Pyrolysis-Crystallinity Relationships in Cellulose

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Abstract—During pyrolysis of pure cellulose, the Crystallinity Index (CrI) remained fairly constant over more than 50% weight loss before dropping rapidly as the X-ray pattern deteriorated. With samples first treated with trace quantities of inorganic salts, heating first increased the CrI—the results implying a preferentially catalyzed decomposition of the amorphous regions. Swelling cellulose in liquid ammonia eliminated the crystalline diffraction pattern, but heating restored a considerable degree of order. The initial weight loss rate in the swelled material was considerably accelerated and the ultimate char residue reduced. The results support the suggestion that inter-ring cross-linking leading to enhanced char formation will occur preferentially in the ordered rather than the disordered regions of natural cellulose.

INTRODUCTION

The subject of thermal decomposition of cellulose has received considerable attention during the past few decades [Broido and Kilzer (1963); Madorsky (1964); Shafizadeh (1968)]. Various theories have been proposed as to the sequence of chemical reactions during pyrolysis. Clearly, at least two competing sequences of reactions occur, in proportions dependent upon such factors as heating rate and purity of the sample [Broido (1966)]. If, as proposed [Kilzer and Broido (1965); Back *et al.* (1967)], at least one of these sequences involves an intermolecular cross-linking, pyrolysis should also depend upon the crystal structure of the cellulose—both initially and as the pyrolysis progresses.

Studies of crystallinity and accessibility in cellulose have led to conflicting descriptions of the shape and distribution of the ordered and disordered regions in the matrix. Naturally occurring cellulose has been described as having a structure ranging from uniformly ordered [Manley (1964)], through sharply demarcated between ordered and disordered regions [Battista (1950)], to gradually varying between highly ordered and totally disordered portions [Hermans (1949)]. Nevertheless, X-ray diffraction measurements do provide a simple and apparently useful indication of the ratio between ordered and disordered portions of cellulose [Wakelin *et al.* (1959); Segal *et al.* (1959); Ant-Wuorinen and Visapaa (1965)].

In particular, the Crystallinity Index (CrI) of

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Segal *et al.* (1959), obtained from measurements made at the diffraction intensity minimum observed at 2θ near 18° and at the intensity maximum observed at 2θ near 23°, gives results consistent with those obtained by the more sophisticated methods. Since the measurement at the minimum, representing the contribution of the amorphous regions, provides an 'internal reference', the CrI determination does not depend on the mass, shape, or size of the cellulose sample. This simple procedure is particularly suited to a study like the present one which only requires measurement of relative rather than absolute changes in the order-disorder relationship in pyrolyzed cellulose.

This paper reports results of CrI measurements as pure or treated cellulose paper samples lose weight in a pyrolysis process. For treatment with small quantities of inorganic additives, two salts were chosen: KCl, which should have minimal interaction with cellulose, and $ZnCl_2$, which in concentrated solutions swells and dissolves cellulose. To investigate the importance of pre-pyrolysis crystallinity, we used cellulose which was first swelled in liquid ammonia to eliminate the crystalline pattern.

EXPERIMENTAL

Materials

The cellulose samples used were 2.5 cm squares cut from circular sheets of Whatman #541 'ashless' filter paper, containing less than 0.01% ash (analysis: 0.008% ash).

For the salt-treated samples, sheets of this paper were first spiked on a vertical glass rod and 1 ml of an aqueous solution of either KCl (Mallinckrodt granular, A.C.S.) or $ZnCl_2$ (Baker and Adamson granular, A.C.S.), at a concentration such that the additive level was 10^{-5} moles of salt per gram of cellulose, was pipetted evenly on each sheet. The samples were air-dried and kept in a desiccator before use.

To prepare swelled cellulose, circular sheets of the standard paper were vacuum dried (10^{-2}–10^{-3} mm Hg) overnight in a container connected to a P_2O_5 drying tube. The container was then cooled to $-60\,°C$ and flushed with dry helium. The samples were then covered with liquid NH_3 (Matheson anhydrous, min. purity 99.99%) while a slight flow of dry helium was maintained through the system. After four hours, the liquid was poured off and the container evacuated until the papers looked dry. They were then transferred to a vacuum desiccator and kept in vacuum over concentrated H_2SO_4 and then P_2O_5 for two weeks, the desiccator being flushed occasionally with dry helium.

Ethylamine-swelled cellulose [Loeb and Segal (1955)] was first prepared in a similar way at $0\,°C$, using an 85% aqueous solution (prepared by adding Eastman anhydrous $EtNH_2$ to Matheson, Coleman and Bell 70% $EtNH_2$ in water). However, even after being pumped for two weeks with helium flushing, these samples still contained 1.6% nitrogen—corresponding to 1 mole of $EtNH_2$ per 5 anhydro-glucose units (AGU). (The $EtNH_2$ could not be removed completely even at 100 °C, where a residue of 1 $EtNH_2$ per 20 AGU still remained.) No such difficulty was encountered with the ammonia-swelled cellulose, since nitrogen analysis gave only 0.18% N, the same analytical result obtained using the original untreated cellulose as a control.

Heat treatment

(1) For each run, six or eight paper samples were threaded on a thin glass spike extending downwards inside a 5 cm I.D. vertical Pyrex cylinder (Figure 1). The lower part of this cylinder was equipped with a vacuum-tight Teflon gland through which a stainless steel tube, hooked at its upper end, could be rotated and moved up and down. Using this hook, samples could be pulled successively to the bottom of the cylinder during a run without breaking the vacuum. The cylinder was heated by a Lindberg Heavy-Duty Tube Furnace, the temperature of which was controlled
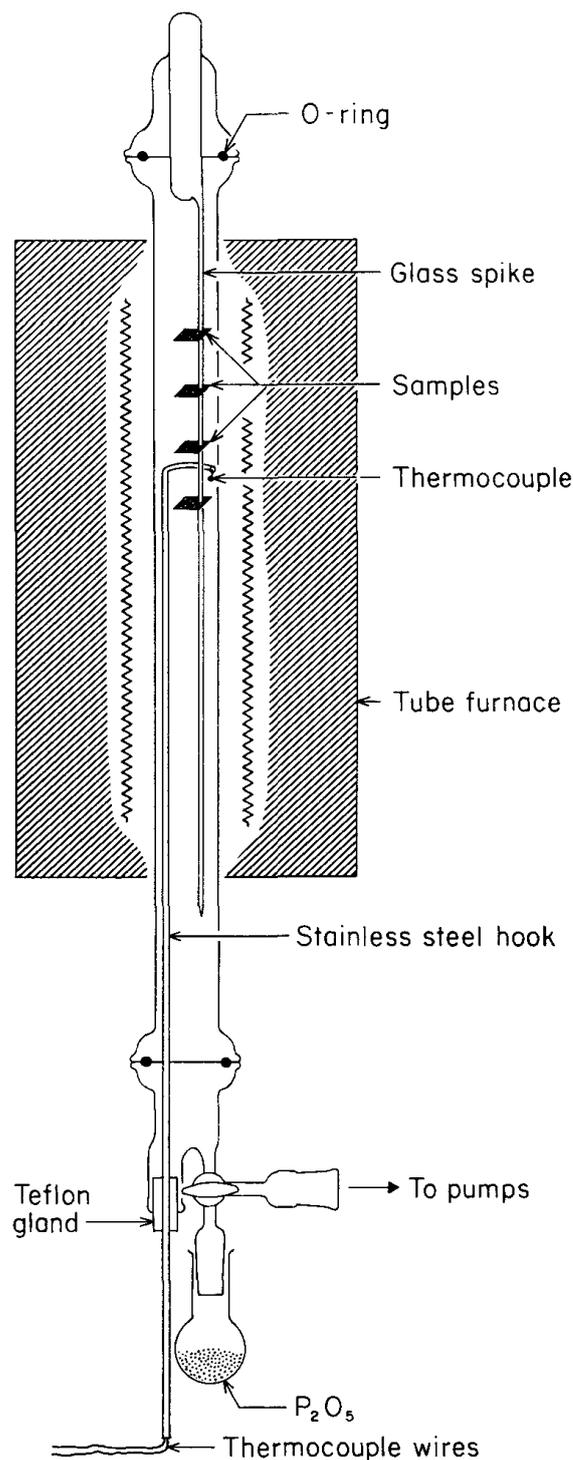

FIG. 1. Schematic of pyrolysis apparatus.

by a Hallikainen 'Thermotrol'. A thermocouple inserted through the stainless steel tube (which was then sealed at its lower end) measured the temperature at any point within the Pyrex cylinder.

For each run, the apparatus was loaded, evacuated (10^{-3} mm Hg) over P_2O_5 and, under continuous pumping, the furnace turned on.

Following a warm-up time of about 40 minutes, the controller kept the temperature constant within ±0.5 °C for the duration of the run. After predetermined periods, samples—two at a time—were pulled out of the furnace into the lower part of the Pyrex tube. After the last samples were withdrawn, the tube was cooled, opened to the atmosphere, and the pyrolyzed samples sealed in individual polyethylene bags.

(2) The isothermal weight loss of similar samples was determined independently under identical thermal conditions in a vacuum Thermogravimetric Analysis (TGA) apparatus using a Cahn RG Electrobalance.

X-Ray diffraction

The X-ray measurements were made on a General Electric Model XRD-3 Diffraction Unit equipped with a No. 1 SPG X-ray Detector. This detector uses an X-ray-sensitive Geiger-Mueller counting tube, Victoreen Thyrode Type 1B89, with a 0.030-inch beryllium window. The reproducibility and accuracy of the crystallinity measurements are much greater than obtainable with a conventional Geiger-Mueller tube, since the Thyrode employs a parallel multiple-cell construction, i.e., the cathode of each cell is tied to the metal shell and one common anode connection is brought out for the high voltage. This design results in a great reduction in apparent dead time because when one cell breaks into discharge the other cells are still sensitive to ionizing events occurring in them. Thus the counting rate is reasonably linear up to 10,000 counts/sec. The counting tube is connected to a logarithmic rate meter for rapid scanning and to a predetermined-count-scalar for accurate measurement.

The same geometry and intensity were used for all measurements: 40 kV and 10 mA Cu K_α beam, Ni filtered, 3° and 0.1° slits at the tube and detector, respectively.

Just before measurement, each sample was taken out of its bag, placed on a 2.5 × 3.8 × 0.3 cm Al plate to provide mechanical stability, and sample plus plate were covered with 10^{-3} cm thick 'dry cleaners' polyethylene foil [Segal (1962)] in order to minimize the effect of changes in moisture content [Ray (1967)]. The reflected X-ray intensity was recorded during a 0.2°/min sweep between 2θ angles of 17° and 19° and again between 21° and 23°, and the exact angles of the minimum and the 002 peak, respectively, were determined. The intensity was counted to a ±0.5% probable error

(16,384 counts) at these two angles. The Crystallinity Index could then be computed as

$$CrI = 100 \frac{I_{max} - I_{min}}{I_{max}} \qquad (1)$$

To minimize the effects of differences in fiber orientation among the various samples, the measurement was repeated with the sample rotated 90° in the cell, and the two measurements were averaged.

Typical intensities, uncorrected for background, were ca. 2000 counts/sec for I_{max} and ca. 700 counts/sec for I_{min}. Background readings with the empty cell in place were typically ca. 400 counts/sec at both angles. Thus, background corrections in the numerator of equation (1) largely cancel out, and background corrections of the denominator typically change the value of CrI by some 20%. To confirm the reasonableness of the measurement for samples whose thickness changed during pyrolysis, CrI values were obtained for multiple layers of the standard paper and for thinner paper layered to give mass-per-unit-area values similar to that of the pyrolyzed samples. Consistent CrI values were obtained when 85% of the counted intensity of the X-ray beam reflected from the empty cell at the corresponding 2θ angles was taken as background. When this empirical correction was applied, the correct CrI was found for samples of known crystallinity obtained from the USDA Plant Fibers Pioneering Research Laboratory.

RESULTS

Each of the CrI values summarized in Tables I–IV is an average of at least four determinations, i.e., two determinations each on duplicate samples. Where samples from two different runs were withdrawn after the same heating time, the reported value represents an average of eight determinations. Whether one considers the two measurements on the same sample, the duplicate samples in a single run, or the duplicate samples from different runs, the reproducibility was quite good, i.e., deviations only rarely exceeded ±2 CrI units. Although the measurement angles selected varied somewhat, especially in the quite flat minimum, the average angles for each result reported in Tables I–III were $(2\theta)_{min} = 18.1 \pm 0.1°$ and $(2\theta)_{max} = 22.7 \pm 0.1°$. For values in Table IV, the corresponding angles were $17.6 \pm 0.2°$ and $21.9 \pm 0.1°$.

TABLE I
Crystallinity Index of Pure Cellulose Samples
Isothermally at 260 °C

Time of heating	Weight loss	Crystallinity index
(hours)	(percent)	
Control	—	81
0[a]	2	77
5	22	74
7	29	73
24	59	71
27	61	63
31	64	42

[a] Samples withdrawn as soon as the reaction temperature was attained (about 40 minutes from start-up).

Pure cellulose samples heated isothermally at 260 °C (Table I) lost 2% of their weight during the heat-up period alone. However, the CrI decreased only slightly for 24 hours—until more than half of the sample weight was lost. Subsequently, the CrI dropped rapidly and after 36 hours, the X-ray pattern had deteriorated to an amorphous pattern closely resembling that of ball-milled cellulose [Patil et al. (1965)].

Similar samples heated at 225 °C lost as much as 2% of their weight only after 16 hours (Table II). Nevertheless, the CrI dropped somewhat during the 40 minute heat-up interval. Subsequently it apparently increased slightly but remained fairly constant for the next 41 hours—through a total weight loss of about 8%. At the comparable weight loss (2%), CrI measurements for the two temperatures were in close agreement.

TABLE II
Crystallinity Index of Pure Cellulose Samples
Isothermally at 225 °C

Time of heating	Weight loss	Crystallinity index
(hours)	(percent)	
Control	—	81
0[a]	0	75
3	0.3	74
6	0.5	77
16	2	76
19	3	78
24	4	76
41	8	76

[a] Samples withdrawn as soon as the reaction temperature was attained (about 40 minutes from start-up).

Treatment of cellulose with very dilute solutions of KCl or $ZnCl_2$ (1 mole salt per 500 AGU) does not change the CrI of the cold samples. By the time the treated samples reached the temperature of the furnace and suffered a weight loss of about 2%, however, the samples acquired a higher CrI than the original paper (Table III). The differences

TABLE III
Crystallinity Index of Treated Cellulose
(10^{-5} moles Salt per Gram of Cellulose)
Heated Isothermally at 250 °C

Time of heating	Weight loss Untreated	Treated	Crystallinity index
(hours)	(percent)		
	KCl—Treated		
Control	—	—	81
0[a]	1	2	85
4	5	9	83
26	30	22	80
	$ZnCl_2$—Treated		
Control	—	—	81
0[a]	1	2	84
3	4	7	83
26	30	28	79

[a] Samples withdrawn as soon as the reaction temperature was attained (about 40 minutes from start-up).

resulted from lower intensity of the diffraction at the minimum and not from intensification of the 002 peak.

The ill-defined X-ray pattern of the unheated NH_3-swelled cellulose resembled that of ball-milled cellulose—too diffuse to detect any superimposed pattern of swelled cellulose III. After heating, however, these samples regain considerable crystallinity (Table IV), although the previously noted shift in angle of both the maximum

TABLE IV
Crystallinity Index of NH_3-Swelled Cellulose
Heated Isothermally at 250 °C

Time of heating	Weight loss Pure	Swelled	Crystallinity index
(hours)	(percent)		
Control	—	—	([a])
0[b]	1	2	68
2	3	12	70
4	5	20	61
25	29	59	51

[a] Pattern similar to ball-milled cellulose, see text.
[b] Samples withdrawn as soon as the reaction temperature was attained (about 40 minutes from start-up).

and minimum indicate a different crystalline modification—either the swelled cellulose III structure or the high-temperature cellulose IV. The cold EtNH$_2$-swelled cellulose gave a CrI of approximately 65, and this value did not change much on heating through a 20% weight loss. However, since these samples retained a considerable quantity of EtNH$_2$, the interpretation of the crystal structure is quite uncertain. Further, since amines markedly affect cellulose pyrolysis reactions, the significance of weight loss results is also unclear.

DISCUSSION

In the temperature range of these experiments, Back et al. (1967) report a thermal softening of cellulose attributable to second-order transitions, followed by a thermal hardening as a result of cross-linking reactions. The thermal softening is consistent with the reported initial sharp drop to a constant degree of polymerization (D.P.) of the order of 200 reported earlier by Golova and Krylova (1960), and such results may account for the apparent drop and then increase in CrI in Table II.

Such correlations are subject to some uncertainty. Small traces of inorganic impurities markedly affect the pyrolysis behavior of cellulose; and Back's heating procedures, involving direct contact of the entire sample surface with steel platens, can perhaps introduce a similar catalytic effect. However, Golova and Krylova found similar D.P. effects for cellulose with ash content 0.22% and 0.001% and Halpern (1969) has confirmed their results for high-purity cellulose, indicating that the rapid decrease in chain length, at least, is insensitive to sample purity.

The increase in CrI of the salt-treated samples on heating, and particularly the lower intensity at the minimum, implies that there is a preferentially catalyzed decomposition of the amorphous regions in these samples. Such a result is not surprising, since the method of treatment does not introduce the additives into the more ordered parts of the matrix [Polcin (1966)]. Although the initial weight-loss rate is higher in these samples than in pure cellulose, the ultimate residue is also higher in the treated samples (~45% for the treated samples vs ~30% for the pure samples after five days at 250 °C). Thus, the additives must catalyze dehydration and other char-forming reactions which compete with the depolymerization process

responsible for most of the weight loss when pure cellulose is heated rapidly.

On the other hand, despite the re-introduction of some crystal structure in the NH$_3$-swelled cellulose, the initial weight loss rate in this material is considerably accelerated, and the ultimate char residue reduced (to ~20% after five days at 250 °C). Thus, the amount of char formed in pyrolysis of cellulose depends also upon the initial order-disorder relationship in the matrix. These results support the suggestion that inter-ring cross-linking leading to enhanced char formation will occur preferentially in the ordered rather than the disordered regions of natural cellulose.

The relative constancy of the CrI values for pyrolyzed cellulose (up to more than 50% weight loss) suggests an unzipping reaction proceeding along chains which continue through both ordered and disordered regions. The fact that catalytic amounts of additives which do not penetrate the crystalline regions can retard or even stop completely the depolymerization [Halpern (1969)] implies that this process starts from active end groups formed in the initial D.P. reduction step and that dehydration or cross-linking occurring at this stage can determine whether a cellulose chain will depolymerize or undergo further char-forming reactions.

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