

Dilute acid-hydrolyzed cotton cellulose

An electron diffraction study

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SUMMARY

A comparative morphological investigation by electron diffraction analysis was carried out on samples of cotton cellulose from different stages of dilute-acid-catalysed hydrolytic degradation reactions. Within the range from \overline{DP}_n 13000 (native material) to 500 only a gentle decrease of the relative crystallinity was observed. For \overline{DP}_n below 500 the crystallinity decreases much faster, together with a simultaneous marked increase in paracrystalline lattice distortion and the show up of crystallographic evidence for a new cellulose phase which became better defined as degradation proceeded. A clearly defined parallel can be established between the different kinetic stages of the degradation reaction and the degree-of-polymerization dependence of the morphological features. The resulting evidence is at odds with the traditionally held views about the effects of acid hydrolysis of cellulose on its morphological fine structure.

INTRODUCTION

In regard to acid-catalysed hydrolytic degradation of cellulose, it has been found that its kinetic course exhibits three different phases according to the range of degree of polymerization (DP) in which hydrolysis takes place (1). In the high-molecular-weight range two kinds of splitting reactions occur simultaneously. They consist in the cleavage of "weak links" (three or four per each cellulose molecule, still native in regard to its DP), and of normal 1,4- β -glucosidic bonds. Since the rate constants of these two splitting reactions differ by a power of 5, high DP cellulose degrades very rapidly and the rate of hydrolysis decreases with the disappearance of the weak links (2). Consequently, the second kinetic phase displays a constant reaction rate, corresponding only to the cleavage of the "normal" 1,4- β -glucosidic bonds. The subsequent third kinetic phase begins from \overline{DP}_n 500 on down and displays a new and continuously decreasing reaction rate. Simultaneously there occurs a systematic decrease of the ability of the cellulose to form nitrates with the standardized degree of substitution (3) of $DS = 2.90 \pm 0.02$, although nitration conditions known to produce this DS in a homogeneous and reproducible manner (4) were applied. Taking into account that the material under study has always been subjected to the same type of degradation procedure it was thought that this kinetic behaviour may have been a consequence of fine structural and morphological changes caused by the acidic reaction. The occurrence of a new polymorphic form under the action of strong acids and higher temperatures has already been described (5). Therefore, a more detailed study on the relationship between hydrolytic degradation and fine structure as a function of time of degradation has been started, with special emphasis on extended degradation times which determine

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in turn, the respective degrees of polymerization.

Morphological and structural studies can be carried out by two main techniques: X-Ray Diffraction and Electron Diffraction. In the present, first part, of the study we have relied mainly on electron diffraction (ED) experiments.

EXPERIMENTAL

The studies were carried out on samples originated in the kinetic studies (2,3), spanning a range of \overline{DP}_n from the native one ($\overline{DP}_n = 13000$) to 160. The different samples were suspended in n-Butanol and homogenized (Edmund Buhler Homogenizator Model, Germany) at 25000 rpm at an approximate temperature of -60°C and for 30 minutes. These conditions, according to our experience, involved the shortest time compatible with an adequate dispersion. Drops of the butanol suspension were deposited on gold-coated copper grids and dried. Although this treatment induces distinct morphological alterations on the specimens, their extent and nature are exactly equivalent for the different samples and do not invalidate the comparative character of the investigation.

The ED experiments were carried out on an electron microscope Siemens Elmiskop-101, at an acceleration potential of 80 kV, with stage-cooling and anticontamination provisions according to a previously described procedure (6).

Densitometric profiles of the ED diagrams were recorded by means of a double-beam microdensitometer Joyce-Loebl MK III. The supporting membranes of gold, in addition to performing as internal calibration standard for the determination of the crystal parameters, provide a convenient conducting contact to help dissipate heat and static charges from the specimens.

RESULTS AND DISCUSSION

The morphological investigations were focussed on the observation of the following parameters and phenomena as a function of molecular weight:

- 1) Lattice spacings (from the positions of the reflections on the ED diagrams).
- 2) Transitions giving rise to new crystal phases (from the occurrence of previously unobserved reflections).
- 3) Relative degree of crystallinity (from the peak heights of the equatorial reflections) (7).
- 4) Lattice disorder of the second (II) kind (from broadening of equatorial ED reflections) (8).
- 5) Degree of uniaxial orientation (from the azimuthal extension of the ED reflections) (9).

All this wealth of information for samples produced at different stages of the acidic degradation, characterized by well-defined DP's, is obtained by analysis of the microdensitometric traces of the ED diagrams. Although the quantitative analysis is concentrated on the equator of the diffractograms and refers, therefore, only to lateral order, qualitative observations on the whole hkl family of reflections indicate that the conclusions can be safely extended to the third dimension of the fibrils.

The results of the overall analysis carried out on samples of 7 different DP's are shown in Table 1. It is seen that the 020 spacings (Cellulose I, monoclinic $a = 8.35$, $b = 7.9$, $c = 10.3$, $\gamma = 96^\circ$ and $z = 2$, ref. 10) follow no significant trend as a function of molecular weight, as they vary at random within the limits of the experimental error ($\pm 2\%$). The degree of orientation is also rather indifferent to the influence of acidic degradation, as shown by its independence from DP.

TABLE 1
Quantitative Parameters of Degraded Cellulose Samples
as a Function of Degree of Polymerization

DP _n	<u>Interplanar Spacings</u>		Degree of orientation ^{a)} f	Relative Crystallinity %	Paracrystalline Distortion %
	020 (Å)	New phase (Å)			
13000 ^{b)}	--	--	0.95	75	2
3120	4.11	--	0.95	75	3
1100	4.12	--	0.95	54	4
940	3.99	--	0.95	56	4
500	3.90	4.34	0.95	50	2
300	4.14	4.34	0.95	28	39
160	4.17	4.34	0.95	14	55

a) The degree of orientation about the c axis is given by $f = \frac{3|\cos^2\phi| - 1}{2}$

where $|\cos^2\phi|$ is an average value describing the distribution of intensity of the reflection concerned about the corresponding direction, f is zero for random orientation and one for the perfect single crystal case.

b) Native material in regard to molecular weight.

Changes in diffraction broadening and relative crystallinity, on the other hand, are of a more significant nature as they display a clear dependence on DP. The former, arising from specimens of different DP but comparable cross section, is directly interpreted in terms of paracrystalline disorder (8) which only starts increasing for samples with number-average degrees of polymerization smaller than 500 and keeps growing up to the smallest DP investigated. The relative crystallinity decreases linearly as a function of molecular weight, whereby for \overline{DP}_n smaller than 500 the "velocity of amorphatization" increases by a whole order (Fig. 1) reaching at $\overline{DP}_n = 160$ a crystallinity which barely shows up in the diffraction pictures (Fig. 2). The corresponding course of these two parameters, degree of crystallinity and paracrystalline distortion, is hardly surprising, of course, in view of the fact that they follow from a model interpretation of two different features of diffraction diagrams which, at least partially, derive from a unique morphological reality (11). $\overline{DP}_n \approx 500$ also marks the onset of degradation at which a solid-solid phase transition begins to take place. This is demonstrated by the occurrence of an incipient shoulder on the 020 reflection, centered at 4.34 Å (as opposed to $d_{020} = 4.07$ Å), which becomes better defined as degradation proceeds (Fig. 3).

Clearly, therefore, a direct parallel can be established between a) the kinetic course of acid-catalysed hydrolytic degradation of cellulose, and its diminishing ability to undergo derivatization, and b) morphological characteristics of the specimens, as revealed by ED. Thus, the slow decrease in relative crystallinity, and the absence of changes on all the other morphological characteristics (Table 1) occur within the same range of \overline{DP}_n (from native to 500) in which the splitting of the 1-4,β,glucosidic bonds is accountable for the constant rate of hydrolytic degradation (second kinetic stage) (1,3). The subsequent stage (\overline{DP}_n from 500 to 160) witness a striking increase in the "velocity of amorphatization" as well as the setting out of a hitherto unobserved solid-solid phase transition, and the start of a progressive lattice-distortion process of the paracrystalline type (8). All these events take place on the same cellulose samples ($\overline{DP}_n \leq 500$ which display the lowest and ever decreasing rates of hydrolytic degradation (third kinetic stage) (1,3)).

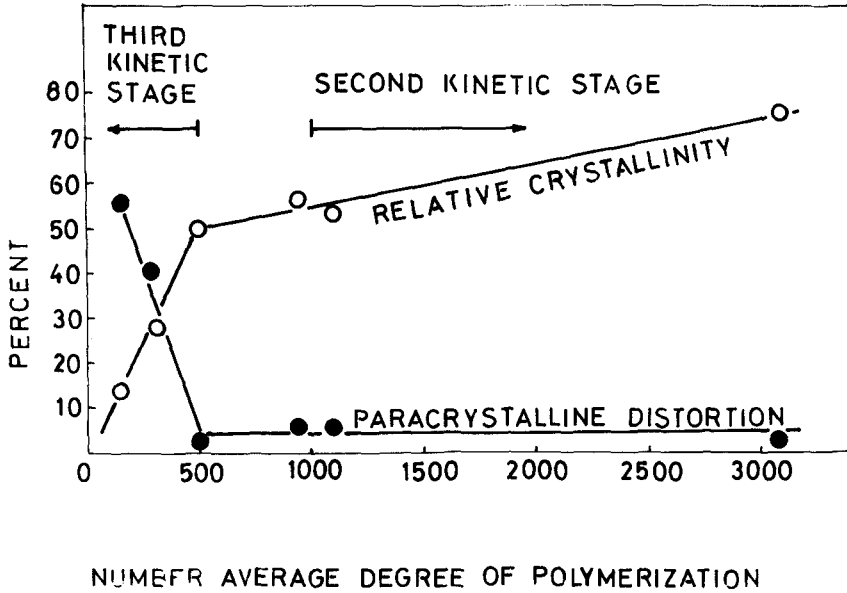


Figure 1.- "Relative crystallinity" and "paracrystalline distortion" respectively vs. number-average degree of polymerization of the hydrolyzed samples of cellulose.

Hydrolysing agent: aqu. solution 0.5 M KSO_4H .

Hydrolysing temperature: DP_n 160, 300, 500, 1100, $t = 60^\circ C$

DP_n 3120 $t = 40^\circ C$

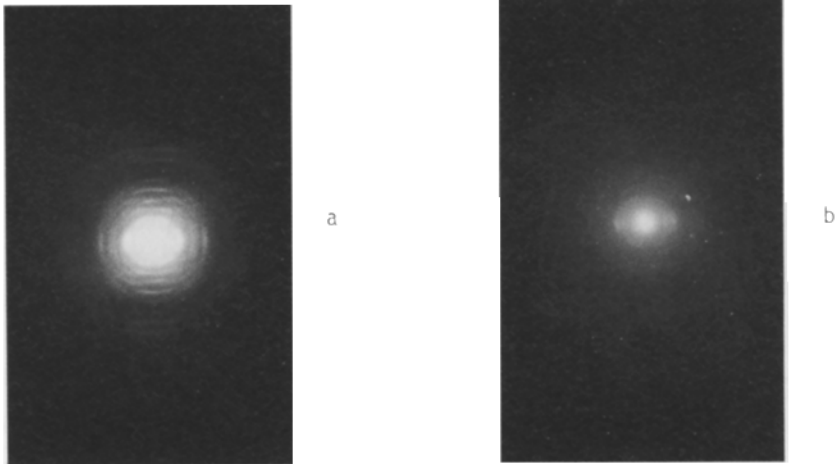


Figure 2.- Electron-diffraction diagrams of cellulose fiber. a) native cellulose, b) samples with $DP_n = 160$. OOL direction (fiber, c axis) is vertical, HKO planes (equator) projected into the horizontal axis.

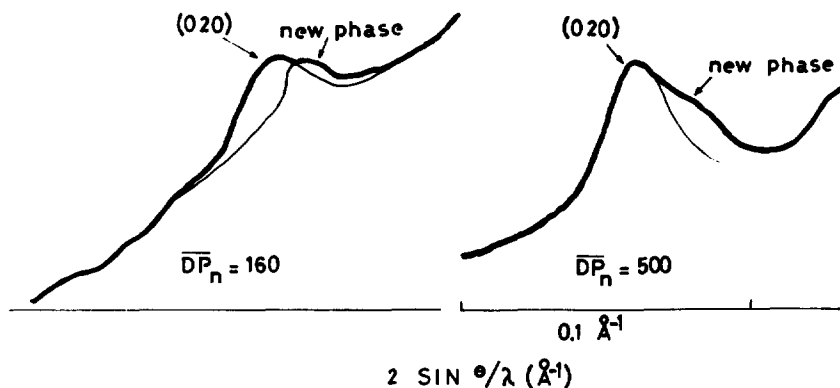


Figure 3.- Partial, microdensitometric equatorial scans of ED diagrams of hydrolytically degraded cellulose samples; (same samples are in Fig. 1).

Considering that sample handling for ED is identical for all specimens studied, and that only relative changes of the properties are considered, it is safe to conclude that the morphological evolutions observed are a consequence of the acidic treatment which, among other effects, induces a progressive decrease on the relative crystallinity of the samples along two well-defined straight lines (Fig. 1) as degradation proceeds. These experimental results are at odds with widespread views on chemical attacks to cellulose, based on the two-phase concept of morphology, which hold that the attacks take place preferentially by initial swelling and subsequent dissolution of the amorphous components (12,13) affecting thus a corresponding increase in the degree of crystallinity. This interpretation, which implies a definite weight loss of sample at each stage of degradation, is also in disagreement with the results of careful gravimetric measurements carried out in the framework of the kinetic experiments (1-3,14), that show no weight loss whatsoever, of the extent that would be expected from that model.

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