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Effect of Chemical Agents on the Fine Structure of Cellulose. Part II. The Action of Acetyl Chloride

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Synopsis

The action of acetyl chloride on the fine structure of regenerated cellulose (fiber and film) has been studied by infrared and x-ray techniques. The two techniques reveal different aspects of the fine structure and are therefore complementary. The changes found on acetylation appear to show that the molecular network theory is inadequate to describe the fine structure of the samples of regenerated cellulose studied. The observed effects can be explained more satisfactorily in terms of a structure in which highly oriented crystallites are interspersed with regions that are highly oriented but not as well ordered, resulting in a variation in density across the cross section.

INTRODUCTION

It is important to know what part the fine structure plays in chemical reactions on cellulose, and also to know how the fine structure changes with the progress of the reaction. In Part I[1] the fine structure of different forms of cellulose was discussed in relation to the methylation reaction with diazomethane; here observations are recorded of two forms of cellulose II in relation to the acetylation reaction with acetyl chloride in presence of pyridine. As before, the evidence is derived from x-ray and infrared measurements.

EXPERIMENTAL

Materials and Their Purification

Fortisan yarn and saponified cellulose acetate film were used to study the acetylation reactions. The Fortisan yarn was 45 den./170 fil. from British Celanese; the individual filaments were 5 μ in diameter, i.e. thin enough for the infrared work. Secondary cellulose acetate film, either commercial Clarifoil or film cast from acetone on a glass plate, was used, and saponified in 2% potassium hydroxide as described in Part I.

The Fortisan was loosely wound on small polyethylene bobbins to form hanks each about 0.1 g. in weight. Twenty of these small hanks were placed in a tall beaker just wide enough to take the hanks flat, each being separated from the next by a polyethylene spacer. The sheet material was sorted into batches 3–4, 6, 8, and 20 μ thick, and each batch

placed in a separate bottle. The Fortisan and the films were treated in 1.52*N* NaOH for 2–3 hr., care being taken to remove occluded air and to prevent the films from curling up. The sodium hydroxide solution was then poured off and the materials treated with saturated sodium chloride solution containing *N*/10 acetic acid for $^1/_2$ hr., after which the samples were thoroughly washed in water. The water was replaced by methyl alcohol, and then this was replaced by pyridine. The Fortisan and the films were left in pyridine until required.

Acetylation

A 1-g. portion of Fortisan and various cellulose films of different thicknesses were placed in a flask together with acetyl chloride and pyridine in molar ratio with the cellulose, and a quantity of specially dried benzene added as an inert diluent. The reaction was allowed to proceed at room temperature with gentle shaking, and at different intervals of time samples were removed from the reaction mixture. These samples were washed in pyridine and then washed in water and dried. Since the fibers and films were already swollen in pyridine before the addition of the acetylation mixture, it was expected that the reaction would take place in all the accessible regions of the cellulose ("quasi-homogeneous" reaction). Other samples were treated in a similar way, except that acetyl chloride was omitted, to act as blanks in subsequent experiments.

The acetyl contents were determined by the method of Nevell and Zeronian[2] and expressed in terms of the degree of substitution (complete acetylation = 3). The samples of Fortisan had degrees of substitution (D.S.) of 0.39, 0.82, and 1.05; the sheets had D.S. = 0.42, 0.9, 1.21, and 1.69.

Infrared Measurements

The infrared results were obtained both with films and with fiber layers prepared from the yarn by a method substantially the same as that described elsewhere.[3] The fiber layers were mounted between two sheets of aluminum foil, each with a cruciform aperture. This shape provided the maximum support for the layer consistent with the necessity of examining it, in two mutually orthogonal directions in the dichroic studies. The fiber layer samples were dried carefully and maintained their cohesion very well during the whole deuteration treatment.

The cell used for deuterating the samples, both films and fiber layers, was the same as in the methylation work.[1] Dichroism measurements were made with a silver chloride polarizer.[3]

Deuteration of Materials

This followed the same procedure as described in Part I,[1] except that some deuterations were carried out with the sample at the same (room) temperature as the D_2O supply to ensure that the relative humidity in the cell was 100%, rather than with the sample at the slightly higher temperature (25°C.) of the spectrometer sample compartment.

The difference technique employed in Part I was again used to determine the onset of deuteration in crystalline regions.

Measurement of Optical Path Length of Films

In Part I the effective film thickness—the optical path length—was measured by a β-gauge. In so doing it was assumed that the relation between the gauge reading and path length was independent of the degree of substitution (D.S.), and this was very probably correct to within the accuracy required by the experiment. In the present investigation, however, the β-gauge measurements proved to be of little use. This was shown by the fact that the relationship between C—H absorption and gauge reading changed enormously over the range of D.S. covered (0–1.21); moreover, by the fact that the changes were in the opposite sense to what might be accounted for by an increase in the C—H absorption due to the introduction of C—H groups by acetylation. Hence, to account for this effect it would appear that the relation between gauge reading and path length must vary with the degree of substitution.

In view of this drawback, and since the C—H absorption is not a suitable internal standard, no reliable estimate of path length is available.

Intensity Measurements of the Crystalline O—H Bands

Effect of C=O Overtone. Even at the highest D.S. (1.21) the C=O overtone (peak ca. 3480 cm.$^{-1}$ in secondary acetate) is of negligible intensity at the frequency of the most intense O—H band, viz., 3450 cm.$^{-1}$ and is of course even less significant at lower O—H frequencies.[4,5]

Effect of Changes in the Orientation of the (101) Planes. If the orientation of these planes relative to the sample surface changes from one sample to another, the intensity per hydroxyl group of the crystalline hydroxyl bands does not remain constant throughout the samples,[6] and the intensity of any one of the bands is not solely determined by the number of crystalline hydroxyl groups present. It was found by Mann and Marrinan,[6] however, that the intensity at ca. 3350 cm.$^{-1}$ does not suffer from this disadvantage, and can therefore be used as a measure of the crystalline hydroxyl groups.

X-ray measurements on the acetylated films used in the present infrared studies showed that the orientation in question did in fact change according to the degree of substitution (see later), whereas in the methylated films it was the same for different degrees of substitution.

X-Ray Measurements

The general details of the x-ray examination were similar to those described in Part I.[1] The Fortisan samples were made into standard 15 mg. bundles 1 in. long, and x-ray fiber photographs were recorded on a cylindrical camera ($R = 5.73$ cm.), and also on a flat-plate camera (film–specimen distance = 5.1 cm.), with crystal-reflected monochromatic copper Kα radiation. Equatorial scans of the fiber photographs taken with a

cylindrical camera were recorded with a microdensitometer, and azimuthal scans around the main equatorial arcs were recorded from the flat plate photographs. Before finally plotting the results, densities were converted to intensities I by reference to a calibration step-wedge imposed on each film; allowance was also made for the fog level of the film.

Although an attempt was made to standardize the x-ray exposure by means of a Goppel device, variable results were obtained. The cause of this variation seemed to be in the different packing densities of the bundles after chemical reaction, since results from the same bundle used on different occasions were in good agreement. In view of these difficulties it was decided to adjust the equatorial scans to have the same intensity for the $(10\bar{1} + 002)$ peak to aid comparison.

A smaller cylindrical camera (R = 3 cm.) was used for the cellulose films, which were made into a small cylinder and rotated during exposure to x-rays. The films were isotropic, and the powder-type photographs produced from them were measured along the equator with the microdensitometer. Again all scans were adjusted to agree in intensity on the $(10\bar{1} + 002)$ combined peak.

Since all the measurements were required for comparison only, it was not necessary to correct them for Lorentz and polarization factors.

RESULTS

Infrared

Films. In the absence of reliable measurements of optical path lengths (see above), there is no very satisfactory way of determining whether the crystalline regions are attacked during acetylation, for to do this a knowledge of the crystalline hydroxyl absorption per unit path length is required. However, it is noteworthy that the ratio of hydroxyl absorption at ca. 3350 cm.$^{-1}$ to the C—H absorption (2896 cm.$^{-1}$) is effectively constant (see Table I). This suggests, without being indisputable evidence, that the crystalline regions as detected by the infrared-deuteration method are not attacked, otherwise this ratio would decrease. It also implies that the contribution of the acetyl C—H groups to the absorption at 2896 cm.$^{-1}$ is not appreciable. In this connection, the ratio of the crystalline hydroxyl absorption at 3449 cm.$^{-1}$ to the C—H absorption increases with increase in degree of substitution. The 3449 cm.$^{-1}$ absorption is dependent on the orientation of the (101) planes, as was discussed above, and one possible explanation for an increase is that it is due to a re-orientation of these planes. Such changes in orientation were in fact detected by x-ray measurements on the films used in these infrared studies. Figure 1 shows the OH bands of the crystalline regions of the various partly acetylated samples; these bands are adjusted to give the same intensity at 3350 cm.$^{-1}$.

The OD bands of the films deuterated in the noncrystalline regions are shown in Figure 2; here the absorbance of each band has been scaled,

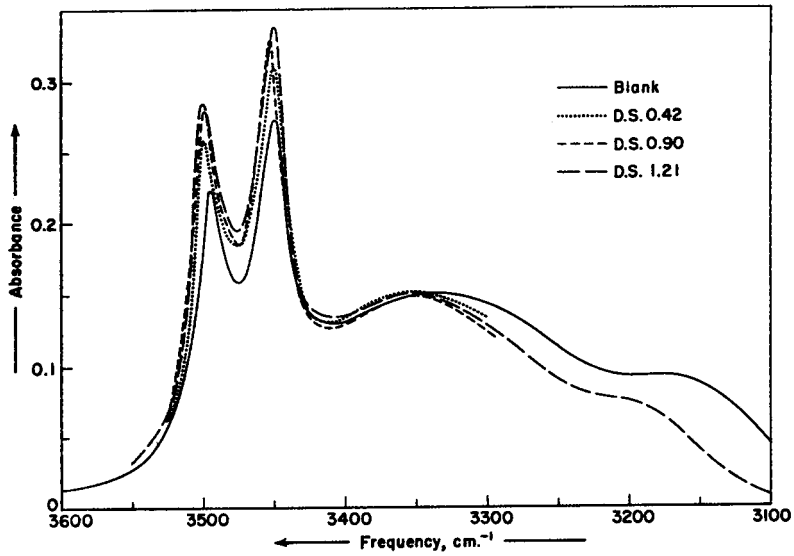


Fig. 1. Change in shape of the OH-stretching band of the crystalline regions detectable by infrared methods, as a result of partial acetylation. (To emphasize change in shape all absorbances have been scaled to give the same value at 3350 cm.$^{-1}$.)

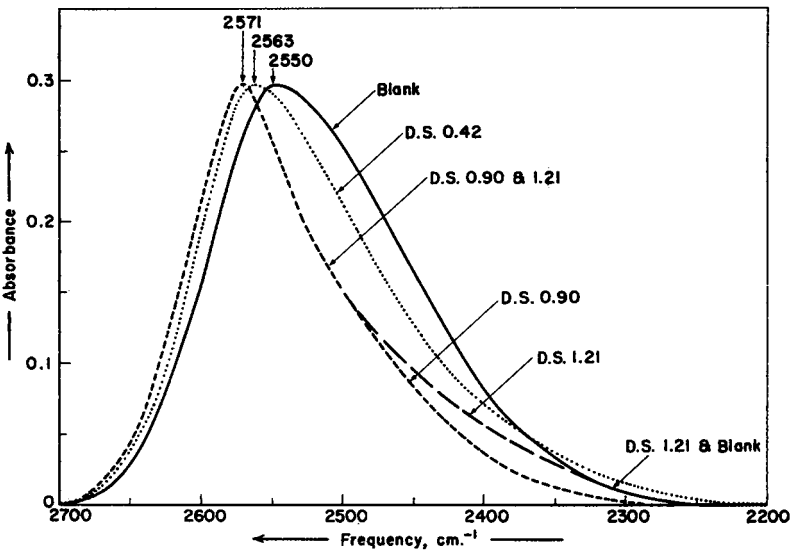


Fig. 2. The OD-stretching bands of the noncrystalline regions of the partially acetylated films (scaled to the same peak intensity).

this time to give the same peak value. The changes on acetylation are pronounced (see also Table I) and are very similar to those produced by methylation. Thus, in both sets of derivatives the OD band narrows and moves to higher frequencies as the degree of substitution increases. These changes again imply that the hydroxyl groups left in the noncrystalline

TABLE I
Measurement of Films Deuterated in the Noncrystalline Regions

Sample	D.S.	A_{OH} (cryst.)/A_{C-H}[a] 3449 cm.$^{-1}$	3350 cm.$^{-1}$	Peak frequency of OD band, cm.$^{-1}$	Half-band width of OD band, cm.$^{-1}$
Unacetylated cellulose (mean)	0	2.00	1.00	2550 ± 3	162
Acetylated cellulose	0.42	2.20	1.05	2563 ± 3	147
	0.90	2.35	1.00	2570 ± 3	118
	1.21	2.35	1.00	2575 ± 3	118

[a] A is the absorbance (optical density).

regions after acetylation are less strongly hydrogen-bonded than those in the noncrystalline regions of the original cellulose, and that the range of hydrogen-bond strengths is narrowed by acetylation. The extents to which these two effects occur are rather different, however, in the two sets of derivatives. The peak frequency of the OD band changes more in the acetylated celluloses than in the methyl derivatives, but the half-band width changes less rapidly. The greater change in peak frequency means that the hydrogen-bond system is weaker in the acetyl than in the methyl derivatives: this is in agreement with published infrared results on highly substituted cellulose derivatives.[5] The difference in the half-band width is also in agreement with these published results, but a complete explanation of the changes has not yet been found.

The changes in the OD band can be interpreted in three ways: (*a*) that the acetyl groups are evenly distributed in the noncrystalline regions and cause a gradual change in hydrogen-bond characteristics from those of regions containing only OH groups, to those of regions containing a preponderance of acetyl groups; (*b*) the characteristics of two regions may be superimposed, i.e., those of the noncrystalline regions with no acetyl content; (*c*) strain caused by the juxtaposition of the two types of regions discussed in (*b*); (*b*) and (*c*), of course, can occur together. In light of the x-ray evidence given later, the most probable explanation is that of (*b*), although (*c*) can also play a part.

The carbonyl frequency also increases steadily from 1743 cm.$^{-1}$ at D.S. = 0.42 to 1752 cm.$^{-1}$ at D.S. = 1.21, showing that hydrogen bonding to the carbonyl groups becomes progressively weaker.

Fibers. Table II refers to measurements on Fortisan fibers, sampled in the form of pressed fiber layers. Owing to unavoidable defects such as cracks in the samples and the relatively poor transmission in comparison to films, absorbances, and half-band widths are approximate only.

In spite of these limitations, the results clearly show that acetylation of the fibers produces the same effects in the OD band as did acetylation of films. It is also noteworthy that the hydrogen bonding of the acetyl groups becomes weaker as the degree of substitution increases, for the carbonyl stretching fre-

TABLE II
Measurement on Fibers Deuterated in the Noncrystalline Regions

Sample	D.S.	A_{OH} (cryst.)/A_{C-H}[a] 3447 cm.$^{-1}$	3345 cm.$^{-1}$	Peak frequency of OD band, cm.$^{-1}$	Half-band width of OD band, cm.$^{-1}$
Unacetylated	0	1.85	1.45	2545 ± 3	~185
Acetylated cellulose	0.39	1.90	1.30	2561 ± 3	~153
	0.82	1.95	1.35	2565 ± 3	~140
	1.05	2.00	1.45	2570 ± 3	~130

[a] A is the absorbance (optical density).

quencies in the three acetylated samples were 1742, 1745, and 1748 cm.$^{-1}$, corresponding to a D.S. of 0.39, 0.82, and 1.05, respectively. These values are very similar to those found in the film spectra (see above). Further, the intensity of the crystalline band at 3345 cm.$^{-1}$ (corresponding to 3350 cm.$^{-1}$ in the films) relative to the CH band again shows no trend with change of degree of substitution, whereas the relative intensity at 3447 cm.$^{-1}$ again increases with degree of substitution. This time, however, the increase is rather less than in the film spectra. The difference is possibly due to the more random orientation, relative to the sample surface, of the (101) planes in the fibers than in the films. It should also be mentioned that the dichroic ratio ($A_{\parallel}/A_{\perp}$) of the band at 3447 cm.$^{-1}$ also varies; as the degree of substitution increases so does the dichroic ratio. The significance of this is not clear, but it is quite possibly related to the orientation of (101) planes, because the dichroic ratio of this band was found to be even higher in stretch films. It should be noted that the orientation measured by this dichroic ratio is that of OH groups relative to the fiber axis, and not to the sample surface as was discussed previously in connection with (101) planes.

Orientation of Noncrystalline Regions Relative to the Fiber Axis

Measurements of the dichroic ratio (D.R.) of the OD band (2550 cm.$^{-1}$) showed a regular increase with degree of substitution, thus; D.S. = 0, D.R. = 1.0; 0.39, 1.2; 0.82, 1.4; and 1.05, 1.5. On the assumption that acetylation does not significantly affect the crystalline regions the increase in dichroic ratio indicates either (*1*) that the more random parts of the noncrystalline regions are acetylated first, and that as acetylation proceeds, the hydroxyl groups remaining in the noncrystalline regions are those that are more highly oriented, or (*2*) acetylation is accompanied by an increase in order of the region acetylated. Measurements of the dichroism of the carbonyl band did not yield any additional information. The dichroic ratio varied between 1.10 and 1.30 but was not related to the value of the degree of substitution. The absence of any such correlation is compatible with the changes in dichroism of the OD band, if these are interpreted as showing

that the acetyl groups enter the less oriented of the noncrystalline regions. The carbonyl group may also rotate about the C—O bond of the ester linkage and so allow the carbonyl bond to become random in direction.

X-Ray

Figure 3 shows the equatorial scans for the acetylated Fortisan samples compared with that for the original cellulose. As with the results on methylation, the main effect appears to be connected with the (101) planes. There is a progressive shift to lower values of 2θ and an increase in the diffracted intensity around 2θ = 8–9°. However, other changes are present that are not so evident from the scans as such.

By plotting the difference between the intensity at a given 2θ value for a given sample and that for the blank at the same 2θ value against 2θ, a difference scan is formed. These difference scans (Fig. 4) show common features. There is evidence for a peak in the region of 2θ = 9–10° and another at 2θ = 17–19°, with a possibility of an additional one at 2θ = 23–25°, although this is not shown on the difference curve for the sample of D.S. 1.05.

In the interpretation of difference scans several points have to be borne in mind. The two scans to be compared should be from samples with the same crystallite orientation, otherwise nonequatorial diffraction phenomena can, because of disorientation, appear on the equator of one scan, and be transferred to the difference scan. If this is suspected, allowance can be made if the orientation is known; alternatively, fully randomized samples can be used, although the resulting patterns will then be less informative. Again, if two scans are identical except for a slight difference in corresponding peak positions, the difference scan will show a series of peaks and troughs modified by the closeness of the peaks in the original scans. Finally, if a scale difference only exists between the scans, provided they are subtracted to give positive differences, a small reproduction of the original scan will be given on the difference scan.

If these possible features are taken into account then it would appear that the peaks at 9–10° and 17–19° occur because the acetylation reaction alters the structure of the sample. It should also be noted that evidence for these peaks appears even in the sample with the lowest degree of substitution, 0.39.

Evidence from the acetylated film is similar. Here the sheets were isotropic, and in consequence only powder-type diagrams were possible. As before, the scans were adjusted to the same intensity on the ($10\bar{1}$ + 002) peak. The results for the sample of D.S. 1.21 fell out of sequence, the exact reason being unknown; the general result, however, is identical with those for the rest of the samples, and can therefore be included in the discussion.

The evidence (Fig. 5) again shows the most prominent reaction to be such that the 101 peak is shifted in position and a new peak at 2θ = 9–10° is apparently starting to develop. Difference scans (Fig. 6) show peaks

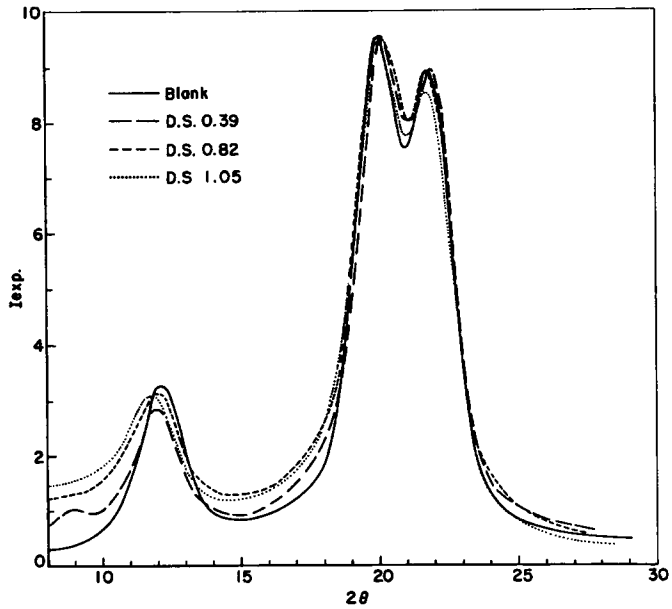
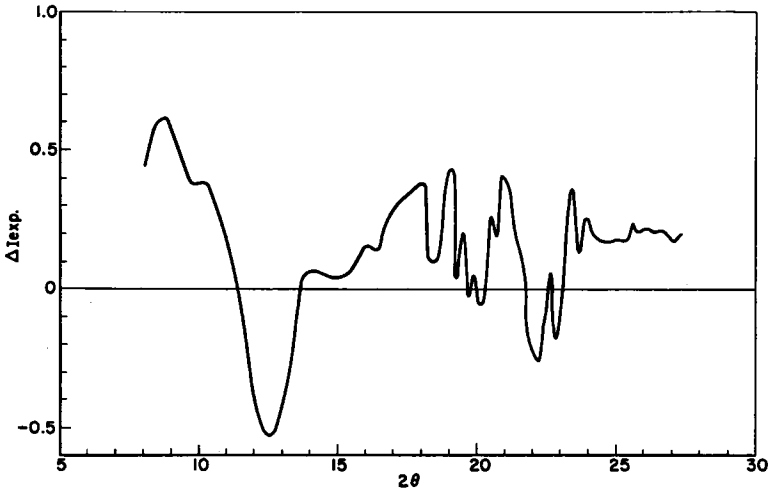


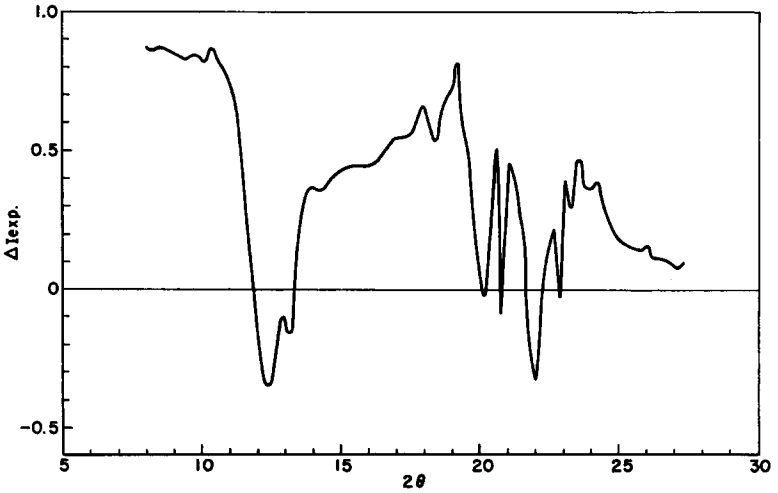
Fig. 3. X-ray equatorial intensity curves of Fortisan acetylated to different degrees.

developing in the regions 2θ = 9–10°, around 17° and 24–25°, i.e., in the same regions as found with treated Fortisan. A scan over an x-ray diagram from Tricel (Fig. 7), a commercial cellulose triacetate, shows a prominent peak at 2θ = 9–10°, and a broad hump that would include a peak at 2θ = 17° and a lesser peak at 2θ = 24°. On this diagram are shown also the positions of the equatorial reflections given by Hess and Trogus[11] (see also Sprague, Riley, and Noether[12]) for cellulose triacetate II. Even for a powder diagram the envelope would not be greatly different in this region because upper layer-line reflections that would overlap here are either weak or absent; hence the data from the isotropic films can also be fitted to these data. On comparing this scan with the difference scans, it seems quite evident that in basic features the two are alike, especially if the evidence from the acetylated sheet is taken into account.

It seems reasonably clear from this evidence that the cellulose triacetate structure is being formed in the fibers even in the samples with the lowest degrees of substitution. These results are quite unlike those given on methylation with diazomethane, where little evidence for a known methylcellulose was found even at the highest degree of substitution attained. There is, however, some similarity between the two systems, in that attack seems to take place preferentially in the (101) plane of the cellulose II structure. This fact is not surprising since both reactions attack the OH groups, and if the crystallites are to be attacked then the (101) planes are the very places at which such attack would be expected to take place. The difference between the mode of reaction in the two systems lies in the



(a)



(b)

subsequent processes. In the methylation of cellulose with diazomethane the solvent was ether saturated with water, which is not a solvent for the full reaction product, whereas in the acetylation processes pyridine was present, which is a potential solvent for the cellulose acetate. In consequence of the difference, further swelling of the material and the rearrangement of chains after reaction, are much more probable in acetylation than in methylation. It is suggested, therefore, that attack takes place in the noncrystalline regions, followed by rearrangement of the acetylated chains into the cellulose triacetate structure facilitated by the solvent action of the pyridine. If reaction had been continued long enough, a fibrous cellulose triacetate would have been formed, but for the purposes of this

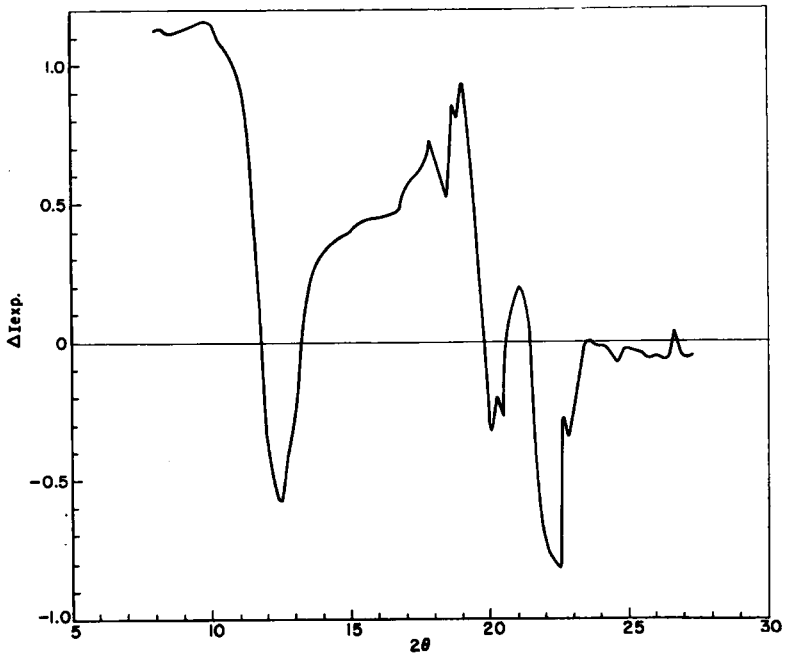


Fig. 4. X-ray difference curves for acetylated Fortisan: (*a*) *I* (D.S. 0.39) vs. *I* (blank); (*b*) *I* (D.S. 0.82) vs. *I* (blank); (*c*) *I* (D.S. 1.05) vs. *I* (blank). Δ *I* indicates the difference in the intensities.

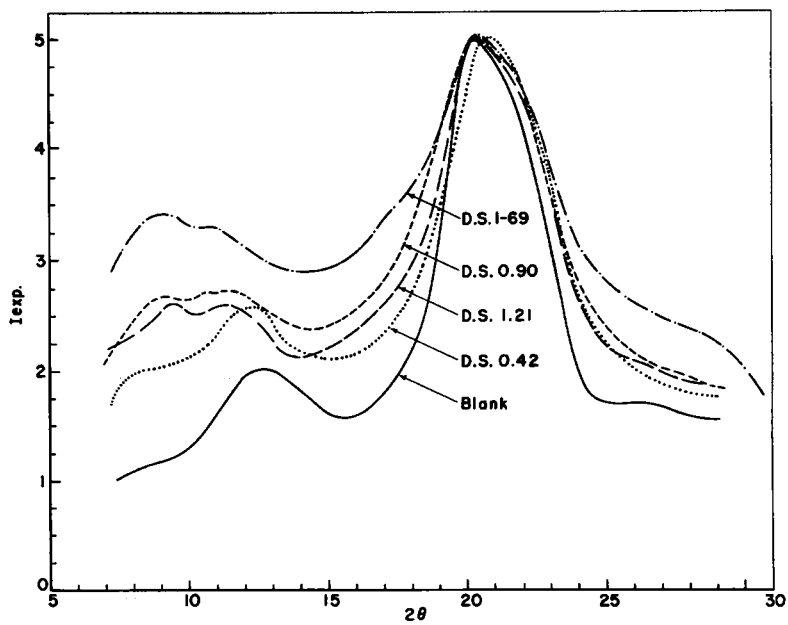


Fig. 5. X-ray equatorial scans for acetylated sheet cellulose.

study of fine structure the reaction was not carried so far. The role of the inert diluent in the reaction would therefore seem to be to restrict the swelling so that solution does not take place, and thus preserving the fibrous form of the sample. The type of acetylation found here is similar to that described by Happey,[7] where the chains in the noncrystalline regions are first acetylated and then by their swelling in the reactants the cellulose

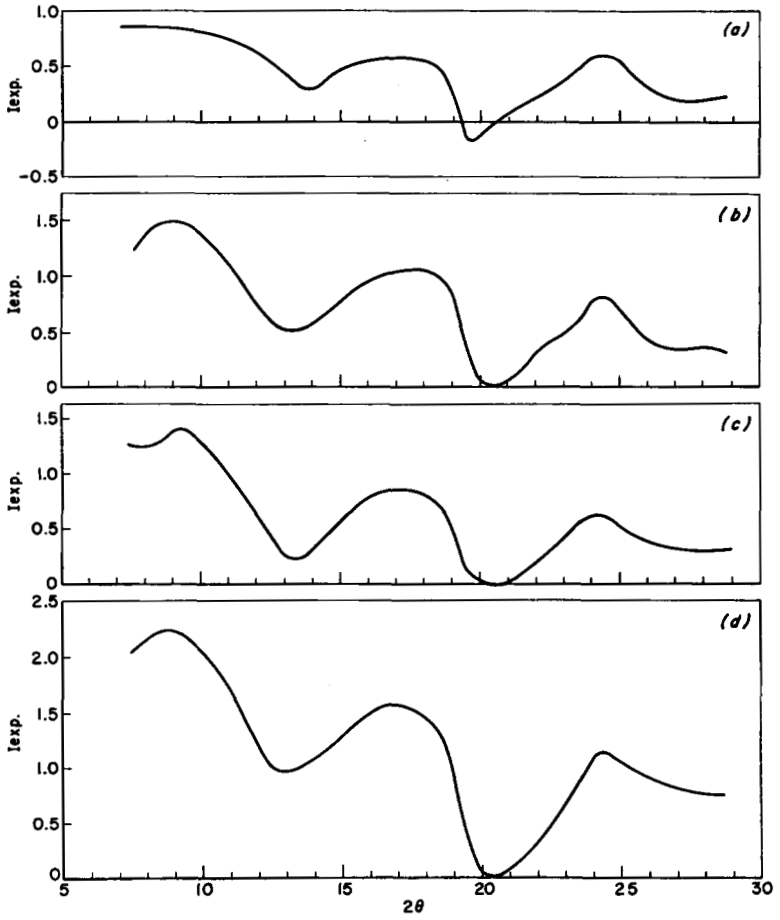


Fig. 6. X-ray difference scans for acetylated cellulose sheet: (*a*) *I* (D.S. 0.42) vs. *I* (blank); (*b*) *I* (D.S. 0.9) vs. *I* (blank); (*c*) *I* (D.S. 1.21) vs. *I* (blank); (*d*) *I* (D.S. 1.69) vs. *I* (blank).

structure is further opened to attack. It is thought, however; that not only do the acetylated regions swell but they also crystallize into the cellulose triacetate II structure.

From a study of the integral breadths of the azimuthal scans around the 101, 10$\bar{1}$, and 002 arcs of the acetylated Fortisan samples it was found that the orientation of these arcs was not greatly altered during the reaction.

The mean integral breadths were, D.S. 0.00, 15.5°; D.S. 0.39, 17.7°; D.S. 0.82, 15.8°; D.S. 1.05, 17.0°. These indicate that within the experimental error the change is small, perhaps a slight disorientation at the beginning of the reaction that does not progress as the reaction proceeds. These results are in full accord with the mechanism proposed, in which the chains on acetylation recrystallize into the cellulose triacetate structure wherever possible. The fact that the orientation is maintained reasonably constant therefore suggests that at no time do the chains curl up or go seriously out of general alignment. This would suggest that in Fortisan there are very few completely randomly disposed chains, and therefore there do not seem to be in Fortisan many, if any, amorphous regions, if we define by this term a region in which sections of chains can be found in

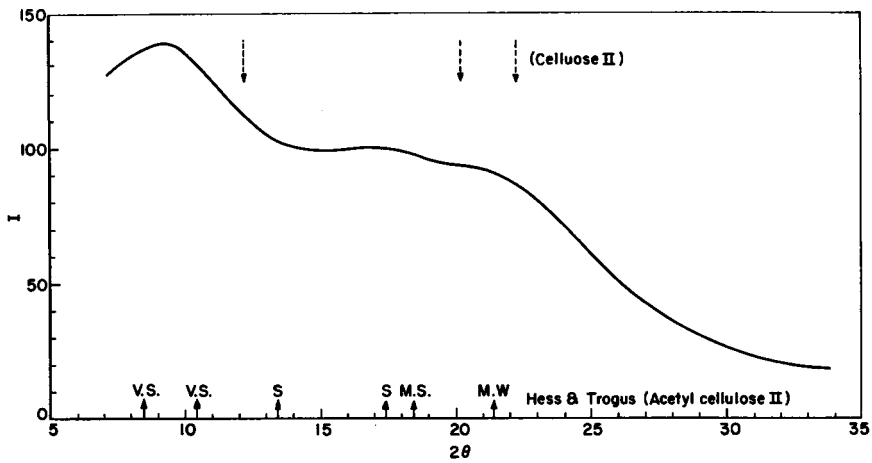


Fig. 7. X-ray equatorial intensity curve for Tricel.

all orientations. However, the evidence is confused by the fact that cellulose triacetate II has peaks in the region where the broad peak of an amorphous cellulose might be expected, that is, on the equatorial scans in the region of $2\theta = 20°$.[8] Against this, however, is the observation that the azimuthal scans around the principal equatorial arcs always descended to the fog level of the film. If any appreciable amorphous halo has been present this would not have happened for one or more of the scans. Furthermore it is also necessary to take into account the evidence from methylation that any randomly arranged material is small in relation to the bulk of the cellulose. Of course it is evident that there are noncrystalline regions, but these regions must have chains approximately parallel to one another but in the wrong position for three-dimensional order to be achieved. It is important to make this distinction between the terms "amorphous" and "noncrystalline" because the former term has a definite meaning in other branches of x-ray work.

DISCUSSION

The important finding of this study is that the rearrangement of the chains to form the crystalline cellulose triacetate II structure takes place at low degrees of substitution, and before any marked cellulose acetate reflection appears on the x-ray diagram of the product, i.e., the difference-scans are indicating these changes before they can be detected visually on the x-ray diagram. This is so both for Fortisan and for the isotropic film. It can thus be inferred that in Fortisan, and in localized regions of the isotropic film, the chains must be approximately parallel, and there must be freedom for the chains to crystallize into the cellulose triacetate structure.

Since evidence of the cellulose acetate structure is found for a degree of substitution as low as 0.4, and there is no infrared evidence for any acetylation of the crystalline regions, it would seem unlikely that the crystalline regions of the acetate are formed directly from those of cellulose II. This evidence implies that the chains not in crystalline regions are relatively free in the presence of a swelling agent to rearrange themselves on acetylation into another crystalline structure. If the structure proposed by Dulmage[9] for cellulose triacetate II is correct then quite considerable rotation of chains would be required. Sprague, Riley, and Noether,[12] however, claim that the structure proposed by Dulmage cannot be correct, since the density calculated from it is too low. Whatever view is taken, however, the fact remains that to form the cellulose triacetate II structure, chain movement is necessary on account of the size of the acetyl groups and the difference in intermolecular bonding between cellulose triacetate II and cellulose II. Furthermore, the achievement of the exact positions of the chains in three dimensions to form crystalline from noncrystalline regions will also require the chains to move lengthwise as well as laterally. Indication that chain movement takes place is shown by the increase in cross-sectional area of the fibers on acetylation, as found by Vermaas and Hermans[13] for rayon and by Tripp, Giuffria, and De Gruy[15] for cotton.

These molecular rearrangements, which are necessary to achieve the formation of the cellulose triacetate II structure at low degrees of substitution, are not readily compatible with the commonly held view of regenerated cellulose structure. This view is that the structure of regenerated cellulose is one of a network of chains held together at junction points that are themselves either crystalline regions or near-crystalline regions, and hence have high cohesive energy. The chains between these junction points, i.e., in the noncrystalline material, are more randomly arranged, and one chain may enter several such regions as well as crystalline regions, because its length is much greater than any individual region. Such a view is sometimes referred to as the molecular network theory and has been used as a basis for following the acetylation reaction in rayon.[13,14] The inadequacy of this structure with the present evidence

arises from the fact that the locking of parts of the chain in crystalline regions would tend to prevent the necessary molecular rearrangements of the reacted portion between the crystalline regions. This would be especially pronounced for highly oriented structures, and it is thus suggested that for Fortisan, at least, the accessible noncrystalline cellulose runs parallel to the more ordered crystalline regions and, although these regions are independent of the crystalline regions, some merging with them must take place to some extent at the boundaries. Kaeppner[16] has recently shown by electron-microscopical evidence that such a structure is very probable for Fortisan. In such a system outlined for Fortisan, the movement of chains and recrystallization to the cellulose triacetate structure would then be possible in the noncrystalline and near-crystalline regions running parallel to the crystalline regions, facilitated by the pyridine. A similar structure might also be present in film, since similar x-ray and infrared data were obtained.

Some further support for these ideas on the fine structure of cellulose II is obtained from consideration of the methylation reaction discussed in Part I,[1] where some evidence for the formation of methyl cellulose was obtained with cellulose II samples methylated to a low degree of substitution. Furthermore, if a swelling agent is present in the methylation reaction, as was present in the experiments of Hess et al.,[10] then there is clear evidence of rearrangement of mercerized ramie to a new crystalline structure at low degrees of substitution. However, although it is believed that the structure is plausible for Fortisan and some other samples of cellulose II, it cannot be claimed, without further work, that it is a general structure for all systems in which crystallites of cellulose II are formed. Each sample of cellulose must be considered on its own merits, and it is conceivable that the molecular network theory is valid for other samples of cellulose II.

These experiments have shown that by a combination of infrared and x-ray methods it is possible to form a clearer view of the fine structure of cellulosic materials. It is believed that an extension of this approach is likely to yield more insight into fine structure than conventional measurements of the crystalline/amorphous ratio carried out by x-ray or infrared methods. Indeed such measurements imply a fine structure rather than reveal its true nature.

This new approach is at the moment exploratory. It is hoped that as more clarified ideas on fine structure are found, models of the proposed structures can be set up and then be tested by mathematical or optical diffraction methods.

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References

1. Spedding, H., and J. O. Warwicker, *J. Polymer Sci.*, **A2**, 3933 (1964).
2. Nevell, T. P., and S. H. Zeronian, *Polymer*, **3**, 187 (1962).
3. Cumberbirch, R. J. E., and H. Spedding, *J. Appl. Chem.*, **12**, 83 (1962).
4. Jeffries, R., private communication.
5. Jeffries, R., *Polymer*, **4**, 375 (1963).
6. Mann, J., and H. J. Marrinan, *Trans. Faraday Soc.*, **52**, 492 (1956).
7. Happey, F., *J. Textile Inst.*, **41**, T381 (1950).
8. Ellefsen, Ø., E. W. Lund, B. A. Tønnesen, and K. Øien, Meddelelse NR 87 Fra Papindustriens Forskninginstitutt (Oslo 1957).
9. Dulmage, W. J., *J. Polymer Sci.*, **26**, 277 ((1957).
10. Hess, K., C. Trogus, W. Eveking, and E. Garthe, *Ann.*, **506**, 260 (1933).
11. Hess, K., and C. Trogus, *Z. Physik. Chem.*, **B5**, 161 (1929).
12. Sprague, B. S., J. L. Riley and H. D. Noether, *Textile Res. J.*, **28**, 275 (1958).
13. Vermaas, D., and P. H. Hermans, *J. Polymer Sci.*, **2**, 397 (1947).
14. Vermaas, D., P. H. Hermans, and A. Weidinger, *J. Polymer Sci.*, **2**, 406 (1947).
15. Tripp, V. W., R. Giuffria, and I. V. De Gruy, *Textile Res. J.*, **27**, 14 (1957).
16. Kaeppner, W. M., *Tappi*, **46**, 637 (1963).

Résumé

On a étudié par infra-rouge et aux rayons-X l'action du chlorure d'acétyle sur la structure fine de la cellulose régénérée (en fibre et en films). Les deux techniques révèlent différents aspects de la structure fine et sont donc complémentaires. Les changements observés lors de l'acétylation semblent montrer que la théorie du réseau moléculaire ne convient pas pour décrire la structure fine des échantillons étudiés de cellulose régénérée. On peut expliquer les effets observés d'une façon plus satisfaisante si on considère une structure dans laquelle les cristallites parfaitement orientés sont entremelés avec des régions bien orientées, mais pas aussi bein ordonnées, ce qui provoque une variation de densité à travers la section transversale.

Zusammenfassung

Der Einfluss von Acetylchlorid auf die Feinstruktur von regenerierter Zellulose (Faser und Film) wurde mit Infrarot- und Röntgenverfahren untersucht. Die beiden Methoden zeigen verschiedene Aspekte der Feinstruktur und ergänzen einander daher. Die bei der Acetylierung auftretenden Veränderungen scheinen zu zeigen, dass die Molekülnetzwerktheorie zur Beschreibung der Feinstruktur der untersuchten Proben von regenerierter Zellulose nicht geeignet ist. Die beobachteten Effekte können besser mit einer Struktur erklärt werden, bei welcher hochorientierte Kristallite mit hochorientierten, aber nicht so gut geordneten Bereichen abwechseln, was zu einer Variierung der Dichte über den Querschnitt führt.

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