CELLULOSE

1. Introduction

Cellulose [9004-34-6], characterized by Anselme Payen in 1838 (1), is the main molecule in cell walls of higher plants. The name cellulose indicates that it is the sugar (the "ose") from cells, and we now know that cellulose consists of a long chain, or polymer, of glucose units (Fig. 1). Cellulose is also formed by some algae, fungi, bacteria, the ameboid protozoan *Dictyostelium discoideum*, and a group of marine animals, the tunicates. It has even been reported in humans suffering from the rare disease of scleroderma (2). The secondary cell walls of cotton fibers are almost pure (about 94%) cellulose. In other plant sources such as the wood of mature trees, cellulose is enmeshed in as much as 36% lignin, a three-dimensional polymer of several aromatic compounds. About 7.5×10^{10} t of cellulose grow and disappear each year, establishing it as the most abundant regenerated organic material on earth.

Natural cellulosic materials such as grass are eaten by grazing animals, and various species build nests or dens with wood. Cellulose in wood (qv), in animal manure, or in bagasse (the stalks of sugar cane after the juice has been pressed out), serves directly as fuel while scientists strive to develop efficient conversion of cellulose to alcohol and other fuels. After minimal processing of natural cellulosic materials, they are used as lumber, textiles, and cordage. After industrial treatment, with and without chemical derivatization, cellulose is made into diverse products including paper, cellophane films, membranes, explosives, textiles (rayon and cellulose acetate), and dietary fiber (see Cellular Esters; Cellulose Fibers, Regenerated). The U.S. consumption of paper and other products made from wood pulp in 1999 was 340 kg per person (3). Besides its use in relatively simple products, cellulose fiber is being used to reinforce plastics in composites. This is an exciting area that can result in strong, lightweight, economical and biodegradable materials (4).

Cellulose is mostly insoluble in natural environments. Its fibers are relatively strong, with ramie and Fortisan (formerly made by Hoechst-Celanese) both having specific breaking stress values of 0.59 $Pa \cdot mm^3/g$, compared with

Kirk-Othmer Encyclopedia of Chemical Technology. Copyright John Wiley & Sons, Inc. All rights reserved.

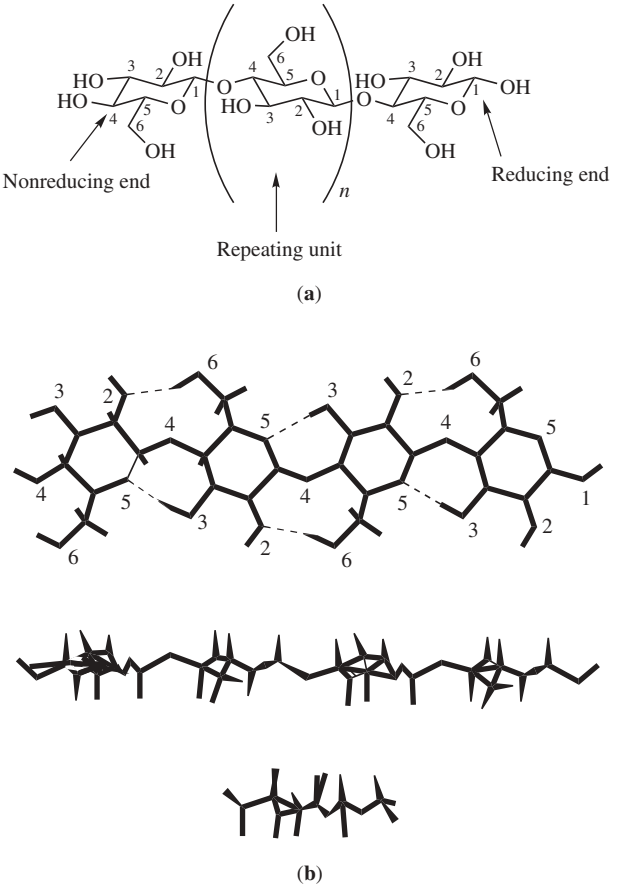

Fig. 1. Drawings of the cellulose molecule. (**a**) The chemist's structural formula for cellulose that shows the β-1,4-linked glucose units, and the numbering of the carbon atoms. (**b**) A segment of a cellulose chain composed of four β-D-glucopyranose residues (cellotetraose) in three different views. The upper image, viewed perpendicular to the flat surface of the molecule, shows the covalent bonds and electron clouds around the atoms. The dotted lines indicate hydrogen bonds between the O6-H and the O2 atoms and between the O3-H and the O5 atoms. Disregarding the ending hydroxyl hydrogen atoms, the molecule has the twofold helical conformation and hydrogen bonding typical of some proposed structures of crystalline cellulose. The middle image shows a view of the long edge of the molecule, and the bottom image shows the end of the molecule.

steel wire, for example, with 0.26 Pa mm^3/g (5). After factoring out their densities, these values can be converted to breaking stress values of 0.9 and 2.0 GPa, respectively. These attributes of strength and insolubility allow cellulose to stabilize the overall structure of plants. The stability of cellulose combined with lignin allows some trees to have very long lives. Some bristlecone pines (*Pinus longaeva (P. aristata)*) in cool, dry mountain regions of Colorado are more than 5000 years old. On the other hand, cellulosic materials in damp, warm conditions are degraded naturally by enzymes collectively known as cellulases that are present in fungi, in bacteria that exist in soil, and in cattle rumen. Cellulases are

also found in protozoa in the gut of insects such as termites. Very strong acids can also degrade cellulose. The human digestive system has little effect on cellulose.

One of the reasons for the stability of cellulose is that it is usually in the form of dense crystals that have extensive van der Waals' attractive forces as well as hydrogen bonds. Although its properties, especially its flexibility, are unlike the properties of materials that are recognizable crystals, cellulose molecules have sufficient regularity to meet the criterion for crystallinity. The main reason for the difference in properties between crystals of cellulose and crystals of molecules that do not form fibers is that typical cellulose crystals are very small crosswise while being relatively long. Cellulose is polymorphic, ie, there are a number of different crystalline forms that reflect the history of the molecule. It is almost impossible to describe cellulose chemistry and biochemistry without referring to these different forms. Briefly, cellulose I, with its subclasses Iα and Iβ, is the form that occurs, with limited exception, as the result of biosynthesis. Cellulose II occurs when cellulose is regenerated from solution, such as during the manufacture of rayon, or when cellulose I is treated with strong alkali, washed, and dried. A major part of this chapter on cellulose is devoted to a more detailed explanation of these and other structures.

Plant cell walls are complicated composites, with primary and oftentimes secondary cell walls. The primary walls are next to the outer lipid membrane, and contain substantial amounts of other compounds, including pectin and hemicelluloses. The primary walls of all higher plant cells are thought to be similar in structure. During growth of the cell, expansin proteins loosen the associations of these polymers so that the cell wall can expand (6). The natural cellulosic fibers of commercial interest are typically the walls of elongated cells. For example, the cellulose-rich cotton fiber (see COTTON) is a single cell that develops on the coat of a cottonseed. Other cellulosic fibers are collections of cells called "ultimate fibers" (7).

In industrial terminology, α-cellulose is mostly β-1,4-glucan, although some insoluble hemicelluloses [9034-32-6] may also be present. Hemicelluloses (qv), which occur along with cellulose in plant cell walls, are polysaccharides such as glucomannan and acetylated glucuronoxylan. Other hemicelluloses are natural derivatives of cellulose itself, with side chains of xylose, galactose, or fucose. Holocellulose is an industrial word for delignified cellulose that still contains the hemicellulose. In the older nomenclature, β- and γ-cellulose are fractions of hemicellulose and partially degraded cellulose that are insoluble and soluble, respectively, after their alkaline solution is neutralized. All of this industrial terminology pre-dates explicit knowledge of the chemical and physical structures of these polysaccharides. The word cellulose means β-1,4-D-glucan, regardless of source.

Because of the importance of cellulose and the difficulty in unraveling its secrets regarding structure, biosynthesis, chemistry, and other aspects, several societies are dedicated to cellulose, lignin, and related molecules. These include the Cellulose and Renewable Resources Division of the American Chemical Society, the Cellulose Society of Japan, TAPPI (the Technical Association of the Pulp and Paper Industry), and Cellucon, which has organized numerous international symposia regarding cellulose. Besides the publication of the Cellulose Society of Japan (*Cellulose Communications*), there are two journals

dedicated to cellulose (*Cellulose* and *Cellulose Chemistry and Technology*). Research results are published in many other journals as well. The 1638 pages of the proceedings of the Tenth Cellulose Conference that were published in 1989 (8) also indicate the vitality and interest in this subject. Several fairly recent books on cellulose have been published (9–14). The history of the proof of chemical structure of cellulose, one of the milestones in organic chemistry, is reviewed in Reference 15. The Cellulose Society of Japan published an encyclopedia of cellulose science and technology in Japanese (16). Another perspective on the long history of cellulose structure is available (17). An overall chapter is included in an encylcopedia on biopolymers (18), and a 1998 book covers many aspects of importance for those wishing to carry out chemical modifications (19).

2. Sources

Cellulose for industrial conversion comes from wood and scores of minor sources such as kenaf. Paper and rayon are now made mostly from wood pulp. Cotton rags were historically important for paper making, and cotton linters (short fibers not used to spin yarns) are now used in high quality writing and currency papers. The importance of cellulose recycling is increasing, especially for paper products. Some cellulose comes from the hairs (trichomes) on seeds, eg, cotton, kapok, and milkweed. Bast fibers are obtained from the stems of plants such as hemp, kenaf, ramie (a perennial Asian nettle), flax (linen), and jute. Besides the "soft" bast fibers, "hard" cellulose fibers are obtained from the leaves of plants such as agave (especially sisal), banana, and pineapple. In some cases, such as corn stover (the stalks and leaves of maize), the substantial amounts of cellulose present are interesting but not extensively exploited.

Celluloses from algae such as *Valonia ventricosa* are of considerable research interest because they occur in large and well-oriented crystallites. Superior structural data can be obtained by various experimental methods when crystallites are larger. However, ramie is also used for such experiments because it represents textile celluloses better than algal or bacterial cellulose. Ramie fibers contain smaller but highly oriented crystallites. Cellulose from the "tunic" of the tunicates has been processed to yield even larger crystals than those from algal celluloses, and these crystals have allowed the determination of the structure of one important form of native cellulose (see Structure, below). Bacterial cellulose is of research interest because the synthesis of cellulose by an individual bacterium, *Acetobacter xylinium*, can be observed directly with a microscope (20). It forms tangled extracellular masses of cellulose called pellicles. The pellicles resemble a nonwoven fabric and can be grown in shapes as complicated as a glove (21). A single thread of bacterial cellulose can grow to a length of a meter, compared with a few centimeters for cotton fibers.

A commercial bacterial cellulose product (Cellulon) was introduced by Weyerhaeuser (22). For use in foods, the product is called PrimaCel and is available from NutraSweet Kelco. The fiber is produced by an aerobic fermentation of glucose from corn syrup in an agitated fermentor (23,24). Because of its small particle diameter (10 μm), it has a surface area 300 times greater than normal wood cellulose, and gives a smooth mouthfeel to formulations in which it is

included. It has an unusual level of water binding and works with other viscosity builders to improve their effectiveness. It is anticipated that it will achieve GRAS (Generally Regarded As Safe) status, and is neutral in sensory quality; microcrystalline cellulose (see below) has similar attributes. Other products made from bacterial cellulose include the oriental dessert, Nata di Coco, high quality loudspeaker cones, and Biofilm, a temporary skin substitute.

Recently, cellulose from sugar beet pulp and from citrus pulp has aroused interest for use as a fat substitute (25). The parenchyma cell walls involved do not contain secondary wall cellulose. The very small microfibrils with some remaining pectin, for example, give this microfibrillated cellulose properties that are similar to Cellulon; but since it is made from low cost by-products, is much less expensive.

3. Biosynthesis

During the past decade or so, we have witnessed major advances in our understanding of the biosynthesis of cellulose. Two areas are of interest, biochemistry and molecular biology.

3.1. Biochemistry. There has been reasonable progress in the biochemistry of cellulose synthesis, but inherent difficulties lie in the isolation and characterization of the proteins that comprise the membrane-bound terminal complex (TC) first described by Brown and Montezinos (26). This complex is associated with the plasma membrane. The discovery of linear and rosette TCs using the freeze-fracture method opened the pathway for the isolation and characterization of these complexes. The first success, in 1989, was the purification of cellulose synthase from the gram-negative bacterium, *Acetobacter xylinum* (27). Extracts were capable of synthesizing cellulose *in vitro*, but only in the cellulose II crystalline form usually found for regenerated (rayon) or mercerized cellulose, not the normal native cellulose I form (see Structure, below). In 1990, Lin and co-workers (28) identified the UDP–glucose binding subunit of cellulose synthase from *Acetobacter xylinum*, using an azido photoaffinity probe. This allowed for the first identification of an 83-kDa polypeptide as the catalytic subunit of cellulose synthase. The polypeptide was subsequently sequenced for the first isolation of a cellulose synthase gene in 1990 by Saxena and co-workers (29) (see below). A comprehensive series of biochemical investigations with cotton membrane extracts (30) and product analysis led to the in vitro synthesis of cellulose II. Kinetic analyses (31) and identification of UDP–glc binding subunits of β-glucan synthases using photoaffinity labeling (32) were made.

In 1994, the first assembly of cellulose I outside of a living cell was conducted using an artificial system by means of a cellulase-catalyzed polymerization of β-glycosyl fluoride substrate (33). Micelles were postulated to organize the polymerizing sites in such a manner that a laboratory synthesis produced cellulose I microfibrils for the first time. This work (R. M. Brown Jr., unpublished) provided insight into the crystallization mechanisms and suggested that a specific association of the catalytic subunits was necessary to produce synthetic cellulose I. This was achieved by a substantial purification of a minor component of

the complete *Trichoderma* cellulase system. Further work (unpublished) showed that a minor 38-kDa endoglucanase is the purified component that synthesizes cellulose I from the artificial cellobiosyl fluoride substrate.

In 1995, the first in vitro synthesis of cellulose I from native plant membrane extracts was achieved (34). The judicious use of MOPs buffer and two independent digitonin solubilization steps led to the synthesis of cellulose I microfibrils in vitro. Cellulose II and callose (β-1,3-glucan) also were assembled in vitro. A comparative study of cellulose I synthesized in vitro from cotton and mung bean revealed apparent differences in crystallinity and resistance to acetic/nitric acid reagent (35). A major breakthrough in the separation of activities leading to cellulose and callose was achieved in 1997 (36). Using native gel electrophoresis under nondenaturing conditions led to the separation of in vitro assembly of cellulose I and callose. Electron micrographs of negatively stained fractions yielded protein complexes of different morphologies involved in the synthesis of cellulose I and of callose, suggesting that the long-standing assumption that the same complex could assemble the two glucans was no longer tenable. This study also initiated a systematic fractionation of the proteins separated on the native gel, and a number of these have been sequenced (R. M. Brown Jr., unpublished). However, other than the cellulose synthases themselves, we do not yet have concrete evidence regarding which polypeptides function or participate in cellulose biosynthesis in vascular plants. Recently, Lai-Kee-Him et al. developed a larger-scale, in vitro synthesis of cellulose microfibrils (37). The cellulose was in the form of cellulose IV (see Structure, below), thought to be a disorganized form of cellulose I. Our understanding of the polymerization events is still fragmentary, as evidenced by a recent paper by Peng and co-workers (38) that discusses sitosterol β-glucoside as a possible primer for cellulose synthesis.

Freeze-fracture labeling studies have given new insight and proven the initial hypothesis that TCs are the sites of cellulose assembly. In 1999, Kimura and co-workers (39) showed the antibody labeling of rosette TCs of cotton fibers. The antibodies were produced against a recombinant polypeptide to the gene sequence of cellulose synthase. Similarly, antibodies to the c-di-GMP-binding protein were produced and tested with freeze-fracture labeling (40), and these localized with the row of the TCs in *Acetobacter* that are responsible for cellulose microfibril assembly. This study provided the first structural evidence for a cellulose-associated polypeptide known to be functional in cellulose biosynthesis in *Acetobacter*. Early work by Mizuta and Brown (41) showed the effects of 2,6-dichlorobenzonitrile and Tinopal LPW on TCs of the alga *Vaucheria*, suggesting that the complex is disrupted by these agents.

Dynamic assembly of cellulose by *Acetobacter* also has provided new understanding of the polymerization and crystallization process. In a series of papers, Cousins and Brown (42–44) showed that cellulose altered during synthesis by the optical brightener, Tinopal, was in the form of monomolecular sheets. Removal of the dye by photoisomerization or acid washing led to the assembly of cellulose I microfibrils. Comparisons of the molecular mechanics energies of different small arrangements of cellulose chain fragments (42) suggested that crystallization involved a two-step association, first to form monomolecular glucan sheets associated with each other by van der Waals' forces, followed by

stacking of these sheets by hydrogen bonding to form the three-dimensional microfibril.

3.2. Molecular Biology and Molecular Genetics. Some of the most important advances in cellulose biosynthesis have originated from the combined areas of molecular biology and molecular genetics. Since the first gene for cellulose synthase in *Acetobacter xylinum* was cloned and sequenced by Saxena and co-workers in 1990 (29), many genes for cellulose synthase have been discovered. Selected mutation of *Acetobacter* cellulose synthase components affected crystallization of the product (45). In 1995, Saxena and co-workers (46) subjected the *Acetobacter xylinum* sequence to hydrophobic cluster analysis and revealed a clearly predictable pattern in processive β-glycosylation reactions. These data revealed a conservative DDD QXXRW amino acid motif common to all living organisms, prokaryotic or eukaryotic, plant or animal, that have processive β-glycosyl transferases. Using these data, the structure–function of cellulose synthase has been recently presented in the form of a genetic algorithm (47). In 1996, Pear and co-workers (48), using the data generated from the hydrophobic cluster analysis of Saxena et al., sequenced a cellulose synthase gene from a vascular plant. Independently, Arioli and co-workers (49) found the same gene in *Arabidopsis*. Since then, many other cellulose and cellulose-like synthase genes have been reported (50). Recent advances in the mutation of cellulose synthase and associated genes have provided more interesting data on the complexities of control and regulation in cellulose biosynthesis in growth and development. For example, Taylor and co-workers (51) demonstrated that the irregular xylem3 locus of *Arabidopsis* encodes a cellulose synthase required for secondary wall synthesis. In the same plant, Nicol and co-workers (52) found that a putative *endo*-1,4-β-D glucanase is required for normal cell wall assembly and may be associated with cellulose synthase. Cellulose synthases also have been isolated from forest trees, particularly *Populus* (53). In 2000, Fagard and co-workers demonstrated that PROCUSTE1 encodes for a cellulose synthase required for normal cell elongation (55). Sato and co-workers (56) found KORRIGAN, an endo-1,4-β glucanase in *Arabidopsis* that may be responsible for cell elongation and cellulose synthesis. Along the same lines, Lane and co-workers (57) found temperature-sensitive alleles that link the KORRIGAN glucanase to cellulose synthesis and cytokinesis in *Arabidopsis*. Zuo and co-workers (58) also studied the KORRIGAN endoglucanase and found that it is essential for cytokinesis. Along another line, Gillmor and co-workers (59) found that α-glucosidase I is required for cellulose biosynthesis and morphogenesis in *Arabidopsis*. Recently the question of whether one or more cellulose synthases are required for normal growth and development has been addressed, and it appears that multiple cellulose synthase catalytic subunits are required (60). Recent work from the lab of Zogaj and co-workers (61) has shown that even pathogenic bacteria produce cellulose in the form of biofilms. They conclude that cellulose biosynthesis may have an underlying function in pathogenicity. In addition, the relationship between herbicide resistance and cellulose biosynthesis was recently described by Peng and co-workers (62).

From the genetic evidence has come exciting new insight on the relationship of cellulose synthase between organisms, especially in terms of phylogeny. The recent discovery of cellulose biosynthesis in cyanobacteria, a group of organ-

isms that have been postulated to be one of the most ancient forms of life on earth, has led to some interesting conclusions (63). For example, the cyanobacterial cellulose synthase is more like that of vascular plants than bacteria and other prokaryotes. This supports the endosymbiotic hypothesis for the early transfer of genes for cellulose synthase from cyanobacteria to a primitive eukaryotic cell that eventually led to the evolution of land plants.

3.3. The Future. With rapid advancements in molecular genetics and the ability to create, manipulate, and utilize individual molecules (nanotechnology), many exciting applications for the design and fabrication of synthetic celluloses may be on the horizon. First, however, we must learn from living organisms how a large multi-subunit enzyme complex can simultaneously polymerize up to thousands of glucan chains, then aggregate them into a metastable crystalline microfibril. It is ironic that a biopolymer made only of the sugar, glucose—one which has been around for some billions of years—is so complex in its function and regulation. A few web sites are recommended for further information (64).

4. Preparation

Wood can be used for structures with little preparation. Cotton fiber is also relatively ready for use in textiles. After it is picked, either mechanically or by hand, the fiber is removed from the cottonseed by ginning. With only some additional cleaning, the fiber is ready for textile manufacture. Bast and some leaf fibers are extracted from their surrounding tissues by various processes such as microbiological "retting," the process of rotting the nonfiber parts of the plant. A mechanical process is called decortication. It involves crushing the leaves and scraping the fibers. Other manual or mechanical stripping operations are also used (65).

Most large-scale manufacturers of cellulosic products other than textiles begin with cellulose that is in the form of pulp. Pulping partially separates cellulose from the and hemicelluloses, leaving it in a fibrous form that is more susceptible to chemical treatment than the starting material. After pulping, the pulp is purified and otherwise treated to tailor it to the required specifications. Following drying, the pulp is shipped in large rolls, to serve as feedstock for papermaking, and for the manufacture of rayon fiber, films, and other products.

High purity chemical cellulose, usually in the form of "dissolving pulp," is not only mostly free of lignin and hemicellulose, but the molecular weight of the cellulose, while fairly uniform, is lowered. This increases solubility in alkali and provides desired viscosity levels in solution. These dissolving pulps are used to make derivatives such as sodium cellulose xanthate [9051-13-2], via alkali cellulose [9081-58-7], and various esters and ethers (see Cellulose Esters; CELLULOSE ETHERS). A description of the technical details of bleaching is also available (66). The final use determines the extent of these treatments. Many steps may be used when edible or transparent films are the final product, but most newsprint receives only a single-step reductive brightening that merely whitens the fibers to an acceptable level without causing weight loss or other physical effects.

While not nearly as widely used as pulping, steam explosion (67–76) is another way to break down lignocellulose [11132-73-3] into a fibrous mulch that has substantially increased accessibility to chemical and biological agents.

These render the mulch partly soluble in organic solvents or alkali (to the extent of 40–60%) and degradable by cellulolytic enzymes. Moisture-saturated wood chips, straw, or other materials are subjected to high pressure steam (3.5–4.0 MPa) and temperature (200–250°C), followed by rapid decompression. The temperatures and pressures used depend on both the type of starting material and the intended use of the product, with more severe conditions providing greater separation of the components and greater degradation of the cellulose molecular weight. Several of the highest-energy treatments yield nearly complete separations into cellulose, lignin, and other carbohydrate degradation products. However, this comes at the expense of molecular degradation to low molecular weight sugars, furfural, and phenolics at higher treatment severities. Products such as chemical cellulose, microcrystalline cellulose, cellulose acetate [9004-35-7], sulfur-free (thermoplastic) lignin, vanillin [121-33-5], and xylose [58-86-6] that require high quality starting materials can even be made from waste materials. Milder conditions are used as an alternative to conventional pulping for the manufacture of high yield pulps for the manufacturing of paper and board. Lignocellulose given weaker treatments can be formed into molded building materials. Steam-exploded wood can be fed to cattle because of its enhanced digestibility. It is also a suitable substrate for fermentation into alcohol and other products.

Microfibrillated cellulose has several preparations, either from wood pulp or from sugar beet or citrus pulp. Sugar beet pulp is first extracted with acid or base hydrolysis to extract the pectins and hemicelluloses. After grinding or other shearing operation, a rapid pressure drop of at least 20 MPa is followed by a "rapid decelerating impact" (25).

5. Structure and Its Relation to Chemical and Physical Properties

As noted by Payen (1), both cellulose and starch can both be degraded to glucose. Yet, the properties and suitable uses of these two molecules are very different. For example, we eat starch, and we wear cellulose. If clothes were somehow made from starch without added protection, they would fall apart if they became wet. Dietary cellulose for humans furnishes no energy, although polygastric animals such as cattle do get calories from cellulose. The reason for the differences in the properties of starch and cellulose is largely the difference in the spatial arrangements of their molecules. The importance of structure was recognized at the same time as the discovery of cellulose. Therefore, cellulose structures have been studied intensively. Some basic information from more than 70 years ago has been important in helping to understand many other polymers. Still, only at the time this is being written are the intra- and intermolecular arrangements of some of the important cellulose forms resolved well enough that most scientists can be comfortable with the results. Especially in the case of natural cellulose fibers, there are many different levels of structure. Ultimately, the properties depend on the structures of these levels, and it is important to understand the role of each level.

5.1. Chemical Structure. Figure 1**a** is a chemist's drawing of the cellulose molecule. On the right is the reducing end, so called because it can reduce

Cu^{2+} ions in Fehlings solution to Cu^{+} ions. The nonreducing end is on the left. When the molecular weight is high, the number of reducing groups for the amount of cellulose is relatively small, and the sample may test as nonreducing. Cellulose molecules are unbranched chains of up to 20,000 1,4-linked β-D-glucose [492-61-5] residues (Fig. 1), but shorter chains occur in the primary walls and under other circumstances. This measure of the molecular mass is called the degree of polymerization (DP), a measure more easily interpreted than the molecular weight in daltons. DP may be multiplied by 162 to get the molecular weight in daltons.

Attack of cellulose with strong acid gives hydrocellulose, cellulose with reduced molecular weight. The prefix hydro is used because each cleavage of the cellulose chain is accompanied by addition of the hydrogen and hydroxyl parts of a water molecule to the new fragments. After two hours in boiling 2.5 *N* HCl, the cellulose reaches the "leveling off degree of polymerization (LODP)". Different sources of cellulose give different values for the LODP, with number-average values of 390 glucose residues for cotton and 200 for Fortisan rayon (77). When cellulose is hydrolyzed with extremely strong acid (eg trifluoroacetic acid) for two hours, molecules with two to seven β-1,4-linked glucose residues (cellobiose to celloheptaose) will remain, along with glucose itself (78). Further attack on these cellodextrins with acid results in just glucose.

The linkage between the glucose rings is not the only location of chemical reactivity. The 2, 3, and 6 hydroxyl groups can be substituted with many different groups, and with widely varying degrees of substitution (see Chemical Reactivity, below). This polyhydroxylic nature of cellulose makes it an attractive polymer for chemical modification. Because cellulose is composed of chiral glucose residues, and because it forms fibers and films, it can be used to separate chiral materials. This is important for various types of organic synthesis, especially for drugs. It can also be used in woven mat form to complex various pollutants.

5.2. Physical Structure. Despite its ultimate degradation to just glucose, one often reads and hears that cellulose is a polymer of cellobiose units. The crystallographic unit cells of numerous forms of cellulose do repeat after two glucose units, but other crystalline cellulose complexes and derivatives have unit cells that repeat after three, four, five (79), or even eight (80), residues. Further, cellulose is not always crystalline. Amorphous and dissolved cellulose do not have geometrically repeated three-dimensional structural units. Therefore, the "polymer of cellobiose units" statement could limit thinking about the range of shapes of this somewhat flexible molecule. Any polymeric molecule that is composed of only β-1,4-linked glucose units is cellulose, regardless of the molecular shape.

Almost all glucose rings in cellulose have chair forms ($^4C_1$) with all of the substituents disposed equatorially. Any of three orientations of the primary hydroxyl oxygen atoms (O6) are possible. When O6 is located as in Figure 1**b**, it is said to be trans (anti) to O5 (the ring oxygen) and gauche (syn) to C4, or tg. When O6 atoms are positioned between O5 and C4, they are in the gauche, gauche (gg) position, and those gauche to O5 and trans to C4 are said to be gt. Other issues include the relative orientations of the adjacent glucose rings in the chain and, if in a crsytal lattice, the screw-axis symmetry.

Cellulose is rarely encountered as isolated individual molecules. Still, this state has been studied because such molecules would be similar to those in the noncrystalline or amorphous state. Also, it should give insight to the intrinsic shape that is preferred by the cellulose molecule. The amorphous form of cellulose is more chemically reactive than others. The range of allowed shapes of the isolated cellulose chain is determined by the fairly rigid glucose rings, which can, to a certain degree, rotate about their interconnecting bonds. An estimate of the flexibility of the linkage can be obtained by studying crystal structures of cellobiose and related molecules. The ranges of rotational orientations about the C1−O1 and O1−C4 bonds for the cellobiose linkages are substantial: 30° for the former and 60° for the latter (81). Compared with other polymers, these fairly large ranges cause relatively little change in the overall shape. There is also one structure with a rotation about the O1−C4 bond nearly 180° from the other conformations that have β-1,4 linkages (82).

Recently, isolated molecules have been imaged with high resolution transmission electron microscopy. Those molecules also have rather extended shapes (83). Computerized molecular modeling studies usually show that the lowest energy for an isolated individual cellulose molecule occurs when it is quite extended, as in Figure 1**b** (84). When dissolved, cellulose molecules are still fairly extended, but they are described as somewhat flexible random coils with relatively large distances between their ends (Fig. 2) (85). This information was also derived from computerized modeling studies in combination with light-scattering and rheological data from solutions of lightly derivatized cellulose chains. The light substitution is used to keep cellulose in solution for the experiments.

Most cellulose exists in small crystals, or crystallites. In some cases, it is thought that the unit of biosynthesis is a crystallite with only six molecules on each side (this is apparently not the case for cotton). In at least some cases, the length may be equivalent to the molecular weight. Such a crystallite is called an elementary fibril. In a nearly square crystallite with 36 chains, the number of molecules on the surface (twenty) exceeds the number in the interior (sixteen). The crystallites in primary wall material are apparently even smaller. In secondary walls of higher plants such as cotton, a few elementary fibrils are combined to form microfibrils. The details of the separation between the microfibrils and elementary fibrils are not known. Perhaps there is a boundary layer of water in the developing cell. In algal, bacterial, and tunicate cellulose, larger microfibrils are found. In cotton, there are several further levels of organization, with the microfibrils of the secondary cell wall being arranged into complex, reversing helical arrangements. Many properties of cotton are therefore different from those of other, simpler cellulosic substances.

Cellulose can be studied with diffraction crystallography. Many of these studies are reviewed in References 86 and 87. The first objective is to learn the nature of the order of the molecules, if any. If the atoms in the sample do not have a regular repeating pattern, the structure is amorphous and only a diffuse halo will result. Crystalline powders with the particles oriented randomly give a pattern of concentric rings. Powder patterns are distinctive “fingerprints” and effectively distinguish among different crystalline forms. Diffraction patterns of aligned fibers, in which the long crystallites are randomly oriented around

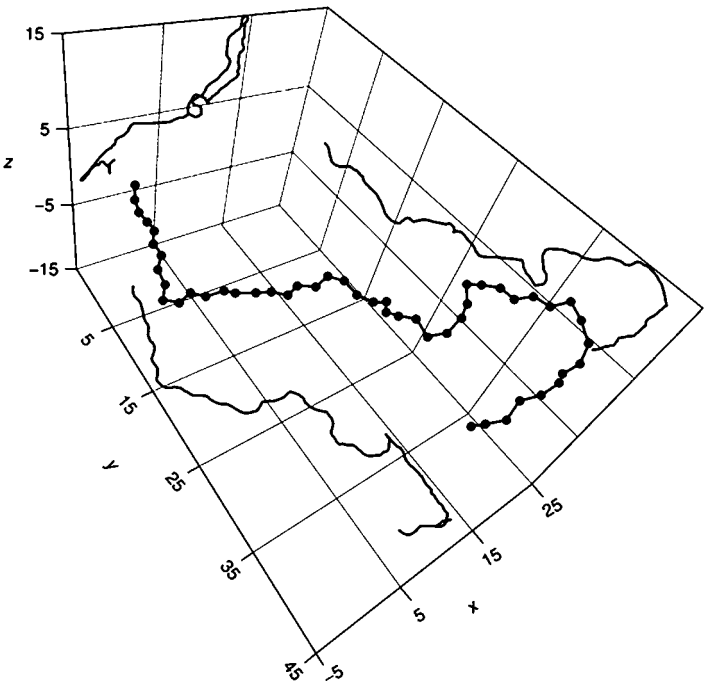

Fig. 2. A representation of the cellulose chain in solution, projected against three two-dimensional surfaces. The circles represent the oxygen atoms that link the individual glucose residues, and the lines take the place of the sugar residues. This result of a modeling study (85) that did not explicitly include solvent molecules indicated that cellulose is somewhat more flexible than found experimentally.

the long axis, give spots on layer lines. The fiber diagrams in Figure 3 show many more spots than those usually obtained from cellulose.

The positions of the diffraction spots depend on the dimensions of the unit cell, the smallest part of the crystal that can reproduce the entire crystal by simple translations of its contents along its edges. (For polymeric samples, the molecules are considered to be infinitely long.) Another objective of the diffraction experiment is to determine the unit cell dimensions. On the basis of the unit cell dimensions, educated guesses can often be made about the arrangement of the molecules. For example, the repeat of 10.38 Å along the meridian is roughly twice the length of a glucose residue. This, along with the missing intensities of the meridional reflections on the odd-numbered layer lines, suggests that the cellulose molecule has twofold screw-axis symmetry and is aligned along the fiber axis.

The final major objective is to determine the positions of the atoms within the unit cell. Until patterns of the quality in Figure 3**a** were obtained, there were always more atomic coordinates to be determined than appearing in diffraction data. Therefore, a completely experimental determination could not be carried out. In such situations, workers rely on computer models to supply information on the positions of the atoms, and calculated intensities from various models are

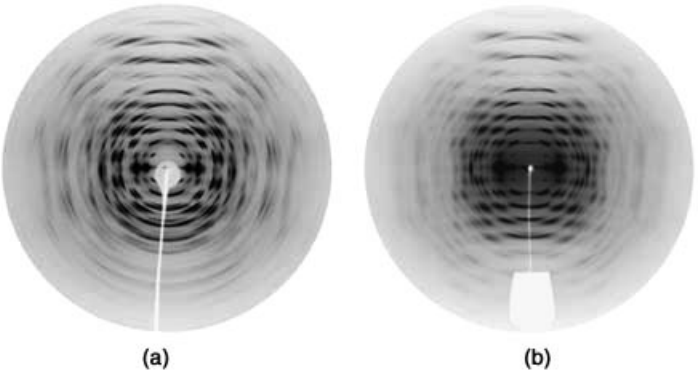

Fig. 3. X-ray fiber diffraction patterns for (**a**) cellulose Iß and (**b**) II. The fibers and the long molecules are vertical in these patterns. The clear areas in the centers are from the shadow of the "beam stop" that keeps the undiffracted main beam from ruining the detector. A horizontal line through the middle is called the equator and the meridional line, which is vertical, also passes through the center. The patterns both show 10 layer lines. The inverse of the distance between the layer lines gives the fiber repeat distance of 10.38 Å for Iß and 10.36 Å for II. The pattern for Iß is not actually from a fiber but instead from a stack of thin films of tunicate crystallites that were dried from a slurry on the sides of a rotating horizontal vial (88). The pattern for II is for repeatedly mercerized flax. From the archives of Prof. HC working in collaboration with Y. Nishiyama and P. Langan.

compared with the observed data. Often the energies of the trial structures are calculated as well, and selection of the final structure takes into account both the extent of disagreement with the diffraction data and the energetic stability of the model (89). Errors in the measured intensities may be important (90), but a more definitive approach is usually not available.

Amorphous Cellulose. Some cellulose is amorphous, from either mechanical action (such as ball milling) or chemical treatment (91,92). Chemical and biochemical reactions of less crystalline cellulose are usually more rapid than those of highly crystalline materials. Most samples of cellulose have some amorphous character. Sources of the amorphous halo include differences in the structures of the surface molecules compared with the structures of the interior molecules; external factors such as scattering from the air and moisture; thermal motion of the atoms; Compton scattering; chain ends, bends, or twists of the crystallites; and other departures from perfection in the array of molecules. Another cause of the background is the very small size of the crystallites. This leads to broad diffraction spots and the disappearance of many weaker spots into the background. Most amorphous cellulose probably retains many of the traits of the original crystalline material. Early textbook examples of disordered polymers in "plate of spaghetti" arrangements are quite exaggerated compared with the situation that pertains to most amorphous cellulose.

Different experiments to determine the amount of amorphous material in a given cellulose sample give different answers (93). These discrepancies, amounting to 20% or more, are thought to be due in part to the different roles of molecules on crystallite surfaces. In some methods such as X-ray diffraction, the surface molecules appear to be crystalline, and in other methods, such as

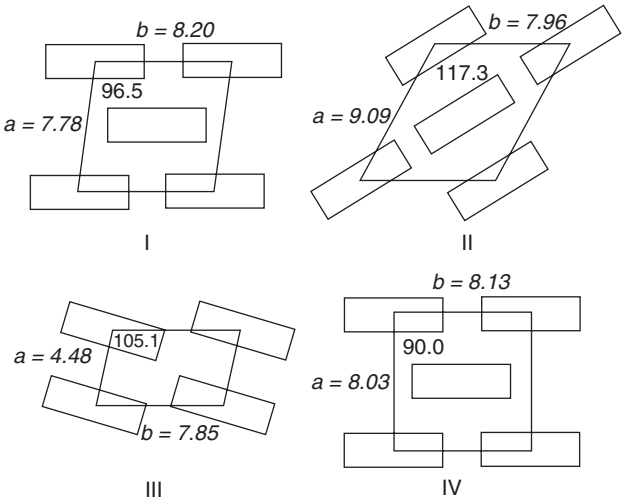

Fig. 4. Comparisons of the unit cells proposed for cellulose I–IV. In all cells, the *c* dimension (perpendicular to the plane of the drawing) is ca 10.31–10.38 Å. The dimensions were taken from References 95–98, respectively.

water sorption, they behave like amorphous material. Even cotton, the most crystalline of the commercial celluloses, has about 20% or more disordered material, including chain ends and crystallite surfaces.

Crystalline Cellulose. There are several different crystalline arrangements of cellulose (Fig. 4), each giving a distinctive diffraction pattern. These polymorphs, or allomorphs, are denoted with Roman numerals I to IV, with some subclasses. Another form is called cellulose x. The particular crystalline form depends on source and treatment. In some cases, more than one form is present in a sample. If so, the fraction of each form can be determined with X-ray diffraction or spectroscopic methods, especially nuclear magnetic resonance (NMR). Again, because they measure different phenomena, different methods will give somewhat different fractions of each form (94). During the allomorphic conversions, many other changes are likely to occur at several levels of structure. Therefore, it is risky to interpret changes in properties solely in terms of crystal form and the underlying changes in chain packing, hydrogen bonding, or molecular conformation. Still, the particular crystal form is an important aspect of solid cellulose.

The microcrystals (microfibrils) are 3–30 nm across (Fig. 5) and perhaps 7 μm in length (99,100). These microcrystals are usually straight, but bent microfibrils have appeared in samples given ultrasonic treatment (101,102). In some cases, such as cotton, the microfibrils organize into macrofibrils 60–300 nm wide. The microfibrils or macrofibrils are then organized into fibers. Diffraction contrast electron microscopy of algal cellulose shows that cross-sections perpendicular to the long axes of microfibrils are nearly square (99,100). This technique produces images that show extended cellulose molecules running parallel to the

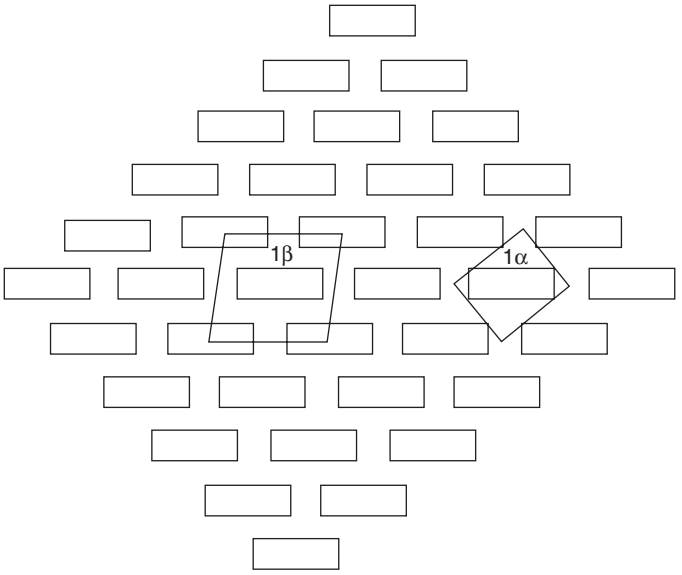

Fig. 5. A cross-section of a nearly square cellulose microfibril, with the individual molecular chains shown as rectangles. Also shown are the one- and two-chain unit cells of Iα and Iβ. This view of the microfibril is parallel to the long axis. The chains are arranged so that the edges of the crystal (microfibril) correspond to diagonals of the two-chain unit cell, or the sides of the one-chain cell (99,100).

long axis of the microfibril (99). Other experiments with atomic force microscopy confirm the conclusions from transmission electron microscopy (103). Cross-sections of other cellulose fibrils have a variety of shapes (104).

Generally speaking, polymer chains can pack efficiently only if their long axes are parallel. The notable differences among cellulose forms relate to the orientations of the rotatable hydroxyl and primary alcohol groups. Those changes permit a variety of hydrogen-bonding and crystal-packing arrangements and result in different availabilities and accessibilities of hydroxyl groups to reagents. There are three ways in which chains could pack in the monoclinic or triclinic crystals found for cellulose (105). If the chains alternate in direction, with half the reducing ends at each end of the microfibril, the packing is "anti-parallel." If all reducing ends are at one of the ends of the microcrystal, the chain packing is "parallel up." If they are all at the other end, the packing is "parallel down." The subtle distinction between the up and down types of parallel packing escaped early workers in the field. Over the years the preferred conventions for describing the unit cell have varied, making the similarity less obvious. For example, the monoclinic angle is currently obtuse, whereas it was formerly acute. Also, the unique monoclinic axis for the older work and small molecule structures is *b*, whereas it is *c* for the current fiber structures.

Cellulose I. Originally, most native cellulose was thought to have the same crystal structure, cellulose I. In the 1950's, it became apparent from infrared spectroscopy (106,107) and electron diffraction (108) that cellulose I from the higher plants was somehow different from that of algal and bacterial cellulose. In

1984, cross polarization magic angle spinning (CPMAS) ^{13}C NMR studies showed that most native celluloses are mixtures of cellulose Iα, prevalent in algae and bacteria, and Iβ, prevalent in higher plants such as flax and cotton (105). Electron diffraction on small areas of large microfibrils from the alga *Microdictyon tenuius* shows that the Iα and Iβ forms both occur in the same microfibril (110). One area of the microfibril gave diffraction spots from a one-chain triclinic unit cell that yields the Iα components of the NMR spectrum. Another area gave the diffraction pattern of the Iβ unit cell, which is essentially the monoclinic, two-chain cell established by Andress (111) and slightly refined by Meyer and Mark (112). At some places along the microfibril, the diffraction pattern is a mixture of the two sets of intensities. In particular, that mixture had led earlier to the proposal of a now-obsolete, eight-chain unit cell for algal and bacterial cellulose I (108).

After many years of controversy, the details of cellulose Iβ (Fig. 6) have been determined to a high level of reliability (113). Extremely crystalline tunicate cellulose was examined by synchrotron X-ray and neutron diffraction analysis. Unlike the 30 or so diffraction spots that can be obtained from samples of ordinary celluloses such as flax, more than 300 spots were recorded (eg Fig. 3**a**). A complete exchange of the hydroxyl hydrogen atoms with deuterium (114) allowed determination of the hydrogen-bonding system through neutron diffraction.

There are two parallel-up cellulose chains, located at the corners and center, in the monoclinic Iβ unit cell. Chains at the corners are linked by hydrogen bonds into sheets, as are the chains at the centers. There are no hydrogen bonds between the chains at the corners of the unit cell and the chains at the centers.

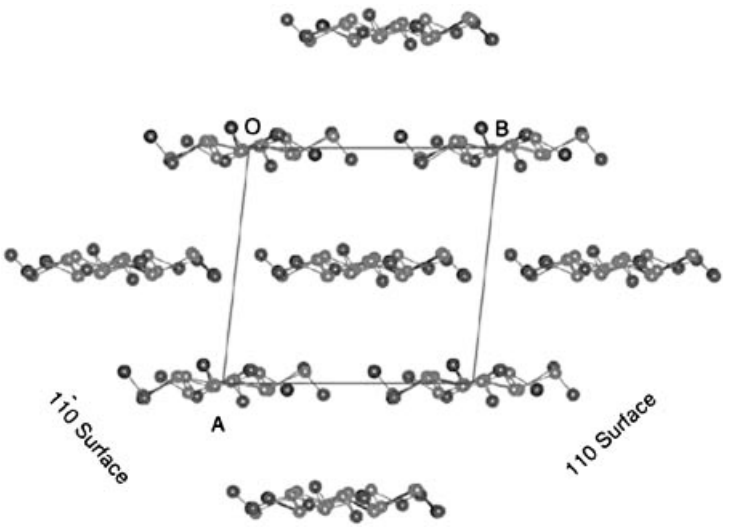

Fig. 6. A segment of the cellulose Iß crystal structure, showing the relationship of the cellulose chains to the unit cell axes *a* and *b* (the origin is O) and to the surfaces of the microfibril. The hydrogen atoms are not shown. The interchain hydrogen bonds would be in directions parallel to the *b* axis. Created from the coordinates in Reference 113.

The chain in the center of the unit cell is shifted along the molecular axis by 0.258 nm relative to the corner chains. Thus, every other sheet of cellulose chains is shifted up from its neighbors. The O6 groups have the unusual tg orientations. Both chains have twofold screw-axis symmetry ($P2_1$ space group) but the structures of the two chains differ. The two unique glucose rings have somewhat different shapes, and the hydrogen bonds for the corner chains and for the center chains are different. The hydrogen atoms on O3 always make hydrogen bonds with O5 on the adjacent glucose ring, but the hydrogen atoms on O2 and O6 are disordered. Those hydroxyls make a variety of different hydrogen bonds. This is thought to allow them to be more reactive than the hydrogen on O3. There is substantial dispersive (van der Waals') attraction between the two different sets of chains, exceeding the strength of the hydrogen-bonding interactions (115).

The chain packing in the Iα crystal structure favored by algal and bacterial cellulose is similar to that in the Iβ crystal. There is only one chain with two glucose residues in the triclinic unit cell, however; so by definition the chains must be packed parallel. Because there is only translational symmetry in the $P1$ space group, the two glucose residues are not identical to each other. There is no symmetry other than translation of the unit cell. The adjacent chains are shifted by approximately the same amount as in Iβ, but the difference is that the shifting is continual, instead of for every other sheet. Although a new crystal structure is being determined (Paul Langan, personal communication), the single chain per unit cell enables a reasonably confident analysis by modeling (116,118). Again the O6 groups have the unusual tg orientation, and disorder of the hydroxyl groups is a possibility. The O6 orientation is not only indicated by modeling, but also found by experimental atomic force microscopy (103).

The Iα crystal structure can be annealed to produce the Iβ structure (119) according to electron diffraction studies, and other studies of the effects of steam on the NMR spectra have been carried out (120). Both cellulose I structures appear in the same microfibrils of most algal and bacterial celluloses (121). The issue of polymorphic composition of native cellulose is further complicated, because sometimes naturally produced cellulose is not in either cellulose I form. Cellulose IV (see below) was found in some primary walls (122), although it can be difficult to distinguish between I and IV when the samples are not very crystalline.

Cellulose II. Rayon, made from dissolved and regenerated wood and/or cotton, has the cellulose II structure, as does cellulose that has been treated with strong NaOH solutions. The effects of alkali treatments were discovered by John Mercer (123) who found that mercerized cotton had improved luster and ability to take up dyes. It also does not shrink. Treatments with alkali are still used to obtain these benefits, but in the textile industry, more dilute solutions are used at higher temperatures. In the laboratory, concentrated, low temperature solutions are most effective at creating the cellulose II crystal structure. (Cold, highly concentrated NaOH can dissolve many cellulose samples (124).) Other systems, such as 65% nitric acid, also swell cellulose and can convert it to cellulose II (125,126).

A good example of the fundamental importance of the particular crystal form is the difference in rate of digestion by bacteria. Bacteria from cattle

rumen rapidly digest cellulose I but degrade cellulose II very slowly (127). Thus, allomorphic form can be an important factor in biochemical reactions of cellulose as well as in some conventional chemical reactions. On the other hand, the improved receptivity of mercerized cotton to dyes may result more from the increased amorphous content, rather than from the packing arrangement of the chains and the hydrogen-bonding system of the new crystal structure.

Besides garments, rayon is used for tire cord and industrial belting. Typical rayon yarns have lower tensile strength than cellulose I yarns, but Fortisan, a heterogeneously saponified cellulose acetate formerly made by Hoechst-Celanese, is a high strength rayon yarn, with its crystallites highly aligned along the fiber axis. The variables in the process of producing rayon fibers allow a large variety of performance characteristics (see Cellulose Fibers, Regenerated).

Some rare bacteria normally create cellulose II instead of I (128,129). Those bacteria apparently have large distances between the synthesizing complexes. This allows the various emerging molecules to fold upon themselves to take advantage of the van der Waals' forces, giving a broad band of cellulose that has its long molecular axes perpendicular to the direction of propagation of the band. Folding often occurs for some synthetic polymers such as polyethylene, but the various proposals of folding for native cellulose I now seem obsolete.

A repeatedly mercerized flax (linen) fiber (which gave an X-ray diffraction pattern similar to Fig. 3**b**) was studied with neutron diffraction to confirm that, unlike the cellulose I crystal structure, the cellulose II structures are composed of antiparallel chains (130). The O6 groups have the more usual gt disposition, and the interchain hydrogen bonding includes links between the corner and center chains as well as between the corner chains and between the center chains. Cellulose II is the most stable known form (117,131,132). Langan, Nishiyama, and Chanzy reject the previously proposed tg orientations for half of the O6 groups (96,133,134), and show the structure of II to be very similar to the structures of methyl cellotrioside (135), and of cellotetraose (136), both of which give cellulose II type powder diffraction patterns. The crystal densities of cellulose Iβ and II are almost identical.

Transformation from I to II. Knowledge is increasing regarding the transformation from the parallel-chain cellulose I structures to the antiparallel cellulose II. In Mercer's experiments the cellulose I yarns were dipped in alkali, then removed and rinsed. While the yarn remained intact (with some shrinkage), the crystal structure had converted from I to II. In the 1970s, when the combination of parallel I and antiparallel II structures was first widely articulated (96,133), many workers found it counterintuitive that such a fundamental change in the molecular orientation could occur with no substantial revisions in gross structure. Several facts, besides these new, well-determined crystal structures of I and II, support this change in chain packing. The parallel-up nature of Iβ has been confirmed in several different experiments, including an elegant electron microscopy study that lays out the relationship of the crystal structure to the fiber morphology (137). A number of cellulose II structures have chain folding, an antiparallel topology (102,129,138).

In the case of isolated or loosely arranged small microfibrils, such as in primary walls, the fibrous nature of the cellulose is completely lost by treatment in

NaOH, although cellulose II is produced (94). Similarly, while large, isolated, untreated crystalline microfibrils of algal cellulose are resistant to alkali, if treated with acid first and then with alkali, "shish kebab" structures are formed. The "shish" retains the cellulose I structure, and the lamellar "kebab" takes the cellulose II structure (138). In these cases, and in the cases of the bacterial cellulose where normal post-biosynthesis crystallization is thwarted, the antiparallel structure occurs through chain folding. Energy calculations show that such folding can occur with little energy penalty (84).

The current understanding (94) is that the fibrous form is retained during conversion from cellulose I to II only in secondary wall cellulose where microfibrils are adjacent to each other. While the molecules within any given cellulose I microfibril are parallel, the adjacent microfibrils in secondary wall material are themselves antiparallel. Thus a swelling of the crystal lattice, caused by the strong aqueous NaOH, allows the interpenetration, or interdigitation, of chains from neighboring antiparallel microfibrils, resulting in an antiparallel crystal (134,139). Such treatments, even when causing a complete transformation from the cellulose I structure, usually cause an increase in the amorphous cellulose content. Perhaps this is caused by folding of loose chain ends.

Other Polymorphs. There are several other cellulose polymorphs. Cellulose exposed to amines or liquid ammonia forms complexes with the swelling agent. Upon removal of the swelling agent, cellulose III is produced. The actual form of III depends on whether the starting material is cellulose I or II, giving III_I or III_{II}. Their diffraction patterns are similar to each other but the meridional intensities differ. Further, both revert to their parent structures if placed in a heated, high humidity environment. Treatment of the algal cellulose (a mixture of $I\alpha$ and $I\beta$) from *Valonia* in ethylenediamine to give cellulose III_I simultaneously induced subfibrillation in the initial microfibril (140). Thus crystallites 20 nm wide were split into subunits only 3–5 nm wide, even though the length was retained. Conversion of this III_I back to I gave a material with an electron diffraction pattern and NMR spectrum similar to that of cotton cellulose $I\beta$. The unit cell for III_I contains only one chain with two glucose residues (97), rendering obsolete a previously proposed two-chain cell. This cell results in a density of only 1.41 g/cm^3, considerably lower than the values 1.63 and 1.61 for cellulose $I\beta$ and II. As in the case of $I\alpha$ the structure of III_I must be composed of parallel chains. At present, a new crystal structure for III is being determined (Masahisa Wada, personal communication).

Similarly, cellulose IV_I and IV_{II}, formed when cellulose is treated in glycerol at temperatures ca 260°C, can revert to the parent I and II structures. Again, differences between the two diffraction patterns are biggest for the meridional reflections. The proposed structures of IV (98) are not stable in energy calculations (115,132), so details of these structures are not discussed here. Long-chain oligomers, eg, with 20 residues, crystallize from solution at high temperatures (90°C) as the IV_{II} form (141).

Cellulose x results from strong hydrochloric or phosphoric acid treatments (142). The degree of polymerization of their samples was as low as 15 or 20 following the strong acid treatment. No molecular arrangements have been proposed for cellulose x.

Conversions from cellulose I to II are widely considered to be irreversible, although there are some reports of regeneration of cellulose I (143,144). The irreversibility is considered to stem from the greater stability of cellulose II, compared with the cellulose I forms, and from the entropic difficulty in segregating the antiparallel chains of II into groups of parallel chains. Cellulose III and IV are thought to have higher energies than I and II, explaining the reversibility of the $I \rightarrow III_I$ and $II \rightarrow III_{II}$ conversions. The fact of parallel I and antiparallel II also explains the difference between the III_I and III_{II} structures. Cellulose x can also convert to cellulose IV_{II}, which can then convert to II.

Cellulose Hydrates. The interaction of cellulose with water is important for many reasons. Initially, cellulose II was incorrectly called cellulose hydrate; cellulose II itself has no crystalline water. Despite the high absorption of moisture, water does not penetrate the crystals in most cases. Instead, it inserts itself into the voids and onto the surfaces of the microfibrils. In some cases, however, there is water inside an otherwise pure cellulose crystal lattice. Cellulose II hydrate is stable at 93% rh (145). It contains four water molecules in a two-chain unit cell. At high hydration, these waters remained after Fortisan was swollen in hydrazine and washed with water. Another cellulose–water complex is called soda cellulose IV. Although soda cellulose I, II, and III (139) all do contain sodium ions, soda cellulose IV is formed as the sodium hydroxide is washed out of the cellulose (146). This structure, with unit cell dimensions different from those of cellulose hydrate, has two water molecules per two-chain unit cell. Two other hydrates were reported earlier (147,148).

General Considerations. All of the above crystal structures repeat in about 10.35 C. This is consistent with two individual glucose residues in the $^4C_1$ conformation. Even if the structures do not possess exact twofold symmetry, such as in Iα, there is only minor distortion from that ideal (except for regions with folds). This corresponds to a ribbon-like shape that is a flattened rectangle in cross-section, as indicated in Figures 1,4,5,6. This shape offers two different types of interaction with neighboring molecules. On the one hand, the short edges of the cross-section present the hydroxyl groups that donate and accept hydrogen bonds with neighboring molecules. The broad edges are the locations of C–H bonds that are perpendicular to the main plane of the glucose rings. These hydrophobic surfaces interact with similar surfaces on other molecules. These properties suit cellulose for its role in nature, with the efficient lateral packing similar to bricks in a wall giving a high density of strong covalent bonds parallel to the fiber axis. Also, solvents must be able to cope with both the network of hydrogen bonds and with the van der Waals' forces. The latter probably exceed those of the hydrogen bonds and contribute substantially to the long-term stability of cellulose.

With so many instances of this twofold ribbon shape, it could be surmised that this is the intrinsically favored shape. Besides the structures already mentioned, there are numerous complexes of cellulose such as those of amines (ethylenediamine, diaminopropane, and hydrazine) (149) in which the cellulose molecule has the same basic shape. The same is true for many chemical derivatives of cellulose, such as the commercially important cellulose triacetate structures (150,151).

However, as mentioned above, other shapes exist. Threefold helical structures, repeating in about 15 C, are the most frequently found alternative. This conformation does not allow an O3−O5′ hydrogen bond. It is frequently found for derivatives such as perethylated cellulose, which because of its ethyl groups is unable to form hydrogen bonds (152). Soda cellulose II is a complex in which the cellulose chain takes a threefold structure (153). Nitrocellulose [9004-70-0] molecules repeat in 25 C, with two helical turns in that distance, each with 2.5 glucose residues (154). When cellulose triacetate complexes with nitromethane, its 40.2 C repeat signifies helices with eight residues in three turns (80). Twofold helices can be considered to be either right- or left-handed, but cellulose structures with more than two residues per turn are apparently left-handed (81,155).

Supramolecular Structure. Cotton fibers have a complex, reversing, helical arrangement of macrofibrils. The properties of cotton fabrics are therefore distinct from properties of fabrics made of ramie and linen fibers. Those and other bast and leaf fibers have crystallites arranged much more parallel to the fiber axis, but there is also a hierarchy of structures. There is the stem of the plant, bast fiber bundles, technical fiber, and finally the plant cell, which is called the elementary fiber. Within that elementary fiber there are again microfibrils. Among cotton varieties, variations in this architecture are associated with differences in strength and other qualities. In addition to diffraction, NMR, and vibrational spectroscopy, two other categories of methods indicate the extent of crystallinity (156). Those involving chemical reaction include acid hydrolysis, formylation, periodate oxidation, and chemical microstructural analysis (CMA). CMA requires reaction with *N*,*N*-diethylaminoethyl chloride [100-35-6] and is based on the relative availability of the hydroxyl groups to that of OH-3, which is least accessible to this agent. Other methods involving sorption include deuteration, moisture regain, and iodine sorption. Both chemical reaction and sorption techniques differ from physical measurements because they measure the fraction of the cellulose that is not readily accessible to a specific reagent. The determined fraction of ordered cellulose varies depending on the method.

Pore Structure. Most cellulosic materials have pores into which reagents must penetrate in order to react. Variations in these pore sizes govern the extent of reaction and quality of finished products (157). In early investigations into pore size distributions, Aggebrandt and Samuelson obtained accessibilities for rayon and cotton fibers with solute exclusion of a series of ethylene glycols (158). Stone and Scallan (159) and Stone and co-workers (160) used individual samples in flasks and conducted the measurements with oligomeric sugars and dextrans of various high molecular weights to measure fiber saturation values, to assess increases in pore sizes with the cell wall during pulping, and to characterize distribution of pore sizes in wood pulps and celluloses. In another paper, Stone and Scallan (161) developed a structural model for the cell wall of water-swollen bleached pine sulfate pulp based on solute exclusion.

Martin and Rowland (162,163) extended the solute exclusion method by developing a chromatographic technique. A series of water-soluble molecules of increasing size are used as molecular probes or “feeler gauges.” Sugars of low molecular weight, ethylene glycols, glymes, and dextrans were included because information on their molecular diameters is available. Also, each probe molecule should penetrate the cellulose sample and not be adsorbed on the cellulosic

surfaces. Their initial experiments involved decrystallized cotton, and subsequently chopped cottons (which retained most of their crystallinity), whole fibers and fabrics. These studies were extended to include the effects of cotton genotype, fabric pretreatments such as scouring, caustic mercerization, and liquid ammonia treatment. Also studied were the effects of cross-linking with the conventional agent dimethyloldihydroxyethyleneurea (DMDHEU) and the formaldehyde-free reagents 4,5-dihydroxy-1,3-dimethyl-2-imidazolidone (DHDMI) and butanetetracarobxylic acid (BTCA). The work with DHDMI compared residual pore volume with dyeability and the study with BTCA compared the effectiveness of different catalysts. Cotton genotypes differ in their pore size distributions (164). Scouring of fabric increases the accessible internal volume, which is substantially enhanced by caustic mercerization (165). Liquid ammonia treatment also increases the internal volume (not to the extent of caustic mercerization) but the degree is dependent upon the technique used to remove the ammonia (166). Water exchange produced the greatest increase, and removal by dry heat the least. The internal volume is substantially reduced by crosslinking with DMDHEU (167) and, to a lesser degree, with DHDMI (168). Fabrics treated with DHDMI are susceptible to dyeing with small direct dyes. The study of BTCA catalysis showed that the residual internal volume in small pores was inversely related to the resilience level achieved (169). This work was recently reviewed (170).

Similar information is obtained from both the static and chromatographic methods. Results give the internal volume in the water-swollen cellulose that is available as solvent to the probes. After the initial equipment setup, the chromatographic technique is preferred for obtaining large amounts of data.

In an entirely different approach Schurz and coworkers (171) have used small-angle X-ray scattering to study the void system and the inner surfaces of fibers. They propose that the cellulose fiber consists of crystalline portions, "amorphous" regions, and air-filled voids. They obtained the ratio of inner surface to the volume of the void and certain average parameters, which characterize the void size, from the tail-end portion of the scattering curve. In their comparison of the regenerated cellulose fibers modal (a high tenacity viscose rayon) and lyocell (see Cellulose Solvents, below) they conclude that a certain void fraction is required for any fiber. The range lies between 0.0005 and 0.01. This represents the "space reserve," which is indispensable for a good fiber. They conclude that it is a very favorable void system, consisting of elongated and well-oriented voids situated between the compact elementary fibrils, which is responsible for the superior mechanical properties of lyocell fibers. Although this technique has provided information about voids in cellulosic fibers, it does not indicate if these voids are accessible to chemical agents. Fischer et al. found lozenge-shaped voids with small-angle neutron scattering (172) of deuterated ramie cellulose but not Fortisan rayon. They attributed these voids to the packing of kinked microfibrils.

6. Microcrystalline Cellulose

Pulverized forms of woodpulp have been widely used as fillers in some foods and pharmaceuticals. However, their utility is limited because the highly fibrous

form results in poor mouthfeel. This problem can be overcome by reducing the woodpulp fibers to colloidal microcrystalline cellulose (173,174). It is made by reducing the particle size and molecular weight by hydrolysis with hydrochloric acid to the point of LODP (see Chemical Structure, above). In aqueous suspensoids, these much finer particles have a smooth texture resembling uncolored butter and exhibit pseudoplastic properties, including stable viscosity, over a wide temperature range. It can therefore be used as a low calorie substitute for fat. Microcrystalline celluloses are important for their heat stability; ability to thicken, with favorable mouthfeel; and flow control. They extend starches, form sugar gels, stabilize foams, and control formation of ice crystals. A few of the foods in which microcrystalline cellulose has been commercially successful are fillings, meringue (cold process), chocolate cake sauce (frozen), cookie fillings, whipped toppings, and imitation ice cream for use as a bakery filling. In the pharmaceutical industry, microcrystalline cellulose is used mostly for tableting. It is used as an excipient to assist in the flow, lubrication, and bonding properties of the ingredients to be tableted, to improve the stability of the drugs in tablet form, and especially to provide for rapid disintegration in the stomach. The determined fraction of ordered cellulose varies depending on the method.

In 2000, 55,000 t of microcrystalline cellulose were sold by the original vendor, FMC, and other companies also sell it. Its utility has led to development of other colloidal polymer microcrystals (see Colloids). For example, polyamides and polyesters from recycled materials can be biodegraded to give microcrystals having a size of 30 nm (175).

7. Chemical Reactivity

Cellulose is chemically like other carbohydrate polymers that consist of pyranose rings bearing hydroxyl groups. These chains of glucose residues include a reducing end unit, a nonreducing end unit, and intermediate units. Most celluloses have a high degree of polymerization; the intermediate glucose residues determine the chemical and physical properties and the end units may be ignored. The glycosidic bonds in cellulose are strong and stable under a variety of reaction conditions. It is a generally insoluble, highly crystalline polymer.

Cellulose can be degraded by acid, or, to a lesser extent, by alkali. The glycosidic bond is susceptible to acid-catalyzed hydrolysis. High yields of glucose can result when hydrolysis proceeds for a long enough time, needing days or weeks. After a few hours under conditions such as room temperature and HCl concentrations around 10 *N* or 0.25 *M* H_2SO_4 at 100°C, noncrystalline cellulose is lost, leaving a more crystalline material. An LODP of 150 or 180 glucose residues is reached (176), with the length depending on the source of the cellulose. Explanations based on chain folding (177) for the various LODP values from different celluloses are not consistent with evidence from other studies of most cellulose structures. However, except for a proposal of periodic weak zones (178), no explanation has been put forth.

While alkaline degradation (179,180) is usually more subtle, losses during pulping of as much as 25% of alpha cellulose have been reported. The problem is exaggerated when excess oxygen is present. Where oxygen has been excluded,

cellulose undergoes endwise degradation, scission of the glycosidic linkages, and, under certain conditions, breakdown to low molecular weight organic acids. Typically, some 50 glucose residues react and are peeled off the end of each cellulose molecule before a stable metasaccharinate (3-deoxy-D-ribohexonate) is formed that blocks further alkaline action.

Oxidation under moderate conditions (181) yields solid products referred to as oxycelluloses. This general term describes various products that must be qualified by indicating the oxidant employed. Among oxidants used are periodate, dinitrogen tetroxide, and sodium hypochlorite. Cellulose is particularly susceptible to oxidation under alkaline conditions.

Industrially important chemical modifications of cellulose generally involve reaction with its 2, 3, and 6 hydroxyl groups. These reactive sites undergo most of the reactions characteristic of alcohols. Etherification and esterification are of particular importance for cellulose (182). Cross-linking of the polymer chains gives durable press properties (183) to cellulosic textiles and dimensional stability to wood products. Reactions with the hydroxyl groups usually take place under heterogeneous conditions because of the insoluble and crystalline nature of cellulose. Under such mild heterogenous conditions, the reactivities of hydroxyl groups may depend on whether they are involved in hydrogen bonds (157). Compared with soluble polysaccharides, therefore, the extents of such reactions are inhibited.

8. Cellulose Solvents

Solvents for cellulose are central to the rayon and cellophane industries as well as being necessary for many analyses. Despite the difficulty of dissolving cellulose in aqueous and organic liquids, several cellulose solvents have been been devised over the last 150 years and reviews have been published (184–187). The solvents fall into several categories; solvents discussed in the following paragraphs do not include processes where cellulose is converted to a derivative that is subsequently dissolved in another medium. For example, cellulose can be gradually dissolved in the mixture of pyridine and acetic anhydride. However, this involves a chemical reaction and the resulting dissolved matter is "cellulose acetate," not "cellulose." The viscose process is the most important industrial method for dissolving cellulose (188). In this process, alkali cellulose [9081-58-7], pulp swollen in NaOH solution, is reacted with CS_2 to give a cellulose xanthate [9032-37-5]. The xanthate is dissolved in aqueous alkali and subsequently spun into the coagulating bath containing sulfuric acid to convert back to cellulose (189). This process, from which cellulose is readily regenerated, is sometimes considered to use a cellulose solution because solvation and derivatization occur simultaneously. Again, the dissolved molecule is a derivative, not pure cellulose. Because of the crystallite size, molecular weight and purity differences in cellulose from various sources, solvents that work well for some celluloses may not work for others. Cellulose subjected to high temperature and pressure during the steam explosion process can be dissolved in strong base (190). It has been exceptionally difficult to find effective solvents that preserve the original molecular weights of high dp samples.

The first solvent systems for cellulose were heavy metal–amine complex solutions. Aqueous solutions of Cu with ammonia (191) or ethylenediamine (192), called "cupra" and "cuen" [111274-71-6], respectively, dissolve cellulose rapidly although cellulose is subjected to progressive, oxidative degradation. The cuproammonium system is used for making high purity dialysis membranes. Instead of Cu, the alternative metals Co, Zn, Ni, and Cd can also be used effectively (193,194). Also discovered early on, some aqueous inorganic salt solutions dissolve cellulose at temperatures above 100°C. However, only a few salts will work, including $ZnCl_2$ [7646-85-7] (195), $Ca(SCN)_2$ [2092-16-2] (196) and NaSCN (197). All of these salt solutions must be highly concentrated to be effective solvents. In addition to the extremely strong, cold NaOH solutions that can dissolve many celluloses; cold, weaker NaOH solutions can also swell cellulose and dissolve 20–30% of the cellulose. Sonication (198) completes the dissolution of these "soda cellulose Q" slurries (199,200).

Reliable nonaqueous salt solutions include thiocyanate/amine and LiCl [7447-41-8]/dimethylacetamide [127-19-5] (DMAc) systems. In the thiocyanate/amine system, ammonia (201), hydrazine (202), and ethylenediamine (203) can be used as the amine. The potent thiocyanates are NH_4SCN in ammonia and NaSCN and KSCN in hydrazine and ethylenediamine. With these thiocyanate/amine solvents, solutions up to about 20% (w/w) of DP210 cellulose can be obtained without heating and/or pretreatment. The LiCl/DMAc system is useful for carrying out chemical modification of cellulose under homogeneous conditions (204) because it has no active functional group to compete with a nucleophilic attack. With DMAc, however, heating to ca 150°C and/or swelling procedures are required for the complete dissolution of cellulose. Both thiocyanate/amine and LiCl/DMAc systems afford liquid crystals of cellulose, suggesting that the chain rigidity of cellulose increases in these solvents. Most other nonaqueous solvent systems, using dipolar aprotic solvents such as dimethyl sulfoxide (203,205) and dimethylformamide (207), cause chemical derivatization even though the derivatives are unstable and readily regenerated to cellulose.

The *N*-methylmorpholine-*N*-oxide [7529-22-8] (NMMO)/H_2O system (208) is the only industrialized solvent for the spinning of cellulosic fiber that is used in place of viscose process. The solutions of dissolved cellulose have liquid crystalline properties (209) so that the lyocell (Tencel) fibers spun from this solvent have high tenacity and modulus. A drawback is that the dissolution of cellulose occurs above 130°C, close to the explosive point of NMMO (150°C). Rosenau (210) has reviewed the cellulose/NMMO system and ways to avoid runaway thermal reactions.

Most cellulose solvents are multicomponent; however, *N*-ethylpyridinium chloride is a single-component system (211). Recently, ionic liquids such as 1-butyl-3-methylimidazolium salts (212) have aroused interest as a single-component solvent system. The primary driving forces behind investigation of new solvents include environmental concerns, the ability to form liquid crystals and single component in the new solvent systems.

9. Liquid Crystals

Many cellulose derivatives form liquid crystalline phases, both in solution (lyotropic mesophases) and in the melt (thermotropic mesophases). The first

report (213) showed that aqueous solutions of 30% hydroxypropylcellulose [9004-64-2] (HPC) form lyotropic mesophases that display iridescent colors characteristic of the chiral nematic (cholesteric) state. The field has grown rapidly and has been reviewed from different perspectives (80,214–217). A major reason for the interest in cellulosic liquid crystals is their role in the production of high strength, high modulus fibers. Cellulose fiber spun from an anisotropic phosphoric acid solution had a breaking stress value of 1.7 GPa, about twice that of the highest-strength native fibers (218). Even higher strengths (2.7 GPa) were reported for fibers spun from liquid crystalline cellulose acetate in trifluoroacetic acid, stretched in steam and then saponified (219,220).

The separation of liquid crystals as the concentration of cellulose increases above a critical value (30%) is mostly because of the higher combinatorial entropy of mixing of the conformationally extended cellulosic chains in the ordered phase. The critical concentration depends on solvent and temperature, and has been estimated from the polymer chain conformation using lattice and virial theories of nematic ordering (221–226). The side-chain substituents govern solubility, and if sufficiently bulky and flexible can yield a thermotropic mesophase in an accessible temperature range. Acetoxypropylcellulose [96420-43-8], prepared by acetylating HPC, was the first reported thermotropic cellulosic (227), and numerous other heavily substituted esters and ethers of hydroxyalkyl celluloses also form equilibrium chiral nematic phases, even at ambient temperatures.

Substituted cellulose chains have chiral twists. This leads to chiral nematic liquid crystals, in which the polymer is oriented in macroscopic helicoidal structures. If the pitch of these helicoidal structures is of the same magnitude as the wavelength of visible light, the samples show striking optical properties, in particular the reflection of circularly polarized light with a wavelength related to the pitch. The wavelength of the reflected light depends on factors such as the nature of the side groups, the degree of substitution, the molecular weight of the polymer, temperature, the nature of the solvent, and the polymer concentration. Hydroxypropylcellulose and several of its ether and ester derivatives form right-handed nematic phases (215,227–229). Ethylcellulose [9004-57-3] in glacial acetic acid gives a left-handed nematic phase (230). A change in the nematic chirality may occur with a change in the side-group substituents (231–234) and solvent (235,236). Thermally induced inversions of the twist sense have been reported for oligomers of tri-*O*-2-(2-methoxyethoxy)ethylcellulose [123423-08-5] (TMEC) and tri-*O*-heptylcellulose [100214-73-1] (237).

The helicoidal structure of such liquid crystals can be carried to the solid state by cross-linking (238,239) or by careful evaporation of solvent (240,241). Underivatized cellulose can also form ordered mesophases (209,242), and gel films precipitated from lithium chloride dimethylacetamide retain some mesophase structure (241).

Interest has been growing in liquid crystalline phases where the ordering species is not a molecularly dispersed cellulosic chain, but rather a colloidal particle of cellulose. Surprisingly, colloidal dispersions of cellulose crystallites, produced by careful sulphuric acid hydrolysis of natural cellulose fibres, were found to self-order into a chiral nematic phase above a critical concentration in water (243). The critical concentration depended primarily on the axis ratio of the rodlike cellulose particles, which typically had widths of a few nanometers, and lengths of tens of nanometers (244,245). The phase separation also depended

on the ionic strength (246) and on the nature of the counterions (247) of the suspension. The chiral nematic order of the suspensions was maintained in films cast from the suspensions (248). The above suspensions were electrostatically stabilized by the presence of sulfate groups on the surface. Stabilization in water by grafting (249) and in nonpolar solvents (250) has been reported. The surface of the crystallites, termed "cellulose nanocrystals," may be modified chemically (251). Many properties of the suspensions have been examined by small-angle X-ray altering, small-angle neutron scattering (253), and induced CD of suspensions (254) and films (255). Flow properties (256) and the interfacial tension between isotropic and chiral nematic phases (257) have been investigated, and the suspension has been proposed as a medium for nmr dipolar coupling (258).

BIBLIOGRAPHY

"Cellulose" in *ECT* 1st ed., Vol. 3, pp. 342–357, by J. Barsha and P. Van Wyck, Hercules Powder Company; in *ECT* 2nd ed., Vol. 4, pp. 593–616, J. K. Hamilton and R. L. Mitchell, Rayonier, Inc.; in *ECT* 3rd ed., Vol. 5, pp. 70–88, by A. F. Turbak, ITT Rayonier, Inc.; D. F. Durso, Johnson & Johnson; O. A. Battista, Research Services Corp.; H. I. Bolker, Pulp and Paper Research Institute of Caroda; and J. R. Colvin, National Research Council, Canada; in *ECT* 4th ed., Vol. 5, pp. 476–496, by Alfred D. French, Noelie R. Bertoniere, Southern Regional Research Center, O. A. Battista, (Microcrystalline Cellulose) Research Services Corporation, John A. Cuculo, (Cellulose Solvents) North Carolina State University, Derek G. Gray, (Liquid Crystals) Pulp and Paper Research Institute of Canada; "Cellulose" in *ECT* (online), posting date: December 4, 2000, by Alfred D. French, Noelie R. Bertoniere, Southern Regional Research Center, O. A. Battista, (Microcrystalline Cellulose) Research Services Corporation, John A. Cuculo, (Cellulose Solvents) Norther Carolina State University, Derek G. Gray, (Liquid Crystals) Pulp and Paper Research Institute of Canada.

CITED PUBLICATIONS

1. A. Payen, *Compt. Rend.* **7**, 1052 (1838).
2. D. A. Hall, F. Happey, P. J. Lloyd, and H. Saxl, *Proc. Royal Soc. (London)* **151**, 497 (1959).
3. *AF&*PA Statistics of Paper, Paperboard and Wood Pulp, American Forest and Paper Association, Washington, D.C., 2001.
4. A. K. Bledzki and J. Gassen, *Prog. Polym. Sci.* **24**, 221 (1999).
5. W. E. Morton and J. W. S. Hearle, *Physical Properties of Textile Fibres*, 2nd ed., The Textile Institute, Manchester, 1993, p. 282.
6. J. Cosgrove, *Nature* **407**, 321 (2000).
7. R. M. Rowell and H. P. Stout, in M. Lewin and E. M. Pearce, eds., *Handbook of Fiber Chemistry*, 2nd ed., Marcel Dekker, Inc., New York, 1998, p. 465.
8. C. Schuerch, ed., *Cellulose and Wood—Chemistry and Technology*, John Wiley & Sons, Inc., New York, 1989.
9. T. P. Nevell and S. H. Zeronian, eds., *Cellulose Chemistry and Its Applications*, Ellis Horwood, Chichester, U.K., 1985.
10. R. H. Atalla, ed., *The Structures of Cellulose—Characterization of the Solid States* (ACS Symposium Series 340), American Chemical Society, Washington, D.C., 1987.

11. R. A. Young and R. M. Rowell, eds., *Cellulose: Structure, Modification and Hydrolysis*, Wiley-Interscience, New York, 1986.
12. J. F. Kennedy, G. O. Phillips, and P. A. Williams, eds., *Cellulose Structural and Functional Aspects*, Ellis Horwood, Chichester, U.K., 1989.
13. R. M. Brown Jr., ed., *Cellulose and Other Natural Polymer Systems: Biogenesis, Structure, and Degradation*, Plenum Press, New York, 1982.
14. H. A. Krassig, *Cellulos—Structure, Accessibility and Reactivity*, Gordon and Breach Science Publishers, Amsterdam, 1993.
15. R. H. Marchessault and P. R. Sundararajan, in G. O. Aspinall, ed., *The Polysaccharides*, Vol. **2**, Academic Press, New York, 1983, pp. 12–95.
16. Serur-osu Gakkai hensh-u, *Serur-osu no jiten*, Asakura Shoten, Tokyo, 2000.
17. A. D. French, in S.-F. Yang, ed., *Discoveries in Plant Biology III*, World Scientific Publishing Company, Hong Kong, 2000, pp. 163–196.
18. D. Klemm, H.-P. Schmaur, and T. Heinze, *Biopolymers*, Vol., **6**, Wiley-VCH, Weinheim, 2001.
19. T. Heinze and W. Glasser, eds., *Cellulose derivatives: Modification, Characterization and Nanostructures* (ACS Symposium Series 688), American Chemical Society, Washington, D.C., 1998.
20. F. C. Lin, R. M. Brown Jr., J. B. Cooper, and D. P. Delmer, *Science* **230**, 822 (1985).
21. D. G. White and R. M. Brown Jr., in Ref. 8, pp. 573–590.
22. J. Krieger, *Chem. Eng. News* 35–37 (May 21, 1990).
23. U.S. Pat. 4,960,763 (Oct. 2, 1990), R. S. Stephens, J. A. Westland, and A. N. Neogi (to Weyerhaueser Co.).
24. R. A. Kent, R. S. Stephens, and J. A. Westland, *Food Technol.* **45**, 108 (1991).
25. U.S. Pat. 5,964,983 (Oct. 12, 1999), E. Dinand, H. Chanzy, M. R. Vignon, A. Maureaux, and I. Vincent.
26. R. M. Brown Jr., and D. Montezino, *Proc. Natl. Acad. Sci. U.S.A.* **73**, 143 (1976).
27. F. C. Lin and R. M. Brown Jr., in Ref. 8, pp. 473–492.
28. F. C. Lin, R. M. Brown Jr., R. P. Drake Jr., and B. E. Haley, *J. Biol. Chem.* **265**, 4782 (1990).
29. I. M. Saxena, F. C. Lin, and R. M. Brown Jr., *Plant Mol. Biol.* **15**, 673 (1990).
30. K. Okuda, I. Li, K. Kudlicka, S. Kuga, and R. M. Brown Jr., *Plant Physiol.* **101**, 1131 (1993).
31. L. Li and R. M. Brown Jr., *Plant Physiol.* **101**, 1143 (1993).
32. L. Li, R. R. Drake Jr., S. Clement, and R. M. Brown Jr., *Plant Physiol.* **101**, 1149 (1993).
33. J. H. Lee, R. M. Brown Jr., S. Kuga, S. Shoda, and S. Kobayashi, *Proc. Natl. Acad. Sci. U.S.A.* **91**, 7425 (1994).
34. K. Kudlicka, R. M. Brown Jr., L. Li, J. H. Lee, and S. Kuga, *Plant Physiol.* **107**, 111 (1995).
35. K. Kudlicka, J. H. Lee, and R. M. Brown Jr., *Am. J. Bot.* **83**, 274 (1996).
36. K. Kudlicka and R. M. Brown Jr., *Plant Physiol.* **115**, 643 (1997).
37. J. Lai-Kee-Him, H. Chanzy, M. Müller, J.-L. Putaux, T. Imai, and V. Bulone, *J. Biol. Chem.* **277**, 36931 (2002).
38. L. Peng, Y. Kawagoe, P. Hogan, and D. Delmer, *Science* **295**, 147 (2002).
39. S. Kimura, W. Laosinchai, T. Itoh, X. Cui, R. Linder, and R. M. Brown Jr., *Plant Cell* **11**, 2075 (1999).
40. S. Kimura, H. P. Chen, G. Kikuchi, I. M. Saxena, R. M. Brown Jr., and T. Itoh, *J. Bacteriol.* **183**, 5668 (2001).
41. S. Mizuta and R. M. Brown Jr., *Protoplasma* **166**, 200 (1992).
42. S. K. Cousins and R. M. Brown Jr., *Polymer* **36**, 3885 (1995).
43. S. K. Cousins and R. M. Brown Jr., *Polymer* **38**, 897 (1997).

44. S. K. Cousins and R. M. Brown Jr., *Polymer* **38**, 903 (1997).
45. I. M. Saxena, K. Kudlicka, K. Okuda, and R. M. Brown Jr., *J. Bacteriol.* **176**, 5735 (1994).
46. I. M. Saxena, R. M. Brown Jr., M. Fevre, R. Geremia, and B. Henrissat, *J. Bacteriol.* **177**, 1419 (1995).
47. I. M. Saxena, R. M. Brown Jr., and T. Dandekar, *Phytochem.* **57**, 1135 (2001).
48. J. R. Pear, Y. Kawagoe, W. E. Schreckengost, D. P. Delmer, and D. M. Stalker, *Proc. Natl. Acad. Sci. U. S. A.* **93**, 12637 (1996).
49. T. Arioli, L. Peng, A. S. Betzner, J. Burn, W. Wittke, W. Herth, C. Camilleri, H. Höfte, J. Plazinski, R. Birch, A. Cork, J. Glover, J. Redmond, and R. E. Williamson, *Science* **279**, 717 (1998).
50. T. Richmond, *Genome Biol.* **1**, 3001.1 (2000).
51. N. G. Taylor, W. R. Scheible, S. Cutler, C. R. Somerville, and S. R. Turner, *Plant Cell* **11**, 769 (1999).
52. F. Nicol, I. His, A. Jauneau, S. Vernhettes, H. Canut, and H. Höfte, *EMBO J.* **17**, 5563 (1998).
53. F. Sterky, S. Regan, J. Karlsson, M. Hertzberg, A. Rohde, A. Holmberg, B. Amini, R. Bhalerao, M. Larsson, R. Villarroel, M. Van Montagu, G. Sandberg, O. Olsson, T. T. Teeri, W. Boerjan, P. Gustafsson, M. Uhlén, B. Sundberg, and J. Lundeberg, *Proc. Natl. Acad. Sci. U.S.A.* **95**, 13330 (1998).
54. L. Wu, C. P. Joshi, and V. L. Chiang, *Plant J.* **22**, 495 (2000).
55. M. Fagard, T. Desnos, T. Desprez, F. Goubet, G. Refrégier, G. Mouille, M. McCann, C. Rayon, S. Vernhettes, and H. Höfte, *Plant Cell* **12**, 2409 (2000).
56. S. Sato, T. Kato, K. Kakegawa, T. Ishii, Y. G. Liu, T. Awano, K. Takabe, Y. Nishiyama, S. Kuga, Y. Nakamura, S. Tabata, and D. Shibata, *Plant Cell Physiol.* **42**, 251 (2001).
57. D. R. Lane, A. Wiedemeier, L. Peng, H. Höfte, S. Vernhettes, T. Desprez, C. H. Hocart, R. J. Birch, T. I. Baskin, J. E. Burn, T. Arioli, A. S. Betzner, and R. E. Williamson, *Plant Physiol.* **126**, 278 (2001).
58. J. Zuo, Q. W. Niu, N. Nishizawa, Y. Wu, B. Kost, and N. H. Chua, *Plant Cell* **12**, 1137 (2000).
59. C. S. Gillmor, P. Poindexter, J. Lorieau, M. M. Palcic, and C. Somerville, *J. Cell Biol.* **156**, 1003 (2002).
60. N. G. Taylor, S. Laurie, and S. R. Turner, *Plant Cell* **12**, 2529 (2000).
61. X. Zogaj, M. Nimtz, M. Rohde, W. Bokranz, and U. Römling, *Mol. Microbiol.* **39**, 1452 (2001).
62. L. Peng, F. Xiang, E. Roberts, Y. Kawagoe, L. C. Greve, K. Kreuz, and D. P. Delmer, *Plant Physiol.* **126**, 981 (2001).
63. D. Nobles, D. Romanovicz, and R. M. Brown Jr., *Plant Physiol.* **127**, 529 (2001).
64. Websites for additional information on cellulose and cellulose biosynthesis: The Cellulose Electronic Network—A website devoted to all aspects of cellulose: http://128.83.195.51/cen/; The Stanford Cell Wall Page—A website devoted to cellulose synthase genes and other aspects of plant cell walls: http://cellwall.stanford.edu/; The Unrooted N J Tree of Processive Glycosyl Transferases—A website devoted to updated cataloging of processive glycosyl transferases, including cellulose synthases: http://www.botany.utexas.edu/cen/library/tree/main.htm.
65. S. K. Batra, in M. Lewin and E. M. Pearce, eds., *Handbook of Fiber Chemistry*, 2nd ed., Marcel Dekker, Inc., New York, 1998, p. 505.
66. R. P. Singh, ed., *The Bleaching of Pulp*, TAPPI Monograph Series, 3rd ed., Technical Association of the Pulp and Paper Industry, Atlanta, Ga., 1979.
67. R. H. Marchessault and J. St. Pierre, in L. E. St. Pierre and G. R. Brown, eds., *Proceedings of the CHEMRAWN Conference, Toronto, Canada, July 1978*, Pergamon Press, New York, 1980, pp. 613–625.

68. R. H. Marchessault, S. Coulombe, T. Hanai, and H. Morikawa, *Pulp. Pap. Mag. Can. Trans.* **6**, TR52–TR56 (1980).
69. B. K. Avellar and W. G. Glasser, *Biomass and Bioenergy* **14**, 205 (1998).
70. W. G. Glasser and R. S. Wright, *Biomass and Bioenergy* **14**, 219 (1998).
71. S. C. Van Winkle and W. G. Glasser, *J. Pulp Pap. Sci.* **21**, J37 (1995).
72. G. O. Phillips and J. Meadows, in J. F. Kennedy, G. O. Phillips, and P. A. Williams, eds., *Wood Processing and Utilization*, Ellis Horwood, Chichester, U.K., 1989, pp. 3–28; R. P. Overend and E. Chornet, pp. 395–400; T. Yamashiki and co-workers, pp. 401–406; K. Shimizu, K. Sudo, H. Ono, and T. Fujii, pp. 407–411.
73. U.S. Pat. 4,645,541 (Feb. 24, 1987), E. A. DeLong.
74. U.S. Pat. 4,947,743 (Aug. 14, 1990), D. B. Brown and H. Malys (to Stake Technology Ltd.).
75. U.S. Pats. 4,119,025 (Oct. 10, 1978) and 4,186,658 (Feb. 5, 1980), D. B. Brown (to Stake Technology Ltd.).
76. U.S. Pat. 4,136,207 (Jan. 23, 1979), R. Bender (to Stake Technology Ltd.).
77. H. Krassig and W. Kappner, *Makromol. Chem.* **44**/46, 1 (1961).
78. K. B. Hicks, A. T. Hotchkiss Jr., K. Sasaki, P. L. Irwin, L. W. Doner, G. Nagahashi, and R. M. Haines, *Carbohydr. Polym.* **25**, 205 (1994).
79. K. Hess and C. Trogus, *Z. phys. Chem. (B)* **13**, 25 (1931).
80. P. Zugenmaier, in Ref. 11, pp. 221–245.
81. Z. Peralta-Inga, G. P. Johnson, M. K. Dowd, J. Rendleman, E. D. Stevens and A. D. French, *Carbohydr. Res.* **337**, 851 (2002).
82. A. Ernst and A. Vasella, *Helv. Chim. Acta* **79**, 1279 (1996).
83. T. Kondo, E. Togawa, and R. M. Brown Jr., *Biomacromolecules* **2**, 1324 (2001).
84. A. D. French, in Ref. 8, pp. 103–118.
85. D. A. Brant and M. D. Christ, *ACS Symp. Ser.* **430**, 42 (1990).
86. P. Zugenmaier, *Prog. Polym. Sci.* **26**, 131 (2001).
87. A. Isogai, in R. Gilbert, ed., *Cellulosic Polymers*, Hanser Publishers Inc., Cincinnati, Ohio, 1994.
88. Y. Nishiyama, S. Kuga, M. Wada, and T. Okano, *Macromolecules* **30**, 6395 (1997).
89. A. Sarko, C.-H. Chen, B. J. Hardy, and F. Tanaka, *ACS Symp. Ser.* **430**, 345 (1989).
90. A. D. French, W. A. Roughead, and D. P. Miller, *ACS Symp. Ser.* **340**, 15 (1987).
91. L. R. Schroeder, V. M. Gentile, and R. H. Atalla, *J. Wood Chem. Technol.* **6**, 1 (1986).
92. A. Isogai, Y. Akishima, F. Onabe, M. Usuda, and R. H. Atalla, in J. F. Kennedy, G. O. Phillips, and P. A. Williams, eds., *Cellulose*, Horwood, Chichester, U.K., 1990, pp. 105–110.
93. Ref. 14, p. 169.
94. E. Dinand, M. Vignon, H. Chanzy, and L. Heux, *Cellulose* **9**, 7 (2002).
95. C. Woodcock and A. Sarko, *Macromolecules* **13**, 1183 (1980).
96. A. J. Stipanovic and A. Sarko, *Macromolecules* **9**, 851 (1976).
97. M. Wada, L. Heux, A. Isogai, Y. Nishiyama, H. Chanzy, and J. Sugiyama, *Macromolecules* **34**, 1237 (2001).
98. E. S. Gardiner and A. Sarko, *Can. J. Chem.* **63**, 173 (1985).
99. H. Chanzy, in J. F. Kennedy, G. O. Phillips and P. A. Williams, eds., *Cellulose Sources and Exploitation*, Ellis Horwood, New York, 1990, pp. 3–12.
100. A. Frey-Wyssling, *Biochim. Biophys. Acta* **18**, 166 (1955).
101. R. St. John Manley, *J. Polym. Sci. Part A-2* **9**, 1025 (1971).
102. F. J. Kolpak and J. Blackwell, *Textile Res. J.* **45**, 568 (1975).
103. A. A. Baker, W. Helbert, J. Sugiyama, and M. J. Miles, *Biophysical J.* **79**, 1139 (2000).
104. E. A. Bayeer, H. Chanzy, R. Lamed, and Y. Shoham, *Curr. Opin. Struct. Biol.* **8**, 548 (1998).

105. K. H. Gardner and J. Blackwell, *Biopolymers* **13**, 1974 (1975).
106. H. J. Marrinan and J. Mann, *J. Polym. Sci.* **21**, 301 (1956).
107. C. Y. Liang and R. H. Marchessault, *J. Polym. Sci.* **37**, 385 (1959).
108. G. Honjo and M. Watanabe, *Nature* **181**, 326 (1958).
109. R. H. Atalla and D. L. VanderHart, *Science* **223**, 283 (1984).
110. J. Sugiyama, R. Vuong, and H. Chanzy, *Macromolecules* **24**, 4168 (1991).
111. K. R. Andress, *Z. Phys. Chem. A* **136**, 279 (1928).
112. K. H. Meyer and H. F. Mark, *Z. Phys. Chem. B* **2**, 115 (1929).
113. Y. Nishiyama, P. Langan, and H. Chanzy, *J. Am. Chem. Soc.* **124**, 9074 (2002).
114. Y. Nishiyama, A. Isogai, T. Okano, M. Mueller, and H. Chanzy, *Macromolecules* **32**, 2078 (1999).
115. A. D. French, D. P. Miller, and A. Aabloo, *Int. J. Biol. Macromol.* **15**, 30 (1993).
116. A. Aabloo, A. D. French, R.-H. Mikelsaar, and A. J. Pertsin, *Cellulose* **1**, 161 (1994).
117. A. P. Heiner, J. Sugiyama, and O. Telleman, *Carbohydr. Res.* **273**, 207 (1995).
118. R. J. Vietor, K. Mazeau, M. Lakin, and S. Perez, *Biopolymers* **54**, 342 (2000).
119. J. Sugiyama, T. Okano, H. Yamamoto, and F. Horii, *Macromolecules* **23**, 3196 (1990).
120. F. Horii, H. Yamamoto, R. Kitamaru, M. Tanahashi, and T. Higuchi, *Macromolecules* **20**, 2949 (1987).
121. T. Imai and J. Sugiyama, *Macromolecules* **31**, 6275 (1998).
122. H. Chanzy, K. Imada, and R. Vuong, *Protoplasma* **94**, 299 (1978).
123. E. A. Parnell, *The Life and Labours of John Mercer*, Longmans, Green & Co., London, 1886, pp. 175–207, 214–216, 317.
124. A. Isogai and R. H. Atalla, *Cellulose* **5**, 309 (1998).
125. J. R. Katz and K. Hess, *Z. Phys. Chem. (Leipzig)* **122**, 126 (1927).
126. J. Chedin and A. Marsaudon, *Chim. Ind. (Paris)* **71**, 55 (1954).
127. P. J. Weimer, J. M. Lopez-Guisa, and A. D. French, *Appl. Environ. Microbiol.* **56**, 2421 (1990).
128. W. A. Sisson, *Science* **87**, 350 (1938).
129. S. Kuga, S. Takagi, and R. M. Brown Jr., *Polymer* **34**, 3293 (1993).
130. P. Langan, Y. Nishiyama, and H. Chanzy, *J. Am. Chem. Soc.* **121**, 9940 (1999).
131. B. G. Ranby, *Acta Chem. Scand.* **6**, 101 (1952).
132. A. D. French, M. K. Dowd, S. K. Cousins, R. M. Brown Jr., and D. P. Miller, *ACS Symp. Ser.* **618**, 13 (1995).
133. F. J. Kolpak and J. Blackwell, *Macromolecules* **9**, 273 (1976).
134. F. J. Kolpak, M. Weih, and J. Blackwell, *Polymer* **19**, 123 (1978); F. J. Kolpak and J. Blackwell, *Polymer* **19**, 132 (1978).
135. S. Raymond, B. Henrissat, D. T. Qui, A. Kvick, and H. Chanzy, *Carbohydr. Res.* **277**, 209 (1995).
136. K. Gessler, N. Krauss, T. Steiner, C. Betzel, A. Sarko, and W. Saenger, *J. Am. Chem. Soc.* **117**, 11397 (1995).
137. M. Koyama, W. Helbert, T. Imai, J. Sugiyama, and B. Henrissat, *Proc. Natl. Acad. Sci. U.S.A.* **94**, 9091 (1997).
138. H. Chanzy and E. Roche, *Appl. Polym. Symp.* **28**, 701 (1976).
139. A. Sarko, H. Nishimura, and T. Okano, *ACS Symp. Ser.* **340**, 169 (1987).
140. B. Henrissat, M. Vincendon, S. F. Tanner, and P. S. Belton, *Carbohydr. Res.* **160**, 1 (1987).
141. I. Quenin and H. Chanzy, *ACS Symp. Ser.* **340**, 189 (1987).
142. O. Ellefsen and N. Norman, *J. Polym. Sci.* **58**, 769 (1962).
143. R. H. Atalla, R. H., and S. C. Nagel, *Science* **185**, 522 (1974).
144. R. E. Whitmore and R. H. Atalla, *Int. J. Biol. Macromol.* **7**, 182 (1985).
145. D. M. Lee and J. Blackwell, *Biopolymers* **20**, 2165 (1976).
146. H. Nishimura and A. Sarko, *Macromolecules* **24**, 771 (1991).

147. I. Sakurda and K. Hutino, *Kolloid Z.* **77**, 346 (1936).
148. P. H. Hermans and A. Weidinger, *J. Colloid Sci.* **1**, 185 (1946).
149. J. Blackwell, D. Kurz, M.-Y. Su, and D. M. Lee, *ACS Symp. Ser.* **340**, 199 (1987).
150. A. J. Stipanovic and A. Sarko, *Polymer* **19**, 3 (1978).
151. E. Roche, H. Chanzy, M. Boudeulle, R. H. Marchessault, and P. Sundrarajan, *Macromolecules* **11**, 86 (1978).
152. U. Vogt and P. Zugenmaier, *Ber. Bunsenges. Phys. Chem.* **89**, 1217 (1985).
153. P. M. Whitaker, I. A. Nieduszynski, and E. D. T. Atkins, *Polymer* **15**, 125 (1974).
154. D. Meader, E. D. T. Atkins, and F. Happey, *Polymer* **19**, 1371 (1978).
155. P. Zugenmaier, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **37**, 223 (1983).
156. N. R. Bertoniere and S. H. Zeronian, *ACS Symp. Ser.* **340**, 255 (1987).
157. S. P. Rowland and N. R. Bertoniere, in Ref. 9, pp. 112–137.
158. L. Aggebrandt and O. Samuelson, *J. Appl. Polym. Sci.* **8**, 2810 (1964).
159. J. E. Stone and A. M. Scallan, *Pulp. Pap. Mag. Can.* **69**, 69 (1968).
160. J. E. Stone, E. Treiber and B. Abrahamson, *Tappi J.* **52**, 108 (1969).
161. J. E. Stone and A. M. Scallan, *Cell. Chem. Technol.* **3**, 343 (1968).
162. L. F. Martin and S. P. Rowland, *J. Chromatogr* **28**, 139 (1967).
163. L. F. Martin and S. P. Rowland, *J. Polym. Sci., Part A-1* **5**, 2563 (1967).
164. N. R. Bertoniere, W. D. King, and S. E. Hughs, in J. F. Kennedy, G. O. Phillips and P. A. Williams, eds., *Lignocellulosics—Science, Technology, Development and Use*, Ellis Horwood Limited, Chichester, U.K., 1992, p. 457.
165. N. R. Bertoniere and W. D. King, *Textile Res. J.* **59**, 114 (1989).
166. N. R. Bertoniere, W. D. King, and S. P. Rowland, *J. Appl. Polym. Sci.* **31**, 2769 (1986).
167. N. R. Bertoniere and W. D. King, *Textile Res. J.* **60**, 606 (1990).
168. N. R. Bertoniere and W. D. King, *Textile Res. J.* **59**, 608 (1989).
169. N. R. Bertoniere, W. D. King and C. M. Welch, *Textile Res. J.* **64**, 247 (1994).
170. N. R. Bertoniere in M. Raheel, ed., *Modern Textile Characterization Methods*, Marcel Dekker, Inc., New York, 1996, pp. 265–290.
171. J. Schurz, J. Lenz and E. Wrentschur, *Angew. Makromol. Chem.* **229**, 175 (1995).
172. E. W. Fischer, P. Herschenröder, R. St. J. Manley, and M. Stamm, *Macromolecules* **11**, 213 (1978).
173. O. A. Battista, *Microcrystal Polymer Science*, McGraw-Hill, New York, 1975.
174. O. A. Battista, in J. I. Kroschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **3**, John Wiley & Sons, Inc., New York, 1985, pp. 86–90.
175. U.S. Pat. 3,536,647 (Oct. 27, 1970), O. A. Battista; U.S. Pat. 3,931,082 (Jan. 6, 1976), M. M. Cruz Jr., N. Z. Erdi, and O. A. Battista.
176. O. A. Battista, *Ind. Eng. Chem.* **42**, 502 (1950).
177. M. Chang, *J. Polym. Sci. C* **36**, 343 (1971).
178. M. Marx-Figini, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **37**, 157 (1982).
179. R. J. Whistler and J. N. BeMiller, *Adv. Carbohydr. Chem.* **13**, 289 (1958).
180. T. P. Nevell, in Ref. 9, pp. 223–242.
181. Ref. 180, pp. 243–265.
182. P. J. Wakelyn, N. R. Bertoniere, A. D. French, S. H. Zeronian, T. P. Nevell, D. P. Thibodeaux, E. J. Blanchard, T. A. Calamari, B. A. Triplett, C. K. Bragg, C. M. Welch, J. D. Timpa, and W. R. Goynes Jr., in M. Lewin and E. Pierce, eds., *Handbood of Fiber Chemistry*, 2nd ed., Marcel Dekker, Inc., New York, 1998, pp. 577–724.
183. S. L. Vail, in Ref. 9, pp. 375–422.
184. S. M. Hudson and J. A. Cuculo, *J. Macromol. Sci., Rev. Macromol. Chem. C* **18**, 1 (1980); A. F. Turbak, R. B. Hammer, R. E. Davis, and H. L. Hergert, *CHEMTECH* **10**, 51 (1980).

185. D. C. Johnson, in Ref. 9, pp. 181–201.
186. B. Philipp, *J. Macromol. Sci., Pure Appl. Chem. A* **30**, 703 (1993).
187. V. V. Myasoedova, in V. V. Myasoedova, ed., *Physical Chemistry of Non-Aqueous Solutions of Cellulose and Its Derivatives*, John Wiley & Sons, Inc., Chichester U.K., 2000.
188. E. E. Treiber, in Ref. 9, pp. 455–479.
189. A. F. Turbak, in J. I. Knoschwitz, ed., *Encyclopedia of Polymer Science and Engineering*, Vol. **14**, John Wiley & Sons, Inc., New York, 1985, pp. 45–72.
190. T. Yamashiki, M. Saitoh, K. Yasuda, K. Okajima, and K. Kamide, *Cell. Chem. Technol.* **24**, 237 (1990).
191. E. Schweizer, *J. Prakt. Chem.* **72**, 109 (1857).
192. W. Traube, *Ber. Dtsch. Chem. Ges.* **44**, 3319 (1911).
193. G. Jayme, in N. M. Bikales and L. Segal, eds., *Cellulose and Cellulose Derivatives*, Vol. **V**, Part IV, John Wiley & Sons, Inc., New York, 1970, pp. 381–411.
194. K. Saalwächter, W. Burchard, P. Klüfers, G. Kettenbach, P. Mayer, D. Klemm, and S. Dugarmaa, *Macromolecules* **33**, 4094 (2000).
195. Br. Pat. 13,296 (1850), J. Mercer.
196. A. Dubose, *Bull. Soc. Ind. Rouen* **33**, 318 (1905).
197. K. Kamide and M. Saito, *Polym. J.* **20**, 447 (1988).
198. U.S. Pat. 5,605,567 (Feb. 25, 1997), E. P. Lancaster (to Weyerhaueser Co.).
199. H. Sobue, H. Kiessig, and K. Hess, *Z. Phys. Chem. (B)* **43**, 309 (1939).
200. A. H. Nissen, G. H. Hungen, and S. S. Sternstein, in N. M. Bikales, ed., *Encyclopedia of Polymer Science and Technology*, Vol. **3**, John Wiley & Sons, Inc., New York, 1965, p. 166.
201. U.S. Pat. 4,367,191 (Jan. 4, 1983), J. A. Cuculo and S. M. Hudson (to Research Corp.).
202. K. Hattori, J. A. Cuculo, and S. M. Hudson, *J. Polym. Sci., Part A: Polym. Chem.* **40**, 601 (2002).
203. K. Hattori, T. Yoshida, and J. A. Cuculo, *224th National Meeting*, American Chemical Society, Boston, 2002. Abstract, BTEC32.
204. T. R. Dawsey and C. L. McCormick, *J. Macromol. Sci., C: Rev. Macromol. Chem. Phys.* **30**, 405 (1990).
205. U.S. Pat. 4,097,666 (June 27, 1978), D. C. Johnson and M. D. Nicholson (to the Institute of Paper Chemistry).
206. B. Philipp, H. Schleicher, and W. Wagenknecht, *CHEMTECH* **7**, 702 (1977).
207. U.S. Pat. 3,669,916 (June 13, 1972), O. Nakao, S. Nakagawa, J. Hirose, S. Yamazaki, T. Amano, T. Nakamura, and H. Yamamoto (to Tomoegawa Paper Manufacturing Co., Ltd.).
208. U.S. Pat. 3,447,939 (June 3, 1969), D. L. Johnson (to Eastman Kodak Co.).
209. H. Chanzy and A. Peguy, *J. Polym Sci., Polym. Chem. Ed.* **18**, 1137 (1980).
210. T. Rosenau, A. Potthast, H. Sixta and P. Kosma, *Prog. Polym. Sci.* **26**, 1763 (2001).
211. U.S. Pat. 1,943,176 (Jan. 9, 1934), C. Graenacher (to Society of Chemical Industry).
212. R. P. Swatloski, S. K. Spear, J. D. Holbrey, and R. D. Rogers, *J. Am. Chem. Soc.* **124**, 4794 (2002).
213. R. S. Werbowyj and D. G. Gray, *Mol. Cryst. Liq. Cryst. (Lett.)* **34**, 97 (1976).
214. D. G. Gray, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **37**, 179 (1983).
215. R. D. Gilbert and P. A. Patton, *Prog. Polym. Sci.* **9**, 115 (1983).
216. D. G. Gray, *Faraday Discuss. Chem. Soc.* **79**, 257 (1985).
217. P. Sixou and A. Ten Bosch, in Ref. 11, pp. 205–219.
218. M. G. Northolt, H. Boerstoel, H. Maatman, R. Huisman, J. Veurink, and H. Elzerman, *Polymer* **42**, 8249 (2001).

219. U.S. Pat. 4464323 (Aug. 7, 1984), J. P. O'Brien (to E. I. Du Pont de Nemours and Company).
220. U.S. Pat. 4501886 (Feb. 26, 1986), J. P. O'Brien (to E. I. Du Pont de Nemours and Company).
221. R. S. Werbowyj and D. G. Gray, *Macromolecules* **13**, 69 (1980).
222. G. Conio, E. Bianchi, A. Ciferri, A. Tealdi, and M. A. Aden, *Macromolecules* **16**, 1264 (1983).
223. S. N. Bhandani, S.-L. Tseng, and D. G. Gray, *Makromol. Chem.* **184**, 1727 (1983).
224. E. Bianchi, A. Ciferri, G. Conio, L. Lanzavecchia, and M. Terbojevich, *Macromolecules* **19**, 630 (1986).
225. G. V. Laivins and D. G. Gray, *Macromolecules* **18**, 1753 (1985).
226. J. M. Mays, *Macromolecules* **21**, 3179 (1988).
227. S.-L. Tseng, A. Valente, and D. G. Gray, *Macromolecules* **14**, 715 (1981).
228. S. Bhandani and D. G. Gray, *Mol. Cryst. Liq. Cryst.* **99**, 29 (1983).
229. A. M. Ritcey and D. G. Gray, *Macromolecules* **21**, 1251 (1988).
230. U. Vogt and P. Zugenmaier, *Ber. Bunsenges. Phys. Chem.* **89**, 1217 (1985).
231. A. M. Ritcey and D. G. Gray, *Macromolecules* **21**, 2914 (1988).
232. J. X. Guo and D. G. Gray, *Macromolecules* **22**, 2086 (1989).
233. W. P. Pawlowski, R. D. Gilbert, R. E. Fornes, and S. T. Purrington, *J. Polym. Sci., Part B: Polym. Phys.* **25**, 2293 (1987).
234. H. Steinmeier and P. Zugenmaier, *Carbohydr. Res.* **173**, 75 (1988).
235. P. Zugenmaier and P. Haurand, *Carbohydr. Res.* **160**, 369 (1987).
236. B. R. Harkness and D. G. Gray, *Can. J. Chem.* **68**, 1135 (1990).
237. T. Yamagishi, T. Fukua, T. Miyamoto, T. Ichizuka, and J. Watanabe, *Liq. Cryst.* **7**, 155 (1990).
238. S. N. Bhandani and D. G. Gray, *Mol. Cryst. Liq. Cryst.* **102**, 255 (1984).
239. S. Suto and H. Tashiro, *Polymer* **30**, 2063 (1989).
240. G. Charlet and D. G. Gray, *Macromolecules* **20**, 33 (1987).
241. J. Giasson, J.-F. Revol, A. M. Ritcey, and D. G. Gray, *Biopolymers* **27**, 1999 (1988).
242. G. Conio, P. Corazza, E. Bianchi, A. Tealdi, and A. Ciferri, *J. Polym. Sci., Polym. Lett. Ed.* **22**, 273 (1984).
243. J.-F. Revol, H. Bradford, J. Giasson, R. H. Marchessault, and D. G. Gray, *Int. J. Biol. Macromolecules* **14**, 170 (1992).
244. J.-F. Revol, L. Godbout, X.-M. Dong, D. G. Gray, H. Chanzy, and G. Maret, *Liq. Crys.* **16**, 127 (1994).
245. X. M. Dong, J.-F. Revol, and D. G. Gray, *Cellulose* **5**, 19 (1998).
246. X. M. Dong, T. Kimura, J.-F. Revol, and D. G. Gray, *Langmuir* **12**, 2076 (1996).
247. X. M. Dong and D. G. Gray, *Langmuir* **13**, 2404 (1997).
248. U.S. Pat. 5,629,055 (May 13, 1997), J.-F. Revol, D. L. Godbout, and D. G. Gray (to Pulp and Paper Research Institute of Canada).
249. J. Araki, M. Wada, and S. Kuga, *Langmuir* **17**, 21 (2001).
250. L. Heux, G. Chauve, and C. Bonini, *Langmuir* **16**, 8210 (2000).
251. W. T. Winter and A. J. Stipanovic, in *221st National Meeting*, Amercian Chemical Society, Orlando, Fla., 2001, Abstract P, CELL-076.
252. T. Furuta, E. Yamahara, T. Konishi, and N. Ise, *Macromolecules* **29**, 8994 (1996).
253. W. J. Orts, L. Godbout, R. H. Marchessault, and J.-F. Revol, *Macromolecules* **31**, 5717 (1998).
254. X.-M. Dong and D. G. Gray, *Langmuir* **13**, 3029 (1997).
255. C. D. Edgar and D. G. Gray, *Cellulose* **23**, 1 (2001).
256. J. Araki, M. Wada, S. Kuga, and T. Okano, *Colloids Surf., A* **142**, 75 (1998).

257. W. Chen and D. G. Gray, *Langmuir* **18**, 633 (2002).
258. K. Fleming, D. Gray, S. Prasannan, and S. Matthews, *J. Am. Chem. Soc.* **122**, 5224 (2000).

ALFRED D. FRENCH
NOELIE R. BERTONIERE
Southern Regional Research Center, USDA
R. MALCOLM BROWN
The University of Texas at Austin
HENRI CHANZY
CNRS-CERMAV
DEREK GRAY
Pulp and Paper Research Centre, McGill University
KAZUYUKI HATTORI
Kitami Institute of Technology
WOLFGANG GLASSER
Virginia Polytechnic Institute and State University