

Further Studies on Cellulose III Polymorphs. Transformations to Cellulose IV Lattices and Subsequent Reactions

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Synopsis

Production of cellulose IV polymorphs, their characterization using X-ray diffraction and infrared spectroscopy, as well as the effect of chemical treatments on these polymorphs have been investigated. Cellulose III_I and III_{II} polymorphs, produced from celluloses I and II using EDA—MeOH treatments, were of particular interest as starting materials in the study. Celluloses IV_I and IV_{II} gave identical equatorial X-ray patterns in the absence of other crystal lattices in the samples. Crystallinity as well as conformation were indicated to influence production and further reactions of the samples. The latter included boiling in water, acid hydrolysis, and treatments with EDA—water, EDA—MeOH, and NaOH solutions. Cellulose IV_I → I, IV_I → I → II, and cellulose IV_{II} → II lattice conversions were demonstrated to occur with EDA—water treatments, thereby providing a new technique for observing these transformations. Conformational differences were apparent among celluloses I, II, III_I, and III_{II}, each produced using different experimental procedures.

INTRODUCTION

Earlier work carried out at our laboratories¹ had indicated certain differences between the radial X-ray diffraction (XRD) patterns of celluloses III_I and III_{II}, prepared by treating natural and mercerized cotton (or ramie) fibers, respectively, with ethylenediamine (EDA) and removing the swelling agent with methyl alcohol (MeOH). The main objective of the present study was to find out whether such differences persist in the XRD patterns of celluloses IV_I and IV_{II} produced using the above cellulose III polymorphs as starting materials. In this context, different procedures were tried to achieve maximum cellulose IV lattice conversion. In addition, a few studies were conducted on the response of the cellulose IV materials to certain selected chemical treatments. Results of these investigations are reported in the present paper.

EXPERIMENTAL

Preparation of Samples

Preparations of cellulose III_I and cellulose III_{II} samples have been described in an earlier publication.¹ Cellulose III_{II} from viscose for the present work was also prepared using essentially the same procedures.

Methods of production of cellulose IV have been recently reviewed by Kulshreshtha.² In the present study, in addition to direct boiling of celluloses I, II

(mercerized cotton or viscose), III_I, and III_{II} (from mercerized cotton or viscose) in glycerol at 260°C, the following variations were also used: (1) presoaking of the samples in glycerol before heat treatment, as described by Loeb and Segal³; (2) presoaking of the samples successively in water, MeOH, and glycerol and then boiling in glycerol, as described by Hermans and Weidinger⁴; (3) presoaking in NaOH, washing with glycerol and boiling in glycerol, as described by Cabradilla and Zeronian⁵; (4) presoaking in EDA, decomposing with DMF and boiling in DMF, as described by Segal⁶; and (5) presoaking in EDA, washing with glycerol, and boiling in glycerol.

After heat treatment in glycerol, the samples were washed with MeOH and air-dried.

Recording XRD Patterns and Infrared Spectra

The XRD patterns were obtained using Cu K_α radiation following procedures described in detail in an earlier paper.

Infrared spectra were recorded in KBr matrix using a Perkin-Elmer Model 457 grating spectrophotometer, under normal slit programme and slow scan mode. Fiber samples were finely cut with scissors, about 2 mg of the cut powder mixed with 120 mg of KBr and pellets prepared for recording the spectra. Absorption intensities were measured by the usual base line technique.

Lattice Conversion and Crystallinity Estimations

The ratio of the intensity at about $2\theta = 15.5^\circ$ (101, 10 $\bar{1}$ peaks of cellulose IV_I) to that at about $2\theta = 11.8^\circ$ (101 peak of cellulose III_I) was used as an index to estimate cellulose III_I → cellulose IV_I lattice conversion. The above index is similar to that employed by Hermans and Weidinger⁴ for evaluating cellulose II → cellulose IV lattice conversion through the ratio of the intensity at $2\theta = 15.5^\circ$ to that at about $2\theta = 12.0^\circ$. The same index could be used for assessing the cellulose III_{II} → cellulose IV_{II} lattice conversion also.

Where an estimate of cellulose I → cellulose IV_I transformation was required for comparison purposes, the ratio of the intensity at $2\theta = 15.5^\circ$ to the sum of the intensities at about $2\theta = 14.8^\circ$ and $2\theta = 16.5^\circ$ was used. The intensities were measured above a background line connecting $2\theta = 10.0^\circ$ and $2\theta = 18.0^\circ$ in the diffractograms. Because of the comparatively better resolution of the (101), (10 $\bar{1}$) peaks for cellulose I, this index would increase with higher transformation to cellulose IV_I.

The crystallinity index (CI) evolved by Segal *et al.*⁷ is one of the simplest measures available for comparison of crystallinities of samples with cellulose I lattice structure. Earlier work⁸ had indicated that this index may well be related to comparatively more absolute measures of crystallinity in systems consisting of cellulose I and amorphous phases. During the present investigations, it was noticed that the same CI can be used for comparing crystallinities in systems containing cellulose I, cellulose II, and amorphous phases. The relationships observed between the total crystallinities of such systems (calculated for various mixtures of pure cotton and mercerized cotton, using values reported for these samples in the literature⁹) and the CI values measured from the x-ray scans are shown in Figure 1. It may be inferred from the figure that CI can be used to compare the crystallinities of samples belonging to each system. Use

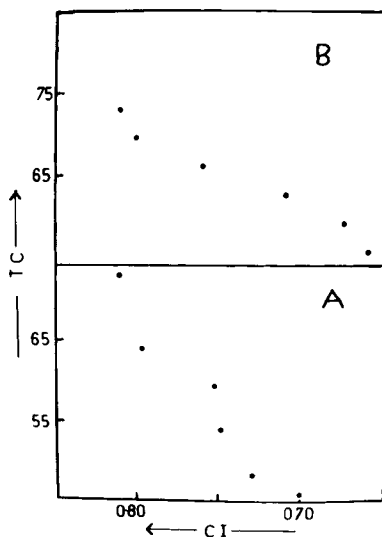


Fig. 1. Relationship between crystallinity index (CI) and total crystallinity (TC). (A): (Cellulose I + Amorphous) system, (B): (Cellulose I + Cellulose II + Amorphous) system.

of CI for comparing samples belonging to the different systems, however, would not be justified, as a particular value of CI would not imply the same crystallinity in such cases.

The types of diffraction patterns usually obtained while studying cellulose III and cellulose IV polymorphs are similar to those of either of the systems discussed in the preceding paragraph. Therefore, the use of CI has been extended to cellulose polymorphs other than cellulose I in the present work, for comparing crystallinities of samples with the same lattice type or the same mixture of lattice types.

Crystallinity values of the samples were also computed from their infrared spectra using the ratios of absorbances of (i) the 1372 cm^{-1} band and 2900 cm^{-1} band¹⁰ and (ii) the 342 cm^{-1} band and 2900 cm^{-1} band.¹¹ The latter index has been shown to be very sensitive to small changes in crystallinity, and both the indices have been shown to be useful for comparison of samples with either the cellulose I or the cellulose II lattice structure.

RESULTS AND DISCUSSION

Production of Cellulose IV Polymorphs

The lattice conversions of different starting materials, brought about by heat treatment in glycerol, are given in Table I. The data on the effect of different pretreatments prior to heating in glycerol are also presented in the table.

It may be seen from the results that it was very difficult to achieve a substantial transformation of native cotton fibers into cellulose IV_I. Out of the different pretreatments used, the maximum conversion was obtained when cotton fibers were decrystallized using EDA or were subjected to treatments with EDA and DMF. Presoaking in NaOH gave a substantially higher conversion index, but in this case the final product was cellulose IV_{II}.

With mercerized cotton fibers, the trend of results was more or less identical

TABLE I
Production of Cellulose IV Polymorphs

Starting material and treatment	Conversion index to	
	IV _I	IV _{II}
<i>Cellulose I (native cotton)</i>		
No treatment ^a	0.41	—
Boiled in glycerol ^b	0.44	—
Presoaked in glycerol	0.42	—
Presoaked in H ₂ O, MeOH, and glycerol successively	0.48	—
Presoaked in 24% NaOH, washed in glycerol	—	2.17
Presoaked in 80% EDA, treated with DMF, and boiled in DMF	0.53	—
Presoaked in 80% EDA, washed in glycerol	0.61	—
Treated with 80% EDA, washed with water, air-dried	0.60	—
<i>Cellulose III_I (cotton)</i>		
No treatment ^a	0.81	—
Boiled in glycerol ^b	2.85	—
Presoaked in glycerol	3.19	—
Presoaked in H ₂ O, MeOH, and glycerol successively	2.92	—
Presoaked in 24% NaOH, washed in glycerol	—	2.09
Presoaked in 80% EDA, treated with DMF, and boiled in DMF.	2.85	—
Presoaked in 80% EDA, washed with glycerol	2.45	—
<i>Cellulose II (mercerized cotton)</i>		
No treatment ^a	—	0.73
Boiled in glycerol ^b	—	0.73
Presoaked in glycerol	—	0.83
Presoaked in H ₂ O, MeOH, and glycerol successively	—	0.89
Presoaked in 24% NaOH, washed in glycerol	—	1.38
Presoaked in 80% EDA, treated with DMF and boiled in DMF	—	1.23
Presoaked in 80% EDA, washed in glycerol	—	1.07
<i>Cellulose III_{II} (cotton)</i>		
No treatment ^a	—	0.63
Boiled in glycerol ^b	—	0.73
Presoaked in glycerol	—	0.81
Presoaked in H ₂ O, MeOH, and glycerol successively	—	0.93
Presoaked in 24% NaOH, washed in glycerol	—	1.00
Presoaked in 80% EDA, treated with DMF and boiled in DMF	—	1.33
Presoaked in 80% EDA, washed in glycerol	—	1.04
<i>Cellulose II (viscose)</i>		
No treatment ^a	—	1.00
Boiled in glycerol ^b	—	1.67
Presoaked in glycerol	—	2.60
Presoaked in 24% NaOH washed in glycerol	—	2.30
<i>Cellulose III_{II} (viscose)</i>		
No treatment ^a	—	1.00
Boiled in glycerol ^b	—	1.60
Presoaked in glycerol	—	1.90
Presoaked in 24% NaOH, washed in glycerol	—	1.76

^a indicates the control sample.

^b indicates boiling for 30 min in glycerol without pretreatment. All other samples were boiled in glycerol for 30 min, after specified pretreatments.

to that obtained with native fibers. However, it was noticed that presoaking the latter in NaOH prior to heat treatment was more efficient than presoaking mercerized fibers in NaOH in achieving lattice transformation to cellulose IV_{II}.

With viscose as the starting material, it was obvious even during preliminary

experiments that this material could be easily converted into cellulose IV_{II}. Hence, the effect of pretreatments were not studied in detail with this material. Nevertheless, it may be observed from Table I that pretreatment with glycerol or NaOH were more or less equivalent as far as the conversion achieved, was concerned. Further, pretreatment with these media gave a higher conversion than that obtained without any presoaking of viscose. It may also be noted that the quantity of cellulose IV_{II} produced by giving pretreatment in NaOH was of the same order as that obtained with identical treatment on native cotton fibers.

As mentioned in the Introduction, our interest in the present study was more on the production of cellulose IV lattice structures from cellulose III structures, and the above studies with starting materials having cellulose I and cellulose II lattices were conducted mainly to obtain guidelines to achieve the maximum conversions of III_I→IV_I and III_{II}→IV_{II}.

The conversion index obtained for cellulose III_I may be noted to be considerably higher than that for cellulose I. Variations in pretreatments did not alter the index substantially, similar to the results obtained with native fibers. A cellulose IV_I sample, with a conversion index value 3.78, obtained by heat treatment of cellulose III_I for 1 h (it was verified that increasing the time further did not improve the conversion) was ultimately chosen for further studies on this polymorph. This sample may be considered to be almost completely converted cellulose IV_I (cotton). The XRD pattern of this sample is given in Figure 2. Presoaking in NaOH yielded quantitatively the same amount of cellulose IV_{II} as that from native fibers, similarly pretreated.

As regards the III_{II} → IV_{II} conversions, it may be seen that, contrary to the results obtained with cellulose I and cellulose III_I, using cellulose III_{II} (cotton) had very little advantage over mercerized cotton. The maximum production of cellulose IV_{II} from cellulose III_{II} resulted when cellulose III_{II} (viscose) was used as the starting material. While a fairly good conversion into cellulose IV_{II}, with a conversion index of 2.80, could be achieved by boiling cellulose III_{II} (viscose) for 1 h, the index remained practically the same whether cellulose III_{II} (cotton) was boiled for 30 min or 1 h.

The XRD patterns of cellulose III_{II} were identical, whether the sample had mercerized cotton or viscose as its precursor. This pattern showed two diffraction maxima at 2θ values 12.0° and 20.8° . The maximum at 20.8° (2θ), which was resolved into two peaks centered at about 20.5° (2θ) and 21.3° (2θ) by using cold MeOH for treatment,¹ could be brought about in the XRD pattern of III_{II} (viscose) also by treating it with dilute ammonia solution (32%, w/w of NH₃), although use of cold MeOH did not bring about this clear resolution as in the case of III_{II} (cotton). This fact indicates that the resolution of the peak at $2\theta = 20.8^\circ$ is probably decided by the lateral order in the material. In view of the above, and due to the ease with which conversion into cellulose IV_{II} could be achieved, the cellulose IV_{II} sample prepared from cellulose III_{II} (viscose) was used for further studies. The XRD pattern of this sample is given in Figure 2.

A good cellulose IV_{II} sample could not be prepared from cellulose III_{II} (cotton). In view of the substantial conversion obtained from NaOH-presoaked native cotton into cellulose IV_{II}, the polymorph thus produced appeared to be the best alternative. Heat treatment in glycerol of NaOH-presoaked cotton for 30 min or 1 h gave cellulose IV_{II} with the same conversion index (ca. 2.17). The XRD

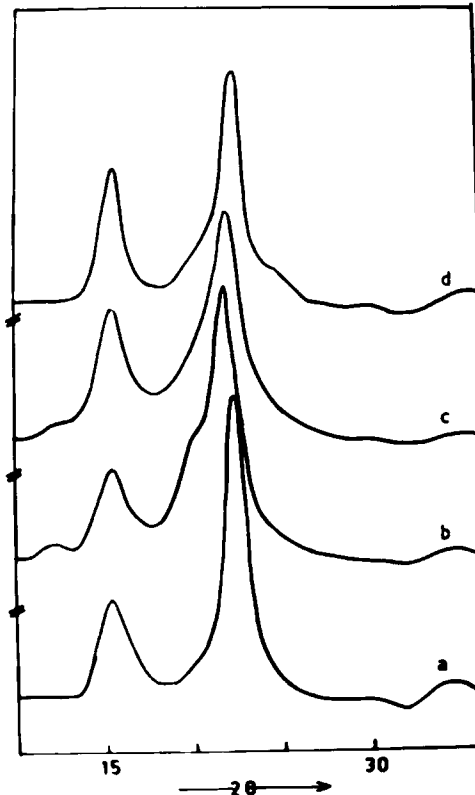


Fig. 2. XRD patterns of (a) IV_I after boiling III_I for 1 h, (b) IV_{II} after boiling III_{II} (viscose) for 1 h, (c) IV_{II} after boiling NaOH pretreated native cotton fibres for 1 h, and (d) same as (b) but after boiling for 6 h.

pattern of this sample (Fig. 2) indicated some presence of cellulose II; however, since its amount was negligible in comparison with the quantity of cellulose IV_{II} in the sample, it was accepted to represent cellulose IV_{II} produced from cotton for further studies. That the polymorph was cellulose IV_{II} was decided from its meridional XRD scans.

Additional attempts were also made, by increasing the time of heat treatment, to find out whether cellulose IV_I and cellulose IV_{II} samples with higher conversion indices could be prepared. The $III_I \rightarrow IV_I$ conversion was not substantially enhanced by this approach. On the other hand, the III_{II} (viscose) sample showed

TABLE II
Characterization of Radial XRD Scans of Cellulose IV Samples

Sample	Half-maximum breadth		R'
	$[(101), (10\bar{1})]$	(002)	
IV_I (cotton) ^a	2.00°	1.35°	0.44
IV_{II} (cotton) ^a	1.80°	1.80°	0.44
IV_{II} (viscose) ^a	1.65°	1.80°	0.65
IV_{II} (viscose) ^b	1.35°	1.35°	0.66

^a After heat treatment of parents for 1 h.

^b After heat treatment of parent for 6 h.

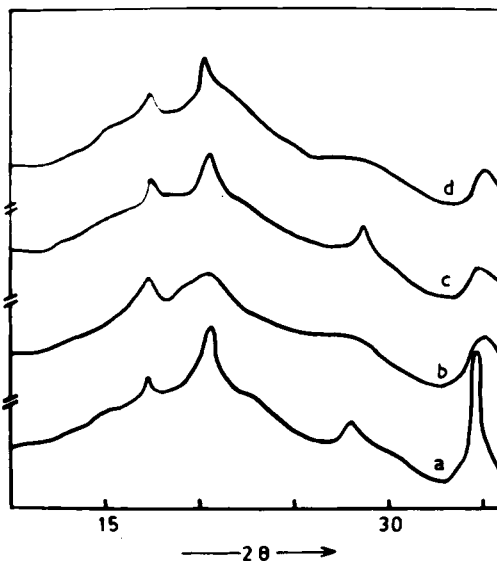


Fig. 3. Meridional XRD patterns of (a) IV_I after boiling III_I for 1 h, (b) IV_{II} (viscose) after boiling III_{II} for 1 h, (c) IV_{II} (cotton) after boiling NaOH pretreated native cotton fibres for 1 h and (d) same as (b) but after boiling for 6 h.

progressive increase in conversion with time of treatment, and a very good cellulose IV_{II} sample with a conversion index value 19.25 could be obtained by boiling the III_{II} parent for 6 h. The XRD pattern of this sample, also given in Fig. 2, did not contain any visible evidence for remnants of cellulose III_{II} and appeared to indicate completely converted cellulose IV_{II} . It may, however, be mentioned that this sample became very brittle, while the samples obtained after boiling for 1 h retained their fibrous nature.

It may be added in this context that increasing the period of heat treatment up to 6 h did not enhance production of IV_{II} from native cotton fibers which were pretreated in NaOH solution.

Characterization of Cellulose IV Lattice Structures

The XRD pattern of cellulose IV_I obtained by boiling cellulose III_I for 1 h consisted of the combined $(101, 10\bar{1})$ maximum at $15.5^\circ (2\theta)$, and the (002) maximum at $22.3^\circ (2\theta)$. The (040) peak could be discerned clearly in its XRD pattern (Fig. 2). In the case of cellulose IV_{II} (viscose) as well as cellulose IV_{II} (cotton), prepared with identical boiling time, the above maxima were located at $15.5^\circ (2\theta)$ and $22.0^\circ (2\theta)$, respectively. These observations are in general agreement with the findings of Segal.⁶ Further, the (040) reflection was weaker in the case of the IV_{II} samples.

The breadths at half maximum intensity of the $(101, 10\bar{1})$ peak was measured above a base line connecting $10^\circ (2\theta)$ and $18^\circ (2\theta)$, and that of the (002) peak above a base line connecting $18^\circ (2\theta)$ and $30^\circ (2\theta)$ from the XRD scans. The values thus obtained for the above IV_I (cotton), IV_{II} (cotton) and IV_{II} (viscose) cellulose samples are given in Table II.

The relative intensity ratio R' of the $(101, 10\bar{1})$ peak to the (002) peak for the above samples are also included in this table. It may be noted that the IV_I

TABLE III
 Characterization of Cellulose Polymorphs by Infrared Spectra

Infrared absorption band (cm ⁻¹)	I (cotton)	III _r (cotton)	IV _r (cotton)	II (cotton)	III _l (cotton)	IV _l (cotton)	II (viscose)	III _l (viscose)	IV _l (viscose)	Distinction between
2920 } 2900 } 2880 }	2900 band strongest, followed by 2880 & poorly defined 2920 bands	2900 band strongest, followed by 2880 & poorly defined 2920 bands	2900 band strongest, followed by 2880 & poorly defined 2920 bands	2880 band strongest, followed by 2920 bands	2880 band stronger than 2900 band; 2920 band poorly defined	Only 2880 band clear	2880 band stronger than 2920 band; 2900 band poorly defined	Equally strong 2880 and 2900 bands; 2920 band poorly defined	Equally strong 2880 and 2920 bands; 2900 poorly defined	(see text)
1440 } 1420 } 1330 } 1310 }	Only 1420 band clear Both bands equally strong	Only 1420 band clear 1310 band stronger	Only 1420 band clear Both bands equally strong	Only 1420 band clear 1310 band stronger	Only 1420 band clear 1310 band stronger	Both bands equally strong	Only 1420 band clear Both bands equally strong	Only 1420 band clear Both bands equally strong	Both bands equally strong 1330 band stronger	IV _r (cotton) & IV _l (cotton) III _r (cotton & IV _r (cotton) III _l (cotton) & IV _l (viscose) & IV _l (viscose) IV _l (cotton) & IV _l (viscose) (see text)
1280 } 1260 } 1230 }	1280 band stronger, followed by 1230 & 1260 bands	1230 band stronger, followed by 1280 & 1260 bands	Equally strong 1230 & 1280, followed by 1260 & poorly defined 1260 band	1230 band strongest, followed by 1280 & 1260 bands	1230 band strongest, followed by 1280 & 1260 bands	1230 band strongest, followed by 1280 & 1260 bands	1230 band strongest, followed by 1260 & poorly defined 1280 bands	Equally strong 1230 & 1260 bands, followed by 1280 band; 1280 band poorly defined	1260 band strongest, followed by 1230 band; 1280 band poorly defined	

sample had a broader (101, 10 $\bar{1}$) peak but considerably sharper (002) peak as compared to IV_{II} (cotton) or IV_{II} (viscose). While R' value of IV_I (cotton) was the same as that of IV_{II} (cotton), that of IV_{II} (viscose) was considerably higher.

The meridional XRD scans from the cellulose IV_I (cotton), cellulose IV_{II} (cotton) and cellulose IV_{II} (viscose) samples, obtained after heat treatment for 1 h in glycerol, are presented in Figure 3. The ratio R of the peak intensity of the (020) reflection to that of the (040) reflection was about 0.17, 0.47, and 0.66 for cellulose IV_I, cellulose IV_{II} (cotton), and cellulose IV_{II} (viscose) samples, respectively. These values agree fairly well with the ratios reported by Hayashi et al.¹²

As regards the cellulose IV_{II} (viscose) sample obtained after heat treatment for 6 h, it was interesting to note that its principal diffraction maxima were located at 15.5° (2θ) and 22.3° (2θ) as in the case of the IV_I sample. The half-breadths of both the principal diffraction peaks were noticeably lower compared to the values obtained after boiling in glycerol for 1 h; however, the R' value was the same for both these samples (Table II). The values of R , obtained from meridional XRD scans, were also identical at 0.66 for these samples.

The R and R' values, therefore, can be used to distinguish between cellulose IV_I and cellulose IV_{II} samples which have identical equatorial x-ray diagrams. However, it is yet to be ascertained whether R' can be used, like R , for characterization of these polymorphs prepared from different sources of celluloses I and II. The same comment also applies to the breadths of the principal diffractions. It is interesting to note from Table II that, for the cellulose IV_I (cotton) and IV_{II} (viscose) polymorphs which indicated almost complete conversion, the (101, 10 $\bar{1}$) breadth was considerably less in the latter, although the (002) breadths were similar. This observation may be related to the directions and strengths of hydrogen bonding in the starting materials and the types of changes occurring in them during the lattice transformations.

The infrared spectra of cellulose polymorphs have been described in detail in articles on this subject.^{13,14} However, most of the discussions pertain to deuterated or polarized infrared spectra, as the differences between various polymorphs of cellulose are clearer in them. In the present work, unfortunately, neither of these classes of spectra was available. However, the normal spectra obtained from the samples prepared during this work did show certain differences between the polymorphic forms. They are described in Table III. It was impossible to unambiguously quantify the absorbances of many of the bands, and, in particular, the definition of some of the bands in the 2920–2880 cm⁻¹ region and 1280–1230 cm⁻¹ region was poor. However, the differences mentioned were easily recognizable, and served to identify the polymorphs in conjunction with x-ray diffraction data. It may be added that the differences could not be simply explained away on the basis of the crystallinity differences between the concerned samples, which are discussed later.

It may also be mentioned in this context that, in addition to the data given in Table III, the cellulose III_I sample showed a band at about 3480 cm⁻¹. Further, there were bands at 1590 cm⁻¹, 920 cm⁻¹, and 870 cm⁻¹ in cellulose IV_{II} (viscose); since absorptions around these regions have been reported from thermally degraded celluloses,¹⁵ it was, however, difficult to decide whether these bands were really characteristic of this cellulose polymorph.

TABLE IV
Crystallinity Data on Cellulose Polymorphs

Sample	Crystallinity Indices		
	X-ray	IR(1) ^a	IR(2) ^b
I (cotton)	0.84	0.78	0.71
III _I (cotton)	0.77	0.58	0.42
IV _I (cotton) ^c	0.80	0.61	0.57
II (cotton)	0.66	0.57	0.34
III _{II} (cotton)	0.65	0.49	0.25
IV _{II} (cotton) ^c	0.71	0.52	0.38
II (viscose)	0.46	0.50	0.26
III _{II} (viscose)	0.45	0.44	0.24
IV _{II} (viscose) ^c	0.67	0.49	0.29

^a IR(1) = a_{1372}/a_{2900} .

^b IR(2) = a_{342}/a_{2900} .

^c Produced after 1 h heat treatment in glycerol.

Results of crystallinity evaluations using x-ray and infrared spectroscopic indices are given in Table IV. The data are presented diagrammatically in Figure 4, which helps to easily rank the various polymorphs according to crystallinity. In addition, it also indicates that x-ray crystallinity index may be related better to that evaluated using the 342 cm^{-1} band than the 1372 cm^{-1} band. The crystallinity of the cellulose III sample was close to (or slightly lower than) its parent (I or II) in both families. The crystallinity of the cellulose IV_{II} sample, however, was noticeably higher than the cellulose III_{II} (viscose) sample from which it was prepared. The difference was less when cellulose IV_I and cellulose III_I samples were compared. Finally, while cellulose IV_I was slightly less crystalline compared to cellulose I, the cellulose IV_{II} samples were more ordered compared to the relevant control samples.

It was mentioned earlier that, except in the case of viscose, increasing the period of heat treatment in glycerol did not improve the production of the IV polymorph. The crystallinity indices of IV_{II} (viscose) obtained after 6 h heat treatment recorded the maximum increase (ca. 18%) over that which was given 1 h treatment. In consonance with the absence of higher conversion, the crystallinity also did not increase significantly for the other samples.

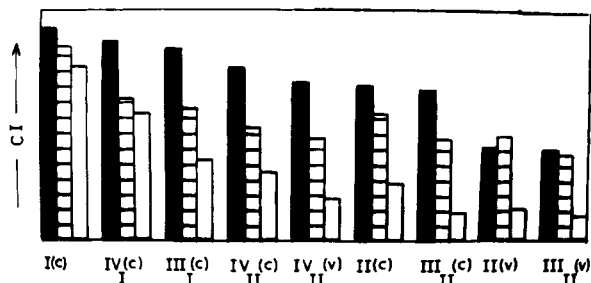


Fig. 4. Ranking of different samples for crystallinity, calculated from X-ray and different infrared indices. (■) X-ray index; (▒) infrared index, a_{1372}/a_{2900} ; (□) infrared index, a_{342}/a_{2900} .

Further Studies on Reactions of Cellulose IV Polymorphs

These studies were made on fibrous cellulose IV samples obtained after 1 h heat treatment of the parents (III_I and III_{II}) in glycerol. Treatment of the cellulose IV polymorphs in water at 30°C did not produce any change in their XRD patterns. Boiling in water for 3 h also gave similar results, except in the case of the cellulose IV_{II} sample, which had narrower XRD peaks as compared to their respective controls after treatment.

Acid Hydrolysis

Acid hydrolysis behaviors of the cellulose IV_I and IV_{II} samples were investigated using 1.0*N*, 2.5*N*, and 4.8*N* HCl at temperatures between 30°C and 100°C, with periods of hydrolysis normally in the range 15 min to 3 h. With lower concentration and temperatures, acid treatment for 24 h was also studied. The trends of results were more or less similar whether IV_{II} (cotton) or IV_{II} (viscose) was used for hydrolysis. However, since the effects were observed more clearly with the latter, the results are presented on this material. Only the significant conclusions which were derived out of the various experiments are summarized below.

As with treatment in boiling waer, hydrolysis with 1.0*N* HCl did not produce any appreciable effect on the XRD pattern of the cellulose IV_I sample. As a typical case, the XRD diagram of this sample after hydrolysis at 65°C for 1 h is presented in Figure 5(a). The X-ray crystallinity index of this sample was 0.83, compared to the value 0.80 before hydrolysis.

Hydrolysis with 2.5*N* HCl of the IV_I sample at 65°C or below for 1 h did not again visibly alter the x-ray diffractogram [Fig. 5(b)]. The X-ray crystallinity of the sample thus hydrolyzed was the same as that hydrolyzed with 1.0*N* HCl at the same temperature and for the same period. When the hydrolysis with 2.5*N* HCl was done at boil, however, even with a short period of treatment of 15 min, the peak at 15.5°(2θ) broadened, and the peak at 22.3°(2θ) shifted to 22.5°(2θ) [Fig. 5(c)]. The crystallinity index of this sample was 0.80. As IV_I → I reversion was indicated by the trends of changes observed in the principal diffraction regions, a reversion index was calculated through $(I_{14.8} + I_{16.5})/I_{15.5}$, where I_x means the intensity at $2\theta = x$ above a background joining $2\theta = 10^\circ$ and $2\theta = 18^\circ$. The value of this index increased to 1.70 for the hydrolyzed sample from 1.21 of the original IV_I sample. When the hydrolysis was carried out for 2 h, a clear reversion to cellulose I was obtained [Fig. 5(d)]. This reconverted cellulose I sample had a crystallinity index of 0.60 and a reversion index 2.12.

As unmodified cellulose I sample was characterized by a crystallinity index of 0.84 and a "reversion index" of 2.40, it may be concluded that hydrolysis under the above conditions results in a substantial IV_I → I reversion with accompanying decrystallization. The latter result indicates that the above hydrolysis should be considered as rather drastic, which could disorganize the crystallites in the IV_I sample (which, incidentally, had a crystallinity of 0.80). Considering the fact that the I sample had nearly the same crystallinity before and after similar hydrolysis, the above results on the IV_I polymorph indicate that even its highly ordered regions are very susceptible to acid attack, in contrast with the case with cellulose I.

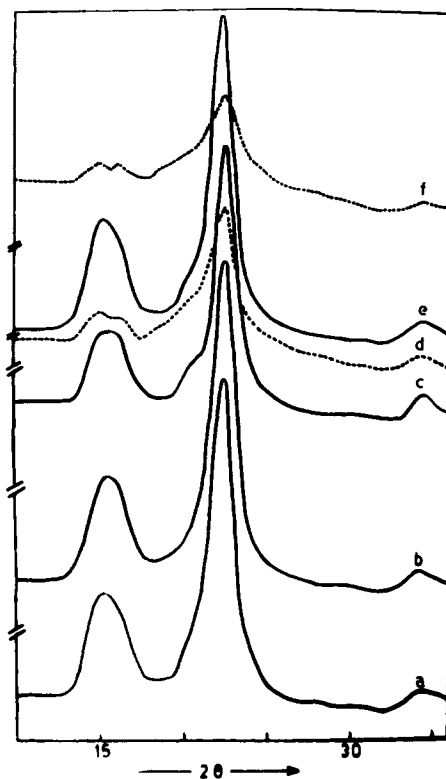


Fig. 5. XRD scans after hydrolysis of IV_I (cotton) with (a) 1.0*N* HCl at 65°C for 1 h, (b) 2.5*N* HCl at 65°C for 1 h, (c) 2.5*N* HCl at boil for 15 min, (d) 2.5*N* HCl at boil for 2 h, (e) 4.8*N* HCl at 30°C for 24 h, and (f) 4.8*N* HCl at boil for 30 min.

With 4.8*N* HCl, the broadening and shifting effects in the XRD diagram were apparent when the cellulose IV_I sample was hydrolyzed even at 30°C for a prolonged period of 24 h [Fig. 5(e)]. The crystallinity index of the hydrolyzed sample was 0.82 and the reversion index was 1.81. Comparing these results with those obtained when 2.5*N* HCl at boil was used (for 15 min), it is seen that the same extent of IV_I → I reversion has been produced in the present case, with only a slightly lower decrystallization. Thus, higher concentrations of acid at lower temperatures seem to produce the same effect as that produced by lower concentrations of acid at higher temperatures, which may not be, perhaps, very surprising. With 4.8*N* HCl at boil, even a period of treatment of 30 min reduced the crystallinity index to 0.51, and yielded a reversion index of 2.00 [Fig. 5(f)]. Comparing these data with the results obtained after hydrolyzing in 2.5*N* HCl at boil for 2 h, it may be concluded that the attack by acid is most drastic when higher concentrations are combined with higher temperatures. The reversion index for hydrolysis with 4.8*N* HCl did not register further increases, probably due to the extreme decrystallization which the sample underwent.

Hydrolysis of the cellulose IV_{II} sample in 1.0*N* HCl produced only narrowing of the principal diffraction peaks, similar to the observations after boiling in water. Figure 6(a) is a typical XRD pattern, obtained on hydrolysis with 1.0*N* HCl at 65°C for 1 h. The X-ray crystallinity index of this sample was 0.72, as compared to the value 0.67 before hydrolysis.

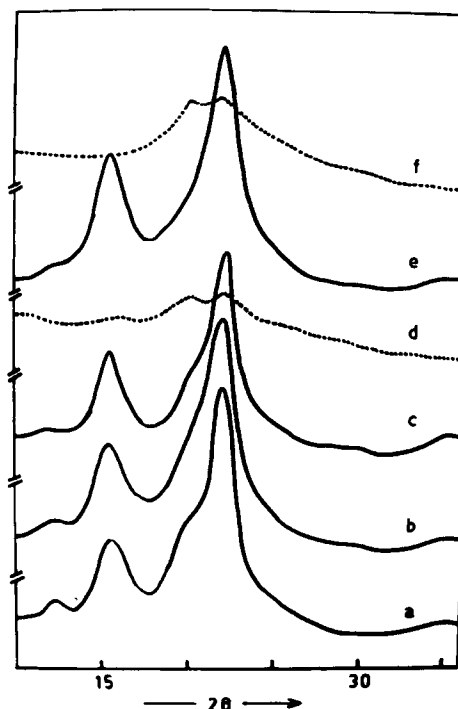


Fig. 6. XRD scans after hydrolysis of IV_{II} (viscose). Explanations as in Figure 5.

Thus, the IV_I and IV_{II} samples behaved identically on hydrolysis under the above conditions.

Hydrolysis with 2.5*N* HCl of the IV_{II} sample at 65°C or below for 1 h also produced the same type of changes in the XRD pattern [Fig. 6(b)]. The crystallinity of the sample hydrolyzed at 65°C was nearly the same as that before hydrolysis. When the hydrolysis was done at boil for 15 min, the peak at 15.5° (2θ) sharpened and the peak 22.0° (2θ) shifted to 22.3° (2θ) [Fig. 6(c)]. The crystallinity index of this sample was 0.70. It may be recalled that a similar shift from 22.0° (2θ) to 22.3° (2θ) was obtained when higher $II \rightarrow IV_{II}$ lattice conversion was achieved. From this fact, it may be concluded that some residual cellulose II was removed during hydrolysis. This conclusion was further supported by the reduction in the (101) intensity of cellulose II (in the XRD patterns of cellulose IV_{II}) as a result of hydrolysis. However, some ordering of cellulose IV_{II} on hydrolysis cannot be entirely ruled out, in view of the sharpening effect on the 15.5° (2θ) peak. In any case, no indications of a clear $IV_{II} \rightarrow II$ reversion was evident under the above conditions of hydrolysis. In this respect, as well as in decrystallization behaviour, cellulose IV_{II} may be seen to be different from cellulose IV_I .

Figure 6(d) shows that, on continuing the hydrolysis with 2.5*N* HCl for 2 h, a clear reversion to cellulose II was obtained. The reconverted sample was very highly decrystallized, with a crystallinity index value of only 0.20. The reversion index ($I_{12.0}/I_{15.5}$) was 1.0, as compared to its value of 0.36 for the unhydrolyzed IV_{II} sample. The values of crystallinity and "reversion index" for the cellulose II sample were 0.46 and 1.0, respectively. Thus, the behavior

of the IV_{II} sample may be seen to be similar to that of the IV_I sample under the above conditions of hydrolysis. It may be added that the crystallinity of the cellulose II sample remained nearly the same on similar hydrolysis.

The conclusions derived from hydrolysis of the IV_{II} sample with 4.8*N* HCl at the different temperatures and for different times were essentially similar to those mentioned while considering the hydrolysis of cellulose IV_I. For the sake of completeness, the XRD patterns obtained after hydrolyzing the IV_{II} sample with this concentration of acid at 30° for 24 h, and at boil for 30 min, are also included in Fig. 6(e) and (f).

The present results on the possibility of achieving IV_I → I and IV_{II} → II reconversions by acid hydrolysis agree in general with earlier reports.^{16,17} However, the effects of concentration of acid and temperature of treatment, reported in the present study, do not seem to have been commented upon earlier. It should be pointed out that these effects may depend upon the types of parent cellulose used and methods employed for preparing the cellulose III polymorphs, which in turn are the precursors for the cellulose IV_I and IV_{II} samples. Anyway, it appears that when 2.5*N* HCl is used for hydrolysis, IV_{II} → II reconversions are a little more difficult to achieve.

EDA Treatments

When the cellulose IV_I sample was treated once with EDA and the swollen sample washed with water, a significant IV_I → I reversion was observed [Fig. 7(a)]. Traces of cellulose II could, however, be discerned in the diffractogram. The crystallinity index of the treated sample was 0.54 and the IV_I → I reversion index was 2.60.

When unmodified cellulose I was treated similarly, the crystallinity index reduced from 0.84 to 0.72 (ca. 15%); the reduction in the case of IV_I, from 0.80 to 0.54 (ca. 33%) again indicates the susceptibility of this sample to chemical treatments. When the treatment was repeated thrice, the XRD pattern resembled that of cellulose II. The sample had the same crystallinity as the once treated sample.

In the case of cellulose IV_{II} samples, clear IV_{II} → II reconversions were obtained even with a single treatment with EDA and water [Figs. 7(b) and 7(c)]. The values of crystallinity index and reversion index obtained for IV_{II} (viscose) were 0.60 and 1.23, respectively. The values for IV_{II} (cotton) were 0.51 and 0.85, respectively. The above data indicate that, the treatment brought about, comparatively, a tremendous reversion with only a little decrystallization in IV_{II} (viscose).

It may be worth adding that the crystallinity index of the reconverted II (viscose) was ca. 30% more than that of unmodified II (viscose), while the value of reconverted II (cotton) was ca. 23% less than that of unmodified II (cotton).

The data from the infrared spectra of samples reconverted thus are given in Table V. Comparison of the details of the reconverted samples with the relevant unmodified samples (Table III) reveals some differences. The spectral details in the region 1280–1230 cm⁻¹, ascribed to bending modes of CH and OH groups,^{13,14} were different for the reconverted and unmodified cellulose I. The spectra were nearly identical in the case of II (viscose) samples, while the 810

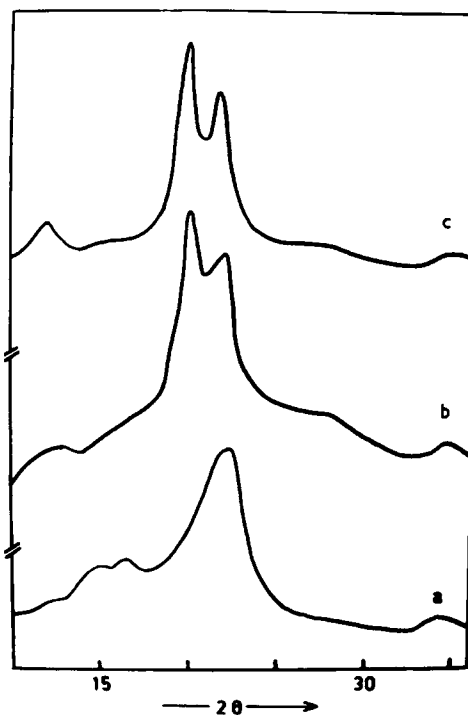


Fig. 7. XRD scans after single step EDA—water treatment on (a) IV_I (cotton), (b) IV_{II} (cotton), and (c) IV_{II} (viscose).

cm^{-1} band, attributed to ring breathing,^{13,14} could be clearly observed only in the spectrum of reconverted II (cotton). Since this sample had a lower crystallinity than unmodified II (cotton), it seems unlikely that the appearance of this band is related to order, and the above changes may be rather related to conformational differences between the molecular chains in the original and reconverted samples, which do not reveal themselves in X-ray diffractograms.

In spite of the above, the present study provides a new route for transforming cellulose lattices IV_I and IV_{II} into I and II, respectively. Besides, the observation that $IV_I \rightarrow I$ (with traces of II) and, subsequently, $I \rightarrow II$ lattice modifications (which represent transformations within the I family and I to II families, respectively) are brought about by the same route may be a point of interest in considerations on cellulose polymorphism. Nevertheless, further spectroscopic and other studies may alone decide whether the reconverted structures are identical *in all respects* to the respective unmodified structures. It may be added that the results obtained on single and multiple step treatments, with EDA and water, of cellulose IV_I are similar to our earlier observations¹⁸ on cellulose I.

In a preceding publication,¹⁹ we have reported that $IV_I \rightarrow III_I$ (cotton) and $IV_{II} \rightarrow III_{II}$ (viscose) reconversions can be induced using EDA and MeOH. The $IV_{II} \rightarrow III_{II}$ (cotton) reversion also has been observed in the present study, using the same method. Besides, the cellulose IV_{II} (viscose) sample used in the previous work was one prepared by treating cellulose III_{II} (viscose) in glycerol for 30 min at $260^\circ C$ and this IV_{II} (viscose) sample had its (002) maximum at 22.0° (2θ). During the course of the present work, the $IV_{II} \rightarrow III_{II}$ (viscose) retrans-

TABLE V
Infrared Absorption Data on Reconverted Cellulose Polymorphs

Infrared absorption band (cm ⁻¹)	I (cotton)	III _I (cotton)	II (cotton)	III _{II} (cotton)	II (viscose)	III _{II} (viscose)
2920 } 2900 } 2880 }	2900 band strongest, followed by 2880 & poorly defined 2920 bands	2900 band strongest, followed by 2880 & poorly defined 2920 bands	2880 band strongest, followed by 2900 & 2920 bands	equally strong 2880 & 2900 bands followed by poorly defined 2920 band	2880 band strongest, followed by 2900 & poorly defined 2920 bands.	only 2880 band clear
1440 } 1420 }	only 1420 band clear	only 1420 band clear	only 1420 band clear	only 1420 band clear	only 1420 band clear	only 1420 band clear
1330 } 1310 }	both bands equally strong in I stronger in I[-III _I -IV _I] 1280 band stronger, 1230 & 1260 bands, in I[-III _I] 1230 band stronger followed by equally strong 1260 & 1280 bands, in I[-III _I -IV _I] & I[-IV _I]	both bands equally strong	1310 band stronger	1310 band stronger	both bands equally strong	both bands equally strong
1280 } 1260 } 1230 }	1280 band stronger, followed by 1230 band, 1260 band poorly defined	1280 band stronger, followed by 1230 band, 1260 band poorly defined	1230 band strongest, followed by 1280 & 1260 bands in II[-III _{II}] 1230 band strongest, followed by 1280 & 1260 bands in II[-IV _{II}] 1230 band stronger, followed by equally strong 1260 & 1280 bands in II[-III _{II} -IV _{II}] present in II[-IV _{II}] very clear in II[-IV _{II}] & in II[-III _{II}] just present in II[-III _{II} -IV _{II}] absent	1230 band stronger, followed by equally strong 1260 & 1280 bands	1230 band stronger, followed by equally strong 1260 & 1280 bands	Equally strong 1260 & 1280 bands, followed by 1230 band
810 } 375 }	absent Just present in I[-III _I] & I[-IV _I] Clear in I[-III _I -IV _I]	absent present	absent present in II[-III _{II} -IV _{II}] very clear in II[-IV _{II}] & in II[-III _{II}] just present in II[-III _{II} -IV _{II}] absent	absent very clear	absent present	clear present
360 } clear }	clear	just present	absent	absent	absent	absent

Note: If the type of reversion is not specified, the observation is valid for all types of reconverted samples.

formation was confirmed for the cellulose IV_{II} (viscose) sample, with its (002) maximum at 22.3° (2 θ), obtained after heat treatment for 6 h in glycerol. This reconverted cellulose III_{II} (viscose) sample, also gave resolved peaks at 20.5° (2 θ) and 21.3° (2 θ), as with the sample used in the earlier study.

Reconversion indices for IV_I \rightarrow III_I and IV_{II} \rightarrow III_{II} transformations were calculated using $I_{11.8}/I_{15.5}$ and $I_{12.0}/I_{15.5}$, respectively. The cellulose IV_I (cotton), IV_{II} (cotton), and IV_{II} (viscose) (obtained after 1-h heat treatment of respective parents in glycerol), had index values of 0.31, 0.36, and 0.53, respectively. On reconversion to the corresponding cellulose III polymorphs, the values were 1.00, 1.28, and 1.05, respectively. In other words, the reconversions were obtained in the order IV_{II} (cotton), IV_I (cotton), and IV_{II} (viscose), respectively. Comparing the crystallinity indices, the decreases for IV_I (cotton), IV_{II} (cotton), and IV_{II} (viscose), respectively, were 0.80 to 0.63, 0.71 to 0.66, and 0.67 to 0.39. That is, the decrystallizations were in the order IV_{II} (viscose), IV_I (cotton), and IV_{II} (cotton). Thus, contrary to the observations made with reference to treatment of cellulose IV_{II} (cotton) and IV_{II} (viscose) with EDA and water, it is seen that IV_{II} (viscose) yielded poorer reconversion to III_{II} while undergoing higher decrystallization, comparatively.

Comparing crystallinity values, the reconverted cellulose III_I (cotton) sample was about 18% less crystalline than the III_I sample prepared directly from cellulose I. The reconverted cellulose III_{II} (cotton) sample had the same order as the directly prepared sample. The reconverted III_{II} (viscose) was about 13% less ordered compared to its direct counterpart.

As regards the infrared spectra of the reconverted and directly prepared samples, differences were noticeable in the 1330–1310 cm⁻¹, 1280–1230 cm⁻¹, 375 cm⁻¹, and 360 cm⁻¹ absorption regions in the case of cellulose III_I (Tables III and V). In the cases of cellulose III_{II} (cotton or viscose), the differences were mainly in the 2920–2880 cm⁻¹ and 1280–1230 cm⁻¹ absorption regions. In the light of the general concepts of band assignments,^{13,14} the above data, if confirmed with more sophisticated techniques, would indicate that conformations of the pyranose ring, as well as the CH₂OH and CHOH groups, may differ in the reconverted and directly prepared cellulose III_I samples, while the conformational differences may mainly pertain to the latter in the cellulose III_{II} polymorphs.

Further Reconversions

Further attempts were made to transform the reconverted cellulose III_I and III_{II} samples into cellulose I and II lattices respectively, by boiling them in water for 15 h. The results are presented in Figure 8. It was found that reconverted III_I (cotton) sample could be further transformed into cellulose I, although a complete transformation was not obtained [Fig. 8(a)]. This III_I \rightarrow I transformation behavior is, nevertheless, similar to that obtained with a directly prepared cellulose III_I sample [Fig. 8(b)]. In the case of reconverted III_{II} (cotton), the XRD scan showed a broadened (002) peak after boiling, which might indicate cellulose II formation [Fig. 8(c)]. However, as the (002) peak was located at the same 2 θ as in the scan of the reconverted III_{II} (cotton) sample, it is difficult to state whether III_{II} \rightarrow II transformation had occurred. The directly prepared III_{II} (cotton) sample, however, readily transformed into cellulose II [Fig. 8(d)]. In the case of reconverted III_{II} (viscose) sample, the reconversion to cellulose II was

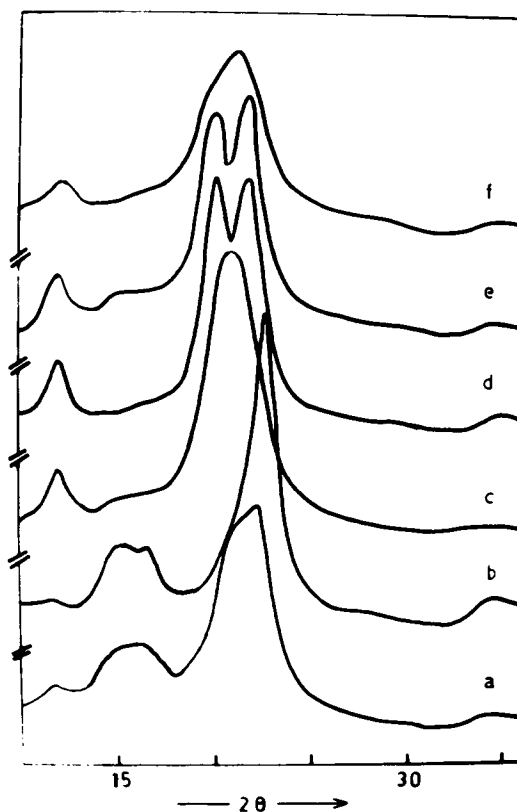


Fig. 8. XRD scans, after boiling in water for 15 h, of (a) reconverted III_I (cotton), (b) directly prepared III_I (cotton), (c) reconverted III_{II} (cotton), (d) directly prepared III_{II} (cotton), (e) reconverted III_{II} (viscose), and (f) directly prepared III_{II} (viscose).

very clear [Fig. 8(e)]. However, in the case of directly prepared III_{II} (viscose) sample, it was again difficult to conclude that the modification to cellulose II was obtained [Fig. 8(f)].

Recalling that the crystallinity values of the directly prepared and reconverted III_{II} (cotton) samples were identical, and that the directly prepared III_{II} (viscose) was only about 13% more crystalline than the reconverted III_{II} (viscose) sample, it is difficult to understand the above results from considerations of this factor alone. It seems more likely that conformational differences influence the lattice transformations involved.

The crystallinity value of the reconverted cellulose I sample was the same as that of the parent cellulose III_I for directly prepared $\text{III}_I \rightarrow \text{I}$ or reconverted $\text{III}_I \rightarrow \text{I}$ transformations. The same observation was applicable in the case of cellulose II (cotton) samples also. On the contrary, the cellulose II sample, obtained by boiling reconverted cellulose III_{II} (viscose), was as much as 64% more crystalline than the latter. The crystallinity of the product obtained after boiling the directly prepared cellulose III_{II} (viscose), however, was only about 16% higher than the latter. The different results between cotton and viscose are interesting, when it is considered along with identical heat treatment effects on unmodified samples of these materials; the crystallinity indices of cellulose I (cotton) and

cellulose II (cotton) did not change appreciably (within ca. 5%) while the index of cellulose II (viscose) registered a 11% increase after treatment.

From Tables III and V, it may be noticed that there are differences between the infrared spectra of unmodified celluloses I and II and their variously reconverted specimens.

NaOH Treatments

Results of treatment of the cellulose IV polymorphs with different concentrations of NaOH at 30°C for 30 min were broadly in agreement with the observations of Hayashi et al.²⁰ Hence, only a brief summary of these experiments are given below. In the present work, treatment of cellulose IV_I (cotton) with 9% NaOH broadened the (002) peak, similar to the trend observed after relatively mild acid hydrolysis. Treatment with 13% NaOH caused the IV_I → II lattice transformation, with the (10 $\bar{1}$) intensity being stronger than the (002) intensity in the X-ray pattern of the product. Treatment with NaOH solutions of 24% concentration also gave the cellulose II lattice, but with the above intensities being nearly equal. When the treatment was repeated twice more, the pattern resembled that obtained after treatment with 13% NaOH solutions. Therefore, it would appear that better swelling of the IV_I sample occurred at this concentration. With the cellulose IV_{II} polymorphs, the trends of results were similar. In the case of IV_{II} (viscose), however, it is to be mentioned that the sample dissolved substantially in 13% NaOH. The undissolved part was verified to be cellulose II, while the dissolved part, obtained by precipitation from the solution by dilution with water, was amorphous (as judged from XRD and infrared scans). Use of 9% NaOH on the IV_{II} (viscose) sample yielded a fairly good IV_{II} → II modification; use of 24% NaOH gave a still better conversion of this type. In short, the above data indicated that this lattice transformation could be induced with lower concentrations of alkali as compared to the IV_I → II modification. It may also be mentioned that the production of cellulose II was considerably higher (by ca. 50%) from cellulose IV_I than from cellulose I, when treated with 13% NaOH. This agrees with the earlier observation that the former was more susceptible to acid hydrolysis.

CONCLUSIONS

Concerning production aspects of cellulose IV polymorphs, it may be concluded that both the structural aspects of the starting material as well as its crystalline order are important. The importance of chain conformation has been commented upon by Sueoka et al.²¹ The data in Tables I and IV, however, also indicate that, within a family, the lateral order in the starting material also influences the transformations.

The observation that NaOH presoaked cellulose I (cotton), rather than similarly pretreated cellulose II (cotton), gives higher conversion to cellulose IV_{II} indicates that the structures of these swollen materials may be different. The fact that the NaOH presoaked cotton fibers transformed into cellulose IV_{II} is somewhat surprising, because treatment of this material with water at high temperatures is reported to have yielded mixtures of cellulose IV_I and cellulose

II.²⁰ Perhaps, the differences in the methods of removal of the swelling agent influenced the course of results in the two cases.

The differences between cellulose II (cotton) and cellulose II (viscose), as regards production of the IV_{II} polymorphs and their reconversion behaviors, may be due to conformational differences²² as well as different lateral orders in polymorphs prepared from cotton and viscose.

The equatorial X-ray patterns of celluloses IV_I and IV_{II}, prepared from celluloses III_I and III_{II}, respectively, were identical when complete transformations were effected. Different 2θ positions of the (002) peak,^{6,19} and consequent differences in the values of the unit cell parameters²³ have been reported for the cellulose IV_I and IV_{II} polymorphs. We are inclined to think that these differences arose, at least partly, due to incomplete transformations to cellulose IV_{II}.

The present study indicates the importance of concentration of acid and the temperature of treatment on the course of hydrolysis of the cellulose IV polymorphs. Further, these results, in conjunction with studies on IV_I → II and IV_{II} → II reconversions using NaOH reveal differences between these polymorphs.

It has been demonstrated that, cellulose IV_I → I, IV_I → I → II, and IV_{II} → II lattice changes can be brought about using EDA and water. This provides a new route for observing IV_I → I lattice transformation. The effect of this treatment on cellulose IV_I is similar to that given to cellulose I.¹⁸

There were differences between cellulose III polymorphs prepared directly from cellulose I and II polymorphs, and those obtained by reconversion from cellulose IV samples, as regards their further reconversion to celluloses I and II. This indicates some differences in structures of the cellulose III samples prepared through the two routes. Similarly, there appear to be differences between the modified and the reconverted cellulose I as well as cellulose II (obtained by different experimental procedures). It would be desirable to confirm these aspects using more sophisticated spectroscopic and allied techniques.

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