Influence of Anomeric Configuration on Mechanochemical Degradation of Polysaccharides: Cellulose versus Amylose

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Cellulose and amylose are (1→4)-linked polysaccharides that are used extensively in the textiles, paper, and food and feed industries and are finding increasing use as alternative fuels and so forth. At the molecular level, cellulose and amylose differ only in their anomeric configuration: β in cellulose, α in amylose. During processing and end use, these polymers experience a variety of mechanochemical stresses, many through contact with transient elongational flow fields. Here, we subject solutions of both polysaccharides to extended periods of ultrasonic irradiation, as the cavitational bubble collapse characteristic of ultrasound experiments creates flow fields strictly analogous to those encountered in other transient elongational flow scenarios. With the use of multidetector size-exclusion chromatography, the effects of anomeric configuration on both the limiting molar mass, beyond which polymers do not degrade in transient elongation flow (M_{lim}), and the rate of degradation have been isolated in these (1→4)-linked polysaccharides. This effect was found to be pronounced; for example, $M_{lim}^{cellulose} = 5(M_{lim}^{amylose})$. Also, while extensive change was observed in molar mass averages, distribution, polydispersity, and size of the analytes during degradation, their structure was found to remain invariant. A modified "path theory" of transient elongational flow degradation was proposed, with the persistence length identified as a parameter which embodies the minimum continuous path length and flexibility requirements of the theory.

Introduction

Cellulose is a structural polysaccharide and the most abundant biopolymer on Earth.[1] Amylose, a storage polysaccharide and a main component of starch, is also a highly abundant renewable resource.[2] Both cellulose and amylose are (1→4)-linked glucopyranosyl-D-glucopyranoses, the molecular-level difference among them being anomeric configuration: β in cellulose, α in amylose. While the main use for cellulose is in the textile and pulp and paper industries, the principal use of amylose remains in foods and feeds, though amylose is finding increasing use in biodegradable products and alternative fuels. Derivatives of both polysaccharides have found application in a wide variety of areas, often interchangeably.

During processing and end-use application, amylose, cellulose, and their derivatives are often subjected to a variety of stresses. The types of stresses which may occur during extrusion, fiber drawing, or sheet forming, for example, are oftentimes elongational in nature and difficult to study in the laboratory. This is particularly true when dealing with stresses and concomitant mechanochemical degradation resulting from the application of transient elongational flow fields, where the velocity time scale of a volume element of fluid is orders of magnitude greater than the relaxation time of a macromolecule.[3,4] Transient elongational flows are encountered in processes such as four-roll Taylor milling or mixing (similar to fiber drawing and to nip−roll processes), in abrupt contraction or expansion flows (encountered in entering and/or exiting extruders, dies, and pipes), in periodic convergent divergent geometries (encountered during passage through filtration beds), and when free jets impinge upon a solid surface (such as when spraying solutions or suspensions).[3] In all of these situations, sample consumption is large and isolation of individual variables difficult, often due to the complicated experimental geometries involved.

An alternative means of mechanochemically degrading polymers is ultrasonication.[5] The flow fields created upon cavitational bubble collapse are also transient elongational, sample consumption is minimal (tens or hundreds of milligrams), and isolation of the variables is relatively straightforward. Additionally, the precursor and degradation products can be conveniently analyzed using techniques such as multidetector size-exclusion chromatography (SEC), which provide a wealth of data regarding degradation.[6–8] The ultrasonically produced flow fields are, from both a fluid mechanics and kinetics points-of-view, strictly analogous to those produced in the aforementioned scenarios (Taylor milling etc.).[3,4,9] Thus, ultrasonication provides a convenient means of studying the mechanochemical degradation of polymers in transient elongational flows.

Two features in particular separate transient elongational from other means of polymer degradation, such as chemical or thermal degradation.[5] First, for linear polymers, transient elongational degradation is nonrandom, producing near-mid-chain scission. Second, rather than the polymer degrading to its constituent monomer or repeat unit, a limiting molar mass (M_{lim}) is reached beyond which no further degradation is possible. M_{lim} has been described as corresponding to the critical molecular length that can diffuse the loaded mechanical stress without a breakage of covalent bonds.[8,10] The effects of long-chain branching on M_{lim} have been discussed elsewhere.[8]

Here, we study the mechanochemical degradation of polysaccharides via ultrasonically generated transient elongational flow fields. We compare the degradation of cellulose to that of amylose; with all experimental factors maintained equal, this comparison permits us to isolate the effects of anomeric configuration on the degradation of (1→4)-linked polysaccha-

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rides. We hope the results of this study will shed light on the degradation of these biopolymers and on the effect of anomeric configuration on M_{lim} and on degradation rate, will show how other polysaccharides may degrade during processing or industrial use, thus permitting for a more informed choice of starting materials and/or processing conditions, as appropriate, and will show how the polydispersity of polysaccharides such as cellulose and amylose, for which narrow standards are not available, can be reduced in solution.

We believe this is the first report regarding the ultrasonic degradation of underivatized cellulose and amylose. A number of studies have examined the ultrasonic degradation of derivatives of both these polysaccharides, noting the effect that varying the substituents has on both M_{lim} and the rate of degradation.[11–15] Unfortunately, the same derivatives of starch and cellulose do not appear to have been examined as part of the same study; that is, the experiments had more than one variable, unlike the experiments presented here, where anomeric configuration is the only variable. As such, the studies involving cellulose/amylose derivatives, while interesting for a variety of reasons, do not provide data sets that can be compared to the cellulose/amylose data sets we obtained.

Experimental Section

Materials. Celluloses and potato amylose were purchased from Sigma-Aldrich. Corn amylose, purified by multiple butanol precipitations according to the Schoch procedure,[16] was a kind gift from Dr. Randy Shogren (USDA/ARS/NCAUR). *N,N*-dimethyl acetamide (DMAc) and LiCl were purchased from Fisher.

Sample Dissolution. Cellulose and amylose were dissolved in DMAc/LiCl,[17,18] as per the procedure described in refs 19 and 20. Final concentrations were ~0.5 mg/mL of cellulose or amylose in DMAc/0.5% LiCl. All solutions were crystal clear and stable at room temperature.

Ultrasonic Degradation. For sonication experiments, ~100 mL of sample solutions were placed in brown glass bottles and sonicated for specified times (see figures) in a Branson 5200 ultrasonic bath operating at 47 KHz and 185 W. The water temperature in the bath was maintained at ~20 °C via a Neslab CFT-75 refrigerated recirculator. Prior to sonication and at each specified time, ~4 mL of solution was removed for SEC analysis.

Size-Exclusion Chromatography. Ultrasonic degradation was monitored using a GPCV 2000 high-temperature size-exclusion chromatograph from Waters Corp. Three detectors were used in series, a DAWN EOS multiangle light scattering (MALS) detector from Wyatt Technology Corp., an Optilab DSP interferometric differential refractometer (DRI; Wyatt), and a triple-capillary, flow-through differential viscometer (Waters). Normalizations of the photodiodes of the MALS unit and interdetector delays were performed using a 19.9 kg/mol narrow polydispersity (PDI = 1.02) polystyrene standard from Polymer Laboratories. The specific refractive index increment, $\partial n/\partial c$, of cellulose and amylose was 0.077 mL/g, as determined in ref 21 under virtually identical experimental conditions. A total of 300 μL of unfiltered sample solution was injected into a set of three Mixed B columns (Polymer Laboratories), at a flow rate of 1.0 mL/min. The sample compartment, column, and detector temperatures were all 80 °C. Flow to the external detectors (MALS and DRI) was through a heated transfer line. Data acquisition and manipulation were performed using Wyatt's ASTRA for Windows software (version 4.9).

Results and Discussion

Molar mass averages and polydispersities of the various celluloses and amyloses examined, prior to sonication, are given in Table 1.

Table 1. Molar Mass Averages and Polydispersities of Celluloses and Amyloses, As Determined by SEC/MALS

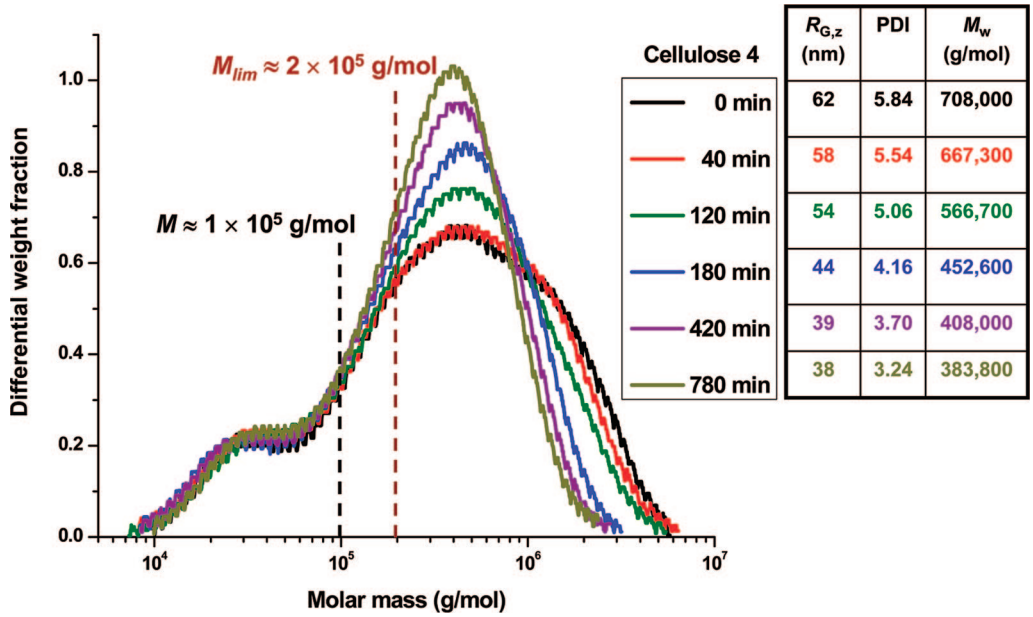
sample[a]	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[b]
cellulose 1	28800	82900	167600	2.88
cellulose 2	25100	63000	119800	2.51
cellulose 3	82800	124300	174400	1.50
cellulose 4	121300	708000	1728000	5.84
amylose 1	83400	148300	245600	1.78
amylose 2	60000	92000	126500	1.53

[a] Cellulose 1: microcrystalline cellulose powder. Cellulose 2: 20 μm cellulose powder. Cellulose 3: native fibrous cellulose. Cellulose 4: acid washed, ashless cellulose. Amylose 1: corn amylose, purified. Amylose 2: potato amylose. [b] PDI = M_w/M_n.

Celluloses 1, 2, and 3 were sonicated for up to 11 h with imperceptible change in their elution profiles and molar mass averages and polydispersity. Unlike celluloses 1 through 3, cellulose 4 did degrade ultrasonically. Evidence of this is seen in Figure 1, which overlays the molar mass distributions (MMDs) of cellulose 4 prior to and at various stages of ultrasonic degradation, up to 13 h. From the figure and embedded table, various features emerge. First, the molar mass distribution of cellulose 4 is observed to narrow with increasing exposure of the solution to ultrasonic irradiation. Second, changes in the MMD occur only at the high molar mass end; no change is observed at the low molar mass end of the MMD below ~100 kg/mol. As ultrasonication in particular and transient elongational flow degradation in general cause near-midchain scission in linear polymers, the limiting molar mass, M_{lim}, should be approximately twice the value at which no changes are observed in the MMD, that is, $M_{lim} \approx 2 \times 100$ kg/mol = 200 kg/mol. It now becomes apparent why degradation was not observed for celluloses 1–3: as seen in Table 1, for all three of these celluloses $M_z < 200$ kg/mol, indicating that virtually all of the MMD for these samples lies below M_{lim}. In hindsight, degradation of these samples, under the given experimental conditions, would not have been expected.

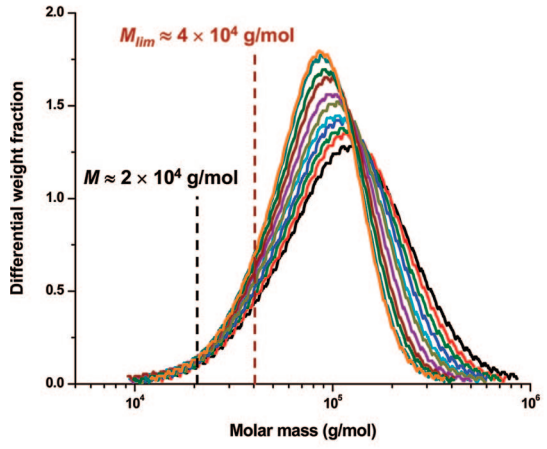
Exhaustive sonication, to the point where the MMD does not change and the primary mode of the distribution corresponds to M_{lim}, may seem like a more suitable method to determine M_{lim}. This approach, however, suffers from the point of view of practicality. As can be seen in Figure 1, even after 13 *hours* of sonication, the primary mode of the distribution is only at ~400 kg/mol, still approximately twice as high as our estimated value of M_{lim}. This, combined with the fact that the polymer will degrade more slowly as its molar mass decreases (i.e., as it approaches M_{lim} from above), indicates that exhaustive sonication experiments may take several *days* to perform. The method presented here appears simpler and robust, as the MMD data obtained by SEC/MALS are quite reproducible and finding a common region in the MMD overlays is not particularly difficult. Also, M_{lim} values obtained by examining the MMD overlays agree almost exactly with the M_{lim} obtained from overlaying the normalized DRI traces. In the latter method, the retention volume where the normalized DRI chromatograms begin to overlap is matched to the molar mass slice (a value obtained using the online MALS detector) corresponding to the particular elution slice. The molar mass value for this slice then corresponds to $M_{lim}/2$.

We also note in Figure 1 that the polydispersity of cellulose 4 decreases by close to a factor of 2 over the course of 13 h of sonication, and the size of the sample, as measured by the *z*-average root-mean-square radius, $R_{G,z}$, decreases by ~40%, from 62 to 38 nm. Additionally, the longest cellulose chains in the original, unsonicated sample of cellulose 4 have a molar



$R_{G,z}$ (nm)	PDI	M_w (g/mol)
62	5.84	708,000
58	5.54	667,300
54	5.06	566,700
44	4.16	452,600
39	3.70	408,000
38	3.24	383,800

Figure 1. Overlay of the MMD of cellulose 4, as determined by SEC/MALS, at various sonication times (to reduce clutter, not all times have been included).



Amylose 1	$R_{G,z}$ (nm)	PDI	M_w (g/mol)
0 min	17	1.78	148,300
20 min	16	1.69	135,000
40 min	15	1.61	128,100
60 min	15	1.61	121,400
120 min	14	1.57	112,200
180 min	14	1.49	112,000
240 min	13	1.48	103,400
300 min	13	1.45	96,400
360 min	13	1.41	93,800
420 min	12	1.38	89,400
480 min	12	1.36	88,600

Figure 2. Overlay of the MMD of amylose 1, as determined by SEC/MALS, at various sonication times.

mass of 5 800 000 g/mol. After 13 h of sonication, the longest chains in the sample are now of molar mass 2 300 000 g/mol. In other words, all material between 5.8 and 2.3 million g/mol has been degraded, but without degrading the chains at the lower end of the MMD.

Figure 2 shows the results of the ultrasonic degradation experiment for amylose 1, purified corn amylose. Here, while results are less dramatic than those observed for cellulose 4, the same features may be observed. Again, the MMD narrows, and the accompanying molar mass polydispersity and sample size decrease with increasing exposure to ultrasonic irradiation. For amylose 1, the longest chains prior to sonication have $M =$ 850 000 g/mol. After 8 h of sonication, all material higher than 365 000 g/mol has been degraded. Equivalent results were observed with amylose 2, potato amylose, though degradation of amylose 2 proceeded more slowly than that of amylose 1, due to the molar mass of the former being smaller than that of the latter (see discussion of rates of degradation below).

It is quite interesting to note that, for amylose 1, the MMD ceases to change at ~20 kg/mol, indicating a value of $M_{\lim}$ for amylose of ~40 kg/mol, *5 times smaller than the* $M_{\lim}$ *value of cellulose under identical conditions.* In other words, all other factors being equal and given enough exposure to ultrasonic irradiation, amylose will degrade to substantially shorter chain lengths than will cellulose, a result strictly due to the difference in anomeric configuration between these (1→4)-linked polysaccharides and to the impact of anomeric configuration on macromolecular structure.[22–24] Said impact is reflected in the difference in the persistence lengths, L_p, of cellulose and amylose. Here, we have calculated L_p using eq 1:[25,26]

$$\left(\frac{M}{R_G}\right)^{1/2} = \left(\frac{3M_L}{L_p}\right)^{1/2}\left(1 + \frac{3L_pM_L}{2M}\right) \qquad (1)$$

where M_L is the molar mass per unit contour length. L_p and M_L are determined from the intercept, $(3M_L/L_p)^{1/2}$, and slope, $(3/2)M_L(3L_pM_L)^{1/2}$, of a plot of $(M/R_G^2)^{1/2}$ versus $1/M$. Equation 1 has been shown to be accurate, within 1%, for cases in which $[(M/(2L_pM_L)] > 2$.[26] Using this relation, we obtain values of L_p for cellulose 4 of 55 ± 3 nm and for amylose 1 of 11 ± 2 nm, in excellent agreement with the difference between the $M_{\lim}$

values for these polysaccharides. While these values are higher than literature values of L_p for cellulose and amylose in DMAc/LiCl,[27,28] it should be noted that the literature values are for solutions with much higher concentrations of LiCl:DMAc with 3% LiCl for amylose and DMAc with 9% LiCl for cellulose, whereas in our experiments for both polysaccharides, the LiCl concentration was merely 0.5%.

A Revised "Path Theory" of Degradation. Traditionally, M_{lim} was described as the molar mass beyond which transient elongational flow degradation does not occur.[3,5] This definition makes no allowance for macromolecular architecture. Previously, we introduced the so-called "path theory" of degradation, to account for the effects of long-chain branching in polymers.[8] The path theory successfully explained the vastly different M_{lim} (and also degradation vs nondegradation) for linear and star polymers of the same chemistry and molar mass. It also explained differences in ultrasonic degradation results between equal chemistry star polymers of differing arm numbers but similar molar masses or of equal arm numbers but differing arm lengths. Briefly, it was suggested that, rather than a minimum molar mass being the requirement for transient elongational flow degradation to occur, a minimum continuous path length within the molecule was needed. For example, given the case of two polymers, one linear and one long-chain branched, of identical chemistry and molar mass, the longest possible continuous path that can be traced (without doubling back upon the path) will be longer in the linear molecule. In this case, M_{lim} of the linear molecule will be lower than M_{lim} of the branched molecule.

It appears, from the present set of experiments, that chain stiffness should also be incorporated as an architectural influence on our understanding of M_{lim}. Thus, not only is a minimum continuous path length within the molecule necessary for transient elongational flow degradation to occur but also this path must have sufficient conformational freedom to diffuse the loaded mechanical stresses via covalent bond rupture. The persistence length is a parameter which embodies both the path length and flexibility requirements. All other factors (e.g., polymer chemistry) being equal, a macromolecule with a smaller value of L_p will degrade to shorter chain lengths and have a lower value of M_{lim} than a macromolecule with larger L_p.

Rate of Degradation. Anomeric configuration is also seen to affect that rate of degradation, k, of polysaccharides. To determine k, we use eq 2:[29]

$$\frac{1}{M_{n,t}} = \frac{1}{M_{n,0}} + k't \qquad (2)$$

where $M_{n,t}$ is the number-average molar mass at sonication time t, $M_{n,0}$ is the number-average molar mass of the unsonicated sample (i.e., at $t = 0$), and $k' = k/M_o$, where M_o is the molar mass of the repeat unit of the polymer (162 g/mol for both cellulose and amylose). Thus, a plot of $1/M_{n,t}$ versus t will give k' and, hence, k. From this relation and the first several (two for amylose, three for cellulose) hours of degradation data, we calculate values of k of $(2.66 \pm 0.19) \times 10^{-6}$ min^{-1} for amylose 1 and $(0.92 \pm 0.18) \times 10^{-6}$ min^{-1} for cellulose 4. The difference of a factor of 3 between the rates of degradation of amylose 1 and cellulose 4 actually *underestimates* the difference in rates, as the molar mass of cellulose 4, even after extended ultrasonic degradation, is still substantially higher than that of amylose 1. Because it has been noted that k scales not with M but with M to the power 1.2−1.4 ($M^{1.2-1.4}$) for most linear polymers,[5,8] a comparison of amylose and cellulose of the same molar mass would certainly show a difference in degradation rates exceeding the factor of 3 calculated above.

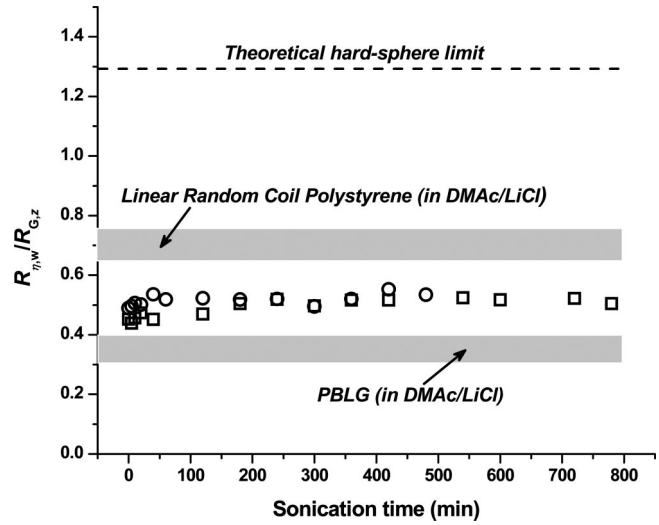


Figure 3. Ratio of the viscometric to root-mean-square radii, $R_{\eta,w}/R_{G,z}$, as a function of sonication time. Circles denote data for Amylose 1, squares data for Cellulose 4, with standard deviations smaller than or equal in size to data points, and therefore, these are not shown. Data for polystyrenes in DMAc/0.5% LiCl from ref 8; data for PBLG in DMAc/0.5% LiCl from ref 37.

Equation 2 is similar to many others used in the literature to determine k for ultrasonic degradation.[30–33] An advantage of eq 2 over several alternative methods is that in eq 2 M_{lim} is not included in the calculation of k. As such, any error or uncertainty in the determination of M_{lim} does not transfer to the determination of k. As with many of the other equations used to determine k, eq 2 models random chain scission. At early degradation times, however, it has been found to adequately represent the nonrandom scission events characteristic of ultrasonic degradation and has been successfully applied to the of study the ultrasonic degradation of native dextran,[34] of various poly(alkyl methacrylates),[29] and of linear and star polystyrenes.[8]

Effect on Structure. While Figures 1 and 2 provide evidence of the large changes in molar mass distribution, polydispersity, and size that occur as a result of ultrasonically induced mechanochemical degradation, Figure 3 shows that the structure of the polysaccharides does not appear to change appreciably during degradation. This figure plots the dimensionless size parameter $R_{\eta,w}/R_{G,z}$, the ratio of the viscometric to root-mean-square radii, as a function of sonication time ($R_\eta = [(3[\eta]_w M_w)/(10\pi N_A)]^{1/3}$, where N_A is Avogadro's number and $[\eta]_w$ is the weight-average intrinsic viscosity). Shown also in the figure are the theoretical hard-sphere limit, the region occupied by linear random coil polystyrenes of various molar masses in DMAc/LiCl, and the region occupied by the synthetic polypeptide poly(γ-benzyl-L-glutamate) or PBLG, which assumes a highly extended conformation in DMAc/LiCl. The lower the value of the dimensionless ratio, the more extended the polymer chain.[35,36] As can be seen in Figure 3, the ratio of the radii for both cellulose and amylose lies below the polystyrene linear random coil region,[8] indicative of the extended nature of the polysaccharides, though not as extended as PBLG, which under identical conditions adopts a structure closer to that of a rigid rod than do the polysaccharides.[37] More importantly, the ratio R_η/R_G for both amylose and cellulose shows almost no change over the course of the sonication experiments, indicating that, while much change is occurring in the MMD, PDI, molar mass averages, and size of the polymers, their structure remains essentially invariant during degradation.

It should be noted that the ratio R_η/R_G only appears to be sensitive to relatively large changes in conformation (e.g., sol

vs linear, random coil vs highly extended). While the persistence lengths of cellulose 4 and amylose 1 differ by a factor of 5, their R_η/R_G ratios are fairly similar, 0.49 ± 0.03 for cellulose and 0.52 ± 0.02 for amylose. These values are higher than the value of R_η/R_G for PBLG in DMAc/0.5% LiCl at 35 °C, found to be 0.36 ± 0.04. Under these conditions, though, the persistence length of PBLG was calculated, using eq 1, to be ~140 nm, substantially higher than the L_p values of cellulose and amylose under virtually identical experimental conditions.

The invariance in R_η/R_G for cellulose and amylose, as a function of sonication time, is in agreement with results obtained by comparing the fractal dimension, d_f, of each polysaccharide as a function of degradation. The fractal dimension, as determined by either light scattering or viscometry (results from both sets of experiments are consistent with each other), remains virtually invariant as a function of degradation, merely oscillating between 1.5 and 1.7 (standard deviations of ± 0.1 or less were obtained for d_f by either viscometry or light scattering). This confirms the R_η/R_G results above, namely that, while large changes in molar mass averages, PDI, MMD, and size occur during degradation, cellulose and amylose retain their original structures throughout the degradation experiments. The fractal dimension is obtained from the slope, α (not to be confused with anomeric configuration), of the so-called "conformation plot" of log R_G versus log M. From this plot, the fractal dimension is obtained via the relation $d_f \equiv 1/\alpha$.[7,35,38] The fractal dimension can also be obtained from the Mark–Houwink plot of log [η] versus log M, where [η] is the intrinsic viscosity of the polymer solution. In this case, the fractal dimension is related to the slope, a, of the plot as per $d_f = 3/(1 + a)$.[7,35,38]

Conclusions

We have studied the ultrasonically induced mechanochemical degradation of cellulose and amylose, two polysaccharides which differ only in their anomeric configuration. This difference, however, has a large effect on the degradation characteristics of the polysaccharides. Under identical experimental conditions, the limiting molar mass beyond which degradation does not occur is 5 times smaller for amylose than for cellulose. Likewise, the degradation rate of amylose is several (at least 3) times faster than that of cellulose. These results can have important implications in what type of material, or which material's derivatives, to use for a particular application, should a choice be possible. We believe this is the first report regarding the ultrasonic degradation of underivatized cellulose and amylose.

Additionally, celluloses where the entire MMD lies below M_{lim} are not observed to degrade, a factor which can also prove of benefit in processing and end-use applications of the material. The existence of M_{lim}, encountered in all forms of transient elongational flow degradation, provides a means of making polymer solutions with decreased polydispersity where commercially available samples or standards with the needed polydispersity are not available. This is especially true for natural polymers such as cellulose and amylose. However, as noted above, degradation will only be possible if a portion of the MMD lies above M_{lim}, and the degradation of material with $M \leq M_{lim}$ will not occur. Also, degradation will proceed more slowly the lower the molar mass and the closer to M_{lim}. At present, this form of making polymers with narrower PDI than originally obtained appears useful for research purposes only, though the increasing use of ultrasonic die extruders may aid in scaleup operations.[39,40]

A modified "path theory" of transient elongational flow degradation was introduced, to help explain the influence of macromolecular architecture on degradation. This theory builds upon the original,[8] which attempted to explain the effects of long-chain branching on degradation. The current theory incorporates the effect of macromolecular conformation on degradation, postulating that a minimum path length of sufficient flexibility is needed for degradation in transient elongational flows to occur. Furthermore, the persistence length was identified as a parameter which embodies both the path length and flexibility requirements. Quantitative agreement was found between the differences in L_p of cellulose and amylose and the differences in M_{lim} of these two polysaccharides, under identical experimental conditions.

Finally, the combination of ultrasonication and multidetector SEC is seen to be extremely powerful for studying mechanochemical polymer degradation. A limited amount of sample is needed for ultrasonic experiments, and isolation of individual variables is relatively straightforward. SEC with viscometric and light scattering detection can provide a number of parameters to characterize the change (or lack thereof) in molar mass averages, polydispersity, distribution, size, and structure of polymers, natural and synthetic, as a function of degradation.

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