

The Interconvertibility of Cellulose's Allomorphs

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ABSTRACT: Seven interconvertible polymorphs (allomorphs) of cellulose, namely I_{α} , I_{β} , II, III_I, III_{II}, IV_I and IV_{II} have been identified. Using cross-polarization magic angle spinning, the sub-polymorphs termed as I_{α} and I_{β} was found to be arisen from the native cellulose (cellulose-I). The cellulose I_{α} is dominant in algal, bacterial and tunicates celluloses, and both I_{α} and I_{β} may be present in celluloses in higher plants. The I_{α} -allomorph can be converted irreversibly to the more thermodynamically stable I_{β} by high-temperatures in various media. Cellulose-I can be converted into cellulose-II by either chemical regeneration or mercerization process. The cellulose-I and II are similar in their diffraction patterns except for their meridional intensities. In contrast to cellulose-I, the chains in cellulose-II has antiparallel arranged-cellulosic chains that makes it more stable for textiles and paper industries. The cellulose-III can be obtained from cellulose-I or II when exposed to gaseous or liquefied ammonia as well as various amine reagents. At these conditions, cellulose-III_I and III_{II} can be produced irreversibly from their parent structures (cellulose I and II, respectively). Both III_I and III_{II}-allomorphs can be reverted to their parents at elevated temperatures and humidity. The allomorphs IV_I and IV_{II} can be synthesized irreversibly by heating cellulose-III_I or III_{II}, respectively up to 260°C in a glycerol media. Both cellulose-I and IV exist in several plant primary cell walls, while cellulose-II and III can be only produced artificially.

KEYWORDS: Native cellulose, Allomorphs of cellulose, Crystallinity, hydrogen bonding.

I. INTRODUCTION

Lignocellulosic fibers are constituted mainly from cellulose, lignin and hemicellulose and secondarily from pectin, pigments and organic extractives. Their chemical composition and cell structure are quite complicated in which the solid cellulosic backbone is embedded in a soft matrix from these materials [1, 2]. The properties of these natural fibers are strongly influenced by many factors such as chemical composition, anatomical structure, microfibril angle, cell dimensions and defects, which differ from different parts of a plant as well as between different plants [3].

Cellulose

Cellulose is the most abundant biomaterial in nature with fascinating structures and characteristics and can be extracted from woody fibers [4, 5] as well as seed flosses. Cellulose content in wood, flax and cotton seed floss was found to be 40 to 50%, 80% and 90%, respectively [6]. Along with higher plants, cellulose can be isolated from bacteria, algae and tunicate [7].

Cellulose microfibrils are the main reinforcement structural component of plant cell walls. It is a linear homopolysaccharide formed of 1-4 β -D-glucopyranose units termed as glucan chain [8,9]. For more illustration, glucopyranose units, the 6-membered rings are joined by single oxygen atoms (acetal linkages) between the C₁-atom of one glucopyranose ring and the C₄-atom of the next ring [9]. Each D-anhydro-glucopyranose monomer bears three hydroxyl groups that able to form hydrogen bonds within the same glucan chain (intra-bonding) as well as between chains (inter-bonding). These hydrogen bonds was reported to play a major role in controlling and directing (conformation) the crystalline packing as well as governing the physical properties of cellulose [10].

The glucan chains aggregate to form a bundle termed as elementary fibril that are aggregated in turn to bigger constructions, namely microfibrils. The diameters of the elementary fibril and the microfibril were estimated to be 3.5nm and 28nm, respectively [11]. The glucan chain that are rotated alternatively by 180° along the polymer axis to

form ribbon-like chains as reported by Harris and DeBolt[12]. It has been established that each glucosyl residue has three substitutionable hydroxyl groups. The tight bonding capacity of the hydroxyl groups via hydrogen bonding are very important for determining the crystalline structure and physical properties of cellulose materials [13]. Ordered crystalline structures are found to be alternated with amorphous zones along the fibril axis. The amorphous zones are recognized as association between hemicellulose and cellulose [14].

Allomorphs of Cellulose

The natural form of crystalline cellulose is cellulose I. Cellulose I can be irreversibly converted into cellulose II, a form that is more stable than the cellulose I [15,16]. Consisting of cellulose I_α and I_β, both forms are composed of parallel glucan chains [17,18,19]. The parallel glucan chains in natural cellulose are compatible with the idea that glucan chains in an elementary cellulose microfibril are made simultaneously [15,20,21]. In higher plants, the ratio of cellulose I_α to I_β varies among different species and types of walls [22,23]. In both forms, each glucose molecule is rotated 180° in relation to its neighboring glucose molecule, forming a flat ribbon in which cellobiose is the repeating unit [24].

For studying the structure of cellulose allomorphs, each of X-ray diffraction and Fourier transform infrared spectroscopy (FTIR) is a key tool [12].

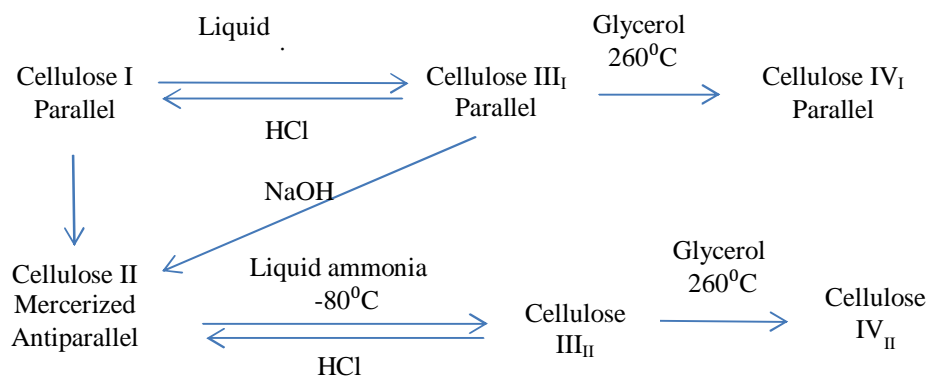


Figure 1. The interconvertibility of cellulose I into its other allomorphs.

In the crystalline regions of cellulose, the chains are tightly contacted together by a network of intra- and intermolecular hydrogen-bonds as well as van der Waals forces [7,22,25] as shown in Figure 2. The hydrogen-bonding network and molecular orientation within cellulosic microfibril can vary widely producing cellulose allomorphs (polymorphs) depending on the parent cellulosic resource and maceration method used [22,25]. Seven interconvertible polymorphs of cellulose, namely, I_α, I_β, II, III_I, III_{II}, IV_I, and IV_{II} have been identified. It was indicated by Matthews et al. [26] that the allomorphs II, III and IV does not occurred naturally (Table 1). By using cross-polarization magic angle spinning, the native cellulose (cellulose I) was found to be divided into two sub-allomorphs termed I_α and I_β, [27,28] in different ratios according to the origin of cellulose [29]. The cellulose I_α is dominant in algal, bacterial and tunicates celluloses, and both I_α and I_β may be present in celluloses in higher plants. The cellulose chain structures of I_α and I_β are similar in parallel configurations, but they differ in their hydrogen bonding patterns which reveals to different crystalline structure. I_α can be converted to the more thermodynamically stable I_β by high-temperatures in various media [30]. However, the conversion of cellulose I to cellulose II has been widely considered irreversible, although a partial regeneration of cellulose I from cellulose II has been reported by Whitmore and Atalla[31] and Habibi et al. [7]. 2010).

Cellulose II, can be obtained cellulose I by two different processes (Figure 1), namely chemical regeneration and mercerization. In the chemical regeneration process the cellulose I is dissolved in a suitable solvent and subsequent re-precipitating it in water, whereas the mercerization can be done by swelling the cellulose I in concentrated alkali solutions such as sodium hydroxide yielding cellulose II [7].

In contrast to cellulose I, which has a parallel up arrangement, the chains in cellulose II are in an antiparallel arrangement yielding a more stable structure preferable for textiles and paper industries. The diffraction patterns of cellulose I and II are similar except for the meridional intensities [32].

It was reported by Kolakovic[33] that there are clear differences between the hydrogen bonding networks for the celluloses I and II. As shown in Figure 2, for both celluloses I and II, an intra-hydrogen bond was arisen between the oxygen atom no. 3 of the left glucan chain for cellulose I and that oxygen atom no.5 within the same glucan chain. On the other hand, an inter-hydrogen bond in cellulose I was detected between O_3 of the left glucan chain and O_6 of the right glucan chain ($O_3 \dots O_6$) and $O_6 \dots O_3$, while in cellulose II the inter-hydrogen bonds was reported were ($O_2 \dots O_6$) and $O_6 \dots O_2$ (Figure 2).

For the cellulose III, it can be obtained from cellulose I or II when exposed to gaseous or liquefied ammonia as well as various amine reagents [7] as shown in Figure 1. However, the inter-sheet hydrogen bond network is similar to cellulose II. The exact structure of cellulose III_{II} is not clearly established yet, but the crystallographic and spectroscopic studies reported recently by Wada et al. [32] indicate that cellulose III_{II} is a disordered phase of cellulose mainly contains a crystalline form having a unit cell occupied by one chain organized in antiparallel fashion, in addition to a second structure, as revealed by CP/MAS ¹³C NMR Furthermore, either of III_I or III_{II} reverts to its parent structure if placed in a high temperature and humid environment.

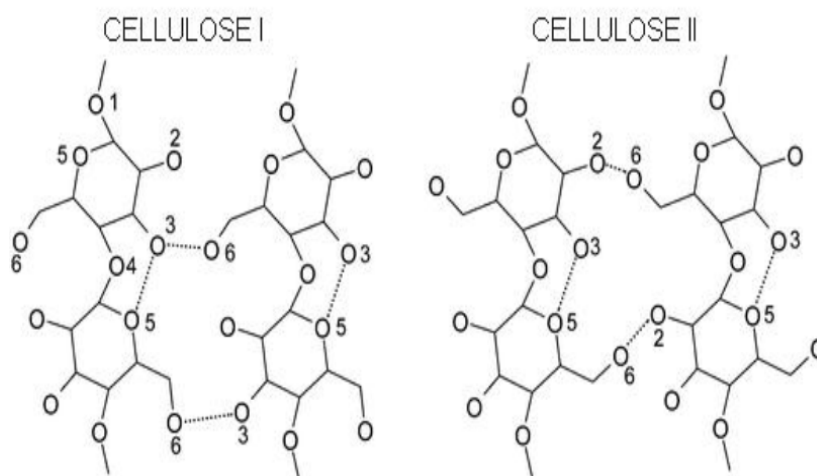


Figure 2. Major supramolecular difference between cellulose I and cellulose II (From Kolakovic, 2013).

The amorphs IV_I and IV_{II} can be produced (Figure 1 and Table 1) by heating cellulose III_I or III_{II}, respectively up to 260°C in glycerol [34] (Gardiner and Sarko, 1985). Like to cellulose III, the IV_I and IV_{II} can revert to their parent structures of celluloses I or II. It was indicated that both cellulose I and IV exist in several plant primary cell walls [35,36].

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Table 1. Differentiation of the cellulosic allomorphs (CA's)

CA	Natural existence	Synthesis	Precursor
I _α	In algal, bacterial and tunicates	Naturally	Glucose
I _β	In primary and secondary cell walls of plants.		
II	Synthetic	Chemical regeneration or mercerization.	Cellulose I
III _I	Synthetic	Exposure to ammonia or amines (reversible reaction).	Cellulose I or II
III _{II}			Cellulose I or II
IV _I	Synthetic and sometimes naturally in primary cell walls.	By heating 260°C in glycerol (irreversible reaction).	Cellulose III _I

It is clear from Figure 3b that the suggested unit cell of cellulose has one cellobiose unit in each corner. Accordingly, eight cellobiose units are packed in each unit cell. The actual values of the three orthogonal angles of the unit cell (α , β , γ) presented in Table 2 are deviated from their origin value (90° , each) as shown in Figure 2a.

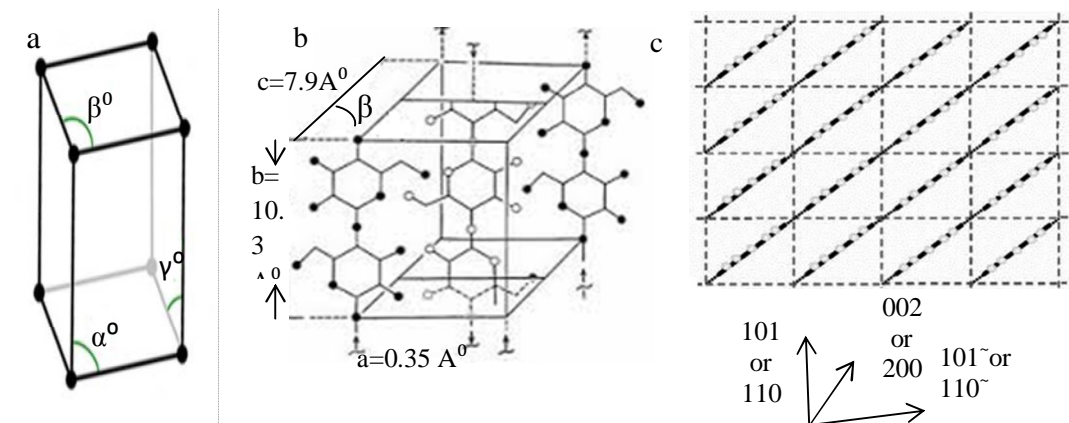


Figure 3. The crystalline structure of cellulose: a) The three angles of the unit cell, b) The Meyer-Misch model of unit cell, c) Sponsler and Dore unit cell of cellulose I.

Based on Table 2, the unit cell volume (UCV) calculated in the current work by multiplying the dimensions (a, b and c), the theoretical unit cell of cellulose is about 28 \AA^3 . In addition, the highest UCV value was calculated for the cellulose II [$805 \text{ (\AA}^3\text{)}$], while the lowest value was obtained for the cellulose III_I and I_α [$360.15 \text{ (\AA}^3\text{)}$].

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Table 2. Dimensions of unit cell of the seven allomorphs of cellulose.

CA	a (Å)	b (Å)	c (Å)	α°	β°	γ°	Reference	UCV* (Å ³)
Meyer-Misch model of unit cell	7.9	10.3	0.35	90	90	90	[37]	28.48
I _α	6.717	5.962	10.40	118.08	114.8	80.37	[38]	416.49
I _β	7.784	8.201	10.38	90	90	96.5	[39]	662.62
II	8.100	9.030	10.31	90	90	117.10	[40,41,42]	754.1
II _a	8.02	9.32	10.77	90.2	91.6	121.5	[43]	805.02
II _b	8.30	8.77	10.73	89.7	91.2	117.1		781.5
III _I	4.450	7.850	10.31	90	90	105.10	[44]	360.15
III _{II}	4.450	14.640	10.36	90	90	106.96 ^A 90.05 ^B	[32]	674.93
IV _I	8.030	8.130	10.34	90	90	90	[45]	675.04
IV _{II}	7.990	8.130	10.34	90	90	90		671.67

^AThe 1st construction

^BThe 2nd construction suggested based on cross-polarization magic angle spinning (CP/MAS)-¹³CNMR.

*Calculations done in the current work.

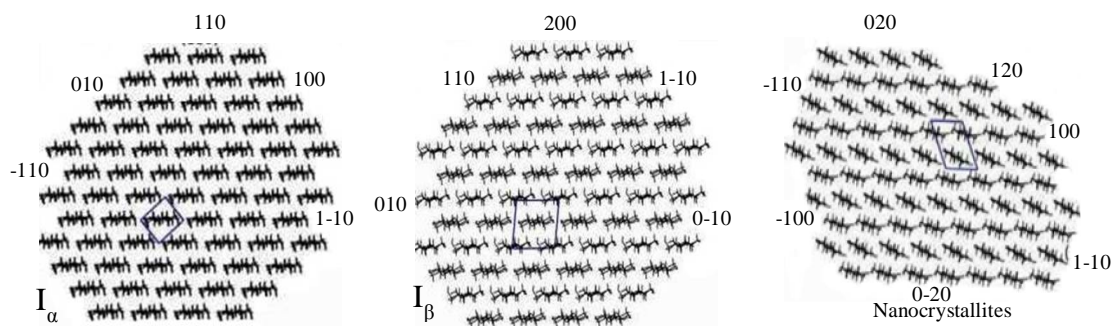


Figure 4. Schematic representatives of crystallographic planes of cellulose structure.

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For the sharp crystalline peaks of cellulose arisen for XRD diffractogram, some researchers have considered the crystallographic planes of cellulose (Figures 3a and 4), namely 101, 101⁻ and 002 [46,47,48,49,50,51], while others used 110, 11⁰ and 200 toward the increasing in the two theta value [43].

Table 3. Typical crystallographic structures proposed for the cellulosic allomorphs¹.

Allomorph Type	Unit cell	Cellulose Chains	Repeat distance, A	Space group	Asymmetric unit
I _α	One-chain triclinic	Parallel	10.35	P1	Two glucosyl
I _β	Two-chain monoclinic	Parallel	10.35	P2 ₁	Two glucosyl
II	Two-chain monoclinic	Antiparallel	10.35	P2 ₁	Two glucosyl
III _I	One-chain monoclinic	Parallel	10.35	P2 ₁	One glucosyl

¹ From Wertz et al., 2010

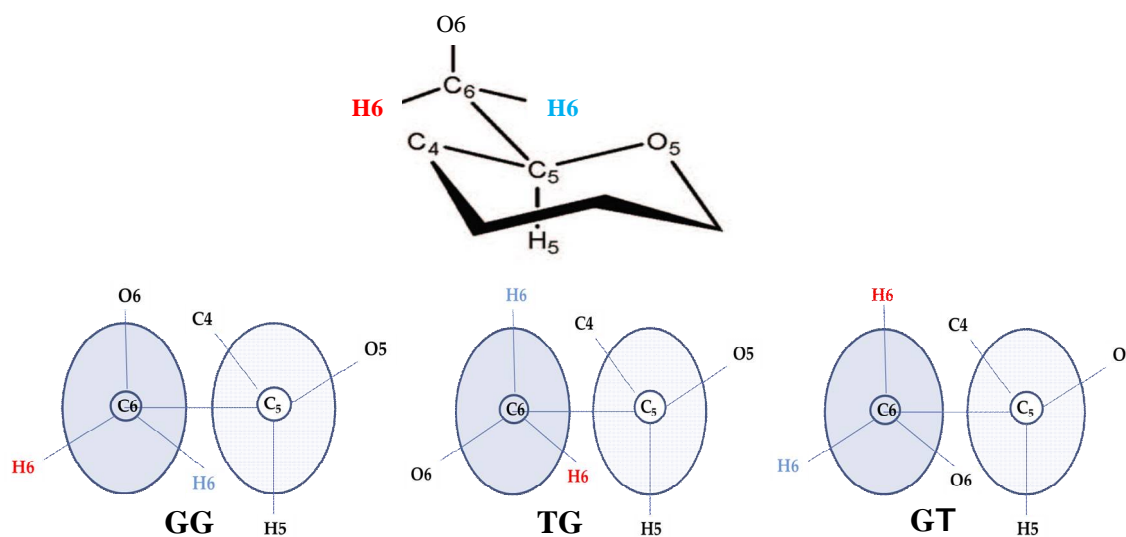


Figure 5. The most probable occurrence of rotational positions of the hydroxymethyl group.

The hydroxymethyl group located at the carbon atom no. 5 can be rotated to different positions. There are three rotational positions with the most probable occurrence defined as GG, TG and GT. For instance, the GT position can be defined by ascertaining the placement of the O6-C6 bond regarding to the O5-C5 and C4-O5 bonds: if O6-C6 is gauche to O5-C5 and trans to C4-C5, then the conformation is called gt, while the other two conformations are referred to as GG and TG (Figure 5).

Examining Table 3 and Figure 5 indicates that each of celluloses I and III_I exists in a monoclinic P2₁ form with one chain in the unit cell (Table 3), displaying parallel chains as observed in cellulose I [32].

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It was indicated that both polymorphic and morphological transformations of cellulosic precursors are strongly related to their properties and subsequent applications, especially for nanocelluloses [53].

II. CONCLUSION

- There are seven interconvertible polymorphs (allomorphs) of cellulose, namely I_{α} , I_{β} , II, III_I, III_{II}, IV_I and IV_{II}.
- Cellulose-I can be converted into cellulose-II by either chemical regeneration or mercerization process.
- The cellulose-I and II are similar in their diffraction patterns except for their meridional intensities.
- In contrast to cellulose-I, the chains in cellulose-II has antiparallel arranged-cellulosic chains that makes it more stable for textiles and paper industries.
- The cellulose-III can be obtained from cellulose-I or II when exposed to gaseous or liquefied ammonia as well as various amine reagents.
- At these conditions, cellulose-III_I and III_{II} can be produced irreversibly from their parent structures (cellulose I and II, respectively).
- Both III_I and III_{II}-allomorphs can be reverted to their parents at elevated temperatures and humidity.
- The allomorphs IV_I and IV_{II} can be synthesized irreversibly by heating cellulose-III_I or III_{II}, respectively up to 260°C in a glycerol media.
- Both cellulose-I and IV exist in several plant primary cell walls, while cellulose-II and III can be only produced artificially.
- The hydroxymethyl group located at the carbon atom no. 5 can be rotated to different positions. There are three rotational positions with the most probable occurrence defined as GG, TG and GT.

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