilization of oxidoreductases, such as glucose oxidase, peroxidase, and lactate oxidase. High enzyme activities of 206 mU cm^{-2} were obtained during the immobilization of peroxidase with glutaraldehyde, for example.[95] These properties of PDA celluloses have triggered broad investigations on the application of such aminocelluloses as polymer supports in fiber-optical biosensors.[96]

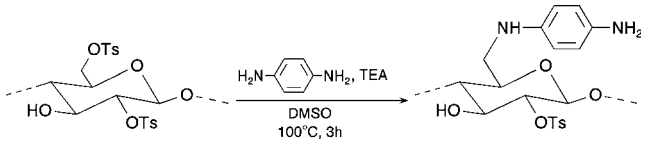
In comparison, aliphatic diamino groups can be introduced into cellulose with diaminoalkanes (H_2N–$(CH_2)_n$–NH_2; $n = 2, 4, 8, 12$) (Scheme 12),[97] by using the S_N2 reaction of cellulose tosylate derivatives (2,3-benzoate, 2,3-carbanilate, and 2,3-methyl ether). Aminocellulose carbanilates produced from 1,2-diaminoethane and 1,4-diaminobutane with $DS_{amin} < 0.4$ are soluble in DMA and DMSO, for example, and the corresponding 2,3-methoxy derivatives are soluble in water, ethanol, and DMSO. Figure 15 shows a typical ^{13}C NMR spectrum of 6-(4-aminobutyl)-6-deoxy-2,3-di-*O*-methyl aminocellulose in D_2O in part b) compared with the spectrum of the starting tosylate in part a).

The films formed from these solutions are suitable for the immobilization of enzymes. In this manner, glucose oxidase was immobilized onto an aminocellulose carbanilate ($DS_{aminobutyl} = 0.49$, $DS_{carbanilate} = 0.58$, $DS_{tosylate} = 0.08$) with an activity of 205 mU cm^{-2} by using benzoquinone as the immobilizing reagent.[97] Aminocelluloses of araliphatic diamines have also been used as enzyme supports.[98]

The synthesis of aminocelluloses based on aliphatic monoamines has been known for a long time, as the following examples illustrate. After the initial investigations between 1978 and 1980,[99a,b] the reaction of cellulose tosylates with monoamines was investigated systematically.[99c–e] Open questions were primarily with regard to the inhibition of crosslinking by multiple reactions of the amine, the extent of aminolysis reactions of the toluene sulfonic acid ester under



Scheme 10. Subsequent reactions of cellulose tosylate.[93]



Scheme 11. Synthesis of PDA-cellulose by reaction of cellulose tosylate with 1,4-phenylenediamine (PDA).

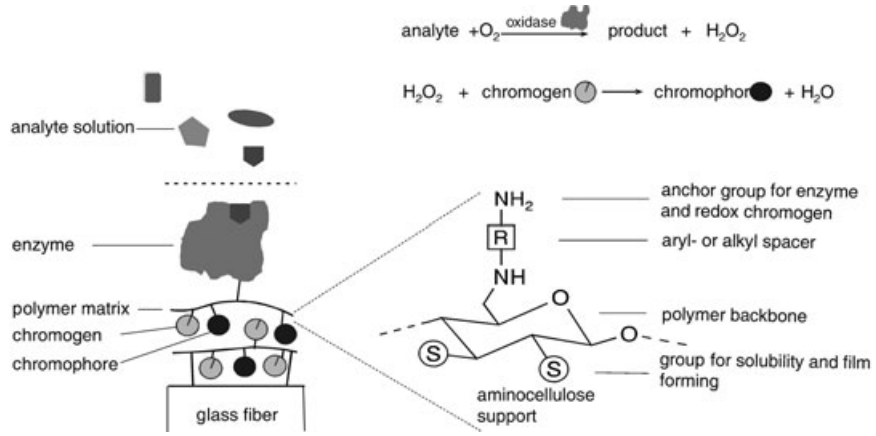
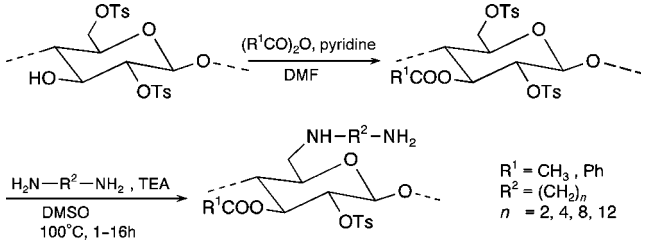


Figure 14. Scheme of an enzyme sensor and structural elements of the aminocellulose support.



Scheme 12. Aminocelluloses synthesized from aliphatic diamines and cellulose tosylate.

the regeneration of OH groups, as well as the selective conversion of primary and secondary tosylate groups. Tosyl cellulose with DS values of 0.1 to 1.1 synthesized under homogeneous reaction conditions reacts with methylamine to form the corresponding methylaminocellulose with comparable degrees of substitution. These cellulose derivatives are to be used as adsorbents for the extracorporeal purification of blood.[99f] Long-chain aliphatic amines can be introduced by the same methods (Scheme 13).[100]

3.3. Supramolecular Architectures

The past 10 years of cellulose research have also been characterized by expanding activity in the design of the supramolecular structure of cellulose derivatives. As a molecular basis in this respect, regioselectively functionalized celluloses have become very important. Preparative and application-oriented work has led to the formation of colloidal superstructures through selective topochemical reactions on crystallites formed by acid-catalyzed hydrolytically degraded cellulose,[101] for example, and to the formation of ultrathin layers of phosphorylated cellulose derivatives on metal surfaces.[102] The following examples are given to illustrate other routes to the formation of supramolecular cellulose architectures and their properties.

3.3.1. Hair–Rod Nanocomposites

Ultrathin mono- and multilayer systems of high order can be constructed with the Langmuir–Blodgett technique from isopentyl cellulose (DS = 2.9), [5-(9-anthrylmethoxy)pentyl]-isopentyl cellulose ($DS_{isopentyl} = 2.8$, $DS_{anthryl} = 0.1$), fumarate-modified isopentyl cellulose, and trimethylsilyl celluloses (DS > 2.5) (Figure 16).[103]

The architecture of these layers is best described by the embedding of molecular rods—in this case, the cellulose polymer backbone—into the matrix of the side-group segments (ether substituents; hair–rod polymers). By subsequent reactions (photo-cross-linking and cycloaddition) or the

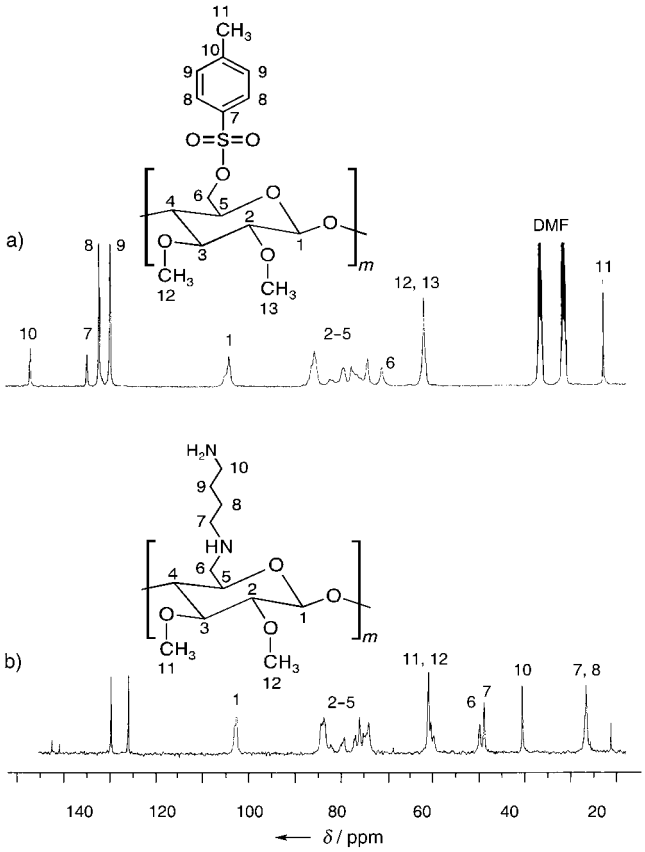
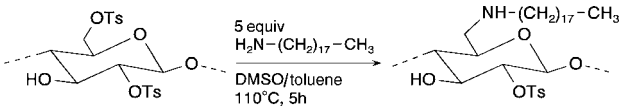


Figure 15. ^{13}C NMR spectra of a) 2,3-di-*O*-methyl-6-*O*-tosyl cellulose in [D_7]DMF and b) 6-(4-aminobutyl)-6-deoxy-2,3-di-*O*-methyl aminocellulose in D_2O.[97]



Scheme 13. Synthesis of 6-(*N*-octadecylamino)-6-deoxycellulose tosylate.

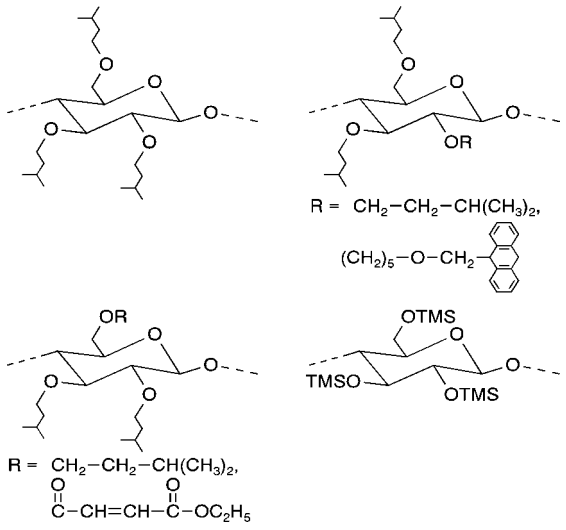


Figure 16. Typical hair–rod cellulose ethers for the construction of nanostructured layers.

regeneration of cellulose through acidic hydrolysis of the TMS-cellulose layers, 3D networks and ultrathin cellulose layers are formed.[104] The latter are important as insoluble and stable hydrophilic films for the adsorption of dyes as well as of synthetic and biogenic polymers. By subsequent introduction of succinate groups into the cellulose films, this behavior can be further amplified.[105] Therefore, ultrathin cellulose layers are very good substrates for diagnostic and analytical purposes. Corresponding 2D cellulose architectures are used for the design of structured ultrathin peptide layers and their use in neurophysiologic growth studies.[106]

3.3.2. NTA Cellulose Films for Protein Fixation

During the course of investigations on the interaction of cellulose and cellulose derivatives with proteins, it was possible to covalently bind nitrilotriacetic acid (NTA) groups onto cellulose.[107a] NTA-cellulose forms thin films on glass substrates from solution in DMSO, which enables a stoichiometric binding of nickel to the NTA substituents upon incubation with an aqueous solution of $NiSO_4$. Treatment of these films with solutions of histidine and fluorescently labeled model proteins, followed by a thorough rinsing to wash away unbound protein yields model protein that is specifically bound to the Ni-NTA groups of cellulose, as substantiated by inverse microscopy. Proteins can then be eluted from the surface by treatment with an imidazole solution (1M).

Figure 17 illustrates the principle assembly of the cellulose–protein complex, containing two histidine units bound at the NTA-modified cellulose film through a Ni^{2+} ion. The

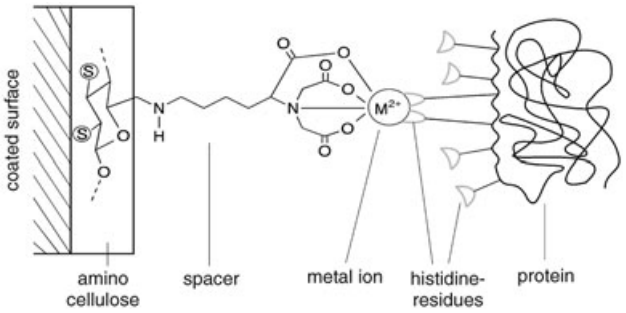
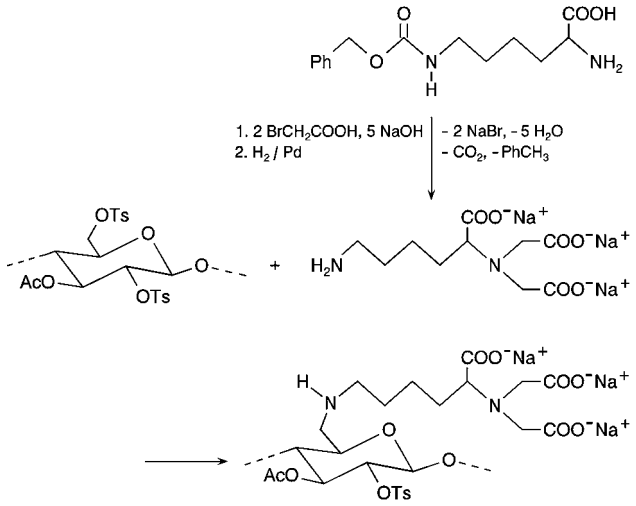


Figure 17. Schematic representation of the immobilization of histidine and fluorescently labeled proteins onto nitrilotriacetic acid (NTA)-modified aminocellulose films by metal complexes (M = Ni, S = control element for solubility and film formation).

synthesis of the cellulose support involved dissolution of cellulose (DP = 800) in DMA/LiCl and tosylation with tosyl chloride in the presence of triethylamine (DS: 1.2–2.0). To introduce the NTA groups, a corresponding H_2N-terminal derivative was prepared. Starting with N_ε-benzyloxycarbonyl-L-lysine, the N_α position was dicarboxymethylated, the protecting group was removed from the N_ε position and persilylated with trimethylchlorosilane in toluol in the presence of triethylamine (for the separation of by-products and improvement of the following S_N2 reaction). In reaction

with the cellulose tosylate in a DMSO/toluene mixture, the nitrilotriacetic acid derivative was synthesized in 24 h at 90 °C (Scheme 14). The His_6 (6 histidine units) and fluorescently labeled model protein were synthesized according to published methods.[107b]



Scheme 14. Synthesis of nitrilotriacetic acid (NTA)-modified aminocellulose.

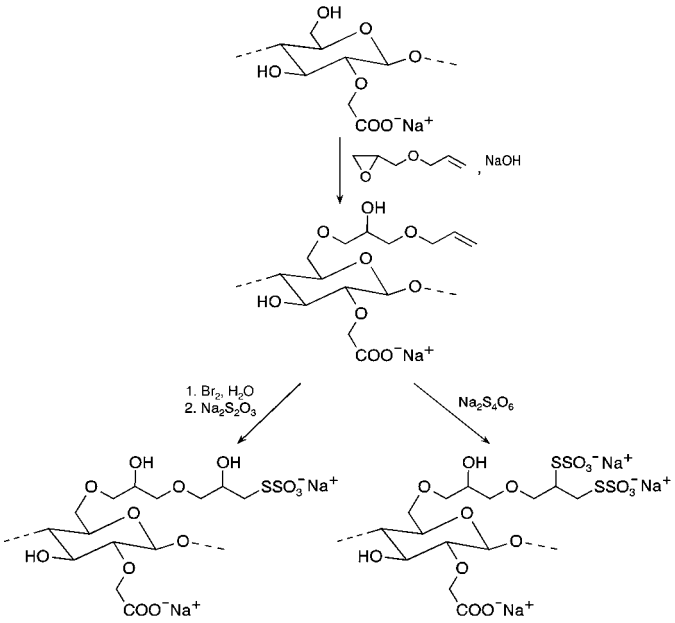
3.3.3. Monolayers of Reactive Cellulose Derivatives

By addition of tetrathionate to 6-*O*-(3-allyloxy-2-hydroxy)-propylcellulose, water-soluble thiosulfates of cellulose can be synthesized to form dense monolayers with a thickness of 4 ± 1 nm on gold surfaces by chemisorption.[108] These layers have been characterized by ellipsometry, AFM, FTIR- and X-ray photoelectron spectroscopy, as well as contact-angle measurements. These investigations have revealed that the thiosulfate groups are homolytically cleaved, and stable gold thiolate anchor groups are formed via thioradical intermediates. The interaction of these cellulose derivatives immobilized on gold surfaces with proteins was investigated. Cellulose thiosulfates of water-soluble carboxymethyl celluloses were included in this work (Scheme 15).

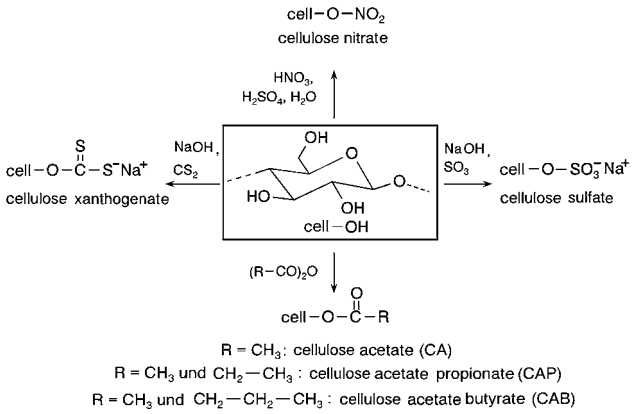
In summary, it was shown that self-assembled monolayers (SAMs) of cellulose derivatives with reactive groups can be synthesized rapidly and with uniform quality. Biomolecules can be linked to these SAMs directly, with controlled density, and with only a small amount of nonspecific interactions. Such SAMs are therefore a suitable platform for the study of molecular recognition on surfaces and for the development of biosensors.

4. Innovative Commercial Esters and Ethers of Cellulose

Cellulose esters of inorganic and organic acids (Scheme 16) as well as cellulose ethers (Scheme 17) were pioneer compounds of cellulose chemistry, and remain the most important technical derivatives of cellulose.[4,21a,d,109] Present developments are therefore aimed at a more detailed understanding of the structure–property relationships, an improved adaptation of these cellulose products to specific and new applications, and to the decreased use of chemicals from an economical and ecological perspective. Continuous investments into the improvement of technical syntheses (pilot and production plants), into sophisticated analysis, and into improved testing methods determine the course of these developments.



Scheme 15. Synthesis of thiosulfates of carboxymethyl cellulose (CMC).

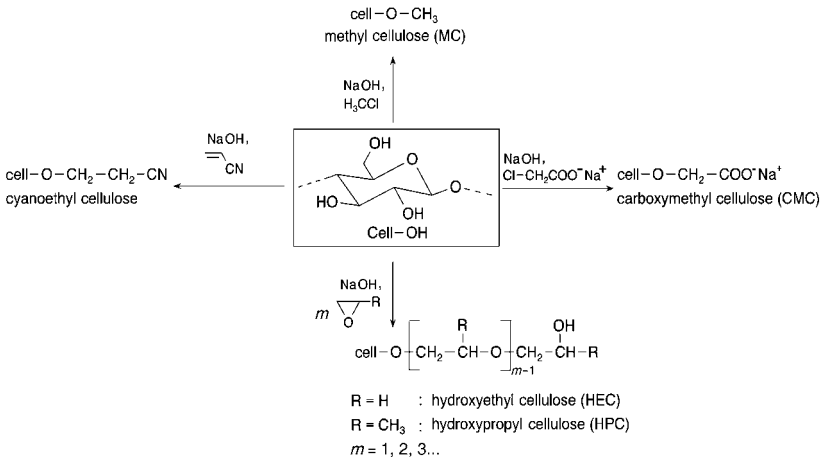


Scheme 16. Typical technical cellulose esters.

4.1. Progress in the Development and Application of Cellulose Esters[110a]

4.1.1. Coatings and Controlled-Release Systems

Materials such as metal, plastic, wood, paper, and leather are coated with polymers primarily for protection and for the improvement of their properties. For this purpose, cellulose



Scheme 17. Examples of commercial cellulose ethers.

acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are the most important classical and solvent-based cellulose esters of the coating industry.

To decrease the amount of organic solvents used in coating systems, there has been an increased development over the past few years of high solid-content coatings, water-based coatings, powder coatings, and radiation-curable polymers as key elements in new technologies. These technologies now meet the requirements of commercial products as well. In view of the EU directive on volatile organic compounds (VOC), solvent-based lacquers are under special scrutiny. In the case of nitrocellulose (NC) lacquers, the aim is to retain these solvent-containing lacquers as powerful alternatives within the provisions of the EU directive through the establishment of a solvent management system.[111a]

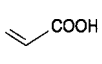
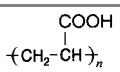
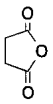
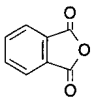
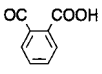
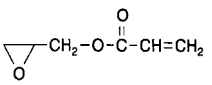
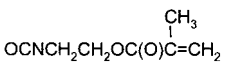
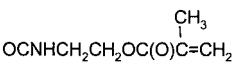
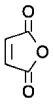
Various concepts were pursued in the development of water-based cellulose ester coatings. Notable examples include the use of conventional as well as high hydroxy group-containing esters in water, the introduction of carboxy groups by radical-initiated graft copolymerization,[112] acylation with dicarboxylic acid anhydrides, and the esterification of carboxymethyl cellulose (Table 3). As the complex structures of these commercial products cannot be characterized completely in many cases, the functional groups are listed without information about their distributions along the polymer. The DS values of the various residues are used for product descriptions. A cellulose acetate butyrate succinate is thus characterized with $DS_{acetate} = 0.09$, $DS_{butyrate} = 1.94$, $DS_{OH} = 0.58$ and $DS_{succinate} = 0.38$. Radiation-curable coatings are synthesized from common cellulose esters by introduction of polymerizable and cross-linkable functionalities (Table 3).

In the field of controlled-release systems, cellulose ester is in an excellent position as a result of its established process and application safety, its readiness toward chemical modifications, and its good handling properties.[110a] New systems were therefore developed on this basis as enteric coatings, hydrophobic matrices, and semipermeable membranes for applications in pharmacy, agriculture, and cosmetics.

4.1.2. *Composites, Films, and Membranes*

Since the commercial production of celluloid, the classical application of cellulose esters has been as thermoplastic materials, and is currently under intense advancement for the creation of high-performance materials that are based on renewable resources.[110a] Topics include the production of

Table 3: Examples of water-based and radiation-curable cellulose ester coatings.

Substrate	Reagent	Product, R in cell-OR			
cellulose acetate propionate (CAP)		H	H_3CCO	H_3CCH_2CO	
cellulose acetate butyrate (CAB)		H	H_3CCO	$H_3CCH_2CH_2CO$	$OCCH_2CH_2COOH$
cellulose acetate (CA)		H	H_3CCO		
carboxymethyl cellulose (CMC)	$(H_3CCO)_2O$, $(CH_3CH_2CH_2CO)_2O$	H	H_3CCO	$H_3CCH_2CH_2CO$	$H_2CCOO^-Na^+$
cellulose butyrate succinate (CB-SU)		H	$H_3CCH_2CH_2CO$	$OCCH_2CH_2C(O)OCH_2CH(OH)CH_2OC(O)CH{=}CH_2$	
cellulose acetate propionate (CAP)		H	H_3CCO	H_3CCH_2CO	
cellulose acetate propionate (CAP)		H	H_3CCO	H_3CCH_2CO	$OCCH{=}CHCOOH$

long-chain cellulose esters and the development of blends with other polymers. Cellulose esters are widely used in composites and laminates as binder, filler, and laminate layers. In combination with natural fibers, they can be used to some extent as composites from sustainable raw materials with good biodegradability.

Cellulose ester films have been used in large quantities as optical media by virtue of their very good mechanical and optical properties and ease of accessibility.[110a] Although other products with a favorable balance of performance and cost have partially replaced cellulose esters in this field, cellulose acetates in particular continue to be an excellent material for photographic films owing to their excellent properties. The development of LCDs were a result of innovations in this field.

An additional domain of cellulose esters is their use as membranes and other separation media.[110a] Cellulose nitrate and cellulose acetate were the first materials to be fabricated into useful membranes. Today, cellulose esters are used in all techniques of separation. Their applications concern water supply, food and beverage processing, as well as applications in medicine and in bioscience research. They cover the entire filtration spectrum from particle-, micro- and ultrafiltration up to nano- and hyperfiltration (reverse osmosis). Superabsorbers are also a form of sorption media in the broadest sense, characterized by their high swelling and water retention capacities and insolubility (through cross-linking).[110b]

4.2. Developments in the Field of Cellulose Ethers[111]

The synthesis of cellulose ethers is an important aspect of commercial cellulose derivatization. The production of methylcellulose (MC) was described for the first time in 1905, followed by other nonionic alkyl ethers of cellulose in 1912, and of carboxymethyl cellulose (CMC) and hydroxyethyl cellulose (HEC) after 1920. Shortly thereafter, the industrial production of these most important cellulose ethers was started.

They have the outstanding properties good solubility and high chemical stability, and are toxicologically innocuous. The especially important matter of water solubility can be controlled to a certain extent by the constitution and combination of the ether groups, the degree of substitution, and the distribution of substituents. Cellulose ethers are processed in a dissolved or highly swollen state. They are the dominant polymers in numerous industrial applications and in convenience goods for matters in which consistency in the quality of aqueous media and water-containing systems is required.

Etherification of cellulose on the industrial scale is performed in aqueous alkaline media in which cellulose is present in a highly swollen state. The dominant approach for this process is O-alkylation with alkyl halides according to Williamson; other approaches include epoxide addition and Michael addition of reagents with activated double bonds. Scheme 17 highlights some typical examples. In contrast to methyl cellulose, carboxymethyl cellulose, and hydroxyalkyl cellulose, the commercial importance of cyanoethyl cellulose remains limited to a few special applications: as an additive in the paper and textile industry, and in the formation of membranes.

4.2.1. Cellulose Ethers for Drilling Technologies and Building Materials[111a]

The use of cellulose ethers as additives to drilling fluids for consistency control is of considerable importance to the drilling of wells for mineral oil, natural gas, and water. Drilling fluids supplemented with cellulose ethers keep rock dust in suspension, cool the drilling head, and stabilize the bore.

Another significant core business in which cellulose ethers are used is the building materials market, which involves a multitude of tailor-made versions of methylhydroxyethyl (MHEC) and methylhydroxypropyl celluloses (MHPC) that control the rheology and processing of plaster systems. As additives that are admixed to the mortar in the range of 0.02–0.70% by mass, they make up a market share of about 90%. Cellulose ether permits the silo transport and machine processing of dry mortar as well as the effective handling of gypsum plasters, knifing fillers, tile adhesives, and joint fillers. They determine the water requirement, the water-retaining power, and the development of consistency in plaster systems.

4.2.2. Pharmaceuticals, Cosmetics, and the Food Market[111a]

In addition to carboxymethyl cellulose, high-purity hydroxypropylmethyl cellulose (HPMC) was synthesized and introduced onto the market for this demanding area of application. HPMC binds water, has good stability in freeze/thaw cycles, mediates the viscosity of liquids, and is odorless and tasteless. In products of this kind, purity and permanent quality play a critical role, as their production must adhere to GMP standards.

Carboxymethyl cellulose is used as a stabilizer in beverages. It has improved the consistency, texture and storage quality of milk products, and ensures that the solids added are kept in suspension. It is also used to stabilize whey-based beverages.

5. Regenerated Cellulose: Environmentally Friendly Technologies on the Advance

5.1. Present Situation

The most important segment by volume in the chemical–technical processing of cellulose is represented by products made of regenerated cellulose (man-made cellulosics), which primarily include regenerated fibers, but also films, membranes, and sponges. At an annual world production of about 2.2 million tons (2002), the viscose method,[113] well over 100 years old, still dominates production methods in which pulp with CS_2 is converted into cellulose xanthogenate as a metastable intermediate. The xanthogenate is soluble in aqueous sodium hydroxide, and can be formed as a viscose solution in a wet process. After precipitation of the shaped

product, the substituent is cleaved off, and high-purity cellulose is regenerated. Viscose fibers (Rayon) have excellent properties for a broad product range, from wet-strength cottonlike textile fibers (Modal fibers) to technical fibers in the form of cord (Rayon) for use in high-performance tires. Viscose technology is still in use today for film (cellophane) production, which is particularly important for food casing products.

The viscose route, however, is technologically complex (see processing scheme in Figure 18), requires highest-quality dissolving pulp, and leads to problematic environmental loads from the use of CS_2, heavy metal compounds (in the precipitation process), and resultant by-products. To decrease emissions and to meet the environmental standards, different methods can be applied.

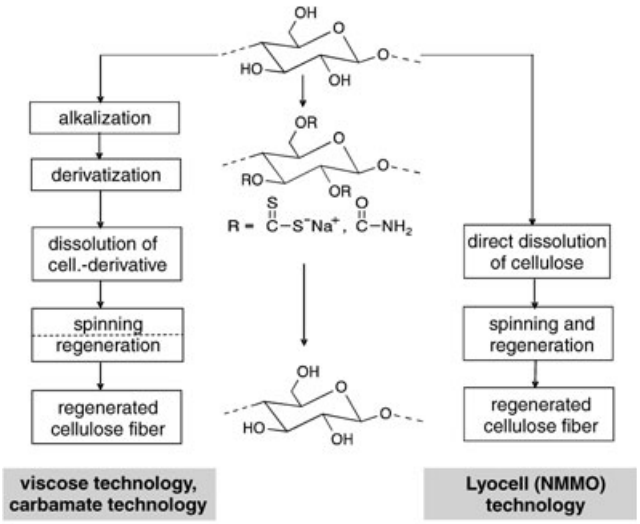


Figure 18. Process principles in regenerated cellulose technologies: left, derivate methods; right, direct methods.

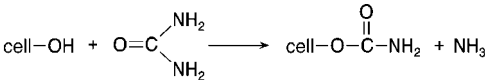
The first (and rather unspectacular) variant to this end is to improve the existing viscose production by optimizing the consumption of chemicals, with particular regard to minimizing the use of CS_2.[114] This variant also includes the refitting of exhaust gas and waste water cleaning equipment, which has been implemented continuously in the viscose industries in western Europe, where today the emissions either meet or lie below the threshold values in place.[115] It is advantageous that existing facilities can still be used for the production of highly sophisticated types of fiber that have been introduced to the market. The increased cost of viscose technology incurred by the purification of exhaust gas and waste water is a disadvantage that must be weighed against the product advantages, in particular, in case of the installation of new production capacities.

Alternate processing technologies should be simpler than the viscose process, and environmentally hazardous materials and side products in general must be avoided (Figure 18). An alternate derivatization method that has been developed to commercial maturity without the use of sulfur-containing compounds, but that retains the viscose spinning technology, is the CarbaCell process,[116] in which a new reaction variant employs urea to convert cellulose into cellulose carbamate, which can be subsequently processed on existing viscose spinning systems.

The direct dissolution and shaping of cellulose without derivatization is possible with copper ammonia technology,[117] which originated as a very early spinning route of cellulose (Cupro silk, Cuprophane). It is rarely used anymore, as it poses environmental hazards. Among others, it has been suggested that the dissolution and shaping of cellulose could be carried out by DMA/LiCl or zinc chloride and in aqueous solution with NaOH (CELSOL process),[118] or phosphoric acid as a direct solvent to spin high-strength cellulose filaments.[119] However, the most advanced development took place beginning in the 1980s with a process based on the NMMO monohydrate solvent system, which was taken to commercial maturity and which made the current industrial breakthrough known as the Lyocell process.[120] This process offers the potential for a revolutionary development in cellulose processing, as it is comparatively simple (Figure 18) and is practically free from emissions as almost all the solvent involved is recovered.

5.2. The CarbaCell Process

The starting point of this development is founded in previous studies[121] of the transformation of cellulose with urea (after urea breakdown) to form cellulose carbamate (Scheme 18), which is soluble and shapeable in sodium



Scheme 18. Formation of cellulose carbamate by transformation of cellulose with urea.

hydroxide solution. The patented CarbaCell technology is based on a synthesis of the cellulose carbamate in xylene as a transfer medium.[116] The technical sequence is similar to the viscose method (Figure 18). The starting cellulose material is initially alkalized and pre-ripened (partial chain degradation); in the synthesis stage it is subsequently derivatized and dissolved in sodium hydroxide solution. The spinning solution is filtered and deaerated prior to wet spinning in an acidic precipitation bath, followed by a salt-containing alkaline decomposition bath for the hydrolysis of the carbamate groups at elevated temperature. The structural changes of the cellulose during processing are clearly illustrated in Figure 19 with ^{13}C-CP/MAS solid-state NMR spectra.

Depending on the derivatization procedure, the transformation of the alkalized cellulose with urea leads to structures that are similar to the cellulose modifications II and IV, and that have either blocklike or statistic distributions of the substituents along the cellulose chain.[38e] Apart from

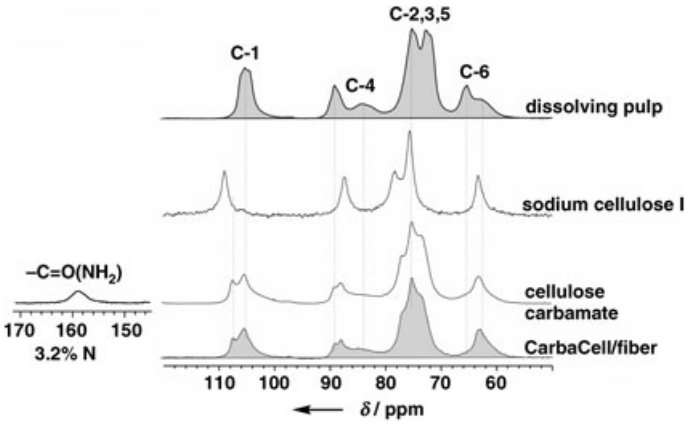


Figure 19. Structural changes of cellulose in the carbamate process as observed with ^{13}C-CP/MAS NMR spectroscopy.[122]

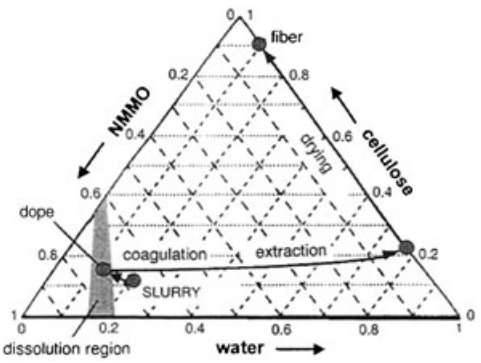


Figure 20. Phase diagram: cellulose/NMMO/water.[124a]

the use of the innocuous urea as a substitute for the toxic CS_2, the advantage of the carbamate process is that the cellulose carbamate is relatively stable at room temperature, which permits storage times of more than a year without loss of quality. Thus, the synthesis of cellulose carbamate can be carried out on a large scale in a central location, from which products can then be shipped to decentralized facilities for processing (such as spinning factories). Industrial tests have shown that cellulose carbamate can be processed without any problems on viscose spinning machines. Despite the advantages of the carbamate process, which could possibly be used for other products such as high-absorbent nonwovens, hollow fibers, sponges, and carpet cleaners, industrial cellulose carbamate production sites have not yet been established.

5.3. The NMMO (Lyocell) Process

Owing to its strong N–O dipole, *N*-methylmorpholine-*N*-oxide (NMMO) in combination with water can dissolve cellulose without prior activation or derivatization. With a water content of 13.3% by mass and a decreased melting point of about 74°C, NMMO monohydrate is significant as a solvent, from a technical standpoint, compared with pure NMMO. The breakthrough of this system for technical applications came with the introduction of stabilizers such as propylgallate, which suppresses the radical separation of the NMMO and scission of the cellulose chain at the required processing temperatures.[123] Solutions with cellulose content of up to 23% can be produced starting with the dispersion of conventional cellulose in NMMO with a high water content (such as 50%). Subsequent concentration of the suspension at higher temperature until the NMMO monohydrate composition is made permits dissolution of the cellulose. In the ternary phase diagram of Figure 20, the path of the cellulose during the solutions production and the technological stages of the NMMO processes (cf. Figure 18) can be followed.

The shaping of the cellulose/NMMO/water solution into fibers takes place at temperatures between 80 and 120°C, at which the semiliquid system (dope), with a cellulose content of 8–23%, is extruded from a nozzle over an air gap with a length of 10–250 mm into an aqueous precipitation bath. There, the cellulose precipitates almost instantaneously. In a closed circle, the industrial recovery of NMMO is 99.6–99.7% from the precipitation bath, with its upgrade and cleaning by an ion-exchange process. In the dry jet/wet-spinning process, any deformation in the region of the nozzle and the following air gap section elicits a significant influence on structure formation (particularly the orientation state) of the thread and its resulting properties. The fundamentals of crystallization and structure formation of the cellulose after precipitation from NMMO solutions were initially analyzed by Chanzy and co-workers,[125] and Dubé and co-workers.[126] A list of the extensive literature concerning the structure formation of cellulose regenerated materials made from NMMO solutions available since the seminal work is given in Ref. [42]

Compared with conventional viscose fibers, today's generation of commercial Lyocell fibers spun from NMMO solution have outstanding properties in certain respects, such as strength in both wet and dry states, modulus of elasticity, sorption behavior, wearing properties, gloss, and touch. However, the distinct wet fibrillation behavior is predominantly disadvantageous, and its suppression still requires additional processing, such as subsequent cross-linking steps (Section 5.5).

The fact that the cellulose/NMMO/water solution can be deformed in the nozzle and the air gap, similar to a melt, opened up the initial possibility to produce cellulose films in a blow-extrusion process[127] (basic sketch in Figure 21). Spun fleeces (melt-blown nonwovens) [128] can also be manufactured analogously to synthetic polymers (polyethylene, polypropylene, and polyethyleneterephthalate) shaped from melt. The blown-film process permits the setting of longitudinal and transverse properties by means of the corresponding orientation states, a feature still not feasible in this manner for cellulose films, on the one hand. On the other hand, the morphology and pore structure of the film can be influenced by the subsequent precipitation process, which is not possible in melt-extruded films from synthetic polymers. This results in versatile application possibilities for the blown films from cellulose, which range from packaging materials and food casings, to dialysis membranes.

Another advantage of the NMMO process is that less expensive cellulose of lower purity (higher hemicellulose

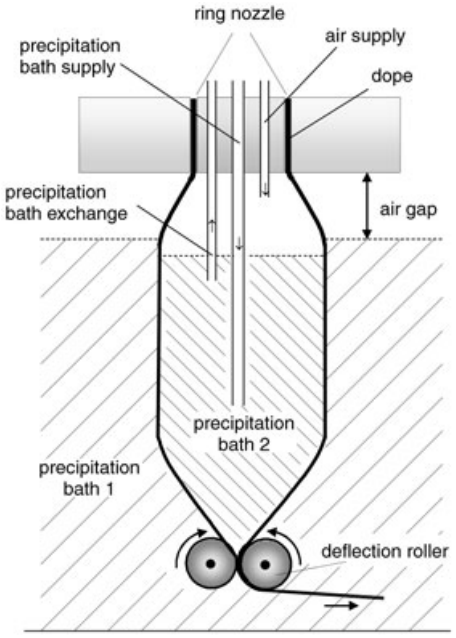


Figure 21. Basic sketch on blow-extrusion of cellulose films made from NMMO solution.

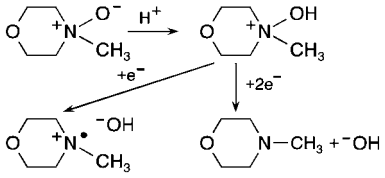
content) can be used; this is a significant benefit for the development and production of melt-blown nonwovens.[128] The pioneering significance of the cellulose/NMMO/water system is also made clear by the fact that apart from classical fibers and films, numerous new products can be produced, thus opening a gigantic field of application for the sustainable polymer raw material cellulose. Developments are currently in progress, including lyophane membranes for water purification,[124b] precursor filaments for carbon fibers,[129] and cellulose-based functional materials[130] such as conductive and piezoelectric fibers, ceramic hollow fibers, pearl cellulose for encapsulation, and highly porous materials for various applications.

Special emphasis must also be placed on the fact that through the industrially applied Lyocell fiber process and the emission-free technical NMMO recovery system developed in this field, a significant drawback to the previous cellulose technologies has been removed. This achievement was acknowledged by awarding the Austrian company Lenzing AG the EU Environmental Award 2000 for the Lyocell process.

5.4. The Chemistry of the NMMO/Cellulose System

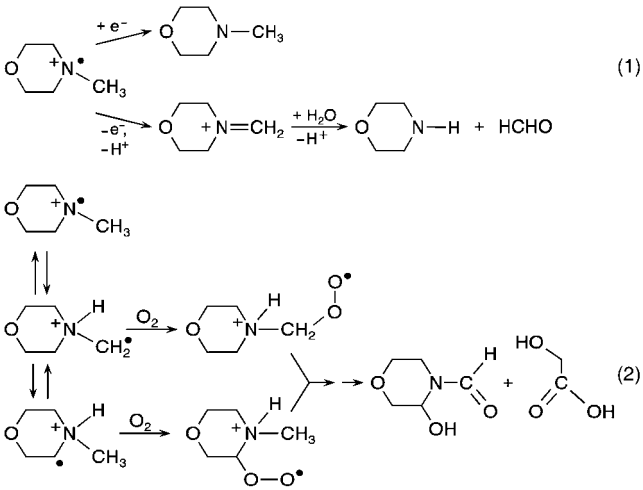
Like all amine-*N*-oxides, NMMO is well-known as an oxidizing agent in organic chemistry. Therefore, its application in an industrial process is not unproblematic. Against this background, systematic and detailed investigations on the chemistry of NMMO were carried out in a series of studies.[131a]

All homolytic reactions of NMMO start with cleavage of the N–O bond with formation of aminium (aminyl) radicals (Scheme 19). In the absence of oxygen, these radicals undergo



Scheme 19. Homolytic and heterolytic bond cleavage of *N*-methylmorpholine-*N*-oxide (NMMO).[131a]

disproportionation or react in redox processes that finally produce *N*-methylmorpholine, morpholine, and formaldehyde (Scheme 20, top). These processes are induced by transition metal ions. In the presence of oxygen, the radicals react with the latter (Scheme 20, top).



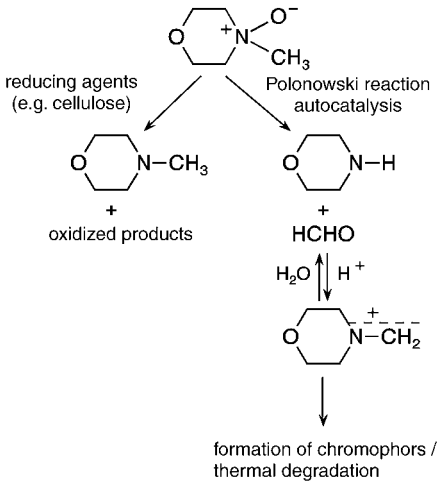
Scheme 20. Reactions in the NMMO/cellulose system starting from the aminyl radicals; products of redox processes in the (1) absence and (2) presence of oxygen.[131a]

The heterolytic reactions in NMMO solution proceed either by reductive deoxygenation of NMMO, which produces *N*-methylmorpholine with concomitant oxidation of reductants such as cellulose, or by the formation of morpholine and formaldehyde by Polonowski-type reactions in intramolecular redox processes (Scheme 21). A third pathway induced by carbenium-iminium ions as an autocatalytic process can cause the quantitative decomposition of NMMO.

The current knowledge of the potential reactions in the cellulose/NMMO/water solvent system is of considerable significance for the safe and economically effective production of cellulose fibers according to the aminoxide process. The strict exclusion of heavy metals such as copper, even at the smallest concentrations, as well as a tightly controlled temperature system are basic safety requirements.

5.5. Structures and Properties of Cellulose Regenerate Fibers and Films

The high stage of development and the vast range of today's viscose products are founded on decades of research



Scheme 21. Reductive deoxygenation and carbenium-iminium ion formation in the NMMO/cellulose system.[131a]

efforts. It results from a largely empirical understanding of the complicated processes of cellulose derivative structure formation from solution which have not always been published, and which are mastered today only by a few specialists in industry and research institutes. The development of new, possibly superior products manufactured through application of the latest environmentally compatible technologies can be realized only through a comparatively thorough understanding of the structure formation process and the connections between manufacturing conditions, structures, and properties. The differences between viscose, carbamate, and Lyocell fibers based on different structure formation conditions are described below. From this, the targets of the structure–property relationships of new products can be derived.

5.5.1. *Cellulose Regenerate Fibers*

Electron micrographs of ultrathin sections of the various regenerate fibers reveal that textile viscose fibers have a lobed cross-section and a skin–core morphology, whereas the round to oval cross-sectional shapes and the homogeneous morphologies of carbamate and Lyocell fibers are distinctly different, and are similar to each other (Figure 22). In the latter case, it is apparent that a fast "hard" precipitation takes place without hydrolysis of the carbamate groups, whereas the precipitation conditions of the viscose process are "softer"; the precipitation, the substituent removal, as well as the transport of the reaction products during regeneration take

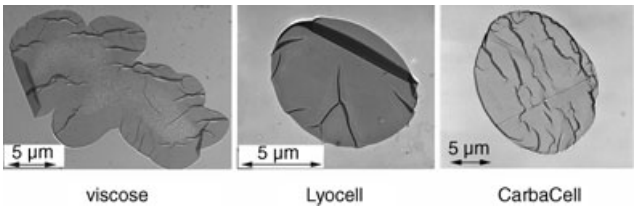


Figure 22. TEM images of cross-sections of various kinds of cellulosic fibers.

Table 4: Degrees of crystallinity (x_c) and crystallite sizes ($D_{(hkl)}$) of regenerated cellulose fibers.

Fiber Type		x_c [%]	$D_{1\bar{1}0}$ [nm]	D_{110} [nm]	D_{004} [nm]
viscose		27–31			
	technical yarn		6.6	3.9	9.7
	textile yarn		5.1	4.5	9.8
Lyocell	filament	35	4.4	3.3	17.5
carbamate	filament	34–43	3.6–4.1	4.1–5.3	10.0–12.4

place as competing processes. Table 4 shows that the degrees of crystallinity (WAXS, Ruland–Vonk method)[132] for carbamate and Lyocell fibers range between 35 and 40 %, above the respective value for viscose fibers of lower crystallinity (≈30 %). A comparison of the crystallite dimensions, also determined by X-ray diffraction and given in Table 4, demonstrates that the Lyocell fiber has narrower and particularly longer crystallites (in the fiber direction).

Distinct differences between the types of fibers are also revealed in their state of orientation, which has significant influence on the mechanical properties. Figure 23 compares the overall orientation (f_t; obtained by birefringence measurements), the orientation of the crystalline ranges (f_c; X-ray

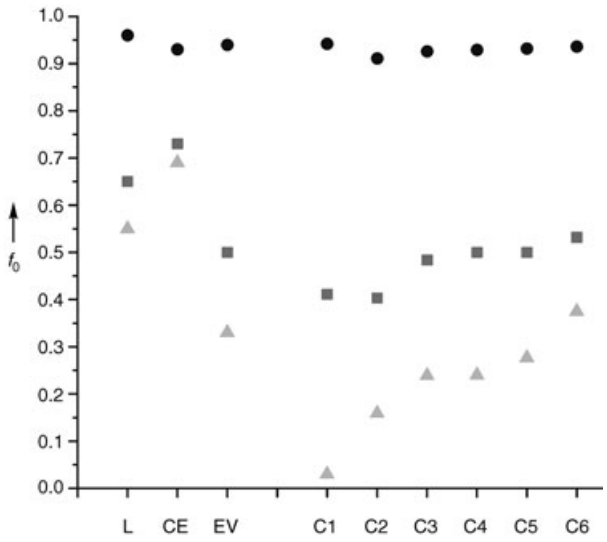


Figure 23. Orientation parameters of different cellulose regenerate fibers:[122] orientation factor, f_o; overall orientation, f_t (■); orientation of crystalline ranges, f_c (●); orientation of noncrystalline chain segments, f_a (▲); fiber types: Lyocell, L; CordEnka, CE; EnkaViskose, EV; Carbamate, C1–C6.

diffraction), as well as the orientation factors calculated for the noncrystalline chain segments (f_a) of commercial fibers and a number of development patterns from the carbamate program.

It is clear that the stiff and fibrillating behavior of the Lyocell fibers is caused by their high orientation in the noncrystalline regions—similar to technical fibers—the lowering of which in combination with a decrease in the degree of crystallinity was, and still is, a central task in the continued development of Lyocell fibers. In the development of

carbamate fibers, however, the problem was to increase the low orientation of the noncrystalline chain segments at the beginning. This problem has been solved in the meantime; today carbamate fibers can be produced with an orientation state and property profile almost identical to those of viscose.

The decrease of crystallinity and orientation of Lyocell fibers is possible by a "softer" precipitation in alcoholic baths. Fibers with a firm, highly oriented core and a soft, non-fibrillating shell can be produced through a two-stage precipitation in alcohol and water (Figure 24).[133]

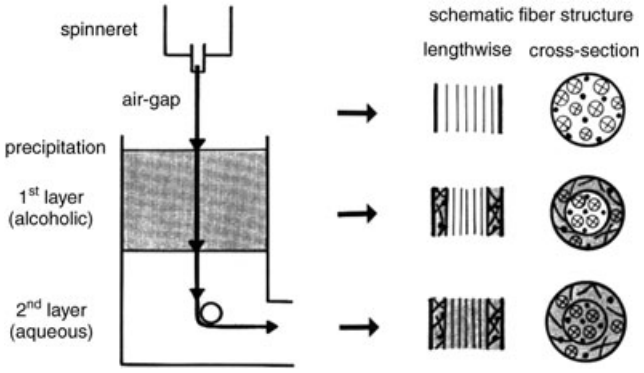


Figure 24. Basic sketch of the double-bath precipitation for Lyocell fibers with a core–shell structure.

This example demonstrates, that knowledge of fiber structures and an understanding of the structure-forming process are important prerequisites for the development of products with the desired properties. A wide range of alternate possibilities for influencing fiber structure and properties, including the downstream cross-linking of molecules in the fiber, can be found in the patent literature. The full potential capacity for such process control, however, has certainly not yet been tapped by the methods currently in use. Therefore, a more thorough understanding of these structure-forming processes is urgently required.

5.5.2. Blown Films Made of Cellulose

As with Lyocell fibers, the precipitation process, which in this case includes inner and outer precipitation baths (see basic sketch, Figure 21), offers considerable possibilities to influence the morphology and pore structure of the product films. Symmetrical (identical precipitation baths inside and outside) and asymmetrical (different precipitation baths inside and outside) film structures can be produced without difficulty (Figure 25). Compared with cellophane and cuprophane films on the market, blown films produced according to the Lyocell process have somewhat lower degrees of crystallinity ($\approx 40\,\%$) and only slightly smaller lateral crystallite dimensions.

An advantage of the blow-extrusion process, which can be transferred to cellulose films as well, is the ability to control the orientation in the machine direction and transverse

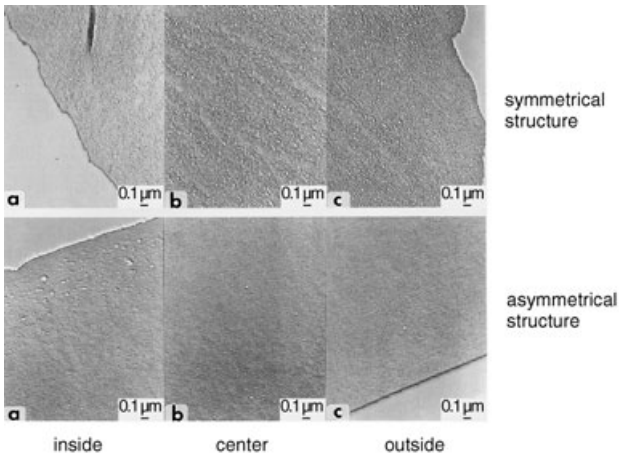


Figure 25. TEM micrographs of symmetrical and asymmetrical structures of blown films.

direction without any problems by means of the draw-down and blow-up ratio. Figure 26 shows the X-ray pole figures in a uniplanar orientation of the $(1\bar{1}0)$ lattice plane, whereby suitably adjusted draw-down and blow-up ratios[127] can be used to produce different orientation states up to almost balanced films (compare longitudinal and transverse strength values of Figure 26).

The orientation distribution of the crystallite longitudinal axis (chain direction) in the film plane can be approximated with the (110) pole figures. Figure 27 shows the corresponding distribution functions of the longitudinal chain axis of differently produced blown films (BF7, 10, and 13) in comparison with commercial cellophane and cuprophane, which substantiates the control possibilities described. It should be emphasized as well that the mechanical properties of the blown films are superior to those of conventional products, and that the separating properties of Lyocell-based films, such as the dialysis and flow rates, are outstanding as a result of their pore structures.[124a]

6. Bacterial Cellulose as a Model Compound and High-Performance Material

6.1. Formation and Structure

The biosynthesis of cellulose takes place not only in plants, but, as already mentioned in Section 1, also in bacteria (such as *Acetobacter*, *Acanthamoeba*, and *Achromobacter* spp.), algae (*Valonia, Chaetamorpha* spp.), and fungi.[134] The formation of cellulose by laboratory bacterial cultures is an interesting and attractive access to pure cellulose for both organic and polymer chemists. By selecting the substrates, cultivation conditions, various additives, and finally the bacterial strain, it is possible to control the molar mass, the molar mass distribution, and the supramolecular structure. Thus it is possible to control important cellulose properties, and also the course of biosynthesis (e.g. kinetics, yield, and other metabolic products).

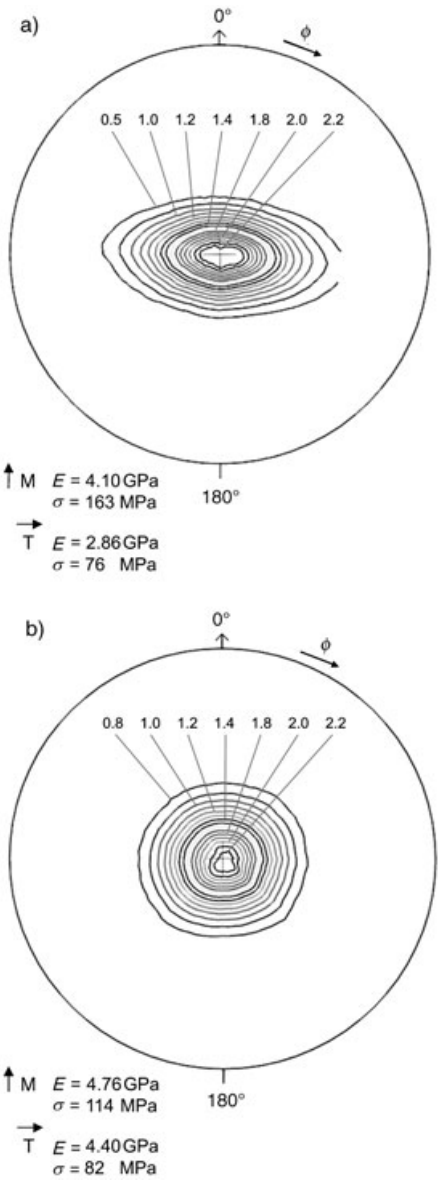


Figure 26. ($1\bar{1}0$) Pole figures and mechanical properties of differently produced cellulose blown films: a) draw-down in machine direction larger than transverse (BF7); b) drawing balanced in longitudinal and transverse direction (BF13).

Amongst the cellulose-forming bacteria, *Acetobacter* strains (reclassified as the genus *Gluconacetobacter*) are especially suitable for the production and investigation of cellulose. These gram-negative and strictly aerobic bacteria form ellipsoidal, straight, or slightly bent rods in the size range of 0.6–0.8 × 1.0–4.0 μm. They are not pathogenic and are commonly found on naturally grown fruits and in fruit products. Strains of the *Acetobacter xylinus* species produce extracellular cellulose that is easily isolated as fiber material. Under static immersed cultivation conditions, a biofilm of varying thickness (fleece) is produced which helps the colonized bacteria to maintain a high oxygen content near the surface, and which serves as a protective barrier against drying, natural enemies, and radiation.

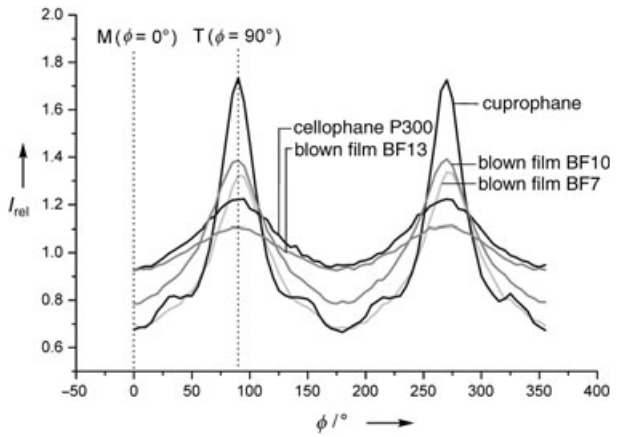


Figure 27. Orientation of the cellulose chains in the film plane (ϕ scan of the (110) pole figure at $\chi = 85°$).

The metabolic products of *A. xylinus* were initially described by A. J. Brown in 1886.[135] He identified a gelatinous mass, formed on the culture solution during the course of vinegar fermentation as cellulose. Thanks to systematic and comprehensive research over the past decades,[17] recent knowledge about the formation and structure of bacterial cellulose is extensive. Moreover, this work is an important part of research investigations of the integration of biotechnological synthesis methods in polysaccharide chemistry and the development of cellulose products with new properties and application potentials.

The synthesis of the bacterial cellulose occurs between the outer and plasma membranes of the cell by a cellulose-synthesizing complex (terminal complex) starting with uridine diphosphate glucose (UDP glucose).[136] This complex is associated with bacterial cell surface pores, which have a diameter of about 3.5 nm. Cellulose synthase catalyzes the addition of UDP glucose to the end of the growing cellulose chain, which exits the cell as an elementary fibril, and then forms a 3D network with other elementary fibrils through formation of microfibrils and ribbons.[136] Crystallization and polymerization of the elementary fibrils are closely linked. One single cell can convert over 100 glucose molecules into cellulose per hour. As the culture medium contains millions of bacteria, the polymer is synthesized practically "before your eyes". The details of the polymerization catalyzed by cellulose synthase have been the subject of controversy.[137] The latest studies seem to indicate that the β-(1→4) linkage starts with the formation of cellobiose as an intermediate at a dual UDP glucose binding site.

A detailed model of the structure (Figure 28) of the bacterial cellulose of *A. xylinus* (strain NCIB 8034) in a never-dried state was determined by synchrotron X-ray diffraction experiments and studies carried out by electron microscopy.[138] Anhydrous units (nanofibrils) with cross-sectional dimensions in the nm range appear hydrated as a whole, and are aggregated to flat microfibrils with a width of 70–150 nm. This model was basically substantiated by means of small-angle X-ray diffraction, and was expanded by the fact

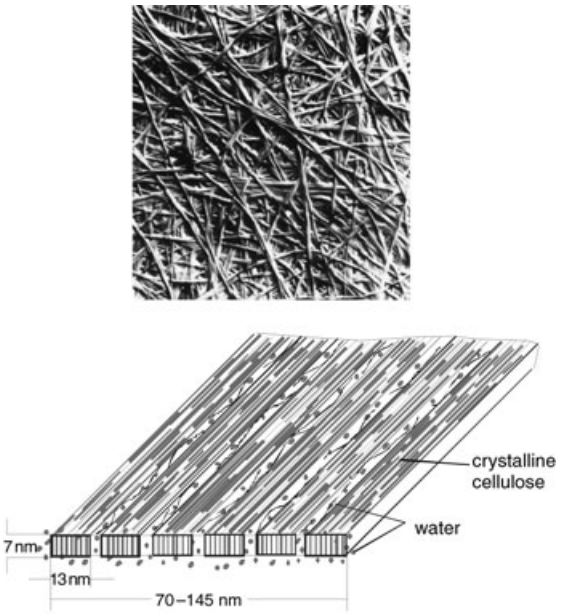


Figure 28. SEM image of dried bacterial cellulose (top) and model of an initially hydrated bacterial cellulose microfibril (bottom).

that a shell of noncrystalline cellulose chains passes around neighboring microfibrils to produce a microfibril band with a width of about 500 nm.[139] After drying, the initially wet and highly swollen cellulose fleece becomes a uniplanar oriented foil with microfibrils partially twisted around the longitudinal axis (Figure 28) which consist of $\approx 80\%$ I_α cellulose.

6.2. Properties and Applications

Although identical to cellulose of plant origin in terms of molecular formula, bacterial cellulose is quite different. The degree of polymerization is very high, with DP values of 2000–8000. Crystallinity is also high, with values of 60–90%. Bacterial cellulose is characterized by its high purity (no association with accompanying substances like hemicelluloses, lignin, or pectin) and by an extremely high water content of 90% or more. Upon complete removal of water by air drying, the bacterial cellulose will only rehydrate to the same low extent as that of plant celluloses after re-exposure to water: about 6%. After gentle freeze-drying, however, it can absorb up to 70% of the original water content by re-swelling.[140a] Through a stepwise exchange of water for other solvents, it is possible to introduce methanol, acetone, or *n*-hexane, for example, at the same volume as water in bacterial cellulose, while maintaining the hollow space and network structure.[140a]

Bacterial cellulose highly swollen with water gives well-resolved ^{13}C NMR spectra without additional pretreatment with conventional techniques (CP/MAS) of solid-state NMR spectroscopy.[138,140a,d,e] Figure 29 shows a typical example. Detailed NMR spectroscopic examinations of bacterial cellulose and of its biosynthetic route were carried out by using ^{13}C-labeled D-glucose.[141a]

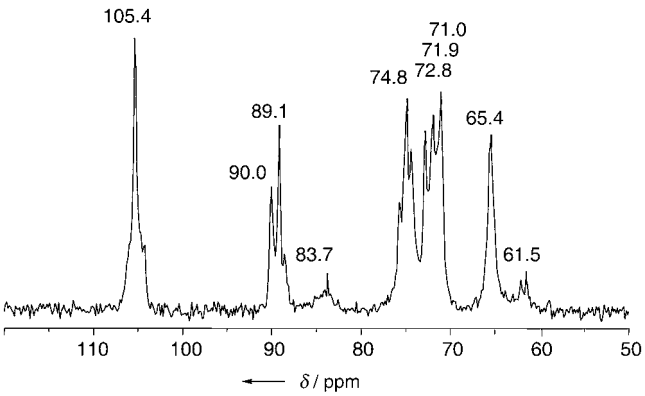


Figure 29. ^{13}C-CP/MAS NMR spectrum of a purified never-dried bacterial cellulose fleece (swelling agent: water).[140a,e]

Because of its crystalline nano- and microfibril structure, bacterial cellulose has excellent mechanical properties[142] (Table 5). It is therefore well-suited as a reinforcing agent for paper and fibers made from glass, carbon, phenol resin, and silicon at small quantities (5%). Owing to the high modulus of elasticity in combination with a large internal loss factor, it is also a superior material for headphone and loudspeaker membranes (Sony Corp.).

Table 5: Mechanical properties of bacterial cellulose and other organic layer materials (from Gilbert[142]).

Material	Young's Modulus [GPa]	Tensile Strength [MPa]	Elongation [%]
bacterial cellulose (BC)	15–35	200–300	1.5–2.0
polypropylene (PP)	1–1.5	30–40	100–600
polyethylene terephthalate (PET)	3–4	50–70	50–300
cellophane	2–3	20–100	15–40

Over the past few years, there has been an increased interest in commercial applications of bacterial cellulose. Important examples include supports for proteins, cell cultures and microorganisms, products for temporary skin and tissue replacement (Biofill, Bioprocess, and Gengiflex), calorie-free food such as Coco de Nata, and additives in the production of lattices and paper. These activities are accompanied by the isolation of new bacterial strains, genetic modifications, and a wide variation of all laboratory culture parameters.[143]

6.3. Biotechnological Synthesis of Blood Vessels from Dextrose

The investigations described below required for the formation, characterization and application of innovative biomaterials for surgery[140] have taken advantage of the powerful *A. xylinus* AX5 strain as a particularly suitable "cellulose factory in the laboratory".[140a] As shown in Figure 30, this strain produces water-soluble D-glucose (dex-

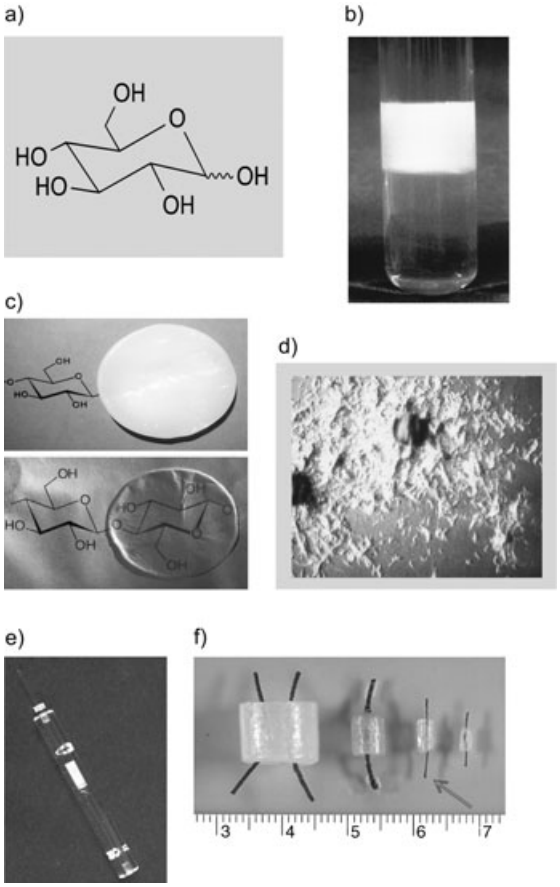


Figure 30. Biotechnological synthesis of bacterial cellulose of varying design: a) substrate D-glucose; b) static culture with cellulose fleece at the interface between Schramm–Hestrin culture medium and air after eight days of cultivation at 28 °C; c) never-dried (top) and completely air dried (bottom) cellulose fleece viewed from the top; d) colony of an *Acetobacter xylinus* strain; e) glass matrix for shaping the bacterial cellulose directly in the culture medium with cellulose tubes formed (see Figure 31); f) cellulose tubes of different dimensions after removal from the matrix and purification (arrow: implants for experimental microsurgery; scale values in cm).[140a]

trose) in static culture with the conventional Schramm–Hestrin culture medium[140a] within eight days, with a yield of 40 % cellulose in the form of a high swollen fleece at the interface between the culture medium and air.

Thus it was demonstrated that bacterial cellulose can be suitably shaped for application during biosynthesis. With the patented matrix reservoir technology developed for this purpose, it is possible to synthesize the cellulose in the shape of formed hollow bodies directly in the culture medium without subsequent treatment.[144] Figure 31 shows a schematic diagram of the cultivation vessel, in which the glass matrix is immersed in a larger volume of nutrient solution. The tube-shaped bacterial cellulose is produced in the nutrient medium which has entered between the outer and inner matrices, and is supplied with oxygen by a second opening to the air space.

The cellulose tubes (brand name BASYC, Bacterial Synthesized Cellulose) formed biotechnologically in this way were investigated for their application as a new type of

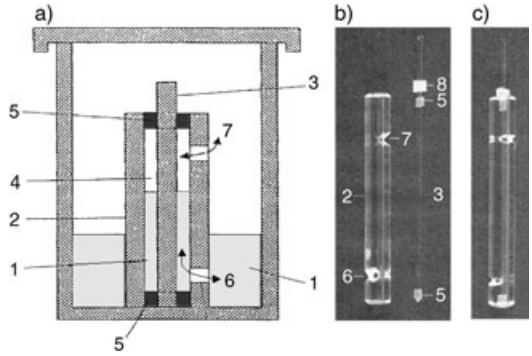


Figure 31. Matrix reservoir cultivation technique for the production of shaped bacterial cellulose (BASYC): a) basic sketch; b) example of the building units of a glass matrix: (1) Schramm–Hestrin culture medium in the reservoir and within the matrix, (2) outer matrix, (3) inner matrix, (4) cultivation space between outer and inner matrix, (5) spacer, (6) opening to the reservoir, (7) opening to the air, (8) stopper; c) ready-to-use matrix.[140a]

biomaterial for microsurgery in a cooperative effort between physicians, biologists and chemists.[140c] Tubular implants with an internal diameter of less than 3 mm were used (Figure 30 f, arrow). This application is derived from new microsurgical techniques that can repair nerves and blood vessels by sutures in a very small diameter range with optical equipment. The well-known synthetic implant materials from the surgery of larger vessels made of polytetrafluoroethylene, polyethylene terephthalate, polyethylene, and polyurethane have been insufficient for the requirements of microsurgery, often resulting in thromboses.

The wall of the BASYC tubes consist of the bacterial cellulose loaded with water at 90 % or greater in the nanofiber network, as described above. The hollow spaces of the BASYC material transport water, monovalent ions, and small molecules, but not biopolymers or corpuscular blood constituents. The stored water not only stabilizes the cellulose network, it also contributes to the tissue and hemocompatibility of BASYC.

For the BASYC vessel implants, the low roughness of the inner surface (feature variations of ≈ 15 nm) is especially significant, and can be obtained with the matrix-reservoir technique. This degree of roughness is within the order of magnitude of that for typical blood vessels in rats. BASYC tubes also meet other significant demands for microvessel replacement: they have a constant shape, are sufficiently stable against internal and external pressure, are flexible and elastic, and are capable of handling a tight microsurgical suture. Figure 32 a shows an example of the microsurgical work with shaped cellulose material. Results of investigations of the microsurgery of nerves and vessels of the rat as an experimental model are shown in Figure 32 b–f.

Upon dissection of the *nervus ischiadicus* and subsequent reconnection by a microsurgical suture, a protective cover (cuff) of BASYC prevents connective tissue from growing into the nerve gap, and favors the adhesion of the fascicles, which facilitates early regeneration of the nerve and a rapid return of muscle function. The good incorporation of bacterial cellulose-forming connective tissue and new blood

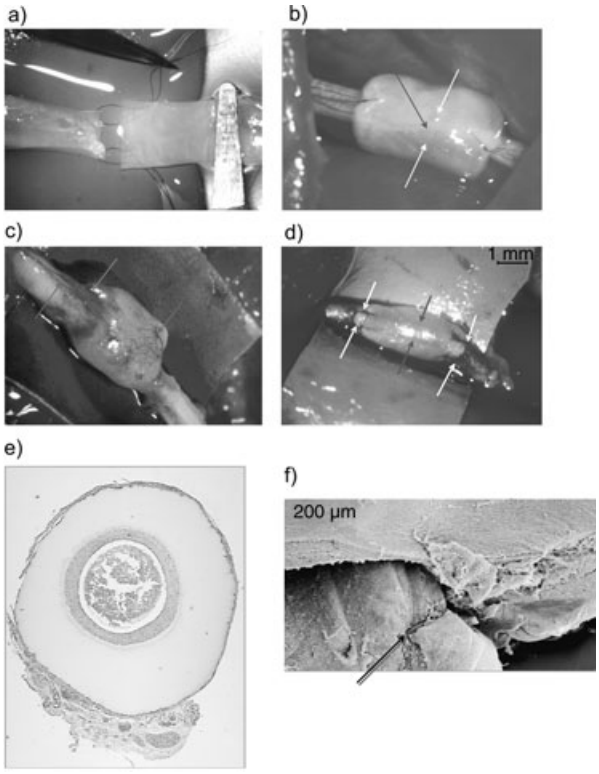


Figure 32. Application of bacterial cellulose tubes (BASYC) for training in microsurgical techniques and for animal experimental microsurgery on nerves and vessels: a) end-in-end connection (anastomosis) of BASYC tubes; b) *nervus ischiadicus* of the rat directly after operation of the dissected nerve (white arrows: anastomosis, black arrow: suture) with BASYC protective cover; c) operating field 10 weeks after the nerve dissection (arrows: new connective tissue and new blood vessels); d) BASYC implant in the carotid artery of the rat directly after operation (white arrows: anastomosis, black arrows: free blood flow, visible through the cellulose tube); e) cross-section of the middle part of a BASYC implant from the carotid artery of the rat after four weeks of residence time in the body as a histological preparation (cf. text); f) SEM image of a longitudinally cut BASYC implant with a homogeneous surface in the cellulose (left) and natural vessel region (arrow: remaining suture material). Magnification: 10 ×: (a, b, c); 6 ×: (d); and 32 ×: (e).[140c]

vessels on the surface of the protective cover is worthy of particular emphasis.

Upon reconnection of a dissected carotid artery (in a rat model) with a BASYC tube, the internal surface of the BASYC material becomes completely covered by an endothelial cell layer after a residence time of four weeks, as determined by histological examination of the preparation along with a specific test for endothelial cells (Figure 32e). Blood remnants can be found in the lumen. As observed by electron microscopy, the complete colonization of the BASYC region with endothelial cells covering both parts of the suture (Figure 32f) can be substantiated. Apparently, the BASYC material is a good substrate for the anchoring of autologous cells.

Upon coverage of longitudinally cleaved tubes with bovine endothelial cells in cell culture tests, a distinct sprouting of the initially spherical cells takes place within 24 h. Electron microscopy shows that the resulting filaments barely differ from the fibers of bacterial cellulose (Figure 33). This structure apparently also benefits the rapid endothelial colonization of BASYC.

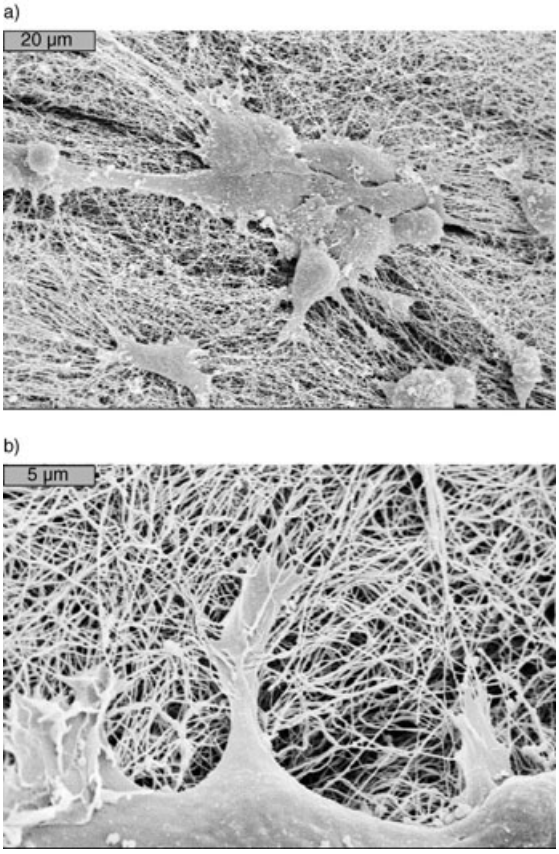


Figure 33. Scanning electron microscopy of the growth of bovine endothelial cells on a BASYC surface 24 h after spreading: a) overview; b) section at 4 × enlargement.[140c]

Notably, further investigations have shown that BASYC microvessel implants can be applied toward vessels under low or high pressure, and that in all cases, thromboses were never observed.

6.4. Bacterial Cellulose for Veterinary Medicine and Cosmetics

The supramolecular structure of bacterial cellulose depends on the method of formation applied. Apart from the methods employed in static cultures and by the matrix-reservoir technique described above, an optimized surface cultivation of *A. xylinus* has been developed.[145] This cultivation system overcomes the transport barrier at the interface between nutrient solution and air for the introduction of the necessary nutrients (carbon and nitrogen sources, inorganic salts, and oxygen) as well as for the removal of the products formed by spraying a substrate aerosol directly on the surface of the immersed culture without causing a mechanical impairment. The cellulose layers of about 10 cm thickness

thus obtained are tested and respectively used for veterinary and cosmetic applications.[146]

7. In-Vitro Syntheses: Ways to New Horizons

The synthesis of a polysaccharide requires frequently repeated glycosylations, including the total control of the configuration at the anomer C atom and of the regioselectivity of the reacting hydroxy group. For this reason, it has only been within the past few years that cellulose could be produced synthetically.

7.1. Enzyme-Catalyzed Cellulose Structure

After many attempts to synthesize cellulose outside organisms, Kobayashi and co-workers[19b] succeeded in 1992 with the enzymatic polymerization of β-cellobiosyl fluoride in the presence of purified cellulase as catalyst in an acetonitrile/buffer solution at 30 °C. Cellulose with a yield of 54 % and a DP value of 22 was formed. The polymer structure as determined by ^{13}C and ^{1}H NMR spectroscopy corresponds well with that of natural cellulose.

Scheme 22 demonstrates that this in-vitro synthesis principle can also be extended to the preparation of amylose and chitin.[19] In continuation of this synthesis work, the in-vitro formation of crystalline cellulose I in an optimized solution system with purified cellulase has been described for the first time.[19d] The generation of this thermodynamically less stable allomorph had been known up to this point in living cells only.

7.2. Ring-Opening Polymerization of Glucose Derivatives

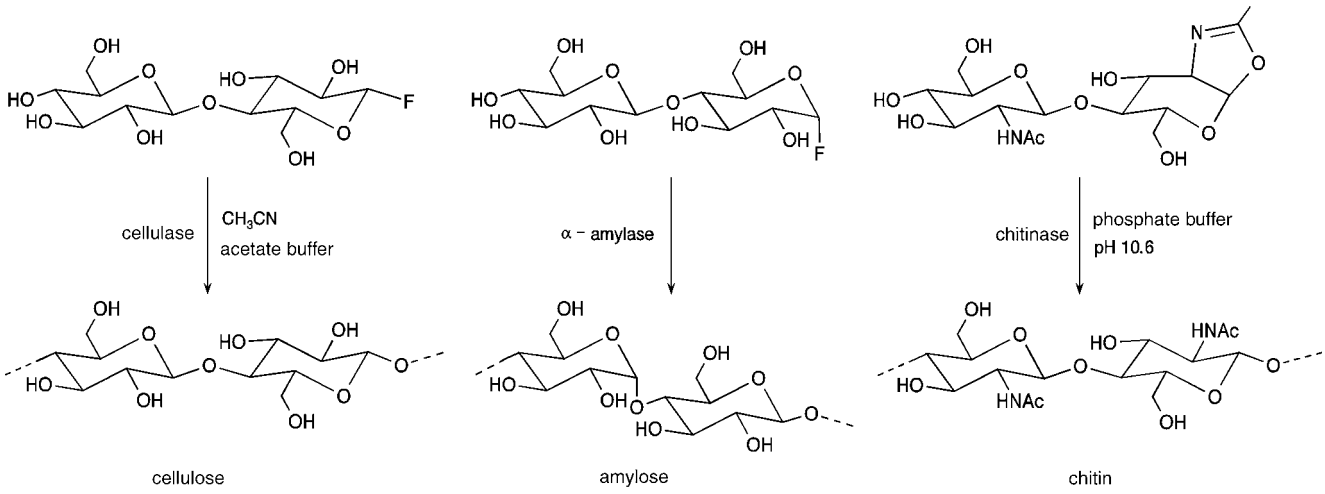
By stepwise synthesis[147] and particularly by cationic ring-opening polymerization of glucose orthoesters, cellulose was synthesized in a purely chemical manner by Nakatsubo and Kamitakahara in 1996 for the first time.[20] Starting with 3-*O*-benzyl-α-D-glucopyranose-1,2,4-orthopivalates with different groups at position 6, cellulose (after deprotection) is accessible according Scheme 23, as well as regioselectively substituted cellulose derivatives.

Scheme 24 shows the corresponding synthesis of uniform methyl celluloses. The DP values of these celluloses are in the range of 20–50. The influence of the glucose substituents on the regio- and stereochemistry of the polymerization could be identified and optimized through systematic work, as well as the availability of the glucose derivatives required and the deprotection chemistry of the product.[148]

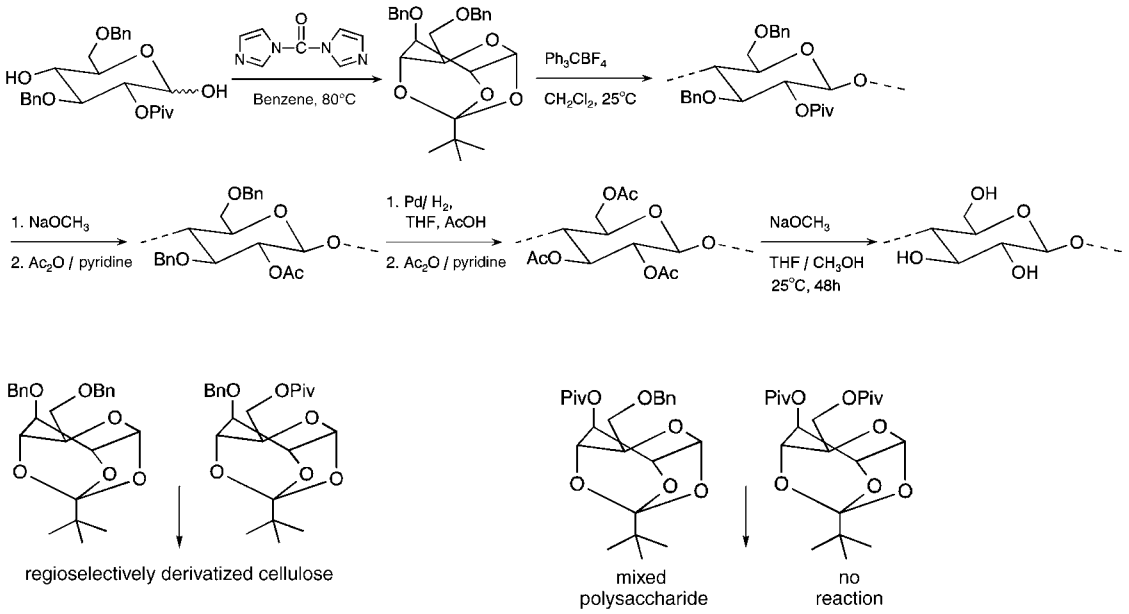
8. Summary and Outlook

Science and technology continue to move toward renewable raw materials and more environmentally friendly and sustainable resources and processes. Cellulose, cellulose derivatives, and polysaccharides as a whole are of growing importance in the development and application of polymer materials. This progression has triggered a distinct renaissance of cellulose research and application all over the world over the past 10 years. In this context, it has been essential to increase the current knowledge of organic and polymer chemistries as well as in the chemistry of low-molecular-weight carbohydrates and other polysaccharides in the basic and application-oriented work in the field of cellulose. Moreover, it has been important to intensify the interdisciplinary interactions between biology, physics, pharmacy, medicine, and the wood industry and chemical engineering.

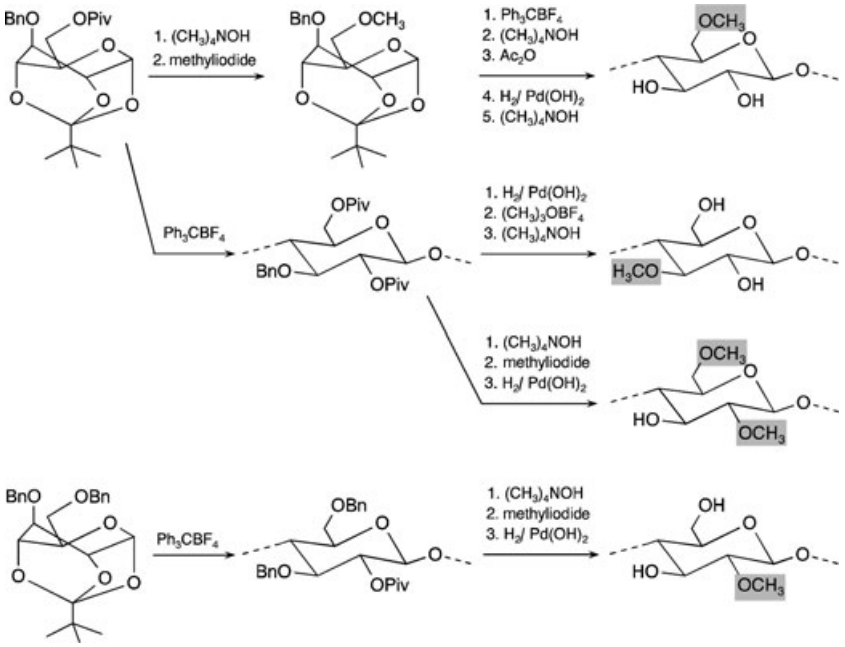
In consequence of this expanding development, groundbreaking insight has been gained on the complex structure of cellulose and cellulose derivatives in the solid state and in solution, on cellulose reactivity, reaction control, and selective syntheses, and regarding supramolecular structure formation as well as the biosynthesis and in-vitro synthesis of cellulose. This includes the rapid development of polysaccharide instrumental analysis and a deeper understanding of the relation between reaction conditions, product structure, and application-oriented properties. Thus, it has been possible to develop new types of cellulose esters and ethers as "polymers



Scheme 22. Enzyme-catalyzed in-vitro synthesis of cellulose and related polysaccharides.



Scheme 23. Chemosynthesis of cellulose by ring-opening polymerization of 3,6-di-*O*-benzyl-α-D-glucopyranose-1,2,4-orthopivalate and the influence of substituents at positions 2 and 3 on the course of the reaction.



Scheme 24. Synthesis of regioselectively substituted methyl celluloses starting from 3-*O*-benzyl-α-D-glucopyranose-1,2,4-orthopivalates.

of the future", for example, toward a wide range of high-quality applications on the industrial scale, which have been established in the market. Fundamental research on the cellulose/NMMO/water system has led to a novel, environmentally friendly technology (Lyocell process) for the production of cellulose regenerate products, which has revolutionized the processing of cellulose, and has at least partially removed the previous disadvantages in comparison with the process steps in the production of synthetic polymers.

All signs and symptoms seem to indicate that the impressive rate of development in the field of cellulose will continue or will even accelerate. The establishment of centers of excellence, new pilot, process, and production plants, the expansion of large-scale technical products, a close cooperation of fundamental and applied research, as well as an effective international cooperation of scientists and facilities are distinct evidence of this fact. New insight into the processes of wood pulping and overall wood processing, into the production of cellulose from other plants as well as into the analysis of cellulose products will help to ensures that the quality, variety of products, and ecological acceptance of the starting materials will grow, along with the consistent ecological orientation of industrial cellulose chemistry.

Fundamental changes regarding the access to cellulose as a raw material are predictable because of the fast growth in understanding cellulose biosynthesis. Indeed, efforts are being made to purify and sequence cellulose synthase and associated proteins to generate a reproducible cell-free system capable of generating crystalline cellulose. By introducing genes to modify cellulose biosynthesis in important cellulose-forming organisms (trees, cotton crops, and bacteria), it should be possible to tailor various types of cellulose for pulp, paper, building materials, textiles, and other fields of application.

If cellulose-forming bacteria could be cultivated on a large technical scale, the requirement of cellulose could be satisfied entirely by this source in the future.

The aim of this paper is to demonstrate the current state of development in the field of cellulose research and application through examples. It should be also pointed out that cellulose as a natural product belongs to the polymers, which hold an impressive future potential for fundamental knowledge as

well as for large-scale production in a wide range of applications.

Glossary

AGU	anhydroglucose unit
BF	blow film
CMC	carboxymethyl cellulose
CA	cellulose acetate
CAB	cellulose acetate butyrate
CAP	cellulose acetate propionate
CE	carbohydrate esterase
CF	cellulose formate
CTFA	cellulose trifluoracetate
DCC	dicyclohexylcarbodiimide
DP	degree of polymerization
DS	degree of substitution
HEC	hydroxyethyl cellulose
HMDS	hexamethyldisilazane
HPC	hydroxypropyl cellulose
HPMC	hydroxypropylmethyl cellulose
MC	methyl cellulose
Ms	mesyl
NC	nitrocellulose
NMMO	*N*-methylmorpholine-*N*-oxide
NMP	*N*-methylpyrrolidone
NTA	nitrilotrieacetic acid
PDA	1,4-phenylenediamine
Piv	pivalate
TDS	thexyldimethylsilyl
TEA	Triethylamine
Thexyl	1,2-dimethyl-butyl-1
TMS	trimethylsilyl
TMSC	trimethylsilyl cellulose
Tr	triphenylmethyl, Trityl
Ts	tosyl
Tf	triflyl
UDP	uridine diphosphate

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