

Chapter 1

Introduction

Cellulose represents a naturally occurring linear macromolecular chain of 1–4-linked β -D-glucopyranose and exhibits great chemical variability and potential in applications. The cell walls of all plants contain fibers of cellulose. Cellulose has long been harvested as commercial fibers from the seed hairs of cotton (over 94% cellulose), as bast fibers (60–80% cellulose) from flax, hemp, sisal, jute and ramie or as wood (40–55% cellulose), which is a common building material or is used as a source for purified cellulose. The chemical compositions of some known species are collected in Table 1.1, which, when purified, serve as cellulose sources. Wood represents a composite material with cellulose as a major part combined in excellent form with lignin and hemicelluloses, creating a unique high-strength and durable material, and recently came again into focus as a renewable energy resource.

Land plants such as forest trees and cotton synthesize cellulose from glucose, produced in the plant cells by photosynthesis. Unicellular plankton or algae in the ocean also generate cellulose by fixation of carbon dioxide as do land plants. Therefore, vast resources of cellulose are available and serve as food for animal life in the ocean or can be harvested. However, cellulose may be also assembled by several animals, fungi and bacteria, which are devoid of photosynthetic ability and require glucose or other organic substrates and are dependent on other organisms.

In the nineteenth century, methods were developed to separate wood cellulose from lignin chemically and to regenerate the cellulose for use as fibers (rayon) and plastics (cellophane). Later, ester and ether derivatives of cellulose were developed and the esters were predominantly used as fibers and plastics and the ethers as binders and additives for special mortars or special chemicals for building and construction as well as viscosity stabilizers in paint, oil exploration, food and pharmaceutical products, etc. Cellulose nitrate (nitrocellulose, made into celluloid) and cellulose acetate (fibers, films and plastics) are important derivatives for solid-state applications. The properties of both these chemical derivatives are based on the cellulose chain structure.

Cellulose also represents the basic materials in papermaking. Its fibers have high strength and durability. They are readily wetted by water, exhibiting considerable swelling when saturated, and are hygroscopic, i.e., they absorb appreciable amounts of water when exposed to the atmosphere. Even in the wet state, natural cellulose fibers show almost no loss in strength. It is the combination of these

Table 1.1 Chemical composition of some typical cellulose-containing materials. (Adapted from Hon 1996)

Source	Composition (%)			
	Cellulose	Hemicellulose	Lignin	Extract
Hardwood	43–47	25–35	16–24	2–8
Softwood	40–44	25–29	25–31	1–5
Bagasse	40	30	20	10
Coir	32–43	10–20	43–49	4
Corn cobs	45	35	15	5
Corn stalks	35	25	35	5
Cotton	95	2	1	0.4
Flax (retted)	71	21	2	6
Flax (unretted)	63	12	3	13
Hemp	70	22	6	2
Henequen	78	4–8	13	4
Istle	73	4–8	17	2
Jute	71	14	13	2
Kenaf	36	21	18	2
Ramie	76	17	1	6
Sisal	73	14	11	2
Sunn	80	10	6	3
Wheat straw	30	50	15	5

qualities with strength and flexibility that makes cellulose of unique value for paper manufacturing.

Dry cellulose has thermosetting behavior, i.e., it forms permanent, bonded structures that cannot be loosened by heat or common solvents without causing chemical decomposition. Its thermosetting behavior arises from strong dipolar attractions that exist between cellulose molecules, imparting properties similar to those of interlinked polymer networks.

In regenerated form, cellulose is used for textile fibers and for producing derivatives. Cellulose fibers and films show excellent tensile properties. Thin sheets of cellulose acetate serve as optical compensators and shields for compounds evaporating from the polarizer in modern liquid-crystalline displays, and cellulose acetate sheets are the base for photographic films.

Composite materials with cellulose are widely used as wood; also worthy of mention are cactus thorns used by the Indians of South America as nails. Synthetic composites have been developed by extruding polypropylene with microcrystalline cellulose obtained by hydrolytic degradation of native cellulose or with regenerated cellulose. These easily accessible composites point towards promising applications. The superiority of cellulose derivatives as the stationary phase in chromatographic procedures separating enantiomeric molecular species should be mentioned as well.

Cellulose as an abundant natural material serving mankind for centuries became the subject of science as soon as appropriate tools for scientific investigations

became available to satisfy human curiosity and to improve the existing properties of materials as well. Therefore, cellulose has to be considered as a major subject in the history of polymer science in the development of the concept of macromolecules and the determination of polymeric crystal structures. These developments represent excellent examples of how science proceeds and develops with the ideas and contributions of many researchers. An involvement with the history of science may rediscover ideas which have been forgotten and lost. At certain times ideas were impossible to follow up because the necessary tools were not available or science took another route.

All native celluloses are organized in fibrils, which represent the association of cellulose molecules and contain ordered and less ordered regions. From a structural point of view cellulose represents a semiflexible molecule and can be described as an extended wormlike chain for short molecular length but as a Gaussian coil with loops and intermolecular contacts for long chains as represented for cellulosic solutions in Fig. 1.1. Stiff wormlike chains are also the prerequisite for the formation of lyotropic liquid crystals with amazing physical properties. The diversity of appearance of cellulose and cellulose derivatives in various polymorphs in the solid state on a molecular and a supermolecular level as well as in solution made it difficult to obtain a clear picture of these structures for a long period of time. Native cellulose in fibers of higher plants possesses a very high degree of polymerization in contrast to treated cellulose used as sources in applications (Table 1.2), and various kinds of morphological structures may occur depending on the chain length. In addition, structural investigations have suffered extensively from insufficient data owing to imperfect structures and methods. In recent years improvements in structural research on the molecular level have led to the proposal of valuable models for the conformation and packing arrangements of chain molecules.

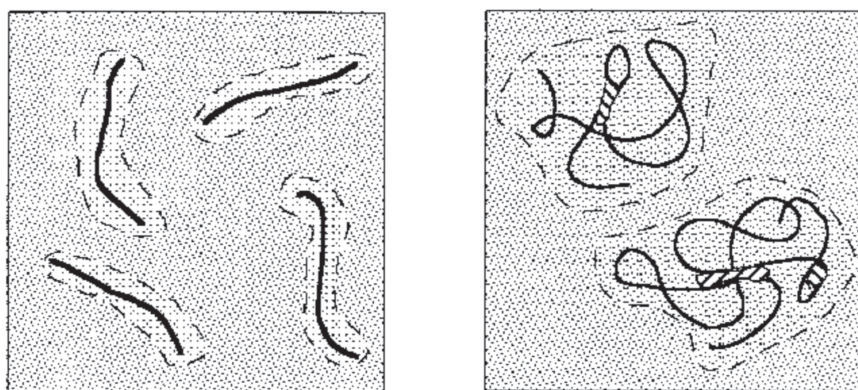


Fig. 1.1 Cellulosic molecules of short and long molecular chain lengths in molecularly dispersed solution. The *broken lines* indicate the solvent shell. Extended molecules are present for short chains and Gaussian coils with loops and intermolecular contacts for long chains

Table 1.2 Average degree of polymerization (average number of monomeric units in one chain, evaluated from the molecular mass distribution) of some selected celluloses

Cellulose	Degree of polymerization
Wood of various species	6,000–10,000
Pulp	500–2,000
Sulfate pulp	950–1,300
Chemical pulp bleached	700
Cotton	10,000–15,000
Cotton linters bleached	1,000–5,000
<i>Valonia</i>	25,000
Bacterial cellulose	4,000–6,000
Ramie	10,000
Textile flax	9,000
Rayon	300–500
Cellophane	300
Cellulose acetate	200–350

A comprehensive evaluation of molecular masses of native celluloses is provided by Schulz and Marx (1954) and Marx-Figini (1982).

In this book we will present a short overview of basic principles in the development of macromolecular science, in particular the development of the macromolecular concept and of the crystal structure of native cellulose. The description of the crystal structures of various polymorphs of cellulose requires some insight into the methods applied for a basic understanding, for a judgment of the goodness of the available data and for further possible improvements of structures as well as developments to proceed to further fields. A survey of cellulosic structures may also lead to extraction of general structural features of cellulosic materials.

Polymeric chain structures are composed of many monomeric units containing numerous atoms but the experimental data sets are very limited. Invariants have to be introduced, such as configuration, bond lengths and angles, derived from oligomeric compounds, and regarded as a necessity to implement the determination procedure of polymeric crystal structures and to supplement missing experimental data of polymeric compounds, e.g., cellulose.

The determination of crystalline structures predominantly rests on diffraction methods such as X-ray, synchrotron, electron and neutron scattering of highly crystalline, highly orientated samples with little disorder. It took a long time until it was realized that native cellulose consists of two crystalline polymorphs, now termed cellulose I α and I β . The cellulose microfibrils from the cell walls of the algae *Cladophora*, *Halicystis*, *Valonia*, etc., contain predominantly well-oriented cellulose I α . In contrast, the microfibrils of cotton, ramie (China-grass), further bast fibers and the tunicin animal cellulose from the mantle of tunicates serve as sources for oriented and highly crystalline cellulose I β .

IR, Fourier transform IR, Raman and NMR spectroscopic techniques have always served as complementary tools, especially if the long-range three-dimensional order is disturbed or totally missing. Some background knowledge will be provided for a fast characterization and judgment of the materials as well as the discussion of the structures.

An overview of cellulosic structures and the representation of experimental data may fulfill many purposes. It serves as a data base for characterizing naturally occurring substances, i.e., for differentiating between various cellulose polymorphs and other polysaccharides. For such a discrimination only fingerprint patterns of diffraction experiments or spectroscopic traces are necessary. A more detailed evaluation of the experimental data is needed to gain insights into the structure at the molecular or the morphological level and to extract information for studying the formation of the structure by nature or to invoke possible changes in the structure to improve properties and find new applications. Such comprehensive structural knowledge is also required for the prediction of pathways of chemical reactions and for the specific interaction sites of small molecules in inclusion complexes or at the surfaces of the crystallites.

Science will rapidly develop further and with the advent of improved and new tools, techniques and with combinations of them, including experiments with further data, such a survey can only serve as a snapshot of our knowledge in this field at the present time.

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