Models of Cellulose Physical Structure from the Viewpoint of the Cellulose I → II Transition

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Synopsis

Supermolecular structure of linters cellulose at the cellulose I–II phase transition is investigated by wide-angle X-ray scattering (quantitative phase analysis, degree of crystallinity by the method of Ruland and Vonk, and lateral crystallite sizes via peak separation by Pearson VII functions). A survey of models of cellulose structure recently discussed in literature is given. The compatibility of these models with the obtained WAXS results is checked. As a conclusion, some of the models especially the parallel–antiparallel transition of chain arrangement are outruled and a nonuniform fringed fibrillar model in connection with a conformation transition from bent to bent and twisted single chain conformation is preferred.

INTRODUCTION

Since the cellulose lattice model of Meyer and Misch had been proposed in 1937, a lot of experimental evidence has become available on the conformation and mutual order of cellulose chains from X-ray diffraction, IR, NMR and Raman spectroscopy, and a somewhat contradictory variety of qualitative and quantitative structural models has been published in the recent two decades. A survey covering present ideas of cellulose structure has been given some years ago by Krässig,[1] and especially a comprehensive review of the field of crystal structure investigations was published by Hayashi.[2] Results of measurements and model calculations with regard to chain conformation and chain arrangement in the lattice cell have been reported by Atalla[3,4] employing ^{13}C-NMR, Raman and X-ray data, by Blackwell et al.,[5–7] Sarko et al.,[8–10] and Hayashi et al.,[11,12] using X-ray diffraction data mainly, and by Zbankov et al.[13,14] on the basis of X-ray diffraction and IR data. Some of these authors derived from these calculations rather clear-cut models not only for chain arrangement in the lattice and for the dimensions of the unit cell of the crystallites, but also for the location and the relative strength of the intra- and intermolecular H bonds in the crystalline and amorphous regions of this polymer. The relevance of structure analysis is generally accepted today not only as a fundamental question per se in cellulose research, but also with regard to a further elucidation of the biogenesis of fibrillar cellulose[15] and with regard to a better understanding of structural transitions and their effects on product properties in technical cellulose processing. Therefore, in checking the reliability of new ideas in structural analysis of cellulose not only the fixed states of this polymer but also structural transitions have to be considered.

In some recent publications[16–22] we presented experimental results on structural changes of cellulose by interaction with aqueous solutions of

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NaOH, employing ^{13}C-NMR spectroscopy, wide angle X-ray-scattering (WAXS), and electron microscopy to study these changes under identical conditions at different structural levels. Particularly on the level of supermolecular structure, further progress in the application of WAXS methods[18,19] permit a deeper insight into phase transition processes. In this contribution, these experimental findings—mainly obtained by WAXS—are discussed more systematically with regard to their consistency with present structural, resp. mechanistic models on the cellulose I → Na–cellulose → cellulose II transformation, in order to find out which one of these models might be the most suitable one for a better understanding of the transformations in technical processes and for conceiving further experimental work in this field.

SYNOPSIS OF EXPERIMENTAL RESULTS ON CELLULOSE I → Na-CELLULOSE → CELLULOSE II TRANSITION

Before turning to current models of cellulose physical structure and their application to the cellulose I → Na–cellulose → cellulose II transition, some of our recent experimental results in this field shall be reviewed briefly (for experimental details compare Refs. 18 and 19). Our WAXS measurements obtained with cotton linters treated at 20°C with aqueous solutions of NaOH are summarized in Figures 1–3, these figures showing relevant X-ray diffraction parameters in dependence of NaOH concentration. As revealed by a quantitative phase analysis of the Na-cellulose to cellulose I ratio of the alkali-treated samples, and of cellulose II to cellulose I ratio after neutralization of a part of the same samples (Fig. 1), not all of the Na-cellulose formed in the "transition range" between 10 and 15% NaOH is converted to cellulose II after neutralization. This means that part of the Na–cellulose obviously can be reconstituted to cellulose I and that alkali

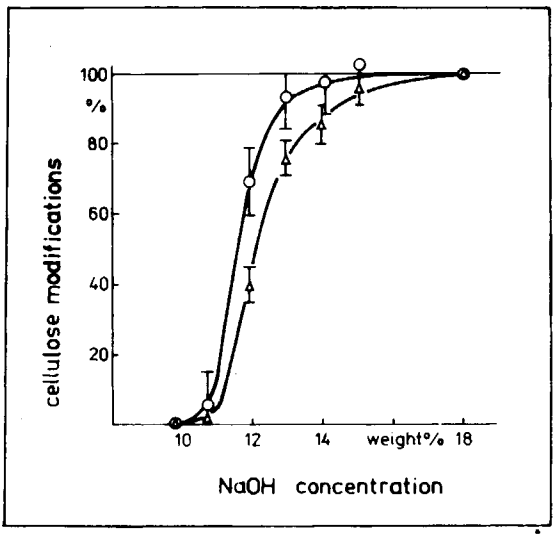

Fig. 1. Lattice conversion from cellulose I to Na-cellulose I and cellulose II depending on steeping lye concentration: (△)-Cellulose II; (○)-Na-cellulose I.

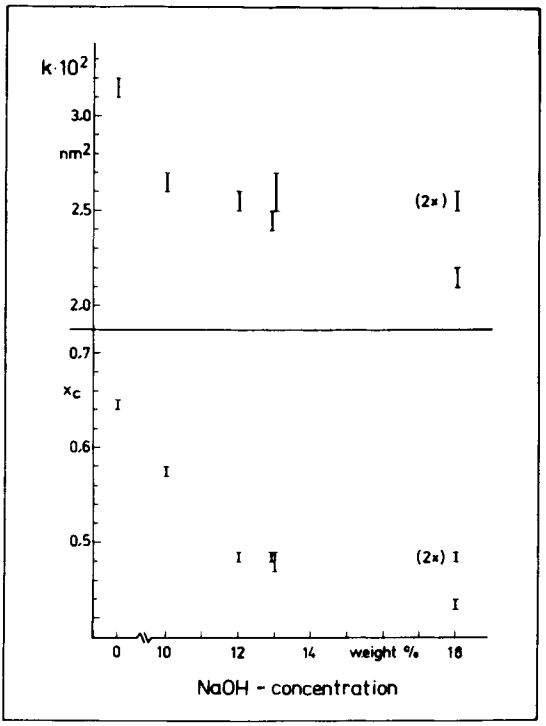

Fig. 2. Degree of crystallinity, x_c, and disorder parameter k depending on steeping lye concentration.

cellulose formation from cellulose I is not to be considered as a completely irreversible step. From quite a different line of experimental work, Hayashi[12] arrived at the same conclusions, as will be discussed later.

Employing the method of Ruland and Vonk,[23,24] a decrease of the degree of crystallinity, but also a decrease of the "disorder parameter" of the crystallites was found by us with increasing steeping lye* concentration. This can be interpreted as an increase in the amount of X-ray amorphous material with increasing degree of lattice transition, while the residual crystalline material simultaneously attains a more perfect order (Fig. 2). Despite some influence of the choice of background scattering curve,[19] it may be mentioned that the degree of crystallinity of all of these samples and, of course, also of the wood pulp samples investigated by us, was well below 80%. Thus, according to Ruland's line of reasoning,[25] all of our samples are to be considered at least as a "two-phase" and not as an imperfectly ordered "one-phase" specimen.

An estimation of minimum lateral crystallite sizes has been performed via peak width at half the maximum height of crystalline peaks. For this procedure background scattering was separated in the same way as for crystallinity determination, whereas overlapping crystalline peaks have been separated by the aid of PEARSON VII functions.[19] The influence of

* The term steeping lye originating from the viscose industry is used here for the aqueous NaOH solution applied in excess for preparing the alkali cellulose.

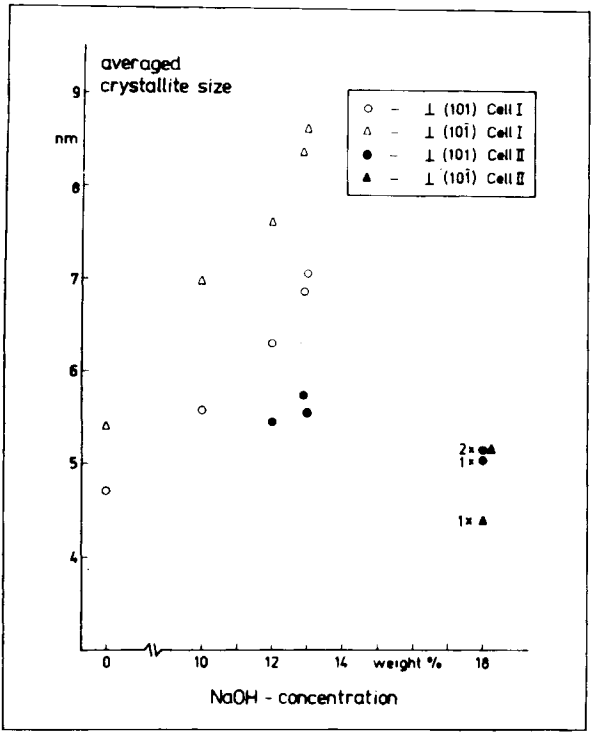

Fig. 3. Averaged lateral crystallite sizes depending on steeping lye concentration (lattice distortions are neglected).

lattice distortions of the second kind has been neglected, as it was estimated to amount to less than 10% of the calculated particle size.[26]

As shown in Figure 3, the average size of the cellulose I crystallites increases with increasing NaOH concentration, while the size of the cellulose II crystallites is rather constant within the concentration range suitable for a quantitative evaluation. If a crystallite size distribution in the original cellulose I sample is assumed, it can be concluded that the largest of the cellulose I crystallites are the most resistent ones with regard to lattice transformation and that lattice transition of these largest crystallites is accompanied by disintegration into smaller cellulose II crystallites.

Though the WAXS data on supramolecular structure are the most relevant ones for reflections on current models in the following, some facts on adjacent structural levels obtained by NMR spectroscopy and by electron microscopy may be additionally considered:

i. As revealed by MAS CP high resolution solid state ^{13}C-NMR spectroscopy, a treatment of linters cellulose with aqueous NaOH solution of increasing concentration results not only in a shift and a change in shape of the C-2, C-3, and C-6 signals due to interaction of the lye with the OH groups of the anhydroglucose units, but also in rather definite changes in the C-1 and C-4 signals, indicating conformational changes at the C–O–C glycosidic linkage.[16,17]

ii. Lattice transition from cellulose I to cellulose II is generally combined with changes in the microfibrillar morphology of cellulose, as detected by

transmission electron microscopy.[20,21] The influence of an aqueous solution of NaOH on the morphological structure was found to be different for different cellulose samples, and there was no evidence for the existence of an *uniform* elementary fibril building up the microfibrils.

SURVEY OF CURRENT MODELS OF CELLULOSE STRUCTURE

Since Naegeli at the end of the last century published his ideas of a "micellar structure" of cellulose in plants tissue, several qualitative one- and two-phase models of supermolecular cellulose structure have been proposed. Most widely known and of large heuristic value was the "fringed micell model" of Hermans (compare Ref. 27) and Kratky,[28] which was further developed and sophisticated by Hearle[29] arriving at the concept of a "fringed fibrilla" and assuming not a constant value, but a rather wide distribution of the size and the perfection of the crystalline regions.

According to this two-phase model, the amorphous part of the structure contains a large amount of tie chains between the fibrillae. Based on this model, the supermolecular structure might be represented by Figure 4. One-phase models to be mentioned in this connection are the "cable model" of Ruck[30] and Blackwell and Kolpak's idea of cellulose structure as being composed of a disordered array of perfectly ordered elementary fibrils.[31,32] This latter model had been developed mainly on the basis of experimental data obtained with Valonia cellulose, the highly ordered physical structures of which are not generalizable to any other type of cellulose samples (compare Ref. 2).

Models of cellulose physical structure so far discussed are based on the assumption of extended polymer chains in the crystalline and the amorphous regions as well. Chain folding has been discussed in connection with cellulose structure by several authors (compare Refs. 33–37). While folded

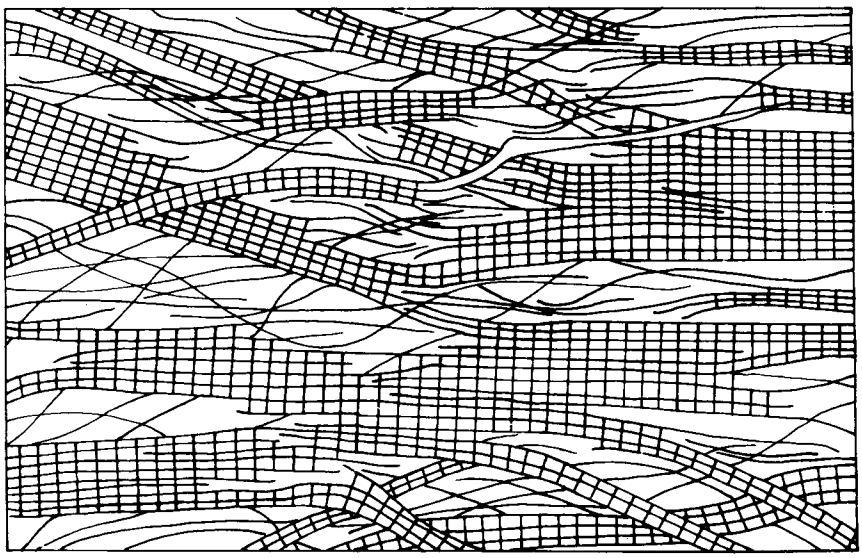

Fig. 4. Fringed fibrillar model of cellulose supermolecular structure.

chains in cellulose I are generally considered as rather improbable today, the question of chain folding in cellulose II is still open to discussion. A very carefully elaborated fold chain model for cellulose II was presented by Watanabe et al.[37] 10 years ago. On the other hand, no explicit experimental proof of this chain folding has been established up to now, and some experiments of our own in connection with this problem also did not lead to a definite conclusion.

The subject of a quantitative modelling has been in recent years the mutual location of cellulose chains in connection with chain conformation and the system of H bonds along and between the chains. In a schematized manner, three lines of reasoning based on different experimental methods and findings can be discerned here; i.e.:

(i) models derived from crystal structure investigations of Blackwell et al.[5-7] and Sarko et al.,[8-10] which are based on a combined stereochemical packing refinement and X-ray diffraction analysis of fiber diagrams, different packing parameters of chains essentially determining the different crystalline cellulose modifications;

(ii) the models stressing differences in chain conformation at the C(1)–O–C(4) glucosidic linkage between the different modifications of cellulose, models of this kind being elaborated by Atalla[3,4] mainly from NMR and Raman spectroscopy data and by Hayashi et al.[2,11,12] from X-ray diffraction data;

(iii) the location and binding strength of H bonds calculated by Zbankov[13,14] for different cellulose modifications in connection with experimental IR data.

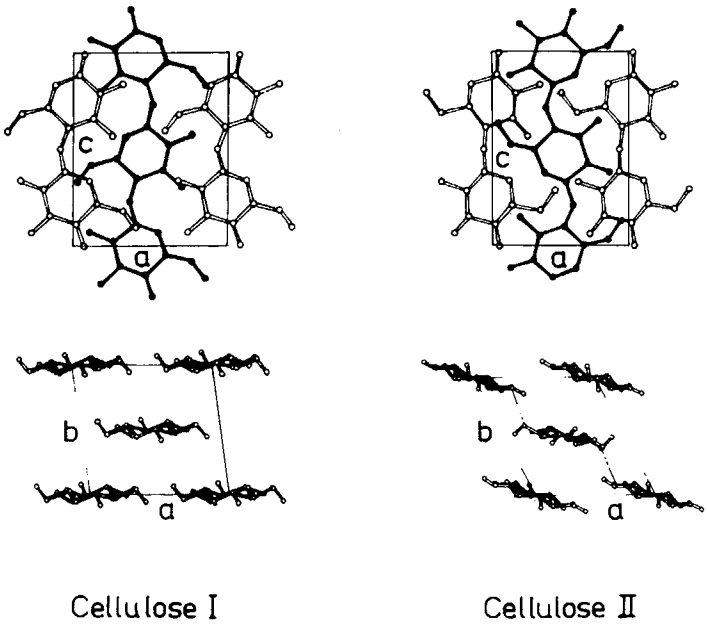

Fig. 5. Cross sections of cellulose I and cellulose II unit cells according to Refs. 5–7.

Blackwell et al.[5-7] and Sarko et al.[8-10] independently suggested a parallel chain arrangement for cellulose I and an antiparallel one for cellulose II (Fig. 5). The starting point of these investigations has been an energy-optimized single chain of a bent backbone conformation with a twofold screw axis in chain direction for both modifications. It may be mentioned here that there are some controversal discussions to method and result of this crystal-structure investigation (for instance, Ref. 2). Without going deeper into this controversy, our following considerations are centered on the cellulose I–II transition. Starting from other premises, Hayashi and co-workers,[11,12] concluded from crystal-structure investigations with a high degree of reliability that differences between cellulose I and cellulose II unit cells are determined mainly by differences in single chain conformation. The so-called "bent" modification of chains with twofold screw axis in cellulose I changes into the "bent and twisted" conformation without twofold screw axis in cellulose II (Fig. 6). According to Ref. 2, the question of chain polarity cannot be solved by crystal structure investigation alone because of the rather low order and, subsequently, the weak reflexes of wood pulp or even cotton cellulose.

Atalla et al.[3,4] arrived at similar conclusions with regard to the glycosidic linkage by analyzing Raman and ^{13}C-NMR measurements. They also assumed different chain conformations between cellulose I and II (with respect to the glycosidic linkage and the C-6 hydroxyl group), and, modelling the cellulose polymorphy, they developed the concept of coexistence of different combinations of stabile basic conformation type.

As to our opinion, these models based on essential conformational differences of cellulose I and II single chains can reasonably account also for the difference in stability between these two modifications of cellulose as well as for understanding further lattice transformations and splitting of lattice types into the I and II families. As an example, the existence of Na–

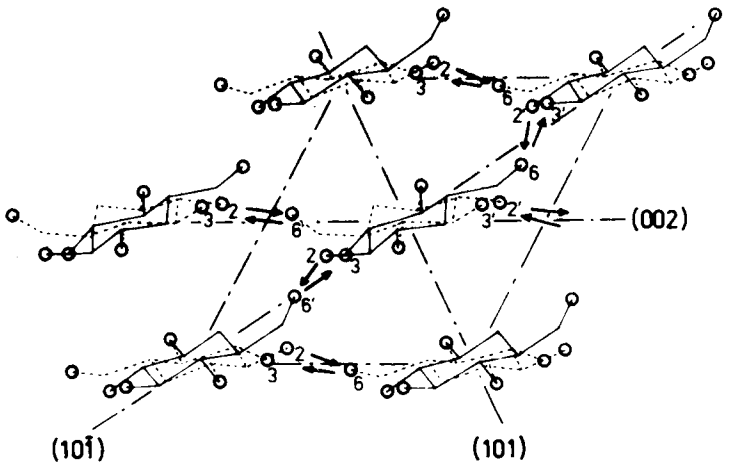

Fig. 6. Cross section of cellulose II unit cell with bent and twisted single chain conformation according to Refs. 2 and 11.

cellulose I_I and Na–cellulose I_{II} with equal packing but different single chain conformation[12] provides a key for understanding the partially reversibility of cellulose I–Na–cellulose I transformation.[18]

Qualitative reasoning and quantitative calculations on H-bond structure in solid cellulose is, of course, closely related to the question of chain packing and chain conformation. Tentative statements on this H-bond structure have recently been published by Zbankov et al.[14] (Fig. 7). By these authors, structural differences between cellulose modifications are considered within the wider frame of similarities and differences in structure of polysaccharides.

DISCUSSION OF STRUCTURAL MODELS WITH REGARD TO EXPERIMENTAL DATA ON CELLULOSE I → II TRANSITION

In comparing the applicability of different structural models for interpreting experimental results on the cellulose I → II transition, it must be kept in mind that in the whole process of the cellulose I → Na–cellulose → cellulose II transformation the cellulose sample is intermediately highly swollen, but, nevertheless, always retains definitely some of its original high supermolecular order and also some morphological structure, at least, if water is employed as a reaction medium. Considering at first the models of Blackwell and Sarko, this implies the transition from a parallel to an antiparallel chain packing of the cellulose moiety still remaining in a more or less ordered solid state. According to Sarko et al.[38,39] (Fig. 8), this transition is achieved by a start of cellulose II formation (via Na–cellulose) in the amorphous regions and a subsequent gradual peeling off (with increasing NaOH concentration) of polymer chains from cellulose I crystallites and attaching of these chains to the crystalline regions of cellulose II. This implies the premise that within one single cellulose I crystallite, of course, all chains have the same direction. But 50% of the crystallites are positioned in one and the other 50% in the opposite direction. With regard to the peeling and attaching of chains, Sarko et al. assume a transport of individual

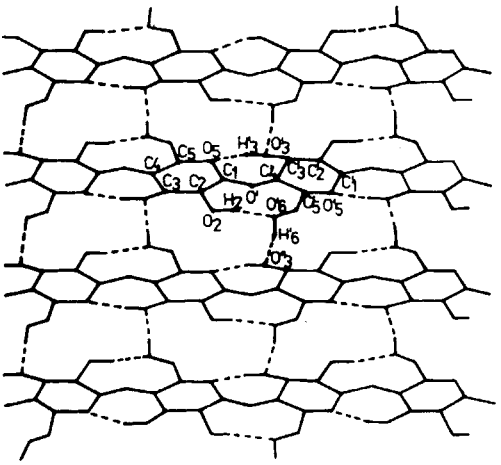

Fig. 7. Schematized crystalline structure of cellulose I with hydrogen bonds (dashed lines).[14]

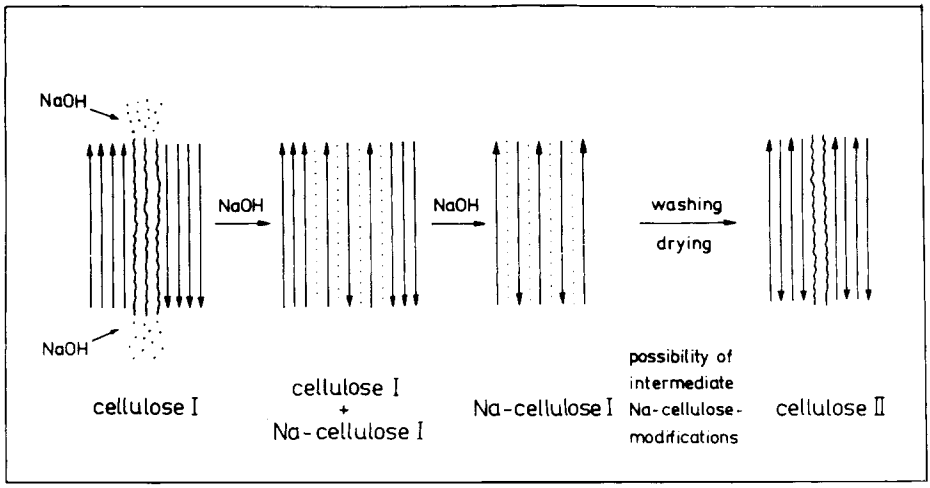

Fig. 8. Suggested cellulose I–II transformation mechanism according to Refs. 38 and 39 (arrows indicate chain direction in the crystallites).

polymer molecules, while Kolpak and Blackwell prefer the idea of a motion of complete layers of chains in a similar manner.[7] Our experimental results cannot be brought into agreement with these considerations insofar as in the peeling and attaching procedure proposed the average size of the cellulose I crystallites should be expected to became smaller with increasing degree of conversion, while the opposite has been observed experimentally. Besides this, the suggested mechanism does not offer a plausible explanation of the decrease in degree of crystallinity observed when enhancing the steeping lye concentration in the transition range.

A chain-folding mechanism in the cellulose I → II transition might give a more reasonable explanation of the transformation of a parallel to an antiparallel packing of the chains and was therefore proposed, for example, by Ruscher[36] (compare Fig. 9). But, unfortunately, no definite experimental evidence is available up to now on a process of this kind, and the postulate of a fold-chain crystal formation during cellulose I → II transition as demonstrated in Figure 9 can barely be reconciled with our experimental findings on cellulose I and II lateral crystallite size depending on NaOH concentration.

Recognizing difficulties in finding an appropriate mechanism for the parallel–antiparallel transition in chain packing and taking into account the results of NMR-investigations of Atalla[3,4] and our group,[16,17] it seems to be much more reasonable to assume the change in single chain conformation at the glycosidic linkage as the decisive step in lattice conversion. Furthermore, we can explain our results of partial reversibility of Na–cellulose I formation (Fig. 1) in the Hayashi scheme of lattice conversions[12] based on two conformation-types with reconversion discussed on the basis of an incomplete hydration in alkalization or regeneration.

Keeping in mind that there is experimental evidence of reconversion of Na–cellulose to cellulose I due to external stress,[40] it might be concluded that some internal stress in linters is responsible for reversible Na–cellulose

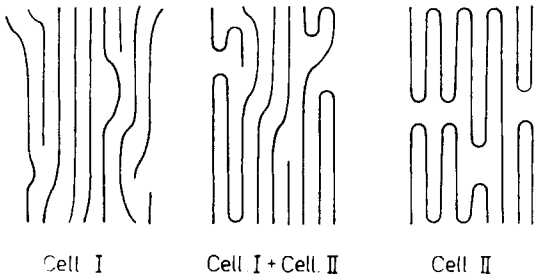

Fig. 9. Suggested cellulose I–II transition as a chain-folding mechanism.[36]

formation in slack mercerization.[19] In a more supermolecular level of structure we have to decide between a one- or two-phase model, at least. Blackwell et al.'s one-phase model of native cellulose being composed of an imperfect array of crystalline elementary fibrils should be considered as a "borderline case" for cellulose samples of very high order as Valonia cellulose, for example. As concluded by Ruland,[25] in employing his method only above a degree of crystallinity of 80%, a polymer structure can be adequately represented by a crystalline one-phase model with lattice distortions. That means lattice distortions can decrease the calculated degree of crystallinity of a complete crystalline sample by not more than 20%. This case is definitely outruled by our experimental results on the alkali treatment of cotton linters; as always—before, during, and after the lattice transition—the degree of crystallinity is well below 80%. Thus, for describing the physical structure of technical cellulose samples including cotton linters as well as wood pulp and cellulose man-made fibres, a two-phase model seems to be preferable.

As detailed subsequently, all of our experimental findings obviously can be adequately represented by combining the fringed fibrillae model of Hearle[29] on the supermolecular level with conformational changes of the single chain during the transformation process: cellulose I → Na–cellulose → cellulose II. The idea of a distribution of lateral crystallite size and crystallite order in this two-phase model is experimentally reflected by the fact that the smallest and most imperfect cellulose I crystallites are attacked first by the alkali, the correlation between chains nearly or completely being abolished and these polymer chains becoming thus part of the amorphous matter. With increasing NaOH concentration crystallites of increasing size are penetrated and lattice converted. The largest and more perfect cellulose I crystallites are the most resistant ones and even remain in a rather well-ordered state after penetration by alkali. After neutralization, these larger crystals are obviously broken down to smaller ones of cellulose II along localized lines of lattice distortions leading to an internal structural stress. This could explain the lack of increase in average cellulose II crystallite dimensions at higher NaOH concentration in the lattice transformation region. Especially in the transition range between 10 and 15% NaOH, i.e., in a highly disturbed state of order of the highly swollen sample, a part of the alkali cellulose formed is reverted to cellulose I, while most of it is irreversibly transformed to cellulose II on neutralization. This means

on a single chain level that the conformationally "labile" alkalized chains can easy be reconstituted to the bent cellulose I conformation or transformed to the bent and twisted cellulose II conformation, depending on state of hydration[12] and/or internal structural stress.[19]

In this way, our experimental results presently available on cellulose I → II transition may be interpreted without resorting to phenomena still open to question like chain folding or turning a parallel to an antiparallel chain arrangement. Shortcomings and open problems of the model considerations presented here still are:

(i) the more qualitative nature of the statements given as compared to the quantitative calculations of crystal structure analysis, but it seems questionable at all, if the methods of crystal structure analysis can validly be applied to the very small number of reflexes of technical cellulose samples and if it is permissible to conclude from these investigations on the cellulose I → II transition in a generalized manner;

(ii) the present scarcity and incompletions of quantitative data on single chain conformational data, although more and more experimental evidence becomes available especially by high resolution solid state ^{13}C-NMR spectroscopy;

(iii) the lack of quantitative information regarding the amorphous phase of the two-phase model employed.

Further progress in solving these problems can be expected from a joint evaluation of results obtained by various methods on different structural levels, i.e., NMR spectroscopy on the molecular, SAXS and WAXS on the supermolecular, and electron microscopy on the fibrillar level. Furthermore, as suggested by Hayashi,[2] chemical reaction behavior of cellulose and the investigation of reversibility of structural transitions are additional important tools in understanding the structure of this polymer.

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