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Cellulose: Structure and Properties

Thomas Heinze

Abstract Cellulose, a fascinating biopolymer and the most common organic compound on earth, is comprehensively reviewed. Details of its crystalline phases are given, starting with a description of molecular and supramolecular structures, including the hydrogen bond systems. Sources of this ubiquitous biopolymer are mentioned, with attention to the special properties of bacterially synthesized nanofibrous cellulose. Nanostructures obtained by disintegration of cellulose fibers (top-down approach) yielding nano- or microfibrillated cellulose and cellulose whiskers are the basis for novel materials with extraordinary properties. Moreover, nanofibers and nanoparticles can be made by special techniques applying the bottom-up approach. Efficient systems to dissolve cellulose by destruction of the hydrogen bond systems using ionic liquids and systems based on polar aprotic solvent and salt are described. Novel cellulose derivatives are available by chemical modification under heterogeneous or homogeneous conditions, depending on the cellulose reactivity. In particular, unconventional nucleophilic displacement reactions yielding products for high-value applications are highlighted. Novel amino cellulose derivatives showing fully reversible aggregation behavior and nanostructure formation on various materials are the focus of interest. Finally, "click chemistry" for the synthesis of novel cellulose derivatives is discussed.

Keywords Amino cellulose · Cellulose · Nanostructuring · Reactivity · Solubility · Structure · Supramolecular architecture

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1 Introduction

Cellulose is the most abundant natural polymer in the biosphere, with a global production (and decomposition) of ~1.5×10^{12} tons per year, comparable to the planetary reserves of the main fossil and mineral sources [1]. In addition to the long-standing scientific interest in cellulose, the use of cellulose as renewable and biodegradable raw material in various applications is a proposed solution to the recent industrial challenge to successfully meet environmental and recycling problems [2]. Versatile structuring of cellulose by various routes of modification, including both physical and chemical methods, has enabled its use in a variety of applications (e.g., fillers, building and coating materials, laminates, papers, textiles, optical films, sorption media, viscosity regulators, and even advanced functional materials) [3].

The earliest systematic efforts that lead to the discovery of cellulose began in 1837 with the work of the French chemist Anselme Payen, who showed that various plant materials yielded a fibrous substance after purification with acid-ammonia treatment and extraction with water, alcohol, and ether. The French Academy finally named the resulting carbohydrate “cellulose” [4]. Nowadays, there are various processes used to isolate cellulose, for example, the alkaline, bisulfite,

and sulfate (kraft-) processes, in combination with thermal and mechanical treatments. The different processes result in varying fiber strengths of the pulp [5, 6].

The aim of this review is to discuss the different structural levels of cellulose and to describe important properties that result from this unique structure. Moreover, advanced micro- and nanostructural materials based on cellulose obtained by physical and hydrolytic treatments (top-down approaches) as well as the bottom-up elaboration of nanostructures by electrospinning and nanoprecipitation are highlighted. Finally, one of the most important paths for the design of highly engineered products, namely chemical modification of cellulose (particularly under homogeneous reactions conditions), is summarized with consideration of our own research in the field of chemical modification of cellulose by advanced organic chemistry.

2 Sources of Cellulose

Cellulose is distributed throughout nature in plants, animals, algae, fungi, and minerals (Fig. 1). However, the major source of cellulose is plant fiber. Cellulose contributes approximately 40% to the carbon fraction in plants, serving as structuring element within the complex architecture of their cell walls. Cellulose can occur in pure form in plants but it is usually accompanied by hemicelluloses,

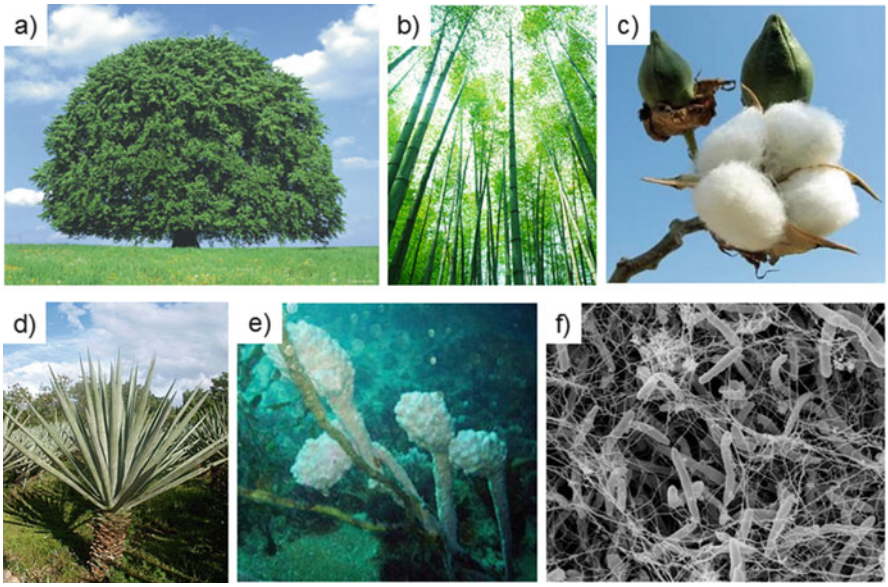

Fig. 1 Selection of important cellulose sources: (**a**) hard wood (beech tree), (**b**) bamboo, (**c**) cotton, (**d**) sisal, (**e**) tunicine, and (**f**) *Gluconacetobacter xylinum* (reproduced with permission from Schubert et al. [7])

lignins, and comparably small amounts of extractives. Wood contains about 40–50 wt% cellulose. Comparable amounts can be found in bagasse (35–45 wt%), bamboo (40–55 wt%), straw (40–50 wt%), and even higher in flax (70–80 wt%), hemp (75–80 wt%), jute (60–65 wt%), kapok (70–75 wt%), and ramie (70–75 wt %). Cotton is a fairly pure cellulose source, containing more than 90 wt% [8]. An impressive amount of cellulose is produced each year, not only in wood fiber from trees (ca. 1,750,000 kt world production) but also in annual plants such as bamboo (10,000 kt), cotton linters (18,450 kt), jute (2,300 kt), flax (830 kt), sisal (378 kt), hemp (214 kt), and ramie (100 kt) [9]. In addition, several fungi and green algae produce cellulose (e.g., *Valonia ventricosa*, *Chaetamorpha melagonicum*, *Glaucocystis*) and some (marine) animals such as ascidians contain cellulose in their outer membrane. Moreover, bacteria of the genera *Gluconacetobacter*, *Agrobacterium*, *Pseudomonas*, *Rhizobium*, and *Sarcina* can synthesize bacterial cellulose from glucose and various other carbon sources [10, 11]. Bacterial cellulose, which is produced directly as a fibrous network, contains no lignin, pectin, hemicelluloses, or other biogenic products; it is very highly crystalline and possesses a high degree of polymerization (DP).

3 Structure of Cellulose

3.1 Molecular Structure

Independent of the source, cellulose consists of D-glucopyranose ring units in the $^4C_1$-chair configuration, which exhibits the lowest energy conformation [12]. Such units are linked by β-1,4-glycosidic bonds that results in an alternate turning of the cellulose chain axis by 180°. Cellobiose with a length of 1.3 nm can be considered the repeating unit of cellulose [13]. Three reactive hydroxyl groups exist in each anhydroglucose unit (AGU) within the cellulose chain, a primary group at C6 and two secondary groups at C2 and C3 that are positioned in the plane of the ring (Fig. 2).

As is typical for a polymer formed by "polycondensation," the chain ends of the cellulose molecule are chemically different [14]. One end contains an anomeric C atom linked by the glycosidic bonds (nonreducing end) whereas the other end has a D-glucopyranose unit in equilibrium with the aldehyde function (reducing end group).

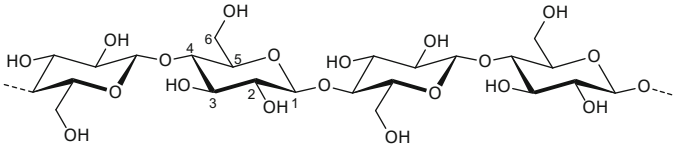

Fig. 2 Representation of a cellulose molecule

Changes in the molecular structure originate from reactions leading to hydrolysis or oxidation of the cellulose chain. Such reactions mainly occur on the surface of the fibrils or in amorphous regions.

The DP of native cellulose of various origins is in the range of 1,000–30,000, which corresponds to chain lengths of 500–15,000 nm. The cellulose samples that are obtained by isolation methods possess DP values ranging between 800 and 3,000 [13]. Cellulose samples are polydisperse, thus, the DP is an average value. There are several techniques that can give information about the molar masses and their distribution, including viscosity measurements, size-exclusion chromatography, and light scattering.

3.2 Hydrogen Bonding

Cellulose possesses various systems of hydrogen bonds, which have a significant influence on properties [15]. For instance, the limited solubility in most solvents, the reactivity of the hydroxyl groups, and the crystallinity of cellulose samples originate from strong hydrogen bonding systems. Cellulose also contains hydrophobic areas (around the C atoms) that have a certain influence on the overall properties, including solubility.

The three hydroxyl groups of the AGU, the oxygen atoms of the D-glucopyranose ring, and the glycosidic linkage interact with each other within the chain or with another cellulose chain by forming intramolecular and intermolecular hydrogen bonds. The hydrogen bonds give rise to various three-dimensional arrangements.

Infrared (IR) [16, 17] and solid state ^{13}C-NMR spectroscopy [18] revealed that the OH group at C3 and adjacent ether oxygen of the AGU units form intramolecular bonds together with those between the oxygen atoms in the hydroxyl group at C6 and neighboring hydroxyls linked to C2. Together with the β-glycosidic covalent linkage, the intramolecular hydrogen bonds are responsible for the rigidity or stiffness of the cellulose polymer [13]. As a result, highly viscous solutions are produced from cellulose relative to those obtained from equivalent polysaccharides bonded by α-glycosidic linkages. This also leads to a high tendency to crystallize or to form fibrillar structures.

Intermolecular hydrogen bonding is responsible for the strong interaction between cellulose chains. The bonds are produced between adjacent cellulose macromolecules located along the (002) plane in the crystal lattice of cellulose I (native cellulose), mainly between the oxygen atom in C3 and the OH at C6 (see Sect. 3.3) [19]. Together, the hydrogen bonding, weak C–H–O bonds, and hydrophobic interactions are responsible for the assembly of cellulose in layers, as elucidated by synchrotron X-ray and neutron diffraction experiments [20].

Cellulose II (see Sect. 3.3) shows a different hydrogen bonding system. Because of the existence of an intermolecular hydrogen bond between the OH groups of C6 and C2 of another chain, the intramolecular bonding of OH in C2 is avoided and an

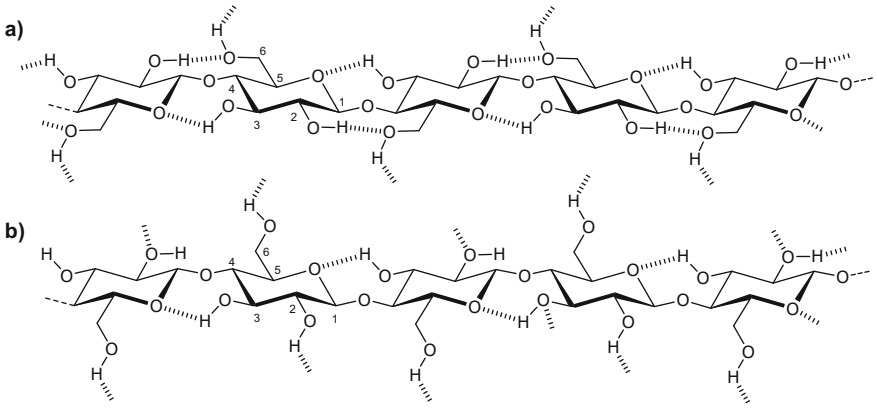

Fig. 3 Hydrogen bonding system of (**a**) cellulose I and (**b**) cellulose II (reproduced with permission from Tashiro and Kobayashi [22], copyright 1991, with permission from Elsevier)

intermolecular hydrogen bond of OH–C2 to OH–C2 of the next chain is formed [21]. In comparison to cellulose I, the cellulose II molecules are more densely packed and strongly interbonded and, therefore, cellulose II is less reactive, as commonly observed [13]. Figure 3 shows a scheme of the hydrogen bonding system in cellulose I and II.

3.3 Crystal Modifications

The regular structure of cellulose leads to X-ray diffraction patterns that reveal its degree of crystallinity. There were a number of inconsistencies in the crystalline structure described for different cellulose modifications after certain treatments [23]. X-ray and NMR experiments confirmed the dimorphism [24]. X-ray diffraction patterns and solid-state ^{13}C-NMR revealed cellulose conformations (Figs. 4 and 5) that were used to elucidate the detailed crystalline structure and the basis for transformation in the various allomorphs [25].

Celluloses from different sources possess comparable crystallinity (i.e., modifications of cellulose I). However, solid state ^{13}C-NMR studies revealed that cellulose can crystallize with varying proportions of two different phases, named cellulose I_α and I_β. Plant cellulose mainly consists of cellulose I_β, whereas cellulose produced by primitive organisms crystallizes in the I_α phase. The monoclinic unit cell of cellulose I_α with a space group $P2_1$ consists of two cellulose molecules, each containing a cellobiose unit in the 002 corner plane and 002 center plane in a parallel fashion [19]. Cellulose I_β corresponds to a triclinic symmetry with space group P_1 containing one chain in the unit cell, as schematically displayed in Fig. 6a.

Cellulose I can be transformed into the thermodynamically stable crystalline form of cellulose II by regeneration from the dissolved state or mercerization.

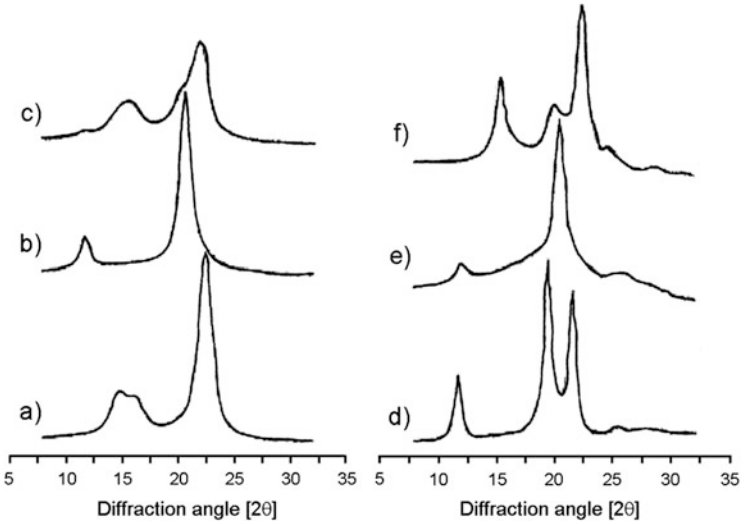

Fig. 4 X-ray diffraction patterns of (**a**) cellulose I_β, (**b**) cellulose III_I, (**c**) cellulose IV_I, (**d**) cellulose II, (**e**) cellulose III_{II}, and (**f**) cellulose IV_{II} (adapted from Isogai et al. [25], copyright 1989 with permission from American Chemical Society)

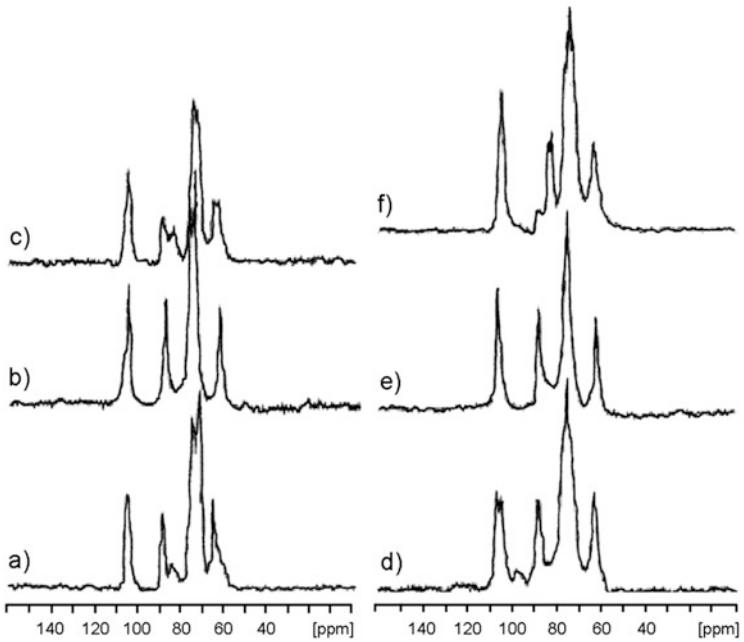

Fig. 5 Solid state ^{13}C-NMR spectra of (**a**) cellulose I_β, (**b**) cellulose III_I, (**c**) cellulose IV_I, (**d**) cellulose II, (**e**) cellulose III_{II}, and (**f**) cellulose IV_{II} (adapted from Isogai et al. [25], copyright 1989 with permission American Chemical Society)

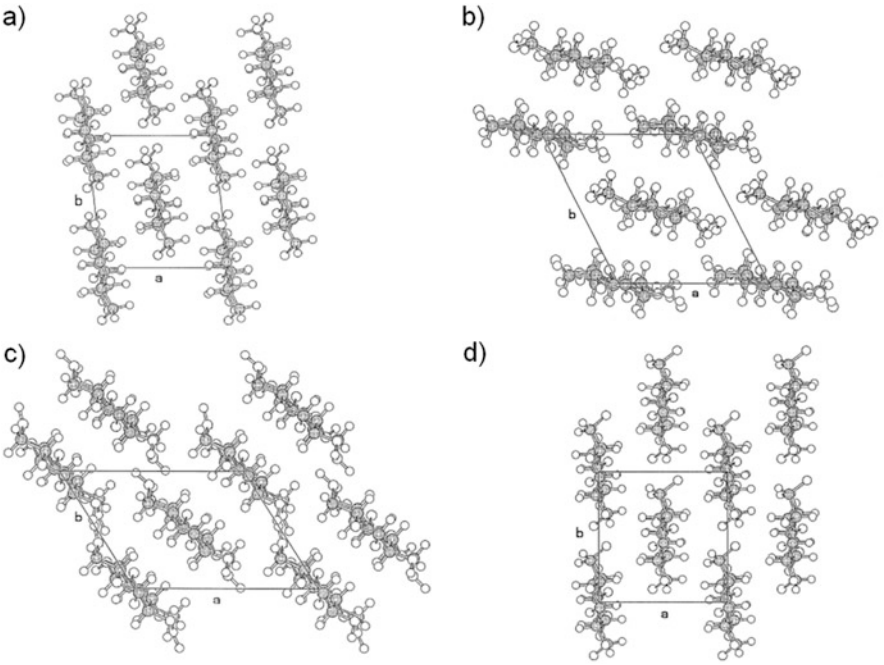

Fig. 6 Models of (**a**) cellulose I_β, (**b**) cellulose II, (**c**) cellulose III_I, and (**d**) cellulose IV_I (reproduced from Zugenmaier [26], copyright 2001, with permission from Elsevier)

Mercerized cellulose II can easily be achieved by treatment of cellulose with alkali at concentrations >18 wt% and subsequent thorough washing. The irreversible transition to cellulose II is used for improving the quality of natural fibers and yarns. Moreover, the treatment of cellulose with aqueous alkali (mainly aqueous sodium hydroxide) is the key step for activating the polymer prior to heterogeneous chemical modification, particularly for commercial etherification. The structure of cellulose II was revised by neutron fiber diffraction analysis [27]. Two chains of cellulose are located antiparallel on the 2_1 axis of the monoclinic cell (Fig. 6b), while the chains are displaced relative to each other by about one fourth of the AGU.

The treatment of cellulose I and II with liquid ammonia and certain amines results in the formation of cellulose III_I and III_{II}, respectively, possessing the same unit cell [26]. The structures can easily be reconverted into cellulose I or II by mild heating. The crystalline structure of cellulose III_I can be described as a one-chain unit cell and a $P2_1$ space group, with the cellulose chain axis on one of the 2_1 screw axes of the cells [28]. A single chain of cellulose III_I is similar to one of the two chains existing in a crystal of cellulose II.

Cellulose III can be transformed into cellulose IV_I or IV_{II} in glycerol at high temperatures, depending on the starting materials used. However, the conversion is

never quantitative, which complicates complete analysis of the crystallinity [29]. The space group P_1 is assumed for both structures.

In addition to the crystalline domains, there are also amorphous or noncrystalline regions in cellulose, which influence the physical and chemical properties of celluloses [30]. Interactions between solid cellulose and water, enzymes, and reactive or adsorptive substances occur first at the noncrystalline, amorphous domains or at the surface of cellulose crystals. Entire amorphous cellulose samples can be prepared by ball-milling of cellulose [31], deacetylation of cellulose acetate under nonaqueous alkaline conditions [32], or precipitation from nonaqueous cellulose solutions into nonaqueous media avoiding stress [33]. However, the amorphous structures are usually unstable in the presence of water and form partly crystalline cellulose II. Interestingly, it was found that Raman and solid state ^{13}C-NMR spectra of amorphous and highly crystalline cellulose IV_{II} are almost identical, which confirms the similarity of the secondary structures of the two cellulose types [34].

Regarding the use of cellulose and its chemical derivatization, the crystal structures of cellulose I and II are important. As far as this author knows, there are no established technical processes nor cellulose-based products using or possessing any other crystalline structures.

3.4 Morphology

3.4.1 Plant Cellulose

Cellulose is organized in parallel assemblies of elementary crystallites, which organize into fibers via hydrogen bonding [13]. Whereas areas of lower order or noncrystalline regions contain turns between neighboring chains, ordered crystallites pack cellulose chains folded in a longitudinal direction. The less ordered regions display a relatively lower density and more random orientation [35]. The cellulose chains arrange as a basic fibrillar unit, the so-called elementary fibrils, which have been reported to be 100 nm in length and have a characteristic lateral dimension of 1.5–3.5 nm [1]. Such elementary fibrils are further assembled as fibrillar bundles, called microfibrils, with widths in the range of 10–30 nm. Also, microfibrillar bands form, of the order of 100 nm in width and lengths of hundreds of nanometers or even a few microns (Fig. 7). Such fibrillar architectures are characteristic of both native and manmade fibers [13]. However, in plant cell walls, a sheath of amorphous cellulose, which is surrounded by hemicelluloses, further covers the microfibrils [9].

Fibers from different sources display different morphologies and dimensions. For example, cotton fibers are twisted (Fig. 8a) whereas those from spruce wood are generally untwisted (Fig. 8b). In contrast, fibers from bast plants are straight and round (Fig. 8c). Interestingly, they all share an internal structure made up of multiple cell wall layers. During the growth period, plant fibers develop a primary

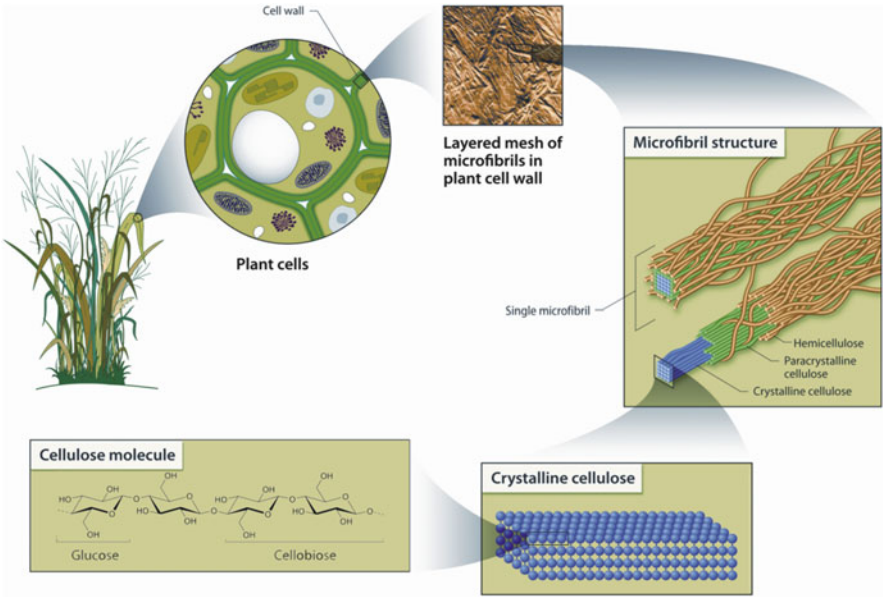

Fig. 7 Association of cellulose molecules in the plant cell wall (reproduced from https://public.ornl.gov/site/gallery/detail.cfm?id=181&topic=&citation=&general=Cellulose&restsection=all, U.S. Department of Energy Genomic Science program, http://genomicscience.energy.gov)

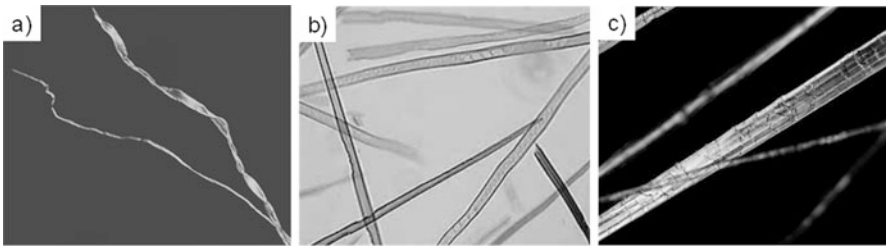

Fig. 8 Micrographs of (**a**) twisted cotton fibers, (**b**) tracheids of spruce wood, and (**c**) straight fibers of ramie (reproduced with permission from Ioelovich and Leykin [36])

cell wall layer (P) that is much thinner than the secondary wall (S), which is formed on its inner side. Further inside, the tertiary cell wall (T) is exposed to an open, hollow area or lumen resulting in typical hollow, cylinder-like plant cells. The cell wall thickness and length of plant fibers are about 4–6 30 μm and 15–30 μm, respectively. The P and T layers contain disordered cellulose nets with dimensions of ~100 nm. The swelling characteristics of fibers (as well as their physical and chemical properties) are influenced by the configuration, composition, and structure of the P layer, which contains microfibrils criss-crossed onto each other to make a network-like helical structure. The secondary layer (~3–5 μm thickness) comprises

three sublayers (S1, S2, and S3) of which S2 is the thickest (2–4 μm). The S2 layer contains microfibrils arranged parallel to each other and oriented at a given average helical angle with respect to the fiber axis, the so-called microfibril angle. It is noteworthy that the tensile strength of the fibers correlates inversely with the microfibril angle [36]. The fibers also display a variety of features and defects that facilitate chemical attack and mechanical failure, including pores or openings (pits), cracks, damage sites, compression failures, nodes, and thinning regions.

The fibrillar arrangement of regenerated cellulose is different; manmade fibers also consist of elementary fibrils but with a random location in the supramolecular structure [37]. Applying a precipitation process without shear forces, the crystallites are randomly distributed in a semi-amorphous matrix, whereas in a film-forming procedure the crystallites are positioned parallel to the film surface with an orientation in the direction of the draw [38]. The crystallites are aligned with the longitudinal axis in the direction of stretch in regenerated cellulose fibers, but with a certain transverse nonuniformity that depends on the spinning conditions applied.

3.4.2 Morphology of Bacterial Cellulose

Compared with plant cellulose, bacterial cellulose (BC) is very pure (contains no hemicelluloses and lignin) and only a very low amount of carbonyl and carboxyl moieties are present [7]. BC possesses high crystallinity (more than 80%), excellent water absorption capacity, and extraordinary mechanical strength, particularly in the wet state, resulting mainly from the presence of nanofibrils of BC rather than microfibers of plant cellulose (see Sect. 4). An important advantage of BC is its in situ moldability (i.e., shaping during biosynthesis) [39].

BC consists of a three-dimensional network of ultrafine cellulose fibrils with a diameter in the range of 80–150 nm and can contain up to 99% water in the initial never-dried state. In addition, the DP value of BC is high, with values of up to 10,000 [40].

Under static culture conditions, layers (sheets) of BC of up to several centimeters thickness are formed on the surface of the culture medium. It is important to control the pH because the accumulation of gluconic-, acetic-, or lactic acids in the culture broth decreases the pH far below the optimum for growth and cellulose production [41]. In the 1980s, Johnson & Johnson (New Brunswick, USA) started to commercialize sheets of BC on large scale for the treatment of different wounds [42, 43]. Independently, a Brazilian company, BioFill Produtos Biotecnologicos (Curitiba, PR Brazil), created a new wound healing system based on BC [1, 44, 45]. At present, commercial products such as Suprasorb X® are distributed by Lohmann & Rauscher (Neuwied, Germany).

In contrast to stationary culture conditions, various reactors (e.g., the rotating disk fermenter) were developed to produce BC under agitated culture conditions that prevent conversion of cellulose-producing strains into cellulose-negative mutants. Morphological differences between the cellulose produced by static and

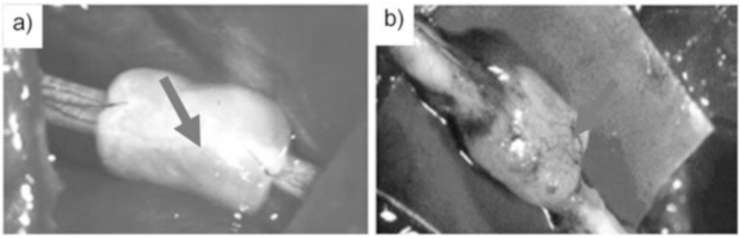

Fig. 9 Sciatic nerve of a rat with a BASYC® tube as protective cover (**a**) immediately and (**b**) 10 weeks after the operation (reproduced from Klemm et al. [47], copyright 2006 with permission from Springer)

agitated cultures contribute to varying degrees of crystallinity, crystalline sizes, and cellulose I_α content. The crystallinity index is closely related to the I_α content [46].

Shaping of BC in a static culture by applying a template matrix can yield different shapes, including tubes of different length, wall thickness, and inner diameter (e.g., BASYC® bacterial synthesized cellulose tubes). The roughness of the BASYC® tubes in the wet state resembles blood vessels and ranges between 7 and 14 nm. Their tremendous mechanical strength provides the stability necessary for microsurgical preparation and to withstand the blood pressure of the living body (Fig. 9) [1, 47].

4 Nanostructures of Cellulose and Their Properties

Natural cellulose can be transformed into micro- and nanoscale materials by applying specific top-down approaches, yielding defined products such as microcrystalline cellulose, microfibrillar cellulose, and whiskers (see Fig. 10) [48].

The micro- and nanoscale materials mainly differ in DP and crystallinity according to the disintegration technique used and, consequently, differ in shape. Figure 11 shows examples of micro- and nanoscaled cellulose samples in comparison with native bacterial cellulose.

4.1 Microcrystalline Cellulose

Microcrystalline cellulose (MC) is a fine, white, and odorless crystalline powder (commercial products include Avicel®, Heweten®, Microcel®, Nilyn®, and Novagel®) used in pharmaceutical (tablet binder), food (rheology control), and paper applications as well as in composite manufacturing [49]. MC is commercially produced by treatment of biomass with aqueous sodium hydroxide to remove other constituents [50], followed by acidic hydrolysis. During hydrolysis, the DP of cellulose decreases with hydrolysis time until reaching a plateau value called

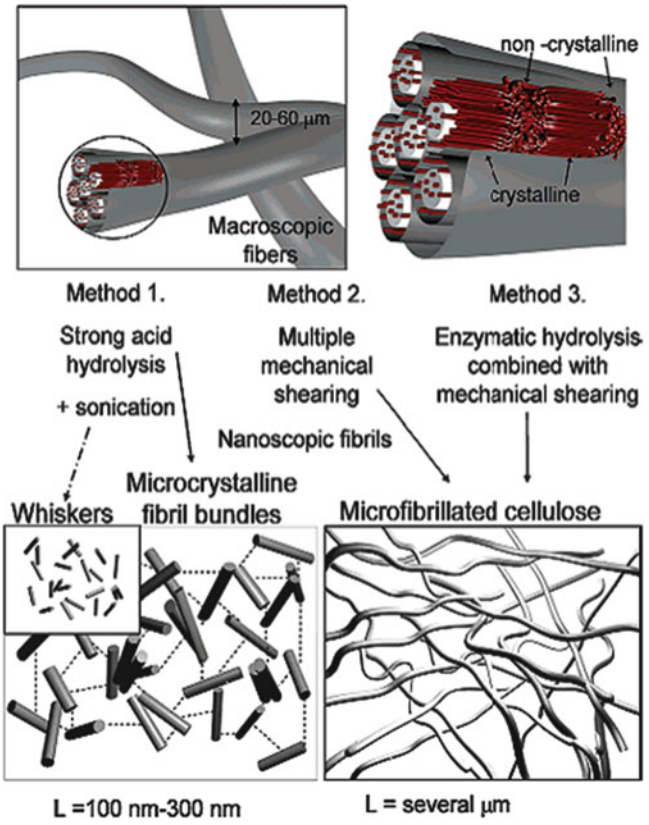

Fig. 10 Mechanical treatment and hydrolysis as top-down approaches for preparing nanoscale cellulosic materials (reprinted from Pääkköö et al. [48], copyright 2007 with permission from American Chemical Society)

"level off DP" (LODP), which ranges between 25 and 300 depending on the cellulose source [51]. The hydrolysis takes place in the less crystalline regions, leaving a solid residue that is water-insoluble and crystalline. As a result of the motion freedom of the hydrolyzed crystallites, structures are produced that have larger dimensions than the original microfibrils [35] forming a stable aqueous dispersion upon vigorous stirring. However, colloidal destabilization of the small crystalline domains can occur upon removal of acid by dialysis followed by spray-drying [52]. In such dry form, MC morphology varies from stubby to fibrillar. Importantly, sulfate half-ester moieties are introduced on the microcrystals (sulfur content 0.5–2%) when sulfuric acid is used for hydrolysis [53, 54]. The negative charge developed in aqueous media by these groups is the main contributor to colloidal stability of the dispersion, and its viscosity has been found to strongly depend on the charge density [55]. HCl is the hydrolytic medium of choice if MC is to be produced for applications that require the absence of electrostatic charges

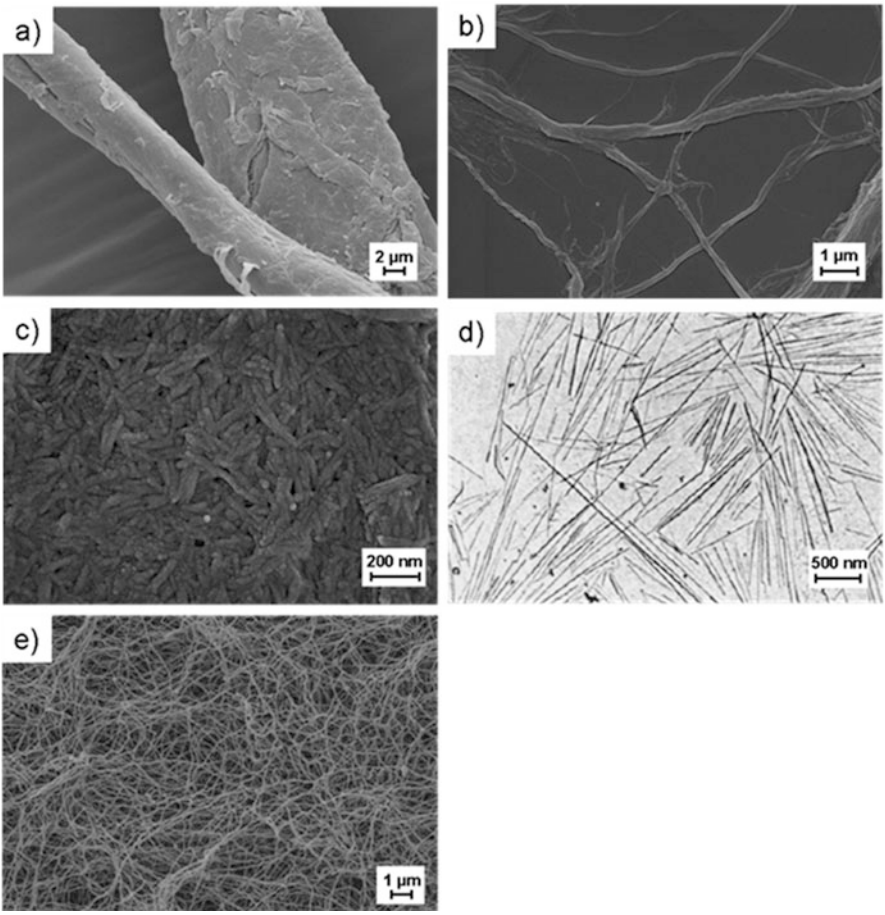

Fig. 11 Scanning electron micrographs of (**a**) fibers of cotton linters, (**b**) microfibrillar cellulose, (**c**) microcrystalline cellulose, (**d**) tunicate whiskers (reproduced from Eichhorn et al. [9], copyright 2001 with permission from Springer) and (**e**) bacterial cellulose

(e.g., in order to enhance enzyme interactions, binding, and attack). Such HCl-hydrolyzed MC is uncharged and can be of similar shape and size to that from sulfuric acid hydrolysis (Fig. 12). Concentrated dispersions of MC obtained with HCl show thixotropy (concentration >5%) whereas antithixotropic behavior is displayed at lower concentrations (<0.3%).

MC cellulose crystallites (and also cellulose nanocrystals or whiskers, see Sect. 4.2) self-assemble in water into chiral nematic phases of a given pitch, P, that reflect circularly polarized light of the same handedness. The value of P is in the order of the wavelength of visible light, giving rise to interesting interactions under illumination. Furthermore, above a critical concentration the cellulose crystallites evolve spontaneously into chiral nematic liquid crystals in water, which upon drying

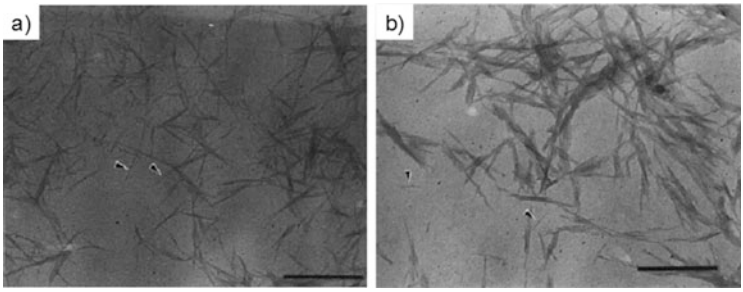

Fig. 12 Transmission electron micrograph of microcrystalline cellulose prepared by treatment with (**a**) H_2SO_4 and (**b**) HCl, with typical single microcrystals marked by *arrowheads*. *Scale bars* indicate 500 nm (reproduced from Araki et al. [53], copyright 1998 with permission from Elsevier)

form regularly twisted fibril layers that resemble the structural organization that evolves in nature [56, 57].

For the synthesis of new cellulose derivatives at the laboratory scale, MC is a convenient starting material of very high purity and sufficiently low viscosity, for example, to acquire well-resolved liquid state NMR spectra for structural analysis.

4.2 Cellulose Whiskers

Intense hydrolysis of cellulose results in crystallites that assemble into rigid rodlike cellulose particles, namely cellulose whiskers, after treatment with ultrasound [50]. Their preparation is also possible using high-energy mechanical treatments that cleave the amorphous parts by mechanical disintegration of a cellulose suspension. An enzymatically produced precursor yields whiskers in a more efficient two-step process [48]. Enzymatic hydrolysis is milder than the more aggressive acid hydrolysis and yields whiskers that are relatively longer and more entangled, resulting in a hydrogel network that possesses much greater strength. Cellulose nanocrystals take rodlike shapes with a typical width of a few nanometers and length of the order of hundreds of nanometers [50]. Such dimensions depend on the cellulose source and amorphous cellulose content, and are thus influenced by the conditions used during hydrolysis. Cellulose nanocrystals display a small number of defects and show no signs of chain folding. A large elastic modulus (~150 GPa) and strength (~7 GPa) have been typically calculated or determined for cellulose nanocrystals, which also possess a very low thermal expansion coefficient ($\sim 10^{-7}$ K^{-1}) [58, 59]. The small nanocrystals can form an isotropic dispersion, whereas larger particles separate into an anisotropic, bottom phase as the concentration increases [60]. Whiskers obtained from tunicate cellulose can be separated by ultracentrifugation using a saccharose gradient [61].

The stability of cellulose whiskers is strongly influenced by the size polydispersity, the dimensions of the particles, and their surface charge. Suspensions of

whiskers prepared with H_2SO_4 (negatively charged) are more stable as a result of electrostatic repulsion [62] than whiskers obtained by hydrolysis with HCl (neutral particles).

The rigid and rodlike nature of cellulose I nanocrystals leads to macroscopic birefringence under observation with crossed polarizers [63]. At low concentrations, cellulose nanocrystals are randomly oriented in water and appear as oval or spherical features [64]. As the concentration is increased, the nanocrystals self-assemble along a vector to yield a typical cholesteric liquid crystalline phase. The chiral nematic order can be retained upon removal of water and results in iridescent films, the color of which can be easily tuned by changing the salt concentration, pH, and temperature of the suspension [65]. At higher ionic strength (e.g., by addition of HCl, NaCl, or KCl), the electrical double-layer effect is screened out and the chiral interactions become stronger. The counter-ion also effects the interactions between particles. In the presence of protons, the cellulose suspensions form ordered phases at the lowest critical concentration. Application of a magnetic field during drying of cellulose films results in perfect orientation of the whiskers, leading to colored materials that can be used as security paper. The color change depends on the viewing angle, which is useful for production of optically variable coatings and inks. Figure 13 shows different domains of the cellulose nanocrystals, suggesting an ordered phase (Fig. 13a) and a well-defined cholesteric phase (Fig. 13b) [35]. Under an external magnetic field, small angle neutron scattering (SANS) experiments indicate that the cholesteric axis of the chiral nematic phase aligns with the magnetic field [66]. Along the cholesteric axis, the distance between the cellulose particles is shorter than perpendicular to it. This evidence suggests a helical twist of the cellulose whiskers.

In cellulose-based nanocomposites, whiskers give excellent properties because their regular and precise rigid-rod shape improves the mechanical characteristics of a variety of natural and synthetic materials. The nanocomposites show significantly enhanced mechanical properties as a result of formation of a rigid whiskers network, even when the whiskers content is only a few percent [67, 68].

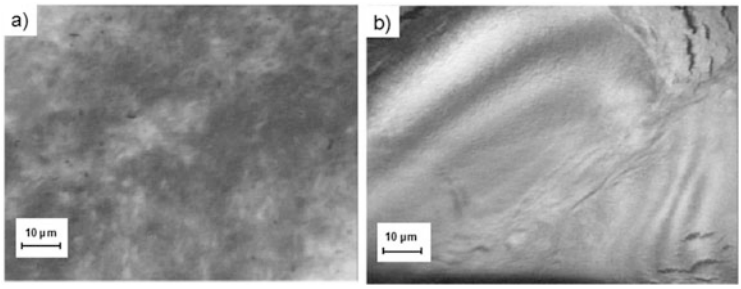

Fig. 13 Cross-polarized optical microscopy images of tunicate whiskers (**a**) at initial ordered phase and (**b**) at cholesteric phase (reproduced from de Souza Lima and Borsali [35], copyright 2004 with permission from John Wiley and Sons)

Cellulose nanocrystals can be dispersed in polar aprotic solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF), for example, for the preparation of films displaying birefringence [69]. Dispersions in dichloromethane allow film-casting with poly(ε-caprolactone) leading to completely biobased composites that possess higher melting and crystallization temperatures, as well as higher glass transition temperatures compared with poly (ε-caprolactone). Poly(β-hydroxyalkanoate), cellulose acetate butyrate, starch, poly (vinyl chloride), polyamide 6, latex, poly(vinyl alcohol), and other synthetic and natural macromolecules have been blended with cellulose whiskers to reinforce the systems [35, 67, 68, 70–76].

Cellulose whiskers can increase the crystallinity of the matrix, with cellulose particles probably acting as a nucleating agent. The nucleating effect is mainly governed by the surface characteristics, whereas unmodified whiskers have the largest nucleation effect [77].

4.3 Microfibrillated Cellulose

Wood pulp is disintegrated by applying high shear force for the preparation of microfibrillated cellulose (MFC). The fibers are moderately degraded and opened into their substructural fibrils and microfibrils [78]. The fibrils and fibril aggregates are highly entangled, inherently connected, and form mechanically strong networks and gels. The inherent interactions result in much stronger gels than those formed only by weak hydrogen bonds between water and fibrils. Various pretreatments, such as mild carboxymethylation, enable MFC to be obtained by a less energy-consuming shearing [79]. Subsequent ultrasound results in smaller and charged MFC. The combination of mild enzymatic hydrolysis with high-pressure shear forces can be used as an additional method for the preparation of MFC with controlled diameter in the nanoscale range. Mercerization can also be an appropriate treatment [80].

MFC can be used to produce patterned surfaces using lithographic techniques [81]. In these cases, MFC improves homogeneity and stability, which is important in various applications. Microcontact printing of oppositely charged poly(ethylene imine) (PEI) on a surface of PEI/poly(styrene sulfonate) followed by MFC treatment (Fig. 14a), or on a PEI-coated poly(dimethyl siloxane) stamp, produces geometric patterns (Fig. 14b). Such surfaces can be used in the development of membranes and filters because the pore geometry and size can be controlled by selection of the appropriate microstamp pattern.

MFC can be chemically modified with different reagents, including *N*-octadecyl isocyanate and others that enable combination with synthetic polymers and produce precursor materials for film casting [82]. Charged groups, reactive vinyl moieties, and polymer chains can be installed on the surface of MFC via treatment with maleic anhydride, glycidyl methacrylate, and succinic anhydride [83]. Hydrophobization via acetylation, silanization, and carboxymethylation as well as corona or

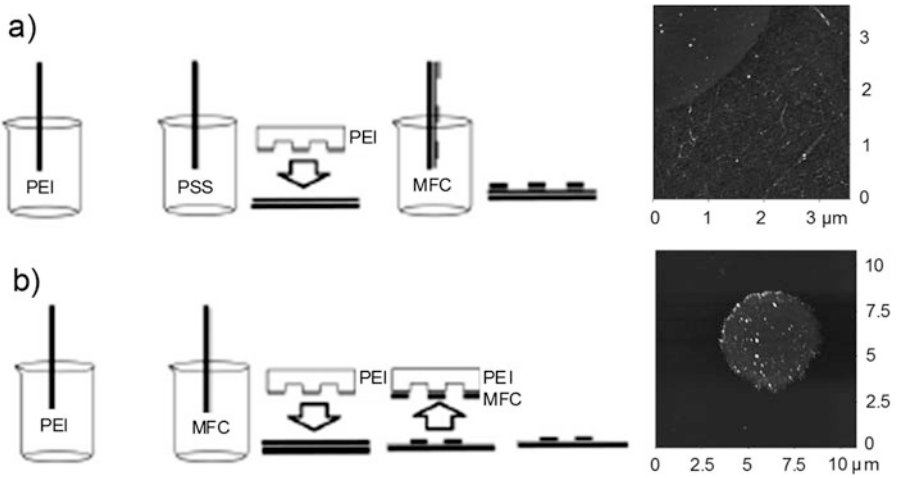

Fig. 14 (**a**) Selective adhesion technique using poly(ethylene imine) (*PEI*) and poly(styrene sulfonate) (*PSS*) to pattern microfibrillated cellulose (*MFC*). (**b**) Lift-off technique, where MFC is partially removed by a PEI-modified stamp. Representative atomic force micrographs are also included (reproduced from Werner et al. [81], copyright 2008 with permission from Royal Society of Chemistry)

plasma treatment can be used to adapt microfibrillated cellulose for given applications [84–88], including oil-in-water emulsions and others.

5 Bottom-up Approaches to Nanostructures of Cellulose

5.1 Electrospinning of Cellulose and Cellulose Derivatives

The electrospinning technique is widely used for the production of nanofibers, which opens a route for production of materials with high effective surface areas [89]. Nanofibers can be produced from different polymers and have applications in various fields, namely biomedicine, composites, filters, catalysts, and textiles [90–92]. Nanofibers regulate water vapor and wind permeability and can improve the thermal isolation of textiles. Moreover, they can possess special properties such as aerosol-filtration, binding of chemical and biological contaminants, or improved surfactant release [93]. Air cleaning of contaminated environments is a typical example of their application [94].

Cellulose dissolved in DMA/LiCl, *N*-methylmorpholine-*N*-oxide (NMMNO) [95], ionic liquids (e.g., BMIMCl) [96], or sodium hydroxide/water/urea [97] can be transferred to nanofibers of different morphology by electrospinning.

Although electrospinning of polyelectrolytes from aqueous solutions is not successful in the majority of cases, water-soluble and bioactive nanofibers of

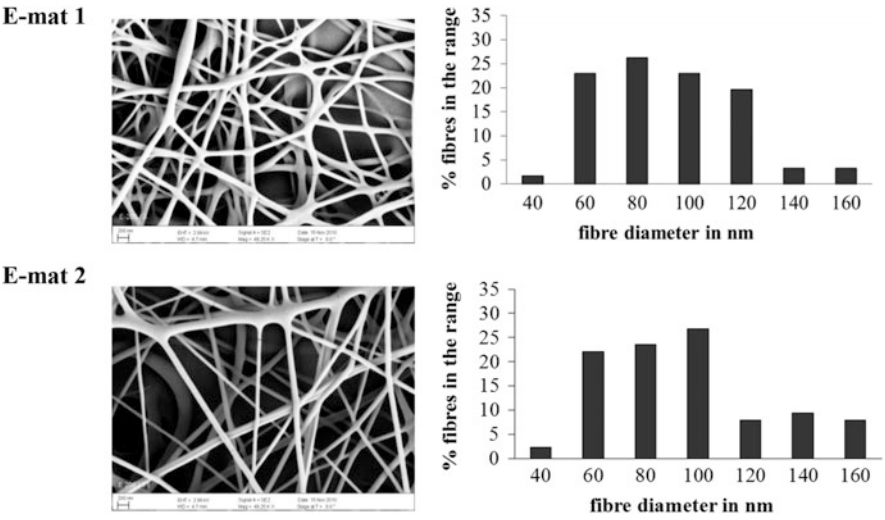

Fig. 15 Scanning electron micrographs of the nanofiber webs of 6-deoxy-6-trisaminoethylamino cellulose/polyvinyl alcohol in the ratio 1:15 (*E-mat 1*) and TEAE cellulose/PVA at 1:18 (*E-mat 2*)

amino cellulose can be prepared using blended solutions of a typical amino cellulose, 6-deoxy-6-trisaminoethyl-amino (TEAE) cellulose, and polyvinyl alcohol (PVA), as shown in Fig. 15. The nanofibers show high antimicrobial activity against *Staphylococcus aureus* and *Klebsiella pneumoniae* [98].

5.2 Nanospheres

Nanoscaled particles can be obtained from different cellulose esters, including commercially available cellulose acetates, cellulose acetate propionate, and cellulose acetate butyrate, and also from some organo-soluble cellulose ethers. Methods commonly used are emulsification solvent evaporation and the low-energy method of solvent displacement by dialysis, inducing nanoprecipitation [99]. Comparing the methods, a large amount of small and uniform nanoparticles can be obtained by the emulsification solvent evaporation procedure, whereas solvent displacement yields narrowly distributed particles. Typical particles obtained from cellulose acetate are shown in Fig. 16 [100]. Dialysis is easy to use and therefore appropriate for laboratory-scale studies. Moreover, very pure suspensions of the nanoparticles can be obtained.

It is important to point out that even spherical nanoparticles of polymers containing hydrophilic moieties such as 6-deoxy-6-(ω-aminoalkyl)aminocellulose-carbamates can be prepared. Such nanoparticles are of particular interest because they possess primary amino groups that can be more easily modified than OH moieties. Thus, labeling with rhodamine B isothiocyanate is simple and does not

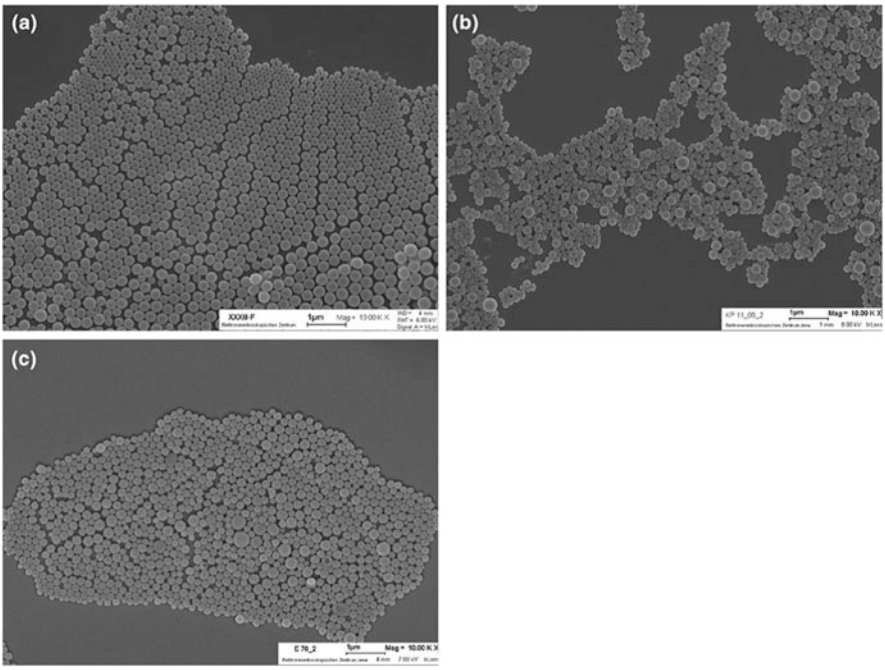

Fig. 16 Field-emission scanning electron micrographs of nanoparticles prepared by (**a**) emulsification–evaporation of cellulose triacetate (CTA) (150 W, 10 s, cW 25 mg/mL), (**b**) by dialysis of CTA (cW 4 mg/mL), and (**c**) by dropping water into a solution of CA, DS 2.45 (cW 6 mg/mL, V(H_2O) 70 mL, rate 10 mL/min)

change the size, stability, or shape of the nanoparticles. Incorporation of such nanoparticles into human foreskin fibroblasts BJ-1-htert and breast carcinoma MCF-7 cells could be successfully carried out without any transfection reagent [101].

Although an organo-soluble cellulose derivative must be used for the technique of nanoprecipitation, even pure cellulose nanoparticles can be prepared. Using trimethylsilyl cellulose (TMSC), the formation of nanoparticles by dialysis of the organic solvent against water is accompanied by complete removal of the TMS functions. Analysis of particle size distribution shows that cellulose particles with a size of 80–260 nm are accessible in this simple manner [102]. Aqueous suspensions of the pure, spherical cellulose nanoparticles are storable for several months without any demixing. Covalent labeling of the cellulose nanoparticles with FITC has no influence on particle size, shape, and stability. The particles can be sterilized and suspended in biological media without structural changes. As can be seen in Fig. 17, FITC-labeled cellulose nanoparticles can penetrate into living human fibroblasts by endocytosis without transfection reagents or attachment of a receptor molecule, as shown by means of confocal laser scanning microscopy [103].

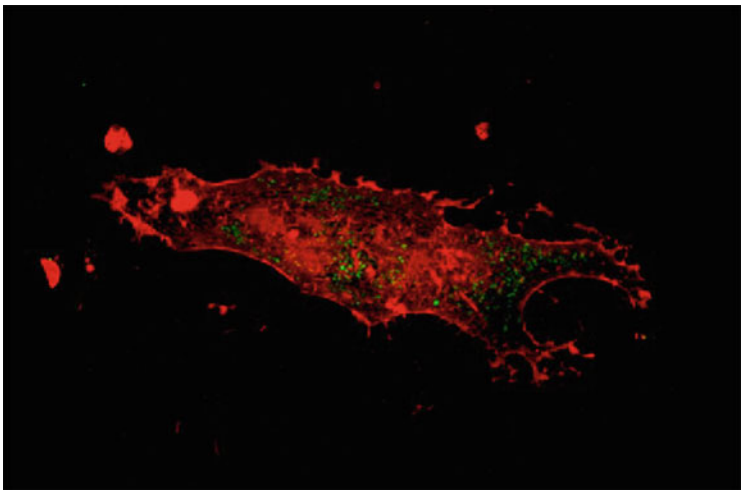

Fig. 17 Confocal micrograph overlay of 21 stacks of human fibroblasts (*red* cell membrane) incubated with FITC-labeled cellulose nanoparticles

6 Solubility of Cellulose

As a result of the extended hydrogen bonds between the cellulose chains, special media and procedures must be applied to dissolve cellulose. Today, solvents are divided into derivatizing solvents (forming covalent bonds of low stability with the polymer) and nonderivatizing solvents (interacting only physically with the polymer). At the industrial scale, cellulose nitrate as a soluble and, thus, formable cellulose derivative can be used. It should be pointed out that cellulose nitrate is a relatively stable cellulose derivative so introduction of ester moieties for "derivatizing dissolution" is somewhat questionable, although regeneration is easy to achieve. The invention of a mixture of copper(II) hydroxide and aqueous ammonia for dissolving cellulose, with subsequent precipitation in dilute sulfuric acid, was followed by probably the most important large-scale technical process in fiber production, the viscose process. Cellulose is transformed into cellulose xanthogenate, with subsequent spinning of the solution in aqueous sodium hydroxide. The Lyocell process is an environmentally friendly alternative to the viscose process, whereby cellulose is dissolved physically in *N*-methylmorpholine-*N*-oxide monohydrate and regenerated in water [104].

The majority of cellulose solvents known today are only applied at the laboratory scale although there are some semitechnical trials being carried out for fiber spinning using novel solvents such as ionic liquids (ILs). Until now there has been no homogeneous chemical modification carried out at technical scales.

6.1 Polar Aprotic Solvents in Combination with Electrolytes

Binary mixtures of organic liquids and inorganic or organic electrolytes are the most-used solvents for cellulose. Typical examples are *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidinone, 1,3-dimethyl-2-imidazolidinone in combination with LiCl, and DMSO with tetra-*n*-butylammonium fluoride × $3H_2O$ [105].

In these solvents, there are ions that can efficiently interact with hydrogen bonds and liquids that can solvate polar polymers such as cellulose. The essential factors required for dissolution of cellulose include:

1. Solubility of a sufficient amount of electrolyte in the organic liquid
2. Adequate stability of the electrolyte/solvent complex
3. Cooperative action of the solvated ion-pair on cellulose hydrogen bonds
4. Sufficient basicity of the anion [106]

For example, to obtain a 3 wt% solution of cellulose in DMAc requires about 4 wt% LiCl, whereas 10 wt% LiCl is needed to dissolve it in DMF. This agrees with the fact that LiCl forms a stronger complex with the former solvent [107]. By contrast, NaCl is not appropriate because it is insoluble in DMAc and DMF. The strength of cation–solvent association of alkali metal chlorides in DMAc and DMF is in the order $Li^+ > Na^+ > K^+ > Cs^+$(as determined by electrospray ionization mass spectroscopy). For LiCl, the strength of cation–solvent association is in the order *N*,*N*-dimethylpropionamide > DMAc ≫ DMF. That is, the association increases as a function of increasing negative charge on the oxygen atom of the C=O group of the solvent [108, 109]. For DMAc, LiCl is more efficient than LiBr for dissolving cellulose, because the later halide ion is less basic than the former.

In general, to design new solvents of this type, the requirements mentioned must be fulfilled. Thus, it was found that quaternary tetraalkylammonium chlorides with one long alkyl chain dissolve in various organic solvents and constitute a new class of cellulose solvents. In contrast to the well-established solvent DMAc/LiCl, cellulose dissolves in DMA/quaternary ammonium chlorides without any pretreatment (Fig. 18). Consequently, use of the new solvent avoids some of the disadvantages of DMAc/LiCl [110].

Highly surprising is the finding that cellulose dissolves quickly even in a mixture of acetone/triethyloctylammonium chloride containing 9 parts of the salt and 20 parts of the organic liquid. No pretreatment or activation of the cellulose is necessary. This has not yet been reported for binary acetone/salt mixtures, including ILs, where acetone has been found to cause immediate cellulose precipitation [111]. Further increase in the amount of triethyloctylammonium chloride does not have an adverse effect on the solution. The ^{13}C-NMR spectrum measured for cellulose dissolved in acetone/triethyloctylammonium chloride verifies that the biopolymer is dissolved without being chemically modified (nonderivatizing solvent) as is the case for all solvents of this class (Fig. 19). Nevertheless, the solvent LiCl/DMAc is still the most extensively employed because it is capable of

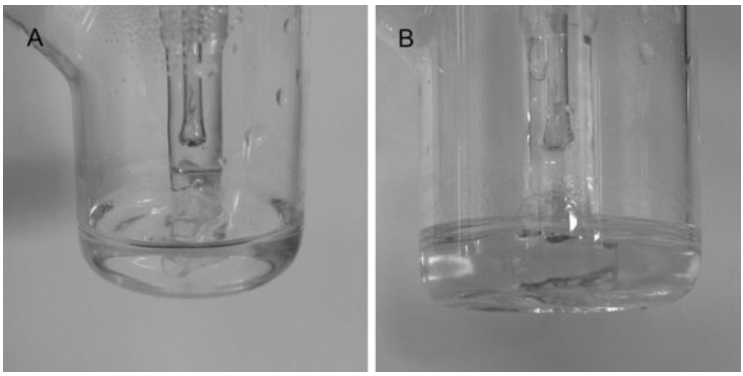

Fig. 18 Cellulose dissolved in *N,N*-dimethylacetamide/triethyloctylammonium chloride after dissolution (**a**) and after 24 h (**b**)

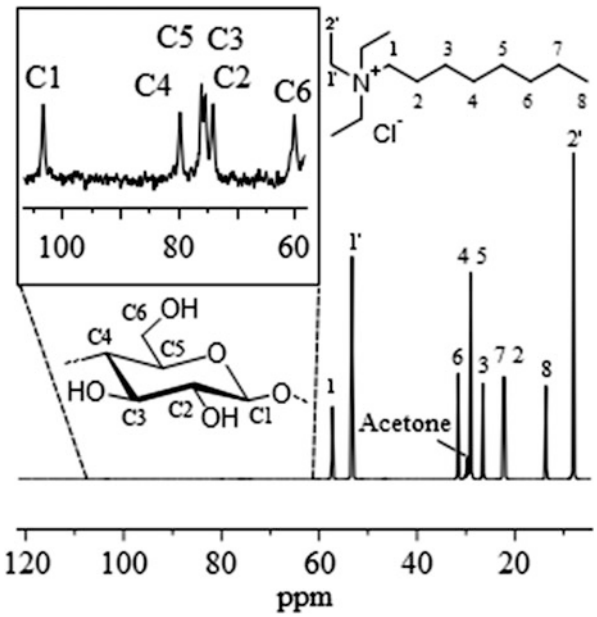

Fig. 19 ^{13}C-NMR spectrum (100 MHz, acetone-d_6) of cellulose in acetone-d_6/triethyloctylammonium chloride

dissolving different celluloses, including samples of high DP and index of crystallinity (e.g., cotton linters and even bacterial cellulose).

The combination of DMSO and tetra-*n*-butyl ammonium fluoride $\times$ $3H_2O$ (TBAF $\times$ $3H_2O$, premixed) dissolves cellulose very efficiently without any pretreatment as a result of the fact that the fluoride ion is a harder base than the chloride ion (LiCl/DMAc). Furthermore, the cation is voluminous and hence acts as

a "spacer," preventing re-attachment [105, 112]. For instance, clear solutions of microcrystalline cellulose were obtained in 15 min at room temperature, whereas fibrous sisal required 30 min at room temperature plus 60 min at 60°C [113].

The commercially available, stable TBAF contains 3 mole of water. The water may influence the chemical modification of dissolved cellulose because of hydrolysis of the reagent. However, the cellulose solution can be partially dehydrated by distilling off about 30% of the solvent before addition of the reagent (e.g., acetic anhydride). The esterification yields products of higher degree of substitution (DS) [113].

Complete dehydration of TBAF × $3H_2O$, resulting in the water-free salt, is impossible because anhydrous TBAF is unstable and undergoes rapid E2 elimination, resulting in the formation of hydrogen difluoride anions [114]. However, preparation of anhydrous TBAF in situ by reacting tetra-*n*-butylammonium cyanide with hexafluorobenzene in dry DMSO has been described [115]. Freshly prepared water-free DMSO/TBAF solution, even in the presence of the by-product hexacyanobenzene, dissolves cellulose very easily. In the water-free solvent, dissolution of bleached cotton fibers with very high DP of 3,743 occurs within a short time, as visualized by optical microscopy (Fig. 20, [116]).

Other ammonium salts have been studied as electrolytes in DMSO-based cellulose solvents, namely tetramethylammonium fluoride (TMAF) and benzyltrimethylammonium fluoride monohydrate (BTMAF × H_2O). At room temperature, 0.94 mol/L TBAF × $3H_2O$ could be dissolved in DMSO, but only 0.025 mol/L of

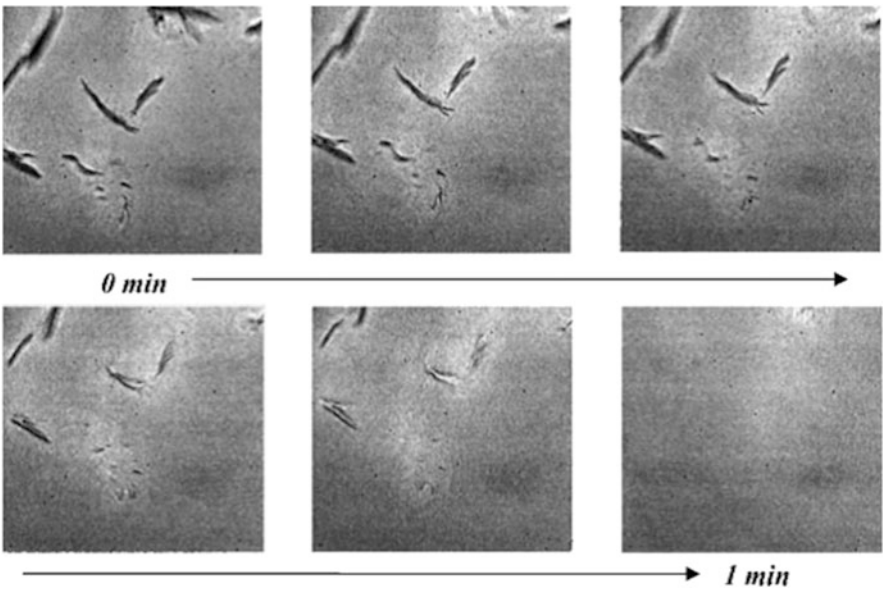

Fig. 20 Optical micrographs showing the dissolution of bleached cotton fibers in dimethyl sulfoxide/water-free tetrabutylammonium fluoride (10 wt%) at 35°C

BTMAF × H_2O dissolves at room temperature, and 0.142 mol/L at 90°C. TMAF is insoluble in DMSO.

Up to 1 wt% of cellulose is soluble in DMSO/BTMAF × H_2O by heating the system to 85°C to maintain an adequate fluoride ion concentration. A minimal amount of 2.2 fluoride ions per AGU is needed. In the case of TBAF × $3H_2O$, the relation between the fluoride ions and AGU depends on the DP of the cellulose (as also known for DMAc/LiCl). Thus, for microcrystalline cellulose (Avicel, DP 332) a ratio of 1:1 (salt/cellulose) is appropriate, whereas for spruce sulfite pulp (DP 600) and cotton linters (DP 1,198) a ratio of 3:1 is needed.

These results again substantiate the simple approach mentioned above for creation of new solvents for cellulose. Following such an approach, another solvent was found very recently; almost anhydrous dibenzyldimethylammonium (BMAF × $0.1H_2O$) in DMSO dissolves microcrystalline and fibrous celluloses [117].

It should be pointed out that clear cellulose solutions are not necessarily molecularly dispersed, but may contain aggregates of still-ordered cellulose molecules [118]. These aggregates were described as forming a "fringed" micellar structure (Fig. 21a) composed of laterally aligned chains, forming a rather compact and possibly geometrically anisotropic core that is immiscible in the solvent. The solvated amorphous cellulose chains form "coronas" at both ends of the particles [119]. The thickness of the coronas and the number of molecular chains forming the aggregate increase as a function of both cellulose concentration and the interfacial tension between the solvent and particle core [120]. Monodisperse solutions of cellulose molecules with small (Fig. 21b), and large (Fig. 21c) DP produced typical features. The length of the short cellulose chain is practically equal to its persistent length, (i.e., there is neither chain coiling nor interaction with other chains). The flexibility of the long chain polymer allows the formation of strong intramolecular hydrogen bonds, provided that the OH groups reside for some time within a "critical

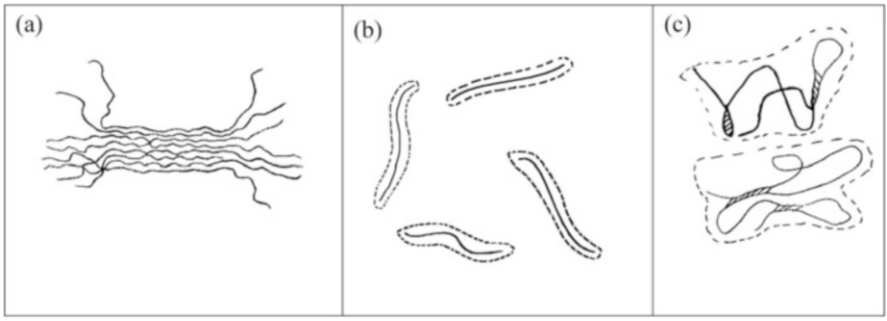

Fig. 21 Cellulose structures in solution: (**a**) "fringed" micellar structure, (**b**, **c**) possible chain conformations of celluloses of different DP. Intramolecular hydrogen bonding is possible for high molecular weight cellulose (**c**)

distance" of each other (ca. 0.3 nm), sufficient for van der Waals forces to operate (Fig. 21c) [121]. As a result, the properties of cellulose (DP, crystallinity, and concentration) affect its solution state and, hence, its derivatization. For the same cellulose, the accessibility of the OH groups increases with decreasing solution concentration. For different celluloses, at a given concentration, only the outer surface of the fringed micellar core is accessible and the area of this part decreases with DP and crystallinity.

Regarding chemical modification, molecularly dispersed solutions are not needed. Moreover, as a result of the change in structure of the cellulose derivative compared with the starting material, and considering the DS, the different structures formed during the course of reaction have different interactions with the solvent components. In some cases the reaction systems can become microheterogeneous, and possibly even complete gelation or precipitation can occur.

6.2 Ionic Liquids

The first ionic liquids (ILs) used for esterification of cellulose were *N*-alkylpyridinium halides, especially *N*-ethylpyridinium chloride (EPyCl) and *N*-benzylpyridinium chloride (BPyCl) [122]. Nevertheless, the most promising ILs for the modification of cellulose are the salts of 1-alkyl-3-methylimidazolium. In 2002, it was shown that such ILs could open new paths for the shaping of polysaccharides [123, 124]. Additionally, they could lead to commercially relevant routes toward homogeneous cellulose chemistry, which would significantly broaden the number of tailored cellulose derivatives. Meanwhile, a huge number of cellulose-dissolving ILs are now known and discussed in various recent reviews (e.g., [125] and references cited therein), and the number of reported low melting organic salts is growing rapidly (Fig. 22). Nevertheless, according to the literature [126, 127] and our own experience, cellulose can be dissolved in ILs with imidazolium, ammonium, and pyridinium. Only organic salts with asymmetric cations give melts that can interact with the backbone of cellulose. Neither sulfonium nor phosphonium salts have so far been able to dissolve cellulose. Dissolution of cellulose in pyridinium salts must be performed under protective gas otherwise degradation results [128]

1-Ethyl-3-methylimidazolium acetate (EMIMAc) ILs have the advantage of not having a reactive side group, such as the unsaturated function of the 1-allyl-3-methylimidazolium (AMIM) ion. Moreover, EMIMAc is considered to be nontoxic, noncorrosive, and even biodegradable. However, EMIMAc reacts with the reducing end groups of cellodextrins, according to the formula depicted in Fig. 23, giving a hemiacetal-type structure [129–131].

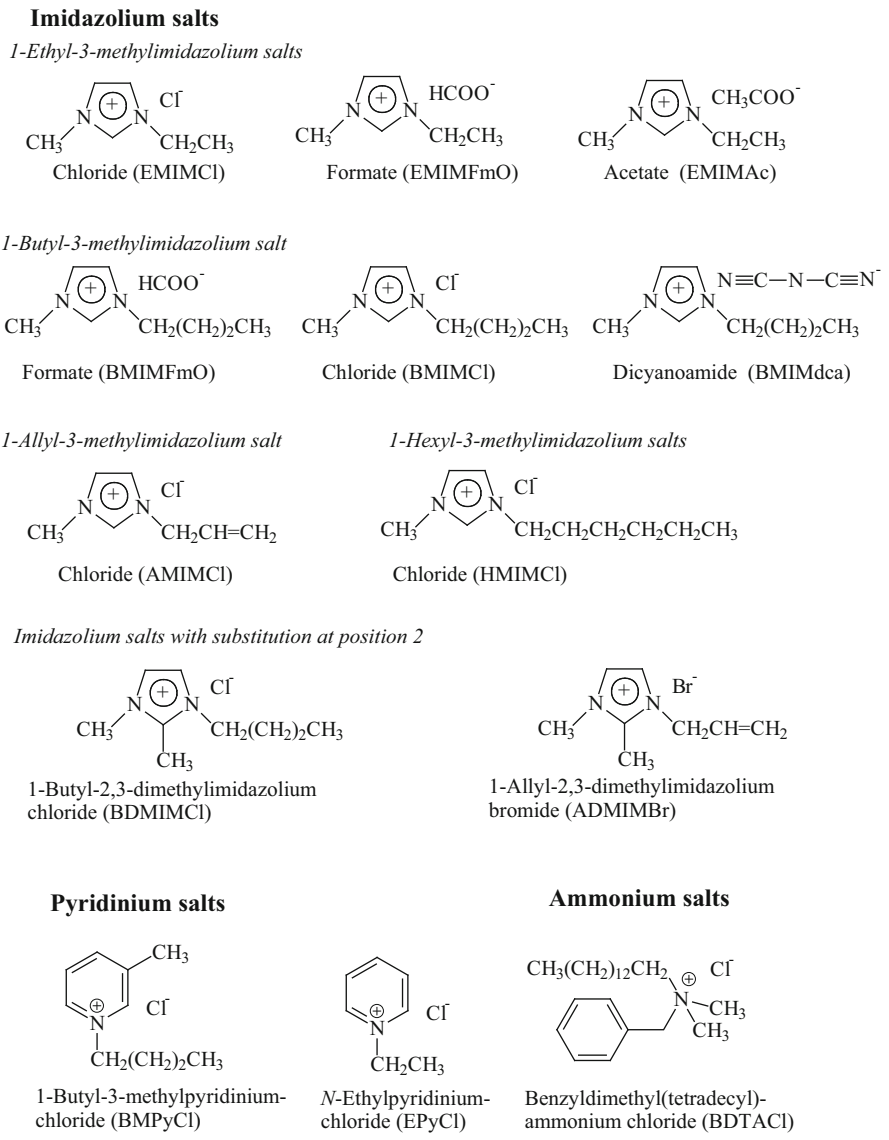

Fig. 22 Examples of ionic liquids suitable for dissolving cellulose

The dissolution mechanism is still the subject of ongoing research. 1-Alkyl-3-methylimidazolium-based ILs yield clear solutions after 15 min without activation of the cellulose. The solubility of cellulose in such ILs is directly related to the length of the alkyl chain. But, the solubility does not regularly decrease with increasing length of the alkyl chain. An odd–even effect was determined for short alkyl chains [132].

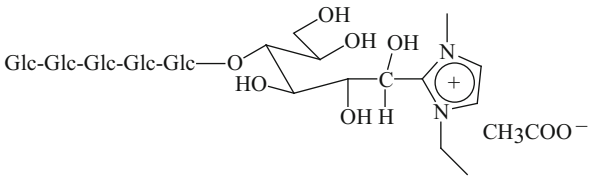

Fig. 23 Structure proposed for conversion of the reducing end group of cellodextrins with 1-ethyl-3-methylimidazolium acetate

Although there is a very high potential for a commercial application of ILs, it is clearly obvious that ILs also possess various disadvantages and further research and development is needed.

6.3 Aqueous Alkali (Base)-Containing Solvents

Mercerization, the treatment of cellulose with aqueous solution of bases such as NaOH, is one of the most important processes prior to cellulose etherification. The phase diagram established by Sobue et al. suggests that there is a dissolution zone of cellulose in aqueous NaOH at a concentration of 7–10% at temperatures below 268 K (Fig. 24, [133]).

Complete dissolution of microcrystalline cellulose in aqueous NaOH is possible [134]. However, linters cellulose had limited solubility (26–37%) applying the same procedure. Kamide and coworkers have applied steam explosion treatments in order to dissolve pulp directly in NaOH [135–139]. In technical papers, they claim that a solution of 5% of steam-exploded cellulose in 9.1% NaOH at 4°C, spun into 20% H_2SO_4 at 5°C, yielded fibers but of poor quality.

Recently, the dissolution and modification of cellulose in mixtures of an aqueous base with urea and thiourea has been the focus of interest [140–143]. Cellulose can be dissolved in an aqueous solution of NaOH (7 wt%)/urea (12 wt%). Starting from a precooled mixture at −12°C, cellulose dissolves within 2 min. The urea hydrates could possibly be self-assembled at the surface of the NaOH hydrogen-bonded cellulose [144]. The solutions are rather unstable and sensitive to temperature, polymer concentration, and storage time [145, 146]. Alternatives include LiOH/urea [147, 148] and NaOH/thiourea [149]. TEM images and wide-angle X-ray diffraction (WAXD) provide experimental evidence for the formation of a worm-like cellulose inclusion complex surrounded by urea (Fig. 25).

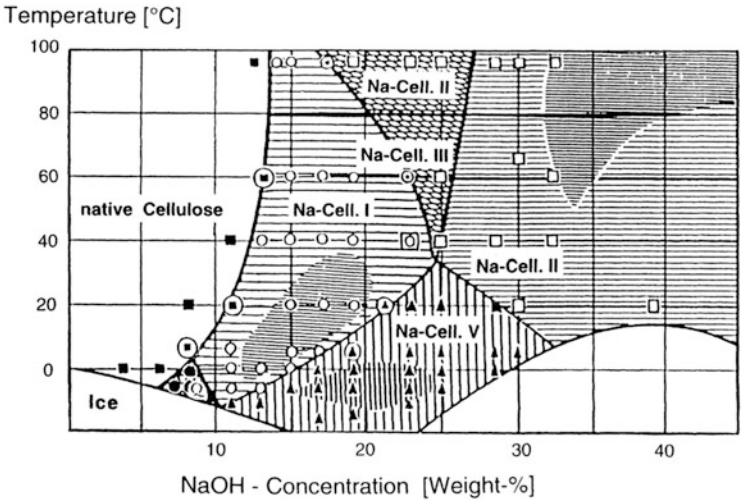

Fig. 24 Phase diagram of ternary cellulose/NaOH/water system

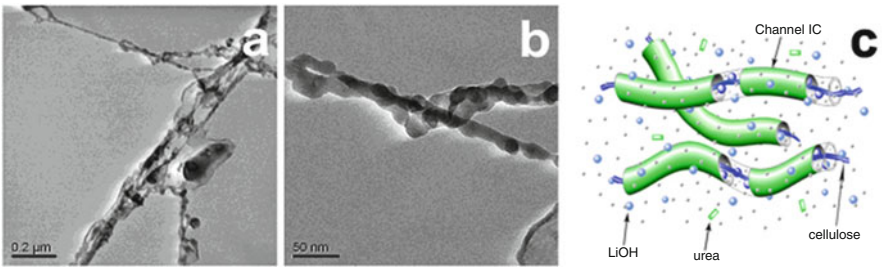

Fig. 25 (**a**, **b**) Transmission electron micrographs of cellulose at concentration of 4.0×10^{-4} g mL^{-1} in aqueous 4.6 wt% LiOH/15 wt% urea. (**c**) Model of inclusion complex

7 Chemical Reactivity

Glucan cellulose was used as a precursor for chemical modification even before its polymeric nature was accepted and well understood. The reactive groups are the hydroxyl moieties. Cellulose nitrate (misnomer, nitrocellulose) of high nitrogen content was an important explosive. Partially nitrated cellulose ester was used as a "plastic" (trade name Celluloid) and is still produced commercially [150]. Methyl-, ethyl-, and hydroxyalkyl ethers as well as cellulose acetate are cellulose products that remain important even decades after their discovery. The same applies to other cellulose products carrying a variety of functional groups, such as ethylhydroxyethyl and hydroxypropylmethyl cellulose, acetopropionates, acetobutyrates, and acetophthalates. Ionic cellulose ethers were introduced a long

time ago and commercial production of the most important ionic cellulose ether, carboxymethyl cellulose (CMC), began in the 1920s [151].

The preparation of commercial cellulose derivatives is exclusively carried out under heterogeneous reaction conditions. In the case of acetylation, the cellulose acetate formed may dissolve during the course of reaction, thus it is not considered a homogeneous reaction.

However, the dissolution of cellulose *prior* to chemical reaction offers a great opportunity for the design of novel and unconventional cellulose derivatives by homogeneous phase chemistry. For homogeneous phase chemistry, either nonderivatizing or derivatizing solvents can be used. In the case of derivatizing solvents, both conversion of the soluble intermediate formed during dissolution and modification of the isolated intermediate (which is re-dissolved in an organic solvent such as DMSO or DMF) are considered homogeneous reactions. By contrast, neither chemical modification of soluble but "stable" cellulose derivatives such as cellulose acetate in DMSO nor chemical modification of cellulose under dissolution of the cellulose derivative formed (as a result of the conversion) are included in the context of homogeneous phase chemistry. In the following section, the synthesis of some cellulose derivatives is discussed.

7.1 Homogeneous Modification of Cellulose

7.1.1 Acylation of Cellulose

Although a wide variety of solvents for cellulose have been developed and investigated in recent years, only a few have shown the potential for controlled and homogeneous functionalization of the polysaccharide (Table 1) [157]. Limitations to the application of solvents result from high toxicity, high reactivity of the solvents leading to undesired side reactions, and loss of solubility during reactions. The latter results in inhomogeneous mixtures through formation of gels and pastes,

Table 1 Solvents and reagents exploited for the homogeneous acetylation of cellulose

Solvent	Acetylating reagent	DS_{max}[a]	Reference
N-Ethylpyridinium chloride	Acetic anhydride	Up to 3	[122]
1-Allyl-3-methyl-imidazolium chloride	Acetic anhydride	2.7	[152]
N-Methylmorpholine-*N*-oxide	Vinyl acetate	0.3	[153]
DMAc/LiCl	Acetic anhydride	Up to 3	[154, 155]
	Acetyl chloride	Up to 3	
DMI/LiCl	Acetic anhydride	1.4	[156]
DMSO/TBAF	Vinyl acetate	2.7	[105, 113]
	Acetic anhydride	1.2	

DMAc *N*,*N*-Dimethylacetamide, *DMI* 1,3-dimethyl-2-imidazolidinone, *DMSO* dimethyl sulfoxide, *TBAF* tetra-*n*-butylammoniumfluoride trihydrate

[a]Maximum degree of substitution

which are difficult to mix, and even through formation of de-swollen particles of low reactivity, which settle out in the reaction medium.

Homogeneous reaction conditions give the opportunity for esterification with state of the art reagents, for example, after in situ activation of carboxylic acids, which is characterized by reacting the carboxylic acid with a reagent to form an intermediate, highly reactive carboxylic acid derivative. The carboxylic acid derivative can be formed prior to reaction with the polysaccharide or converted directly in a one-pot reaction. Modification of cellulose with carboxylic acids after in situ activation has made a broad variety of new esters accessible, because common reactive derivatives such as anhydrides or chlorides are not accessible for numerous acids (e.g., unsaturated or hydrolytically instable acids). The mild reaction conditions applied for in situ activation avoids side reactions such as pericyclic reactions, hydrolysis, and oxidation [158]. For example, a reaction with enormous potential for cellulose modification is the homogeneous one-pot reaction after in situ activation of carboxylic acids with *N*,*N*′-carbonyldiimidazole (CDI), which has been well known in bioorganic chemistry since 1962 [159]. The reactive imidazolide of the acid is generated, and the by-products CO_2 and imidazole are nontoxic (Fig. 26). The pH is almost constant during the conversion, resulting in negligible chain degradation. In comparison to dicyclohexylcarbodiimide (DCC), the application of CDI is much more efficient, avoids most of the side reactions, and allows the use of DMSO (a good solvent for most complex carboxylic acids).

7.1.2 Sulfation of Cellulose

Although studied for decades, sulfation of cellulose is still of interest because the products show pronounced bioactivity and can be used for self-assembly systems such as polyelectrolyte complexes. A very elegant method offers the sulfation of cellulose dissolved in ILs. Cellulose dissolved in BMIMCl/co-solvent mixtures can be easily converted into cellulose sulfate (CS) by using SO_3-Py, SO_3-DMF, or $ClSO_3H$ [160]. Highly substituted CS with DS values up to 3 has been reported for sulfation in BMIMCl at 30°C [161]; however, it should be noted that cellulose/IL solutions slowly turned solid upon cooling to room temperature, depending on the cellulose and moisture content. Synthesis of CS with an even distribution of sulfate groups along the polymer chains requires a dipolar aprotic co-solvent that drastically reduces the solution viscosity and does not significantly influence the reactivity of the sulfating agent [162]. At a 2:1 molar ratio of SO_3-DMF/AGU, the sulfation of microcrystalline cellulose in BMIMCl and BMIMCl/DMF mixtures leads to comparable DS values of about 0.86. Whereas CS synthesized without co-solvent is insoluble, the other readily dissolves in water.

Homogeneous sulfation of cellulose in IL allows tuning of CS properties simply by adjusting the amount of sulfating agent and choosing different types of cellulose. If conducted at room temperature, the reaction leads only to minor polymer degradation. This makes the procedure valuable for the preparation of water-soluble CS over a wide DS range. In particular, capsules of CS with low DS can

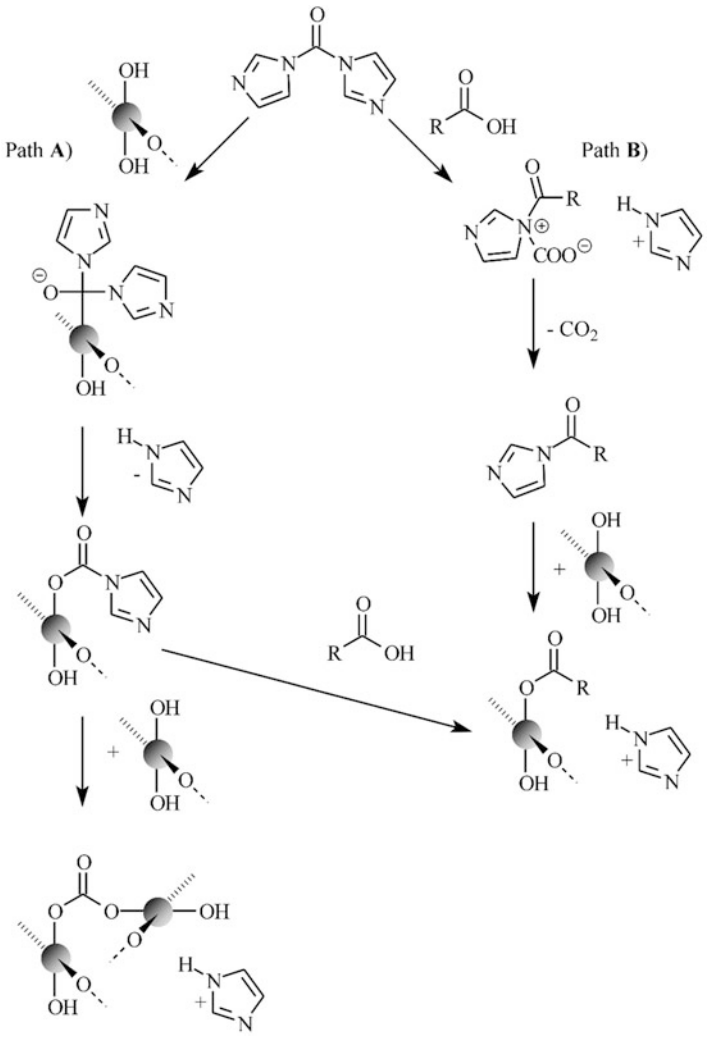

Fig. 26 Mechanism of activation of carboxylic acids with *N*,*N*′-carbonyldiimidazole

be prepared efficiently in IL/co-solvent mixtures and are of interest for bioencapsulation applications [162].

7.1.3 Structural Design of Cellulose by Nucleophilic Displacement Reactions

In addition to typical modification of the hydroxyl groups of cellulose, chemical modification can be carried out by reaction at the C atoms of the AGU. Nucleophilic displacement (S_N) reactions with cellulose are based on the transformation of

Table 2 Typical products of nucleophilic displacement reactions of cellulose tosylate

Reagent	Product	Reference
$Na_2S_2O_3$	6-Deoxy-6-*S*-thiosulfato cellulose	[165]
$NaSCH_3$,	6-Deoxy-6-thiomethyl-2,3-di-carboxymethyl cellulose	[166]
$NaSO_3$	Sodium deoxysulfate-*co*-tosylate cellulose	[167, 168]
NaN_3	6-Deoxy-6-azido cellulose	[169]
Iminodiacetic acid	6-Deoxy-6-iminodiacetic acid cellulose sodium salt	[170]
Triethylamine	6-Deoxy-6-triethylammonium cellulose	[171]
N,*N*-Dimethyl-1,3-diaminopropane	6-Deoxy-6-(*N*,*N*-dimethyl-3-aminopropyl)ammonium cellulose	[171]
2,4,6-Tris(*N*,*N*-dimethylaminomethyl)phenol	6-Deoxy-6-(2,6-di(*N*,*N*-dimethylaminomethyl)phenol)-4-methyl-*N*,*N*-dimethylamino cellulose	[171]
R(+)-, *S*(−)-, and racemic 1-phenylethylamine	6-Deoxy-6-(1-phenylethyl)amino cellulose	[172]
Aminomethane	6-Deoxy-6-methylamino cellulose	[173]

hydroxyl groups of the biopolymer to a good leaving group, mainly by tosylation [163, 164]. A broad variety of cellulose derivatives are accessible, as summarized in Table 2. The S_N reaction occurs almost exclusively at the primary position of the repeating unit, most probably for steric reasons. The S_N of a tosylate moiety occurs via a S_N2 mechanism (i.e., a transition state appears containing five atoms that is hardly formed at the secondary positions of the modified AGU).

7.2 Amino Cellulose

Conversion of cellulose tosylate with diamines or oligoamines yields polymers of the type P-CH_2-NH-(X)-NH_2 (P = cellulose; X = alkylene, aryl, aralkylene, or oligoamine) at position 6 (Fig. 27). These cellulose derivatives can form transparent films and can be used for the immobilization of enzymes such as glucose oxidase, peroxidase, and lactate oxidase. The products are useful as biosensors. Soluble and film-forming cellulose derivatives with redox–chromogenic and enzyme-immobilizing 1,4-phenylenediamine groups have been reported [174–178].

Thus, it is possible to design amino celluloses with properties that differ in, for example, the distance of the terminal NH_2 groups from the cellulose backbone (spacer effect), basicity, and reactivity. Moreover, di- and oligoamines provide different properties such as pH value and charge distribution, control of hydrophilic/lipophilic balance, and redox–chromogenic properties. Chromogenic properties (electron mediator) play an important role in the use of amino cellulose derivatives as transducers in the field of biosensors [179].

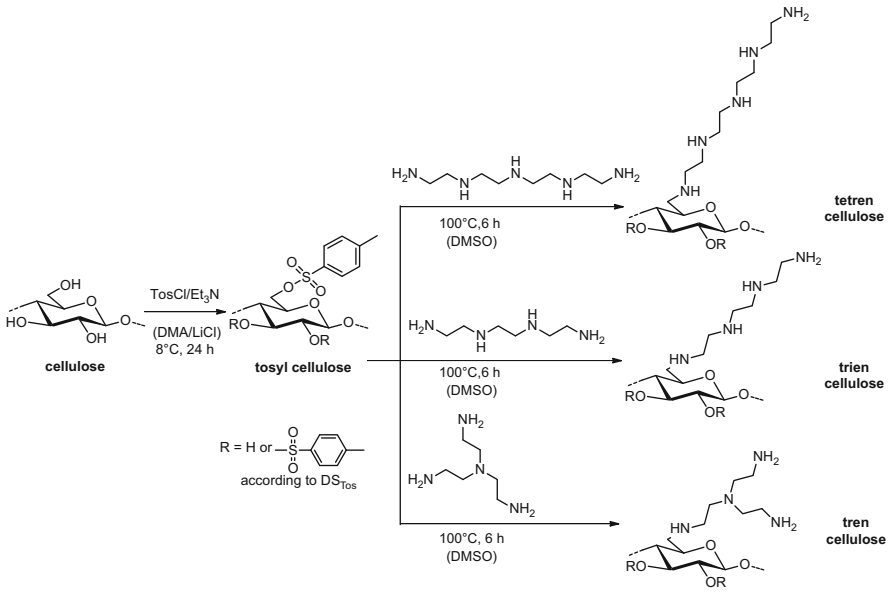

Fig. 27 Reaction path for the synthesis of 6-deoxy-6-amino cellulose ester derivatives by nucleophilic displacement of tosyl cellulose

Because of the multifunctionality of cellulose and the stability of tosylates, modification of the secondary OH groups prior to the S_N reaction can also be carried out to design the properties of the products. The OH groups at positions 2 and 3 are preferably esterified to adjust the properties, including the solubility of the polymer. Whereas amino celluloses possessing mainly OH groups at the secondary positions are water soluble, the additionally esterified polymer derivatives are soluble in organic solvents such as DMAc and can form nanoparticles (see Sect. 5.2).

6-Deoxy-6-amino cellulose forms multiple oligomeric species that were discovered using the hydrodynamic technique of analytical ultracentrifugation as a probe. For every amino cellulose studied, the sedimentation coefficient distributions indicate 4 or 5 discrete species, with a stepwise increase in sedimentation coefficient. This was found in every case across a range of six different solute loading concentrations (from 0.125 to 2.0 mg/mL). For example, the lowest sedimentation coefficient of 6-Deoxy-6-(2-(bis(2-aminoethyl)aminoethyl)amino) cellulose was 1.8 Svedberg (S). Additional species sedimenting at peak maxima of 2.8, 4.0, 5.1 and 6.5 S were also clearly found (Fig. 28).

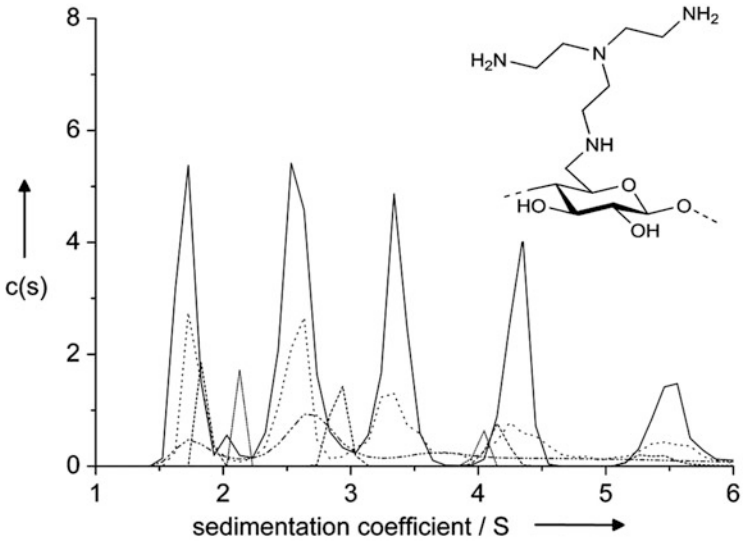

Fig. 28 Representative sedimentation coefficient distributions of 6-deoxy-6-(2-(bis(2-aminoethyl)aminoethyl)amino) cellulose $DS_{Amine} = 0.60$, at various concentrations: *solid* (——) 2.0 mg/mL; *dash* (– –) 1.0 mg/mL; *dot* (·····) 0.5 mg/mL; *dash dot* (– · – ·) 0.25 mg/mL; *short dot* (·····) 0.125 mg/mL. Sedimentation velocity patterns from the Rayleigh interference optical system of the Beckman XL-I ultracentrifuge were analyzed using the SEDFIT procedure of Schuck and Dam [180]. Sedimentation coefficients were extrapolated to zero concentration to correct for non-ideality effects [181]

It is obvious that even a fully reversible self-association (tetramerization) within this family of 6-deoxy-6-amino celluloses can occur (Fig. 29). Remarkably, these carbohydrate tetramers are then seen to associate further in a regular way into supramolecular complexes.

This behavior was found for the first time for carbohydrates, whereas it is well known for polypeptides and proteins such hemoglobin and its sickle cell mutation [182]. The large self-assembling cationic structures render them possible candidates for mimicking the properties of histones and using as condensing or packing agents in DNA-based therapies [183]. Most importantly, however, our traditional perceptions as to what is “protein-like” and what is “carbohydrate-like” behavior may need to be reconsidered [184].

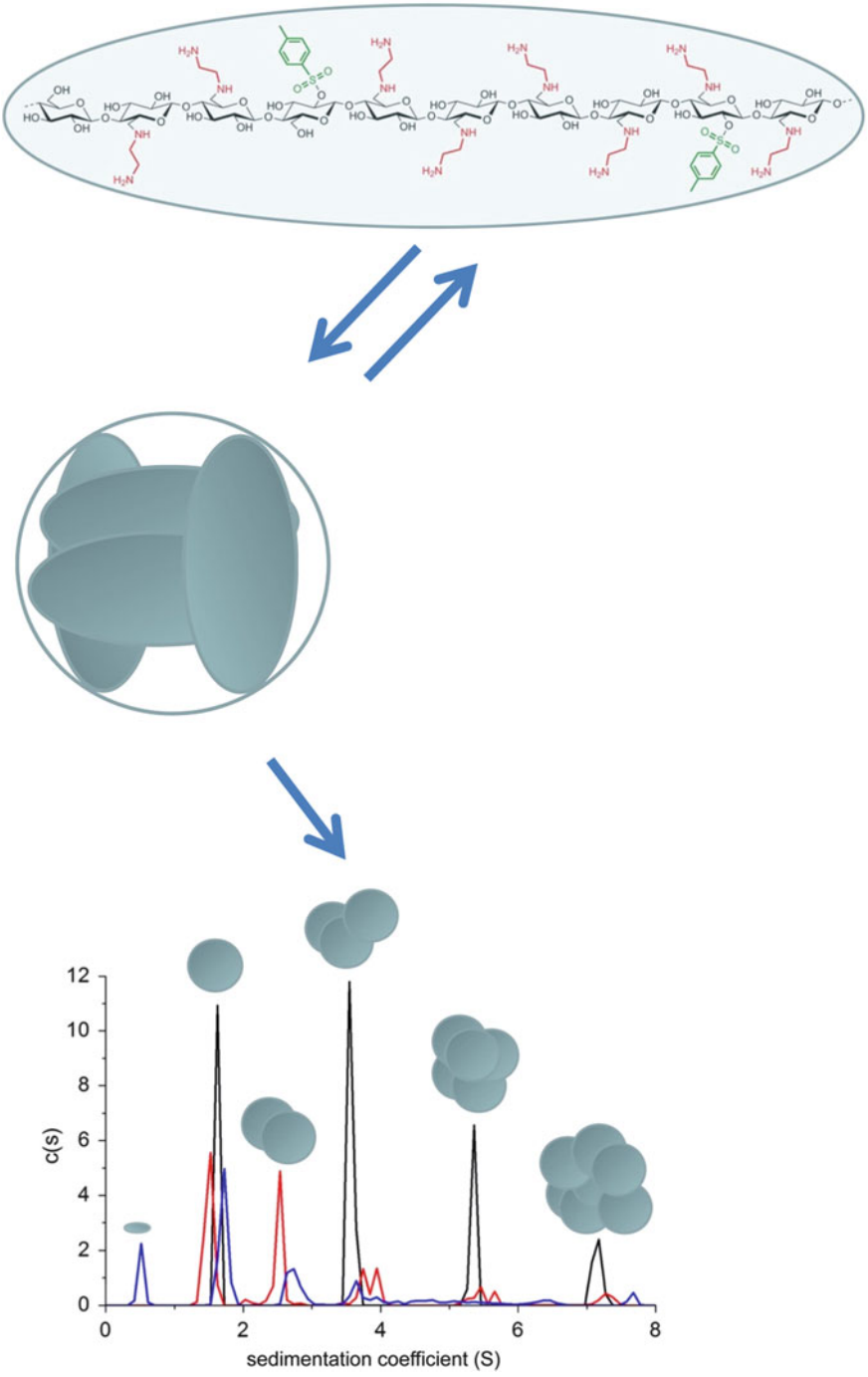

Fig. 29 Reversible tetramerization and further higher-order association of the polysaccharide 6-deoxy-6-(*ω*-aminoethyl)aminocellulose (AEA cellulose). *Top*: Monomer unit of DP ~10, degree

7.3 Reactions of 6-Deoxy-6-Azido Cellulose

S_N reaction of tosyl cellulose with sodium azide and subsequent copper-catalyzed Huisgen reaction (click chemistry) is another promising path to new cellulose derivatives not accessible by conventional etherification and esterification. Thus, 1,4-disubstituted 1,2,3-triazols formed as linker yield novel cellulose derivatives with methylcarboxylate, 2-aniline, 3-thiophene, and acetylenecarboxylic acid dimethyl ester moieties without any side reaction, with a conversion of up to 98% (Fig. 30) [185, 186].

The chemoselective introduction of dendrons into cellulose is achieved by homogeneous reaction of 6-deoxy-6-azido cellulose with propargyl-polyamidoamine (PAMAM) dendrons in DMSO and ILs or heterogeneously in methanol in the presence of $CuSO_4 \cdot 5H_2O$/sodium ascorbate (Fig. 31) [187–189].

The HSQC-DEPT NMR spectrum of second generation PAMAM-triazolo cellulose (DS 0.59) allows complete assignment of the signals of the protons of the substituent in ^{1}H-NMR spectra (Fig. 32).

In Fig. 33, a comparison of ^{13}C-NMR spectra of first, second, and third generation PAMAM-triazolo cellulose synthesized in EMImAc demonstrates the possibility to assign the signals of the dendrons and the AGU. However, the intensity of the peaks of the carbon atoms of the repeating unit decreases as a result of the large number of branches and corresponding carbon atoms.

Even water-soluble deoxy-azido cellulose derivatives are accessible by carboxymethylation, applying 2-propanol/aqueous NaOH as medium [190]. The carboxymethyl deoxy-azido cellulose provides a convenient starting material for the selective conversion by Huisgen reaction, yielding water-soluble carboxymethyl 6-deoxy-(1-*N*-(1,2,3-triazolo)-4-PAMAM) cellulose derivatives of first to third generation (Fig. 34).

Chemoselective synthesis of dendronized cellulose could be a path not only to regioselective functionalization of propargyl cellulose in position 6 [191] but also to functionalization at position 3 [192]. By nucleophilic displacement of 6-*O*-tosylcellulose (DS 0.58) with propargyl amine, 6-deoxy-6-aminopropargyl cellulose is formed and provides an excellent starting material for reaction, including dendronization of cellulose by the Huisgen reaction to yield 6-deoxy-6-amino-

Fig. 29 (continued) of substitution at C-6 $DS_{Amine} = 0.83$, and degree of substitution at C-2 of tosyl residues $DS_{Tosyl} = 0.2$, yielding molar mass $M \sim 3{,}250$ g/mol and sedimentation coefficient $s \sim 0.5$ S. *Middle*: Assembly into tetramers with $M \sim 13{,}000$ g/mol and $s \sim 1.7$ S. *Lower*: Sedimentation coefficient distribution for AEA cellulose at different concentrations: 2.0 (*black*), 1.0 (*red*), 0.75 (*blue*), 0.25 (*green*), and 0.125 mg/mL (*pink*). Based on the $s \sim M^{2/3}$ scaling relationship, the supermonomers associate into supertrimers, superhexamers, and super-9-mers. There is also evidence for some superdimers, although they were not evident at the highest loading concentration. The proportion of supermonomers drops relative to the higher-order species indicates partial reversibility, even with the higher-order association

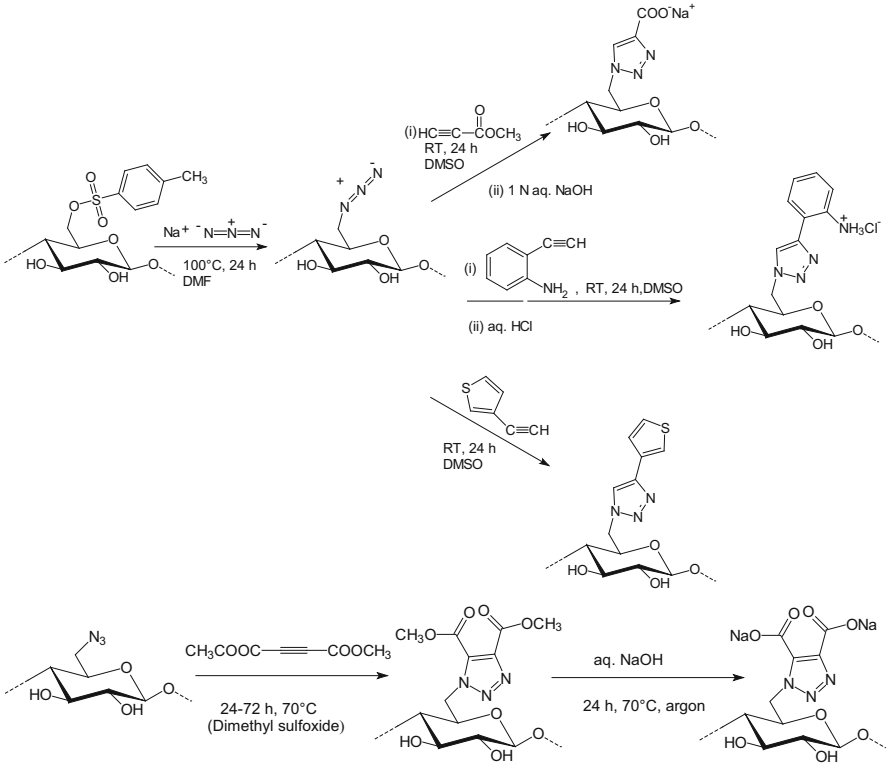

Fig. 30 Reaction path for synthesis of 6-deoxy-6-azido cellulose and subsequent copper-catalyzed Huisgen reaction of 1,4-disubstituted 1,2,3-triazols used as linker for the modification of cellulose with methylcarboxylate, 2-aniline, 3-thiophene moieties, and acetylenecarboxylic acid dimethyl ester

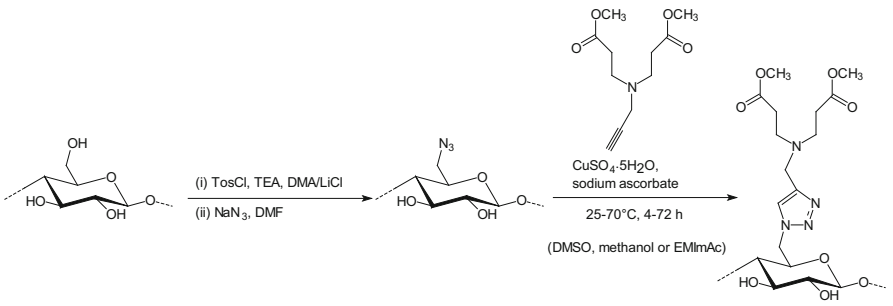

Fig. 31 Reaction path for conversion of cellulose with first generation propargyl-PAMAM dendron via tosylation, nucleophilic displacement by azide, and conversion with the dendron

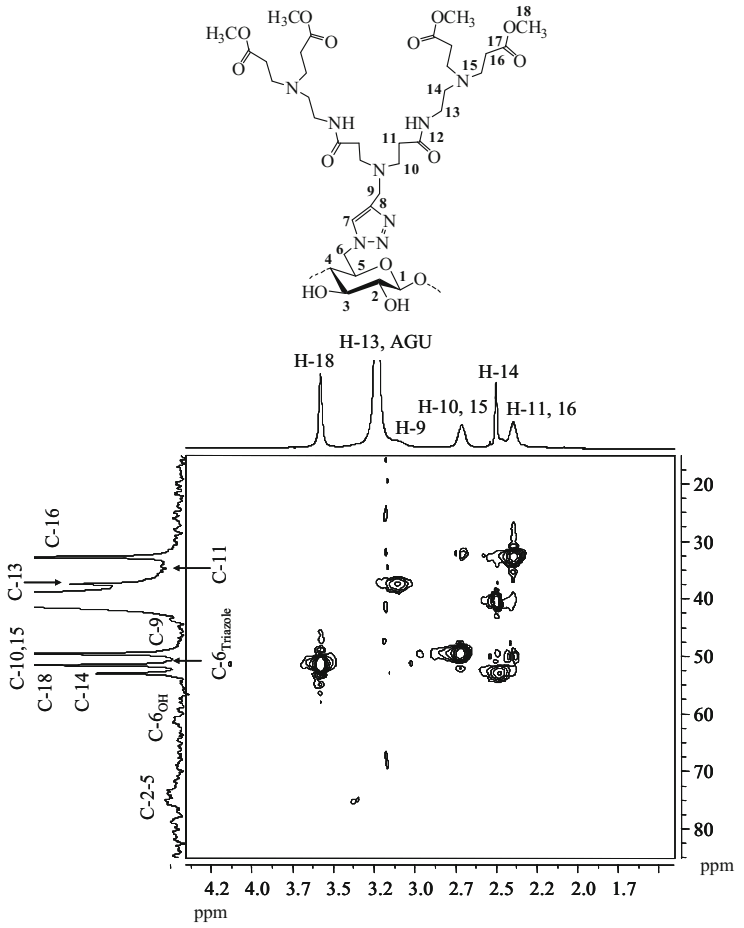

Fig. 32 HSQC-DEPT NMR spectrum of second generation PAMAM-triazolo cellulose (DS 0.59). *AGU* anhydroglucose unit. Adapted from [187]

(4-methyl-(1,2,3-triazolo)-1-propyl-polyamido amine) cellulose derivatives (Fig. 35).

3-Mono-*O*-propargyl cellulose can be produced by reaction of 2,6-di-*O*-thexyldimethylsilyl cellulose with propargyl bromide in the presence of sodium hydride, followed by subsequent treatment with tetrabutylammonium fluoride trihydrate for complete removal of the silicon-containing moieties of 3-mono-*O*-propargyl-2,6-di-*O*-thexyldimethylsilyl cellulose. Cu-catalyzed Huisgen reaction with azido-propyl-polyamidoamine of first and second generation dendrons leads to cellulose regioselectively functionalized with 3-*O*-(4-methyl-1-*N*-propyl-polyamidoamine-(1,2,3-triazole)) ([192], Fig. 36).

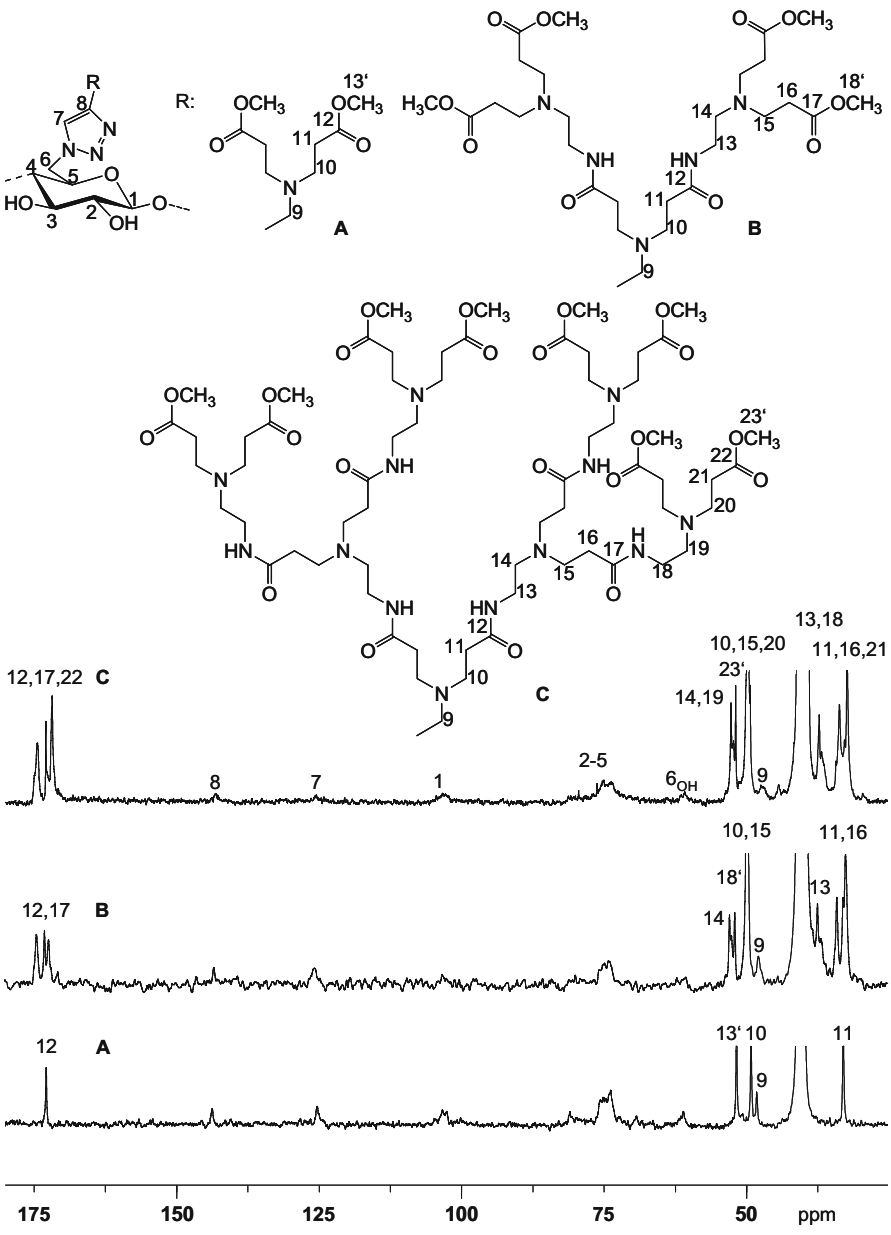

Fig. 33 ^{13}C-NMR spectra of first (DS 0.60, *A*), second (DS 0.48, *B*), and third (DS 0.28, *C*) generation PAMAM-triazolo cellulose in DMSO-d_6 at 60°C

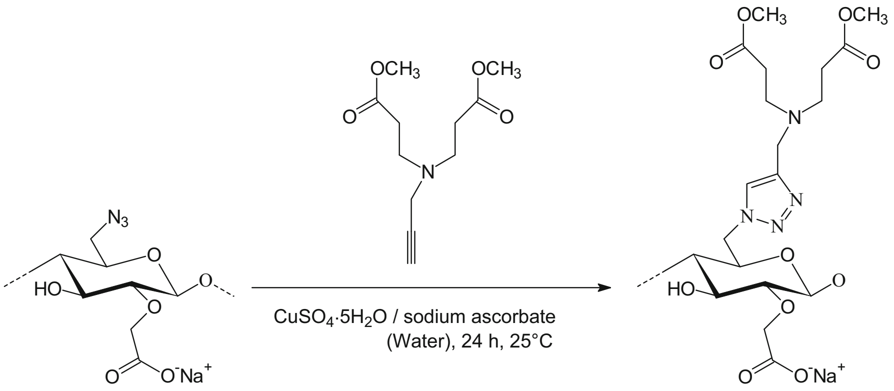

Fig. 34 Homogeneous conversion of carboxymethyl 6-deoxy-6-azidocellulose (DS_{Azide} 0.81, DS_{CM} 1.25) with first generation propargyl-polyamidoamine dendron via the copper-catalyzed Huisgen reaction

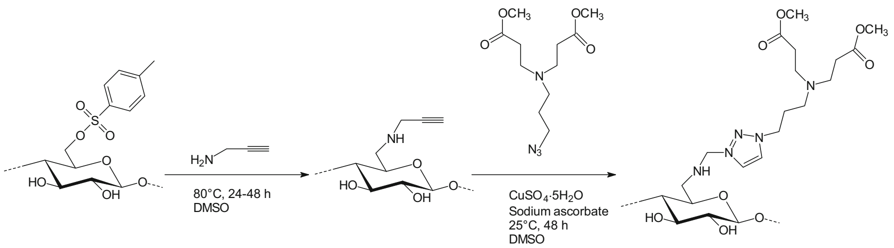

Fig. 35 Reaction path for the synthesis of 6-deoxy-6-amino-(4-methyl-(1,2,3-triazolo)-1-propyl-polyamido amine) cellulose derivatives of first generation (DS 0.33) via 6-deoxy-6-aminopropargyl cellulose

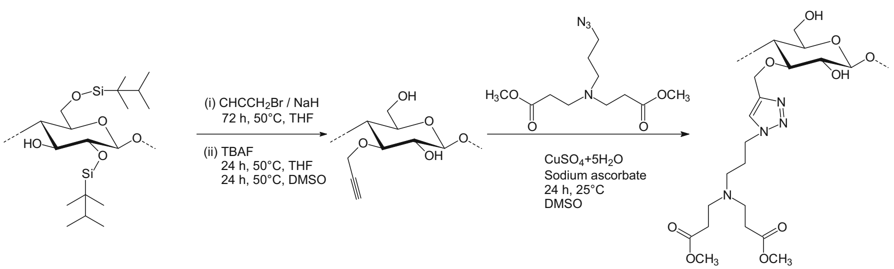

Fig. 36 Synthesis reaction of first generation 3-*O*-(4-methyl-1-*N*-propyl-polyamidoamine-(1,2,3-triazole)) cellulose via 3-*O*-propargyl cellulose

7.4 Cellulose Carbonate as Reactive Intermediate

Polysaccharide aryl carbonates are easily accessible reactive derivatives useful for a variety of reactions [193]. Easily soluble cellulose aryl carbonates can be synthesized by applying phenyl chloroformate, phenyl fluoroformate, and *p*-NO_2-phenyl chloroformate under homogeneous reaction conditions with DMAc/LiCl as reaction medium. Pyridine should be used instead of triethylamine to reduce the nucleophilicity of the hydroxyl groups of the polymer and to exclude formation of cyclic or intermolecular carbonates [194–196].

The synthesis of cellulose phenyl carbonates in the IL 1-butyl-3-methylimidazolium chloride/pyridine is even more efficient. The DS can be controlled, and completely functionalized products are available as a result of the less pronounced side reactions than with tertiary amide solvents [197].

A variety of novel cellulose derivatives are accessible based on cellulose phenyl carbonate. For instance, poly-zwitterions can be produced (Fig. 37). Cellulose phenyl carbonate can be allowed to react with equimolar amounts of β-alanine ethyl ester and *N-tert*-butoxycarbonyl-1,2-ethanediamine. The aminolysis produces (3-ethoxy-3-oxopropyl-*N*-Boc-2-aminoethyl) cellulose carbamate with a $DS_{alanineester}$ of 0.88 and a $DS_{Boc-EDA}$ of 0.95. Thus, there is indication of similar reactivity of the amines, together with a very high conversion (95% of the carbonate moieties into carbamate).

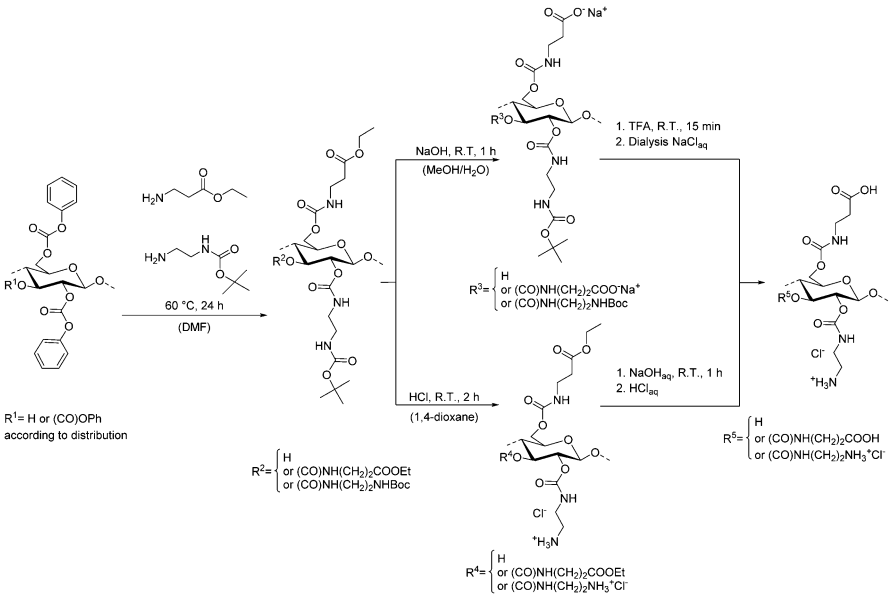

Fig. 37 Reaction scheme for the synthesis of anionic, cationic, and ampholytic cellulose carbamate

A polyanion, polycation, and poly-zwitterion can be obtained from cellulose carbamate because of the orthogonal protecting groups. Synthesis of (2-carboxyethyl-*N*-Boc-2-aminoethyl) cellulose carbamate by alkaline cleavage of the ethyl ester has been carried out homogeneously in methanolic/aqueous NaOH solution to mediate the solubility of educt and product. By applying gaseous hydrogen chloride, acidic cleavage of the Boc group leads to the polycation. Also, (2-carboxyethyl-2-aminoethyl) cellulose carbamate, a poly-zwitterion, can be produced by acidic treatment of the polyanion.

8 Conclusions

Cellulose is the most important renewable resource and a unique polymer in terms of its structure and properties. Because of its unique properties, cellulose can serve as starting material for various products and processes for a sustainable world and the development of a country's bioeconomy. Physical and chemical modification reactions yielding fibers, film, sponges, and cellulose ethers and esters are of high commercial importance today. However, research and development in the field of nanostructuring of cellulose and cellulose derivatives, homogeneous chemistry with cellulose applying various solvents (including molten salts, ionic liquids, and water-based systems) can open new avenues for product design with modern organic chemistry. It can be expected that homogeneous phase chemistry will enter the technical scale in the future. Not only chemical modification of the bulk, but also surface modification (i.e., products with low DS) can provide important novel materials. Last but not least, as discussed in this review paper, depending on its nano- and microstructured architectures, versatile characteristics of the biopolymer cellulose can be achieved and addressed to a specific function. Consequently, cellulose is a promising and broadly applicable material not only (as commonly known) in the paper and textile industries but also for medical and pharmaceutical devices, among others. The applications of nano- and microstructured cellulose can further be broadened by chemical and physical surface treatments.

However, there is still a need for research and development investment in science and engineering to produce advanced and cost-competitive cellulose nanoscale products. It is necessary to obtain a better understanding of the adhesion interactions beyond hydrogen bonding, including mechanical interlocking and interpenetrating networks, on a fundamental level to improve the interfacial properties of cellulose composite materials.

From the author's point of view, cellulose and other polysaccharides and their derivatives obtained by physical, biological, and chemical processes and combinations thereof have a bright future.

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