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Structure of Cellulose. 2. Low-Energy Crystalline Arrangements

Istvan Simon,[†] Leslie Glasser,[‡] and Harold A. Scheraga*

Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853-1301

R. St. John Manley

Pulp and Paper Institute of Canada and Department of Chemistry, McGill University, Montreal, Canada H3A 2A7. *Received June 23, 1987*

ABSTRACT: Low-energy conformations and arrangements of cellulose chains in a crystalline structure have been investigated. Both metastable parallel and stable antiparallel arrangements exist. By analogy with the unit cell parameters and hydrogen bond networks suggested from X-ray diffraction data, the most stable parallel and antiparallel arrangements correspond to the cellulose I and II structures, respectively. Some low-energy structures obtained in the computations might correspond to cellulose III and IV, but the available experimental data are too incomplete to enable a definite identification to be made. Our data also suggest the presence of some structural inhomogeneity along and on the surface of the microfiber. Such inhomogeneities have been reported earlier, based on electron microscopy. A two-chain and an eight-chain unit cell model have been compared. The differences in conformation, packing arrangements, and energy are quite small and are at about the limit of experimental accuracy. A model is suggested for the transformation from metastable parallel-chain cellulose I to the more stable antiparallel chain cellulose II during mercerization.

Introduction

Early attempts to propose packing schemes for cellulose date back to the 1930s.[1] Although there are only a few stable conformations of a single chain,[2] these can be packed in several different arrangements. Thus, chains may be placed in parallel or in antiparallel alignment and, in both cases, one or more minimum-energy arrangements can be expected depending on the relative positions of the chains. By increasing the number of single-chain conformations involved, the number of theoretically possible packing arrangements increases dramatically. Many of these packing arrangements, however, may never appear because the corresponding local-minimum energies are too high relative to other minimum-energy arrangements. On the other hand, metastable packing arrangements may persist if large activation energies are necessary to alter the structure. Certainly, those transformations which involve a parallel ↔ antiparallel rearrangement must have large activation energies.

At least six different cellulose structures are known at present.[3] The best characterized are native cellulose (cellulose I), which is suggested to have a parallel arrangement[4-6] of chains, and mercerized cellulose (cellulose II), which can be produced from native cellulose by treatment with alkali and is suggested to have an antiparallel arrangement.[7-10] Less detailed information is available for cellulose III_I and III_{II}, which are produced from cellulose I and II, respectively, by liquid-ammonia treatment at −80 °C, and for cellulose IV_I and IV_{II}, which are products of glycerol treatment of cellulose III_I and III_{II} at 260 °C[3] (see Figure 1). It has been suggested that some among these six cellulose structures may represent the same conformation and packing but differ in the spatial arrangements of the microfibers.[3]

Most X-ray diffraction data indicate that the unit cell of the crystalline structure contains one disaccharide portion of each of two cellulose chains.[3] The more detailed diffraction patterns for cellulose I and II also show a few low-intensity reflections, the appearance of which depends on the source of the sample, which cannot be indexed on the basis of the simple two-chain unit cell model;[4,8] these data rather suggest that the unit cell dimensions normal to the fiber axis might each be twice as large as in the two-chain model so that the unit cell contains eight disaccharides.

The simplest, but fairly effective, hard-sphere calculations on cellulose packing[6,11,12] ignored the attractive terms involving the atomic interactions and took into account only repulsions. More detailed energy calculations, combined with X-ray, electron, and neutron diffraction data, led to the proposal that various hydrogen-bonded networks stabilize the structures of native and of processed cellulose.[5,7,13] Pizzi and Eaton[14-16] used conformational energy

[†] Institute of Enzymology, Hungarian Academy of Sciences, P.O. Box 7, Budapest 1502, Hungary.
[‡] Department of Chemistry, University of the Witwatersrand, Wits 2050, South Africa.

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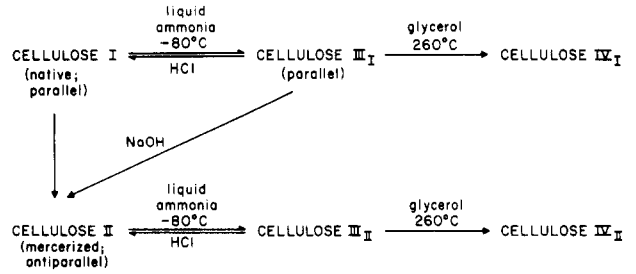

Figure 1. Schematic description of the various forms of cellulose and the conditions for their interconversion.[3]

calculations to determine the conformation and the packing of di- and tetrasaccharides in a crystalline array; their simplified calculations involved the energy of the intermolecular interactions within only pairs of di- or tetrasaccharides.

In the present paper, the low-energy conformations and arrangements of infinitely long cellulose chains in crystalline form are reported. The calculations were performed by using the FORTRAN program WMIN (revised version of March, 1984),[17] with an improved optimization routine POWELL,[18,19] and vectorized here for the IBM 3090-400 VF supercomputer of the Cornell–NSF Theory Center. A possibly unique feature of the present work is the extension of these lattice energy calculations to infinite chains, by constraining the unit-cell dimensions and the asymmetric unit position along the chain axis. The method presented here for generating infinitely long chains should be applicable to the study of other polymers as well.

Methods

A. Generating the Crystalline Lattice. X-ray diffraction data[4-10] show that cellulose chains have twofold screw symmetry along the crystalline microfibrils, while Figure 2 of the accompanying paper[2] shows that none of the conformations corresponding to energy minima of a single chain have such a symmetry. However, the virtual-bond dihedral angle (C5′–C3′–C5‴–C3‴ between the second and fourth glucose units; see Figure 1 of the accompanying paper[2]) differs from 180° by only a few degrees in each of the six low-energy conformations. For a glycosidic C–O–C bond angle of 113.1°, this dihedral angle can be reduced by 1° either by increasing ϕ by 1.90° or ψ by 1.74°; therefore, ϕ and ψ were altered in a ratio of 1.90:1.74 until the twofold screw symmetry was reached. This process increases the conformational energy of the chains to various extents, depending on how far the original minimum-energy positions on the (ϕ,ψ) map are from the straight line [ψ (deg) = $-234.48 - 0.9225\phi$] corresponding to two-fold screw symmetry. Hence, we checked if any of the structures in the accompanying paper[2] in the minimum-energy region I, with energies between 4 and 10 kcal/mol, might appear in the lower energy range of the conformations with twofold screw symmetry. No such structure was found. Therefore, we used only those low-energy structures shown in Figure 4 and 5 of the accompanying paper.[2]

To build a crystalline structure, we start with a hexasaccharide having twofold screw symmetry, produced by the slight alterations in ϕ and ψ mentioned above. The unit cell contains the second and third glucose residues; i.e., the "molecule" inside a unit cell starts with atom O4′ and terminates with atom C1″, while O4‴ bound to the residue containing C1″ belongs to the glucose residue of the next unit cell along the X axis. Only this disaccharide portion of the original hexasaccharide is used in the subsequent calculations. The glycosidic oxygen, O4′, between the first and second pyranoside rings, is taken to define the origin of the coordinate system. The X axis is defined by the vector from O4′ to O4‴, and the Y axis is parallel (the Z axis perpendicular) to the C5′C3′C5‴ plane. The two-chain unit cell also contains one disaccharide portion of a second chain. In the parallel alignment, the second disaccharide is set parallel to the first; the first O4 atom of the first disaccharide is placed at the origin of the unit cell (as mentioned above), and the corresponding O4 atom of the second disaccharide is placed at $(a/4, b/2, c/2)$, where a, b, and c are the unit cell dimensions along the X (fiber), Y, and Z axes, respectively. In the antiparallel alignment, the second disaccharide is antiparallel to the first, and the O4 atom is placed at $(3a/4, b/2, c/2)$. In both cases, the planes of C5′C3′C5‴ of both chains are parallel.

These arrangements were suggested on the basis of X-ray data and were used as starting structures in the energy-minimization process. While carrying out the energy calculations, we found that there is another energy minimum for parallel packing when O4 is near the $(3a/4, b/2, c/2)$ position and for antiparallel packing when O4 is near the $(a/4, b/2, c/2)$ position. These two structures differ significantly from those mentioned above in most cases, except when both disaccharides of the unit cell have the same type ...i–i–i... conformation,[2] i.e., when each overlapping disaccharide has the same conformation in the cellulose chain. We started energy minimization from both positions of the second chain.

The unit cell length parameters b and c and the angles α, β, and γ were generally taken from the Meyer and Misch model[1] and allowed to vary during energy minimization, as described in section B, while the length parameter a (along the chain axis) was taken as the distance between O4′ and O4‴ in the hexasaccharide with 2_1 symmetry and was treated as a direct function of ϕ and ψ, rather than using X-ray data. The latter choice was necessary to maintain the fixed length of the covalent bond between two consecutive units cells.

B. Conformational Energy Calculations. The conformational energy of the asymmetric unit was calculated as a sum of nonbonded, electrostatic, and hydrogen-bonding interactions between pairs of atoms and of intrinsic torsional energies, as reported earlier.[2,20,21] The calculated total energy consisted of three terms. The first ("internal" energy) involves the interactions between all pairs of atoms whose distances of separation are not constant and all intrinsic torsional energies within the asymmetric unit that are not constant, plus the torsional energies around the C1″–O4‴ bond which connects adjacent unit cells along the fiber axis. The second term involves an accelerated convergence calculation of the electrostatic interactions between atoms in the structure,[22] while the third ("external") term treats nonbonded and hydrogen-bonding interactions between the atoms of the asymmetric unit and those within a given radius from each atom of the asymmetric unit. This radius was set to 10 Å after checking for covergence,[23] in that further increase of this distance did not alter the structure corresponding to the energy minimum.

WMIN does not recognize the bond between C1″ and O4‴ of two adjacent disaccharides of the chain as covalent because they are in different unit cells; interactions between atoms belonging to the two adjacent unit cells are calculated as 1–5 interactions. Therefore, the energies of interaction of those atoms which are in 1–2 or 1–3-positions because of the existence of the C1″–O4‴ bond are set to zero and the energies between atoms in 1–4-positions are calculated explicitly as 1–4 interactions.

Table I
Energy and Unit Cell Data[a] of Nine Pairs of Structures

corner/center	ΔE	a^b	b	c	α	x_0	y_0	z_0	D
				Parallel					
$(AA)_n/(AA)_n$	11.14	10.28	8.40	7.93	81.01°	0.244	0.487	0.499	−1.74°
$(BB)_n/(BB)_n$	0.00	10.23	8.28	8.21	76.15°	0.241	0.489	0.505	2.57°
$(CC)_n/(CC)_n$	10.25	10.23	8.18	10.00	122.44°	0.278	0.454	0.504	−0.41°
$(AB)_n/(AB)_n$	9.42	10.28	8.38	8.08	78.23°	0.242	0.487	0.501	−2.15°
$(AC)_n/(AC)_n$	23.62	10.28	8.38	8.72	72.16°	0.203	0.519	0.513	−4.20°
$(BC)_n/(BC)_n$	14.50	10.23	8.27	8.68	79.21°	0.219	0.536	0.522	2.56°
$(AA)_n/(BB)_n$	6.42	10.23	8.33	8.01	88.86°	0.260	0.468	0.484	−7.64°
$(CC)_n/(AA)_n$	11.53	10.23	8.40	9.30	60.48°	0.232	0.482	0.508	−10.37°
$(CC)_n/(BB)_n$	1.34	10.23	8.07	9.65	58.69°	0.228	0.491	0.503	11.57°
				Antiparallel					
$(AA)_n/(AA)_n$	9.24	10.28	8.40	7.65	90.28°	0.599	0.643	0.499	10.34°
$(BB)_n/(BB)_n$	−2.07	10.23	8.24	7.71	90.18°	0.623	0.664	0.500	0.89°
$(CC)_n/(CC)_n$	12.33	10.23	11.45	6.28	89.91°	0.822	0.484	0.500	−9.32°
$(AB)_n/(AB)_n$	8.35	10.28	8.47	7.68	90.10°	0.613	0.649	0.500	7.00°
$(AC)_n/(AC)_n$	23.30	10.28	8.65	8.25	89.04°	0.605	0.376	0.501	2.36°
$(BC)_n/(BC)_n$	9.98	10.23	7.79	8.89	90.33°	0.629	0.536	0.499	−4.24°
$(AA)_n/(BB)_n$	5.67	10.23	8.52	7.64	92.87°	0.614	0.659	0.497	−0.98°
$(AA)_n/(CC)_n$	−5.95	10.23	7.74	9.75	122.46°	0.620	0.613	0.457	12.15°
$(BB)_n/(CC)_n$	11.63	10.23	8.18	9.52	120.75°	0.577	0.621	0.475	9.56°

[a] a, b, and c are the unit cell dimensions in Å. α is the unit cell angle around the X axis (fiber axis). x_0, y_0, and z_0 are the fractional coordinates of the O4 atom of the second disaccharide. D is the virtual-bond dihedral angle between the planes of the two disaccharides. ΔE is the energy (in kcal/(unit cell mol)) of the specified structure relative to the energy of the most stable structure. [b] a was determined by a grid search for the minimum-energy value of ϕ, which also determines ψ and a.

C. Energy Minimization. WMIN was used to optimize the given starting structures of various conformations and arrangements of the cellulose chains to reach local energy minima. For a fixed glycosidic bond angle, only one of the three variables ϕ, ψ, and the unit cell length a can be varied independently; the other two are then fixed by the requirement for twofold screw symmetry. However, in order to maintain a covalent bond between atoms in adjacent unit cells during energy minimization, all three variables (ϕ, ψ, and a) were kept constant. Then a grid search was made to find the value of ϕ (and corresponding values of ψ and a) which yields the lowest energy. An initial step size of 5° was used for the search; then the final values of ϕ were determined by quadratic interpolation between the 5° steps.

Energy minimization with WMIN, including POWELL, was carried out in consecutive steps, i.e., by adding more and more variables successively. It was first assumed that the unit cell has two disaccharides with the same conformation, i.e., that the asymmetric unit consists of one disaccharide. In this stage of energy minimization, the dihedral angles of the functional groups of the asymmetric unit were allowed to vary. a was fixed according to the corresponding value of ϕ, the b and c dimensions were taken from the X-ray data,[4] and α, β, and γ were each set to 90°. The latter assignments are necessary for building an antiparallel unit cell.

In the next stage, we started with the results of the first minimization. We now combined conformations so that the conformation of the second disaccharide could differ from that of the first. It must be noted that only conformations with the same values of a, b, c, α, β, and γ can be combined. During minimization, the dihedral angles of all functional groups, the relative positions and orientations of the two disaccharides of the unit cell, and the five unit cell parameters b, c, α, β, and γ were allowed to vary; for an antiparallel unit cell, α, β, and γ were maintained at 90°.

Finally, for the most stable parallel and antiparallel structures, the unit cell dimensions b and c were both doubled, so that the unit cell contained eight disaccharide units. During subsequent energy minimization, the dihedral angles of all of the functional groups, the relative positions and orientations of the disaccharides, and all the unit cell parameters, except a, altogether 98 variables, were allowed to vary.

Results

A. Two-Chain Unit Cell. In both parallel and antiparallel alignments of chains, the energy minimizations show that there are two energy minima for the relative positions of the two chains. In one case, the two chains are shifted relative to each other by about $a/4$ and, in the other case, by about $3a/4$. Shifting the second chain by $3a/4$ results in the same structure as interchanging the two chains (between the corner and center of the unit cell) and shifting by $a/4$. Therefore, we report the results for only one of these pairs.

To reduce the number of possible arrangements, it is generally assumed[4-10] (a) that the two chains of the unit cell have the same conformation and (b) that the interaction pattern stabilizing the overlapping disaccharides is the same, i.e., that the chain conformation is of type ...i–i–i... With both of these conditions, three parallel and three antiparallel structures can be built from the single chains: $(AA)_n$, $(BB)_n$, and $(CC)_n$. If, however, only condition (a) is maintained, three additional pairs of structures can be built from the single chains: $(AB)_n$, $(AC)_n$, and $(BC)_n$ (six structures in all). When only condition (b) is maintained, three other pairs of structures may be built from $(AA)_n$, $(BB)_n$, and $(CC)_n$ when the conformation of the corner chain differs from that in the center (another set of six structures).

These nine pairs of structures (parallel and antiparallel) were examined initially. Table I lists the conformational energy (ΔE) relative to that of the most stable parallel structure, the dimensions of the unit cell (a, b, c, and α), the coordinates of the O4 atom of the center chain (x_0, y_0, z_0), and the orientation of the central chain, i.e., the virtual-bond dihedral angles between the C5, C3 vectors of the two chains. β and γ of the unit cell were also allowed to vary but they remained very close to 90° during energy minimization.

There are 12 additional pairs of structures when neither of the conditions, (a) and (b), mentioned above are maintained. It is worth noting that, in a crystalline

Table II
Calculated Unit Cell Parameters, Fractional Coordinates of the O4 Atom of the Center Chain, and Virtual-Bond Dihedral Angle between Two Chains in the Most Stable Parallel and Antiparallel Arrangements as Well as X-ray Diffraction Data for Cellulose I and II[a]

	corner/center	ΔE	a	b	c	α	β	γ	x_0	y_0	z_0	D
						Parallel						
	cellulose I (X-ray)[1]		10.3	8.35	7.90	84°	90°	90°				
1	$(BB)_n/(BB)_n$	0.00	(10.23)[c]	8.28	8.22	76.15°	90.74°	89.85°	0.241	0.487	0.505	2.57°
2[b]	$(CB)_n/(BB)_n$	0.49	(10.23)	8.13	9.66	58.70°	91.43°	89.33°	0.228	0.491	0.505	−9.90°
3	$(CC)_n/(BB)_n$	1.34	(10.23)	8.07	9.62	58.68°	91.00°	89.83°	0.228	0.491	0.503	11.57°
						Antiparallel						
	cellulose II (X-ray)[3]		10.36	8.01	9.04	117.1°	90°	90°				
4	$(AA)_n/(CC)_n$	−5.95	(10.23)	7.74	9.75	122.46°	90.09°	89.66°	0.620	0.613	0.457	12.15°
5	$(BB)_n/(BB)_n$	−2.07	(10.23)	8.24	7.71	90.18°	89.99°	90.32°	0.623	0.664	0.500	0.89°

[a] See footnote in Table I for definition of symbols. [b] This does not appear in Table I because the two chains in the unit cell do not have the same conformation, and their interactions are not of the i–i–i type. [c] Values in parentheses were the results of a grid search for the minimum-energy value of ϕ, which also determines ψ and a.

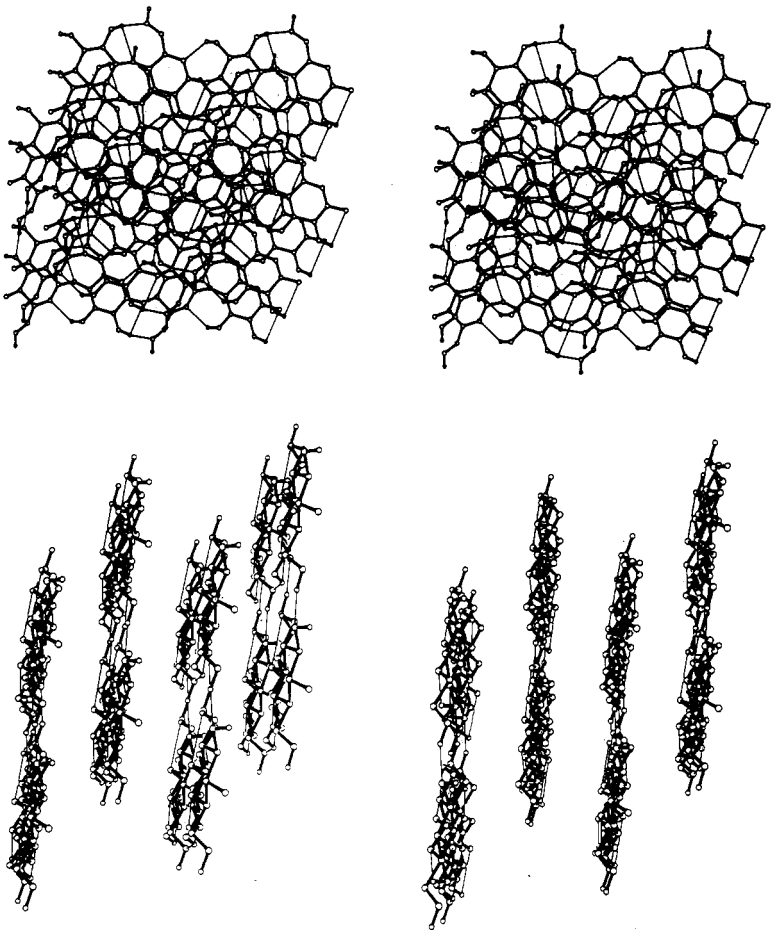

Figure 2. (Top) Stereoviews of eight two-chain (or two eight-chain) unit cells of the structure parallel $(BB)_n/(BB)_n$ (corner/center). Thin lines indicate hydrogen bonds, not longer than 2.8 Å ($E \geq 0.1$ kcal/mol). (Bottom) The same structure as at the top but from a perpendicular direction.

structure in which the chains are arranged in sheets, the atoms of a glucose residue can make direct contact only with atoms of 27 residues as follows: the residue to which the atom belongs, the two adjacent residues in the chain, three adjacent residues in different chains on each side of the chain in question in the same sheet, and nine adjacent residues each in the sheets below and above this sheet. All the possible relative positions and pairings already appear in the nine pairs of interactions listed in Table I. The number of structures that need to be considered as starting conformations may be reduced by omitting those that contain mainly energetically unfavored interactions.

After energy minimization from all reasonable starting structures, we found three low-energy structures among the parallel structures in a 2 kcal/(unit cell mol) interval, with no other stable structure in a further 2 kcal/(unit cell mol) interval. Among the antiparallel structures, two were found with energy lower than that of the most stable parallel structure, with no other structure in the next 3 kcal/(unit cell mol) interval. Data for these five structures are listed in Tables II–IV, and they are shown in Figures 2–6 as stereoviews.

B. Eight-Chain Unit Cell. A comparison between the unit cell parameters and hydrogen bonds of the most stable parallel and antiparallel structures with the available diffraction data suggests that they are the structures of cellulose I and II, respectively. Because of the experimental uncertainty in the size of the unit cell of these two

Table III
Dihedral Angles Determining the Conformation of the Two Disaccharides of the Unit Cell[a]

	exocyclic dihedral angles, deg															
	corner disaccharide								center disaccharide							
struct[b]	3	4	5	6	9	10	11	12	3	4	5	6	9	10	11	12
1	280	201	74	84	280	201	74	84	281	203	73	77	280	204	73	76
2	282	211	96	92	69	65	75	103	282	206	83	87	280	195	74	90
3	73	65	94	101	68	65	94	101	281	197	81	89	281	196	84	89
4	280	107	157	108	200	111	157	106	63	75	91	132	64	75	92	127
5	281	254	70	93	279	254	71	94	281	254	70	93	279	254	71	94

[a] For a backbone conformation of $(\phi, \psi) = (-97°, -145°)$. [b] These structures are the five in Table II.

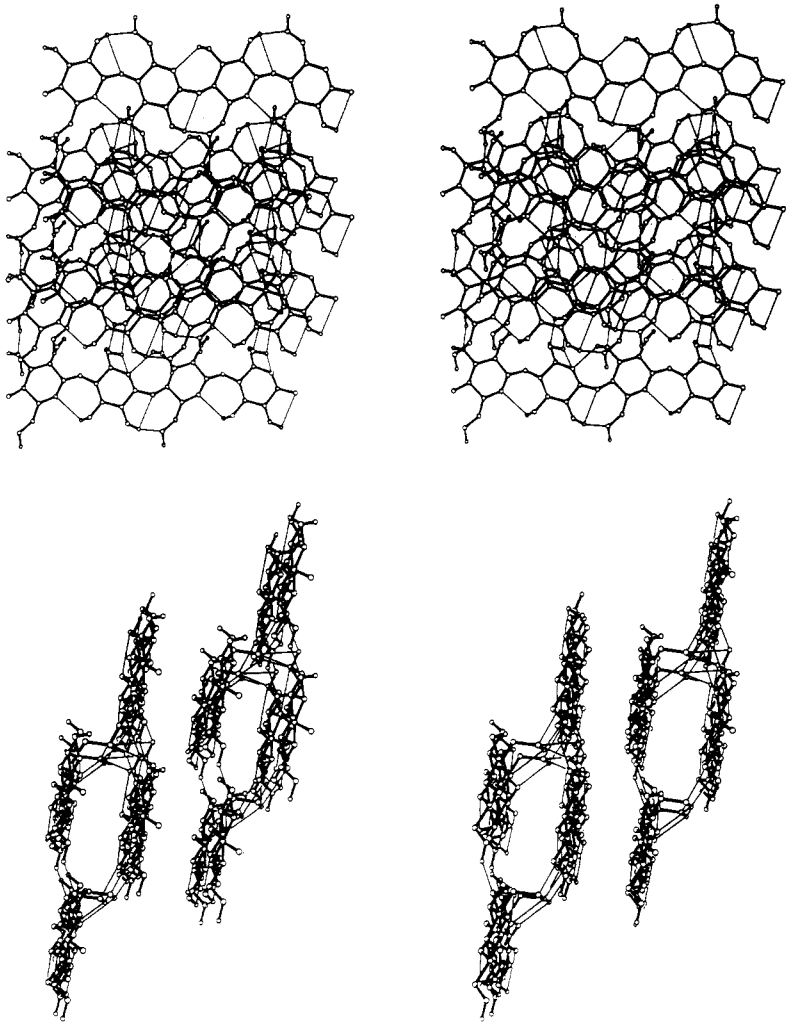

Figure 3. Same as Figure 2 for parallel $(CB)_n/(BB)_n$.

structures, we also studied the energetics of the eight-chain unit cell. Energy minimization results in almost no change in the conformations, packing arrangements, and energies in the parallel case and a more pronounced, but still very small, change in the antiparallel case. A comparison of the two-chain and the eight-chain models is presented in Table V. The differences are so small that stereoviews of their structures cannot be distinguished from those shown in Figures 2 and 5.

Discussion

Low-energy conformations and packing arrangements of cellulose chains in crystalline lattices were investigated. Among the parallel structures, the most stable seems to be the one corresponding to native cellulose. This is the only low-energy structure with no intersheet hydrogen bonds, and its unit cell dimensions are similar to those determined by Mayer and Misch[1] (see Table II). The next two structures in energetic order have almost the same conformational energy but, because of the great differences between the unit cell dimensions c and α, the two structures cannot be mixed in one sheet of the crystalline array.

On the other hand, structures **2** and **3** of Table II have very similar unit cell dimensions and do not differ much in energy. Therefore, it is very probable that these structures can appear in an equilibrium mixture as a structure of a polymorphic form of cellulose or on the surface of a microfibril whose bulk consists of structure **1**.

One chain of structure **2** has a $(BB)_n$ conformation while the other chain has a $(CB)_n$ conformation. For structure **3**, one chain has the $(BB)_n$ conformation, but the other chain has the $(CC)_n$ conformation. On the basis of the energy differences, the main portion of the structure could be expected to exhibit structure **2** with a relatively frequent appearance of the CC disaccharide. If the latter occurs

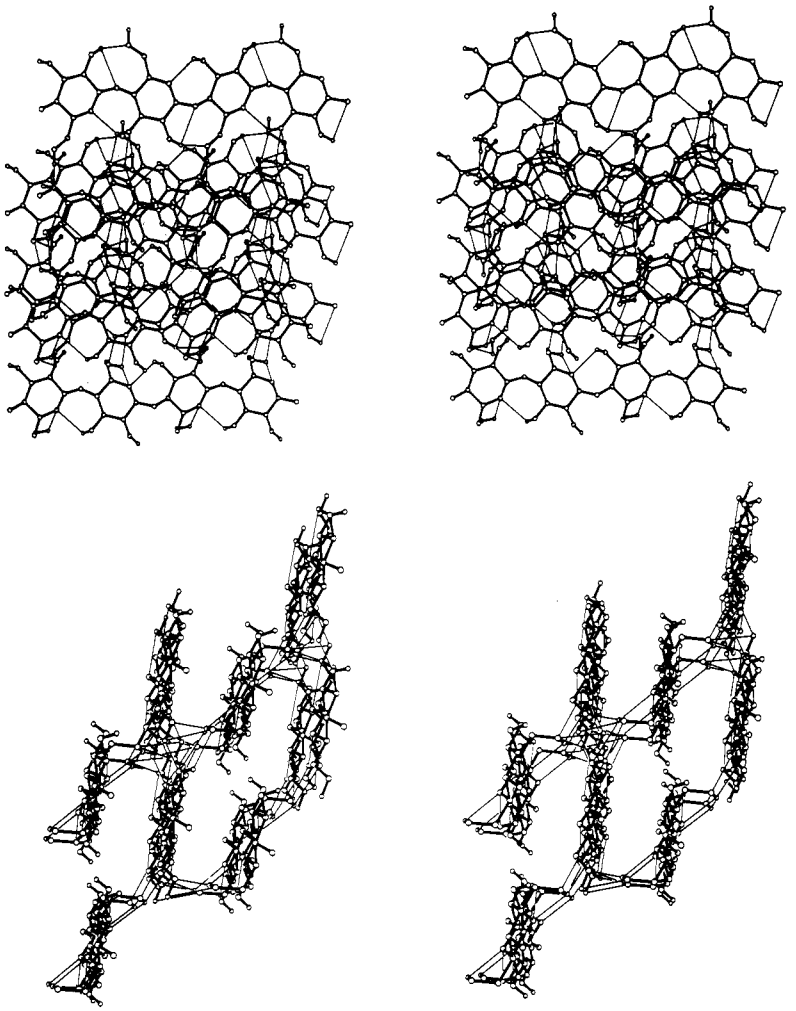

Figure 4. Same as Figure 2 for parallel $(CC)_n/(BB)_n$.

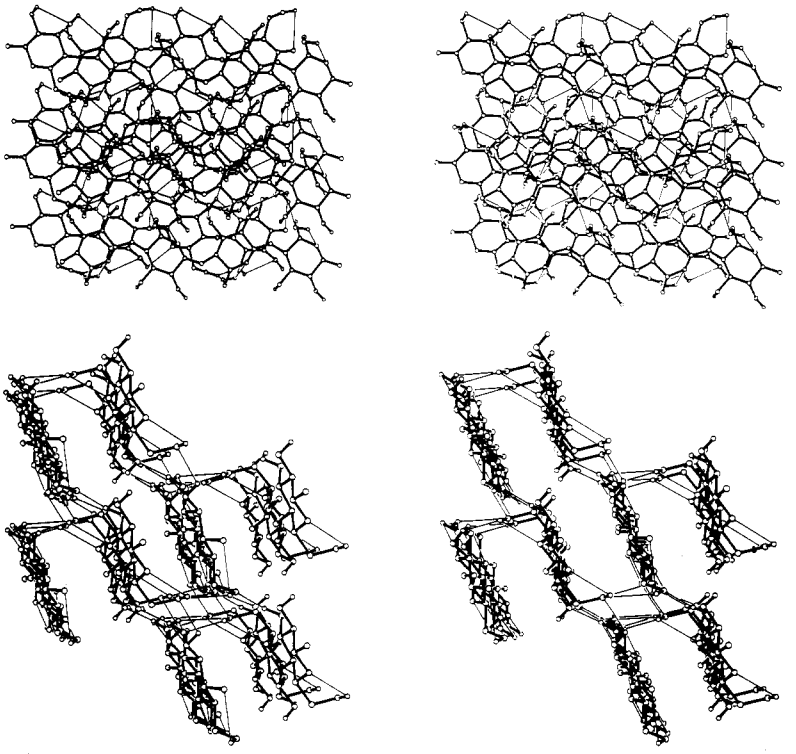

Figure 5. Same as Figure 2 for antiparallel $(AA)_n/(CC)_n$.

in the surface of the microfiber, a structural inhomogeneity (i.e., a different hydrogen-bonding arrangement; see below) would appear along the microfibril axis. This inhomogeneity is a surface effect and, therefore, could not be ob-

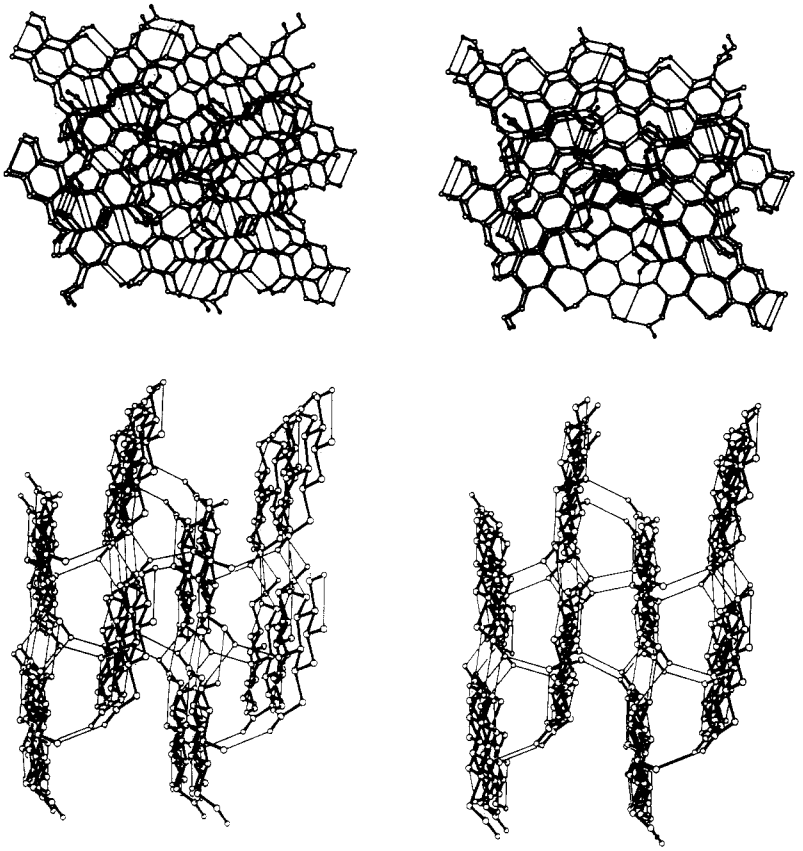

Figure 6. Same as Figure 2 for antiparallel $(BB)_n/(BB)_n$.

Table IV
Lengths (Å) of Hydrogen Bonds[a] Stabilizing Cellulose Structures

struct[b]	intrachain[c]	intrasheet[d]	intersheet[d]
	Parallel (Cellulose I)		
1	O4···H2 (2.62)	O3···H6 (1.79)	none
	O5···H3 (2.15)		
	O6···H2 (1.76)		
2	O4···H2 (2.62)	O3···H6 (1.76)	O3···H6 (2.61)
	O5···H3 (2.27)		O6···H2 (1.87)
	O5···H6 (2.44)		O6···H3 (2.23)
	O6···H2 (1.75)		O6···H6 (1.84)
3	O4···H2 (2.71)	O3···H6 (1.77)	O3···H6 (2.61)
	O5···H3 (2.30)		O6···H2 (1.87)
	O5···H6 (2.40)		O6···H3 (2.23)
	O6···H2 (1.85)		O6···H6 (1.84)
	Antiparallel (Cellulose II)		
4	O2···H6 (1.73)	none	O2···H2 (1.80)
	O3···H2 (2.69)		O2···H6 (2.33)
	O4···H2 (2.80)		O6···H3 (1.73)
	O4···H6 (2.80)		O6···H6 (2.74)
	O5···H3 (2.56)		
	O5···H6 (2.58)		
5	O4···H2 (2.59)	O3···H6 (2.67)	O4···H6 (2.18)
	O5···H3 (2.35)	O6···H3 (2.66)	
	O6···H2 (1.74)		

[a] Only those hydrogen bonds with an O···H separation of <2.8 Å are listed. [b] These structures are the five in Table II. [c] The atoms in this column belong to the same cellulose chain, but not always to the same glucose unit. [d] The O and H atoms in these columns belong to separate cellulose chains.

Table V
Comparison of Eight-Chain Unit Cell Dimensions[a] before and after Energy Minimization with X-ray Data and ΔE (for Eight Disaccharides)[b]

	a	b	c	α	ΔE
	Structure 1[c] (Cellulose I)				
before minimization	10.23	16.56	16.44	76°	
after minimization[d]	10.23	16.57	16.47	76°	−0.01
X-ray data[3]	10.38	15.72	16.34	83°	
	Structure 4[c] (Cellulose II)				
before minimization	10.23	15.49	19.50	122.5°	
after minimization[d]	10.23	16.29	18.43	121.6°	−3.57
X-ray data	10.3	15.7	18.4	117°	

[a] The eight-chain unit cell is the same as the two-chain one, except that b and c are twice the values of the two-chain unit cell. The experimental X-ray data[3] quoted here are more recent ones than those quoted in Table II. Different sets of experimental data are used in these two tables because each set was interpreted in terms of different numbers of chains per asymmetric unit. [b] See footnote in Table I for definitions of symbols. Unit cell lengths are in Å, and energies are in kcal/(unit cell mol). [c] These structures are numbers 1 and 4 in Table II. [d] The fractional coordinates of the atoms of the asymmetric unit in these structures are available in the microfilm edition of this Journal.

served by X-ray diffraction, which averages over the whole fiber, but might be detected by other methods such as electron microscopy. In fact, structural inhomogeneity along the fiber axis was detected by electron microscopy as early as 1964.[24] In the CC-type disaccharide conformation, there is no hydrogen bond between O2 and O6′ (since O6′ is hydrogen bonded to O5′); this phenomenon (involving differences in the positions of O6′ and H6′) can result in differential staining (in the region of the missing hydrogen bond) during sample preparation for electron microscopy.

Only limited data are available for cellulose III, but the suggested hydrogen bonds[3] (from infrared data) may indicate that this corresponds to structure **2** or a mixture of structures **2** and **3**. It should be considered that, because of the mixing entropy, the free energy difference between structure **1** and the mixture of structures **2** and **3** would be even smaller than the energy difference which can be seen in Table II.

The most stable antiparallel structure seems to corre-

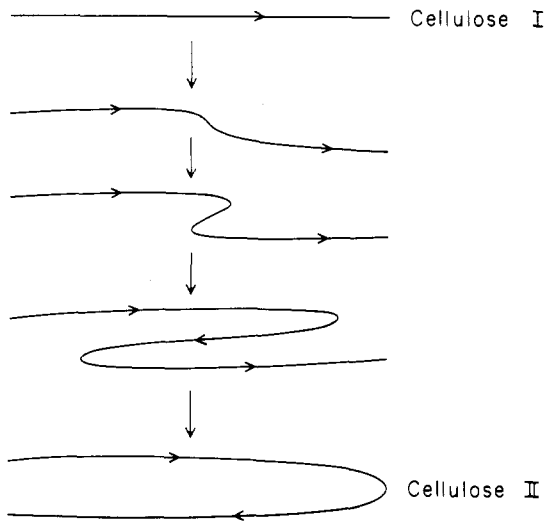

Figure 7. Schematic representation of successive stages of the transformation from a parallel to an antiparallel arrangement of cellulose chains during mercerization.

spond to the structure of cellulose II, according to its unit cell parameters (see Table II) and hydrogen-bond network. This is the only structure with an O2–H2···O2′ hydrogen bond reported for cellulose II.[3] The second most stable structure has similar unit cell parameters to that of cellulose IV, but the latter is so poorly characterized that it is difficult to identify.

Table V shows that the unit cell parameters of the eight-chain unit cell are very similar to those of the (doubled) two-chain model. The differences between the atomic positions are generally less than 0.01 Å, which will be difficult to detect in an X-ray diffraction experiment. It is obvious that detectability depends on the quality of the sample, which may explain why the unit cell suggested depends on the source of the sample.[3]

In the accompanying paper,[2] we showed that a sharp fold in the chain increases the conformational energy by at least 40 kcal/mol. Possible twists in the pyranoside rings or in the valence angle in the glucoside bonds would increase this energy even further, say, to 60 kcal/mol. Therefore, in order to produce a sharp fold leading to an antiparallel arrangement, it would be necessary to overcome this penalty of approximately 60 kcal/mol. Such compensating energy can be gained from the conversion of a parallel structure to an antiparallel one since the latter is 6 kcal/(unit cell mol) lower in energy (see Table II); thus, two straight-chain segments of 10 disaccharide units each in antiparallel arrangement could provide enough attractive interactions to induce a sharp fold. Conceivably, if flexibility of the pyranoside ring is allowed, the energy requirement to make a sharp turn might be a little lower than 60 kcal/mol, and possibly fewer than 10 disaccharide units might be involved in stabilizing such a turn. However, since the crystallite length in cellulose fibers is generally greater than 200 Å (or about 20 disaccharide units),[3] at most only one chain fold per crystallite length could arise from such energy compensation.

It is of interest to speculate why the natural form of cellulose (parallel chains) exists in a metastable state and can be transformed *irreversibly* to the more stable form (antiparallel chains) by mercerization. The biosynthetic apparatus consists of closely packed structures which produce many cellulose chains simultaneously and in close proximity to each other.[25] As these chains are spewed out in a parallel arrangement, they form interchain hydrogen bonds, thereby becoming trapped in a metastable state, with a high activation energy preventing them from achieving the more stable antiparallel arrangement. This view would appear to be supported by experiments on the synthesis of bacterial cellulose, in which the microfibrils are extruded from a linear row of pores along one side of the cell and associate to form a ribbon of cellulose composed of microfibrils.[26]

The transformation from a parallel to an antiparallel arrangement during mercerization might occur by a mechanism shown schematically in Figure 7. Treatment with NaOH would disrupt the hydrogen bonds of cellulose I and swell the fiber, thereby enabling the chains to undergo a conformational change. As discussed above, *long* antiparallel chains can support the chain fold indicated in Figure 7. In the swollen state, the activation energy for the transformation would be lowered, and the chains could then take on their more stable antiparallel arrangement.

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Note Added in Proof. Very recently, Horii et al.[27] reported the results of NMR studies of two slightly different native cellulose structures, called I_a and I_b; one is a cotton-type and the other is a bacterial-type cellulose. According to this paper, and to the references cited therein, these may correspond either to the two-chain and eight-chain models, or the differences between them may be attributed to different influences of the structures of the surface chains. Our calculations on an infinitely large cellulose matrix led to essentially the same structure for both the two-chain and eight-chain models of cellulose I (and different from that of cellulose II). We also pointed out that the structures of the surface chains may differ significantly from those of the interior chains. Therefore, a possible reason for different structures of native cellulose from various sources may lie in different surface structures which result from different cross-sectional dimensions of the microfibrils.

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Supplementary Material Available: Tables of computed fractional coordinates in the eight-chain unit cell for cellulose I and II after minimization (9 pages). Ordering information is given on any current masthead page.

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Methylenebis(*p*-phenyl isocyanate)-Based Polyurethane Ionomers. 1. New Small-Angle X-ray Scattering Model

Day-chyuan Lee,[‡] Richard A. Register, Chang-zheng Yang,[†] and Stuart L. Cooper*

Department of Chemical Engineering, University of Wisconsin—Madison, Madison, Wisconsin 53706. *Received July 28, 1987*

ABSTRACT: Small-angle X-ray scattering (SAXS) data have been obtained on a series of elastomeric MDI-based polyurethane model ionomers. Unlike random copolymer ionomers, the ionizable groups of the polyurethane ionomers are regularly spaced. The SAXS data for these ionomers show both the usual ionomer peak and a prominent shoulder at higher angle, suggesting an ordering of the ionic microdomains. The data are fit to a scattering model based on ionic microdomains organized as micronetworks of beads and springs, dispersed in the polymer matrix with a liquidlike order. The model parameters include the ionic aggregate (bead) radius, the distance between aggregates, the average cross-link functionality of the aggregates, the effective radius of the micronetwork, and the volume fraction of micronetworks in the material.

Introduction

Polymers containing a small fraction of ionic comonomer, termed ionomers, form a class of theoretically interesting and commercially important materials. Considerable research effort has been directed toward understanding the microstructure of ionomers, which strongly affects their physical properties.[1-7] Eisenberg[8] postulated the existence of two types of ionic aggregates, termed multiplets and clusters. A multiplet is a group of a few tightly bound ion pairs, which substantially excludes chain backbone material. If the multiplets are assumed to be spherical, geometric constraints limit their size to about 0.6 nm in diameter. At higher ion contents, Eisenberg suggested the formation of clusters, defined as domains containing several multiplets as well as a significant amount of hydrocarbon. The cluster diameter is presumed to be on the order of 2-10 nm.

Electron microscopy is a popular tool for studying polymer morphology, but due to the very small size of the ionic aggregates and the difficulty of preparing very thin samples, electron microscopy has had little impact on the study of ionomers,[9] whose morphology has generally been probed by small-angle X-ray scattering (SAXS).[10-20] The appearance of a peak in the SAXS pattern in the q range ($q = (4\pi/\lambda) \sin \theta$) of a few reciprocal nanometers is a common feature of ionomer systems. This "ionomer X-ray peak" has been taken as a signature of ionic aggregation since it was first observed.[10] Two basic interpretations of the ionomer scattering pattern have been proposed: an interparticle interference between ionic aggregates, distributed on a paracrystalline lattice[11] or arranged in liquidlike order,[16] and an intraparticle interference due to the internal organization of spherical[12] or lamellar[13] ionic clusters. An accurate model of ionomer morphology should include the size, shape, number density, internal structure, and spatial organization of the ionic aggregates. Most of the ionomers studied to date have ionizable groups randomly spaced along the polymer chain, but a better understanding of ionomer structure might be obtained by studying ionomers with a more regular chain architecture. The two papers in this series describe a family of polyurethane ionomers, prepared by sulfonating the urethane linkages in 1:1 copolymers of methylenebis(*p*-phenyl isocyanate), MDI, and one of several polyols. This paper describes a new morphological model, developed for the more ordered morphology exhibited by these materials, while the second paper in this series describes the physical properties of these ionomers.

Experimental Section

A. Sample Preparation. The general synthetic route to these polyurethane ionomers has been described previously[21] and is

* To whom correspondence should be addressed.
[†] Present address: Department of Chemistry, Nanking University, People's Republic of China.
[‡] Present address: Exxon Research and Engineering Co., Annandale, NJ 08801.

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