Resolution of Molecular Weight Distributions in Slightly Pyrolyzed Cellulose Using the Weibull Function

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Synopsis

Even before weight loss in the low-temperature pyrolysis of cellulose becomes significant, the average degree of polymerization of the partially pyrolyzed samples drops sharply. The gel permeation chromatograms of nitrated derivatives of the samples can be described in terms of a small number of mixed size populations—each component fitted within reasonable limits by a Weibull distribution function. The modal value of each component is taken as an integral multiple of a "macromonomer" of nominal degree of polymerization 228.4. Thus, the data are consistent with a model in which the degradation process is assumed to involve bond rupture at specific "weak links" into particularly favored molecular sizes. Such a mechanism provides a plausible alternative to the commonly assumed random breakdown along the length of the molecule.

INTRODUCTION

Weight loss in the low-temperature pyrolysis of cellulose is preceded by an "incubation period" during which the weight change is negligible,[1] but the average degree of polymerization of the pyrolyzing sample drops sharply.[2] The absence of significant sample volatilization rules out one process commonly involved in such size degradation—the "peeling off" of monomer from one end of the polymer molecule. However, no comparable gross observation is available to distinguish between two other degradation processes: (1) random breakdown along the length of the molecule or (2) breakdown at specific "weak links" into particularly favored molecular sizes.[2]

For polymers, sample-to-sample size comparisons are usually made in terms of the weight- and number-average molecular weights and graphic displays of the frequency distributions. With typical polydispersities, only rarely would such comparisons be expected to distinguish between the random and nonrandom breakdown processes, especially during the early degradation phases. However, if a particular size frequency distribution can be represented as consisting of appropriate proportions of mixed size populations, such distinction would be greatly enhanced.

A procedure has been developed whereby a size frequency distribution may be decomposed into a small number of subsidiary distributions.[3] In this pro-

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cedure, the experimental distribution is fitted within reasonable limits by a statistical continuous univariate distribution function, the Weibull, or by a synthesis of several such functions. An attempt can then be made to find a small number of such distributions with modal values common to all samples, regardless of the extent of degradation. The present paper describes the utility of this procedure in interpreting molecular weight distribution changes reported earlier[2,4] for samples of cellulose nitrate obtained from slightly pyrolyzed filter paper samples.

EXPERIMENTAL

Samples of "ashless" cellulose filter paper (Whatman #541) and similar samples decrystallized by swelling in liquid ammonia had been pyrolyzed in vacuo to a weight loss ranging from <0.1% to nearly 20%.[2] The samples were then nitrated, dissolved in tetrahydrofuran, and their molecular weight distributions determined by gel permeation chromatography.[2,4] The computer-linked data reduction process provided a normalized chromatogram, but the present computations utilized a modification to the original calibration procedure.[3]

For each GPC run, the original recorder tracing provides a plot of refractometer signal versus retention volume. The calibration provides a linear relationship between retention volume and the logarithm of the degree of polymerization (ln w). In the normalizing procedure, the original chromatogram is divided into ν volume (consequently, ln w) increments and the incremental areas normalized in terms of the total. Thus,

$$A_i' = A_i/A_T \tag{1}$$

where

$$A_T = \sum_{i=1}^{\nu} A_i \tag{2}$$

is the total area of the chromatogram and A_i is the area under the chromatogram for the ith increment. There is a direct linear relationship between the refractometer signal and the corresponding weight concentration of the polymer. Consequently, A_i' is identical with f_i, the molecular weight frequency distribution on a weight basis, i.e.,

$$A_i' = f_i = \frac{n_i w_i}{\sum_i n_i w_i} \tag{3}$$

in which n_i is the number of molecules of molecular weight w_i. Similarly, the cumulative distribution, i.e., the weight fraction of molecules with degree of polymerization $\leq w_j$, is given by

$$F_j = \sum_{i=1}^{j} f_i = \sum_{i=1}^{j} A_i' \tag{4}$$

Curve Fitting Procedures

The Weibull distribution function may be fitted to the molecular weight distribution data on either a weight or a number basis.[3] The weight basis was

chosen for the present discussion since its use involves minimum data manipulation. Thus, the Weibull cumulative distribution function may be written as

$$F = 1 - \exp\{-[(w - \gamma)/\alpha]^\beta\} \tag{5}$$

in which γ is the threshold parameter, α the scale parameter, and β is the shape parameter. The normalized experimental chromatogram corresponds to a plot of $dF/d(\ln w)$ versus $\ln w$. The theoretical equivalent of the ordinates, then, is

$$f - dF/d(\ln w) = w\, dF/dw = (\beta/\alpha^\beta)\, w(w - \gamma)^{\beta-1} \exp\{-[(w - \gamma)/\alpha]^\beta\} \tag{6}$$

For such a distribution, there is a single mode at w_m, defined by

$$[(w_m - \gamma)/\alpha]^\beta + (\gamma/\beta w_m) = 1 \tag{7}$$

The weight-average degree of polymerization $\overline{M}_w$ may be computed simply as

$$\overline{M}_w = \gamma + \alpha\Gamma[(\beta + 1)/\beta] \tag{8}$$

in which $\Gamma[r] = \int_0^\infty x^{r-1}e^{-x}dx$, the gamma function. Unfortunately, there is no comparable general solution for the number-average degree of polymerization $\overline{M}_n$, which must be evaluated numerically.

Consideration of the various experimental and data processing errors led us to accept as a "good fit" between a theoretical curve and the experimental data an agreement within 1% in the cumulative distribution and within 10% in the differential curve.[3] With these criteria, the calculated values of $\overline{M}_w$ and $\overline{M}_n$ give excellent agreement with the experimental values. The "good fit" requirements and the sharpness of the peak in the distribution curve establish criteria for acceptable differences between theoretical and experimental values of w_m.

Within the criteria of a "good fit," Weibull parameters were found to fit the experimental curves for unheated filter paper control samples.[3] However, polydispersities of microcrystalline cellulose samples were much higher than those of the filter paper and could not be fitted by a single-population Weibull distribution curve. Instead, each such chromatogram could be represented as composed of two overlapping Weibull distributions, with the major component covering the higher molecular weight region and generally representing about 80% of the sample weight.

The major component of all the microcrystalline cellulose samples had modal values near 230, while the modal values for the single-component Weibull fits to the filter paper chromatograms were very nearly four times as large. If, then, a degree of polymerization of 230 were considered to represent a macromolecular "monomer," the filter paper samples would be comprised of tetramers. Then, as the average molecular weight of such samples dropped during pyrolysis, the degraded chromatograms might be resolvable in terms of appropriate fractions of trimers, dimers, and monomers.
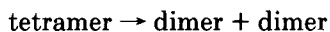
RESULTS

On the basis of all the data, the degree of polymerization of the macromonomer was computed to be 228.4. Consequently, w_m for the dimer, trimer, and tetramer would be 456.8, 685.2, and 913.6, respectively. For each of the 12 samples,[2] an attempt—successful only for the two controls—was first made to fit the chro-

matogram with any single Weibull distribution. Then, all of the chromatograms were fitted (Tables I–III) with a logical minimum of distributions with the above modal values, on the assumption that only the following reaction could occur:

$$\text{tetramer} \rightarrow \text{trimer} + \text{monomer}$$

or, less likely,

$$\text{tetramer} \rightarrow \text{dimer} + \text{dimer}$$

$$\text{trimer} \rightarrow \text{dimer} + \text{monomer}$$

$$\text{dimer} \rightarrow \text{monomer} + \text{monomer}$$

$$\text{monomer} \rightarrow \text{degradation products, including volatiles.}$$

Consider, for example, the decrystallized cellulose control—sample D-1. A good single-component Weibull distribution curve fit can be found for its chromatogram (Table III). However, the average molecular weight of this sample is somewhat lower than those found later for additional controls.[3] Correspondingly, the modal value for the Weibull approximation is low.

Suppose that during the decrystallization, the nitration, the solution, or the analysis of this sample partial degradation occurred, with each decomposing tetramer molecule ($w_m = 913.6$) breaking down into a trimer ($w_m = 685.2$) and a monomer ($w_m = 228.4$). Of course, the weight yield of the trimer would be just three-fourths of the tetramer loss and the yield of monomer would constitute the remaining one fourth. Such a composite solution (Table I) falls well within the criteria for a "good fit" and gives excellent agreement with the experimental values for $\overline{M}_w$ and $\overline{M}_n$ (Table III).

In this manner, for each of the least degraded samples, its chromatogram was assumed to consist of residual tetramer plus trimer and monomer formed during pyrolysis (Tables II and III). With major degradation (including weight losses of 1–5%), the fit was obtained using dimer and monomer only. For the most degraded samples (weight loss 15–20% and degree of polymerization comparable with that for microcrystalline cellulose), the fit involved use of the monomer and a minor "degradation product."

DISCUSSION

The computer printout of the experimental chromatogram provides a histogram rather than a continuous curve. The number of increments is sufficiently large to keep trivial the error thus introduced in computation of average molecular weights. However, the computational procedure does introduce a decided uncertainty in the determination of w_m, and the peaks of the chromatograms are sufficiently flat to permit the appearance of major discrepancies between experimental and theoretical curves.

For example, the data in Table I may leave the implication that experimental and theoretical modes differ by more than 60 units, with the experimental peak at 723.4 and the theoretical peak at 784.9. However, these two values of w represent successive increments. While there is no way to compute the "exact"

TABLE 1
Treatment of Gel Permeation Chromatography Data of Sample Number D-1 Using Weibull Distribution Function[a]

ln w	w	F_1	F_2	F_3	F_{calc}	F_{exp}	f_1	f_2	f_3	f_{calc}	f_{exp}
5.115	166.4	0.0	0.0	0.0	0.0	0.1	.0	.0	.0	.0	1.6
5.196	180.6	0.0	0.0	0.0	0.0	0.2	.0	.0	.0	.0	2.7
5.278	196.0	5.9	0.0	0.0	0.3	0.4	143.5	.0	.0	8.0	3.8
5.360	212.6	16.1	0.0	0.0	0.9	0.7	159.4	.0	.0	8.8	5.1
5.441	230.7	26.9	0.0	0.0	1.5	1.1	162.5	.0	.0	9.0	7.0
5.523	250.3	37.7	0.0	0.0	2.1	1.7	158.6	1.0	.0	9.0	9.3
5.604	271.6	48.0	0.2	0.2	2.8	2.4	149.8	4.7	5.4	13.3	12.2
5.686	294.7	57.6	0.7	0.7	3.9	3.3	137.2	10.3	10.8	17.7	15.8
5.768	319.8	66.3	1.6	1.6	5.2	4.5	122.1	18.0	16.3	22.5	20.4
5.849	347.0	73.9	3.1	2.9	6.9	6.0	105.4	28.2	22.4	27.9	26.5
5.931	376.5	80.4	5.4	4.6	8.9	8.0	88.2	40.9	29.0	34.3	34.1
6.013	408.5	85.7	8.7	6.8	11.5	10.6	71.3	56.4	36.2	41.5	42.9
6.094	443.3	90.0	13.0	9.5	14.5	13.8	55.6	74.4	44.0	49.7	52.3
6.176	481.0	93.2	18.7	12.7	18.1	17.6	41.7	94.2	52.3	58.7	62.1
6.257	521.9	95.6	25.6	16.5	22.4	22.1	29.9	114.5	61.0	68.2	72.5
6.339	566.2	97.3	33.9	20.8	27.3	27.3	20.5	133.5	69.9	77.7	82.5
6.421	614.4	98.4	43.4	25.8	32.8	33.1	13.4	148.4	78.6	86.6	91.0
6.502	666.7	99.1	53.6	31.3	38.8	39.4	8.3	156.4	86.8	94.0	97.4
6.584	723.4	99.5	64.1	37.4	45.3	46.1	4.8	154.6	94.0	99.1	100.0
6.666	784.9	99.8	74.0	43.9	52.0	52.8	2.6	141.6	99.7	101.3	99.8
6.747	851.6	99.9	82.8	50.7	58.7	59.5	1.3	118.4	103.3	100.1	98.2
6.829	924.1	100.0	89.7	57.6	65.3	65.9	0.6	88.7	104.3	95.9	93.9
6.910	1002.7	100.9	94.6	64.5	71.5	72.0	0.3	58.0	102.3	89.3	88.0
6.992	1087.9	100.0	97.6	71.2	77.2	77.7	0.1	32.2	97.2	81.0	80.0
7.074	1180.5	100.0	99.1	77.5	82.3	82.7	0.0	14.7	88.9	71.6	69.8
7.155	1280.8	100.0	99.7	83.1	86.8	87.1	0.0	5.2	78.0	61.5	59.5
7.237	1389.8	100.0	99.9	87.8	90.5	90.7	0.0	1.4	65.1	50.9	49.1
7.319	1508.0	100.0	100.0	91.7	93.6	93.6	0.0	0.3	51.4	40.1	39.1
7.400	1636.2	100.0	100.0	94.7	95.9	95.9	0.0	0.0	38.1	29.7	29.4
7.482	1775.4	100.0	100.0	96.9	97.6	97.6	0.0	0.0	26.3	20.4	21.0
7.563	1926.4	100.0	100.0	98.3	98.7	98.7	0.0	0.0	16.6	12.9	14.0
7.645	2090.2	100.0	100.0	99.2	99.3	99.4	0.0	0.0	9.5	7.4	8.5
7.727	2268.0	100.0	100.0	99.6	99.7	99.8	0.0	0.0	4.9	3.8	4.3
7.808	2460.9	100.0	100.0	99.9	99.9	100.0	0.0	0.0	2.2	1.7	1.2

[a] $F = 1 - \exp[-\{(w - \gamma)/\alpha\}^\beta]$, with w given as degree of polymerization. Three Weibull distribution functions are assumed to represent the experimental data with, for component 1, percent = 5.6, $\alpha = 125.2$, $\beta = 1.15$, $\gamma = 185.0$, $w_m = 228.4$, for component 2, percent = 16.8, $\alpha = 478.4$, $\beta = 2.30$, $\gamma = 240.0$, $w_m = 685.2$; for component 3, percent = 77.6, $\alpha = 731.9$, $\beta = 1.70$, $\gamma = 225.0$, $w_m = 913.6$.

TABLE II
Weibull Parameters and Weight- and Number-Average Degree of Polymerization for
Pyrolyzed Samples of Cellulose Filter Paper.[a]

Sample	wt %	α	β	γ	$\bar{M}_w$		$\bar{M}_n$		w_m	
					Expt	Calc	Expt	Calc	Expt	Calc
0-1										
1 component		738	1.70	186	860	844	664	665	794	867
tetramer	84.0	752	1.61	240						
trimer	12.0	516	2.25	200		860		665		812
monomer	4.0	179	1.10	150						
0-2										
trimer	10.7	493	1.50	290						
dimer	44.9	345	1.57	165	397	391	217	223	409	411
monomer	44.0	216	1.40	25						
0-3										
dimer	58.0	357	1.75	136	372	363	244	245	409	409
monomer	41.0	206	1.34	46						
0-4										
dimer	36.1	337	1.85	154	298	295	170	166	320	320
monomer	63.5	224	1.70	6						
0-5										
dimer	21.8	340	1.91	148	281	275	171	171	272	295
monomer	77.5	212	1.38	32						
0-6b										
dimer	9.4	425	1.09	154						
monomer	88.5	228	1.09	4	237	247	67	58	235	245
minor	3.0	12	2.00	0						

[a] The values of w_m for the individual "macrooligomers" are appropriate multiples of 228.4.

experimental peak, the true theoretical peak can be computed, by eq. (7), to occur at 797, providing an indication of the magnitude of the error thus introduced. Further, even if the experimental peak were truly at 723.4, the theoretical value at that point is 97.8% of the theoretical peak frequency—well within experimental error. Thus, the apparent discrepancies in w_m are not overly significant.

Although each of the 30–100 increments into which each chromatogram is divided is not exactly an independent observation on the size distribution of the molecules which constitute that sample, for curve fitting purposes each may be treated as an individual observation. Thus, it is of more than passing interest that the control chromatograms can be fitted by a single Weibull distribution, but the degraded samples cannot.

The introduction of a second Weibull distribution in fitting an experimental curve adds four or five additional parameters (four if the fraction of the two components must add to exactly 100%; five if the two fractions are totally inde-

TABLE III
Weibull Parameters and Weight- and Number-Average Degree of Polymerization for
Pyrolyzed Samples of Ammonia-Swelled Cellulose.[a]

Sample	wt %	α	β	γ	$\bar{M}_w$ Expt	$\bar{M}_w$ Calc	$\bar{M}_n$ Expt	$\bar{M}_n$ Calc	w_m Expt	w_m Calc
D-1										
1-component		683	1.68	215	832	826	663	668	723	834
tetramer	77.6	732	1.70	255						
trimer	16.8	478	2.30	240		834		660		797
monomer	5.6	125	1.15	185						
D-2										
tetramer	46.5	765	1.57	228						
trimer	40.5	499	2.25	219	731	740	561	564	667	707
monomer	13.5	228	1.00	154						
D-3										
tetramer	44.0	780	1.30	278						
trimer	42.0	514	1.85	222	769	774	557	558	681	703
monomer	14.0	228	1.00	145						
D-4										
dimer	38.5	374	1.65	120						
monomer	61.5	221	1.40	14	308	308	164	164	320	320
D-5										
monomer	84.0	210	1.20	53						
minor	16.0	33	1.55	20	216	217	115	114	181	230
D-6b										
monomer	55.4	226	1.11	15						
minor	44.1	47	1.11	7	158	153	48	48	68	71

[a] The values of w_m for the individual "microoligomers" are appropriate multiples of 228.4.

pendent). Thus, with a relatively small number of independent Weibull distributions, it should be possible to fit almost any experimental chromatogram. However, the procedure adopted here does place rather major restrictions on the permitted alternatives. First, only a single common value is permitted for w_m for the "macromonomer" of all of the samples. Second, except for the small "degradation products" in the most severely degraded samples, all other components have modal values which are an integral multiple of that for the macromonomer. Finally, the proportions of the various "macrooligomers" must be logically consistent with the permitted reactions, e.g., the degradation of a tetramer to yield a trimer must also yield a monomer.

Obviously, the particular combination of oligomers chosen for any fit is not unique. For the very slightly degraded samples, the amount of monomer included in the fitting process is so small that a fit using only tetramer and trimer is quite likely. Where the calculated curve involves tetramer, trimer, and mo-

TABLE IV
Weight- and Number-Average Degree of Polymerization for Monomer Components
with Modal Value 228.4

Sample	Wt %	α_1	β_1	γ_1	$\Gamma\{(\beta_1+1)/\beta_1\}$	$(\bar{M}_w)_1$	$(\bar{M}_n)_1$
0-1	4.0	179	1.10	150	0.965	323	270
0-2	44.0	216	1.40	25	0.911	222	139
0-3	41.0	206	1.34	46	0.918	235	163
0-4	63.5	224	1.70	6	0.892	207	125
0-5	77.5	212	1.38	32	0.913	226	147
0-6b	88.5	228	1.09	4	0.968	224	71
D-1	5.6	125	1.15	185	0.952	304	278
D-2	13.5	228	1.00	154	1.000	383	297
D-3	14.0	228	1.00	145	1.000	373	286
D-4	61.5	221	1.40	14	0.911	215	122
D-5	84.0	210	1.20	53	0.940	249	168
D-6b	55.4	226	1.11	15	0.962	232	106

nomer, small but appreciable quantities of dimer could be added without jeopardizing the fit.

Since population distributions are most commonly represented by their means and we have somewhat arbitrarily chosen to emphasize instead their modes, the range of mean values accompanying a fixed mode deserves some discussion. Perhaps the best indication of the range of value of $\overline{M}_w$ for a fixed w_m comes from consideration of the monomer, since it is the only component common to all 12 samples. The weight-average degree of polymerization may be computed from eq. (8). For the monomer, $1 \leq \beta \leq 1.7$ (Table IV), so $1 \geq \Gamma[(\beta + 1)/\beta] \geq 0.892$. Thus, within an error of about 5%,

$$\overline{M}_w = \gamma + 0.95\alpha \qquad (9)$$

For all samples in which the monomer constitutes more than 15% of the sample, $\overline{M}_w$ and w_m agree within 10% (Table IV). The four cases of serious disagreement have the following characteristics in common: (1) small fraction of the total sample, (2) large γ (i.e., appreciable truncation of the low end of the distribution), and (3) low polydispersity (i.e., a relatively sharp component peak). Thus, the disagreement may simply be attributable to the relatively larger uncertainties in the early portion of the experimental chromatogram. The third characteristic serves to call attention to another fact which lends credence to the "macrooligomer" concept. In general, the polydispersity for each component is lowest in the least degraded sample and increases with increasing sample degradation (Table V).

Very much more data will have to be obtained before we can establish unequivocally the distinction between random breakdown and rupture at specifically spaced weak links in cellulose degradation. Nevertheless, the results presented

TABLE V
Polydispersity of the "Macrooligomer" Components

Sample	$\bar{M}_w$ Expt'l	Component Polydispersity			
		Monomer	Dimer	Trimer	Tetramer
O-1	860	1.20		1.14	1.25
D-1	832	1.10		1.10	1.21
D-2	731	1.29		1.11	1.27
D-3	769	1.31		1.16	1.32
O-2	397	1.60	1.19	1.17	
O-3	372	1.44	1.19		
D-4	308	1.77	1.24		
O-4	298	1.66	1.15		
O-5	281	1.54	1.15		
O-6	237	3.15	1.39		
D-5	216	1.48			
D-6	158	2.20			

here do indicate the possible validity of a "weak link" mechanism. Further, they are sufficiently consistent to suggest that a reexamination of older data, as well as the obtaining of new, may be in order.

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