Ain Shams University
Faculty of women for Arts, Science and Education
Physics Department

"Preparation of Nano-Fibers of chitosan derivatives by using electrospinning technique and characterization by using computer software"

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To My Family
Specially
To
The Soul of My Mother, May Her Soul Rest In Peace.
And
Everyone who lighted me a candle
to keep me on the right track

“Be wise enough to know that you do not know everything”.

A. M. El Masry

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1.1. Cellulose

In ***1838*** the French chemist ***Anselme Payen*** produced a resistant fibrous compound towards nitric acid and sodium hydroxide solutions; that was named “cellulose” in 1839 ***(Heuser, 1944)***. The cellulose chain consists at one end of a D-glucose unit with an original C-4-OH group (the nonreducing end); the other end is terminated with an original C-1-OH group, which is in equilibrium with the aldehyde structure (the reducing end) ***(Klemm et al, 2005 and Cazacu and Popa, 2005)***. The molecular structure of cellulose is shown in Figure 1.1 ***(Heinze and Liebert, 2001)***.

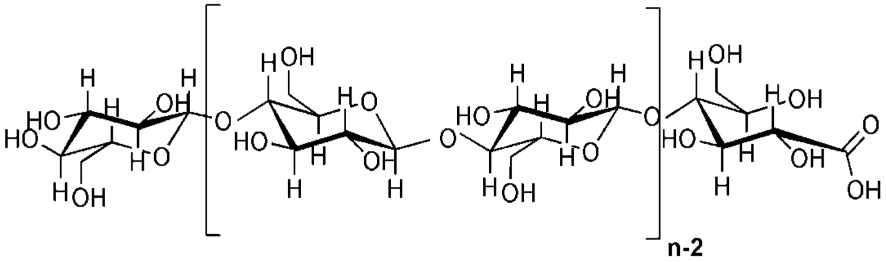

Figure 1.1: Molecular Structure of Cellulose polymer chain (n = DP, Degree of Polymerization) ***(Heinze and Liebert, 2001)***

Cellulose is the most common organic polymer and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products. Wood pulp remains the most important raw material source for the processing of cellulose, most of which is used for the production of paper and cardboard. Cellulose differs from synthetic polymers by virtue of its distinct polyfunctionality, its high chain stiffness, and its sensitivity toward the hydrolysis and oxidation of the chainforming acetal groups, which determine its chemistry and handling. ***(Klemm et al, 2002 and Kaplan, 1998)***

The chain length of cellulose expressed in the number of constituent AGUs (degree of polymerization, DP) varies with the origin and treatment of the raw material. In case of wood pulp, the values are typically 300 to 1700. Cotton and other plant fibers have DP values in the 800–10000 range, depending on treatment; similar DP values are observed in bacterial cellulose. Regenerate fibers from cellulose contain 250–500 repeating units per chain. By acid treatment and cellulose catalyzed hydrolysis, cellulose can be quantitatively decomposed to d-glucose. Partial chain degradation yields powdery cellulose substrates of the microcrystalline cellulose type ***(Jiijma & Takeo 2000 and Humphreys, 1996)*** (such as Avicel) with DP values between 150 and 300. A β (1-4) linked glucan with 20–30 repeating units offers all properties of cellulose**.** ***(Kobayashi et al, 2001)*****.**

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

Cellulose is difficult to process in solution or as a melt because of the large numbers of intra- and intermolecular hydrogen bonds in cellulose, which form a highly organized network system surrounding the single polyglucan chain and interrupt the dissolution of cellulose solid into solution. Thus the key to the application of cellulose is to search for a solvent that can effectively destroy the intra- and interchain hydrogen bonding in cellulose. A nontoxic and easy dissolution system for cellulose has been developed, and it includes indirect and direct solvent systems. In indirect solvent systems, such as dimethylformamide/pyridine, dimethylformamide/N_2O_4, and dimethyl sulfoxide/N_2O_4, cellulose forms derivatives during dissolution. Direct solvent systems such as trifluoroacetic acid/dichloromethane, liquid ammonia/ NH_4SCN, dimethylacetamide/LiCl, and NMMO/H_2O may form complexes withcellulose, but the molecular structure of cellulose is not altered ***(Kim et al, 1999)***. A suitable classification of cellulose solvents identifies five types of systems as follows: NMMO Solvent System ***(Woodings, 2001, Fink et al, 2001 and Heinze and Liebert, 2001),*** LiCl/DMAc Solvent System ***(Heinze and Liebert, 2001)***, Aqueous Metal-Based Solvent System ***(Saalwǟchter et al, 2000)***, Ionic Liquid Solvent System ***(Turner et al, 2004; Heinze et al., 2005 and Zhang et al., 2005)***, and NaOH/Urea Aqueous Solvent System ***(Zhang et al., 2005, Cai et al., 2007a, b).***

The cellulose chains within the cotton fibers tend to be held in place by hydrogen bonding. These hydrogen bonds occur between the hydroxyl groups of adjacent molecules and are more prevalent between the parallel, closely packed molecules in the crystalline areas of the fiber as shown in Figure 1.2. ***(Venkataraman et al, 1987).***

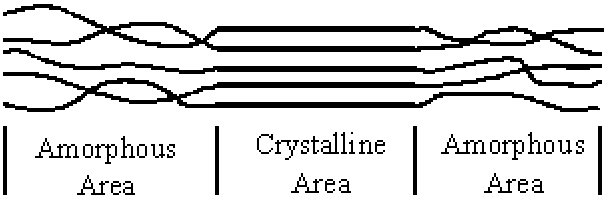

Figure 1.2 Crystalline and amorphous structure of cellulose

1.1.1. Structure and Properties of Cellulose

As shown in the molecular structure represented in Figure 1.1, the hydroxy groups of β-1,4-glucan cellulose are placed at positions C-2 and C-3 (secondary, equatorial) as well as C-6 (primary). The CH_2OH side group is arranged in a trans-gauche position relative to the O_5-C-5 and C-4-C-5 bonds. As a result of the supra-molecular structure of cellulose, the solid state is represented by areas of both high order (crystalline) and low order (amorphous) ***(Zugenmaier, 2001, Sullivan, 1997).***

The crystal structure of native cellulose (cellulose I) determined by X-ray diffraction can be described by a monoclinic unit cell which contains two cellulose chains in a parallel orientation with a twofold screw axis**.** ***(Gardner and Blackwell, 1974)*** In the 1980s, 13C-CP/MAS NMR spectroscopy was used in the initial discovery that native cellulose is present in two different crystalline cellulose I modifications (I_α and I_β), which can be found alongside each other; the I_α/I_β ratio depends on the origin of the cellulose**.** ***(Atalla and Van der Hart, 1984)***.Cellulose II can be formed from cellulose I by treatment with aqueous sodium hydroxide (mercerization) or by dissolution of the cellulose and subsequent precipitation/regeneration, as is done in the formation of fiber and film; cellulose III can be prepared by the treatment of native ramie, cotton, hemp, mercerized ramie, Fortisan rayon with liquid ammonia and cellulose IV produced from cellulose III sources by heating in glycerol at 260°C for 20 min. ***(Klemm et al., 2005 and Zugenmaier, 2001).***

1.1.2. Cellulose Chemistry

The insolubility of cellulose in water and in most organic solvents caused by its supramolecular structure is the reason behind the fact that all commercially available products are currently produced through reactions of cellulose in the solid, or more or less swollen state (heterogeneous reactions).***(Fredriksson et a, 1998)***. Because each repeating unit of cellulose has three hydroxyl groups available for reaction, and the stability of the chain forming acetal groups toward various reagents, oxygen, and mechanical and thermal load is limited, additional questions emerge over substituent distribution in the product and over chain degradation during synthesis.

In case of heterogeneous reactions, the accessibility and reactivity of the OH groups are clearly determined by hydrogen bond-breaking activation steps ***(Hanashiro et al, 1996)*** and by interaction with the reaction media (e.g. swelling). ***(Koch et al, 1998)*** Thus, the “linear” transfer of the typical reactions of organic chemistry to cellulose is not easily done. However, the control of cellulose activation and of the type of heterogeneous reaction permits effective synthesis of cellulose products with desired degrees of reaction, reproducible substitution patterns, and targeted properties at both the laboratory and production scales.

Using specific cellulose solvents, ***(Klemm et al, 1998)*** which disrupt hydrogen bonds and thus dissolve the adducts formed, the influence of the supramolecular structure of cellulose on the reaction procedure is almost eliminated completely. In this context, a solution of LiCl in DMA (DMA/LiCl) is one of the most important solvent systems for cellulose in organic syntheses ***(Dawsey & Mc Cormick, 1990)*** as well as for analytical purposes. ***(Burchard et al, 1994)*** The structure of this binary medium, the mechanism of dissolution, the influence of water on the dissolving activity, and the state of dissolution of cellulose have been investigated in detail. ***(Bruglachner et al, 2002 and.Burchard, 2003)*.**

Over the past few years, it was demonstrated that tetrabutylammonium fluoride trihydrate in DMSO (DMSO/TBAF) effectively dissolves cellulose and is very useful for homogeneous syntheses ***(Ciacco et al, 2003).*** Fundamental progress also has been made in the classical field of metal-containing cellulose solvents like cuprammonium hydroxide ***(Saalwāchter et al, 2000).*** In doing so, the solution structure of cellulose in this copper-containing medium was elucidated. (***Burchard et al 1994)***.

Extensive preparative work on the laboratory scale has been carried out over the past 20 years with cellulose solvent systems. As a result, new types of cellulose derivatives have been synthesized and the knowledge of reaction mechanisms, reaction control, structure–property relationships (solubility, film formation, stability), and structure analysis has been increased. ***(Klemm et al, 1998).*** Until now, it has not been possible to transfer the homogeneous reactions to technical scale, as the handling of aprotic dipolar media and salt components poses an obstacle. Of course, partially substituted soluble cellulose derivatives are also good substrates for reactions under homogeneous conditions. ***(Vieira et al., 2001)*** Cellulose ethers have proven particularly useful as intermediates and regioselective protecting groups. Typical examples include trityl, methoxy-substituted trityl,bulky silyl, as well as allyl and benzyl ethers. ***(Gomez et al., 1996 and Kern et al., 2000)***.

Limited chain degradation can be accepted in most reactions of cellulose without loss of the product properties, if chain lengths beyond the convergence range of the material parameters are not obtained. Transformation of cellulose with phenyl isocyanate (carbanilation) and silylation take place without chain degradation, for example. ***(Vieira et al., 2001).***

1.1.2.1. Chemical Modification of Cellulose

The purposes of chemical modifications of cellulose are to produce modified cellulosic materials having specific properties at commercial levels, to characterize cellulosic materials at laboratory levels, and to approach the nature of cellulose for scientific interests. Furthermore, since there are still many unsolved and mysterious subjects in cellulose science, chemical modifications are sometimes used to study fundamental research subjects of cellulose, such as solid-state structures of cellulose (hydrogen bonding patterns, chain conformations, crystal and amorphous structures, etc.).

The typical modifications of cellulose are esterifications and etherifications at hydroxyl groups of cellulose. Most water-soluble and organic solvent-soluble cellulose derivatives are prepared by these substitution reactions, and drastic changes in the original properties of cellulose can usually be achieved by these chemical modifications. Others are ionic and radical grafting, acetalation, deoxyhalogenation and oxidation. Since the usual cellulosic materials originating from wood and cotton pulps have aldehyde and carboxyl groups in quite