

# MODERN METHODS OF DETERMINING CRYSTALLINITY IN CELLULOSE

J. MANN\*

*British Rayon Research Association, Heald Green Laboratories,  
Wythenshawe, Manchester, U.K.*

## INTRODUCTION

The existence of three-dimensional order in celluloses is shown conclusively by X-ray and electron-diffraction diagrams of such materials as ramie fibres<sup>1</sup>, *valonia ventricosa* cellulose<sup>2</sup> and Fortisan fibres<sup>1</sup>. These diagrams exhibit many sharp reflections which can only be accounted for in terms of three spatial co-ordinates. All the reflections from regenerated celluloses which possess the cellulose II structure can be accounted for in terms of a monoclinic unit cell of approximate dimensions<sup>3</sup>  $a = 7.92$  Å,  $b = 10.34$  Å,  $c = 9.08$  Å,  $\beta = 62.7^\circ$ . Similarly the reflections of ramie (cellulose I) can be accounted for by a monoclinic unit cell of approximate dimensions<sup>3</sup>  $a = 8.17$  Å,  $b = 10.34$  Å,  $c = 7.85$  Å,  $\beta = 83.6^\circ$ . The electron-diffraction diagrams<sup>2</sup> of *valonia ventricosa* cellulose however suggest a unit cell of triclinic symmetry for this material in which the  $a$  and  $c$  axes are double those quoted for ramie cellulose.

Although these observations show the existence of three-dimensional crystalline order they do not prove that all the regions which contribute to the sharp reflections of the diffraction diagrams show the same high degree of three-dimensional order. Such a conclusion would be warranted only if good agreement between calculated intensities for an ordered crystal structure model and the observed intensities could be obtained. This has not yet been shown to be possible<sup>4</sup>. Indeed observations made by Hermans and Weidinger<sup>5</sup> suggest that different degrees of ordering may exist along different directions in cellulose II crystallites. In using the term crystalline to discuss cellulose structure it should be remembered, therefore, that this does not necessarily imply the existence of full three dimensional order and that there is an element of ambiguity in the use of the term.

The non-crystalline portion of celluloses is frequently called amorphous, and a similar ambiguity is attached to this term which is often used to mean complete lack of order. Although the nature of the non-crystalline or amorphous regions is still largely a matter for speculation, it is clear that there can be no sudden transition from three-dimensional order to complete absence of order, since the long chain cellulose molecules are known to pass through both crystalline and amorphous regions. The possibility of the existence of a continuous range of degrees of order in celluloses must be admitted.

\* Present address: Shell Chemical Co. Ltd., Carrington Research Laboratories, Urmston, Manchester, U.K.

The use of the terms *crystalline* and *amorphous*, or the division of a cellulose into crystalline and non-crystalline regions, provides a valuable way of picturing cellulose structure in spite of these theoretical objections and the lack of precision attached to the terms. The simple crystalline-amorphous concept of cellulose structure implies that structure can be pictured in terms of only two types of regions of widely different properties, one highly ordered and the other highly disordered, these regions having the same structure and properties in different celluloses. The extent to which this simple picture provides an adequate approximation to the true structure of celluloses is a matter for experimental investigation. Whatever the answer to this question, however, it is reasonable to try to determine the fraction of a cellulose which is crystalline towards a particular experimental technique.

### DETERMINATION OF CRYSTALLINITY

Many different techniques have been used to determine crystallinities of celluloses and it has been found that results from different methods are rarely in agreement<sup>6</sup>. The significance of this fact is not clear however, since most of the methods measure properties of cellulose which are connected with crystallinity in a rather indirect way, *e.g.* the rates or extents of chemical reactions and physical properties such as moisture sorption.

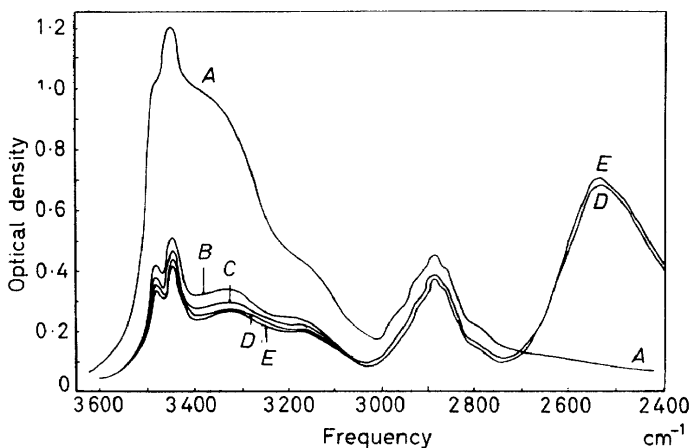


Figure 1. Viscose film—exchanged with  $D_2O$  vapour: A: dry viscose undeuterated; B: Deuterated for 5 min; C: deuterated for 30 min; D: deuterated for 60 min; E: deuterated for 120 min

Since the phenomenon of crystallization is due to the orderly arrangement of molecules relative to one another, the most significant measurements of crystallinity are those obtained by physical techniques which study order in a rather direct way and are based on principles which are thoroughly understood. It is only in terms of the results obtained by such techniques that the significance of measurements by other methods can be understood.

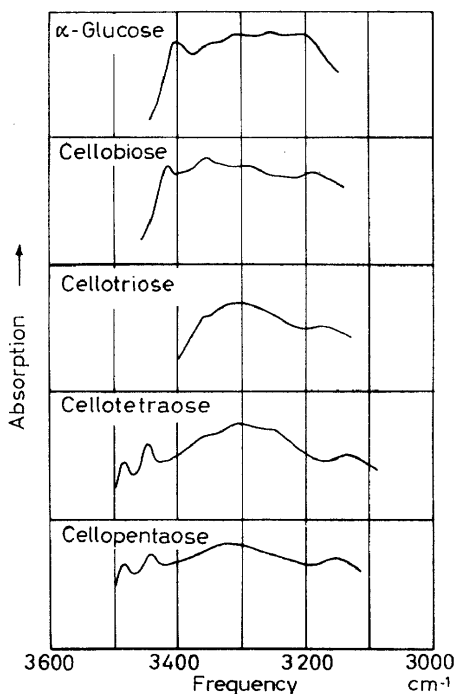
The two properties of cellulose which are most closely related to the presence of intermolecular order are its X-ray diffraction pattern and its infra-red spectrum. X-ray diffraction must be regarded as the basic

## METHODS OF DETERMINING CRYSTALLINITY IN CELLULOSE

method for all crystallization studies because of the direct relation between the diffraction pattern and order. The infra-red spectrum of a material is less closely connected with the presence of order, and its importance in the case of cellulose lies in the great sensitivity of bands due to stretching of OH groups to the local environment around such groups.

### INFRA-RED STUDIES OF CRYSTALLINITY

When  $D_2O$  vapour is passed over a thin film of cellulose there is a rapid exchange reaction in which OH groups are converted into OD groups. This reaction produces changes in the infra-red spectrum<sup>7</sup> which are illustrated in *Figure 1* for a regenerated cellulose. The band due to stretching of OH groups, which extends over the frequency range  $3500-2950\text{ cm}^{-1}$ , is reduced in strength and there is a corresponding increase in absorption in the  $2500\text{ cm}^{-1}$  region caused by the appearance of a band due to stretching



*Figure 2.* Infra-red spectra of oligosaccharides

of OD groups. The reduction in the optical density of the OH band is due to the removal of a broad diffuse absorption similar in shape to the OD band. As the reaction proceeds the reduction in the optical density of the OH band continues; after about 1 hour, the broad OH band has disappeared completely, leaving four well-resolved absorption bands. Further deuteration leads to a very slow decrease in the optical density of all four bands with no change in their relative peak heights.

These four resolved bands are due to OH groups in crystalline regions which are hydrogen bonded in a regular manner. This can be shown from the spectra of the oligosaccharides illustrated in *Figure 2*. Cellotetraose and cellopentaose show the same four bands as cellulose, and X-ray diffraction diagrams prove that these materials are fully crystalline and have monoclinic unit cells of similar dimensions to the cellulose II lattice of regenerated cellulose<sup>3</sup>.

Since it is known from X-ray diffraction that the regenerated cellulose contains only one type of crystal lattice, the broad diffuse absorption band which is removed by deuteration must correspond to absorption by OH groups in non-crystalline regions. This is consistent with our knowledge of absorption by hydroxyl groups in liquids and amorphous solids. The diffuseness of the absorption band is presumably due to the fact that the hydroxyl groups are hydrogen bonded in an irregular manner. This leads to a continuous range of hydrogen bond strengths and, consequently, to a series of absorption bands of different frequencies which overlap and are unresolved. In contrast, only a limited number of different hydrogen bond strengths exists in crystalline regions, leading to discrete, resolved absorption bands.

Quantitative measurements of the decrease in the optical density of the OH band with time have shown that all the OH groups in non-crystalline regions can be deuterated before appreciable deuteration of OH groups in crystalline regions has occurred. At this stage of the reaction therefore, the ratio of the optical densities of the OH and OD bands of the dry film gives a measure of crystallinity; determination of this ratio for different

Table 1

Cellulose	Crystallinity (%)
Saponified acetate	25
Viscose rayon	26
Precipitated cellulose	32
Viscose treated with NaOH	33.5
Mercerized bacterial cellulose	33
Bacterial cellulose	70

celluloses gives relative crystallinities. Absolute values of crystallinity can be obtained by estimating the deuterium content of the cellulose. This can be done by extracting the deuterium from the cellulose with a known amount of H<sub>2</sub>O and estimating the deuterium content of the water by measuring its refractive index<sup>8</sup>. Absolute crystallinities obtained in this way can then be used to calibrate the infra-red method so that absolute crystallinities on further samples can be determined by infra-red spectroscopy<sup>9</sup>.

The method can also be used to determine crystallinities of native celluloses which possess the cellulose I crystal lattice. A separate calibration of the infra-red method is required for these celluloses, however, since the bands due to stretching of OH groups in crystalline regions are different from those of regenerated celluloses<sup>7</sup>.

Some crystallinity values determined by the infra-red method are given in *Table 1*. These crystallinities will not necessarily be the same as crystallinities measured on the same samples by other techniques, and it is important to bear in mind what the infra-red method measures. The crystallinity measured by the infra-red method described above is the fraction of *OH* groups which are hydrogen bonded in the regular manner characteristic of crystalline material. It can be readily appreciated that the X-ray method, for example, measures a somewhat different quantity, ideally the fraction of *molecules* which are arranged in a regular repeating pattern.

### X-RAY STUDIES OF CRYSTALLINITY

The existence of crystallinity in celluloses was first revealed by X-ray diffraction<sup>10</sup> and this technique must still be regarded as the basic method for studying crystallization. However, despite the excellent pioneering work of Hermans<sup>11</sup> and many subsequent investigations, it must be admitted that we still cannot determine absolute crystallinities of celluloses in a completely objective way by this method. It is even doubtful whether reliable relative crystallinities can be obtained.

The basic step in determining the crystallinity of any polymer from its X-ray diffraction pattern is to separate the total scattering curve into scattering from crystalline material and scattering from non-crystalline material. This is a simple matter with polymers such as natural rubber where only the amorphous regions contribute to the scatter at lower angles. In the case of cellulose, however, the scattering from crystalline and non-crystalline material overlap seriously and it is doubtful whether there is any angle at which accurate measurements can be made where only one type of material scatters. In these circumstances, an objective separation of the total curve into its component parts can be made only if the precise forms of *both* scattering curves are known.

Following the work of Hermans and Weidinger<sup>11</sup>, ball-milled cellulose has frequently been used as a standard for amorphous cellulose in X-ray work. The suitability of this material as a standard has been reinforced by observations of Ellefsen *et al.*<sup>12</sup> on lichenin and  $\beta$ -methyl cellobioside glass and by recent work carried out at the British Rayon Research Association<sup>13</sup>.

The monomer of cellulose, glucose, and its polymers, cellobiose to cellohexaose have been obtained in the amorphous state by freeze drying their aqueous solutions. The X-ray diffraction curves of these substances are shown in *Figure 3* together with the curve for ball-milled cellulose. The latter curve was found to be the same within experimental error for ball-milled cellulose prepared from cotton (cellulose I) or from Fortisan H (cellulose II). It can be seen that the scattering curves are all very similar, particularly in the position of the maximum and the shapes of the high angle sides of the curves. The main difference between cellulose and its lower homologues is the shoulder exhibited by cellulose on the low angle side of the maximum. However, this feature fits in with a trend observed in the shapes of the oligosaccharide curves. The curve of glucose is convex to the  $2\theta$  axis on the low angle side of the maximum and the curves of the higher members of the series become progressively less convex until with cellohexaose this part of the curve is almost linear. This comparator

suggests, therefore, that ball-milled cellulose is a suitable standard for amorphous cellulose.

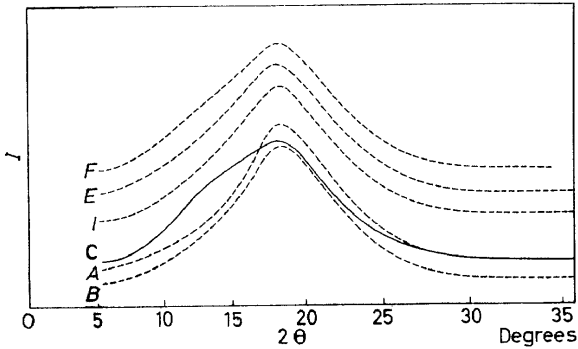


Figure 3. Scattering curves of amorphous oligosaccharides and ball-milled cellulose; curves displaced along intensity axis: *A*: glucose and cellobiose; *B*: cellotriose; *l*: cello-tetraose; *E*: cellopentaose; *F*: cellohexaose; *C*: Ball-milled cellulose

The scattering curves for ball-milled cellulose and some cellulose derivatives which have been subjected to ball-milling or quenched from the melt also form a regular series, as can be seen from Figure 4. All the cellulose derivatives show two maxima, the positions and shapes of the higher angle maxima being very similar to that of cellulose. The maxima at lower angles vary in position however, there being a trend towards higher angles as the size of the substituent decreases. The shoulder of the cellulose curve fits in with this trend.

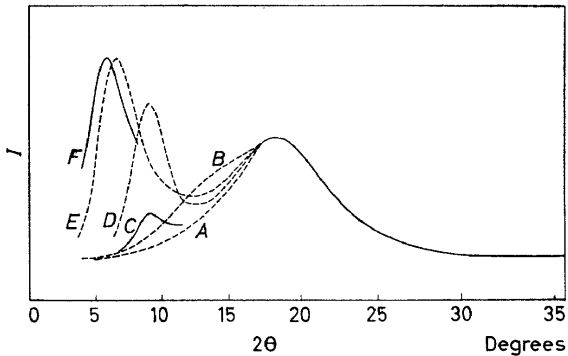


Figure 4. Scattering curves of ball-milled cellulose and its derivatives: *A*: amorphous glucose; *B*: cellulose; *C*: sodium carboxymethyl cellulose; *D*: methyl cellulose; *E*: ethyl cellulose; *F*: cellulose tributyrate

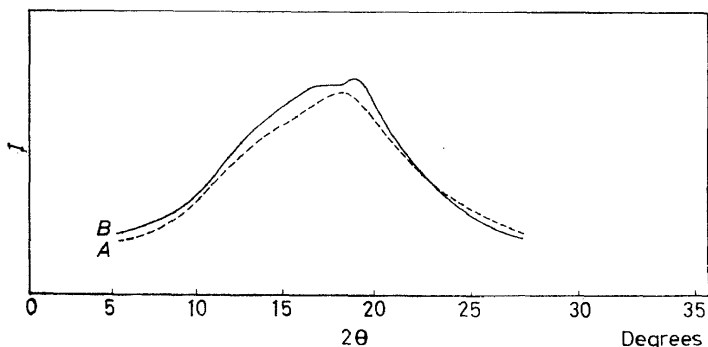
Since no part of the non-crystalline scattering from a partially crystalline cellulose can be measured with certainty free from overlap by crystalline scattering, an objection can be raised against the use of ball-milled cellulose as a standard for crystallinity determinations. The objection is that there is no proof that there are regions in a partially crystalline cellulose which

## METHODS OF DETERMINING CRYSTALLINITY IN CELLULOSE

have the same structure and scattering curve as ball-milled cellulose. For this reason the X-ray diagram of highly oriented Fortisan H has been examined<sup>13</sup>.

The crystalline reflections from this material are observed as short arcs because of the high orientation. On photographs exposed for long times a weak halo can be seen which is strongest near the equator where it merges with the 002 and  $\bar{1}01$  crystalline reflections and which extends outwards towards the meridian. This halo can be photometered without too great an interference from crystalline reflections and the resultant curve is shown in *Figure 5*. It can be seen that the form of the curve is generally similar to that of ball-milled cellulose. It seems reasonably certain, therefore, that there are regions in partially crystalline cellulose which scatter X-rays in a way similar to ball-milled cellulose.

Unfortunately, we do not possess similar information concerning the shapes of the X-ray reflections from crystalline regions and it follows, therefore, that we cannot obtain an absolute crystallinity from the X-ray diagrams of celluloses. It is possible to fix a minimum for the absolute crystallinity, however, by carrying out the separation of the total scattering curve according to the procedure used by Ellefsen *et al.*<sup>12</sup>. It is obvious that the amorphous scattering cannot be larger than the total scattering at any point on the curve. Thus, if the separation is carried out in such a way



*Figure 5.* A: ball-milled cellulose; B: Fortisan halo

that the amorphous scattering curve touches the total scattering curve at some point, it follows that this must represent a maximum for the amorphous scattering. If ball-milled cellulose is used as a standard for completely amorphous cellulose, a maximum of amorphous content *i.e.* a minimum crystallinity can be obtained. This is the only quantity which can be determined without making any assumptions. It is worth noting that the minimum crystallinity determined in this way represents an absolute quantity which is valid even if celluloses do not possess a simple crystalline-amorphous structure, but have a structure of varying degrees of order as suggested by Howsmon<sup>14</sup>. It would also be valid even if celluloses possess no highly disordered amorphous regions, a situation which Hosemann's theories concerning the X-ray diagrams of cellulose would allow<sup>15</sup>. For

this reason, the term *minimum crystallinity* is to be preferred to Ellefsen's term *amorphicity* for the quantity obtained as described above.

Norman and co-workers<sup>16</sup> have shown that the X-ray diagram of a given cellulose leads to a much higher crystallinity if the not unreasonable assumption is made that the shapes of crystalline reflections are Cauchy distributions. The Cauchy distribution has long tails which lead to appreciable overlap between different crystalline reflections in the X-ray diagram. In consequence, the amorphous scattering has to be drawn in much lower if this assumption is made than is the case in the minimum crystallinity method. *Table 2* shows values of minimum crystallinity and crystallinity values assuming the Cauchy distribution as determined by Norman and co-workers<sup>16</sup>. The difference between the two crystallinities is particularly striking with the cellulose I samples, since overlap between different crystalline reflections is greater with cellulose I than with cellulose II.

*Table 2*

	<i>Minimum crystallinity (%)</i>	<i>'Cauchy' crystallinity (%)</i>
Acetate grade wood pulp	53	95
H <sub>2</sub> SO <sub>4</sub> treated surgical cotton	62	95
Acetate grade wood pulp mercerized in 18% NaOH	43	60
Acetate grade wood pulp treated with 39% HCl	49	60

Further progress in the determination of absolute crystallinities from X-ray diffraction patterns must depend on experimental determinations of the shapes of crystalline reflections. This is not a simple matter however, since it is difficult to be certain whether any of the reflections which can be observed free from non-crystalline scatter are in fact produced by only one type of crystallographic plane<sup>1</sup>. Until decisive evidence is obtained on this point it must be admitted that the X-ray diffraction pattern of a cellulose is consistent with a range of crystallinities.

## COMPARISON OF X-RAY AND INFRA-RED CRYSTALLINITIES

In an attempt to throw light on the structure of celluloses and the significance of crystallinity measurements, a comparison has recently been made of the minimum X-ray crystallinity and the infra-red-deuteration crystallinity of a regenerated viscose rayon film<sup>13</sup>.

The film was studied in an unoriented form and in a form showing high planar orientation; both ball-milled cellulose and amorphous cellotetraose were used as 100 per cent amorphous standards. The diffraction curves of these materials are shown in *Figures 6* and *7* standardized to amount of X-radiation scattered per unit weight of irradiated material per unit amount of incident X-radiation. Crystal reflected monochromatic radiation was used and the X-ray beam was monitored with a Goppel camera<sup>17</sup>. The radiation was recorded photographically in a vacuum camera. The



METHODS OF DETERMINING CRYSTALLINITY IN CELLULOSE

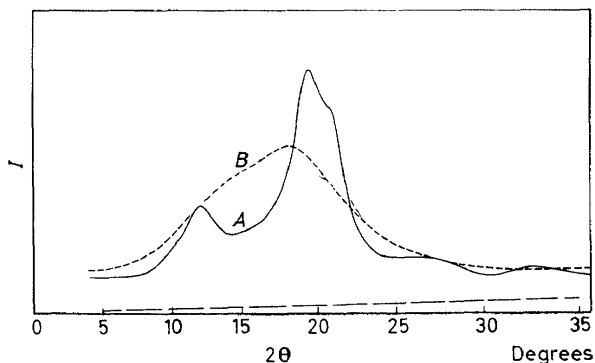


Figure 6. Normalized scattering curves: A: unoriented viscose rayon; B: ball-milled cellulose

weight of the samples per unit area was the same within 5 per cent and no correction was made for absorption of the X-ray beam. The level of incoherent radiation shown in Figures 6 and 7 was assessed from the theoretical calculations of Ellefsen *et al.*<sup>12</sup>. The determination of the infra-red crystallinities has already been described<sup>9</sup>.

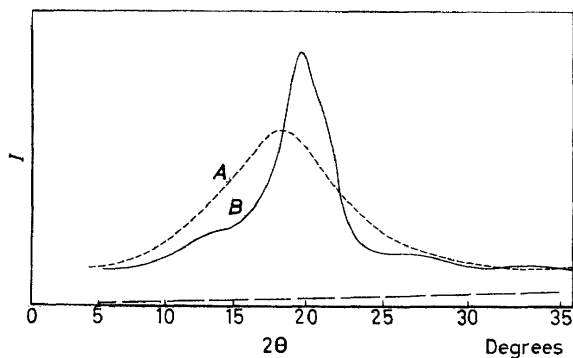


Figure 7. Normalized scattering curves: A: planar oriented viscose rayon; B: amorphous cellotetraose

The results of the determinations are shown in Table 3. The agreement between the figures for minimum X-ray crystallinity obtained with the two amorphous standards suggests that this crystallinity is not very sensitive to the precise shape of the scattering curve assumed for non-crystalline material. It can also be seen that the minimum crystallinity is not very sensitive to the degree of planar orientation present. The significance of this is doubtful, however<sup>13</sup>.

The difference between the minimum X-ray crystallinity of 40 per cent and the infra-red crystallinity of 26 per cent is large and implies that although a minimum of 40 per cent of the cellulose chains is arranged in a crystalline way only 26 per cent of the OH groups are hydrogen bonded in the regular crystalline manner.

Now OH groups which show the characteristic absorption pattern of crystalline material deuterate only slowly and this must imply that they are not easily accessible to  $D_2O$ ; the deuteration reaction is extremely rapid and the rate of deuteration is determined by the rate at which  $D_2O$  molecules are able to reach OH groups. It must be assumed, therefore, that such OH groups are protected from easy access by  $D_2O$  by being in the interior of crystallites. OH groups which lie in the surfaces of crystallites are presumably readily accessible to  $D_2O$  molecules and will deuterate rapidly.

Table 3

	<i>X-ray minimum crystallinity</i>		<i>Infra-red crystallinity (%)</i>
	<i>Ball-milled cellulose as standard (%)</i>	<i>Amorphous cellostetraose as standard (%)</i>	
Unoriented film	43	40	26
Planar oriented film	43	42	26

Since the OD band of deuterated cellulose shows no trace of structure, the vast majority of surface OH groups must be hydrogen bonded in an irregular amorphous fashion. This conclusion provides an obvious qualitative explanation of the crystallinity results and approximate calculations can be made to test this explanation quantitatively.

It is well established that cellulose II crystallites are tabular in shape with the crystallographic 101 plane as the plate face<sup>18,19</sup>. In addition, our knowledge of the crystal structure shows that the planes of the glucose units are roughly inclined in the crystallographic  $\bar{1}01/002$  planes<sup>4</sup>. From this information it can be calculated that for crystallites 29 Å by 65 Å in cross-section 35 per cent of the OH groups will lie in the surfaces of crystallites. The crystallinity measurements show that at least 35 per cent of the OH groups of crystalline chains are hydrogen bonded in an irregular manner. Thus the difference between the minimum X-ray crystallinity and the infra-red crystallinity can be accounted for in terms of crystallites of cross-section 29 Å by 65 Å. The size of this crystallite is consistent with our present knowledge of crystallite size obtained from electron microscopy<sup>18,20</sup> and low-angle X-ray scattering<sup>21</sup>.

### NATURE OF INFRA-RED AMORPHOUS MATERIAL

Although the difference between the minimum X-ray crystallinity and the infra-red crystallinity seems to be consistent with our knowledge of crystallite size, this is only so if *all* the OH groups which lie in the surface of crystallites are hydrogen bonded in an irregular manner. Now the two sharp infra-red bands of crystalline cellulose at 3485 and 3445  $cm^{-1}$  are due to intramolecular hydrogen bonds which join successive glucose units of the cellulose chain<sup>22</sup> and, therefore, characterize molecular form. The fact that there seem to be no OH groups in the surface of crystallites which

## METHODS OF DETERMINING CRYSTALLINITY IN CELLULOSE

show these bands suggests that the material which is crystalline towards X-ray diffraction but amorphous to infra-red spectroscopy does not possess the precise molecular form characteristic of crystalline chains. The extent of this departure from the perfect crystalline molecular form is uncertain but may not be great in view of the sensitivity of O—H stretching frequencies to the hydrogen bond length<sup>23</sup>.

This line of reasoning suggests that the infra-red amorphous material can be divided into two parts. The first is amorphous material of unknown structure and the second chains in crystalline regions which are somewhat distorted from the characteristic crystalline form. It might be expected, therefore, that the structure of the infra-red amorphous material would vary from one cellulose to another, *e.g.* with varying crystallinity. One aspect of the structure of the amorphous material which can be studied is the distribution of hydrogen bond strengths. This can be examined by measuring the shape of the amorphous OD band, since, as was mentioned earlier, this is related to the distribution of hydrogen bond strengths (strictly deuterium-bond strengths).

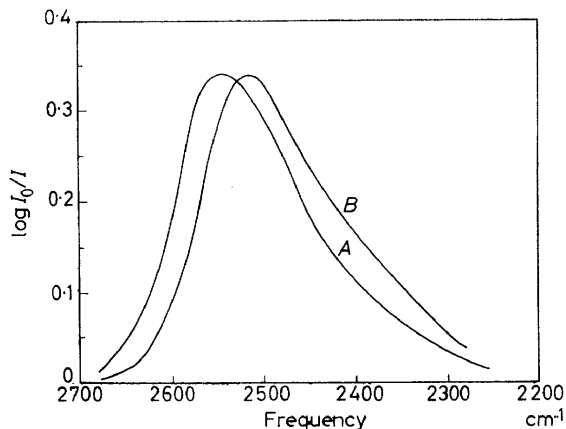


Figure 8. OD band of celluloses: A: regenerated cellulose; B: bacterial cellulose

The amorphous OD band has been carefully measured for five regenerated and one native cellulose<sup>13</sup>. The bands of the regenerated celluloses were found to be the same within the experimental error but the OD band of bacterial cellulose was found to be significantly different, as shown in Figure 8. Although the shape of the band is very similar to that of the regenerated cellulose bands, the whole band seems to be shifted towards lower frequencies, the maximum being some 20–30  $\text{cm}^{-1}$  lower than with the regenerated celluloses. This difference shows conclusively that the infra-red amorphous material in bacterial cellulose is different in structure from the infra-red amorphous material of the regenerated celluloses, and suggests that the average hydrogen bond strength in bacterial cellulose is greater than in the regenerated celluloses.

The fact that no differences were found between the regenerated celluloses studied may simply be due to the fact that they did not vary greatly

in crystallinity. The bacterial cellulose differs from the regenerated celluloses not only in its crystal lattice but also in having a very much higher crystallinity<sup>8</sup>.

The difference between the OD band of bacterial cellulose and the bands of regenerated cellulose suggests that the absorption bands of the material which is crystalline to X-rays but amorphous to infra-red may be blurred versions of the crystalline absorption bands. This could account for the bacterial cellulose band being at lower frequencies, since the strongest crystalline band of this material is lower in frequency than the corresponding band of regenerated celluloses.

In a highly oriented cellulose the material which is crystalline to X-rays but amorphous to infra-red must be highly oriented. If the absorption bands of this material are in fact blurred versions of the crystalline absorption bands, the amorphous OD band should exhibit dichroism when studied with plane-polarized radiation. Dichroism of this band in a highly oriented regenerated cellulose was observed several years ago during work with plane-polarized radiation<sup>22</sup>, but the results were not reported since their interpretation was not clear. In the frequency region corresponding to the two parallel type bands of crystalline material which characterize molecular form, the OD band showed parallel dichroism; however, there were no signs of any absorption peaks. This observation now seems to provide support for the view that part of the infra-red amorphous material shows bands which are a blurred version of the crystalline bands, at least in the high frequency region. It is reasonable to identify this material as that which is crystalline to X-rays but amorphous to infra-red.

### NATURE OF CRYSTALLINE MATERIAL

The crystallinity measurements show that 26 per cent of the viscose rayon film is crystalline towards both X-ray diffraction and infra-red spectroscopy. Study of the deuteration reaction shows, however, that this material must possess varying degrees of order.

It is known<sup>7-9</sup> that although this crystalline material deuterates slowly only a limited fraction can be deuterated, the remainder being extremely resistant towards deuteration. Work by Heritage at B.R.R.A. has shown<sup>24</sup> that OH groups in the crystalline oligosaccharides which are hydrogen bonded in the same way as the OH groups in crystalline regions of cellulose deuterate rapidly. The actual deuteration reaction seems to be extremely fast even with OH groups involved in a strong intramolecular hydrogen bond and in a non-polar environment, *e.g.* salicylic acid in carbon tetrachloride<sup>24</sup>. The slow rate of deuteration of crystalline OH groups in cellulose is a measure, therefore, of the rate of diffusion of D<sub>2</sub>O molecules into the crystals. Since a substantial fraction of these OH groups cannot be deuterated at all, however, it would seem that the deuteration must occur at regions of imperfection. Thus, the existence of varying degrees of perfection in the crystalline regions seems to be established by these observations, and a study of the detailed course of the deuteration of crystalline regions may throw further light on these imperfections.

Published measurements<sup>8,9</sup> suggest that between a quarter and a third of the infra-red crystalline material in viscose rayon films can be deuterated.

With bacterial cellulose this figure was found to be about 15 per cent. Recent work by Jeffries<sup>25</sup> at B.R.R.A., however, suggests that the fraction of the infra-red crystalline material which can be deuterated in viscose rayon films is higher than reported in the previous work, namely about 60 per cent.

### ORDER IN CELLULOSES

The measurements by X-ray diffraction and infra-red spectroscopy which have been outlined above show that four types of material which differ in the degree of orderly arrangement of molecular chains can be distinguished in celluloses. This statement applies to both regenerated and native celluloses, though a complete set of quantitative measurements has only been made on one viscose rayon film<sup>13</sup>. The four types of material are outlined below with reference to this rayon and the percentages of OH groups which show the different types of order.

(i) Material which is crystalline towards both X-ray diffraction and infra-red spectroscopy and which is inaccessible to water. This is the most perfectly ordered material and constitutes approximately 8 per cent by weight of the viscose rayon film.

(ii) Material which is crystalline to both X-ray diffraction and infra-red spectroscopy and is accessible to water. This may be termed imperfect crystalline material and constitutes approximately 17 per cent by weight of the viscose rayon film.

(iii) Material which is crystalline to X-ray diffraction and amorphous to infra-red spectroscopy. This material can be reasonably termed material of intermediate order, *i.e.* material which shows a degree of order intermediate between that of crystalline material and amorphous material. The molecular chains of this material are arranged in a regular crystalline manner, though the chains are somewhat distorted from the form characteristic of crystalline material and form hydrogen bonds of a continuous range of strengths. This material constitutes *at least* 13 per cent of the viscose rayon film, and our present knowledge of crystallite size is consistent with all this material lying in the surfaces of crystallites.

(iv) The remainder of the material is of unknown structure and may tentatively be called amorphous. The hydrogen bonds formed by this material are irregular and cover a continuous range of strengths. It is possible that some of the chains of this fraction may be arranged in an orderly way. This fraction constitutes *at most* approximately 62 per cent of the viscose rayon film.

These facts prove that the simple crystalline-amorphous concept of structure does not provide a close approximation of the true structure of celluloses. Four different degrees of order can be clearly distinguished and quantitatively measured by physical methods. This seems to provide strong support for the ideas on cellulose structure put forward by Howsmon<sup>14</sup>.

It has been stated earlier that since the long chain molecules pass through both crystalline and non-crystalline regions there cannot be an abrupt change from a high degree of order to complete disorder. Howsmon's suggestion is that in celluloses this transition is very gradual and a significant

proportion of the total material lies in the transition region. The curve relating quantity of material and degree of order is visualized as being continuous with two peaks, one relating to the highly ordered or crystalline material and one relating to the poorly ordered or amorphous material. The positions and shapes of both peaks are visualized as varying from one cellulose to another. Howsmon and Marchessault<sup>26</sup> have further suggested that the degree of order within the disordered or amorphous material can be described in terms of a distribution of hydrogen bond strengths.

The present measurements provide striking confirmation of two of Howsmon's predictions, namely the existence of material of intermediate order and differences between the distributions of hydrogen bond strengths of infra-red amorphous material in different celluloses. It should be remembered, however, that these facts can be accounted for in terms of the chains lying in the surfaces of crystallites, whereas it is an essential feature of Howsmon's view of structure that the material of intermediate order is located between the crystalline and amorphous regions. A closer estimate of X-ray crystallinity than is afforded by the minimum crystallinity method seems desirable in this respect.

### VALUE OF CRYSTALLINITY MEASUREMENTS

The validity and usefulness of measurements of crystallinity on celluloses is called into question by the results which have been discussed. The order present in celluloses cannot be characterized by a single quantitative measurement of crystallinity; indeed it must be admitted that even the term crystallinity cannot be defined in a unique way.

The usefulness of crystallinity measurements by a particular method depends entirely on how well we understand what aspect of structure it measures. The X-ray and infra-red methods which have been discussed at length must be regarded as the basic methods to which other techniques can be referred. The X-ray diffraction method is applicable to all types of material but demands expensive equipment and very careful experimental work. The infra-red method suffers from the severe limitation that it can be easily applied only to film samples. Of the other techniques which have been applied to cellulose, acid hydrolysis and water sorption seem, to the writer, to be the most useful.

Many variants of the acid hydrolysis technique have been described in the literature. The method of Sharples<sup>27</sup> in which the initial rate of hydrolysis is measured is probably the most fundamental of these. The quantitative results obtained from this method seem to be very similar to the crystallinities determined by X-ray diffraction using the assumption of a Cauchy distribution for the shape of crystalline reflections<sup>16</sup>.

The value of the water sorption method lies in its simplicity and in the fact that water sorption seems to be related to infra-red crystallinity<sup>28,29</sup>. It must be emphasized that an exact quantitative relation has not yet been established between these two quantities but there can be no doubt that water sorption and infra-red crystallinity show a parallel trend.

There can be little doubt that measurements of crystallinity will continue to play an important part in the study of cellulose structure and its relation to properties. The simple crystalline-amorphous concept also has its part

to play, despite the fact that the true structure of cellulose is more complex than this concept allows. Its value lies in its simplicity and it is unlikely to be abandoned until it is shown that another concept of structure is capable of giving a better *quantitative* account of cellulose properties.

## References

- <sup>1</sup> J. Mann, L. Roldan-Gonzalez, and H. J. Wellard. *J. Polymer Sci.* **42**, 165 (1960).
- <sup>2</sup> G. Honjo and M. Watanabe. *Nature* **181**, 326 (1958).
- D. G. Fisher and J. Mann. *J. Polymer Sci.* **42**, 189 (1960).
- <sup>3</sup> H. J. Wellard. *J. Polymer Sci.* **13**, 471 (1954).
- <sup>4</sup> D. W. Jones. *J. Polymer Sci.* **42**, 173 (1960).
- <sup>5</sup> P. H. Hermans and A. Weidinger. *J. Polymer Sci.* **4**, 135 (1949).
- <sup>6</sup> *Cellulose and Cellulose Derivatives* E. Ott and H. M. Spurlin, p. 251. Interscience Publishers (1954).
- <sup>7</sup> J. Mann and H. J. Marrinan. *Trans. Faraday Soc.* **52**, 481 (1956).
- <sup>8</sup> J. Mann and H. J. Marrinan. *Trans. Faraday Soc.* **52**, 487 (1956).
- <sup>9</sup> J. Mann and H. J. Marrinan. *Trans. Faraday Soc.* **52**, 492 (1956).
- <sup>10</sup> S. Nishikawa and S. Ono. *Proc. Phys.-Math. Soc.* **7**, 131 (1913).
- <sup>11</sup> P. H. Hermans and A. Weidinger. *J. Appl. Phys.* **19**, 491 (1948).
- <sup>12</sup> O. Ellefsen, E. W. Lund, B. A. Tonnesen, and K. Oien. *Saertrykh Narsk Skojindustri* **11**, 284, 349 (1957).
- <sup>13</sup> K. J. Heritage, J. Mann, and L. Roldan-Gonzalez. *J. Polymer Sci. in press.*
- <sup>14</sup> *Cellulose and Cellulose Derivatives* E. Ott and H. M. Spurlin, p. 277. Interscience Publishers, (1954).
- <sup>15</sup> *Die Physik der Hochpolymeren* H. A. Stuart, Springer-Verlag, Volume 3, p. 275 (1955).
- <sup>16</sup> J. Gjønnes, N. Norman, and H. Viervoll. *Acta Chem. Scand.* **12**, 489 (1958).
- <sup>17</sup> J. M. Goppel. *Appl. Sci. Research* A(1), 3 (1949).
- <sup>18</sup> S. M. Mukherjee and H. J. Woods. *Biochim. Biophys. Acta* **10**, 499 (1953).
- <sup>19</sup> B. Baule, O. Kratky, and R. Trear. *Z. Physik Chem. (Frankfurt)* **B50**, 255 (1941).
- <sup>20</sup> F. F. Morehead. *Textile Research J.* **20**, 549 (1950);  
A. Vogel. *Makromol Chem.* **11**, 111 (1953).
- <sup>21</sup> D. Heikens, P. H. Hermans, P. F. Van Velden, and A. Weidinger. *J. Polymer Sci.* **11**, 433 (1953).
- <sup>22</sup> J. Mann and H. J. Marrinan. *J. Polymer Sci.* **32**, 357 (1958).
- <sup>23</sup> C. G. Cannon. *Spectrochim. Acta* **10**, 341 (1958).
- <sup>24</sup> K. J. Heritage. To be published.
- <sup>25</sup> R. Jeffries. To be published.
- <sup>26</sup> J. A. Howsmon and R. H. Marchessault. *Textile Research J.* **27**, 30 (1957).
- <sup>27</sup> A. Sharples. *J. Polymer Sci.* **13**, 393 (1954).
- <sup>28</sup> L. Valentine. *Chem. & Ind. (London)* **1956** (1279).
- <sup>29</sup> J. A. Howsmon. *Textile Research J.* **19**, 152 (1949).