A Note on the Theoretical Consideration of the Crystalline and Amorphous Regions in a Cellulose Fiber

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The observed behaviour of some basic parameters such as levelling-off degree of polymerization (LODP) and degree of crystallinity of cellulose are correctly predicted from basic theoretical arguments and a simple statistical mechanical fiber model.

On the molecular level the cellulose molecule is a chain-like polymer composed of 1,4-β-D linked polyanhydro glucopyranose units. The molecular lengths vary greatly from below 1000 up to 15 000 glucose units, depending on origin and extent of degradation during isolation.[1] On the supramolecular level these chains are aggregated into bundles of fibrilles of varying degree of order ranging from that of the pure crystalline state to that of the amorphous state, and on the morphological level the spatial arrangement and orientation of the fibrilles make up the macroscopic cellulose fiber.

The chemical and physical properties of cellulose can be explained only by combining knowledge of the chemical nature of the cellulose molecules and of their structural and morphological arrangement in the solid state.

To date, only average properties of the macroscopic fibres (such as average molecular weight, viscosity, fiber length, degree of crystallinity etc.), have been used as a means of characterizing different products and their suitabilities for various uses, while the actual origin of the variation in these properties on the molecular to supermolecular level often has been ignored. Recently, techniques such as NMR and Raman spectroscopy and refined crystallographic methods have been shown to provide powerful methods for probing the inner secrets of polymeric materials. Today, rapidly developing computational facilities provide the possibility of applying basic physicochemical arguments in a more quantitative manner for explaining the supermolecular structure of biopolymers such as cellulose.

In the following we attempt to describe some properties of the cellulose supramolecular structure, such as degree of crystallinity, length of "crystallites" and frequency of amorphous regions from basic theoretical arguments.

A fibrille may be pictured as a bundle of chains of parallel cellobioside units. For simplicity, the smallest unit can, as a first approximation, be taken as consisting of only two parallel chains linked to each other by intramolecular hydrogen bonds[2] (Fig. 1). In fact, it has been noticed that the experimental fiber diffraction data can be adequately indexed on the basis of a two-chain model.[3]

Neighbouring chains along the *a* axis are linked by an intermolecular hydrogen bond such that the chains form hydrogen-bonded sheets of chains parallel to the *a* axis. There are no hydrogen bonds along the unit cell diagonals; van der Waals forces are believed to be solely responsible for the stability of the structure in these directions.

The opposing segments of the parallel chains can be either bound to each other in a "crystal-like" conformation C or lie at a distance from each other in an "amorphous" state A. In a simplified manner, a fibrille can then be pictured as a chain of *n* segments with altering crystalline and amorphous regions CCCCAACCA. This naive representation allows us to investigate some of the important physical features of the system in much the same manner as has been done earlier for the phase transition between helix and random coil in polypeptide chains.[4]

This model is able to distinguish between the contribution of bonded and unbonded segments to the partition function, and it further considers the influence of the state of neighbouring segments on these contributions.

Before going on to construct the partition function for a

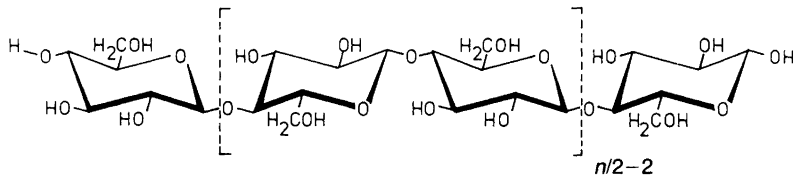

Fig. 1. Schematic representation of the position of the stronger H-bonds between two parallel chains of indefinite length in the body of the crystal.[2]

chain of parallel segments we recall that a fibrille is composed of a great number of such parallel chains. If these were independent of each other the total partition function would be the product of the partition functions for the individual chain pairs. If the chains interact (which they do) the formal treatment becomes more complicated unless we consider the interaction to be very strong, in which case the partition function would simply reduce to the partition function for a chain pair. This could be envisaged as a template for the crystal formation. Experimental observations of strong periodicity between crystal and amorphous regions along the whole fibrille suggest that the latter case applies.[5]

In the following we assume the strong interaction to apply, and the fibrille partition function is assumed to be of the form

$$\Omega = Q^{\circ} \cdot \sum_{1} W(E_i)\exp(-E_i/kT) \qquad (1)$$

Where E_i stands for all the energy states of a single chain pair, $W(E_i)$ is the multiplicity of each energy state and the constant Q° stands for all other interactions. If E_0 is taken as reference state we can write (1) as

$$\Omega = Q^{\circ} \cdot e^{-E_0/kT} \left\{1 + \sum_{i} g_i \exp(\Delta\varepsilon_i/kT)\right\} = Q^{\circ} \cdot Q \qquad (2)$$

where $\Delta\varepsilon_i$ stands for the energy difference of all possible states i with respect to E_0*) and g_i is the number of times such a state can occur in a chain of length n.

*In our case it is convenient to consider the non-bonded fragment as reference. Further, a chain length of minimum 3 monomers is postulated (the first three segments are taken to be non-bonded).

Before we go on to construct the partition function Q for the chain, we will make some specific assumptions about the statistical weights to be attached to the particular states. As we limit ourselves to the thermodynamics associated with the transmission from the crystalline to the amorphous state it is not necessary to consider the quantum states of the individual segments as long as the relative weights of crystalline and amorphous states are correctly represented. We assign the following statistical weights to the different states of the chain.

- Unity for each unbonded segment
- The quantity s each time a crystalline (hydrogen-bonded) position follows another
- The quantity σs each time a hydrogen-bonded position follows a non-bonded one (boundary between bonded and unbonded segments).

The meaning of these weights can be interpreted as follows:[4] s corresponds to the equilibrium constant for the tendency of the crystalline section to grow at the expense of the amorphous region. The quantity σs is a measure of the tendency toward nucleation of crystalline sections. The value unity is thus an arbitrary reference point for a segment which is not bonded, corresponding to 50 % crystallinity, and the factor s is a measure of the contribution to the partition function of a bonded segment relative to an unbonded one.

The larger decrease in statistical weight assumed by the first bond formation after one (or several) unbonded segments is due to restricted freedom of motion, not only of the segment to be bonded but also of the preceding un-

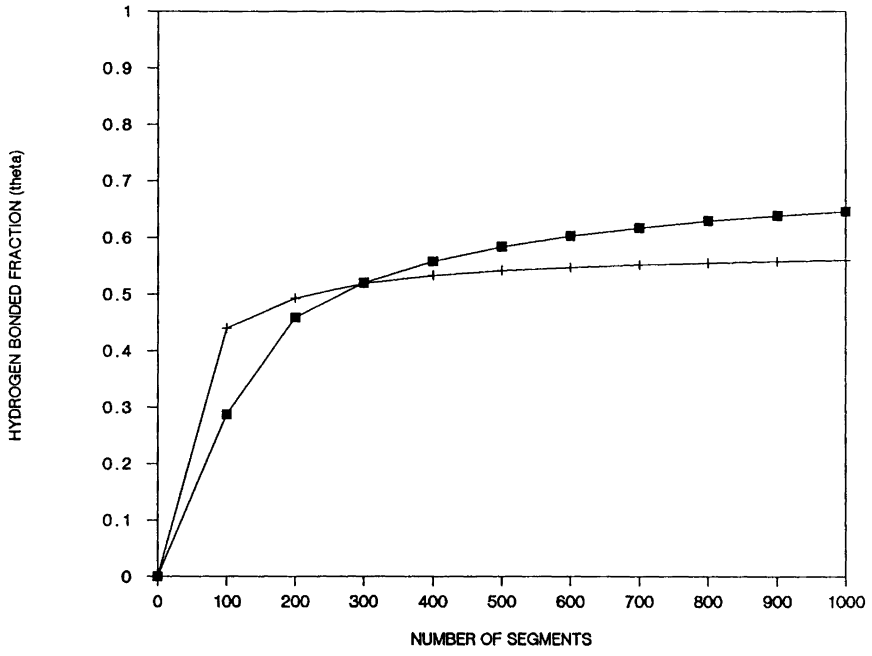

Fig. 2. Hydrogen-bonded fraction, $s = 1.01$; ■ $\sigma = 0.0001$, + $\sigma = 0.001$.

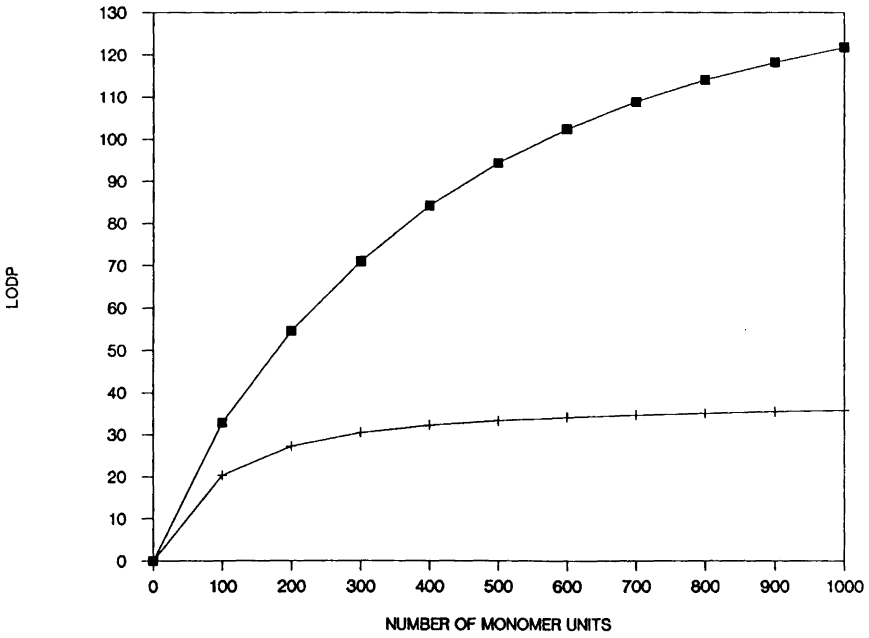

Fig. 3. Lower DP values as a function of sigma; ■ σ = 0.0001, + σ = 0.001.

bonded segment(s). Since the same Boltzmann factor is involved, the contribution to the partition function is written as σs where $\sigma < 1$.

A formal representation of the partition function Q may be obtained for a chain of n segments from the above assumption by simply enumerating the various ways of arranging a given number of bonded and unbonded segments.

$$Q = 1 + \sum^{(n-2)/2} \sigma^l \sum_{l}^{n-l-2} \frac{(k-l)!(n-k-2)!s^k}{l!(l-1)!(k-l)!(n-k-l-2)!} \qquad (3)$$

where the first summation extends over k and the second over l, and $(n\text{-}2)/2$ is the largest integer less than $(n\text{-}2)/2$. Unfortunately the expression for Q obtained in such a way is of a rather complex algebraic form and unattractive for general calculations. Some fundamental features can, however, be derived from the above expression:

As derived from (3), the fraction of bonded segments is given by [4]

$$\Theta = \frac{1}{n-3} \frac{\mathrm{d} \ln Q}{\mathrm{d} \ln s} \qquad (4)$$

Similarly, the number of amorphous (or crystalline) regions in the "fiber" is given by:[4]

$$\nu = \frac{\mathrm{d} \ln Q}{\mathrm{d} \ln \sigma} \qquad (5)$$

The actual behaviour of Q as a function of n is shown in Fig. 2 for some values of s and σ close to the values thought to apply for the cellulose fiber.

In order to obtain plausible estimates for the parameters used in our simplified chain model it is necessary to refer to the molecular structure of cellulose as represented in Fig. 1.

As mentioned earlier, the quantity s can be viewed as the equilibrium constant for a process in which an amorphous section is incorporated into the crystalline section. For this we have the familiar relation (6):

$$\frac{\mathrm{d} \ln s}{\mathrm{d} T} = \Delta H/RT^2 \qquad (6)$$

where T is the absolute temperature and ΔH is the enthalpy change for converting one segment from the amorphous to the crystalline form.

Experimental evidence gives at least a clue to the likely order of magnitude of the parameters s and σ: The fact that the crystallinity of cellulose is about 50–60 %[3] indicates that s must be very close to 1. Such a small stabilization energy in an essentially stable polymer is understandable if we remember that this value is composed of the difference between the energies of hydrogen bonds between chains and the corresponding energies of hydrogen bonds between single strands and the water solvent molecules.[§] Support for such a small stabilization energy value is also provided by the fact that the transformation of wet native cellulose to wet unmercerized cellulose has been found to be weakly exothermic (~ 2 cal per g cellulose).[6]

An order of magnitude of σ can be obtained if we consider that an energy of $kT/2$ is to be attributed to each degree of freedom from both the kinetic and potential energy terms of an unbonded segment. Assuming that the bonding of an unbonded fragment will result in the loss of

[§]A theoretically derived value for the H-bonds in cellulose is ~ 4.75 kcal mol^{-1},[7] while similar values for H-bonds involving water are ~ 4.7 kcal mol^{-1}.[8]

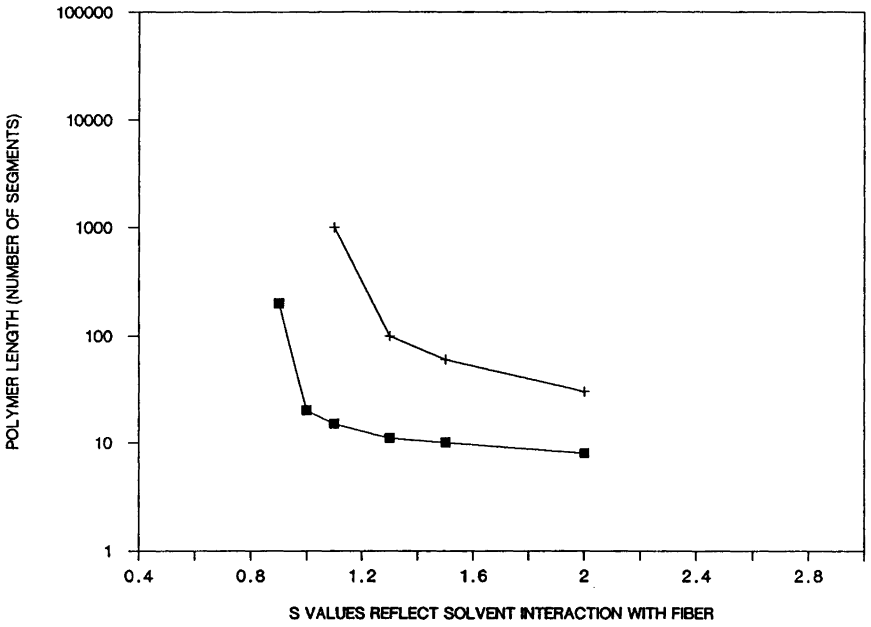

Fig. 4. Phase diagram for an H-bonded polymer. Area between curves indicates "mixed" polymer with amorphous and crystalline character; ■ $\Theta = 0.1$, + $\Theta = 0.9$.

1–2 degrees of freedom for the two segments closest to the interface, an energy loss corresponding to a σ value larger than 10^{-4} but smaller than 10^{-2} will result.

The values $s = 1.01$ and $\sigma = 10^{-3}$ predict a LODP (levelling-off DP) value of about 35 for an initial DP of 1000 (Fig. 3), which is in good agreement with the experimental values[5] of around 40 found for most celluloses. Assuming that solubility requires a high degree of amorphous character and that $\Theta > 0.1$ implies insolubility, these values also correctly indicate that molecular fragments of a DP value greater than 20 should be essentially insoluble in water (Fig. 4). A predicted degree of crystallinity of about 56 % (Fig. 2) for a DP value of 1000 is also consistent with experimental evidence.

The influence of swelling on, for example, the LODP could shed additional light on the validity of a statistical treatment of the above kind, although the interpretation of such data, if existent, would be difficult as it includes contributions from both intra- and interfibrillar changes.

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