The Heterogeneous Character of the Dilute Acid Hydrolysis of Crystalline Cellulose

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Synopsis

The end-attack model proposed by Sharples [*Trans. Faraday Soc.*, **53**, 1003 (1957)] for the dilute acid hydrolysis of crystalline cellulose was tested using the results from the size-exclusion chromatographic analysis of samples of crystalline cellulose I and cellulose II hydrolyzed in 6.1*N* HCl at 107°C. The differential number distribution of the molecular weight of hydrolyzed cellulose was found to be approximately exponential, a result which is consistent with the end-attack model. Differences in the rates of hydrolysis of cellulosic materials appear to arise from differences in both the degree of polymerization and the microstructure of hydrolyzed cellulose. Evidence is also presented which suggests that the recrystallization upon hydrolysis results in part from the lateral accretion of chains which are cleaved during the hydrolysis of amorphous regions in the cellulose microfibrils.

INTRODUCTION

Cellulose, a naturally abundant polymer formed by plants, exists as distinct structural units called microfibrils. Although many models have been proposed for the structure of cellulose microfibrils, it is generally recognized that the microfibrils contain both regions of highly ordered cellulose molecules called the crystalline regions and regions of less ordered molecules called the amorphous regions. Cellulosic materials from all natural sources have the same crystalline structure. This structure is referred to as cellulose I or native cellulose. When the crystalline structure of native cellulose is disrupted by a dissolving or swelling agent, the regenerated cellulose exhibits a different crystalline structure called cellulose II.

The dilute acid hydrolysis of cellulosic materials has been extensively studied both as a means of elucidating the fine structure of this polymer and as a means of producing fermentable glucose from biomass. In this paper, dilute acid hydrolysis is defined as any reaction in which the crystalline regions of the cellulose are not penetrated by the acid solution. By this definition, dilute acid hydrolysis covers a broad range of conditions since fairly concentrated acid solutions (e.g., greater than 10*N* HCl[1]) are needed to disrupt crystalline cellulose. Therefore, in dilute acid hydrolysis, the reactive

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Journal of Applied Polymer Science, Vol. 37, 1373–1394 (1989)
 CCC 0021-8995/89/051373-22$04.00

unit of cellulose is not an individual molecule of cellulose but rather the cellulose microfibril. Many of the characteristics of the dilute acid hydrolysis reaction may then be attributed to the structural features of the microfibril.

For example, at short hydrolysis times, the weight and degree of polymerization (DP) of the cellulose decrease rapidly during hydrolysis of its readily accessible, amorphous component. Following removal of this readily hydrolyzable fraction, the resultant material, commonly called hydrocellulose, takes the form of rod-shaped particles. Since these particles arise from the crystalline regions originally present in the microfibrils, they are often referred to as crystallites.

Further hydrolysis of these crystallites proceeds at a rate which is 1–2 orders of magnitude less than that of the amorphous cellulose.[2,3] Although the hydrolysis of crystalline cellulose is heterogeneous, the weight loss may be effectively modeled as a pseudo-homogeneous, first-order reaction for both celluloses I and II.[4]

Another characteristic of the hydrolysis of crystalline cellulose is that several properties of the cellulose remain constant in spite of the removal of as much as 80% of the material. For example, the moisture regain,[4] particle length,[5] molecular length,[4] and degree of crystallinity[5] remain relatively unchanged during the reaction. Since the degree of polymerization of cellulose decreases rapidly at short hydrolysis times, then levels off, the DP of hydrolyzed cellulose is often referred to as the leveling-off degree of polymerization (LODP).[6] The LODP and the rate of hydrolysis of crystalline cellulose depend upon both the source and prior history of the cellulose.[4] The first-order weight loss and constant molecular length are observed under all conditions of dilute acid hydrolysis (i.e., nonswelling conditions). Reviews of the dilute acid hydrolysis of cellulose have been given by Nevell[7] and Sharples.[8]

Sharples[9] has proposed a model for the heterogeneous hydrolysis of crystalline cellulose which explains the observed first-order weight loss and the invariant properties of a given hydrocellulose during hydrolysis. In this model, hydrolysis of the amorphous regions in the microfibrils results in the generation of a system of cellulose crystallites which are assumed to be uniformly crystalline, to have constant cross-sectional area Θ, and to have an exponential distribution of lengths x. Therefore, the initial population density of the particles may be expressed in terms of x as

$$n_0(x) = a_0 \exp(-bx) \tag{1}$$

where $n_0(x)$ is the number of particles having a characteristic length and where a_0 and b are parameters of the distribution. Sharples noted that such a distribution would arise if the amorphous regions are located randomly along the length of the microfibrils.

Sharples assumed that further hydrolysis of the crystallites occurs only through scission of the bonds at the ends of the cellulose chains. He hypothesized that the resistance to hydrolysis of the nonterminal linkages in the crystallites may be the result of the crystalline structure of cellulose. He noted that chains broken in the surfaces of the crystallites are held by hydrogen bonding with adjacent chains in a position which is sterically favorable for the recombination reaction. Therefore, the glycosidic bonds in the surfaces are

continually broken and reformed. In order for a soluble fragment to detach itself from the surface, two breaks separated by a distance less than the solubility limit would need to exist simultaneously. Sharples proposed that the probability of this event would be much less than that for the removal of a fragment from the end of the crystallite since the latter process requires only a single bond to be broken.

Thus, if the crystallites are hydrolyzed solely along the length (x) dimension, the reactive surface will then consist of the two ends of the particle with a concomitant total area of 2Θ. The rate of weight loss of any particle of length x may then be written as

$$dw/dt = -2B\Theta \tag{2}$$

where w is the weight of the crystallite and B is a rate constant. Hence, for each crystallite, the weight loss obeys zero-order kinetics.

The weight of each crystallite may be expressed in terms of x by recognizing that $w = \rho\Theta x$, where ρ is the density of the crystalline cellulose. Therefore, eq. (2) may also be written in terms of x as

$$dx/dt = -2B/\rho \tag{3}$$

Upon integration, eq. (3) yields

$$x_0 - x_t = 2Bt/\rho \tag{4}$$

where x_0 and x_t are the lengths of the crystallite at times zero and t, respectively. Thus, the x dimension of each particle decreases by an amount $2Bt/\rho$ in time t until a point is reached when the particle becomes soluble in the acid medium.

Since the lengths of all of the particles decrease at the same rate, the population density at any time t is related to the initial population density by

$$n_t(x) = n_0(x + 2Bt/\rho) \tag{5}$$

or, after substitution into eq. (1),

$$n_t(x) = a_0 \exp(-2bBt/\rho)\exp(-bx) \tag{6}$$

Therefore, a unique property of the exponential distribution is that the particle length distribution at any time t retains its exponential dependence on length x; however, the zero length intercept decreases exponentially with time.

At any time t, the total weight of crystallites is given by

$$W_t = \rho\Theta \int_S^\infty x n_t(x)\, dx \tag{7}$$

where S represents the length below which the crystallites become soluble in the acid hydrolysis medium.

Equations (6) and (7) may be used to arrive at the following expression for the ratio of the total weight remaining at any time t to the initial weight:

$$W_t/W_0 = \exp(-2bBt/\rho) \tag{8}$$

Equation (8) represents the integrated form of a first-order weight loss expression where the first-order rate constant is given by

$$k = 2(B/\rho)(b) \tag{9}$$

Sharples[10] showed that the parameter b may be approximated by the expression

$$(1/b) \cong (\mathrm{DP}_w/2) - [(S^2)/(\mathrm{DP}_w + 2S)] \tag{10}$$

where DP_w is the weight average of DP of the crystalline cellulose and S is the degree of polymerization corresponding to the solubility limit for chain fragments produced via hydrolysis. Since b and S are both constants, eq. (10) indicates that the average degree of polymerization of the residual solid remains constant despite the fact that each crystallite is decreasing in length.

The relationship given by eq. (9) suggests that a plot of $1/k$ vs. $1/b$ should be linear if B and ρ are constants for all cellulosics. Since $1/b$ is related to the DP of the crystalline cellulose [eq. (10)], the end-attack model predicts that differences in the rates of hydrolysis of cellulosics are due to differences in their degrees of polymerization. Sharples[10] has experimentally verified this relationship; however, his data included only two samples from higher plants (cotton and ramie), and all of his samples of cellulose II were from regenerated cellulose.

It is apparent that Sharples' end-attack model is consistent with the first-order weight loss and constant DP which have been observed for the hydrolysis of crystalline cellulose. The end-attack model also suggests that differences in the rates of hydrolysis of cellulosics are due to differences in their degrees of polymerization.

Although Sharples' end-attack model explains many of the characteristics of the dilute acid hydrolysis reaction, the model has not been universally supported by size-exclusion chromatography (SEC) studies on hydrolyzed cellulose. For example, Chang et al.[11] concluded from their SEC studies that hydrolysis occurs predominantly through attack on the lateral surfaces of the cellulose crystallites. In addition, a basic tenet of the end-attack model is that the differential number distribution of molecular weight in hydrolyzed cellulose is exponential. The polydispersities reported by Van Lancker[12] and Krassig[13] for hydrolyzed cellulose are not in agreement with the theoretical value of 2 expected for an exponential distribution. On the other hand, Lauriol et al.[14] and Marx-Figini[15] found that the molecular weight distribution was exponential. Finally, Sharples' model suggests that hydrolyzed cellulose from both celluloses I and II consists of a continuous distribution of crystallite lengths. However, Yachi et al.[16] used the results from SEC analysis to support their hypothesis that hydrolyzed cellulose consists of discrete particles whose lengths are integral multiples of 200 Å. Nevell[7] recently noted that further

work is desirable in this area before discarding the end-attack model on the basis of the SEC studies.

In this paper, the results from the SEC analysis of several different forms of hydrolyzed cellulose were used to test the end-attack model proposed by Sharples. Although only one set of reaction conditions was employed (i.e., 6.1*N* HCl at 107°C), the results from this study should be valid for any acid hydrolysis reaction of crystalline cellulose occurring under nonswelling conditions.

EXPERIMENTAL

Materials

The nine cellulosic materials used in this study included:

1. Ramie—bleached, commercial fiber.
2. Linen—unbleached, commercial yarn.
3. Cotton—bleached fiber.
4. α-Cellulose—high cellulose pulp from Sigma, probably obtained from wood pulp.
5. Rayon—commercial fiber.
6. Mercerized ramie—derived from 1.
7. Mercerized linen—derived from 2.
8. Mercerized cotton—derived from 3.
9. Mercerized α-cellulose—derived from 4.

It should be noted that samples 1–4 are all examples of native cellulose and as such contain the cellulose I crystalline polymorph. Sample 5, rayon, which is a regenerated cellulose, and the mercerized cellulosics are all examples of the cellulose II crystalline polymorph.

The samples of mercerized cellulose were prepared by soaking 5 g of air-dried native cellulose in 300 mL of 18% NaOH for 48 h at room temperature.[17] The mercerized cellulose was then filtered onto a coarse-porosity glass filter and washed successively with distilled water, 1% acetic acid, and then distilled water. Finally, the cellulose was dried *in vacuo* at 60°C.

The carbohydrate compositions of all the samples were determined by the method described by Pettersen et al.[18] The mercerized samples of cellulose and the ramie and cotton contained at least 95% cellulose. The linen and α-cellulose also contained hemicellulosic sugars (< 10%).

The azeotrope of hydrogen chloride and water was employed in both batch hydrolysis and percolation hydrolysis reactors (see descriptions below). At 1 atm, the azeotrope has a boiling point of 108.5°C and a composition of 20.2% HCl by weight (approximately 6.08*N* HCl). The variation of the boiling point temperature and composition of the azeotrope with barometric pressure have been given by Millet et al.[4] and by Foulk and Hollingsworth,[19] respectively. Over the range of barometric pressures encountered in this study, however, the composition of the azeotrope may be assumed to be approximately constant.

Hydrolysis in a Batch Reactor

The weight loss kinetics of the nine samples of cellulose were determined using a batch hydrolysis technique similar to that described by Philipp et al.[20] Approximately 0.25 g of cellulose was placed in a preweighed 25 × 200 mm test tube and dried overnight *in vacuo* at 60°C. After cooling over P_2O_5 in a desiccator, the test tube containing the cellulose was weighed and the dry weight of the cellulose determined by difference.

The hydrolysis reactions were carried out in a constant-temperature oil bath maintained at 107.0°C. The reactions were started by adding 25 mL of preheated azeotropic HCl to the cellulose samples. Small flasks were inverted on the tops of the test tubes during the reaction in order to condense the HCl vapors. The reaction temperature (107.0°C) is slightly less than the normal boiling point of the HCl azeotrope at the barometric pressures observed during the study.

In order to quench the reaction, the test tube and contents were rapidly transferred from the oil bath to an ice-water bath. After cooling, the contents of the test tube were filtered onto a preweighed, coarse-porosity, glass filter and washed thoroughly with distilled water. The weights of the hydrolyzed samples of cellulose were determined after drying the filters and residues. The hydrolysis residues were analyzed for their carbohydrate contents using the method described by Pettersen et al.[18]

At longer reaction times the hydrolysis residues became increasingly darker due to contamination of the cellulose by the humic substances formed from the glucose degradation products.[20] Nevertheless, it was possible to determine the weight loss of just the cellulosic fraction of each sample from the total weight loss value by using the values of the cellulose contents of the sample before and after hydrolysis. Millett et al.[21] also used this method to correct their weight loss values for the accumulation of humic substances.

Hydrolysis in a Percolation Reactor

While the weight loss kinetics were easily corrected for the presence of the humic substances by analyzing the hydrolysis residues for their cellulose contents, the effect of these substances on the molecular weight distribution study was uncertain. Thus, a percolation reactor similar to the one described by Millett et al.[4] was employed to prepare highly degraded samples of cellulose which were free of contamination by humic substances.

The essential feature of this reactor is that the azeotropic HCl percolates through the cellulose sample which is supported on a sintered glass frit. The percolating acid removes the glucose produced via hydrolysis from the reaction zone before decomposition of the glucose can occur.

The nine samples of cellulose were subjected to a prehydrolysis treatment prior to hydrolysis in the percolation reactor. Prehydrolysis consisted of boiling 10 g of each cellulosic material in 300 mL of azeotropic HCl for 2 min. The hydrolyzed cellulose was then filtered onto a glass filter and washed thoroughly with distilled water. A portion of the wet, prehydrolyzed cellulose was freeze-dried for further characterization by SEC. The remainder of the prehydrolyzed cellulose was air-dried and stored at ambient conditions for use in the percolation reactor.

The prehydrolyzed samples of cellulose were subjected to hydrolysis in the percolation reactor for various periods of time. After hydrolysis, each sample was thoroughly rinsed and freeze-dried in preparation for the molecular weight distribution (MWD) study.

SEC Analysis

The molecular weight distributions of the nine samples of prehydrolyzed cellulose and the samples prepared in the percolation reactor were determined using size-exclusion chromatography (SEC). The tricarbanilate derivative of cellulose was used to render the hydrolysis residues soluble in the tetrahydrofuran (THF) used in the SEC analysis.

The majority of the samples was derivatized using the following procedure. Approximately 20 mg of cellulose and a magnetic stirring bar were placed in a 10 mL vial which had a Teflon-lined cap. The vial and contents were dried overnight *in vacuo* at 60°C. The vial was then placed in a constant-temperature oil bath maintained at 80°C. Five milliliters of anhydrous pyridine (dried over molecular sieves) was pipetted into the vial. While the suspension was stirred, 0.6 mL of phenyl isocyanate was added to the vial which was then capped.

The carbanilation reaction of the cellulose proceeded in the well-stirred solution for 48 h. At this time the clear yellow solution was removed from the oil bath and 0.6 mL of methanol added to react with the excess phenyl isocyanate to form methyl phenylcarbamate. The reaction time (48 h) and temperature (80°C) utilized are those recommended by Schroeder and Haigh[22] to prevent depolymerization of the cellulose during the reaction.

In some cases (e.g., the rayon samples), a considerable amount of solid material was still present after the 48 h reaction period, a result suggesting that these samples had not been completely derivatized. The derivatization reaction could be promoted in such samples by first soaking the cellulose in water and then solvent-exchanging the water for pyridine.[23]

To prepare a cellulose tricarbanilate (CTC) sample for SEC analysis, a 2-mL aliquot of the pyridine reaction mixture was pipetted into an 8-mL vial, and the pyridine evaporated with a stream of nitrogen. The syrupy liquid remaining in the vial was dried overnight at 60°C in order to remove the last traces of pyridine. The nonvolatile products were then redissolved in approximately 7 mL of THF. This THF solution was used as the stock solution for the SEC analysis.

It should be noted that the CTC was not separated from the reaction byproducts by precipitation of the CTC in a nonsolvent such as methanol or ethanol; rather all of the nonvolatile products from the derivatization reaction were analyzed. This method of sample preparation was necessary because low molecular weight CTC cannot be precipitated in methanol; thus, the MWD of the precipitated CTC prepared from hydrolyzed cellulose is not representative of the MWD of the original sample.[24]

Samples from the THF stock solutions were diluted and filtered through a 0.45 μm filter prior to analysis. After dilution, the resultant polymer concentrations were approximately 0.01% (w/w) for all samples. A constant injection volume of 100 μL was used.

The CTC samples were analyzed on a Spectra-Physics SP8100 liquid chromatograph using Shodex KF803, Shodex KF805, and μ-Styragel 100 Å SEC columns connected in series. A flow rate of 1 mL/min was used for the THF eluent.

The cellulose tricarbanilate in the eluent was detected using a UV spectrophotometer (Spectra-Physics SP8400) operated at 235 nm. The signal from the UV detector was fed to an Apple IIe computer for data storage and calculation of the molecular weight distributions.

The correlation of molecular weight with retention volume for the CTC samples was obtained using the universal calibration procedure.[25] Polystyrene standards were used to establish the primary calibration curve which was linear over the range of retention volumes encountered in this study. The Mark–Houwink coefficients for CTC in THF used in this study were those reported by Danhelka et al.[26] ($K = 0.0053$, $a = 0.84$). The coefficients used for polystyrene were an average of those reported by Kolinsky and Janca[27] ($K = 0.0112$, $a = 0.72$). In both cases, the coefficients are based on the same units for intrinsic viscosity (mL/g).

RESULTS AND DISCUSSION

Hydrolysis Kinetics

Following an initially rapid decrease in weight, the weight loss behavior of all nine cellulosics used in this study could be effectively modeled with first-order kinetics. The weight loss data obtained from batch hydrolysis of the cotton and mercerized cotton samples are shown in Figure 1. By extrapolating the first-order weight loss curve to zero reaction time, it was possible to determine the weight fraction of each sample which is resistant to hydrolysis. The first-order rate constant and crystallinity of each sample were determined

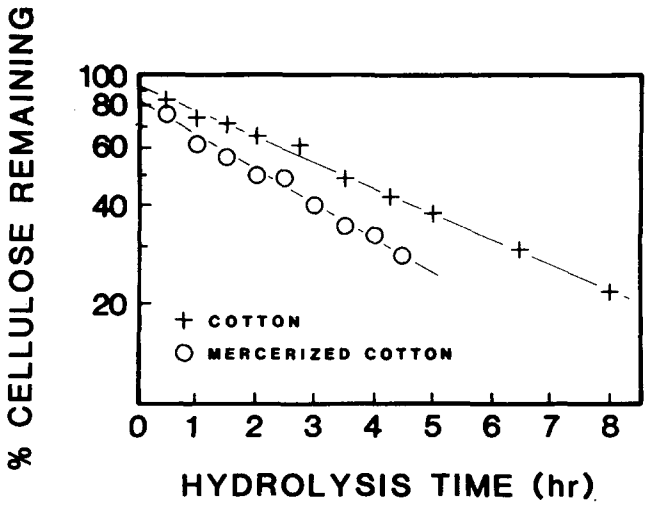

Fig. 1. Semilog plot of weight loss data for the cellulose fraction of cotton (+) and mercerized cotton (O) on hydrolysis in 6.1*N* HCl at 107°C.

TABLE I
First-Order Rate Constants, Crystalline Fractions, Degrees of Polymerization, and Intrinsic Rate Constants Determined in This Study

Material[a]	k (min^{-1})	Crystallinity (%)	DP_w^b	DP_n^b	DP_w/DP_n	B/ρ (min^{-1})
1. Ramie	0.00273	90	188	69	2.7	0.13
2. Cotton	0.00293	92	179	74	2.4	0.13
3. Linen	0.00596	97	168	51	3.3	0.23
4. α-Cellulose	0.00955	98	98	33	3.0	0.25
5. Mercerized ramie	0.00295	77	106	37	2.9	0.08
6. Mercerized cotton	0.00390	81	88	34	2.6	0.09
7. Mercerized linen	0.00354	82	125	39	3.2	0.07
8. Mercerized α-cellulose	0.00642	85	44	21	2.1	0.11
9. Rayon	0.0323	76	16	11	1.5	0.08

[a]Samples 1–4 represent the cellulose I polymorph; samples 5–9 are cellulose II.
[b]The degrees of polymerization correspond to the DP of the sample at approximately 50% weight loss for the crystalline fraction.

from linear regression of the weight loss data obtained from the batch hydrolysis technique. These values are presented in Table I.

The rates of hydrolysis of the nine cellulosics varied by more than a factor of 10. As expected, the crystallinity values determined from acid hydrolysis decreased in the order: native cellulose > mercerized cellulose > regenerated cellulose.

One interesting thing to note from the values given in Table I is the variable effect of mercerization on the rate of hydrolysis of crystalline cellulose. For ramie and cotton, mercerization increased the rates of hydrolysis by 8% and 33%, respectively. On the other hand, mercerization decreased the rates of hydrolysis of linen and α-cellulose by 41 and 33%, respectively. Thus, it is apparent that conversion of cellulose I to cellulose II has a variable effect on both the magnitude and the direction of change in the rate of hydrolysis of crystalline cellulose.

Millett et al.[4] found that mercerization increased the rates of hydrolysis of ramie and cotton by 69 and 88%, respectively. They also noted that mercerization decreased the rate of hydrolysis of one of their wood pulp samples by 3%. These results agree with our experimental results in terms of the direction of change; however, the magnitudes of the changes are considerably different. Philipp et al.[20] found that the rate of hydrolysis of cotton decreased 8% after mercerization, a result which does not agree with the experimental results obtained in the present study. The reason for the discrepancy is uncertain.

Molecular Weight Distributions

The chromatograms of the cellulose tricarbanilate obtained from the prehydrolyzed sample of ramie and the three samples of ramie which were hydrolyzed more extensively in the percolation reactor are shown in Figure 2. The first peak in each chromatogram, eluting before a retention volume of 27 mL, may be attributed to the cellulose tricarbanilate. The large peak eluting after a retention volume of 28 mL results from the byproducts of the

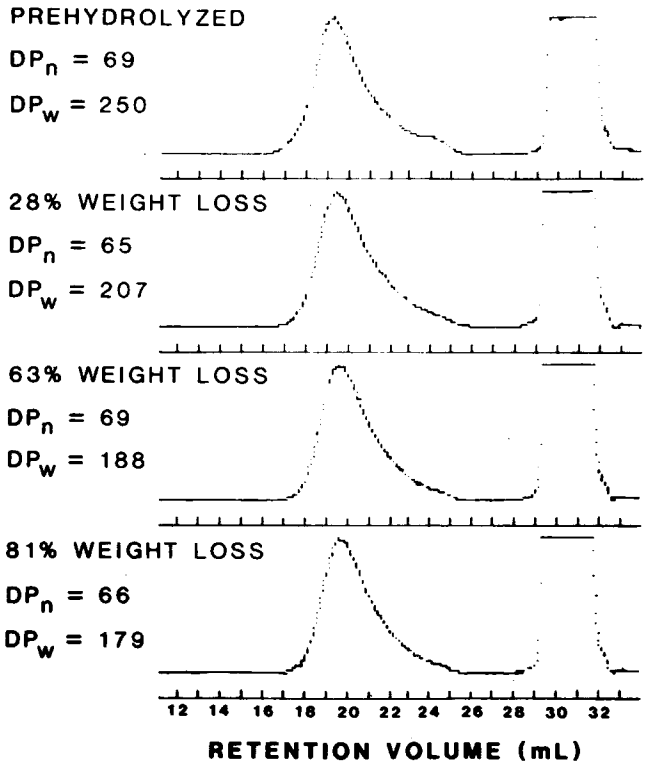

Fig. 2. Chromatograms of cellulose tricarbanilate derived from hydrolyzed samples of ramie.

derivatization reaction. Each chromatogram has been baseline corrected by subtracting the baseline from the entire chromatogram. Note that the column train used in this study afforded baseline resolution of the CTC and byproduct peaks.

Indicated on each chromatogram are the number and weight average degrees of polymerization for the sample determined with the data handling program. Although the molecular weight of the monomeric unit of CTC (519) is higher than the molecular weight of the monomeric unit in underivatized cellulose (162), the degrees of polymerization should be the same for both materials.

The weight loss values given with the chromatograms represent the weight loss of just the crystalline fraction of the cellulose as calculated from the batch hydrolysis kinetics. This weight loss value corresponds to only the weight loss of the fraction of the cellulose which hydrolyzes by first-order kinetics and does not include the initial weight loss due to hydrolysis of the amorphous fraction. The prehydrolysis time (2 min) was added to the hydrolysis time in the percolation reactor to determine the weight loss values.

The weight loss values were calculated from batch kinetics data taken at 107.0°C; however, the operating temperature of the percolation reactor was typically 107.5–108.0°C (corresponding to barometric pressures from 730 to 745 mm Hg). Since the weight loss values were used only to obtain a measure

of the extent of degradation, no attempt was made to correct the values for this small temperature difference.

The chromatograms of the four ramie samples given in Figure 2 change very little in relative shape up to 81% weight loss of the crystalline fraction. All of the chromatograms consist of a single peak with a long, low molecular weight tail. Yachi et al.[16] and Chang et al.[11] noted similar shapes for their chromatograms of hydrolyzed native cellulose.

The weight average degree of polymerization (DP_w) of the ramie samples decreased throughout the reaction from 250 in the prehydrolyzed sample to 179 at 81% weight loss. However, it should be noted that DP_w decreased only slightly for the three samples hydrolyzed more extensively than the prehydrolysis treatment. Millett et al.[4] and Chang et al.[11] also observed a slight decrease in molecular weight of extensively hydrolyzed cellulose. Nevertheless, the decrease in DP_w of the more extensively hydrolyzed samples is relatively small compared to the total weight loss.

The low molecular weight tails in the chromatograms from the ramie samples do not increase in relative significance with increasing extent of hydrolysis. This result indicates that low molecular weight material does not gradually accumulate. This situation is also reflected in the relatively constant values of the number average degree of polymerization (DP_n). (This parameter is sensitive to the low molecular weight region of the chromatogram.) If the crystalline particles were hydrolyzed predominantly through random scission

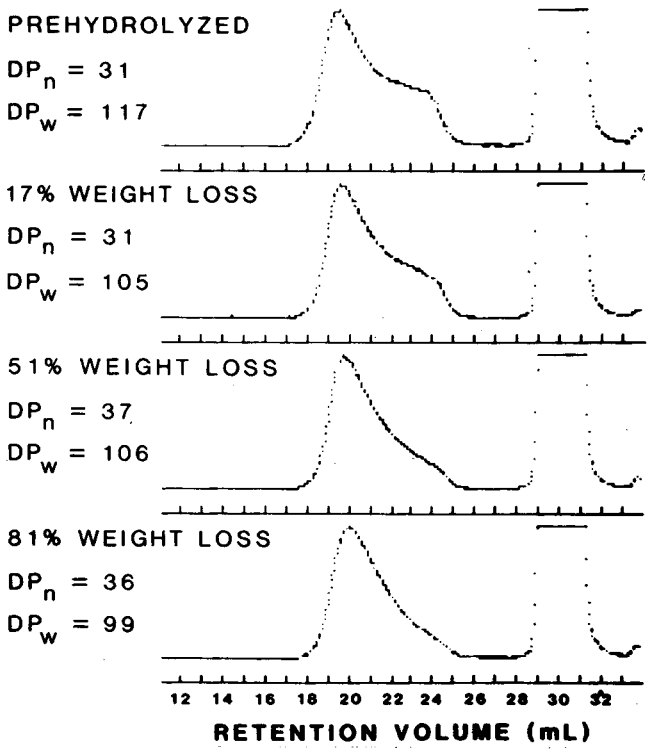

Fig. 3. Chromatograms of cellulose tricarbanilate derived from hydrolyzed samples of mercerized ramie.

and solubilization of the chains on their lateral surfaces,[11, 28] then one would expect to observe a gradual increase in the relative amount of low molecular weight cellulose since the randomly cleaved surface chains would constitute an increasingly larger fraction of the total material as the reaction proceeds.

The chromatograms of the hydrolyzed samples of mercerized ramie are given in Figure 3. Again, the weight average DP is highest for the prehydrolyzed sample but remains relatively constant over the range of conversions from 17 to 81%. Unlike the situation for the samples of hydrolyzed ramie, there is a prominent, low molecular weight shoulder present in the chromatogram of the prehydrolyzed sample. This shoulder decreases in magnitude in the chromatograms of the samples subjected to further hydrolysis. The number average DP actually increased from 31 to 36 over the course of the reaction because of the disappearance of the constituents responsible for the low molecular weight shoulder. Similar behavior was observed in the other three samples of mercerized cellulose. The chromatogram of hydrolyzed, mercerized cellulose presented by Yachi et al.[16] also consisted of a main peak with a prominent, low molecular weight shoulder. A possible explanation for the generation of this low molecular weight fraction will be discussed later.

The chromatograms of the hydrolyzed samples of rayon are shown in Figure 4. The rayon samples are somewhat unique in that their chromatograms exhibit a high molecular weight tail, whereas the chromatograms of all of the other samples had low molecular weight tails.

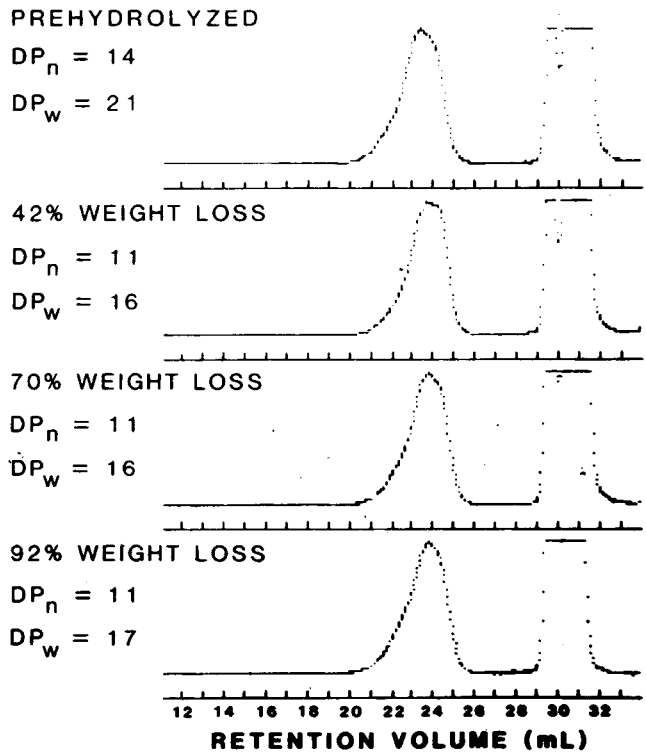

Fig. 4. Chromatograms of cellulose tricarbanilate derived from hydrolyzed samples of rayon.

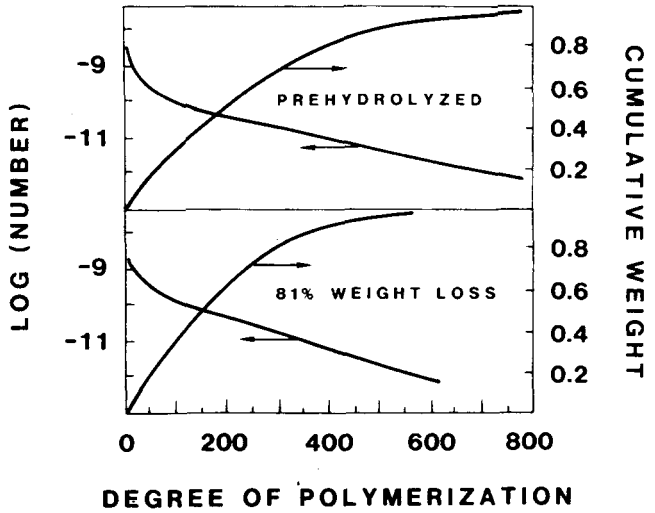

Fig. 5. Differential number and cumulative weight distributions of degree of polymerization for hydrolyzed ramie.

The chromatograms of the remaining samples of native cellulose and mercerized cellulose were qualitatively similar to those of ramie and mercerized ramie, respectively. The weight and number average degrees of polymerization of each of the samples are given in Table I. These values represent the degrees of polymerization of the sample whose weight loss for the crystalline fraction was closest to 50%.

The molecular weight distributions of the hydrolyzed samples of ramie and mercerized ramie are shown in Figures 5 and 6. Each figure contains the differential number distribution of DP and the cumulative weight distribution of DP for the prehydrolyzed sample and the most extensively hydrolyzed

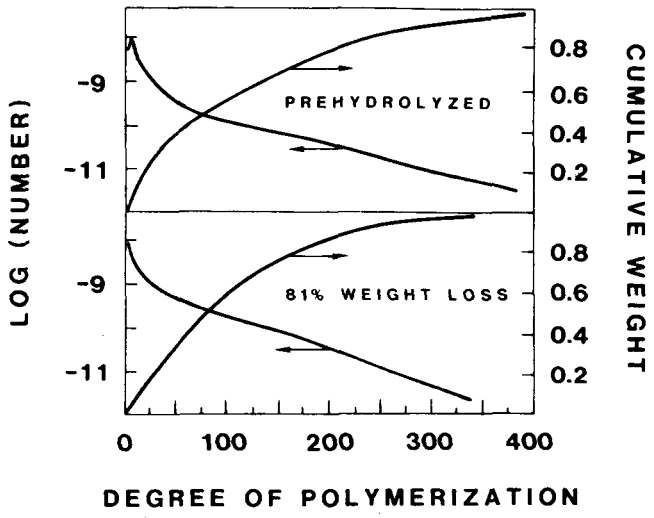

Fig. 6. Differential number and cumulative weight distributions of degree of polymerization for hydrolyzed, mercerized ramie.

sample. The cumulative weight distribution represents the total weight fraction of the cellulose with a degree of polymerization less than a given value.

The differential number distributions for the two samples of hydrolyzed ramie (Fig. 5) appear to be exponential down to a DP of approximately 50. However, below this DP there is an excess of low molecular weight material over that predicted by an exponential distribution. From the cumulative weight distributions, it is apparent that the weight fraction of the hydrolyzed ramie with a degree of polymerization below 50 is less than 20%. Thus, the exponential distribution effectively models the differential number distribution of more than 80% of the weight of the hydrolyzed ramie. The molecular weight distributions of the hydrolyzed samples of mercerized ramie are qualitatively similar to those of the ramie samples.

If the differential number distributions were exactly exponential, then the polydispersities of the samples should be equal to 2. However, with the exception of rayon, the polydispersities of all of the samples shown in Table I were somewhat greater than 2. Again this result is consistent with the observation that there was an excess of low molecular weight material over that predicted by an exponential distribution.

The molecular weight or chain length distribution determined in this study by SEC was used to infer the shape of the crystallite length distribution. It is possible that the crystallite length distribution is exponential as predicted by Sharples[9] but that the chains on the lateral surfaces of the crystallites are subject to hydrolysis. In this case, the contribution to the MWD from the randomly cleaved chains on the lateral surfaces of the particles would lead to an excess of low molecular weight material in the chain length distribution. It is interesting to note that Sharples proposed that the bonds on the lateral surfaces are continually cleaved and recombined.

One of the most probable explanations for the excess of low molecular weight material is that the calibration curve may have been inaccurate for low molecular weight cellulose tricarbanilate. CTC undergoes a change in configuration from a random coil to a rigid rod at low molecular weights.[29] The data presented by Cael et al.[30] suggest that this configurational change may invalidate the use of the universal calibration technique for CTC below a DP of approximately 200. Danhelka et al.[26] have experimentally confirmed the validity of the universal calibration technique for CTC in THF down to a degree of polymerization of approximately 40.

If the universal calibration technique is valid down to a DP of approximately 50, then the DP_w values of the hydrolyzed samples of ramie, cotton, and linen should be fairly accurate since less than 20% of the weight of these samples had a DP below 50. The weight average degrees of polymerization given in Table I for cotton, linen, and ramie are consistent with the viscosity average DPs given by Millett et al.[4] (Table II). Therefore, it appears that the universal calibration technique is not greatly in error above a DP of approximately 50.

On the other hand, almost all of the hydrolyzed rayon had a DP less than 50; thus, the MWDs of these samples are the most uncertain of those reported in this paper. Literature values for the viscosity average DP of hydrolyzed rayon are typically in the range 30–40.[2,4,10] The discrepancy between the

TABLE II
Values of B/ρ Calculated from the Data Presented by Millett et al.[4a]

Material[b]	k (min^{-1})	DP_v^b	B/ρ (min^{-1})
1. Ramie	0.00298	184	0.14
2. Cotton 1	0.00306	175	0.14
3. Cotton 2	0.00349	178	0.16
4. Linen	0.00480	164	0.20
5. Wood pulp 1	0.00654	125	0.21
6. Wood pulp 2	0.00612	140	0.21
7. Wood pulp 3	0.00789	137	0.27
8. Wood pulp 4	0.00685	123	0.21
9. Wood pulp 5	0.00913	134	0.31
10. Wood pulp 6	0.00518	135	0.18
11. Mercerized ramie	0.00505	88	0.11
12. Mercerized cotton 1	0.00575	80	0.11
13. Mercerized wood pulp 1	0.00632	66	0.10
14. Tire-cord rayon	0.0192	31	0.14
15. Fiber G rayon	0.00979	37	0.09

[a] Rate constants corrected to 107.0°C.

[b] Samples 1–10 represent the cellulose I polymorph; samples 11–15 are cellulose II.

[c] The viscosity average degrees of polymerization (DP_v) are at 50% weight loss for the crystalline fraction.

literature and experimental values is probably due to the inaccuracy of using the universal calibration technique in this range.

In order to more accurately determine the molecular weight distribution of CTC obtained from hydrolyzed cellulose, it may be necessary to use a calibration method based on a broad molecular weight distribution standard of CTC.[31] Such a calibration procedure was used by Marx-Figini,[15] who reported that the MWD of cellulose nitrate obtained from hydrolyzed cellulose was exponential. Alternately, a low-angle laser-light scattering detector could be used to continuously monitor the molecular weight of the CTC in the eluent, thereby eliminating the need to use a calibration technique.

As noted earlier, the chromatograms of the prehydrolyzed samples from mercerized cellulose contained low molecular weight shoulders which decreased in magnitude for samples subjected to further hydrolysis. One possible source of this shoulder is low molecular weight material generated by the simultaneous hydrolysis and crystallization of the amorphous fraction in the microfibrils.

It is well recognized that the recrystallization of cellulose occurs concurrently with acid hydrolysis.[32-34] Some investigators have proposed that recrystallization results in part from accretion of low molecular weight chains of cellulose formed during hydrolysis of the amorphous regions.[2,34,35] In this case, the recrystallized cellulose would represent a system of particles whose average length is different from the system of particles which arise from the original crystalline regions in the microfibrils.

In order to determine whether recrystallization may account for the low molecular weight shoulder observed in the mercerized samples, the insoluble

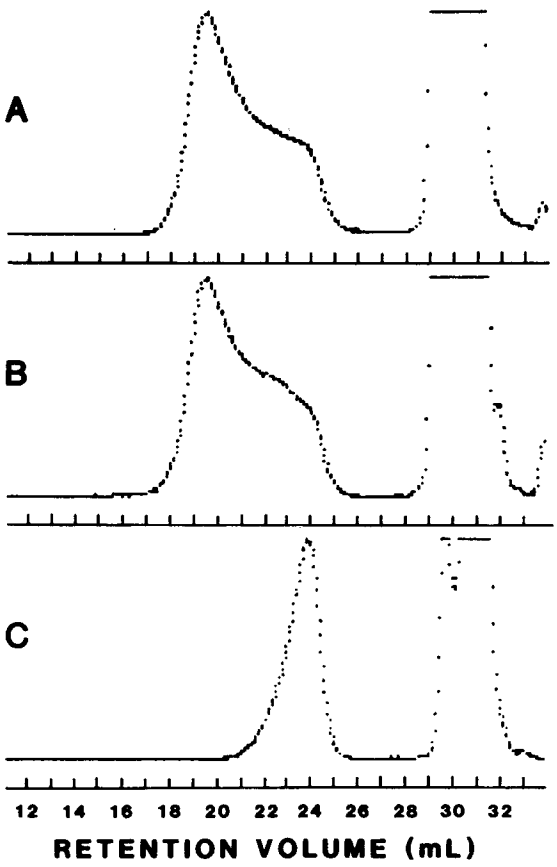

Fig. 7. Comparison of chromatograms of prehydrolyzed samples of (A) mercerized ramie (DP_w = 117; DP_n = 31); (B) mercerized linen (DP_w = 123; DP_n = 33) with chromatogram of (C) recrystallized cellulose (DP_w = 17; DP_n = 13).

products resulting from the hydrolysis of ball-milled cellulose were analyzed by SEC. Extensive ball-milling destroys the crystalline nature of cellulose, thereby producing completely amorphous cellulose.[36] The insoluble residue obtained by hydrolyzing ball-milled cellulose should thus be representative of recrystallized cellulose.

A sample of ramie was treated in a vibratory ball mill for 2 h. The ball-milled cellulose was subjected to the prehydrolysis treatment described earlier. The insoluble products were filtered, washed, freeze-dried, and then prepared for SEC analysis.

Figure 7 compares the chromatograms of the prehydrolyzed samples from mercerized ramie and mercerized linen with the chromatogram of the recrystallized cellulose. The low molecular weight shoulder apparent in the prehydrolyzed samples of mercerized cellulose appears to elute between approximately 21 and 25 mL, a position which coincides with the range of retention volumes of the recrystallized cellulose. Therefore, the SEC results on the MWD of ball-milled cellulose after hydrolysis are consistent with the

hypothesis that the low molecular weight shoulder results from the recrystallization of the amorphous cellulose in cellulose II.

The decrease in the magnitude of the shoulder throughout the hydrolysis reaction indicates that the particles formed via recrystallization are more susceptible to hydrolysis than the remainder of the cellulose. If hydrolysis of crystalline cellulose occurs by end attack, then one would expect the rate of hydrolysis of the recrystallized cellulose to be greater since it has a lower degree of polymerization and hence there are more crystallite ends present per unit weight. Nelson[2] suggested that the more rapid hydrolysis of the recrystallized particles resulted in deviations in her weight loss data from a first-order reaction at short hydrolysis times. From her weight loss data and Sharples' model, Nelson determined that the particles arising from the amorphous regions in mercerized cotton have an average degree of polymerization of 17.

It should be noted that a prominent shoulder was not apparent in the samples of hydrolyzed ramie. This result is consistent with the observation that recrystallization is minimal in samples of native cellulose.[37]

It is interesting to note that the molecular weight of the recrystallized cellulose is approximately the same as the molecular weight of the hydrolyzed rayon. Thus, it appears that a large fraction of the insoluble material resulting from the hydrolysis of rayon may be due to recrystallization of the amorphous cellulose. Howsmon[38] estimated that 30–40% of viscose rayon recrystallizes upon hydrolysis.

In their chromatograms of hydrolyzed samples of mercerized cellulose, Yachi et al.[16] also observed a prominent shoulder which eluted in the same region as the chromatogram from hydrolyzed, regenerated cellulose. They hypothesized that the microfibrils in all cellulosics contain defect regions at intervals of 200 Å. The fraction of these regions which is susceptible to hydrolysis depends upon the severity of any prior treatments performed on the cellulose. Such a structure results in a quantum mode of hydrolysis wherein the hydrolysis products have lengths which are integral multiples of 200 Å. The chromatograms obtained in this study are consistent with those presented by Yachi et al.[16]; however, the above discussion indicates that recrystallization phenomena can explain much of the observed behavior.

Correlation between Rate of Hydrolysis and Molecular Weight

Equations (9) and (10) relate the rate of hydrolysis of crystalline cellulose to its average degree of polymerization. Therefore, given values for k, DP_w, and S, it should be possible to calculate a value for the parameter (B/ρ) for a sample of hydrolyzed cellulose. If the end-attack model is a valid representation of the hydrolysis reaction, then one might expect that the values of (B/ρ) would be the same for all samples of cellulose.

The values of the parameter, (B/ρ), calculated from the experimental data are given in Table I. The solubility limit S of DP = 9 determined by Sharples[9] was used to determine values for $(1/b)$ from eq. (10). Except for the rayon sample, the value of $1/b$ is fairly insensitive to the value used for the solubility limit. For most of the samples, the average degree of polymerization is much greater than S so that $1/b \cong DP_w/2$. The values of (B/ρ) calculated

from the data given by Millett et al.[4] are given in Table II. The rate constants given in Table II have been corrected to the reaction temperature used in this study (107.0°C).

The values of (B/ρ) given in Tables I and II display a fair amount of scatter especially for the samples with cellulose I morphology. In both sets of data, the values of (B/ρ) for linen and wood pulp (or α-cellulose) are consistently higher than the values for ramie and cotton, a fact which suggests that the variation observed for samples of cellulose I is not strictly due to experimental error. It should be noted that Sharples[10] did not include any samples of wood pulp or linen in his analysis of the predicted correlation between hydrolysis rate and DP.

If the end-attack model is a valid representation of the dilute acid hydrolysis of cellulosic materials, then it is interesting to consider the physical significance of the parameter B/ρ.

The rate of decrease in length of the crystallites is given by eq. (3); however, the rate of decrease in length may also be expressed as

$$dx/dt = -2\bar{x}_s k_e \tag{11}$$

where $\bar{x}_s$ is the average length of the fragments produced by hydrolysis at the ends of the molecules and k_e is an average rate constant for the production of these fragments. A factor of 2 is introduced to indicate that hydrolysis occurs at both ends of the crystallites. In eq. (11), k_e represents an intrinsic rate constant for the hydrolysis of the glycosidic bonds in the cellulose chains.

By equating eqs. (3) and (11), one obtains the following expression for the parameter B/ρ:

$$B/\rho = \bar{x}_s k_e$$

Therefore, if the soluble fragments produced from hydrolysis at the ends of the particles have the same average length x_s in all cellulosics, then the parameter B/ρ should be directly proportional to the rate constant for the production of soluble fragments. Further, if one assumes that the soluble fragments have an average length of 1 (i.e., that they are monomers and are thus single molecules of glucose), then B/ρ is simply the rate of hydrolysis of the glycosidic bonds at the ends of the cellulose chains. (Sharples[9] reported that the average length of the soluble fragments was 1.7. In this case the rate constant for the intrinsic rates of hydrolysis, k_e, is less than the parameter B/ρ determined from the end-attack model.)

It is interesting to note that the values of B/ρ for linen and α-cellulose are approximately twice those for the cotton and ramie samples. Marchessault and Ranby[39] found that the rate of homogeneous hydrolysis of wood pulp was approximately twice that of cotton. They felt that chemical modifications introduced into the cellulose during pulping accounted for the difference in the rates of hydrolysis. Therefore, it is possible that the differences which were observed in the intrinsic rate constants B/ρ determined from heteroge-

neous hydrolysis data may arise from the same factors which affect the homogeneous hydrolysis reaction.

The differences in the intrinsic rates of hydrolysis may also reflect differences in the perfection and/or size of the crystalline regions in the cellulose from wood pulp and cotton. Warwicker et al.[40] noted that the transition from cellulose I to cellulose II occurs at a lower concentration of alkali in wood pulp than in cotton. In addition, the diffraction peaks in X-ray diagrams of wood pulp are often broader than the peaks in diagrams of cotton.[5] Warwicker et al.[40] pointed out that both of these observations suggest that the crystalline regions in wood pulp are either less perfect or smaller than the crystalline regions in cotton. Therefore, the greater intrinsic rate constants which were found for the α-cellulose and linen samples may result from an overall lower order in the crystallites in these materials. Because of these considerations, it would be difficult to reject the end-attack model for cellulose I solely on the basis of the differences which were found in the values of the parameter B/ρ.

As noted earlier, the intrinsic rate constants determined for cellulose II were more nearly constant than those determined for cellulose I. This result suggests that any microstructural differences present in the samples of cellulose I are eliminated upon conversion to cellulose II.

From the relationship given in eq. (9), it is apparent that the first-order rate constant k for the hydrolysis of crystalline cellulose may be increased by either lowering the average degree of polymerization of the cellulose (i.e., lowering $1/b$) or increasing the rate of hydrolysis at the end of the crystallites (i.e., increasing B/ρ). Upon mercerization, the weight average DP of both cotton and ramie decreased by approximately 50%. If the intrinsic rate of hydrolysis were unaffected by the conversion to cellulose II, then one would expect the first-order rate constant to double after mercerization. However, an additional fact to consider is that the values of B/ρ given in Tables I and II indicate that mercerization may lower the intrinsic rate constant for the reaction occurring at the ends of the crystallites. In both the ramie and cotton samples, the effect of the decrease in the intrinsic rate constant does not offset the effect of the decrease in DP on the overall rate of weight loss. Thus, the overall effect of mercerization is to increase the rate of hydrolysis in cotton and ramie. On the other hand, the decrease in the intrinsic rate constant is much greater for the α-cellulose and linen samples. Therefore, in these samples, mercerization actually decreases the rate of weight loss, even though the average DP is less in the mercerized samples. An attractive feature of the end-attack model is that it suggests why mercerization may have net effects which act in opposite directions for different types of cellulose.

Atalla[41] has suggested that the rate of hydrolysis of crystalline cellulose II is greater than that of cellulose I because the conformation of the cellulose I chain leads to a shielding of the glycosidic oxygen. However, our results indicate that the intrinsic rate of hydrolysis of cellulose II is less than that of cellulose I. The higher rate of hydrolysis often observed in samples of cellulose II must be attributed to a lower degree of polymerization in these samples. It has been proposed that hydrolysis of crystalline cellulose involves the cleavage of both glycosidic bonds and hydrogen bonds.[9] Since the unit cell structure of cellulose II is more extensively hydrogen bonded than the unit cell of cellulose I,[42] one might expect the intrinsic rate of hydrolysis of cellulose II to be less.

It is interesting to compare the values of B/ρ obtained from Tables I and II to the rate constant for the hydrolysis of cellobiose under similar reaction conditions. Although a value is not available for the rate of hydrolysis of cellobiose in azeotropic HCl (6.08N) at 107°C, this value may be estimated from pertinent data in the literature. In 4.475N HCl, the rate constant for the first-order disappearance of cellobiose at 80°C is 5.6×10^{-2} min^{-1}.[43] Under these same conditions, the activation energy for the reaction is approximately 25.0 kcal/mol.[43] Hence, the Arrhenius relation indicates that in 4.475N HCl at 107.0°C, k(cellobiose) = 0.70 min^{-1}.

The logarithm of the rate constant for the hydrolysis of glycosides is typically linear in the Hammett acidity function.[44] Values of the Hammett acidity function for solutions of HCl at different temperatures were determined from the data presented by Rochester.[45] The proportionality constant between the logarithm of the rate constant and the Hammett acidity function was determined by combining the kinetics data presented by Moiseev et al.[43] with the acidity function data given by Rochester.[45] The first-order rate constant for the hydrolysis of cellobiose in 6.08N HCl at 107.0°C was estimated from these data to be 2.2 min^{-1}.

As is apparent from the data presented in Tables I and II, the intrinsic rate constants for the hydrolysis of the glycosidic bonds at the ends of the crystallites are an order of magnitude less than the rate of hydrolysis of cellobiose at the same conditions. These results suggest that the resistance of crystalline cellulose to dilute acid hydrolysis arises from two factors. First, only a small fraction of the bonds in crystalline cellulose (i.e., those at the ends of the crystallites) is susceptible to hydrolysis. Second, the hydrolysis of these reactive bonds is hindered by the crystalline structure of the cellulose.

CONCLUSIONS

The results presented in this paper from the SEC analysis of hydrolyzed cellulose are consistent with the end-attack model proposed by Sharples for the heterogeneous hydrolysis of crystalline cellulose. For example, the weight average DP of the crystalline cellulose remains relatively constant even for samples hydrolyzed as extensively as 80–90% weight loss of the crystalline fraction. The gradual accumulation of low molecular weight material expected for a lateral attack mechanism is not apparent in the chromatograms. The differential number of distributions obtained for the hydrolyzed cellulose are to a first approximation exponential; however, in all cases there is an excess of low molecular weight cellulose. One possible explanation is that the crystallite length distribution is exponential but the chains on the lateral surfaces are subject to hydrolysis. However, because of uncertainty in the calibration curve in the low molecular weight region, it is difficult to attach much significance to this hypothesis.

The chromatograms of the prehydrolyzed samples from mercerized cellulose displayed a low molecular weight shoulder, which decreased in magnitude with further hydrolysis. Similar behavior was not observed in the samples of cellulose I. The low molecular weight material probably originates from recrystallization of the chains which are cleaved during the hydrolysis of the amorphous regions in the microfibrils.

Intrinsic rate constants calculated from the end-attack model for the hydrolysis of the glycosidic bonds at the ends of the crystallites are greater in samples of α-cellulose and linen than in samples of cotton and ramie. Evidence is available in the literature to suggest that the differences in reactivity may be the result of differences in the crystalline orders of these samples of cellulose I. The variable effect of mercerization on the rate of hydrolysis of cellulose from different sources may reflect the fact that the overall rate of hydrolysis is influenced by both the degree of polymerization and the intrinsic rate of hydrolysis.

The intrinsic rate constant which was determined for the reaction at the ends of the crystallites was an order of magnitude less than that estimated for the hydrolysis of cellobiose under identical conditions. This result suggests that the resistance of crystalline cellulose to dilute acid hydrolysis arises from two factors. First, only a small fraction of the bonds in crystalline cellulose is susceptible to hydrolysis. Second, the rate of hydrolysis of these reactive bonds is hindered by the crystalline structure of cellulose.

B. F. Wood would like to thank the Exxon Corporation for financial assistance in the form of an Exxon Teaching Fellowship. Additional financial support of this research project was provided by the U.S. Forest Products Laboratory and U.S.D.A., Forest Service, Competitive Grant No. 85-08120. The authors thank Marilyn Effland and Virgil Schwandt for performing sugar analyses.

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Received May 20, 1987
Accepted February 29, 1988