

Molecular Weight Decrease in the Early Pyrolysis of Crystalline and Amorphous Cellulose

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Synopsis

Samples of ordinary "ash-free" cellulose papers and similar samples decrystallized by swelling in liquid ammonia were pyrolyzed in vacuo to a weight loss ranging from <0.1% to nearly 20%. The samples were then nitrated and their molecular weight distributions determined by gel permeation chromatography. When weight loss reached 1%, both the ordinary and the ammonia-swelled celluloses showed a large drop in average degree of polymerization (D.P.). However, the ordinary cellulose showed this sharp drop long before there was any measurable weight loss; the ammonia-swelled cellulose changed D.P. only gradually in the early stages. Further, x-ray diffraction measurements showed that by the time the D.P. of the ammonia-swelled cellulose had dropped appreciably, the material had developed a significant crystalline pattern. These results support the suggestion that initial rupture of the cellulose molecule occurs at strain points at the crystalline-amorphous boundaries.

INTRODUCTION

The thermal decomposition of cellulose involves at least two competing sequences of reactions in proportions depending, inter alia, on the crystal structure of the cellulose.¹ Although almost all studies of crystallinity and accessibility in cellulose indicate the existence of ordered (crystalline) and disordered (amorphous) regions in the matrix, the exact shape and distribution of such regions are still in dispute. One of the simplest descriptions pictures naturally occurring cellulose as consisting of sharply demarcated alternating crystalline and amorphous regions.² Hydrolysis of the smaller "amorphous" fractions has been used by Battista and Smith² to produce "microcrystalline cellulose" with a leveling-off average degree of polymerization (D.P.) below 200. Similarly, other investigators^{3,4} have found that by the time cellulose was pyrolyzed to only about 2% weight loss, its average D.P. had dropped from about 2000 to about 200, subsequently dropping only slightly through an additional weight loss of 50%.

When Broido and Weinstein⁵ found that weight loss in low-temperature cellulose pyrolysis was preceded by an "incubation period" of negligible

weight change, it became of interest to see if the initial sharp drop in D.P. actually occurs during this period, that is, before the first 1% or 2% weight loss. If so, this sharp drop could be explained by assuming that formation of crystalline regions in cellulose introduced an increasing strain in the molecule and that, when such a strain was sufficiently severe, it prevented continuing crystal growth until relieved by an amorphous region. When the material is heated, rupture would then occur at the sites of maximum strain—the boundaries between the crystalline and amorphous regions. If this explanation were correct, then decrystallized cellulose, which should have no such strain points, should not show the same sharp drop in D.P. Finally, for all such experiments, we were interested in determining the size distribution of the molecules rather than just the average D.P.

EXPERIMENTAL

Materials

Parallel studies were conducted on samples of "ordinary" and "decrystallized" cellulose. The ordinary samples were cut from Whatman #541 "ashless" filter (ash content less than 0.008%). The amorphous samples were cut from similar papers which had been swelled in liquid ammonia.¹ Removal of the swelling agent was confirmed by nitrogen analysis and by comparing the thermogravimetric analysis (TGA) curve with that previously obtained.⁶ Rectangular samples of approximately 250 mg were vacuum dried (10^{-4} mm Hg) over P_2O_5 for at least 16 hr at room temperature before pyrolysis.

For D.P. determinations, the heated samples and the controls were nitrated by the conventional procedure⁷ and aliquots submitted for nitrogen analysis by the ultramicro method.⁸ In all but one case discussed subsequently, the nitrogen content of the samples fell in the range of 13.3–13.7%, so no correction for incomplete nitration was needed.

Pyrolysis Apparatus

Most of the samples were dried and pyrolyzed individually in a TGA apparatus only slightly modified from that described previously.⁶ The power-proportioning temperature programmer was set at 5°C/min to heat the samples (except the controls) to a certain weight loss or, when weight loss was negligible, to a chosen temperature. To ensure that the weight loss was not due to adsorbed water, the heated samples were initially heated to 175°C, cooled to room temperature, and then heated to the desired temperature or weight loss. In all these cases, the weight of the sample at 175° was the same in the second heating step as in the first. The initial heating also served as a check on the linearity of the instrumental drift caused by thermomolecular flow and electrostatic effects in the system.⁶

To eliminate the possibility of slight differences in temperature histories for successive experiments with the two types of samples, we conducted a final series of experiments with both ordinary and decrystallized cellulose

heated simultaneously. These last experiments were confined to the temperature region of trivial weight loss. Therefore, no attempt was made to follow the individual weight changes, and the initial heating-cooling sequence was eliminated.

Gel Permeation Chromatography

To determine molecular weight distributions, we dissolved cellulose nitrate samples in tetrahydrofuran (THF) to a concentration of 0.15 g/100 ml. The dissolved samples were then filtered, using a Waters Associates pressurized filter, for gel permeation chromatography (GPC). The GPC apparatus was a Waters Associates Model 200 equipped with an automatic six-station sample injection system and modified for computer-controlled operation.^{9,10}

The GPC system was calibrated against polystyrene standards and an appropriate model was used to calculate molecular weights.¹¹ Comparisons with viscometric measurements of the same cellulose nitrate solutions gave agreement within 10% in the retention range for which standards were available, with increasing deviation at higher D.P. The size of the deviations depends somewhat on the particular model assumed here and in the literature sources of data. As a further check at the low molecular weight end, measurements were repeated using the best available standard, microcrystalline cellulose. Even for this material, however, D.P. values reported in the literature are variable—ranging at least from 150 to 200. In any case, applicable data corrections should not affect the major conclusions of this paper.

X-Ray Diffraction

Diffraction spectra on the "ordinary" control material and all of the ammonia-swelled samples were obtained on fractions mounted as previously reported.¹ For added protection, the mounted samples were kept in a desiccator and removed only for mounting on the General Electric XR-5 diffractometer used. A constant-power setting of 50 kV, 30 ma was used to get a Ni-filtered Cu $K\alpha$ x-ray beam. Slits of 1° and 0.1° for the tube and detector, respectively, were used.

Viscosity

Samples were dissolved in THF by shaking for 1 hr at room temperature before equilibrating in a water bath controlled at $25.11 \pm 0.01^\circ\text{C}$. An Ubbelohde viscometer was used for the measurements.

RESULTS AND DISCUSSION

With the exception of the samples pyrolyzed to over 15% weight loss (samples O-6A and O-6A in Table I), all nitrated samples dissolved readily in THF. Nitrated samples of O-6a and D-6a dissolved very slowly and incompletely. The N content of sample O-6a was more than 13% and approximated that of the readily soluble samples. Hence, it seemed un-

TABLE I
Change in Weight-Average Degree of Polymerization With Heat
Treatment of Ordinary and Ammonia-Swelled Cellulose Samples

Sample no.	Weight loss, %	(D.P.) _w ^a	(D.P.) _{peak}	Polydispersity
Microcrystalline cellulose standard ^b	0	180	190	1.81
Ordinary cellulose				
O-1	0	2650	2200	2.10
O-2 ^c	^d	600	460	3.07
O-3 ^c	^d	520	455	1.92
O-4	1.02	375	420	1.97
O-5	5.68	350	340	1.87
O-6a		205	170	2.23
	15.46			
O-6b		220	180	3.40
Decrystallized cellulose				
D-1	0	1970	1450	2.00
D-2 ^c	^d	1580	1140	2.06
D-3 ^c	^d	1230	700	2.37
D-4	1.05	410	390	2.20
D-5	3.98	260	200	1.99
D-6a		85	50	2.03
	17.60			
D-6b		145	60	3.10

^a Computed from GPC data.

^b D.P. by viscometry = 200.

^c Heated to 175°.

^d Negligible weight loss.

^e Heated to 225°.

likely that the difficulty in solubility could be attributed to incomplete nitration. For sample D-6a, the nitrogen content was only 12.7%, so incomplete nitration was a possible explanation. In any case, aliquots of both samples were renitrated, and, although nitrogen analysis showed no significant change for either sample, both renitrated samples dissolved without difficulty. The ease of solution for the renitrated sample can probably be explained by an alteration in the physical state of the sample. On renitration, the sample became more brittle and powdery. The decreased particle size thus provided increased surface area to facilitate solvent-polymer interaction.

The GPC analyses of the fraction that dissolved for the singly nitrated sample (O-6a) and the renitrated sample (O-6b) showed an increase in weight-average D.P. from 205 to 220. The polydispersity index indicated a wider molecular weight distribution for O-6b. The elution curves (Fig. 1) show O-6a and O-6b peaking at D.P. 170 and D.P. 180, respectively, and an increase in the higher-D.P. components for O-6b. It appears that in the incomplete solution of the sample, the higher-D.P. components were preferentially left behind in the insoluble fraction. This effect was even more

pronounced for the decrystallized cellulose. Renitration increased the weight-average D.P. from 85 to 145. Although curves D-6a and D-6b (Fig. 2) are quite similar from the low end through the peak, curve D-6a drops off much more sharply at the high-D.P. end.

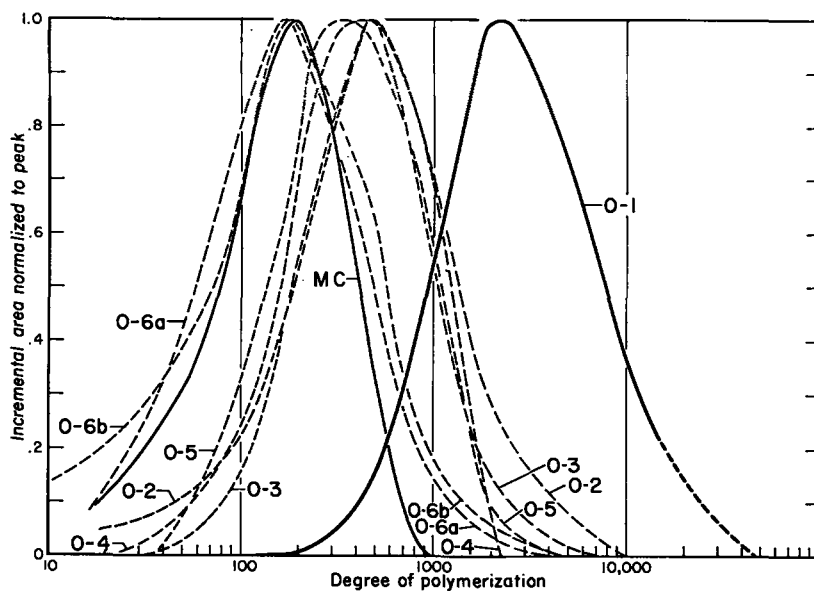


Fig. 1. Change in molecular weight distribution curves with heat treatment for ordinary cellulose.

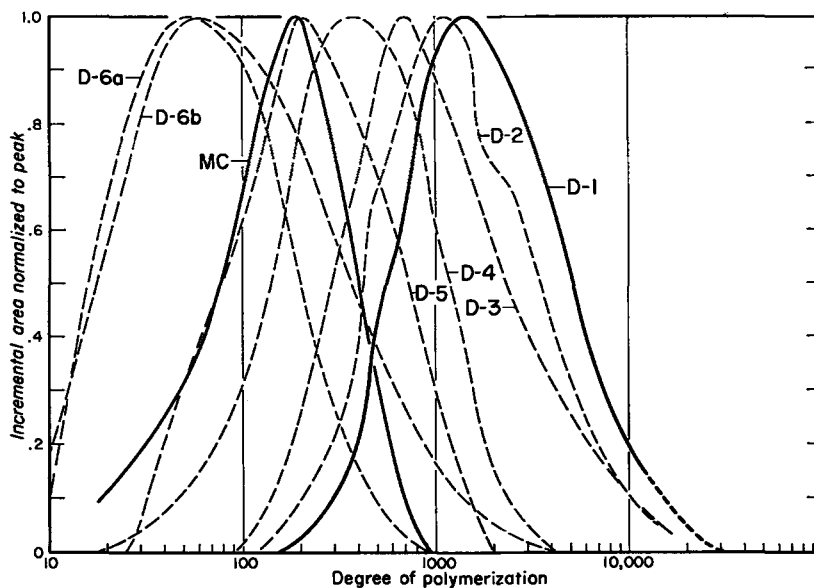


Fig. 2. Change in molecular weight distribution curves with heat treatment for ammonia-swelled cellulose.

For the ordinary cellulose, a remarkable drop on D.P. occurred by the time the sample was heated to 175°C—long before a loss in weight was observed. Progressive heating of the cellulose caused only a small additional decrease in D.P. (Table I). The rate of decrease was progressively slower, indicating a leveling-off of the D.P. The average D.P. for sample 6 approaches that reported by both Golova and Krylova³ and Halpern and Patai⁴ and that of microcrystalline cellulose which is suggested to be the length of a single crystallite.

The shift in the entire distribution curve accompanying the decrease in average D.P. (Fig. 1) occurs in a straightforward way. After the initial marked shift, the elution curves change only slightly, in agreement with the concept of a leveling-off D.P.

The pattern of change in D.P. as the amorphous cellulose samples were heated to various stages of pyrolysis was quite different (Table I). At 1% weight loss, the D.P., in fact, had fallen to a value comparable to that of regular cellulose at 1% weight loss. However, for the less severe treatments—heating to 175° and 225°—only a relatively small decrease in D.P. occurred. On the other hand, with continued heating the D.P. decreased faster than did that of regular cellulose and to much lower values. Thus, at 17% weight loss, the D.P. was lower than that of the microcrystalline cellulose.

A continuously shifting molecular weight distribution for the ammonia-swelled cellulose accompanies the continuous drop in D.P. (Fig. 2). The distribution curve for sample D-5 is remarkably similar to that for microcrystalline cellulose from the low end through the peak, but sample D-5 contains appreciably more of the higher D.P. fractions. The curve for sample D-6 is clearly to the left (lower D.P.) of that for microcrystalline cellulose.

These results provide evidence for the presence of strain points in the ordinary cellulose structure and suggest that these strain points occur at regular intervals comparable in magnitude to the length of a single crystallite. On the other hand, ammonia-swelled cellulose samples lack the regular crystalline and amorphous site arrangement found in ordinary cellulose. The drastic drop in D.P. on initial heating does not occur because strain points for the cleavage are nonexistent in the "decrystallized" samples. However, as noted by Weinstein and Broido,¹ heating such material rapidly restores crystallinity, and the x-ray diffraction spectra of these samples (Fig. 3) indicate that this effect occurs early in the heating schedule. Thus, by 175°C, the amorphous sample has already begun to acquire some crystalline structure. By 225°C, this crystallinity is quite clearly indicated, e.g., by the appearance of the minimum around 18°. When weight loss reaches 1%, much of the ultimate crystallinity has been regained by the sample. Note the definite minimum around 18°. Crystallinity indices, calculated according to Segal et al.¹² for samples 4, 5, and 6, are comparable.

The major implications of these results are highly dependent on the heating regimen before any significant weight loss can provide an additional

TABLE II
Change in Viscometric Degree of Polymerization for Ordinary
and Swelled Samples Heated Simultaneously

Maximum temperature	Degree of polymerization	
	Ordinary	NH ₃ -swelled
Ambient	1100	1140
175°C	820	1170
185°C	710	1170
195°C	460	900
225°C	290	560

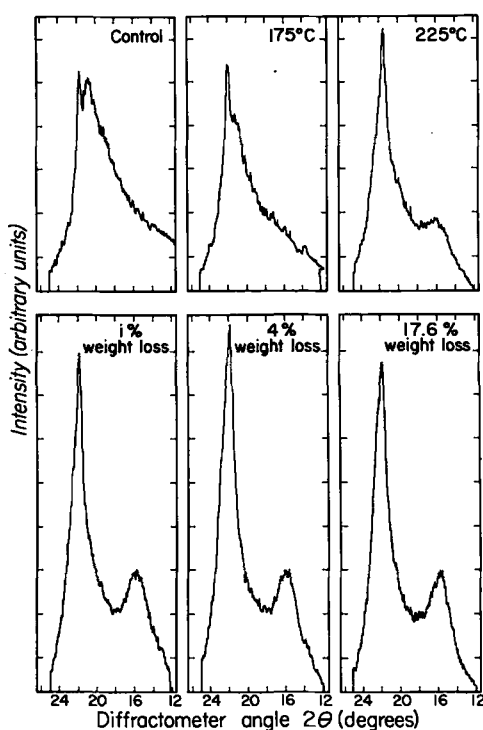


Fig. 3. X-Ray diffraction spectra of the heated ammonia-swelled cellulose samples.

check on small differences in successive experiments. Therefore, we conducted an additional series of experiments. For each experiment in this series, two samples, one of ordinary cellulose and one of the NH₃-swelled material, were mounted together in the apparatus and heated simultaneously at 5°/min to the desired temperature. Upon reaching this temperature, the furnace was lowered and the samples cooled. Each sample was then nitrated and its average D.P. determined viscometrically. Elimination of the initial heating-cooling cycle provided a somewhat different

temperature history for these samples than that of the earlier experiments. The results (Table II) are in essential agreement with those obtained earlier.

In relating the GPC and the x-ray diffraction results, then, a reasonable explanation for the decrystallized cellulose results is suggested. When heated to 175–185°C, the amorphous sample has started to develop some crystalline structure, but not enough rearrangement has taken place to permit a significant amount of cleavage at strain points. When heated to 225°C, more strain points have been created and further cleavage has caused a further slight decrease in average D.P. When weight loss is 1%, much of the ultimate crystalline cellulose structure had been restored so that a more extensive breakdown has occurred.

The subsequent further decrease in D.P. for the NH_3 -swelled samples indicates that in the process of regaining crystalline structure, more cleavage points were created than existed before swelling, i.e., in the restored crystalline structure the crystallite size is smaller. We have no direct evidence concerning the crystallite size in the recrystallized material. Unfortunately, the most reliable method of determining crystallite size—hydrolysis to a leveling-off D.P.—cannot be used because wetting the decrystallized material causes rapid restoration of crystallinity.

CONCLUSIONS

This study has provided evidence that:

1. Fracturing of the cellulose molecule to smaller polymer lengths occurs before any measurable weight loss takes place.
2. In amorphous cellulose, some rearrangement to a crystalline structure takes place before a detectable weight loss.
3. The decrease in the degree of polymerization of the decrystallized cellulose follows the development of crystallinity.

The results support the contention that in the ordinary cellulose structure, strain points exist where cleavage occurs, giving rise to much shorter polymeric chains. Further, the fact that the leveling-off D.P. on pyrolysis of ordinary cellulose approaches the D.P. of microcrystalline cellulose supports the argument that the strain points occur at the crystalline–amorphous interfaces.

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References

1. M. Weinstein and A. Broido, *Combustion Sci. Technol.*, **1**, 289 (1970).
2. O. A. Battista and P. A. Smith, *Ind. Eng. Chem.*, **54** (9), 20 (1962).
3. O. P. Golova and R. G. Krylova, *Doklady Akad. Nauk SSSR*, **135**(6), 1391 (1960).
4. Y. Halpern and S. Patai, *Israel J. Chem.*, **7**, 673 (1969).
5. A. Broido and M. Weinstein, *Thermal Analysis*, Vol. 3, Hans G. Wiedemann, Ed., Birkhäuser, Basel, 1972, pp. 285-296.
6. A. Broido and M. Weinstein, *Combustion Sci. Technol.*, **1**, 279 (1970).
7. W. J. Alexander and R. L. Mitchell, *Anal. Chem.*, **21**(12), 1497 (1948).
8. C. W. Koch and E. E. Jones, *Mikrochim. Acta*, **4**, 734 (1963).
9. A. R. Gregges, B. F. Dowden, E. M. Barrall, II, and T. T. Horikawa, *Separation Sci.*, **5**(6), 731 (1970).
10. A. C. Ouano, *J. Polym. Sci. A-1*, **9**, 2179 (1971).
11. A. C. Ouano, A. Broido, Edward M. Barrall II, and A. C. Javier-Son, *Recent Trends in the Determination of Molecular Weight*, M. Ezrin, Ed., American Chemical Society Advances in Chemistry Series, in press.
12. L. Segal, J. J. Creely, A. E. Martin, Jr., and C. M. Conrad, *Text. Res. J.*, **29**, 786 (1959).

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