Stability of Cellulose Structures Studied by MD Simulations. Could Mercerized Cellulose II Be Parallel?

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ABSTRACT: By extensive and systematic molecular dynamics simulations eight stable cellulose crystal structures have been identified. We organized them in a coherent scheme, which gives a clue to possible interconversions between the various structures. From this scheme it can be inferred that mercerized cellulose II could in fact be a parallel structure or contain parallel regions. This parallel cellulose II structure fits into the same unit cell dimensions as antiparallel cellulose II and therefore can remain unnoticed. Regenerated cellulose II is likely to have all hydroxymethyl groups in the *gt* conformation similar to what was found in two recent determinations of the cellotetraose structures. Due to its characteristic layer structure cellulose I could crystallize in several different packing modes. Biosynthesis, however, enforces a parallel packing. It is shown that Iα and Iβ have a similar and specific parallel packing mode.

Introduction

Cellulose is the most abundant biological macromolecule on earth. The polymer, consisting of $\beta(1\rightarrow4)$ linked glucose residues, forms fibrous structures with high crystallinity. In nature it occurs in all plant cell walls, usually embedded in a lignin and hemicellulose matrix, and in the cell walls of algae, and also some bacteria produce cellulose. Examples of more or less pure native cellulose are cotton, ramie, and algal cellulose. Each of these fibers is an intimate mixture of crystalline and amorphous regions. Research on the structure of the crystalline part has been going on since the 1930s.[1] Still, considerable controversies and questions remain up till today.

Cellulose exhibits considerable polymorphism. A phase diagram is shown in Figure 1. The major polymorphs are cellulose I (recently subdivided in Iα and Iβ[2,3]) and II. All native celluloses are found in the I form or rather they are mixtures of Iα and Iβ. Treatment of native cellulose materials in order to form better oriented fibers, invariably leads to the other major polymorph: cellulose II. Two distinctly different processes are known. In the mercerization process recrystallization takes place after swelling in 18% NaOH solutions without any extensive molecular reorientation.[1] In the regeneration process an isotropic solution of cellulose in the form of a derivative is made, which is extruded through a spinning hole after which cellulose recrystallizes during coagulation.

In the 1970s several X-ray fiber diffraction structure determinations were carried out on cellulose Iβ[4−6] and regenerated and mercerized cellulose II.[7−9] A critical re-evaluation of the data was carried out by French.[10] Both structures have two independent chains traversing the unit cell (origin and center). The chains possess a symmetry close to that of space group $P2_1$. Deviations from the latter are indicated by the presence of weak 001 and 003 reflections. Nonetheless, refinements carried out both with $P2_1$ symmetry[4,7,9] and $P1$ symmetry[6,8] indicate that the cellulose I and II structures are both reasonably well described by $P2_1$ symmetry. The fact that the two chains are crystallographically independent allows the possibility of different orientations and molecular conformations in these two chains. There is considerable consensus on the facts that cellulose I has a parallel packing, while cellulose II has an antiparallel packing. Other experimental evidence for the parallel orientation[3,11,12] of cellulose I is available. For cellulose II the situation is somewhat less well established. In all structural models for cellulose I both the origin and center chains are thought to have the hydroxymethyl group *tg*[13] conformation. In the case of cellulose II preference is given, on the basis of the diffraction data, to the *gt* conformation of the hydroxymethyl group in the origin chain and to the *tg* conformation in the center chain. However, several studies[14,15] suggest that all chains have the *gt* conformation.

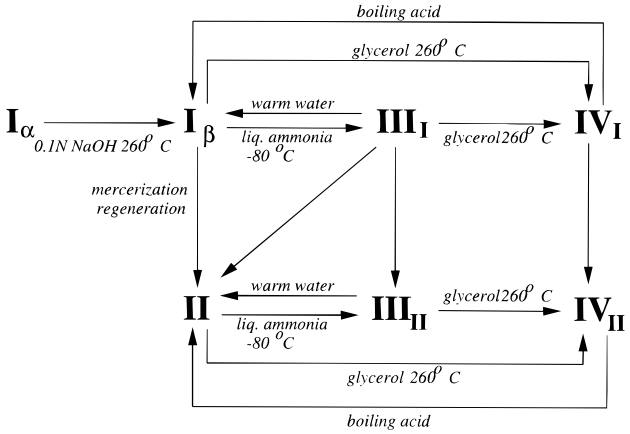

Figure 1. Polymorphy of cellulose.

The finding that cellulose I has a parallel orientation of the chains, whereas cellulose II has an antiparallel orientation, was the cause of many debates. For, how could the II form be antiparallel while it can be obtained from the parallel I form through mercerization, in which no molecular reorientation takes place? Several mechanisms have been proposed to explain this finding. Nishimura and Sarko[16] showed that the original cellulose I crystallites are lost during mercerization, and the amorphous regions take part in the newly formed antiparallel Na−cellulose I crystallites. It is still puzzling how cellulose could organize into a neatly ordered

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up−down array of molecules. A different mechanism was suggested by Simon et al.[17] During mercerization, where the distance between the molecules is substantially increased due to swelling, the chain molecules would fold and both ends would glide along one another. Thus each molecule would end in a once-folded antiparallel shape.

X-ray diffraction data are not particularly sensitive to the parallel or antiparallel packing due to limited resolution of the data. This makes it difficult to obtain conclusive evidence from X-ray data alone. The interaction between the molecules, however, is completely different for the various packing modes. In this paper we describe the results of a systematic analysis of possible packing modes by molecular dynamics (MD) simulations. Several less elaborate efforts have been made in the past.[5,17,18−21] MD simulations have the advantage of not being strictly limited to nearby local minima. Energy barriers on the order of a few kT can be overcome. Only recently were three MD studies on models of cellulose Iα, Iβ, and II carried out, starting from a single initial packing mode for each of these,[22−24] of which some physical and hydrogen bonding properties were calculated. In contrast to these studies we apply constant pressure simulations (NPT ensemble), which turned out to be crucial in proving the instability of some packing modes and selecting those modes that are consistent with diffraction data. Our systematic study led to eight stable and ordered allomorphs within an energy range of 12 kJ/mol (3 kcal/mol). The relation between these allomorphs and their possible interconversion suggests a possible phase scheme, and generates an alternative view on the mercerization process. This hypothesis will be tested experimentally in the near future.

Computational Procedures

MD simulations are carried out with the program package GROMOS[25] with the standard force field for carbohydrates.[26] The program is restricted to a monoclinic system. Periodic boundary conditions were used in a simulation box of 3 × 3 × 2 unit cells for the monoclinic systems, giving a total of 18 cellotetraose fragments and of 3 × 2 × 2 super triclinic cells for the Iα structure, having a b-axis twice the size of the monoclinic b-axis, giving a total of 24 cellotetraose fragments. The glucose residues are covalently bonded across the periodic box in the direction of the chain axis. A special adaptation of the Gromos pressure scaling algorithm[27] was used because of this polymeric character. The variations of the monoclinic γ angle were made possible by a special adaptation.[28] Symmetry and crystallographic translations are not fixed within the computational box. The degree of conservation of the approximate 2-fold screw axis and the crystallographic translations is an indication of the compatibility of the simulated model with experimental diffraction data. A cutoff radius for long-range interactions of 9 Å was used throughout. All structural models were first subjected to energy minimization before the actual MD simulation was started. Initial velocities were taken from a Maxwellian distribution at 300 K. The time step was 0.002 ps. All bond lengths were kept fixed through the SHAKE algorithm.[29] The temperature was kept at 300 K by loose coupling to a temperature bath with a relaxation constant of 0.1 ps. Anisotropic pressure scaling was performed at 1 atm with a pressure relaxation constant of 2 ps and a compressibility of 1.0×10^{-5} bar^{-1} in the c-axis direction and 4.9×10^{-5} bar^{-1} for the other directions. The first 10 ps of each simulation were used as equilibration. After that, each 0.2 ps coordinates, energies, and box dimensions were stored. Both constant pressure (NPT) and constant volume (NVT) simulations were performed. The simulations were carried out for 100−500 ps each after 10 ps equilibration time.

Table 1. Average Potential Energies and Cell Dimensions

		a (Å)	b (Å)	c (Å)	γ (deg)	$\langle E\rangle_p$[a]	$\langle E\rangle_v$[b]
			Cellulose I				
X-ray		8.17	7.86	10.38	97.0		
βp1	*tg*/*tg*	8.1	7.6	10.4	84		
βp1	*tg*/*gt*	8.1	7.8	10.3	94	308.6	310.6
βp2	*tg*/*tg*	8.1	7.6	10.4	95	297.3	306.1
βa1	*tg*/*tg*	8.1	7.7	10.4	93	296.1	302.2
βa2	*tg*/*tg*	8.1	7.5	10.4	90	296.5	308.9
αp1	*tg*/*tg*	8.1	7.7	10.4	82[c]		
αp2	*tg*/*tg*	8.1	7.7	10.9	97[d]	298.9	305.0
			Cellulose II				
X-ray		8.01	9.04	10.36	117.1		
p1	*gt*/*gt*	8.1	8.7	10.3	116	305.6	313.6
a2	*gt*/*tg*	8.0	9.2	10.4	121	302.6	308.1
a2	*gt*/*gt*	8.1	8.9	10.3	119	302.9	310.9

[a] Average potential energy (kJ (mol of cellobiose)$^{-1}$) at constant pressure. [b] Average potential energy (kJ (mol of cellobiose)$^{-1}$) at constant volume. [c] Equivalent monoclinic unit cell dimensions are given. The triclinic unit cell can be generated by $\mathbf{a}' = {}^1/_2\mathbf{a} - {}^1/_2\mathbf{b} + {}^1/_4\mathbf{c}$, $\mathbf{b}' = {}^1/_2\mathbf{a} + {}^1/_2\mathbf{b} + {}^1/_4\mathbf{c}$, and $\mathbf{c}' = -\mathbf{c}$. [d] Converting this unit cell to triclinic gives $a' = 6.5$, $b' = 5.8$, $c' = 10.4$ Å and $\alpha = 109.7$, $\beta = 108.9$, $\gamma = 82.3°$.

Possible packing modes and definitions are based on a paper by Kolpak and Blackwell.[7] It is firmly established by all diffraction experiments that the two independent chains have a relative stagger of approximately ${}^1/_4$ in the fiber axis direction (c-axis). Two parallel modes (p1, parallel-up; p2, parallel-down) and two antiparallel modes (a1, origin chain up and center chain down with $-c/4$ shift; a2, idem but with $+c/4$ shift) can then be considered.[30] These were all investigated in all *gt*/*tg*[31] combinations of the hydroxymethyl groups in both the cellulose Iβ and II unit cells. Since the X-ray structures lack the positions of the hydroxyl hydrogen atoms, these were generated in an arbitrary fashion. It was expected that the hydroxyl group dihedrals will automatically turn to more favorable positions. This was more or less the case, but sometimes the most ordered and lowest energy structure could only be arrived at by starting in ideal hydrogen-bonded positions, i.e. those positions that initial simulations tended to converge to. In total this led to over 70 simulations. An alternative is to use simulated annealing. Although this approach is very effective in changing dihedrals, the structures did not come to a large degree of order, even after 1 ns of simulation after cooling. The initial unit cell dimensions for cellulose Iβ were taken from Gardner and Blackwell[4] (a = 8.17 Å, b = 7.86 Å, c = 10.38 Å, and γ = 97.0°) and those for cellulose II from Kolpak and Blackwell[7] (a = 8.01 Å, b = 9.04 Å, c = 10.36 Å, and γ = 117.1°). The unit cell parameters used to build the initial Iα structure were based on the unit cell by Gardner and Blackwell. Transformation to the triclinic unit cell using the relation at the bottom of Table 1 gives the cell dimensions a = 6.54, b = 5.91, and c = 10.38 Å and α = 109.3, β = 108.6, and γ = 82.8°. This transformation was taken from the paper by Sugiyama et al.[3] During the constant pressure simulations no restriction is put on the unit cell, only the ${}^1/_4$

Table 2. Hydrogen Bonds in the Cellulose I and II Models

	origin		center	
Iβp2*tg*/*tg*	O2o−H···O6o	intra	O2c−H···O6c	intra
	O3o−H···O5o	intra	O3c−H···O5c	intra
	O6o−H···O3o	intraplane	Oc6−H···O3c	intraplane
Iβp1*tg*/*gt*	O2o−H···O6o	intra	O2c−H···O6c	intraplane
	O3o−H···O2c	interplane	O3c−H···O5c	intra
	O6o−H···O3o	intraplane	O6c−H···O1o	interplane
Iβa1*tg*/*tg*	O2o−H···O6o	intra	O2c−H···O6c	intra
	O3o−H···O5o	intra	O3c−H···O5c	intra
	O6o−H···O3o	intraplane	O6c−H···O3c	intraplane
Iβa2*tg*/*tg*	O2o−H···O6o	intra	O2c−H···O6c	intra
	O3o−H···O5o	intra	O3c−H···O5c	intra
	O6o−H···O3o	intraplane	O6c−H···O3c	intraplane
Iαp2*tg*/*tg*	O2−H···O6	intra		
	O3−H···O5	intra		
	O6-H···O3	intraplane		
IIp1*gt*/*gt*	O2o−H···O6c	interplane	O2c−H···O3o	interplane
	O3o−H···O5o	intra	O3c−H···O6o	interplane
	O6o−H···O2o	intraplane	O6c−H···O2c	intraplane
IIa2*gt*/*tg*	O2o−H···O2c	interplane	O2c−H···O6c	intra
	O3o−H···O5o	intra	O3c−H···O5c	intra
	O6o−H···O2o	intraplane	O6c−H···O3c	intraplane
IIa2*gt*/*gt*	O2o−H···O2c	interplane	O2c−H···O6c	intraplane
	O3o−H···O5o	intra	O3c−H···O5c/O6c	intra[a]
			O6o	interplane[a]
	O6o−H···O2o	intraplane	O6c−H···O6o	interplane

[a] The O3c−H hydroxyl group shows large mobility and therefore has disordered hydrogen bonding.

stagger of the chains is approximately imposed by the monoclinic periodic box.

Results

Several models turned out to be unstable in the constant pressure (NPT) simulations, and they either converted into a different packing mode or became completely disordered. In total eight stable and ordered structures have been found and their final equilibrated unit cell dimensions, average energies and hydroxymethyl group conformations are listed in Table 1. Four cellulose Iβ structures seem possible. Three of these have the *tg*/*tg* conformations and are characterized by hydrogen-bonded *ac*-layers (for hydrogen bonding see Table 2) that are packed together by van der Waals interactions, two of which are antiparallel and one of which is parallel. The energy differences between these structures are small and slightly in favor of the antiparallel models. In all cases the *b*-axis is contracted by 0.2 Å (2−3%). The most notable result is the instability of the Iβp1*tg*/*tg* mode.[32] The initial structure is that proposed by Gardner and Blackwell[4] (parallel-up). The monoclinic angle γ changes from 97 to 84°. This change represents a shift of the *ac*-layers with respect to each other. No notable shift in the *c*-direction was observed. Close inspection shows that what happened is the conversion into the parallel-down structure (p2). Indeed, the Iβp2*tg*/*tg* structure is stable and from comparison with the experimental cell dimensions (especially γ) it can be inferred that this is the most likely Iβ structure. This is the structure that was proposed by Woodcock and Sarko.[6,33] A similar situation occurs for the triclinic Iα structure. This structure can be based on either the p1 or p2 structure (parallel-up or parallel-down). Again, the Iαp1*tg*/*tg* structure converts to the Iαp2*tg*/*tg* structure. Thus a choice between the two possible models proposed by Sugiyama et al.[3] is now made. Another notable result (not shown in Table 1) is that if in the cellulose II cell, the p2 packing mode is chosen with the *tg*/*tg* conformations, the structure readily converts to cellulose I (Iβp2*tg*/*tg*).

The fourth cellulose Iβ structure, Iβp1*tg*/*gt*, is higher in energy and could be an intermediate structure that

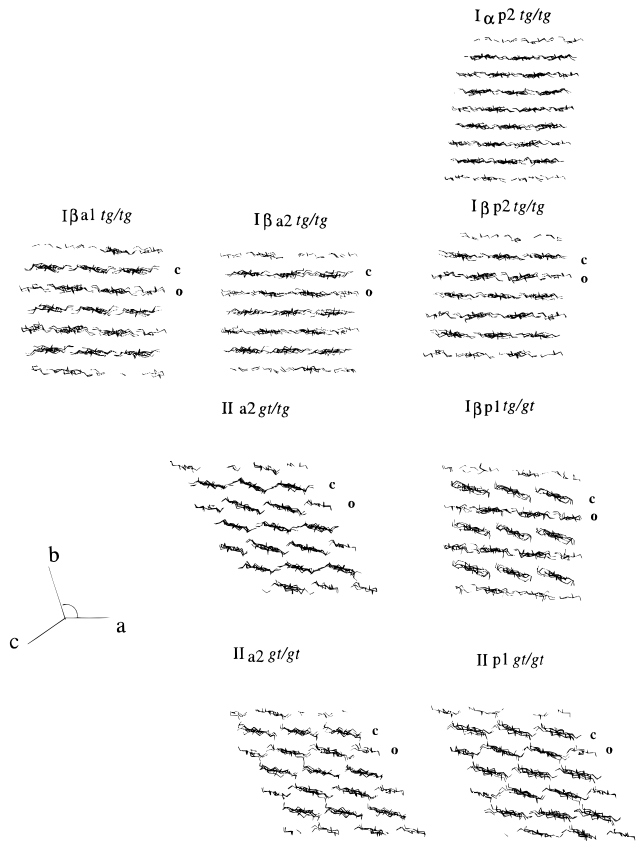

Figure 2. Projections of MD snapshots of the stable cellulose structures down **c**. Origin layers indicated by **o** and center layers by **c**. The structures are arranged according to the scheme in Figure 3.

fits perfectly in the cellulose Iβ unit cell. The center chains have rotated quite significantly with respect to the other Iβ structures. This rotation is in fact characteristic for the cellulose II structures. The *ab*-projections are shown in Figure 2.

For cellulose II three possibilities remain. One antiparallel model in two possible combinations of the hydroxymethyl groups: IIa2*gt*/*tg* and IIa2*gt*/*gt*. Though

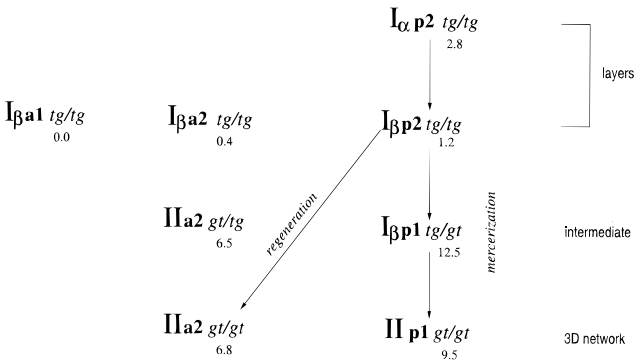

Figure 3. Scheme to show the relation between stable MD structures. The right part represents structures that could occur in the mercerization process. The numbers represent the average relative potential energies in kJ (mol of cellobiose)$^{-1}$ residues in the constant pressure simulations.

the energy of the *gt*/*tg* structure is somewhat lower, it turned out that it was stable only when all hydroxyl groups were initially placed in ideal hydrogen-bonding positions. In any other case the structure readily converted into *gt*/*gt*. On the basis of the unit cell dimensions, especially γ, one would tend to choose IIa2*gt*/*gt* as the structure of regenerated cellulose fibers. In contrast IIa2*gt*/*tg* was preferred by Kolpak and Blackwell[7] as well as by Stipanovic and Sarko[8] on the basis of diffraction data. Basically the structure was also preferred on the basis of diffraction data on mercerized cellulose II.[9] In addition to these IIa2 structures we have also found the possibility of a p1-packing mode: IIp1*gt*/*gt*. This structure fits nicely into the cellulose II cell dimensions. The energy is somewhat higher. Detailed analysis of the various structures and averaged coordinates will be described in a separate paper. Presently, we want to focus on the implications for the phase behavior of cellulose.

Discussion

Organizing the stable structures into the scheme shown in Figure 3 illustrates their structural interrelation. Not all of these structure need to be real observable polymorphs. The structures on the left side are related to each other, as are those on the right side. It has been shown that hydrothermal heating in the presence of NaOH[34] converts the Iα to the Iβ structure. This suggests that Iα is metastable. This is not obvious from the energies in Table 1. The mechanism of this conversion, however, can be easily understood from the simulations. The *ac*-layers are only packed through hydrophobic, rather nonspecific, interactions, and slipping of the layers relative to each other (in the *c*-direction) could be achieved by only a small activation (Iαp2*tg*/*tg* → Iβp2*tg*/*tg*). Hardy and Sarko[23] proposed that the hydrogen bonds in the *ac*-layers of the Iα structure could break by hydrothermal stress, after which the chains could rotate around *c*, which is equivalent to a $^1/_2c$ shift, and in this way convert to the Iβ structure. In our proposal breakage of hydrogen bonds is not necessary.

Iβp1*tg*/*gt* is clearly an intermediate structure between Iβp2*tg*/*tg* and IIp1*gt*/*gt*. Transition of the hydroxymethyl groups of the center layer to *gt*, rotation of the center molecules, and subsequent shift of the layers along *a* would be sufficient to arrive at the intermediate structure, after which also the origin chains could adopt the *gt* conformation followed by a shift along *a* to the larger monoclinic angle to adopt eventually the cellulose II unit cell (see Figure 2). These shifts of layers are particularly easy to imagine in the swollen state as occurs in the mercerization process (the *b*-axis, representing the interlayer distance, increases by ~1 Å[35]). The actual mercerization process goes through a Na−cellulose I phase. What our scheme suggests is that the Iβp1*tg*/*gt* and IIp1*gt*/*gt* structures are favorable arrangements and that the mercerized, or at least part of the mercerized, structure is in fact parallel. This idea is not completely new (see, e.g., Turbak et al.[20]) but was never proposed in such a coherent way. Nishimura and Sarko[16] showed that a lot of the original crystallites are lost during the mercerization process. It is possible that part of the originally amorphous regions take part in the newly formed crystallites. These molecules could be oriented antiparallel. It is essential for the cocrystallization of parallel and antiparallel structures that they fit into the same lattice, which they are seen to do.

Although the energy of the IIa2*gt*/*gt* is found to be somewhat larger than that of IIa2*gt*/*tg*, we believe that IIa2*gt*/*gt* is the cellulose II structure that is obtained after regeneration. Once the cellulose molecules are dissolved, the hydroxymethyl groups take the *gt* (or *gg*) conformation. The *tg* conformation is not found in polar solutions,[36] thus prohibiting the crystallization of molecules in this conformation. Moreover, recently two independent crystal structure determinations of cellotetraose where carried out,[37−39] whereby is was found that all hydroxymethyl groups are in the *gt* conformation and that the packing and hydrogen bonding is remarkably similar to that of our IIa2*gt*/*gt* structure.

No simple physical relationships exist between the parallel on one side and the antiparallel structures on the other side. From the nature of the interaction between the hydrogen-bonded *ac*-layers in the *tg*/*tg* structures of cellulose I, it is evident that several packing modes must be nearly equal in energy. Therefore, in our view, cellulose I could equally well be parallel as antiparallel; if not, the biosynthesis process and the immediate crystallization of cellulose would impose a parallel orientation[12] (Iβp2*tg*/*tg*). During the mecerization process the orientations of the molecules do not change and, as mentioned before, mercerized cellulose could be parallel (IIp1*gt*/*gt*). When cellulose is regenerated through an intermediate isotropic solution, conversion of the parallel alignments of molecules to antiparallel is very likely to occur. The polar solution will exclude the *tg* conformation and during the recrystallization the only choice is between IIa2*gt*/*gt* and IIp1*gt*/*gt*. The first one has a better packing interaction and is the most likely regenerated cellulose II form. It is not evident from the simulations that cellulose II is necessarily the more stable form of the major polymorphs.

None of the low-energy cellulose I structures has interplanar hydrogen bonds and they exhibit a kind of sheet like packing. In cellulose II the hydrogen bonds turned to a 3D network, and the structure is more tightly packed.

During the many MD simulations no clear light on the cellulose III and IV crystal forms could be shed. A remarkable finding, though, is that the Iβa2*tg*/*tg* structure is very similar (with respect to the packing, conformation, and cell dimensions) to the cellulose IV$_{II}$ structure proposed by Gardiner and Sarko.[40] A parallel cellulose IV structure (IV$_I$ according to Gardiner and Sarko) could not be found. Also no ordered cellulose III structure could be found. The unit cell dimensions of

cellulose III[41] were only approached in rather disordered structures. It is very likely that cellulose III does not present a stable structure but is left over from a liquid ammonia treatment of cellulose I or II, and indeed, it converts easily to either cellulose I or II.[40]

In conclusion we can state that the polymorphic behavior of cellulose is afflicted with metastable structures because the polymer always crystallizes under conditions in which no thermodynamical equilibrium is reached. This means that we should not necessarily regard the lowest energy structures as those that actually will be observed. Kinetical aspects of the crystallization could have a prominent influence on the observed polymorphs.

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References and Notes

(1) Meyer, K. H.; Misch, L. *Helv. Chim. Acta* **1937**, *20*, 232−244.
(2) Atalla, R. H.; van der Hart, D. L. *Science* **1984**, *223*, 283−285.
(3) Sugiyama, J.; Vuong, R.; Chanzy, H. *Macromolecules* **1991**, *24*, 4168−4175.
(4) Gardner, K. H.; Blackwell, J. *Biopolymers* **1974**, *13*, 1975−2001.
(5) Sarko, A.; Muggli, R. *Macromolecules* **1974**, *7*, 486−494.
(6) Woodcock, C.; Sarko, A. *Macromolecules* **1980**, *13*, 1183−1187.
(7) Kolpak, F. J.; Blackwell, J. *Macromolecules* **1976**, *9*, 273−278.
(8) Stipanovic, A. J.; Sarko, A. *Macromolecules* **1976**, *9*, 851−857.
(9) Kolpak, F. J.; Weih, M.; Blackwell, J. *Polymer* **1978**, *19*, 123−131.
(10) French, A. D. *Carbohydr. Res.* **1978**, *61*, 67−80.
(11) Chanzy, H.; Henrissat, B. *FEBS Lett.* **1985**, *184*, 285−288.
(12) Haigler, C. H.; Brown, R. M., Jr.; Benziman, M. *Science* **1980**, *210*, 903−906.
(13) The symbol *tg* stands for a *trans* conformation of O5−C5−C6−O6 and a *gauche* conformation of C4−C5−C6−O6.
(14) Horii, F.; Hirai, A.; Kitamaru, R. *Polym. Bull.* **1983**, *10*, 357−361.
(15) Kroon-Batenburg, L. M. J.; Kroon, J.; Northolt, M. G. *Polym. Commun.* **1986**, *27*, 290−292.
(16) Nishimura, H.; Sarko, A. *J. Appl. Polym. Sci.* **1987**, *33*, 867−874.
(17) Simon, I.; Glasser, L.; Scheraga, H. A.; St. John Manley, R. *Macromolecules* **1988**, *21*, 990−998.
(18) French, A. D.; Miller, D. A.; Aabloo, A. *Int. J. Biol. Macromol.* **1993**, *15*, 30−36.
(19) Pertsin, A. J.; Nugmanov, O. K.; Marchenko, G. N.; Kitaigorodsky, A. I.; *Polymer* **1984**, *25*, 107−114.
(20) Turbak, A. F.; Sakthivel, A. *Chemtech* **1990**, July.
(21) Aabloo, A.; French, A. D. *Macromol. Theory Simul.* **1994**, *3*, 185−191.
(22) Heiner, A. P.; Sugiyama, J.; Telleman, O. *Carbohydr. Res.* **1995**, *273*, 207−223.
(23) Hardy, B. J.; Sarko, A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1995**, *36*, 640.
(24) Reiling, S.; Brickmann, J. *Macromol. Theory Simul.* **1995**, *4*, 725−743.
(25) van Gunsteren, W. F. GROMOS, Groningen Molecular Simulation Package, University of Groningen, The Netherlands, 1987.
(26) Koehler, J.; Saenger, W.; van Gunsteren, W. F. *Eur. Biophys. J.* **1987**, *15*, 197−210.
(27) van Eijck, B. P. *Mol. Simulation* **1994**, *13*, 221−230.
(28) Kouwijzer, M. L. C. E.; van Eijck, B. P.; Kroes, S. J.; Kroon, J. *J. Comput. Chem.* **1993**, *14*, 1281−1289.
(29) van Gunsteren, W. F.; Berendsen, H. J. C. *Mol. Phys.* **1977**, *34*, 1311−1327.
(30) Unfortunately, the definitions of Kolpak and Blackwell and Gardner and Blackwell are different from a structural point of view for the antiparallel structures. We adhered to the definition of Kolpak and Blackwell, and consequently, our Iβa2 structure is Gardner and Blackwell's a1 structure and vice versa. The reason we did this is that only in such a way can the similarity between the IIa2 and Iβa2 structures be seen.
(31) From the diffraction studies it is quite evident that the hydroxymethyl groups must either be in a *gt* or *tg* position.
(32) Iβ stands for the cellulose Iβ unit cell; p1 for the p1 packing mode; and tg/tg for the conformation of the hydroxymethyl groups in the origin and center chains, respectively.
(33) The definition for up and down depends on the choice of the *a*- and *b*-axes, which unfortunately is different for the Gardner and Woodcock structures. What in Woodcock's case is an up structure is the down structure of Gardner.
(34) Yamamoto, H.; Horii, F.; Odani, H. *Macromolecules* **1989**, *22*, 4130−4132.
(35) Nishimura, H.; Okano, T.; Sarko, A. *Macromolecules* **1991**, *24*, 759−770.
(36) Kroon-Batenburg, L. M. J.; Kroon, J. *Biopolymers* **1990**, *29*, 1243−1248.
(37) Raymond, S.; Heyraud, A.; Tran Qui, D.; Kvick, A.; Chanzy, H. *Macromolecules* **1995**, *28*, 2096−2100.
(38) Gessler, K.; Krauss, N.; Steiner, T.; Betzel, C.; Sandmann, C.; Saenger, W. *Science* **1994**, *266*, 1027−1029.
(39) Gessler, K.; Krauss, N.; Steiner, T.; Betzel, C.; Sarko, A.; Saenger, W. *J. Am. Chem. Soc.* **1995**, *117*, 11397−11406.
(40) Gardiner, E. S.; Sarko, A. *Can. J. Chem.* **1985**, *63*, 173−180.
(41) Sarko, A.; Southwick, J.; Hayashi, J. *Macromolecules* **1976**, *9*, 857−863.

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