The Acid-Catalyzed Degradation of Cellulose Linters in Distinct Ranges of Degree of Polymerization

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Synopsis

Cellulose linters with starting degrees of polymerization between $100 < DP_n < 6000$ had been hydrolytically degraded (0.5 M aqueous solution of $KHSO_4$, degradation temperature 40°C and 60°C) and the results compared with those obtained in a former study on pure cotton cellulose using the same degradation conditions. A complete coincidence in the degradation characteristics of both is shown, distinguishing the latter one by the following features: (1) different kinetic behavior according to the molecular weight range in which degradation takes place; (2) those corresponding to the very high as well as to the very low range of DP reveal a notable decrease of reaction rate; (3) a simultaneous systematic decrease of derivatization capacity occurs in the low molecular weight range; (4) There is no systematic increase of soluble material in the acidic medium with degradation time; (5) in the low molecular weight range, the polidispersity index derived from the molecular weight distributions remains near $DP_w/DP_n = 2.0$, except when the hydrolysis had been carried out on already technologically digested materials, causing in these cases a certain increase. The possible reasons for the distinct features of degradation behavior are discussed.

INTRODUCTION

Recent detailed studies on the acid-catalyzed degradation of cotton cellulose with initial degrees of polymerization (DP) ranging from $DP = 13,000$ to $DP < 200$ revealed the following features:[1-3]

In the high molecular weight range, two kinds of splitting reactions occur simultaneously, namely the cleavage of four "weak" links per native molecule* and that of the normal 1,4-β glucosidic ones. The rate constants of these two reactions differ by a power of 5.[1] Therefore, in the early stages of hydrolysis, high molecular weight cellulose with average degrees of polymerization (DP_n) exceeding 4000 degrades very rapidly at moderate temperatures such as 40°C. As the weak links disappear, the degradation decreases to a constant rate until the medium range molecular weight is reached, and thus a second kinetic phase. The "weak links" can be attributed to genuine chemical alterations in the cellulose molecule rather than supermolecular arrangement.[2] A subsequent third kinetic phase shows a continuous decrease of reaction rate beginning with $DP_n \cong 500$.[3] This is well observable at somewhat higher temperatures (60°C), at which the "critical" DP is reached more rapidly and the decrease in velocity, therefore, is more pronounced. Consequently, the

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*i.e., Cellulose molecule which did not suffer any alteration after its biosynthesis.

lower the starting DP of the respective material in hydrolysis, the lower is the individual initial reaction rate.

With a $DP_n \equiv 350$ or lower, the decrease in reaction rate is accompanied by a systematic decrease of the degree of substitution (DS) of the respective nitrates,[3] in spite of the fact that nitration conditions known to produce a homogeneous and reproducible DS of 2.90 ± 0.02[4] were applied. The chain length distributions arising in the range $DP_n < 500$ do not deviate notably from the most probable one even at very extended stages of hydrolysis. Also, dissolution of degraded material in the acidic medium does not systematically increase with increasing time of hydrolysis.

All cited investigations had been carried out with cellulose isolated from cotton seed hairs according to mild laboratory procedures known to conserve the native molecular and supermolecular properties.[5] Most of them were then brought to the desired distinct ranges of DP by a first preparative degradation step ("predegradation"). The hereby applied reaction conditions were the same as in the following proper kinetic experiments and did not introduce, therefore, any other alteration in the cellulose as a hydrolytic splitting of the β-glucosidic bonds. As a consequence, the samples used in the cited kinetic studies can be considered as representative for a pure cellulose, and the results obtained on them can be taken as a reference to evaluate the effects of alterations eventually occurring in celluloses of technological use, on their hydrolytic behavior.

In the present investigation, linter samples of different origins, stored at different conditions or already technologically treated were used. The respective results are presented and compared with those obtained on a pure cotton cellulose below.

EXPERIMENTAL

The kinetic experiments were conducted essentially as described previously,[1,2] namely by using a 0.5 M $KHSO_4$ aqueous solution as degradative agent with a constant 3 to 1 (mg/ml) cellulose/solution ratio at degradation temperatures of $40\,^\circ C$ and $60\,^\circ C$.

As has been proved, these conditions provoke a homogeneous swelling of cellulose, thus avoiding the involvement of diffusion effects in the resulting kinetics.

After an exhaustive washing with bidistilled water, the degraded specimens were subjected to a successive passage through H_2O-methanol and methanol-benzene mixtures with increasing proportions of the less and nonpolar component, respectively. Finally, they were freeze dried from a suspension in pure benzene.

Using raw linters as primary material, the cellulose had been previously isolated from the noncellulosic components according to previously described procedures.[5]

A portion of the raw linters cellulose had been "predegraded" with $KHSO_4$ solution to a DP comparable to that of the technological samples.

Before converting into their nitric acid derivative according to Ref. 4, each degradation specimen had been measured viscosimetrically at standard conditions in CuEn using Eqs. (1a) and (2a) to derive the corresponding viscosity

average degree of polymerization DP_η.[6] On the nitrates, the intrinsic viscosities had been measured at standard conditions in acetone[7] and converted in degrees of polymerization by Eqs. (1b) and (2b):[7] If $DP \ll 1000$ ml $\cdot$ g^{-1}

$$[\eta]_{CuEn}(ml \cdot g^{-1}) = 0.42 \times DP \tag{1a}$$

$$[\eta]_{Ac}^{Nitr}(ml \cdot g^{-1}) = 0.82 \times DP \tag{1b}$$

If $DP \gg 1000$ ml $\cdot$ g^{-1}

$$[\eta]_{CuEn}(ml \cdot g^{-1}) = 2.29 \times DP^{0.76} \tag{2a}$$

$$[\eta]_{Ac}^{Nitr}(ml \cdot g^{-1}) = 4.46 \times DP^{0.76} \tag{2b}$$

The corresponding number average degrees of polymerization had been determined by use of a Hewlett Packard Membranosmometer, Model 501, or by deriving it directly from the DP_η by means of a $DP_\eta - DP_n$ calibration curve.[1]

The distribution of DP had been determined by gel permeation chromatography (GPC) according to Ref. 8 in tetrahydrofuran (THF) as eluent, using a WATERS Liquid Chromatograph equipped with an ultraviolet spectrophotometer as detector and a set of μ-Styragel columns 10^6–10^5–10^4–10^3.

RESULTS

Table I lists the starting materials used, together with an indication of their origin and their respective average values of DP_η and DP_n. The latter represent the starting degrees of polymerization in the corresponding kinetic experiments.

As is commonly known, the hydrolytic degradation of cellulose obeys to a law of first order and can be expressed by Eq. (3)[9]

$$1/DP_{n(t)} - 1/DP_{n(0)} = k \cdot t \tag{3}$$

where DP_t and DP_0 mean the number average degrees of polymerization at the times t and 0, respectively. If degradation occurs throughout statistically, the inverse number average degrees of polymerization at different degradation times t must form a straight line cutting the ordinate at the inverse $DP_{n(0)}$. The foregoing studies on pure cotton cellulose had shown, however, that in the range of high molecular weights this is not the case. Here, the first degradation stages distinguish also at moderate temperatures (40°C) by a rapid decrease of the reaction rate before constancy is reached.[1,2] The same behavior had been found in the present study on high molecular weight cellulose linters as in Figure 1. In the same graph, the data obtained formerly[1] on a representative high molecular weight cotton cellulose sample were also included to facilitate comparison.

Similar to cotton cellulose, at a degradation temperature of 40°C, the decreasing reaction rate of the initial phases of degradation of linter cellulose approaches a constant value when DP_0 approaches the range of $DP_{n(0)} < 3000$. On the other hand, in the same range of DP but at degradation temperatures

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TABLE I

Origin and Average Degrees of Polymerization $\overline{DP}_\eta$ and $\overline{DP}_n$
of the Used Linters Cellulose Samples

Sample no.	Material	% Cellulose[b]	DP_η	DP_n
I	2nd cut raw linters (stored for some years before use)	88	8450	5450
II	2nd cut raw linters (strongly damaged during storage at open air)	58	4745	2600
III	Linters from I, technologically digested (stored for some years before the present study)	[a]	700	350
IV	Sample III, technologically bleached (stored for some years before the present study)	[a]	600	300
V	Sample III, weakly predegraded according to Ref. 3	[a]	600	300
VI	Linters from II, technologically digested and bleached (stored for some years before the present study)	[a]	360	180

[a] Used without further purification.
[b] Material not soluble in boiling 2% NaOH aqueous solution.
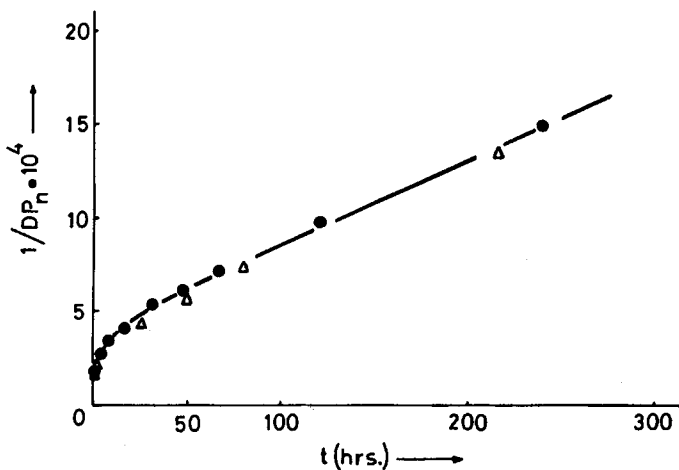

Fig. 1. Inverse number average degree of polymerization as a function of time of degradation. $DP_{n(0)} \equiv 5400$. Degradation temperature: 40° C; ● linters cellulose (sample I); △, cotton cellulose.

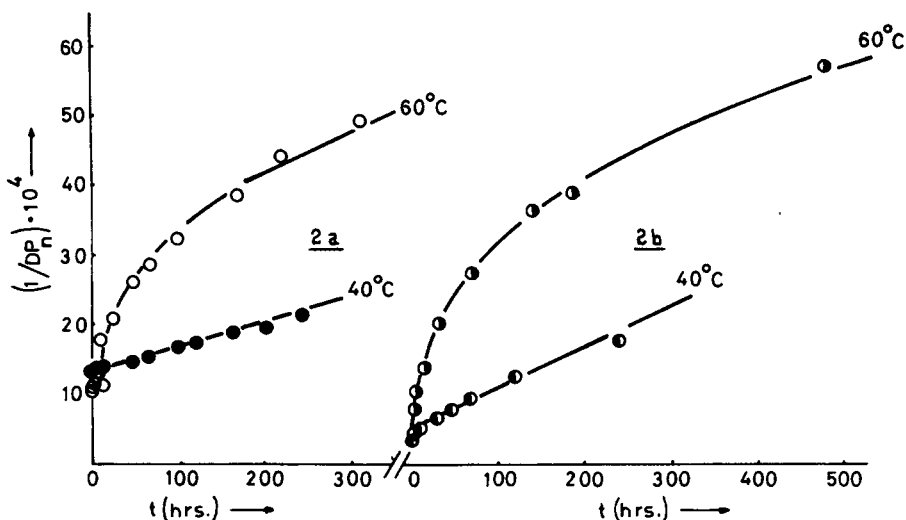Fig. 2.   Inverse number average degree of polymerization as a function of time of degradation at temperatures of 40° and 60°C. $1000 < DP_{n(0)} < 3000$. (a): ●○, cotton cellulose;[1,3] (b): ◑ ◐, linters cellulose (sample II).

of 60°C, a notable decrease of reaction rate is observed, although in a somewhat later degradation stage. This is shown by the Figure 2 on the example of a linter and a cotton cellulose in the range of $1000 < DP_{n(0)} < 3000$.

As it is shown in the Figure 3, when $DP_{n(0)} > 2500$, the degradation rates at 60°C of the initial phases are still independent from DP_0 and seem to agree with those found on cotton cellulose for the slow degradation stage in the range of high molecular weight.[3] Also, by $DP_{n(0)} \ll 1000$, the degradation
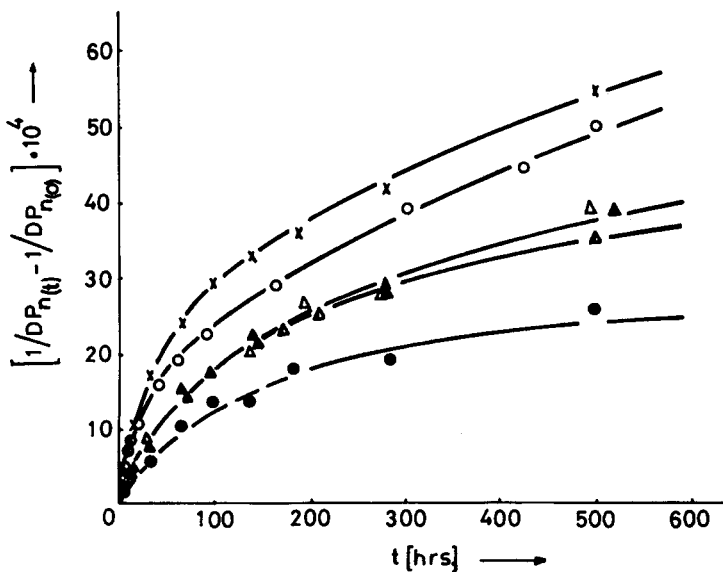

Fig. 3.   Inverse number average degree of polymerization as a function of time according to Eq. (3). Degradation temperature: 60°C. $1000 < DP_{n(0)} \ll 3000$: ×, ○; $DP_{n(0)} \ll 1000$: ▲, △, ▲, ●. ×, sample II; ○, cotton cellulose; ▲, sample III; △, sample IV; ▲, sample V; ●, sample VI.

TABLE II

Intrinsic Viscosity Ratio $[\eta]_{Ac}^{Nitr.}/[\eta]_{CuEn}^{Cell.}$ as a function of the Degree of Polymerization of Hydrolytically Degraded Linters Cellulose from Different Origins

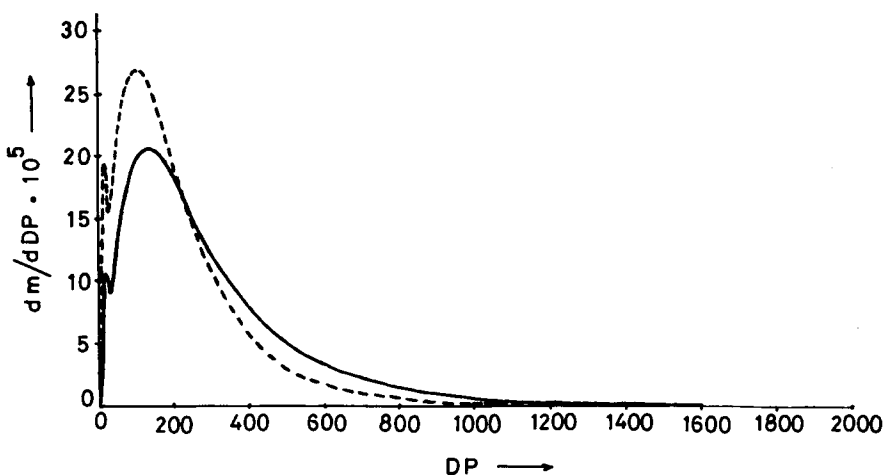| Time of Degradation	Cotton cellulose		Sample II		Sample III		Sample IV		Sample V		Sample VI	
	DP_n	$\dfrac{[\eta]_{Ac}}{[\eta]_{CuEn}}$	DP_n	$\dfrac{[\eta]_{Ac}}{[\eta]_{CuEn}}$	DP_n	$\dfrac{[\eta]_{Ac}}{[\eta]_{CuEn}}$	DP_n	$\dfrac{[\eta]_{Ac}}{[\eta]_{CuEn}}$	DP_n	$\dfrac{[\eta]_{Ac}}{[\eta]_{CuEn}}$	DP_n	$\dfrac{[\eta]_{Ac}}{[\eta]_{CuEn}}$
0	1650	1.93	2600	1.95	347	1.81	324	1.93	300	1.77	180	1.80
4	1100	—	1225	2.00	310	1.79	297	1.86	298	1.77	184	1.55
8	970	1.93	950	1.97	298	1.77	279	1.89	280	1.75	1.73	1.69
16	680	1.95	700	2.00	293	1.72	250	1.75	266	1.68	166	1.65
30	542	1.94	473	1.92	268	1.55	2.39	1.65	247	1.77	164	1.62
65	385	1.86	359	1.81	225	1.69	199	1.63	214	1.68	157	1.58
100	320	1.78	342	1.77	215	1.60	197	1.63	207	1.69	154	1.52
140	265	1.67	270	1.83	196	1.59	185	1.65	183	1.71	147	1.62
200	—	—	252	1.63	169	1.72	170	1.55	170	1.65	144	1.67
280	220	1.69	219	1.68	173	1.43	161	1.47	164	1.64	129	1.52
500	170	1.67	171	1.64	147	1.47	151		145	1.52	132	1.52

Fig. 4.   Distribution curve of the degree of polymerization of a hydrolytically degraded cotton[3] and linters cellulose (sample II). ---, cotton cellulose: $\overline{DP_w}$ = 218; $\overline{DP_n}$ = 105; —linters cellulose: $\overline{DP_w}$ = 309; $\overline{DP_n}$ = 145.

behavior equals that of cotton cellulose showing a continuous decrease of the degradation rate with decreasing DP, and consequently, a pronounced dependence of the individual initial degradation rate on the degree of polymerization at time 0.

As it can be seen from the Table II, cotton and linters cellulose agree also in the simultaneous decrease of degradation rate and derivatization capacity from a $DP_n \cong 350$ or lower. The latter being revealed by a systematic decrease of the ratio between the intrinsic viscosity of the nitrates and the corresponding intrinsic viscosity of the unsubstituted celluloses. Normally this ratio is independent from the degree of polymerization,[6] as it had been corroborated in the former investigation especially for DP < 350.[3] Considering the polymer analogue's course of nitration at the applied standardized nitration conditions, a decrease of the intrinsic viscosity ratio can only be caused by a too low intrinsic viscosity of the nitrate as a consequence of an inferior DS, taking into account that $[\eta]$ is not only a function of DP but also of DS.[4]

Also the molecular weight distributions of the degradation specimens of cotton and linters cellulose do not differ notably from each other, considering samples of comparable average degrees of polymerization. This is shown in the Figure 4 by two representative distribution curves belonging to a cotton and to a linters specimen which lead to polydispersity indices of DP_w/DP_n = 2.08 and 2.13, respectively.

On the contrary, degradation specimens of already technologically digested linters exhibit deviations from this value, as it results from the distribution curves shown in the Figure 5, the polydispersity indices of which are DP_w/DP_n = 2.30 and 2.42, respectively.

The percentage of strongly degraded material which dissolves in the acidic medium during degradation had been found, in the case of linters, to be only slightly, but not significantly, higher than in the case of cotton cellulose (20% and 13%, respectively). As with cotton cellulose, no systematic increase of loss with time could be observed.
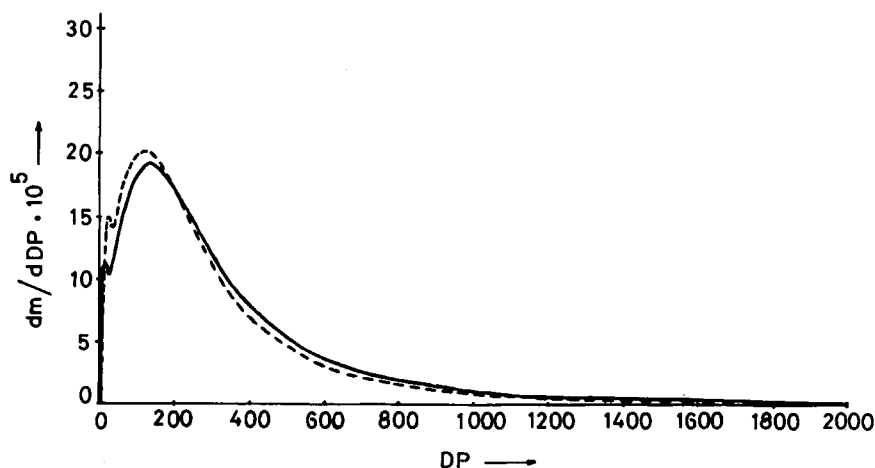
Fig. 5. Distribution curve of the degree of polymerization of two degradation specimens of a technologically digested linters cellulose (sample III). —, $\overline{DP_w}$ = 351; $\overline{DP_n}$ = 153; ---, $\overline{DP_w}$ = 324; $\overline{DP_n}$ = 134.

DISCUSSION

The results of the present study show that the acid-catalyzed degradation of linters cellulose exhibits all the characteristic kinetic features found on a pure cellulose and corroborate the conclusion that the hydrolytic behavior of cellulose is principally governed by its macromolecular properties. It is, therefore, obvious why strongly biodeteriorated cellulose (sample 2), when separated quantitatively from the deterioration products, obeys to the same kinetics as a pure cotton cellulose. Consequently, the molecular weight distributions of cotton and linters cellulose during degradation coincide, provided that the materials were not previously subjected to technological processes.

However, on the degradation specimens of a linter previously technologically treated with strong alkaline, notably higher polydispersities are observed, but without changing the characteristic features of the degradation kinetics. In order to interpret this effect, one may take into account that strong alkaline medium in connection with oxygen brings about degradation reactions obeying chemical and kinetic mechanisms other than the acid-catalyzed one. Linters industrially processed by digestion may exhibit, therefore, no defined alterations in their molecular and macromolecular properties. In addition they may display considerable inhomogeneity in the degree of alkaline/oxydative degradation which influence the molecular weight distribution arising in a subsequent acid hydrolysis on them.

The reasons for the decrease in degradation rate and obtainable degree of derivatization, characteristic for cellulose in a range of DP_n < 350, are not yet clear. The simultaneous occurrence of both events let suspect that they may be related. But definite proof for this does not yet exist. As a preliminary hypothesis one may propose that from a certain "critical" range of DP on downwards and favored by somewhat elevated temperature, the acidic action provokes a change in the molecular conformation followed by a supermolecular rearrangement, making the cellulose less accessible to chemical reagents.

Similar interpretations had been given recently to results of conformation and packing analysis obtained on celluloses subjected to short-term heating and concentrated acid treatments.[10-12]

The complete lack of a systematic increase of degraded portions soluble in the acid medium does not agree with the suggestion of a preferential hydrolysis in amorphous regions. The existence of well defined crystalline and amorphous phases (two-phase model) may appear, therefore, doubtful. At least, the hydrolytic degradation does not serve as a proof of it.

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