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Crystalline cellulose: structure and hydrogen bonds

V I Kovalenko

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Abstract. The state-of-the-art studies of the cellulose structure, major cellulose polymorphs, the crystal packing, conformers and hydrogen bond systems are analyzed based on publications of the last decade. The bibliography includes 50 references.

I. Introduction

The role of cellulose as a renewable source of materials gradually increases. Non-traditional applications of cellulose include its use in composite materials, as fillers for plastic materials (for example, as nanofibres), as a high-strength material for membranes and filters (nanopaper),[1] as liquid-crystalline and micellar self-organizing systems providing the drug delivery and as a new type of biofuel (utilization of cellulose waste). Recently, it has been shown that cellulose can be used as a smart material capable of producing directed bending at low voltage, which is termed as electroactive paper.[2] Suspensions of small-sized cellulose fibres (whiskers) in water and cyclohexane are well-oriented in the electric field, thus allowing the preparation of highly ordered dry cellulose samples.[3] It is suggested that the positive dielectric anisotropy of the material plays a key role in this orientation. Cellulose-based materials, such as synthetic fibres and films, have found wide application. Cellulose ethers and esters are produced on a large scale. However, many problems associated with the structure and transformations of this complex natural polymer remain to be solved. Hence, this field of research continues to develop.

V I Kovalenko A E Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, ul. Akad. Arbuzova 8, 420088 Kazan, Russian Federation. Fax (7-843) 273 22 53, Kazan State Technological University, ul. K Marksa 68, 420015 Kazan, Russian Federation. Fax (7-843) 273 18 72, tel. (7-843) 273 22 83, e-mail: koval@iopc.knc.ru

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The history of research of cellulose includes periods when interest in this material was high and periods when this interest fell. For example, in 1980s many experimental and theoretical methods were applied in this field and the number of publications substantially increased, the contribution of Russian scientists being substantial. In 2000s, the interest in cellulose was renewed. Japanese researchers, often in collaboration with scientists from other countries, performed extensive studies.

Two decades after the publication of the monograph[4] on the biosynthesis and structure of cellulose and its revised version,[5] several new books on this subject were published. For example, let us refer to the monograph by Kamide 'Cellulose and Cellulose Derivatives' published[6] in 2005 and the book 'Cellulose: Molecular and Structural Biology'[7] published in 2007. The latter is an up-to-date treatise on the most advanced research into the biosynthesis of cellulose. The monograph by Kamide examines developments in chemistry and engineering of cellulose acetates, takes an in-depth look at the topic and summarizes the results of studies on the cellulose structure published up to 2004. However, in the past five years the cellulose structure was extensively studied. The results of these studies are considered in the present review with emphasis on the state-of-the-art knowledge on the cellulose structure, which can be useful for its practical application.

There are great difficulties in studying cellulose associated with fine poorly known mechanisms of its biosynthesis, methods of isolation of cellulose from natural sources and its morphological diversity. Lower (fresh-water and marine algae) and higher (bushes and trees) plants, bacteria and animals (for example, tunicates†) are well-known natural sources of cellulose. Although the cellulose biogenesis in these natural objects has common features, there are differences associated with a particular source. These differences were discussed in detail in the publications.[7 – 10]

† Cellulose from mantles of tunicates is called tunicin.

II. Main structural elements of the cellulose macromolecule

Cellulose is a polymer whose macromolecule consists of β-D-glucopyranose rings. The repeating unit of the polymer chain of cellulose is composed of two β-D-glucopyranose rings rotated with respect to each other (Fig. 1 *a*). Nowadays, the conformation of the glucopyranose ring is not a subject of discussion because numerous X-ray diffraction and other physicochemical studies (see, for example, Ref. 11) provided evidence that this ring adopts a chair conformation designated $^4C_1$ (in cellulose esters or ethers, the ring retains this conformation [12]).

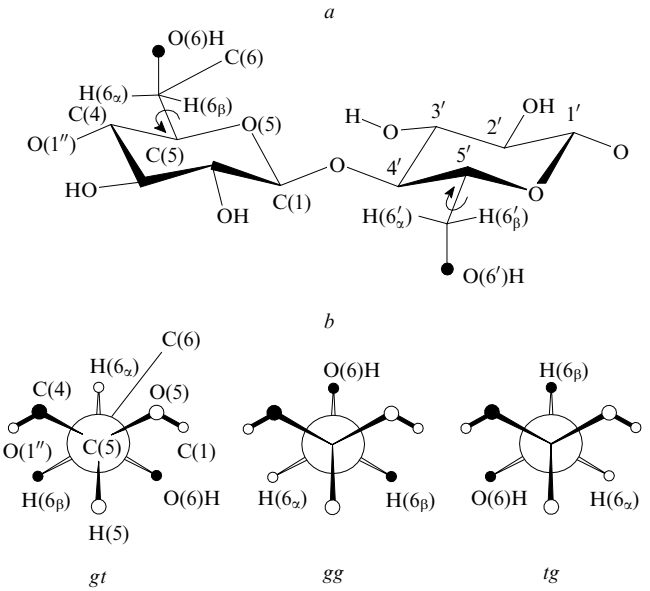


Figure 1. Atom numbering scheme for the repeating unit of cellulose (*a*) and the view of glucopyranose conformers along the C(5)−C(6) bond (*b*).

According to the X-ray diffraction data, the C(1)−O−C(4′) bond angle (τ) between two β-D-glucopyranose rings is ∼116°.[4,5] The bond lengths, bond angles and dihedral angles in the glucopyranose rings of the cellulose macromolecule adopting a chair conformation are similar to those in other glucoside molecules.[13–20]

The conformational state of cellulose polymorphs can be described by the following parameters:

— the Φ[O(5)−C(1)−O−C(4′)] and Ψ[C(1)−O−C(4′)−C(3′)] dihedral angles characterizing the mutual arrangement of a pair of adjacent glucopyranose rings;

— the χ[O(5)−C(5)−C(6)−O(6)] and χ'[C(4)−C(5)−C(6)−O(6)] dihedral angles bearing information on the orientation of the primary hydroxy group O(6)−H with respect to the O(5)−C(5) and C(4)−C(5) bonds in the corresponding glucopyranose ring.[21]

For the dihedral angles χ and χ', the following notations are used: *t* is the *trans* conformation and *g* is the *gauche* conformation; for example, *gg*, *tg* or *gt* (Fig. 1,*b*); the first and second letters refer to the dihedral angles χ and χ', respectively. It is known that the dihedral angles for *t* and *g* are ±180° and ±60°, respectively. For cellulose, the symbols *t* and *g* indicate that the dihedral angles in a particular conformer have the numerical values close to ±180° and ±60°, respectively.

III. Hierarchy of structural levels of cellulose

There are several hierarchical levels of the structural organization of wood cellulose, from the macroscopic (plant cell walls, macrofibril) to nanosize (microfibril) levels (Fig. 2).[22] In the present review, primary attention will be paid to microfibrils because they are of great importance for the supramolecular architecture of cellulose regardless of its origin.

In the cellulose biosynthesis, the polymerization of glucopyranose residues and the formation of microfibrils are interrelated. These processes continue to be the subject of extensive studies (see, for example, Refs 7–9). At the microfibril level, the principal physical and physicomechanical properties of cellulose are manifested. The characteristic features of cellulose are taken into account when developing main methods for the processing of cellulose, such as the mercerization (the treatment with an alkaline solution), regeneration, esterification, *etc*.

The microfibril is a supramolecular unit of cellulose consisting of several (sometimes up to several tens) parallel polymer chains. The cross-section of cellulose microfibrils varies from nanometres to tens of nanometres.[9] Recently, the X-ray diffraction and ^{13}C NMR spectroscopic studies have shown [23] that cellulose microfibrils from petioles of celery (*Apium graveolens* L.) have the diameter of approximately 2.5 nm. The length of the microfibril also depends on the source of cellulose. It is many times larger than the cross-section and is abount tens of micrometres. There is evidence [9] that the length of microfibrils in cellulose isolated from algae is up to parts of a millimeter.

The microfibril consists primarily of crystalline domains (regions of ordered chains) and amorphous regions. The percentage of crystalline domains in cellulose isolated from bacteria and algae can reach 100%, whereas the percentage of ordered chains in cellulose from higher plants is smaller and the latter contains also regions of disordered chains. Earlier, it has been believed that disordered chains are located primarily on the surface of microfibrils. However, Nishiyama *et al.*[24] have recently shown that the crystallite size (d ∼150 nm) of hydrolyzed samples of ramie cellulose are equal to those in microfibrils of nonhydrolyzed samples (Fig. 3). Based on these data and the results of analysis of the sizes of regions accessible to deuteration, which were determined by small-angle neutron scattering, it was concluded that disordered regions are periodically distributed in ramie cellulose microfibrils.

In recent years, disordered regions of the cellulose structure have attracted growing interest because of the high potential of modern methods of investigation. Apparently, the role of these disordered regions in modifications of cellulose is high, although it was not confirmed experimentally.[14,21,25,26] Thus the concept of glucan chain association termed 'nematic ordered cellulose' has recently been proposed. Amorphous cellulose was suggested to be divided into disordered and nematic-ordered types; the latter type borders crystalline cellulose.[21] This differentiation can be useful for the explanation of the details of biosynthesis of major cellulose polymorphs.

Transparent amorphous cellulose was prepared under the combined action of pressure, shear stress, and laser radiation resulting in the 'melting' of fibrillar cellulose.[27]

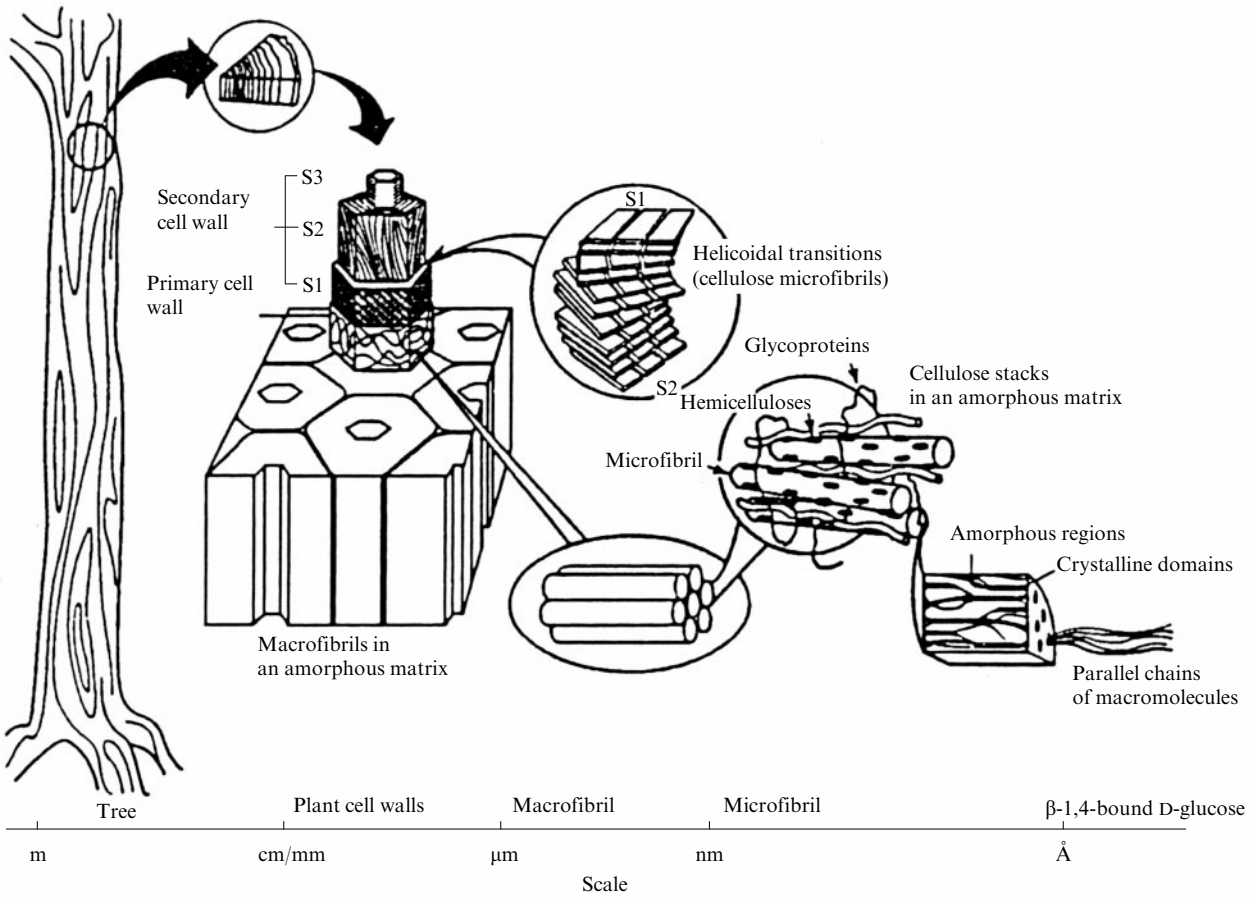


Figure 2. Scheme of hierarchical levels of the structural organization of wood cellulose.[22]

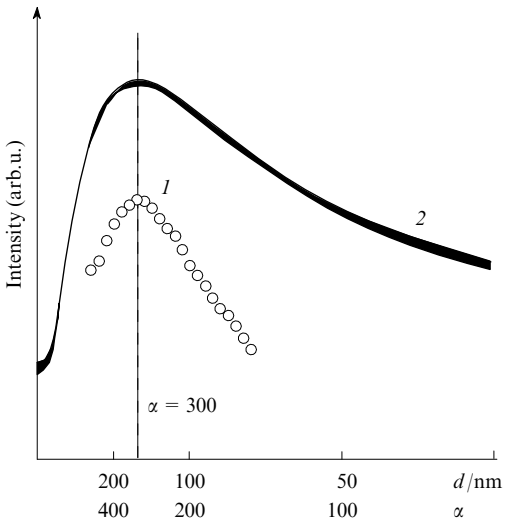


Figure 3. Small-angle neutron scattering data for ramie cellulose (*1*, scale d) and gel permeation chromatography data (*2*, scale α) for the hydrolysis product of the same sample of ramie cellulose [α is the degree of polymerization (the number of glucopyranose rings in the macromolecule), d is the length of the crystallite].[24]

The IR spectra of cellulose samples recorded before and after the action appeared to be identical, indicating that destructive processes do not occur.

IV. Polymorphism of cellulose

In spite of the almost century-long history of research on the structure of crystalline cellulose [the first X-ray diffraction study of cellulose dates to 1913 (cited from the publication [28])], investigations of the characteristic features of the crystalline state of this natural polymer are at their infancy. This is due not only to the complex structure of cellulose but also to the differences in its sources and methods of isolation, as well as due to the absence of informative experimental technique.

Cellulose has several polymorphs. The polymorphism is most typical of crystals of organic compounds whose molecules contain groups capable of hydrogen bonding.[29] The repeating unit of the cellulose macromolecule includes six hydroxy groups and three oxygen atoms. Therefore, the presence of six hydrogen bond donors and nine hydrogen bond acceptors provides great possibilities for forming various hydrogen bond systems. Due to different mutual arrangements of the pyranose rings and possible conformational changes of the hydroxymethyl groups, cellulose chains can exhibit different crystal packings.

Several cellulose polymorphs, such as cellulose I, II, III and IV and their varieties Iα, Iβ, III_I, IV_I, III_{II} and IV_{II}, are known. Cellulose II can be prepared by either the mercerization of native cellulose I or the regeneration of certain derivatives accompanied by their dissolution.

In the past decades, many data on the polymorphism of cellulose were refined and revised. The most reliable data

were published after 1984, when Atalla and Van der Hart [30] reported the results of NMR spectroscopic studies of cellulose. The authors showed that native cellulose I is a composite consisting of two polymorphs, *viz*., Iα and Iβ. It appeared that form Iα prevails in the major part of cellulose isolated from bacteria (for example, from *Acetobacter xylinum*) and in cellulose from fresh-water algae *Glaucocystis nostochinearum*.[9, 15, 31] Polymorph Iβ is the major form in cotton and wood celluloses, ramie cellulose and animal celluloses, for example, in tunicin from *Halocynthia roretzi* (Sea pineapple).[9, 13, 14] Cellulose from the marine algaes *Cladophora* sp. and *Valonia ventricosa* is a mixture of both forms, with polymorph Iα predominating.

The content of polymorphs in cellulose changes under external actions. For example, ramie cellulose contains about 90% of cellulose Iβ; however, the percentage of this modification reaches almost 100% after the hydrothermal treatment (0.1 N NaOH, 260 °C). After the hydrothermal treatment of cellulose from *Cladophora* sp., the percentage of polymorph Iβ is >90%. Crystalline samples of these native celluloses can be transformed into cellulose Iβ under the action of ammonia followed by refluxing in glycerol.[10]

The transitions between the major cellulose polymorphs [32, 33] can be represented schematically (Fig. 4). As can be seen from Fig. 4, the hydrothermal treatment leads to the irreversible transformation of cellulose Iα into cellulose Iβ.

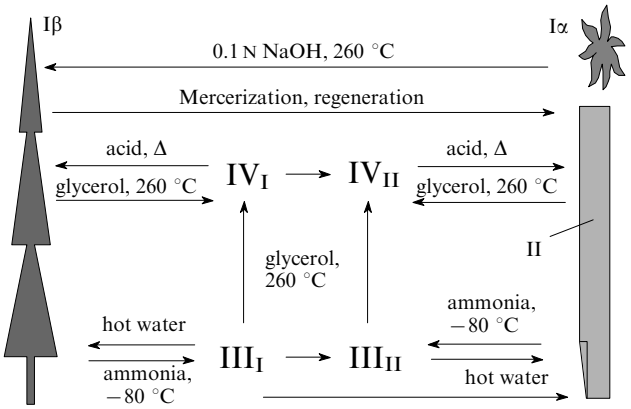


Figure 4. Cellulose polymorphs and transitions between them.

Cellulose I can also be irreversibly transformed into cellulose II by either the mercerization or the regeneration. The mercerization of cellulose in alkaline solutions leads only to its swelling, but not to dissolution. There are several industrial processes for the regeneration of cellulose: fortisan (is not used nowadays), viscose, copper ammonium and *N*-methylmorpholine *N*-oxide processes, special processes developed by DuPont, Michelin, *etc*. All these processes include the dissolution of the corresponding cellulose derivative followed by the formation of regenerated cellulose fibres. The treatment of celluloses I and II with liquid ammonia at −80 °C or with amines leads to their transformation into celluloses III$_I$ and III$_{II}$, respectively. In turn, polymorphs III$_I$ and III$_{II}$ can be transformed into the starting celluloses by the treatment with hot water or by heating.[34] Crystalline celluloses I (III$_I$) and II (III$_{II}$) are transformed into the corresponding polymorphs IV$_I$ and IV$_{II}$ under the action of glycerol at 260 °C, and the latter modifications are transformed into the starting forms I and II after the treatment with acids (for example, with phosphoric acid).

V. Molecular structure and hydrogen bonds in major cellulose polymorphs

At the turn of the 21st century, progress has been made in studying the geometry of major cellulose polymorphs. This is due to the use of synchrotron X-ray diffraction and neutron diffraction methods, as well as due to the improvement of methods for the isolation of highly crystalline samples and their careful preparation.[13–20, 28] Table 1 gives the unit cell parameters for some cellulose polymorphs.

Due to the replacement of hydroxy groups in cellulose by OD groups, the atomic coordinates of deuterium in crystals of celluloses Iα, Iβ and II were determined for the first time, resulting in the refinement of the geometric parameters of hydrogen bonds. The geometry of the intramolecular O(3)H···O(5) hydrogen bond,‡ which plays a great role in the rigidity of the cellulose chain, was most precisely determined.

In spite of evident achievements of these investigations, the detailed determination of the structural features of the crystal packing of cellulose macromolecules is far from being completed, because thousands of reflections are required, which are nowadays impossible to obtain. The methodological approach to the solution of this problem remains the same as that used 30 years ago:[35] the construction of a theoretical model and the fitting of the latter to experimental data (diffraction data, NMR, IR, Raman spectra, *etc*.).

1. Cellulose Iβ

Two parallel chains pass through the unit cell of cellulose Iβ (see Table 1).[13] The corner (or origin) chain passes through the origin of coordinates, and the centre chain passes through the centre of the unit cell. In the case of the parallel packing of two polymer chains in the unit cell, their directions, which are specified, for instance, by the C(1)→C(4) bond vector of the glucopyranose unit, coincide with each other. In the antiparallel packing, the vectors point in the opposite directions. (Running ahead, it should be noted that, according to the commonly accepted view, the antiparallel packing is typical of cellulose II.) The identity period (parameter *c*) includes two glucopyranose rings. The conformational parameters of the corner chain differ from those of the centre chain [13] (Table 2). This fact is an important addition to the earlier structural studies of cellulose Iβ by high-resolution solid-state ^{13}C NMR spectroscopy, where this difference has been found.[36]

The presence of a large number of various hydrogen bonds in the crystal packing of cellulose Iβ was mentioned.[13, 14] In these studies, two types of hydrogen bond networks (networks **A** and **B**) were identified (Fig. 5, Table 3). Two types of hydrogen bond networks are formed due to the involvement of the groups O(2)H and O(6) in hydrogen bonding. The percentage of both types of networks in the cellulose sample under study was estimated. It was shown that the percentage of the network **A** reaches

‡ Hereinafter, the atoms in adjacent glucopyranose rings are unprimed for simplicity.

Table 1. X-ray diffraction and neutron diffraction data for cellulose polymorphs.

Poly-morph	Natural source		Temperature /K	Unit cell parameters [a]						Ref.
	type	name		*a*	*b*	*c*	α	*β*	*γ*	
I_β	A	Tunicate *Halocynthia roretzi*	293	7.784(8)	8.201(8)	10.380(10)	90	90	96.5	13
I_α (see [b])	P	Fresh-water algae *Glaucocystis nostochinearum*	293	6.717(7)	5.962(6)	10.400(6)	118.08(5)	114.80(5)	80.37(5)	15
III_I	P	Marine algae *Cladophora*	293	4.450(4)	7.850(8)	10.310(10)	90	90	105.10(5)	16
II	HP	Ramie cellulose (mercerized)	293	8.10(1)	9.03(1)	10.31(1)	90	90	117.10(5)	17
II	HP	Fortisan (regenerated cellulose)	293	8.03(1)	9.04(1)	10.35(1)	90	90	117.11(2)	18
			100	8.03(1)	9.02(1)	10.34(1)	90	90	117.11(2)	18

Note. A is an animal, P is a plant, and HP is a higher plant. [a] The bond lengths are given in Angstroms, the angles are given in degrees (the unit cell parameters determined by both methods are identical). [b] The space group $P1$, triclinic system, $Z = 1$ (Z is the number of cellulose chains per unit cell); in the other cases, the space group $P2_1$, monoclinic system, $Z = 2$.

Table 2. Conformational parameters of major cellulose polymorphs.[19]

Polymorph	Fragment	Torsion angles /deg			
		Φ	Ψ	χ	χ'
Iβ	Origin chain	−99	91	170	−70
	Centre chain	−89	95	158	−83
II	Origin chain	−97	95	72	−165
	Centre chain	−94	87	58	−175
Iα	First glucopyranose unit	−98	99	167	−75
	Second glucopyranose unit	−99	95	166	−74

Note. In the studies,[13, 15, 16, 19] different values of the dihedral angles were reported; hence, the dihedral angles determined in the most recent publication [19] are given.

80%; correspondingly, the fraction of the network **B** is about 20%.[13] As mentioned above, the O(3)H···O(5) hydrogen bonds that are present in both networks are the strongest bonds. The strength of the hydrogen bond was evaluated based on a combination of two geometric parameters, *viz*., the hydrogen bond length $d(H\cdots O_A)$ and the $O_D-H\cdots O_A$ angle between the O_D-H covalent bond and the $H\cdots O_A$ hydrogen bond (D and A are the proton donor and acceptor, respectively). In the series of hydrogen bonds found in X-ray diffraction studies (see Table 3), the hydrogen bonds with $d(H\cdots O_A) < 2$ Å and the angle $O_D-H\cdots O_A > 130^\circ$ are assumed to be strong.

An important question about the coexistence of two types of hydrogen bonds is as follows: whether these bonds are in dynamic equilibrium or they are formed independently in different parts of crystalline cellulose? Theoretical calculations and experimental neutron diffraction data showed that both hydrogen bond networks statistically coexist at room and lower temperatures,[14, 37, 38] whereas these networks can be dynamically transformed into each other at high temperatures.[14] The topology of these networks in microfibrils is unknown. Thus it remains unclear whether these networks are present in different crystallites or within the same crystallite.

In the study [13] it was first established with certainty that the origin and centre chains form two-dimensional sheets, in which the chains are cross-linked by intermolecular hydro-

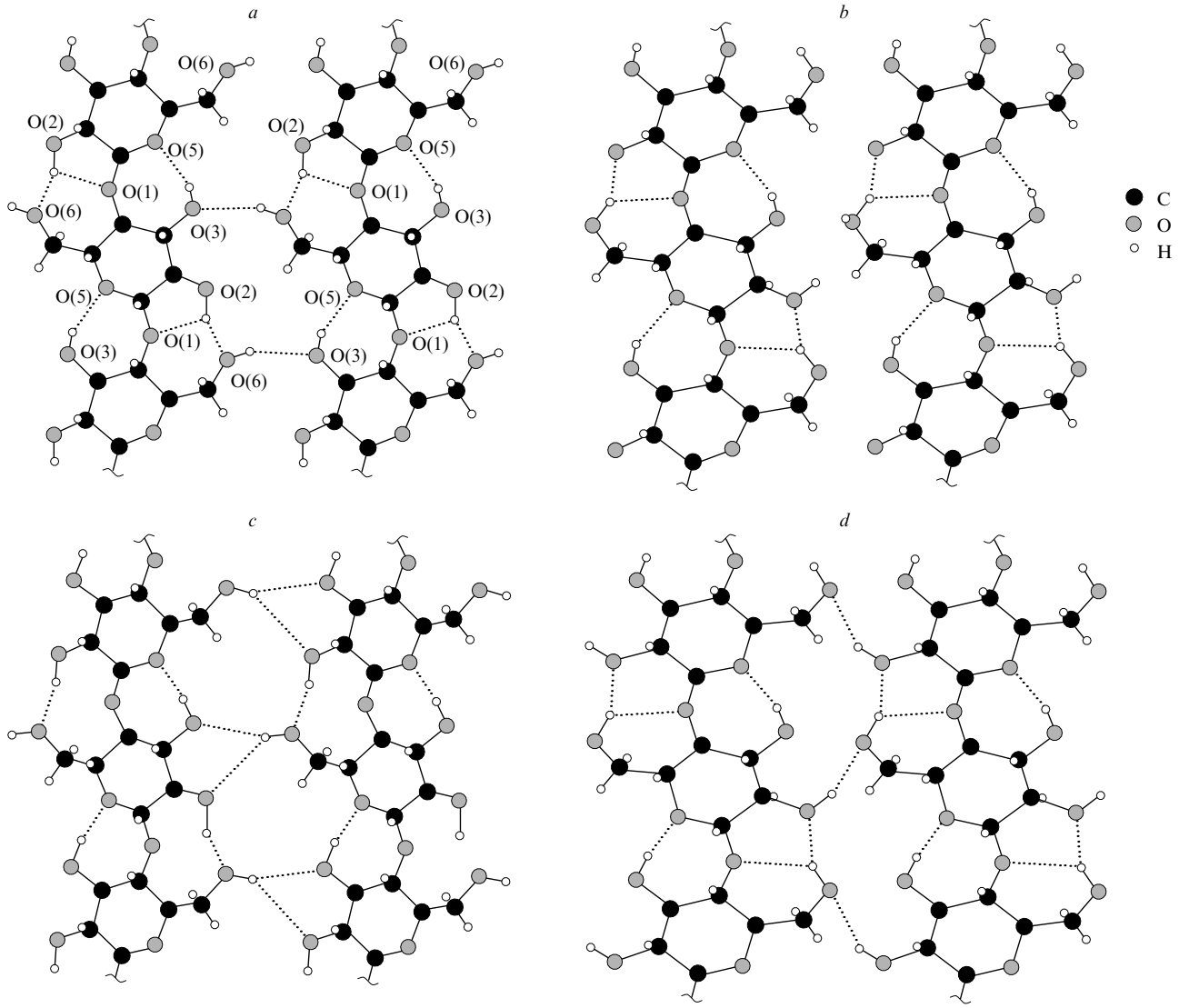


Figure 5. Scheme of hydrogen bonds in the sheet of the crystal structure of cellulose Iβ for the origin (*a*, *b*) and centre (*c*, *d*) chains in the networks **A** (*a*, *c*) and **B** (*b*, *d*).[13]

Table 3. Geometric parameters of hydrogen bonds in cellulose Iβ.[13]

$O_D-H\cdots O_A$ bond	Hydrogen bond type [a]	Distance /Å			$O_D-H\cdots O_A$ angle /deg
		O_D-H [b]	$H\cdots O_A$	$O_D\cdots O_A$	
O(3)H···O(5)	IntraHB	0.98/0.98	1.97/1.75	2.76/2.71	137/162
Network **A**					
O(2)H···O(6)	IntraHB	0.98/0.98	1.83/1.90	2.77/2.87	159/165
O(2)H···O(1)	IntraHB	0.98/–	2.30/–	2.80/–	110/–
O(6)H···O(3)	InterHB	0.98/0.99	2.04/1.78	2.89/2.71	144/157
O(6)H···O(2)	InterHB	–/0.99	–/2.54	–/3.21	–/125
Network **B**					
O(6)H···O(2)	IntraHB	0.97/0.98	1.88/1.97	2.77/2.87	150/152
O(6)H···O(1)	IntraHB	0.97/0.98	2.15/2.24	2.79/2.89	122/123
O(2)H···O(6)	InterHB	–/0.98	–/2.44	–/3.21	–/135

Note. The parameters separated by a slash refer to the corner chain/centre chain.
[a] Here and in Tables 5 and 6, IntraHB and InterHB are intra- and intermolecular bonds, respectively. [b] The O_d-H distance was fixed by the authors.

gen bonds. Therefore, sheets of corner chains alternate with sheets of centre chains to form a three-dimensional packing. In this study, the authors also showed that there are no strong hydrogen bonds between the sheets. The sheets are linked to each other by weak dispersion forces and weak CH···O hydrogen bonds. Consequently, the mutual shifts of the sheets with respect to each other are the most probable shifts in crystallites. (There is a certain analogy with the sheet-like structure of graphite.) Due to this packing, the hydroxy groups of cellulose are accessible, for example, to the nitrating agent, which is important for the reactivity of cellulose.[12] Presumably, the space between the sheets is most suitable for the diffusion of the agent. The anisotropy of the properties of crystalline cellulose Iβ. is convincingly supported by changes in the unit cell parameters with temperature.

Studies of the expansion or contraction of crystallites of celluloses Iβ and II (Table 4) with changes in the temperature of the samples showed that, as expected, the distances between the sheets of the molecules (parameter *a*) in cellulose Iβ vary most substantially. In the sheet, where the chains are linked to each other by strong hydrogen bonds (parameter *b*), these changes are small, which was demonstrated experimentally.[24, 25, 35] The cellulose chains (parameter *c*) behave similarly, which is also in good agreement with the formation of strong intramolecular hydrogen bonds.

The molecular dynamics calculations [41] of the thermal expansion of the unit cell parameters of cellulose Iβ are well consistent with the experimental results (except for the parameter *b*). The data for native cellulose obtained by dynamic Fourier-transform infrared spectroscopy are also in good agreement with the X-ray diffraction data.[42, 43]

Table 4. Changes in the unit cell parameters (%) of the cellulose polymorphs Iβ and II with changes in the temperature.

Source	*T*, °C	Parameter			Ref.
		Δ*a*	Δ*b*	Δ*c*	
Cellulose Iβ					
Tunicin	from 25 to −170	−0.9	–	–	18
Wood	from 25 to 250	+4.2	−0.7	+0.1	39
Abstract cellulose [a]	from 25 to 270	+7.4	+6.0	−0.5	40
Cellulose II					
Regenerated	from 25 to −170	−0.25	−0.22	−0.10	18
Mercerized	from 25 to 250	+0.5	+3.4	−0.1	41

Note. The dash means that no changes were observed.
[a] The calculated data.

2. Cellulose Iα

Crystalline cellulose Iα has the triclinic (space group *P*1) unit cell containing one chain. The repeating unit contains a pair of geometrically identical glucopyranose moieties related by a pseudo-twofold screw axis. In the crystal of this polymorph, the cellulose chains are parallel to each other, like those in cellulose Iβ. The characteristic features of the hydrogen bonds in crystalline cellulose Iα were determined by synchrotron X-ray diffraction and neutron diffraction methods.[15] In polymorph Iα, as in polymorph Iβ, adjacent glucoside units are linked by the strong intramolecular O(3)H···O(5) hydrogen bond (Table 5), and two different hydrogen bond networks are formed.

Two types of hydrogen bond networks (**A** and **B**) in cellulose Iα (Fig. 6), as those in polymorph Iβ, are determined by the type of hydrogen bonds with the participation of the hydroxy groups O(6)H and O(2)H. Thus, the network **A** is characterized by the presence of the strong intramolecular O(2)H···O(6) hydrogen bonds in both glucopyranose rings and the strong intermolecular O(6)H···O(3) hydrogen bond of the second pyranose residue (see also Fig. 7). In the network **B**, the intramolecular O(6)H···O(1) hydrogen bond is the strongest one (see Table 5). The ratio between the networks **A** and **B** in modification Iα was estimated [15] as 55 : 45, unlike that in cellulose Iβ, where the network **A** prevails (~80%).[13] Celluloses Iα and Iβ are similar in that the planes of the glucopyranose units in the chains coincide, and the chains cross-linked by hydrogen bonds form two-dimensional sheets, which are arranged in stacks in crystallites. An important fact is that there are no

Table 5. Geometric parameters of hydrogen bonds in cellulose Iα.[15]

$O_D-H\cdots O_A$ bond	Hydrogen bond type	Distance /Å			$O_D-H\cdots O_A$ angle /deg
		O_D-H [a]	$H\cdots O_A$	$O_D\cdots O_A$	
O(3)H···O(5)	IntraHB	0.99/0.98	1.95/2.07	2.92/2.87	164/138
O(3)H···O(1)	IntraHB	0.99/–	2.39/–	2.99/–	119/–
Network **A**					
O(2)H···O(6)	IntraHB	0.97/0.98	1.69/1.76	2.47/2.48	134/127
O(2)H···O(3)	IntraHB	–/0.98	–/2.18	–/2.87	–/118
O(6)H···O(3)	InterHB	0.98/0.98	2.18/1.85	2.82/2.77	122/154
O(6)H···O(2)	InterHB	0.98/0.98	2.79/2.54	3.61/3.64	141/135
Network **B**					
O(6)H···O(1)	IntraHB	0.98/0.98	1.89/1.96	2.79/2.81	150/145
O(6)H···O(2)	IntraHB	–/0.98	–/1.97	–/2.48	–/110
O(2)H···O(3)	IntraHB	0.98/0.99	2.28/2.36	2.87/2.85	117/110
O(2)H···O(6)	InterHB	0.98/0.99	2.68/3.02	3.61/3.64	157/122

Note. The parameters separated by a slash refer to the first/second glucopyranose rings of the cellulose unit. [a] The O_D-H distance was fixed by the authors.

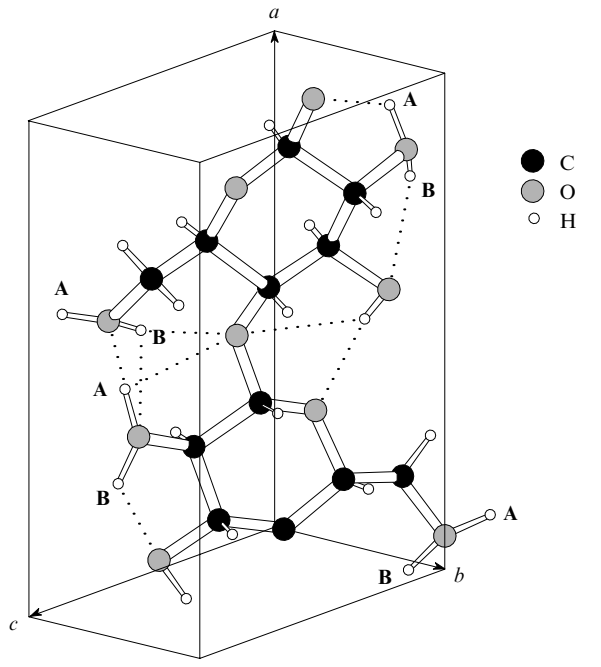


Figure 6. Scheme of intramolecular hydrogen bonds in the sheets of the crystal structure of cellulose Iα.[15]
A and **B** are hydrogen bond networks.

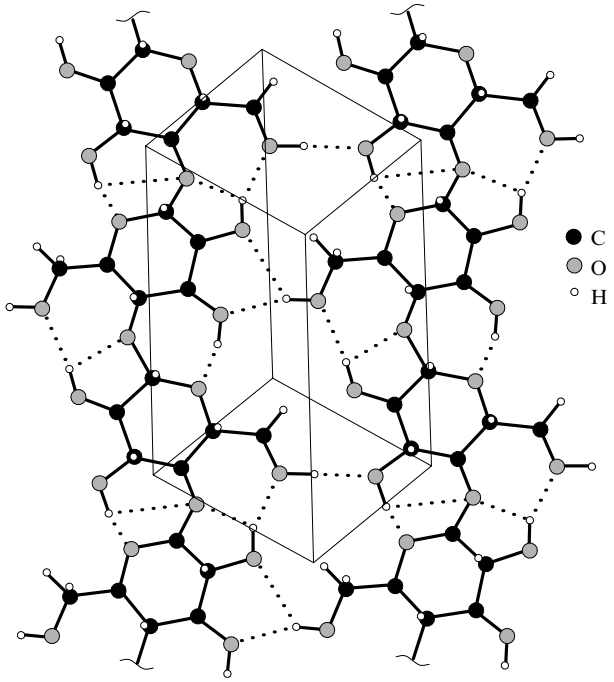


Figure 7. Scheme of hydrogen bonds in the sheets of the crystal structure of cellulose Iα,[31] which is identical to the hydrogen bond network **A** found in the study.[15]

strong intermolecular interactions between the sheets. It was suggested that, due to the absence of strong hydrogen bonds between the sheets, the latter can be shifted with respect to each other under certain actions, resulting in the polymorphic transition of cellulose Iα into cellulose Iβ.[15]

Recall that many difficulties and discrepancies in the interpretation of the structural and other data are associated with the diversity of natural sources of cellulose, their isolation, experimental conditions of transformations, *etc*. Investigations of cellulose Iα by X-ray diffraction and neutron diffraction methods,[15] on the one hand, and high-resolution solid-state ^{13}C NMR spectroscopy,[31] on the other hand, is a typical example. Witter *et al*.[31] found that the crystal structure of cellulose Iα (see Fig. 8) is in good agreement only with the hydrogen bond network **A** published in the study.[15] However, Nishiyama *et al*.[15] suggested that the fraction of the network **B** in the structure of cellulose Iα is essential. This is most likely attributed to the fact that the authors studied cellulose from different natural sources, such as the bacteria *Acetobacter xylinum*[31] and the fresh-water algae *Glaucocystis nostochinearum*.[15]

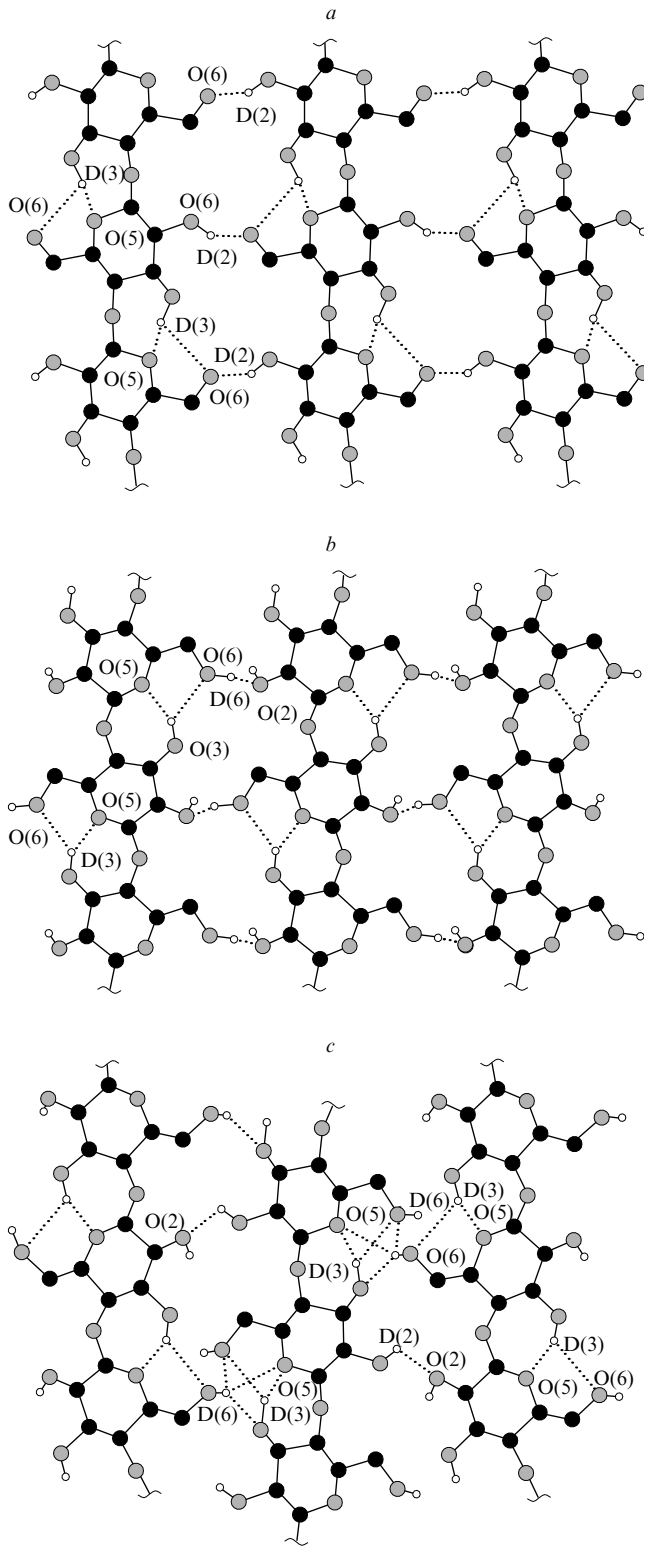


Figure 8. Scheme of intra- and intermolecular hydrogen bonds in crystalline deuterated cellulose II: in the sheets of the origin (*a*) and centre (*b*) chains and between the sheets (*c*).[28]

The dynamics of the transformation of polymorph Iα into Iβ was studied under heating of cellulose Iα in an inert atmosphere. Powder X-ray diffraction and two-dimensional Fourier-transform infrared correlation spectroscopic studies showed that a 'high-temperature' intermediate is formed at a temperature of about 200 °C.[44, 45]

3. Cellulose II

Cellulose II, like cellulose Iβ, has the monoclinic unit cell (space group $P2_1$). The origin and centre chains pass through the unit cell, and a pair of monosaccharide residues of each chain are related by a twofold screw axis (see Table 1). As mentioned above, the different arrangement of the chains (parallel in cellulose Iβ and antiparallel in cellulose II) is the most substantial difference between these two polymorphs.

The origin and centre chains form the corresponding alternating planar sheets, in which the chains are linked to each other by intermolecular hydrogen bonds, *viz*., by the O(6)H···O(2) hydrogen bonds in the sheets of the origin chains and by the O(2)H···O(6) hydrogen bonds in the sheets of the centre chains (Fig. 8, Table 6). Among intramolecular hydrogen bonds, let us mention the O(3)H···O(5) bond between adjacent glucopyranose units. The important difference between cellulose II and the other polymorphs under consideration is that there is a three-centre hydrogen bond between the group O(6)H of the origin chain and the O(3), O(5) and O(6) atoms of the centre chain and a hydrogen bond between the group O(2)H of the centre chain and the O(2) atoms of the origin chain in crystallites of cellulose II (see Fig. 8 and Table 6). All these bonds are weaker than the above-mentioned bonds; however, their number (four hydrogen bonds per glucopyranose residue) is sufficiently large to have an effect on the properties of this polymorph.

This fact is confirmed by the data[18] on the thermal contraction of the unit cell upon cooling of cellulose to 100 K (see Table 4). It is particularly interesting that it is the interlayer hydrogen bonds that are substantially redistributed (the parameter *b* substantially increases) upon heating, which is accompanied even by a decrease in the distance along the chain (the parameter *c*).[40]

The cellulose macromolecule is highly rigid due to the presence of a three-dimensional hydrogen bond network in addition to the C—O—C bonds between the glucopyranose rings. In the absence of such hydrogen bond networks (for example, in cellulose esters), the chains are much more flexible. These hydrogen bonds are responsible for both the poor solubility of cellulose and the difference in the reactivity of the hydroxy groups in esterification reactions. As shown above, there are the strong O(3)H···O(5) and O(6)H···O(2) (or O(2)H···O(6)) hydrogen bonds located on both sides of the C—O—C glycosidic bond in the network **A** (or **B**) in cellulose Iβ (see Fig. 5 and Table 3). In cellulose Iα, the strong O(3)H···O(5) and O(6)H···O(2) hydrogen bonds are present only in the network **A** (see Figs. 7 and 8 and Table 4). In cellulose II, there is only the O(3)H···O(5) hydrogen bond between the pyranose rings (as in the network **B** in cellulose Iα). However, in cellulose II the absence of the second hydrogen bond along the chain is compensated by the presence of four weak hydrogen bonds between the sheets, which provides the more uniform (three-dimensional) distribution of the hydrogen bond network. Evidently, the analysis of the cellulose structure is made possible due to the reliable experimental data on the geometry of different polymorphs.

Table 6. Geometric parameters of hydrogen bonds in cellulose II.[17,28]

$O_D-H\cdots O_A$ bond	Hydrogen bond type [a]	Distance /Å			$O_D-H\cdots O_A$ angle /deg
		O_D-H	$H\cdots O_A$	$O_D\cdots O_A$	
O(3)H···O(5)	IntraHB	0.98/0.98	1.92/1.85	2.66/2.73	130/148
O(3)H···O(6)	IntraHB	0.98/0.98	2.80/2.50	3.31/3.22	113/130
O(2)H···O(6)	InterHB	0.98/–	1.82/–	2.71/–	151/–
O(6)H···O(2)	InterHB	–/0.98	–/1.78	–/2.68	–/150
O(6o)H···O(6c)	IL	0.98	2.02	2.64	120
O(6o)H···O(3c)	IL	0.98	2.22	3.05	142
O(6o)H···O(5c)	IL	0.98	2.49	3.12	122
O(2c)H···O(2)	IL	0.98	2.21	2.78	116

Note. The parameters separated by a slash refer to the original (o) or origin chain/centre chain (c). [a] IL is an interlayer hydrogen bond. [b] The O_D-H distance was fixed by the authors.

VI. Conclusion

Large organic molecules, including polymers, are characterized by the complex potential energy surface determined by the energy difference between possible conformers. Since the energy difference is small, there is a high probability that such compounds have several (sometimes coexisting) polymorphs. The result is determined by the crystallization conditions for each polymorph, as well as by a system of intermolecular interactions that occur in the crystal structures. This is clearly manifested in the natural polymer cellulose. The hydrogen bond network has a substantial effect on both the conformational state and the mutual arrangement of the cellulose chains.

Polymorphs are characterized by the possible existence of one or several metastable phases, *i.e.*, phases, which appear under special conditions and which cannot be formed during phase transitions of this substance. It is probable that two varieties of cellulose I, *viz.*, Iα and Iβ, which are produced in the biosynthesis, can be assigned to metastable phases. Nowadays, there are different views [14,46,47] on the mutual arrangement of the crystalline domains in the coexisting polymorphs of cellulose I; however, this question remains open.

On the whole, the anisotropy of the properties of cellulose Iβ crystallites is an important factor providing insight into the diffusion of reactants during the esterification of cellulose. This anisotropy is determined by the sheet packing of the macromolecules and was revealed in the studies published in the last decade.[13,14,18] It is likely that the diffusion of esterifying agents occurs between the sheets of cellulose molecules.

The transformation of cellulose I into cellulose II, resulting in the transformation of the parallel arrangement of the chains in the crystallites of the former polymorph into the antiparallel orientation (!) in the latter polymorph, also remains unclear. The production of regenerated cellulose II in chemical (for example, the synthesis of cellulose xanthate) and phases (for example, the dissolution of xanthate) processes followed by the transformation into cellulose II does not contradict the possibility of a change in the mutual arrangement of the macromolecules upon the transformation of cellulose I into more stable cellulose II. However, the mercerization does not lead to the transition to the liquid phase, and crystalline cellulose I is transformed into crystalline cellulose II without dissolution. The question arises as to how the parallel chains are reoriented to form an antiparallel packing?

It is most likely [32] that the transformation of cellulose I into cellulose II during mercerization is associated with the appearance of crystallization centres in disordered regions of cellulose I. In these regions, the crystallization is accompanied by the formation of the antiparallel arrangement of the chains and the destruction of crystallites of cellulose I. The regeneration of cellulose leads to the dissolution of the intermediate xanthate. The crystallization of the latter from solution results in the antiparallel arrangement of the chains. Actually, all methods of the preparation of cellulose II lead to the successive or competitive disorder or amorphization of cellulose I and result in the antiparallel arrangement of the chains of cellulose II. This process occurs in the case of both the polymorphic transition through dissolution (regeneration) and the solid-phase transition (mercerization).

The recent data on [48] the mechanochemical treatment of cotton cellulose I support this suggestion. The authors convincingly showed that the milling of dry cotton cellulose (the moisture content was ~0%) in a ball grinder leads to its amorphization. At the same time, according to the X-ray diffraction data and high-resolution solid-state ^{13}C NMR spectroscopy, the mechanochemical treatment of cellulose samples containing ~30% of moisture affords cellulose II. Apparently, in addition to the destruction, which can be caused by this treatment, the presence of moisture leads to an increase in the lability of cellulose chains, which is favourable for their antiparallel arrangement.

Alternatively, this transformation can be attributed to the mutual penetration of the chains on the surface of the differently oriented crystallites. This explanation has been suggested recently [49] based on the analysis of electron diffraction data. It was also shown that cellulose II can be produced in the biosynthesis of bacterial cellulose from *Acetobacter xylinum* under an external action.[50] Recall also the suggestion [32] that the chains in cellulose II are arranged in a parallel fashion. To conclude, let us note that the problem of the formation of the antiparallel arrangement of macromolecules in cellulose II remains to be solved.

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