# Fine Structural Changes in Native and Mercerized Fibrous Cellulose Brought About by Ethylenediamine and Methyl Alcohol

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## Synopsis

X-Ray diffraction (XRD) studies were made on native as well as mercerized ramie and cotton fibers after swelling them in ethylenediamine (EDA) solutions and washing out the swelling agent using methyl alcohol (MeOH). These treatments are shown to convert the cellulose I and II lattices into cellulose $III_I$ and $III_{II}$ type lattices, respectively. Treatment of the $III_I$ and $III_{II}$ samples in boiling water or hydrochloric acid results in reconversions of their crystal lattices into the respective parent types. Alkali treatment causes a III → II type conversion. Studies using alkali-swollen fibers as well as fibers of different lateral order as starting materials indicate the importance of the structural organization in the cellulosic materials in the production of the cellulose III lattices. Possible mechanisms involved in the lattice transformations in cellulose brought about by the EDA and MeOH treatments are discussed.

## INTRODUCTION

The effect of aqueous solutions of ethylenediamine (EDA) on the fine structure and properties of native as well as mercerized cotton cellulose has been studied by many workers.[1–4] The results of these studies indicate that native cotton retains the cellulose I lattice structure on washing the EDA-swollen fibers with water. Similarly, the cellulose II lattice structure of mercerized cotton appears to be unaffected by such treatments, although EDA produces considerable decrystallization in both cases. The retention of the parent lattices is believed to be due to the restrictions to rotation and relative motion imposed on neighboring cellulose chains by EDA molecules which, due to their bifunctional nature, lead to bridge formation. Contrary to the above results, Lokhande[5] presented deuterated infrared spectroscopic evidence for the conversion of cellulose I to cellulose II on treating native cotton fibers with 75% (w/w) aqueous EDA solutions and removing the swelling agent subsequently with water. The finding was explained by suggesting that EDA behaves as a monoamine under suitable conditions.

Additional evidence for the cellulose I → cellulose II conversion was later obtained by x-ray diffraction methods,[6] and it was demonstrated that repeated swelling of native cotton in EDA solutions progressively enhances the lattice conversion. Furthermore, work[7] carried out recently at the laboratories of the authors has also revealed that yet another lattice modification, viz., cellulose III, can be brought about by washing out the EDA from swollen native fibers with

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methyl alcohol (MeOH). The different effects observed with the use of water and MeOH for washing was tentatively explained on the basis of their different polarities and functional nature in the above study. In the present paper, studies are reported on the behavior of mercerized cotton and ramie fibers when subjected to swelling in EDA solutions followed by washing out the reagent with MeOH. In addition, results of experiments conducted with a view to gaining more information on the mechanism of the lattice transformations brought about by such treatments are also discussed.

## EXPERIMENTAL

Purified fibrous cotton and ramie samples were mercerized by soaking them in 7.5*N* aqueous NaOH solutions for 1 hr at 27°C and subsequently washing the swollen samples in acidified and then in distilled water till the alkali was removed completely. Swelling of samples in NaOH solutions of other concentrations was carried out similarly. All the samples were dried in the atmosphere after washing.

The treatments with EDA were carried out using aqueous 75% (w/w) EDA solutions. The samples were soaked for 1 hr at 27°C in the solutions with constant stirring. The excess reagent was squeezed out at the end of the above period and the sample dipped into a large volume of MeOH. The washing was continued using fresh lots of MeOH and the samples finally air dried.

Ni-filtered $CuK_\alpha$ radiation from a Philips stabilized x-ray generator with diffractometer and recording accessories was used for obtaining XRD patterns. Fibers weighing about 150 mg were cut into fine powder, filled in the standard specimen holder, and the patterns recorded using reflection geometry. Flat-film photographs were obtained from fiber bundles with a specimen-to-film distance of 3 cm.

Acid hydrolysis was carried out in 1.0*N* HCl at 65°C for the desired time. After hydrolysis the samples were washed thoroughly with water and dried in air. For preparing highly crystalline cellulose I and cellulose II materials, purified cotton fibers and thrice-mercerized cotton fibers, respectively, were hydrolyzed for 24 hr.

Amorphous samples were prepared using a vibrating ball mill.

## RESULTS

The XRD patterns from purified as well as mercerized cotton and ramie fibers obtained on swelling them in EDA and removing the swelling agent using MeOH are shown in Figure 1. It is clear that the patterns in the range of 20°–22° ($2\theta$) of the samples prepared from mercerized fibers are comparatively broader and consist of two components, centered at about 20.5° and 21.3° ($2\theta$). Using cold (ca. 5°C) MeOH for washing the EDA-swollen samples resulted in an improvement of the resolution of the two peaks. On the other hand, the patterns of samples prepared from native fibers consisted of a sharp peak at 21° ($2\theta$).

When the region 3°–10° ($2\theta$) was scanned separately using appropriate slit assemblies, no evidence was obtained for any XRD peak. This observation rules out the possibility that the diffractograms arise from EDA–cellulose complexes.

Flat-film x-ray photographs of the treated samples prepared from nonmer-

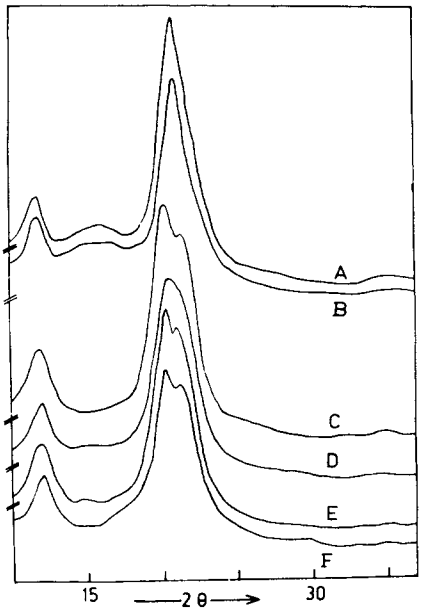



Fig. 1. XRD scans of cellulose III prepared from (A) ramie, (B) cotton, (C) mercerized ramie, and (D) mercerized cotton by EDA treatment and MeOH washing at 27°C. The patterns from mercerized ramie and mercerized cotton obtained on cold MeOH washing are (E) and (F), respectively.

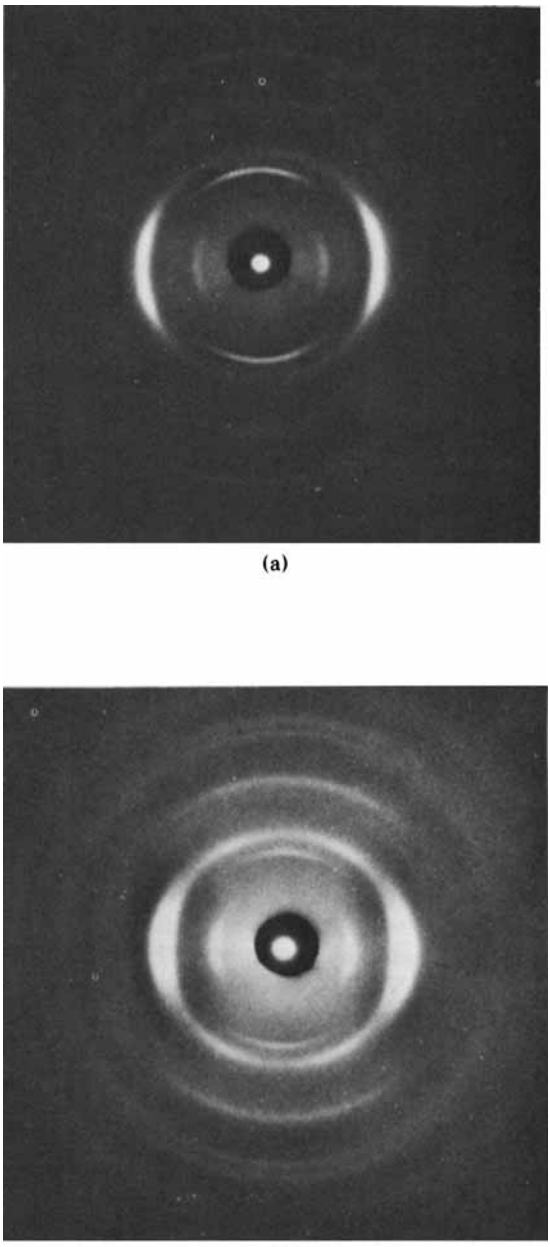
cerized fibers (hereafter referred to as $III_I$) and mercerized fibers (hereafter referred to as $III_{II}$) are shown in Figure 2. As some differences in the relative intensities of the meridional reflections between the x-ray diagrams of $III_I$ and $III_{II}$ were apparent, meridional scans (Fig. 3) of these samples were taken following the method of Hayashi et al.[8] The relative intensity ratio of (020) to (040) reflections for $III_I$ and $III_{II}$ were 2.0 and 0.6, respectively. These values are in close agreement with those reported by the above workers.

Using fibers treated with NaOH solutions of other concentrations (in the range of 4.0–14.5*N*) as starting materials did not significantly change the XRD pattern of $III_{II}$ given in Figure 1. The patterns were composed of the $III_I$ and $III_{II}$ profiles in the case of samples treated with lower concentrations of NaOH in the above range and consisted of only the $III_{II}$ profile for the others. Although the region 20°–22° ($2\theta$) showed some variations in profile shape, no definite trends could be established.

Multiple treatments did not improve the $III_{II}$ patterns, as observed[7] in the case of the diffractograms of $III_I$.

Wetting of $III_{II}$ samples with water at room temperature caused an overall broadening of their XRD patterns. In the case of $III_I$ samples, however, a small amount of reconversion to cellulose I lattice could be observed, in addition to the broadening, on water-treatment (Fig. 4). Keeping the $III_{II}$ and $III_I$ samples in boiling water for about 5 hr caused larger reconversion to the respective parent lattices.

Results obtained on the effect of acid hydrolysis appeared to be similar to the action of boiling water. The XRD patterns obtained after hydrolyzing the $III_I$ and $III_{II}$ samples for 2 hr and 24 hr, respectively, are shown in Figure 5. The reconversion into parent lattices was more obvious in the samples which were hydrolyzed for 24 hr.



(a)

(b)

Fig. 2. Flat-film x-ray fiber photographs of (a) cellulose $III_I$ and (b) cellulose $III_{II}$.

Treatment of $III_I$ or $III_{II}$ samples with NaOH solutions of mercerizing strength transformed the lattice structure into cellulose II.

With a view to investigating the effect of the order of the starting cellulosic material on the ease of production of cellulose III, highly crystalline cellulose I and cellulose II materials as well as amorphous celluloses (prepared from native as well as mercerized fibers) were given the EDA–MeOH treatment and their XRD scans recorded [Figs. 6(a) and 6(b)]. The highly crystalline cellulose I sample was converted into cellulose $III_I$ readily, as in the case of normal fibrous

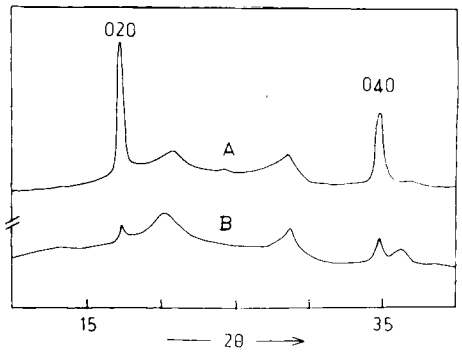



Fig. 3. Meridional XRD scans of (A) cellulose $III_I$ and (B) cellulose $III_{II}$.

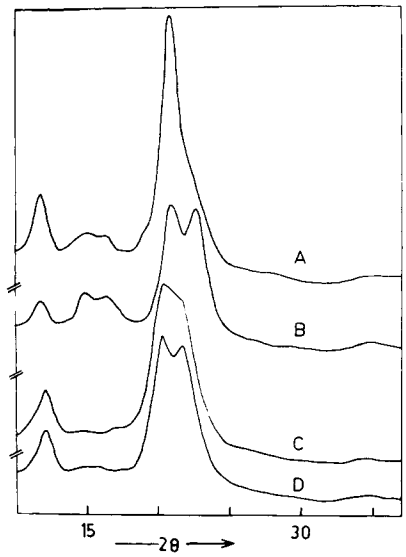



Fig. 4. XRD patterns of $III_I$ samples after (A) water wetting for ca. 2 hr, (B) boiling in water for ca. 5 hr, and of $III_{II}$ sample after (C) water wetting for ca. 2 hr, and (D) boiling in water for ca. 5 hr.

samples. The pattern from the ball-milled cellulose I samples, on the other hand, was not so well defined and appeared to arise from either cellulose II or cellulose $III_{II}$ types of lattices, or from a combination of both types [Fig. 6(a)].

It may be seen from Figure 6(b) that the lattice of the highly crystalline cellulose II samples was apparently unchanged by the treatments. Increasing the time of soaking the sample in EDA to 24 hr did not produce any different results. On the other hand, the amorphous sample prepared from cellulose II may be observed to have recrystallized into cellulose $III_{II}$ lattice type.

A number of experiments were carried out to investigate the effects of altering the conditions of treatment on the formation of the $III_{II}$ lattice. When fibrous samples, swollen in NaOH solutions of mercerizing strength, were transferred *directly* to EDA solutions and then washed with MeOH, the x-ray diffractogram did not change into cellulose III type (Fig. 7). The differences in this scan from the usual cellulose II XRD pattern, noticeable in the range of 10°–13° ($2\theta$), were probably due to residual NaOH which could not be removed easily from the

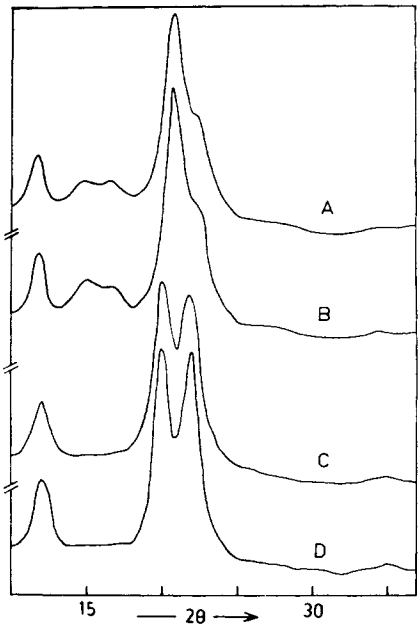
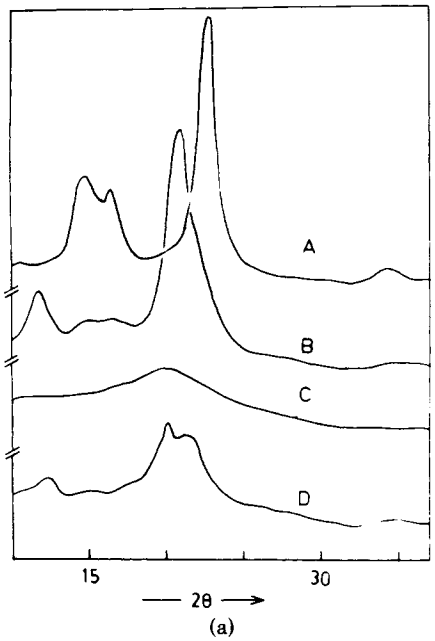



Fig. 5. XRD scans of cellulose $III_I$ hydrolyzed for (A) 2 hr and (B) 24 hr. The patterns from cellulose $III_{II}$, after identical treatments, are (C) and (D), respectively.

sample. When the alkali-swollen fibers were washed with MeOH before treating them in EDA and washing with MeOH, the results obtained were identical. However, when alkali-swollen and MeOH-washed samples were thoroughly dried before swelling them in the diamine and giving subsequent MeOH washes, $III_{II}$ was readily formed.

## DISCUSSION

The most striking feature of the results obtained in the present study is the fact that the diffractometer scans of the $III_I$ and $III_{II}$ samples show definite differences. Earlier studies in this regard generally report that the equatorial XRD patterns of these samples are identical. Clark and Parker[9] found that materials prepared by the action of liquid ammonia on native and mercerized samples gave identical cellulose III x-ray diagrams on driving out the ammonia by heating at 105°C. Hayashi et al.[8] observed that equatorial XRD patterns of $III_I$ and $III_{II}$ samples, prepared using liquid ammonia on a variety of native and mercerized celluloses, were all similar. Although results obtained using infrared techniques[10] and relative intensities of meridional x-ray reflections[8,11] indicate that the molecular conformation in the $III_I$ and $III_{II}$ forms are not the same, no differences in their equatorial XRD patterns seem to have been observed so far. In the present study, the resolution in the region 20°–22° ($2\theta$) was consistently noted in the case of samples prepared from mercerized ramie under all conditions of treatment and in samples from mercerized cotton when cold MeOH was used for washing out the EDA. It is likely that the EDA–MeOH system used in the present study differs in its ability to bring about II → $III_{II}$ transformation when compared to liquid ammonia or short-chain aliphatic amines. Comparative studies on $III_{II}$ samples prepared using different swelling systems are warranted to ascertain this possibility. If it is assumed, for the time



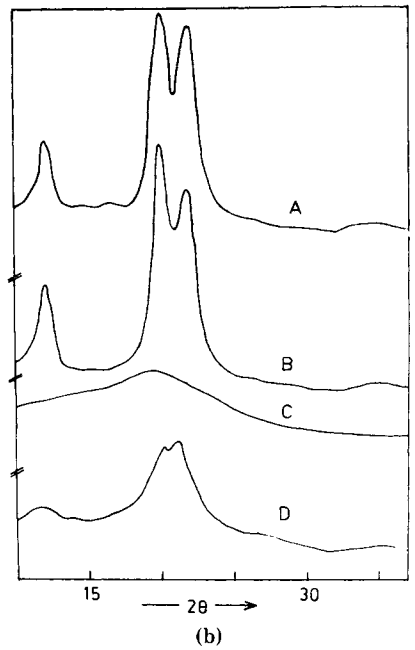




Fig. 6(a) XRD scans of (A) highly crystalline cellulose I sample, (B) sample at (A) treated with EDA and MeOH, (C) amorphous cellulose I, and (D) sample at (C) given identical treatment. (b) XRD scans of (A) highly crystalline cellulose II sample, (B) sample at (A) treated with EDA and MeOH, (C) amorphous cellulose II, and (D) sample at (C) given identical treatment.

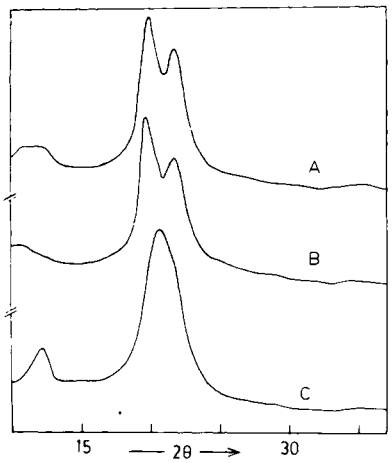



Fig. 7. XRD scans obtained from (A) alkali-swollen sample transferred directly to EDA and MeOH-washed, (B) alkali-swollen, MeOH-washed sample transferred to EDA and MeOH-washed, and (C) alkali-swollen, MeOH-washed, dried sample transferred to EDA and MeOH-washed.

being, that the resolution observed is a real characteristic of the $III_{II}$ cellulose polymorph, minor revisions of the generally accepted unit cells[12] become necessary. For example, if a monoclinic unit cell is accepted, after Legrand,[13] the $d_{10\bar{1}}$ and $d_{002}$ values woud be about 4.33 and 4.16 Å, respectively, instead of both being 4.33 Å. On the other hand, if the hexagonal cell of Hess and Gundermann, which is supported by Wellard,[11] or the recently proposed monoclinic cell of Sarko et al.[14] is taken as the correct structure, it will be necessary to examine whether the present data can be accommodated into it. It is interesting to note in this context that Wellard found certain differences in lattice spacings between $III_I$ and $III_{II}$ samples, but they were reported to lie in the range of experimental error. Further, these variations were of a different nature from what is observed in the present work.

The meridional scans of the $III_I$ and $III_{II}$ samples are in conformity with the patterns reported by Hayashi et al.[8] The relative intensity ratios of (020) to (040) reflections, $R$, agree well with their results and appear to confirm that the swelling and washing treatments used do produce cellulose $III_I$ and $III_{II}$. It was also observed that the value of $R$ did not differ between $III_{II}$ samples produced using MeOH at ambient or lower temperatures. This observation indicates that the crystal lattice of the samples which give resolved profiles in the range of 20°–22° ($2\theta$) is likely to be of the $III_{II}$ type only.

The reconversion effects obtained on water or acid treatment of the $III_I$ and $III_{II}$ samples agree with earlier reports.[10,13]

In our earlier publication,[7] a tentative mechanism based on the monofunctional nature of MeOH was proposed for the $I \rightarrow III_I$ lattice conversion brought about by the EDA–MeOH treatment given to cotton cellulose. If this were the one and only factor responsible, it can be expected that similar effects might occur in samples swollen with other swelling agents as well on washing with MeOH. On the other hand, if the structure of the swollen material or the type of interaction of the swelling agent with the cellulose chains are also important, such lattice transformations need not occur in all cases. Even though studies on the effects of alcoholic removal of the swelling agent from alkali-swollen cotton fibers have been reported earlier,[15] it is difficult to decide from them whether the x-ray

diffractograms of the treated materials contained any evidence of $III_{II}$ lattice formation.

Therefore, a series of samples were swollen in various concentrations of aqueous NaOH solutions and the excess alkali washed out by repeated treatments with MeOH. Their XRD patterns were recorded after drying the samples (Fig. 8). The patterns obtained on removing the alkali with water in the usual way are also included in the figure for comparison.

It may be observed that none of the diffractograms of the samples washed with MeOH contains features which would help to unequivocally establish the presence of $III_{II}$ lattice, although some ill-defined shoulders at various Bragg angles are present in the scans. As suggested by Jeffries and Warwicker,[15] these might represent just various organizations of sheets of cellulose chains and nothing more. The higher lattice conversion in the alcohol-washed samples has been observed by others and has already been commented upon.[15,16]

It is interesting that the lattice transformation to $III_{II}$ is not obtained if samples swollen in alkali are transferred directly to EDA and subsequently washed with MeOH. Similarly, alkali-swollen and MeOH-washed samples do not seem to get converted to $III_{II}$ if they are not dried before treating them in EDA and MeOH. On the other hand, washing with alcohol of samples swollen in EDA brings about the transformation readily. It appears, therefore, that excess alkali or alcohol, if present in a sample when it is brought into contact with EDA, hinders the formation of cellulose $III_{II}$. Similarly, the results obtained on treating celluloses of different crystallinity indicate that the structural organization in the starting materials influences the course of their reactions with EDA and MeOH.

Segal and co-workers have conducted detailed studies on EDA–cellulose

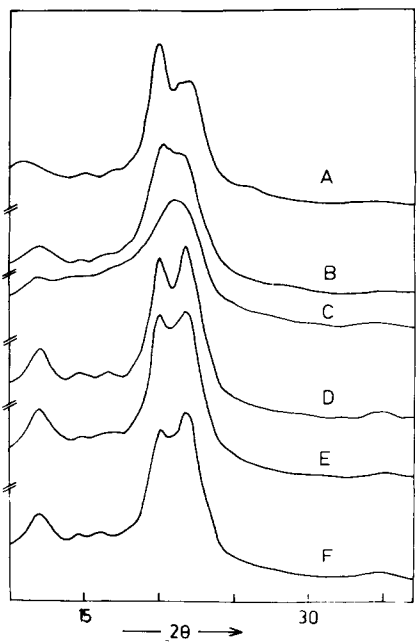



Fig. 8. XRD scans of cotton fibers swollen in (A) 4.0*N* NaOH, (B) 5.5*N* NaOH, and (C) 9.8*N* NaOH and MeOH-washed. The patterns obtained on aqueous removal of alkali are (D), (E), and (F), respectively.

complexes and the decomposition products obtained from them on removing the diamine using different methods.[1-3] In one of their studies,[1] the EDA–cellulose complex, prepared by vacuum drying of cellulose swollen with EDA, was washed with various solvents and the changes occurring in the XRD pattern of the complex were examined. While nonpolar solvents did not alter the pattern of the complex appreciably, polar solvents containing oxygen tended to restore the pattern to that of cellulose I; no evidence for formation of cellulose III lattice was apparent in their XRD scans. The different results obtained in our studies might be due to a difference in experimental procedure; while a *dried* complex containing about 20% EDA was treated with MeOH by Segal et al., the EDA-swollen fibers, containing *excess* diamine, were washed with MeOH in the present work. In the infrared work of Evans and Jeffries[17] wherein evidence for cellulose III formation on swelling cotton fibers in EDA and washing with alcohols was reported, the experimental procedure employed appears to have been similar to ours. However, the extent of formation of ordered cellulose III was reported to be about 5%–10% in samples washed with MeOH in the above work; the present x-ray evidence suggests that it is far higher.

Thus, an excess amount of diamine, before the washing with MeOH is given, seems to be a prerequisite for obtaining cellulose III. Swelling the fibers in mixtures of EDA and EtOH is also known[17] to produce this lattice modification of cellulose. A few preliminary experiments conducted by us have shown that this effect can be obtained by swelling the fibers in mixtures of EDA and MeOH, too. Complex formation between EDA and MeOH can occur under favorable conditions as discussed by Loeb and Segal[1]; if such a complex is responsible for the I $\rightarrow$ $III_I$ and II $\rightarrow$ $III_{II}$ lattice transformations, it will have to be postulated that the complex is formed during washing of the EDA-swollen samples with MeOH. Furthermore, this complex must act on the cellulose chains almost simultaneously to produce stable structural changes in the fibers. Studies under way are expected to clarify these aspects.

## CONCLUSIONS

Swelling native and mercerized cellulosic fibers in EDA and subsequent removal of the swelling agent with MeOH changes the parent cellulose I and cellulose II lattices into cellulose $III_I$ and cellulose $III_{II}$ type lattices, respectively. X-Ray diffractometer scans of $III_I$ and $III_{II}$ samples exhibit definite differences.

Meridional x-ray scans of the samples appear to confirm that the lattices formed by the EDA–MeOH treatment are of the cellulose III type.

Treatment with boiling water or hydrochloric acid converts the III type lattices into the respective parent types. Treatment with alkali converts them into cellulose II.

It was not possible to decide from the XRD scans of fibers swollen in NaOH solutions and washed with MeOH whether these samples contained any cellulose III lattices. Results obtained on treating samples containing excess alkali or alcohol with EDA and subsequently removing the EDA with MeOH indicate that the structural organization in the swollen material influences the formation of cellulose III. Observations on starting materials with different lateral order support this view.

Presence of EDA in excess of that necessary for formation of the EDA–cellulose

complex seems to be essential for obtaining cellulose III by the present system of treatments. The possibility that an EDA–MeOH complex might be responsible for the structural changes observed cannot be ruled out and needs further investigation.

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