

A Study of the Fine Structure of Cellulosic Fibers by Level-Off Degree of Polymerization Measurements

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Synopsis

The crystallization of disordered and partly disordered cellulose on hydrolysis with boiling dilute mineral acid was studied and the level-off degree of polymerization (LODP) of cotton after treatment with inter- or intracrystalline swelling agents was determined. The LODP, of cotton and of cotton which had been swollen in morpholine were similar, indicating that the LODP of cotton cellulose was not affected by this intercrystalline swelling agent. It appears that the aggregates of cellulose chains present in cotton which has been treated with aqueous NaOH of mercerizing strength and then washed with water are not uniformly accessible to hydrolyzing acid and that the accessibility to the acid is not changed when the cellulose is dried. The LODP of samples of mercerized, ethanol-washed, never-dried cotton that had been acetylated was obtained and the results are discussed in terms of current views on the fine structure of cotton.

INTRODUCTION

When cellulose is hydrolyzed with boiling dilute mineral acids, the degree of polymerization of the product falls sharply and then attains a relatively constant value called the "level-off degree of polymerization" (LODP). Battista¹ has provided a comprehensive review of early work in this area. The LODP can be multiplied by the length of an anhydroglucose unit (5.15 Å) to give a measure of the length of the crystallites present in the cellulose.²⁻⁴ However, it has been suggested that during hydrolysis of cotton, crystallization of the cellulose can take place.^{4,5} Thus it is possible that crystallite lengths determined from the LODP measurements cannot be used as absolute values, although they may still remain of value for placing celluloses of differing crystallite length in relative order.

The purpose of this investigation was to study the crystallization of cellulose on hydrolysis with boiling dilute mineral acid and to determine the LODP of cotton cellulose that had been treated with inter- or intracrystalline swelling agents.

EXPERIMENTAL

Commercially kier-boiled cotton yarn (80/2s filling twist) and acetate filament yarn (150-2Z-40) were used as starting materials. Cupriethylene-diamine hydroxide solution was obtained from Ecusta Paper Div., Olin-

Matheson Chemical Corp., Pisgah Forest, N. C. All other chemicals were reagent grade.

Methods of Treatment

Mergerized Cotton. Cotton yarn was immersed in 20% NaOH solution (4 g per 200 ml of solution) for 1 hr at 21°C in a stoppered, ground-glass bottle. The alkali was filtered off, and the sample was washed in several changes of distilled water before being steeped in 10% acetic acid for 15 min. The cotton was rewashed in distilled water until it was free of acid and then dried by exposure to an atmosphere of 65% R.H. and 21°C.

Mergerized Cotton (Never-Dried). Cotton yarn was cut into short lengths (0.5–1.0 cm) and then treated with 20% NaOH solution as described above. However, the sample was not dried after washing with distilled water. Instead, it was washed in several changes of 2.5*N* HCl at room temperature and then hydrolyzed immediately with 2.5*N* HCl at the boil in the manner described below.

In another experiment, the alkali was extracted from the sample by washing several times with 2.5*N* HCl at room temperature and then hydrolyzed immediately with 2.5*N* HCl at the boil as described below.

Swelling of Cotton with Morpholine. The cotton yarn was cut into short lengths and then immersed (3 g per 150 ml of solution) in morpholine or a 40% solution of morpholine in distilled water for 1 hr at 21°C in a stoppered, ground-glass bottle. The swelling agent was filtered off and the cotton was washed in several changes of distilled water. The sample was then washed with methanol and afterward with ether. Finally, the sample was conditioned in an atmosphere of 65% R.H. and 21°C.

Acetylation of Mergerized, Ethanol-Washed, Never-Dried Cotton. The procedure was as previously described for the preparation of mergerized, ethanol-washed, never-dried cotton and for its acetylation.⁶

Preparation of Cellulose Triacetate from Cotton. Cotton yarn which had been cut into short lengths was fully acetylated by the fibrous process, using a procedure similar to that of Tanghe and co-workers.⁷ The water-washed product was dried at room temperature.

Preparation of Disordered Cellulose. Disordered cellulose was prepared using a method described by Jeffries.⁸ Cotton cellulose triacetate or acetate filament yarn (1 g per 100 ml solution) was immersed in a 1% solution of NaOH in ethanol for 24 hr at 25°C. The product was then treated by one of the following methods: (i) washed in several changes of ethanol at 25°C over a 24-hr period and then dried at room temperature; (ii) washed in several changes of distilled water at 25°C over a 24-hr period and then given two washes with ethanol before being dried at room temperature; (iii) washed over a 24-hr period in several changes of distilled water, including an immersion in boiling distilled water for 3 hr; after the sample had cooled, it was washed twice with ethanol before being dried at room temperature.

Hydrolysis. Samples (1 g cellulose per 50 ml solution) were hydrolyzed in boiling 2.5*N* HCl using a procedure that was essentially similar to that of Battista.¹ When air-dry samples were being weighed out for hydrolysis, allowance was made for the moisture present in the samples. In the case of acetylated materials, allowance was also made for the acetyl content.

After the hydrolysis had been terminated, the samples were dried in an air oven at 105°C for 90 min. The residues were then calculated as a percentage of the dry weight of the starting material. Finally, the samples were conditioned in a constant temperature and humidity room at 65% R.H. and 21°C.

Characterization of Products

Acetyl Content. This was determined as described previously.⁹

Hygroscopicity. To determine moisture regains, samples (0.5–1.0 g) of the materials were dried in an air oven at 110°C for 3 hr and then exposed in a constant temperature and humidity room at 65% R.H. and 21°C until they reached a constant weight. In order that the moisture regains could be converted to sorption ratios, the moisture regain of the starting cotton was determined under the same set of conditions. Sorption ratio is defined as the ratio of moisture regain of a cellulose to that of cotton at the same relative humidity and temperature.

Intrinsic Viscosity. Cannon-Fenske viscometers were used to determine intrinsic viscosity values in cupriethylenediamine hydroxide, using a method essentially the same as ASTM D1795-62.¹⁰ Intrinsic viscosity was converted to degree of polymerization (*DP*), using the relation of Immergut and co-workers¹¹:

$$DP = 124 [\eta]$$

where *DP* < 300.

Infrared Spectra. Spectra were obtained with a Perkin-Elmer Model 257 spectrophotometer, using a potassium bromide pellet technique similar to the method of O'Connor and co-workers.¹²

X-Ray Diagrams. Samples were held in thin-walled, cellulose acetate capillaries, and the photographs were taken with nickel-filtered copper K_{α} radiation.

RESULTS AND DISCUSSION

Cotton hydrolyzed for 15 min with boiling 2.5*N* HCl yielded a product with a LODP of 131. The weight loss was 6%. The LODP of mercerized cotton which had been washed with water and dried was 83, and the weight loss was 8%. When the time of hydrolysis was increased to 90 min, the LODP of cotton dropped to 129 and that of mercerized cotton to 82, whereas the weight losses increased to 11% and 21%, respectively. The reductions in LODP with the longer time of hydrolysis were within the limits of experimental error.

Hydrolysis of Disordered Cellulose

The sorption ratio (SR) was 2.55 for the disordered cellulose prepared from acetate rayon filaments by deacetylation followed by washing with ethanol (Table I). The fraction of accessible or amorphous material (F_{am}) in the product was calculated as 98%, using Valentine's relation¹³

$$SR = F_{am} 2.60.$$

When the deacetylated acetate rayon was washed with water either at 25°C or at the boil, the dried product was only partly disordered. This was indicated by the lower sorption ratios for the water-washed products than for the product that had been washed only with ethanol (Table I).

TABLE I
Effect of Washing Treatment on Properties of Disordered Cellulose
Prepared from Acetate Filament Yarn

Sample	Sorption ratio of sample	LODP ^d	Residue, ^d %	F_{am} ^e
Disordered ^a	2.55	21	62	0.98
Partly disordered ^b	2.02	24	55	0.78
Partly disordered ^c	1.81	24	61	0.70

^a Deacetylated sample washed with ethanol at 25°C and then dried at room temperature.

^b Deacetylated sample washed with distilled water and then ethanol at 25°C before drying at room temperature.

^c Deacetylated sample washed with distilled water at 25°C, then with boiling distilled water, and finally with ethanol at 25°C before drying at room temperature.

^d Level-off degree of polymerization and per cent residue determined after 15 min of hydrolysis with boiling 2.5*N* HCl.

^e Fraction of amorphous material.

Thus, crystallization occurred in the deacetylated acetate rayon as it was washed with water. The role of water in inducing the formation of interchain hydrogen bonds in cellulose⁹ and in inducing crystallization¹⁴ has been discussed previously. However, on hydrolysis for 15 min, similar values for both LODP and per cent residue were obtained with both the disordered and the partly disordered samples (Table I). When the time of hydrolysis was raised to 90 min, the LODP of the samples did not change but the amount of residue fell in all cases by roughly 50%. It can be deduced from the LODP values that the length of the crystallites produced by crystallizing disordered cellulose either by water or by boiling 2.5*N* HCl was similar. It is not known whether further crystallization of the partly disordered cellulose occurred during hydrolysis. If further crystallization did take place, it occurred with little change in the LODP, and it maybe speculated that such additional crystallization resulted either through the formation of new crystallites or by crystallization on the surface of existing crystallites, rather than by extension of the existing crystallites. Thus, it

appears that the possibility of crystallization occurring during hydrolysis does not negate the use of LODP as a relative measure of crystallite length.

The x-ray diagram of the disordered sample which had been hydrolyzed for 15 min corresponded to the pattern of cellulose II (Fig. 1). The diagram was not as well defined as that obtained from a mercerized cotton sample which had also been hydrolyzed for 15 min (Fig. 2). This is to be expected since the crystallites produced from the disordered cellulose were

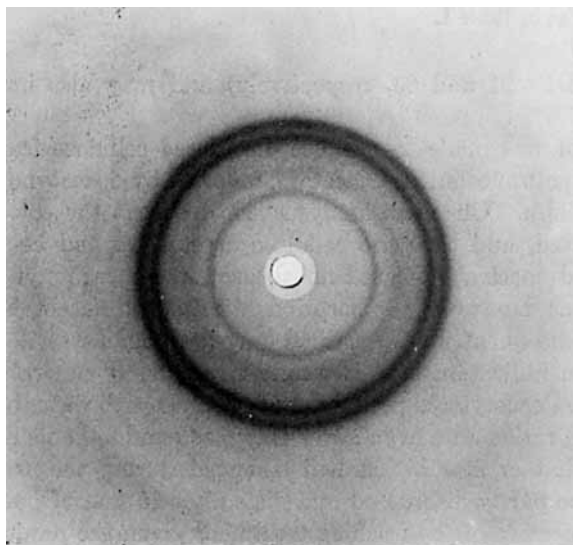


Fig. 1. X-Ray diagram of disordered cellulose hydrolyzed for 15 min in boiling 2.5*N* HCl.

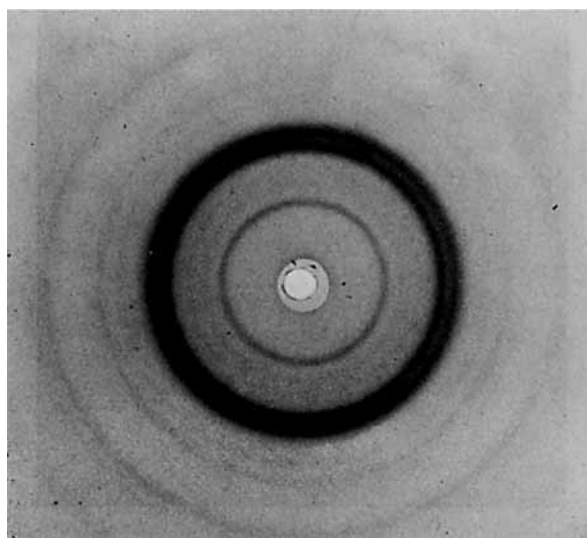


Fig. 2. X-Ray diagram of mercerized cotton hydrolyzed for 15 min in boiling 2.5*N* HCl.

TABLE II
Effect of Washing Treatment on Properties of Partly
Disordered Cellulose Prepared from Cotton

Sample	Sorption ratio of sample	LODP ^d	Residue, ^d %	F_{am} ^e
1 ^a	1.93	43	85	0.74
2 ^b	1.51	42	90	0.58
3 ^c	1.44	45	91	0.55

^{a,b,c,d,e} Same as in Table I.

smaller (LODPs 21 and 83, respectively) and may also have been less perfect.

An attempt was made to produce disordered cellulose from cotton by formation of cotton cellulose triacetate, followed by deacetylation in a non-aqueous medium. Chemical analysis revealed that the cotton had been fully acetylated, and thus the cellulose crystallites had been destroyed. Also, infrared spectra indicated no absorption for carbonyl groups after deacetylation. However, the sorption ratio of the deacetylated product which had subsequently been washed only in ethanol was 1.93 (sample 1, Table II), an indication that it was not completely amorphous ($F_{am} = 0.74$). If the deacetylated products were washed with water before drying, their sorption ratios were even lower (samples 2 and 3, Table II), indicating once more that crystallization had occurred during the washing. The LODPs of the partly disordered materials after 15 min of hydrolysis were similar, irrespective of the washing treatment given the products after de-

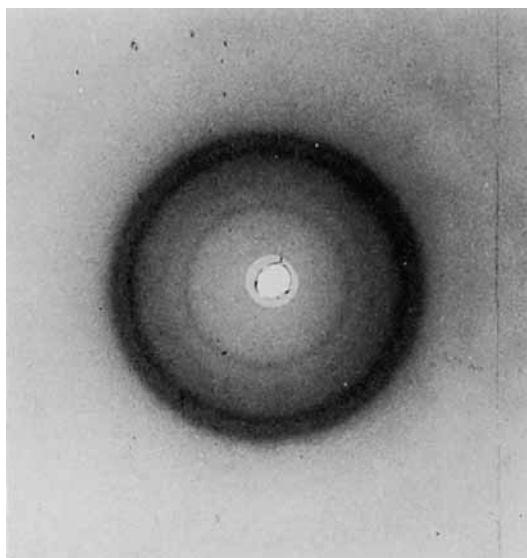


Fig. 3. X-Ray diagram of partly disordered cellulose prepared from deacetylated cotton triacetate (sample 1, Table II) and then hydrolyzed for 15 min in boiling 2.5N HCl.

acetylation. It can be inferred from these results, therefore, that when the deacetylated cotton cellulose triacetate was washed with water, the crystallization that occurred took place by a mechanism similar to that suggested for deacetylated acetate rayon.

The x-ray diagram of deacetylated cotton triacetate that had been washed with ethanol and then hydrolyzed with boiling 2.5*N* HCl was of the cellulose II form (Fig. 3) and not of the cellulose I form found in the starting cotton. For comparison, the x-ray diagram of hydrolyzed cotton in the cellulose I form is included (Fig. 4).

It is of interest to compare the properties of the partly disordered cotton celluloses with those of mercerized cotton, since the crystallites in mercerized cotton also have the cellulose II form. The sorption ratio of mercerized cotton was 1.64, and its LODP was 83 after 15 min of hydrolysis.

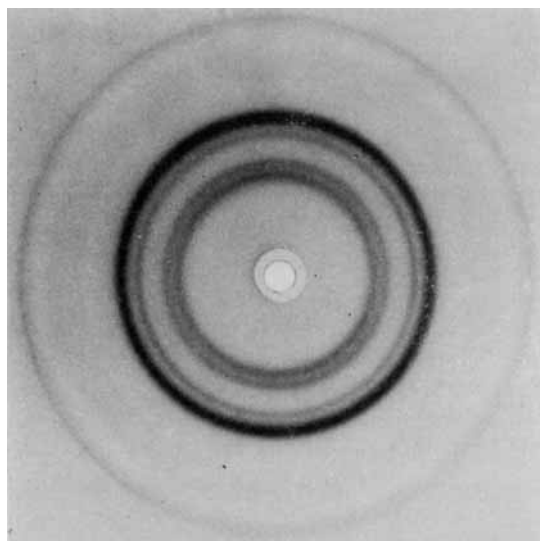


Fig. 4. X-Ray diagram of the starting cotton hydrolyzed for 15 min in boiling 2.5*N* HCl.

It appears, therefore, that all the partly disordered cotton celluloses (Table II), irrespective of the washing medium that was used after deacetylation, had shorter crystallites than did the mercerized cotton. The comparison is especially noteworthy for the partly disordered cotton celluloses that had been washed with water after the deacetylation step (samples 2 and 3, Table II). Both these samples had lower sorption ratios and therefore lower accessibilities than did the mercerized cotton. It has previously been claimed that there is a direct correlation between LODP and per cent accessibility of cotton treated with alkaline or acid swelling agents, and that LODP decreases as the accessibility increases.¹⁵ The reason that such a relation does not hold for the present results may be due to the marked differences in the methods used to modify the fine structure of the starting cotton.

LODP of Cotton Treated with Morpholine

Morpholine is an intercrystalline swelling agent which causes considerable swelling at the microfibrillar level.¹⁶ After 15 min of hydrolysis, the LODPs of cotton cellulose treated with morpholine or with a 40% solution of morpholine in water were 131 and 133, respectively, and the residue values were 96% and 97%, respectively. The values for untreated cotton were similar (LODP 131, residue 94%). Since the LODP of cotton cellulose was not affected by this intercrystalline swelling agent, the results are consistent with the theory that LODP can give a relative measure of crystallite length.

LODP of Cotton Treated with Sodium Hydroxide

Cotton which had been swollen with 20% aqueous NaOH and washed with water was not dried, but the water was displaced with 2.5*N* HCl and then the sample was hydrolyzed for 15 min with boiling 2.5*N* HCl. The LODP and per cent residue of the products were 79 and 91%, respectively. In another experiment, the cotton cellulose that had been swollen with 20% aqueous sodium hydroxide was washed with 2.5*N* HCl and hydrolyzed for 15 min in the boiling acid. The LODP and per cent residue of the products were 78 and 89%, respectively. Both sets of values are similar to those for mercerized cotton that had been washed with water and dried before hydrolysis (LODP 83, residue 92%). Thus, the length of the crystallites in mercerized cotton is not influenced by drying the sample. It would appear, therefore, that the aggregates of cellulose chains present in cotton that has been treated with aqueous sodium hydroxide of mercerizing strength and then washed with water are not completely accessible to hydrolyzing acid. Furthermore, the accessibility to the acid is not changed when the cellulose is dried. This is in marked contrast to the behavior of mercerized cotton on acetylation. Cotton that has been treated with aqueous NaOH of mercerizing strength and washed with water is more reactive, as indicated by acetylation, if it is not dried prior to the acetylation.⁶

When the alkali-swollen cotton is washed with dilute HCl, the product is also not uniformly accessible to acid hydrolysis. Thus, the water present during the washing appears to cause the formation of inaccessible regions.

LODP of Acetylated Samples

It was previously shown⁶ that the products of cotton which had been swollen in aqueous NaOH of mercerizing strength, washed with ethanol, and then solvent exchanged with pyridine before partial acetylation had a higher accessibility than mercerized cotton which had been washed with water before solvent exchanging with pyridine followed by acetylation. The higher accessibility was attributed to the difference in hydrogen-bonding capacity of ethanol and of water. A value of 1.97 was obtained as

TABLE III
Level-Off Degree of Polymerization (LODP) and Per Cent
Residue of Acetylated Cotton^a

Acetyl content of starting material, %	LODP	Residue, ^b %
8.2	67	83
14.0	68	69
20.5	66	62
28.5	58	51

^a Cotton was mercerized, washed with ethanol, and then solvent exchanged to pyridine before acetylating.⁶ Samples were hydrolyzed with boiling 2.5*N* HCl for 90 min.

^b Residue calculated on the weight of cellulose present in the starting material.

the sorption ratio of mercerized, ethanol-washed cotton which had not suffered a loss in accessibility by washing with water and drying.⁶

In the present study, the LODPs of samples of mercerized, ethanol-washed, never-dried cotton that had been acetylated were obtained to determine the effect of the mercerization and of the acetylation on crystallite size. An examination of the infrared spectra of the hydrolysis residues revealed no absorption for carbonyl groups after 90 min of hydrolysis in boiling 2.5*N* HCl. Thus, all the acetylated samples were hydrolyzed for this length of time. The x-ray diagrams of the hydrolyzed products indicated that the crystallites were in the cellulose II form. As the acetyl content of the samples was progressively increased from 8.2% to 28.5%, the LODP fell 13%, and the per cent residue fell 39% (Table III). It should be noted that the residue values were based on the weight of cellulose present in the starting material. The LODP and per cent residue of mercerized cotton that had been similarly hydrolyzed were 82 and 79%, respectively. Thus, if the loss in accessibility which accompanies washing with water and drying is prevented in mercerized, ethanol-washed cotton by solvent exchanging with pyridine and then acetylating, the length of the crystallites will be less than that in mercerized cotton. The acetylation was not the cause of the reduction in the LODP of the mercerized, ethanol-washed cotton. The LODP of cotton which had been swollen in NaOH solution of mercerizing strength and then water washed, solvent exchanged, and acetylated to an acetyl content of 17.7% was 78, which is close to the LODP of mercerized cotton. As stated earlier, the accessibility of the product is lowered if cotton, after mercerization, is washed with water rather than with ethanol.

Warwicker and co-workers¹⁷ have suggested that any disorder in cotton must be either on the surface of the elementary fibrils or periodically disposed along their length and that the important factor in the reactivity of cellulose is the accessibility to the surface of the fibrils. They consider the regions where lattice imperfections extend across the fibril to be short in length and not of the nature of a noncrystalline region into which molecules can readily enter.

The sites of the imperfections extending across the elementary fibrils are probably the regions where breakage into crystallites occurs on acid hydrolysis. Although the importance of the accessibility of the fibril surfaces to the reactivity of cellulose cannot be disputed, results in the present study indicate that molecules can enter the fibrils when cellulose is swollen with an intracrystalline swelling agent. As noted earlier, the LODP of mercerized cotton was markedly lower than that of the starting cotton (83 and 131, respectively), but the decrease in residue was small (92% and 94%, respectively). Thus, it seems that mercerization caused additional sites of lattice imperfection along the length of the fibrils. In addition, it has been shown that cotton which has been swollen in aqueous NaOH of mercerizing strength, washed in ethanol, and then acetylated to prevent a loss in accessibility on drying has a lower LODP than does mercerized cotton. It therefore appears that acetylation occurred in areas of lattice imperfections in the fibrils and that the acetyl groups prevented a reduction in accessibility in these regions when the acetylated samples were dried.

It is interesting to compare the LODP of the acetylated samples with that of partly disordered cellulose prepared from cotton cellulose triacetate. As noted earlier, the purpose of the acetylation was to prevent a loss of accessibility when the mercerized, ethanol-washed sample was washed with water and dried. In addition, it was noted that the sorption ratio of mercerized, ethanol-washed cotton that had not suffered a loss in accessibility was 1.97. This value is slightly greater than that of the partly disordered cellulose produced from cotton cellulose triacetate (sample 1, Table II). Since the acetylation prevented a loss in accessibility in the mercerized, ethanol-washed cotton, it may be assumed that the acetylated samples had an accessibility equivalent to that of the mercerized, ethanol-washed cotton. However, the LODP of the partly disordered cotton cellulose was lower than that of the acetylated samples (43 and 58–67, respectively), but the percentage residue of the disordered cotton cellulose was generally greater (85% and 51–83%, respectively). Thus, the process of decrystallization of cotton by mercerization followed by ethanol washing appears to differ considerably from that which follows deacetylation of cotton cellulose triacetate in a nonaqueous medium.

The author thanks Dr. K. J. Palmer, Western Regional Research Laboratory, U.S.-D.A., Albany, California, for the x-ray diagrams of the cellulosic samples.

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Received November 4, 1970

Revised December 30, 1970