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MODERN IDEAS ON THE SUPERMOLECULAR STRUCTURE OF CELLULOSE

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According to modern ideas, cellulose macromolecules form long, unbranched, elastic threads, consisting of D-glucopyranose residues linked by β-glucoside bonds in the 1,4-position.

Since each glucopyranose residue contains alcoholic hydroxy-groups, the cellulose molecule with a degree of polymerisation of 1000 contains 3000 hydroxy-groups. These groups screen the adjacent units in the cellulose macromolecule, and are responsible for rigidity and elasticity; they also determine the nature of the bonds between the macromolecules. The way in which the cellulose macromolecules are mutually arranged in natural and synthetic fibres and in films has an important effect on the strength, stretch, elasticity, hygroscopicity, reactivity, solubility, capacity to undergo wet grinding, ability to take dyes, and many other properties of these fibres.

Unfortunately, we still know very little about the supermolecular structures that are responsible for these properties of cellulose. Nevertheless, it is in this field that we must look for an explanation of processes that lead to the preparation of ultra-strong cellulose fibres, highly reactive celluloses, and other materials of great industrial importance.

Numerous electron microscope studies of natural cellulose fibres carried out in the last 10–15 years have shown that these have a fine fibrillar structure, the diameter of the elementary fibrils varying from 70 to 150 Å, depending on the origin of the preparation [1-5]. However, it has recently been shown that, in an aqueous medium, the microfibrils of some samples of natural cellulose can be cleaved by ultrasonic vibrations into smaller microfibrils with a diameter of about 35 Å. [6,7]

The structure of artificial cellulose fibres depends on a number of factors, the most important being the degree to which they are drawn [8,9]. The more the hydrocellulose fibres are drawn during their formation, the more well defined is their fibrillar structure. X-Ray and electron diffraction studies of natural fibrils suggest that these are made up of macromolecules, arranged parallel to and along the fibril [1,4].

Ranby and other workers have shown that, when natural or regenerated cellulose is subjected to mild heterogeneous hydrolysis, the microfibrils do not react in a uniform manner along the main axis [10,11]. It would appear that the microfibrils are constructed of continuously alternating sections that differ in the rate at which they are hydrolysed. After the readily hydrolysable sections have been dissolved, the microfibrils are broken up by ultrasonic vibrations into short spindle-shaped fragments. The average length of the cellulose macromolecules in these particles, or "micelles", as Ranby calls them, measured in the electron microscope, is about the same as the average length of cellulose residues determined by viscosimetric, diffusion, or sedimentation methods.

This made it possible to evaluate the length of the sections of the cellulose macromolecule that are difficult to hydrolyse from a knowledge of the average degree of polymerisation of the residue after hydrolysis (limiting degree of polymerisation), which was determined from the viscosity of solutions of nitrates or copper complexes [12-22]. The size of the sections of the microfibrils that are difficult to hydrolyse is not constant and depends on the origin of the cellulose sample. Thus, observations with the electron microscope have shown that, after mercerisation or regeneration of cellulose from solution, the length of the microfibrils that are difficult to hydrolyse is reduced by a factor of 2–4. [10,11]

Studies on the limiting degree of polymerisation have shown that there is a great difference in supermolecular structure between natural and artificial cellulose fibres. The limiting degree of polymerisation of wood cellulose is 400, [23] but in cord fibres of viscose origin this value varies between 40 and 20.

It is interesting that, in the preparation of ultra-strong fibres, the degree of polymerisation decreases instead of increasing, as might be expected [24,25]. A similar phenomenon is observed in the decomposition of viscose in a precipitation bath with an increasing content of salts [26]. This example shows that in nature cellulose is formed with large sections that are difficult to hydrolyse, but in the preparation of artificial hydrocellulose fibres these sections are 1/10 to 1/20 the size of the natural sections.

Studies carried out in recent years have shown that the readily hydrolysable sections of cellulose macromolecules undergo oxidation [27], thermal decomposition [18,28], enzymic hydrolysis [29], and alcoholysis [30] much faster than the other sections.

Using the electron microscope, Hess and coworkers showed that, after treatment with iodine, the microfibrils are not uniformly stained, and alternating dark and bright sections are formed [31]. In size the bright sections were similar to Ranby's micelles that were difficult to hydrolyse. It was concluded that the dark sections containing iodine are readily accessible amorphous components of cellulose.

Similar lack of uniformity in these microfibrils was observed by Manly, who subjected the fibrils to preliminary treatment with an aqueous solution of uranyl acetate or phosphotungstic acid [7]. After this treatment, the microfibrils of the Valonia algae showed the presence of a "bead-like" structure, with individual oval-shaped beads, 175 Å wide and 200 to 400 Å long. Dark coloured connective tissue was present between these formations. The microfibrils of ramie, cotton, and wood cellulose 35 Å in diameter, obtained after vigorous treatment of larger microfibrils with ultrasonic vibrations, also had a bead-like structure. Manly has suggested that this periodicity along the microfibril axis might be due to the formation of the fibril from a band folded into a spiral. However, sufficient evidence to support this has not been obtained, because the measurement is at the limit of the resolving power of modern electron microscopes, and the use of ultrasonic vibrations might lead to further profound structural changes.

It has been shown that the easily hydrolysed fraction of cellulose is hydrolysed 50–60 times more rapidly than the fraction that is difficult to hydrolyse [32]. But there is no sharp transition between these two fractions; this has led some workers to suggest that there is an intermediate mesomorphic cellulose fraction that is hydrolysed at a rate between the rates for the two extreme fractions [14].

It has recently been shown that the density of the cellulose fraction that is difficult to hydrolyse is much greater than that of the easily hydrolysable fraction, and this density varies with the type of cellulose [33,34].

It was also found that the rate of heterogeneous hydrolysis or alcoholysis of the fraction difficult to hydrolyse decreased as the density increased [33,34]. Measurement of the true specific gravity of cellulose during hydrolysis showed that the easily hydrolysed fraction becomes somewhat more dense and its reactivity decreases [35]. This effect is due to the rupture during hydrolysis of strained sections of the macromolecule with the formation of a denser structure.

The increase that occurs in the density of cellulose in the presence of water has been studied from several points of view. It has been shown that cellulose regenerated from its derivatives, for example, the acetate [36] or the xanthogenate [26], generally forms a loose low-density structure that readily undergoes ethanolysis and hydrolysis. When moistened with water, these types of cellulose rapidly become more dense and less reactive.

An especially large density effect was observed when loose cellulose obtained by dry grinding in special mills was moistened with water [37-40].

In recent years the use of alcoholysis [30,35,38-42] and dioxanolysis [35,43] instead of hydrolysis has facilitated studies on the increase in density of reactive cellulose. This change in methods of cleaving cellulose has to a great extent reduced its tendency to increase in density and so has limited the distorting effect of density increase on the quantitative determination of the portion of cellulose that reacts easily [35,38] and also of the maximum degree of polymerisation [44]. As the same time the use of hydrolysis and

alcoholysis in the investigation of various cellulose samples enabled a quantitative study to be made of the spontaneous increase in density that occurs when cellulose is cleaved in polar liquids[23-35].

As mentioned above, the cellulose macromolecules in natural and artificial microfibrils form alternating dense and loose sections along the main axis; this variation appears to be due to the tendency of the long cellulose macromolecules to undergo mutual orientation when highly swollen structures are dehydrated and their orientation is destroyed. The sections of the macromolecule between the dense, oriented sections must cause mutual lack of uniformity in the arrangement of the chains, and this must be reflected in the formation of looser, less oriented, structures in these sections, which are therefore more accessible to reagents. It is quite possible that the size of the oriented and of the loose sections along the microfibril depends on the initial orientation of the macromolecules produced under the conditions of formation of the sample. The greater the orientation in the initial swollen sample, the greater will be the tendency to form dense, highly oriented (crystalline) sections instead of sections with a loose (amorphous) structure, and vice versa.

Studies on the limiting degree of polymerisation of various cellulose samples have shown that the size of the dense, oriented, and more reactive sections depends on the method and conditions of regeneration of the cellulose[26]. Thus, for example, the presence in the precipitation bath of sodium sulphate, zinc sulphate, and especially of modifiers, promotes the preparation from viscose of cellulose with a large number of loose sections and small dense, oriented sections. The double-bath method of regenerating cellulose enhances this effect still further.

On the other hand, stretching increases the proportion of the less reactive fraction by increasing the proportion of oriented sections in the macromolecules[35]. This effect is still further increased by the swelling of hydrocellulose fibres, for example, in aqueous alkali[44]. Thus, the size of the dense and loose sections in cellulose depends on the origin of the cellulose and can be controlled within certain limits.

A study of the stability of fluctuations along the microfibrils of cellulose is of great interest. Recently this process has been elucidated using a method in which hydrogen of the hydroxy-groups in cellulose is exchanged for deuterium or tritium.

It had previously been shown that, when cellulose is immersed in heavy water, the hydrogen of the hydroxy-groups in the loose sections of the molecule is readily exchanged for deuterium[45,46].

Under these conditions, the hydrogen of the hydroxy--groups of the dense sections is not exchanged. To determine the mobility of this equilibrium, Sepall and Mason[47,48] repeatedly moistened cellulose samples with deuterium oxide or tritium oxide, drying them after each immersion. They found that, after 100 to 200 treatments, virtually all the hydrogen atoms of the cellulose hydroxy-groups had been exchanged for deuterium or tritium; the proportions of dense and loose sections of the macromolecule remained constant. With a single treatment, deuterium and tritium became inaccessible after penetrating into the densely packed sections of the macromolecule and were not exchanged for ordinary hydrogen.

According to Sepall and Mason, this observation indicates that fluctuations in the macromolecules in the microfibrils are not constant, and when the cellulose is alternately moistened with water and dried, the dense and loose sections in the microfibrils can be displaced along the fibril axis. It is interesting that the rate of replacement of hydrogen in the densely packed sections increases with the degree of swelling of the cellulose and with the temperature of the water.

Thus, the periodic increases in density in the bundles of cellulose macromolecules described above are not stable.

The nature of the bonds between adjacent macromolecules is of particular interest from the point of view of the supermolecular structure of cellulose. As early as 1926, Slonsler and Dore and then Higgins and Park advanced the hypothesis, on the basis of analogies with other compounds containing hydroxy-groups, that the hydroxy-groups of adjacent cellulose macromolecules form hydrogen bonds. But it was not until 1940 that Ellis and Butt[49] showed by means of infrared spectroscopy that all the hydroxy-groups of cellulose are in fact linked by hydrogen bonds. This conclusion was later confirmed by many workers and it is now fully accepted.

It must, however, be borne in mind that a small proportion of the hydroxy-groups, situated on the external and internal surfaces of cellulose fibres or films, must remain free for reasons of geometry. Direct estimation of these free groups with CH_3MgI in ethyl ether by Tserevitinov and Chugaev's method shows that the number of free hydroxy--groups in cellulose fibres accessible to the Grignard reagent is 5% of the total number of groups[50]. The remaining hydroxy-groups appear to be linked by intramolecular or intermolecular hydrogen bonds. The energy of these bonds varies from 2–3 to 6–7 kcal $mole^{-1}$, and it depends on the spacing between the groups and on steric hindrance.

The closer are the hydroxy-groups of adjacent cellulose macromolecules the stronger are the hydrogen bonds between them. For this reason, the thermodynamic method should be the best method for evaluating the bonding energy of adjacent molecules in a unit volume of cellulose. Unfortunately, such methods are not yet available, and the strength of the hydrogen bonds must therefore be measured by an indirect method. Infrared spectra are most generally used for this purpose.

The vibrations of free alcoholic hydroxy-groups correspond to an absorption maximum at 3570–3580 cm^{-1}. When hydrogen bonds are formed between the hydroxy-groups, absorption bands appear in the 3550–3000 cm^{-1} region, and the stronger the hydrogen bond the greater is the deviation from the absorption band of free hydroxy-groups. Examination of the spectra obtained shows that cellulose preparations give a broad set of absorption bands in the hydrogen--bond region[51]. This indicates the presence of hydrogen bonds of different strengths, which are responsible for the properties of the given type of cellulose. It is therefore possible to characterise the hydrogen bonds between the macromolecules by measurements based on indirect properties, such as the ability of certain reagents to penetrate deeply into the cellulose and rupture these bonds.

The most widely used and the simplest method of this kind is the determination of the absorption of water from air at a definite relative humidity. The ratio of the amount of moisture absorbed by the cellulose to the amount of moisture absorbed under the same conditions by cotton cellulose is termed "accessibility". It has been shown that the value of this accessibility depends on the structure of the cellulose and is independent of the relative humidity of the air[52].

Since, in air of low relative humidity, absorption of water is due to binding by alcoholic hydroxy-groups of the cellulose on the accessible surface of the sample, the quantity of water absorbed is a measure of the area of this surface. Here it must be borne in mind that water molecules that penetrate into the capillaries of the cellulose can break weak hydrogen bonds and penetrate into the depth of the cellulose, causing it to swell. Thus, it should be noted that the term "accessibility", measured by absorption of moisture, refers not only to the surface of the dry sample, but also to the surface that is formed as a result of swelling[53-57].

X-Ray studies have shown that water is absorbed by the loose part of the cellulose and does not penetrate deeply into the tightly packed sections of the macromolecules.

Methods of measuring the swelling of cellulose and in particular its dissolution are widely used in determining the intensity of intermolecular interaction in cellulose. These methods are based on the hypothesis that the most weakly bound macromolecules are the first to pass into solution. For the differential evaluation of the strength of the hydrogen bonds, methods are used in which the cellulose preparations under test are treated with solvents of gradually increasing dissolving power. This enables an arbitrary spectrum of bond strengths to be determined for different cellulose preparations[58].

However, the increase in the solubility of cellulose when its degree of polymerisation is reduced must be taken into account; intermolecular interaction is obviously no less decisive.

The methods to be considered here include those based on the swelling and dissolution of cellulose in ethylenediamine and its complexes, in cuprammonium solution, in solution of iron tartrate complex, in aqueous solutions of alkalis, sodium zincate, quaternary ammonium bases, calcium thiocyanate, chloral hydrate, zinc chloride, concentrated sulphuric acid and phosphoric acids, etc.[59-67].

Important results have also been obtained by measuring the rate of reaction of cellulose under heterogeneous conditions. Thus, for example, Nickerson and Troitzsch and other workers[68,69] used a method in which cellulose was partially formylated with formic acid of different concentrations at different temperatures.

In 1953 the present author in collaboration with Korol'kov and Garmanova[70] used the oxidation of cellulose with nitrogen dioxide, in the gaseous state or dissolved in carbon tetrachloride, for this purpose; this method was also used later by Roseveare and Spaulding[71]. Hydrolysis, ethanolysis, etc. may also be mentioned here.

Attempts have been made to evaluate the strength of the bonds between the macromolecules by measuring the amount of heat evolved in the mercerisation of cellulose by alkali solutions of increasing concentration[58], and also from the changes in the X-ray diffraction pattern of cellulose (as a result of the transition from cellulose I to cellulose II) after treatment with such solutions[72,73], and by measuring the rate of decrease of the degree of polymerisation of cellulose subjected to mild hydrolysis[74], etc. By means of these methods, data were obtained characterising the degree of lateral order in the whole mass of cellulose, that is, in the dense and loose regions.

To determine the degree of lateral order in the dense sections alone, some workers treated the cellulose in two stages; the first consisted of mild hydrolysis or ethanolysis to destroy loose regions, and in the second stage the residue was dissolved in aqueous solutions of sodium hydroxide of increasing concentration[75,76].

The methods enumerated above have been used to evaluate the heterogeneity of the energy of the lateral bond in various cellulose preparations and the variations have been represented on histograms. These methods have recently been used to characterise cellulose.

However, the heterogeneity of cellulose fibres due to their different anatomical structure must also be taken into account, and also heterogeneity due to compounds associated with cellulose which affect its solubility and tendency to swell.

The elucidation of the phase diagram of cellulose is of particular interest. At present the most widely held view is that cellulose consists of two phases, an amorphous and a crystalline phase; the amorphous phase is identified with the loose, readily accessible portion of cellulose, and the crystalline phase with the dense, oriented portion, which has a low reactivity. Such an interpretation applied to a polymer is usually associated with the presence of an interface between the two phases. It should, however, be noted that the presence of this interface has still not been demonstrated, and it is unlikely that such an interface exists. In this connection, many workers consider that cellulose may be partly in the mesomorphic or transition state; this state is characteristic of the boundary region between the amorphous and crystalline sections. Mark, in a typical statement, classifies cellulose as a stereoregular polymer, the rigidity of these polymers being due to the rigidity of the glucopyranose rings themselves and to strong intermolecular bonds[77]. When the molecules are arranged parallel to one another, these bonds promote the formation of crystal--like packets or aggregates. The terms "crystallite" and "crystallisation" are used with reference to certain regions within the cellulose system that show a state of three--dimensional order similar in some respects to the order in crystals of ordinary low-molecular compounds, such as sucrose, maleic anhydride, etc. However, the crystalline regions in cellulose do not have the regular shapes characteristic of ordinary crystals. They are much smaller and they are much more defective. Here the crystalline regions are linked with the non-ordered, amorphous regions by chains passing through both regions. Thus, there is no sharp boundary between the ordered (crystalline) regions, in which the molecules are arranged parallel to one another, and the non-ordered (amorphous) sections. Many workers share the view that cellulose is a single-phase crystalline system with a large number of dislocations[78]. In isolated sections of such a structure, the incidence of defects may be so great that the compound in these sections can be regarded as amorphous. In natural microfibrils highly oriented and poorly oriented sections regularly alternate along the length of the fibril, forming a bead-like structure. As mentioned above, the proportions in which these sections are present depend on the origin of the sample.

The alternation of sections differing in orientation is also found in regenerated cellulose, which does not have a microfibrillar structure, but here the regularity is less marked.

The variations mentioned in the structure of cellulose are similar among themselves and are based on the general idea that defect crystalline structures are present in cellulose.

Numerous X-ray structure studies on cellulose, especially those carried out in recent years[79-81], have definitely confirmed that cellulose contains three-dimensionally ordered regions with unit cells of fixed dimensions.

The degree of mutual orientation of cellulose macromolecules, measured by X-ray diffraction, varies within wide limits in different samples of cellulose. According to Ranby's studies, this orientation reaches a high degree in animal and bacterial cellulose and gradually decreases in cotton, and particularly in wood cellulose (Fig. 1).[82] Crushing and, in particular, dry grinding reduces the degree of orientation of natural cellulose[39,83,84].

The degree of orientation of highly stretched hydrocellulose fibres is much greater than that of isotropic fibres. However, the intensity of interaction (hydrogen bonds) between the macromolecules of natural and regenerated cellulose differs greatly, as is indicated by variations in the tendency to swell and to dissolve. The interaction between the macromolecules in natural fibres is much stronger than that in artificial fibres. For example, the solubility of natural cellulose in 10% aqueous sodium hydroxide solution generally does not exceed 10–20%, but under the same conditions regenerated cellulose in the form of fibres or films dissolves to the extent of 40–90%.

The energy of the interaction of macromolecules in "polynose" fibres is much greater than that in ultra-strong cord fibres. The difference in the packing of macromolecules is also displayed in a number of other properties. For example, natural cellulose has a higher density (1.55–1.60) than hydrocellulose fibres or films (1.495–1.530),[35] and it is hydrolysed[85-86] and ethanolysed[33] more slowly.

The special features of the supermolecular structure of cellulose mentioned above confirm that modifications of this structure exist with high bond energy (natural fibres) and low bond energy (hydrocellulose fibres). Each modification may show a different degree of mutual orientation of its macromolecules. The X-ray diffraction patterns of these two basic types of cellulose are different, which indicates a difference in the spatial arrangement of the macromolecules in a three-dimensional lattice. These two types of cellulose have been named cellulose I and cellulose II.

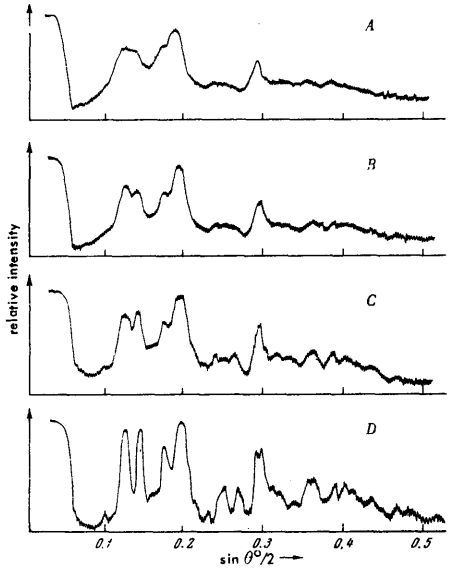


Fig. 1. X-Ray powder diffraction patterns of natural cellulose of different origins:
A) wood cellulose; *B*) cotton cellulose; *C*) animal cellulose (tunicine); *D*) cellulose from valonium algae[82].

It should be noted that this division of cellulose according to the strength of the side bonds and the structure of the unit cell is somewhat arbitrary, since cases are known in which there is a relatively strong side bond in cellulose II (for example, in "polynose" fibres).

At present, cellulose III and cellulose IV[87-88] are also known, the latter being formed from cellulose II by heating. In older papers reference was made to the conversion of cellulose II into cellulose I under these conditions, but this has not been confirmed by later studies[87,88]. A new, fifth modification of cellulose (cellulose X) has recently been described[89,90].

The unit cell of natural cellulose, or cellulose I, has been most studied[89,91-96]; this cell is monoclinic and has the following dimensions: a = 8.35 Å; b = 10.3 Å; c = 7.9 Å; angle β = 84°; volume 672 Å^3.

Wellard[97], who recently studied a large number of different natural celluloses, showed that the dimensions of their unit cells vary within comparatively narrow limits. Mercerised natural and highly oriented regenerated cellulose have the monoclinic cell of cellulose II with the following dimensions: a = 8.02 Å; b = 10.3 Å; c = 9.03 Å; angle β = 62.8°.[91-96,98-100]

Cellulose III is obtained by treating natural cellulose with non-aqueous liquid ammonia[101,102] or ethylamine[103]. Its unit cell has the following dimensions: a = 7.74 Å; b = 10.3 Å; c = 9.90 Å; angle β = 58°.

Cellulose IV, which is obtained by heating cellulose II in water or glycerol at high temperatures[87], has a unit cell of the following dimensions: a = 8.12 Å; b = 10.3 Å; c = 9.03 Å; angle β = [value omitted in Russian original (Ed. of Translation)].

Cellulose X, a new modification that has been little studied, was obtained by the regeneration of natural cellulose from its solutions in 40.3% hydrochloric or 85% phosphoric acid[89,90].

It is of interest to note that cellulose III is the only modification that can be converted into the initial natural cellulose I; up to now celluloses II, IV, or X have not been converted into cellulose I.[104]

All these modifications of cellulose give different X-ray diffraction patterns (Fig. 2); this appears to be due to differences in the configurations of the unit cells[91-96].

Thus, polymorphism is observed in cellulose. It is of interest that cellulose I is the only cellulose formed in nature, and has not yet been prepared in the laboratory.

The crystalline nature of cellulose has been demonstrated in different samples by studies on double refraction[105,106], magnetic anisotropy[107], fluorescence[108], and the piezoelectric effect[109-111].

The crystalline structure of highly oriented cellulose is indicated by the splitting (dichroism) of the absorption bands in the infrared spectra[112], and also by the X-ray diffraction patterns of true crystals of oligosaccharides obtained by the

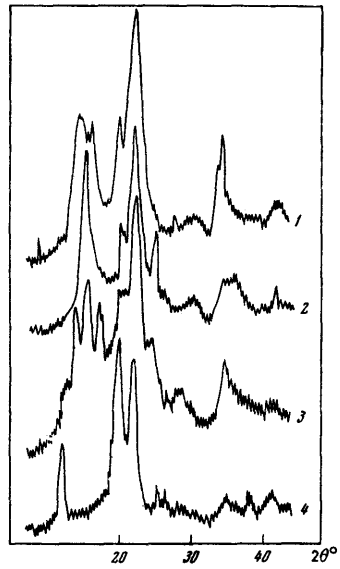


Fig. 2. X-Ray powder diffraction patterns of various modifications of cellulose:
1) cellulose I; 2) cellulose IV; 3) cellulose X; 4) cellulose II; the absorption intensity is plotted on the ordinate and the double angle (2θ) on the abscissa.[96]

extensive cleavage of cellulose (from cellulose to cellohexaose). In the latter case, after acetolysis of the cellulose and subsequent chromatography on a celite column, well crystallised oligosaccharides with a degree of polymerisation between 2 and 7 were separated[113]; these were identified after saponification. Oligosaccharides with a degree of polymerisation of 4 or more showed X-ray diffraction patterns virtually identical with the patterns of cellulose II. Thorough chromatographic separation of the oligosaccharides ensured that compounds of longer chain length did not appear in these fractions. Thus, typical crystals of higher oligosaccharides of cellulose obtained from aqueous solutions gave X-ray diffraction patterns characteristic of one of the modifications of cellulose that is also only formed in the presence of water (cellulose II).

The X-ray diffraction method, which shows the presence of regions of varying degree of orientation in cellulose, is widely used for the qualitative and quantitative evaluation of the extent to which cellulose occurs in the crystalline form[95,114-117].

It should, however, be noted that this method of quantitatively evaluating the crystallinity of cellulose is to a large extent arbitrary and should be used with great caution. For example, comparison of the X-ray diffraction patterns of hydrocellulose fibres[118] before and after removal of the easily hydrolysed (amorphous) fraction showed that the fibres contained virtually the same amount of "crystalline" fraction, although the proportion of the crystalline fraction would be expected to increase greatly after hydrolysis. It has been reported in other papers, however, that a slight increase in the proportion of crystalline fraction is observed when various celluloses are subjected to mild hydrolysis[119].

Various physical and chemical methods have been used in determining the degree of crystallinity of cellulose. Some of these are based on the removal of the amorphous fraction by hydrolysis with dilute acids[120-125], or by oxidation with periodic[26] or chromic[126] acids. In other methods the degree of crystallinity is determined from the absorption of water[127,128], from the rate of exchange of hydroxy-group hydrogen atoms for deuterium[45,46], or tritium[47,48], from the density of the crystalline and amorphous sections[106,129], from the heat of wetting[130], from the absorption of iodine from aqueous solutions[131,132], and from the exchange of hydroxy-group hydrogen atoms of the amorphous sections for thallium in solutions of thallium ethoxide[133], or for sodium in solutions of sodium in liquid ammonia[134].

Methods based on differences in the rate of esterification of the amorphous and crystalline fractions of acetylation[135] or formylation[136-138] form a separate group.

It should be noted that none of these methods gives a clear idea of the degree of crystallinity; they merely indicate the density of packing, the degree of orientation, and the strength of intermolecular bonds; this must be taken into account in the evaluation of the results obtained. Thus, at present we have no reliable methods for determining the degree of crystallinity of cellulose.

This is obviously due, firstly, to the absence of a clear boundary between the crystalline and non-crystalline sections, and, secondly, to the failure of many workers to distinguish properly between "crystalline" and "dense" sections; not all densely packed sections and sections difficult of access can be regarded as crystalline.

Of the methods enumerated above, the X-ray diffraction method appears to be the most suitable for determining the crystallinity of celluloses, but even this method must be used with great caution.

Another point of view on the phase state of cellulose is based on the hypothesis that it has an amorphous structure. Kargin is the founder of this theory in the Soviet Union. Over a period of many years, he and his students have systematically supported and advocated the theory that cellulose is an amorphous polymer with an anisotropic structure[139-149]. He considers that clear X-ray diffraction patterns obtained on a number of vegetable fibres have been incorrectly evaluated by some workers as providing proof of the crystalline structure of the polymer. According to Kargin and coworkers, it is necessary to distinguish between the elements of order responsible for the mutual arrangement of the chains and the order that arises on crystallisation of the polymer[146]. In the latter case additional bonds are formed without substantial change in the order of the arrangement of the macromolecules, but the proportion of these bonds is not great compared with the degree of order in oriented samples.

To determine the phase composition of cellulose, Kargin and coworkers used a method based on the dependence of the interference width on the wavelength of the beam used in systems with long-range order. For this purpose, they studied the interference obtained by the reflection of X-rays (wavelength 1.54 Å) and an electron beam (wavelength 0.05 Å). Since they found no such dependence, they concluded that cellulose has an amorphous structure.

Unfortunately, the electron diffraction method as applied to cellulose has serious disadvantages, and for this reason the results obtained have been criticised by some workers[81].

Evidence in favour of the amorphous structure of cellulose is also provided by the change that occurs in the X-ray diffraction pattern of an isotropic viscose film when the latter is stretched. It has been shown that, when signs of

a high degree of orientation of the film appeared in the X-ray patterns, there were no new interferences that could be ascribed to the crystallisation of the cellulose [141]. These experiments confirm that no phase transition from the amorphous to the crystalline state occurs, provided that these two states show different interferences, which has not yet been confirmed.

In this respect, the changes in X-ray interferences in natural and highly oriented, artificial cellulose fibres that have been subjected to dry grinding are interesting. Under these conditions, it is characteristic that the interferences in the natural cellulose entirely disappear (Fig. 3) without new ones appearing [39,83,84], although the cellulose retains most of its properties (transition to the amorphous state). When ground cellulose from highly oriented viscose fibre is treated with water, the initial X-ray diffraction pattern of the fibre is partly restored.

In developing the theory of the amorphous structure of cellulose, Kargin et al. attempted to change the second-order transition temperature of cellulose, that is, the transition point at which it changes from the vitreous to the highly elastic state, by the introduction of plasticising additives [145]. Under these conditions, the amorphous polymers show a reduction of the second-order transition temperature. Experiments in which triethylphenylammonium hydroxide was added as a plasticiser to cellulose confirmed that this transition temperature is reduced; it was therefore concluded that cellulose always exists in the vitreous state.

By measuring the integral heats of solution in triethylphenylammonium hydroxide of cellulose fibres with differing degrees of orientation, Mikhailov and Fainberg attempted to show that these fibres undergo a phase transition [150]; no appreciable difference in the heats was observed. This was interpreted as demonstrating that cellulose was amorphous in all the samples examined.

In 1962 these workers determined the heat capacity of isotropic and highly oriented cellulose fibres and observed no appreciable difference; this was also interpreted as proof that cellulose is amorphous [151].

The experimental results mentioned above obtained by Kargin and his students led them to conclude that cellulose fibre is a body that is solid in its state of aggregation but liquid in its phase state, with oriented anisodiametric molecules. Therefore, cellulose fibre is an anisotropic liquid phase the equilibrium state of which corresponds to a completely disoriented structure. Under normal conditions this process [attainment of equilibrium (Ed. of Translation)] is inhibited by the existence of a fixed structure [144].

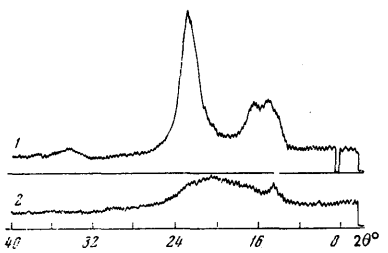


Fig. 3. X-Ray powder diffraction patterns of natural cotton cellulose before (1) and after (2) dry grinding.[39]

In later work Kargin and coworkers studied the supermolecular structure of viscose ultra-strong cord fibres and observed that these contained "ordered structural forms", which, however, were not internally perfect [152]. This indicated that cellulose undoubtedly shows a high degree of order. This interpretation that cellulose has an amorphous structure with a high degree of order agrees with the interpretation previously advanced that in amorphous cellulose the unfolded chains form packets (clusters), with isolated macromolecules passing through several packets.

These considerations are largely in agreement with modern views on cellulose accepted by advocates of both the crystalline and the amorphous hypotheses. The differences between the advocates of the two hypotheses appear to be mainly differences in terminology, the physical interpretations being very similar.

Now the main question in dispute is what name should be given to the "packet", which is recognised by all: should it be regarded as a crystal or as a highly oriented amorphous formation? Discussions in Soviet journals have shown that at present this question cannot be unambiguously answered because of the absence of reliable methods of investigation [78,154-159].

A final decision can probably only be reached by a study of an artificial cellulose crystal, with well defined boundaries, that can be assigned to a definite crystallographic system. If such a crystal had a diffraction pattern and other properties similar to those of highly oriented natural and regenerated cellulose, this would indicate that cellulose has a crystalline structure; on the other hand, if these properties were different, the crystallinity of cellulose would not be demonstrated. In this connection, work on the preparation of crystals of linear polysaccharides is of great importance; these polysaccharides include amyloses [160,161], inulin, mannan [162-164], xylan [164-167], and in particular cellulose [167]. Plane orthorhombic crystals of cellulose have been obtained by the slow saponification of low-molecular acetylcellulose in a dilute solution of alkali.

X-Ray and electron diffraction studies on these crystals have shown that they consist of a system of parallel plates in which the macromolecules are arranged perpendicular to the plane of the plate. The thickness of the plate varies over a range of 100 Å, i.e. it is much smaller than the length of the cellulose molecule from which the crystal is formed. It has been shown that amylose has a similar laminar-crystalline structure [160]. This phenomenon, which is characteristic of many crystallisable high polymers of linear structure [169-172], is also encountered in cellulose [167,168]. This crystalline structure of linear polymers can be explained if it is assumed that at the edge of the crystal the polymer chain turns through an angle of 180° to re-enter the lattice. Thus, the crystals described above are formed by the folding of long macromolecules in a plane perpendicular to the plane of the plate.

Manely has now obtained acetylcellulose crystals of similar structure [168-173]. When these crystals were saponified in an aqueous medium, cellulose that had a polycrystalline structure with folded macromolecules was obtained [174].

X-Ray diffraction studies on Ranby's cellulose crystals showed the presence of interferences in the same positions and of the same intensity as those found with highly oriented hydrocellulose fibres (cellulose II); no new interferences were noted (Fig. 4).

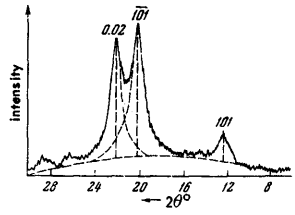


Fig. 4. X-Ray diffraction pattern of crystalline cellulose II powder.[167]

It is interesting that up to 50–60% of all the hydroxy--groups in these crystals are readily exchanged for deuterium in heavy water, that is, they behave in the same way as the groups in ordinary cellulose. Like ordinary hydrocellulose fibres and films, cellulose crystals obtained at a temperature of 30–90° form cellulose II, but those obtained at 120–150° form cellulose IV. The paper by Wolfrom and Dacons[113] mentioned above also provides evidence for the existence of cellulose crystals; these workers showed that, in the crystalline state, the products of the partial hydrolysis of cellulose — from cellotetraose to celloheptaose — gave X-ray diffraction patterns typical for cellulose II.

Whistler made a similar observation for linear xylan molecules[175], the only difference being that here the lowest compound to give a pattern similar to that of crystalline xylan was the hexasaccharide.

These examples show that crystalline formations in cellulose II give X-ray diffraction patterns similar to the patterns for oriented regenerated cellulose. If these formations are regarded as polymer (cellulose) crystals — and there are sufficient grounds for this assumption — we must recognise that similar crystalline structures are present in fibres and films of regenerated cellulose. Obviously, this conclusion can also be extended to natural fibres.

Since macromolecules with a folded structure were found to occur in the interior of various polymers of a crystalline nature, it must be assumed that similar formations can occur also in the interior of regenerated cellulose. It is assumed that in natural microfibrils the macromolecules are arranged longitudinally, but in the microfibrils of regenerated cellulose folded and unfolded macromolecules are present in various proportions.

How the packets or crystalline formations made up of folded macromolecules form sufficiently strong fibres is still obscure. It has been suggested that one end of some macromolecules enters one packet while the other end enters another packet, and in this way a mutual bond is formed along the fibre[172].

In contrast to this view, some workers regard the microfibrils as tubes formed from a solid band folded spirally in which the cellulose macromolecules are arranged perpendicular to the axis of the band in the folded state, as in crystals[160]. It should, however, be noted that these hypotheses need to be critically evaluated.

On the basis of the experimental work cited here, natural and highly oriented regenerated cellulose can be regarded as linear polymers made up of alternate highly oriented and poorly oriented sections. The highly oriented sections are similar in structure to the crystalline formations characteristic of a number of linear polymers.

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MACROKINETICS OF CHEMICAL PROCESSES

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I. INTRODUCTION

A characteristic feature of modern chemical processes, occurring at high rates at high temperatures and pressures in multiphase systems, is their great complexity. This complexity is shown in the large number and wide variety of the parameters determining the course of the processes and the large number of internal relations between the parameters and their mutual influence, the change in one parameter entailing a non-linear change in others. The complexity is enhanced by the occurrence of feedback between the parameters and also by the development of competing modes of the process, whereby the course of the latter is altered.

The complexity of a chemical process makes it necessary to understand it in terms of *models*, i.e. systems which reflect the individual aspects of the phenomena in a given process, restricted to the required conditions. Models are represented in terms of a definite mathematical notation, which establishes the relation between the parameters of the process, using both theoretical methods and experimental data. In their analysis and use, such models are usually divided into separate blocks, purely chemical phenomena, determined by classical chemical kinetics, being considered separately; blocks taking into account mass and energy transfer during the chemical reaction are distinguished. In this connection it has become usual to distinguish the micro- and macro-kinetics of chemical processes. This subdivision is of course to a certain extent arbitrary, but it makes