Degradation of a Water-Soluble Polymer: Molecular Weight Changes and Chain Scission Characteristics

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ABSTRACT: Computer simulations in conjunction with molecular weight distributions, obtained from gel permeation chromatography (GPC), are used to obtain physical insights on the mechanisms of degradation of guar galactomannan, a naturally occuring polysaccharide. Two different modes of degradation, sonication and enzymatic hydrolysis, are compared. Both modes of guar degradation reveal similar features in terms of changes in molecular weights, a rapid reduction followed by a slow decrease. However, the molecular weight distributions are significantly different, with ultrasonication leading to a narrowing of the molecular weight distribution and enzymatic hydrolysis resulting in its broadening. Sonication of guar results in a random degradation of chains, so that all bonds have equal probability of cleavage. In contrast, enzymatic degradation does not follow any of the typical modes of chain scission (random, Gaussian, and central), indicating that enzymatic hydrolysis of guar does not obey a "single scission" pathway. Plots of the zero shear viscosity, η_o, as a function of number-average molecular weight, M_n, show enzymatically degraded guar to possess a much higher viscosity compared to a sonicated guar, at the same M_n. This contrasts the behavior of zero shear viscosity, η_o, vs weight-average molecular weight, M_w, where both systems are identical despite the large differences in polydispersity. We infer that, for polydisperse systems, the steady shear rheological properties are not very sensitive to the entire molecular weight distribution and can be adequately described by M_w, the molecular weight average that is primarily controlled by the high molecular weight fraction.

1. Introduction

Polymer degradation is possible through several methods, including chemical, enzymatic, radiative, mechanical, and ultrasonic means. While it is often a limiting factor for polymer stability and utilization, polymer degradation finds use in a variety of applications including drug delivery devices[1] and oil/gas exploration[2] and in alternatives to fossil fuels for energy sources.[3] Polymer degradation was first analyzed theoretically by Kuhn[4] and Simha,[5] who detailed a statistical method to obtain molecular weight averages for random scission of monodisperse polymer chains. Subsequently, an analytical model[6] was developed to predict the entire molecular weight distribution (MWD) rather than only average molecular weights. Experimentally, the development of gel permeation chromatography (GPC) to measure the MWD has proved to be an important technique for investigating polymer degradation. By combining these analytical and experimental methods, significant insights into the kinetics and mechanisms of polymer degradation have been realized for systems such as acid hydrolysis of dextran,[6] enzymatic degradation of polyglutamine,[7,8] ultrasonication of nucleic acids,[9] and degradation of polystyrene.[10]

In this paper, we present our initial findings on the mechanisms of degradation of guar galactomannan and the concomitant changes in viscosity. Guar is a water-soluble polysaccharide consisting of a linear backbone of β-1,4 linked mannose units with α-1,6 linked galactose units as side chains; the ratio of mannose to galactose units being ~1.6:1.[11,12] Guar is used extensively in industry due to its excellent viscosifying properties, natural abundance, and low cost.[13,14] In many of these applications, such as in food and oil production, guar needs to be depolymerized in a controlled manner.[15,16] Our earlier work[15] focused on developing a kinetic model for the enzymatic hydrolysis of guar solutions. However, no effort was made to understand the mechanism of degradation, which plays a crucial role in achieving optimal performance in the application of these materials. The goal of this study, therefore, is to obtain physical insights on guar degradation effected through two different approaches, ultrasonication and enzymatic hydrolysis. To this end, changes in molecular weight (MW) and molecular weight distribution (MWD) of guar solutions are measured by GPC. These data are compared with calculations based on mathematical modeling of degradation through different modes of chain scission. Finally, structure−property relations for guar solutions degraded by enzymatic action and ultrasound are investigated using steady shear rheology.

Ultrasonication and Enzymatic Degradation. High molecular weight polymer chains degrade to smaller sizes upon exposure to ultrasound radiation. Although the exact mechanism of degradation is unclear, it has been attributed to cavitation, the formation and collapse of microscopic vapor bubbles generated by the strong sound waves. The resultant shock waves impart energy to the macromolecules, which results in scission if the macromolecule is unable to dissipate this energy.[17] Although the mechanism in ultrasound degradation is different[18] than the hydrolysis observed in enzymatic degradation, we use ultrasonication in this study as it is an established/well-studied technique for polymer degradation and provides a basis to compare enzymatic degradation with.

Pathways for enzymatic degradation of polymers can be broadly divided into two types, single and multiple-

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scission.[19] In the single scission pathway, only one bond is hydrolyzed per enzymatic attack, whereas the multiple attack pathway consists of an initial attack on a substrate molecule, followed by several secondary cleavages on one of the fragments produced by the initial scission. For random hydrolysis (all bonds being equally susceptible to enzymatic attack) via single scission pathway, a plot of the reciprocal of chain length (or molecular weight) vs time is linear.[20] This linear relation was observed for enzymatic degradation of guar solutions and gels.[15,16] It needs to be mentioned, however, that this kinetic data ($1/M_w \propto t$, where M_w is the weight-average molecular weight) does not provide conclusive evidence for the single scission pathway as this relationship is insensitive to the primary difference between the single and multiple attack pathways, viz. the relatively large concentration of small oligosaccharides accumulated for the multiple scission pathway. For this study, we consider the single scission pathway to verify if the molecular weight patterns obtained upon enzymatic degradation are consistent with this particular pathway.

2. Model Description

A general model proposed by Basedow et al.[6] is utilized here to describe the degradation of the guar chain backbone by ultrasonication or enzymatic action. To obtain a molecular level picture of guar degradation by sonication, we need to know (a) the rate at which a species with i monomer units breaks and (b) the rate at which a bond breaks according to its position in the chain. For this, the Basedow model uses two parameters, (i) the individual rate constants k_i for the degradation of polymer chain species with i monomer units and (ii) $k_{i,j}$, the rate constant for the breakage of a chain into two fragments, a j-mer and an $(i-j)$-mer. Clearly, k_i is the sum of all $k_{i,j}$. The model also assumes that the degradation is first order with respect to the concentration of i-mer chains (if $k_{i,j}$ is independent of molecular weight). A mass balance for the species of polymer with i units then gives

$$\frac{dn_i}{dt} = -(\sum_{j=1}^{i-1} k_{i,j})n_i + (k_{i+1,1} + k_{i+1,i})n_{i+1} + ... + (k_{r,i} + k_{r,r-1})n_r ... \quad (1)$$

where dn_i/dt is the reaction rate of the species i (molecules containing i subunits), $k_{i,j}$ is the individual rate constant, n_i is the number of molecules of species i, and r is the highest degree of polymerization under consideration. A system of r simultaneous, first-order linear differential equations is thus obtained for both sonication and enzymatic degradation.

It should be mentioned that other models of polymer degradation have also been proposed. For example, a continuous model for polymer fragmentation has been proposed by Ziff and McGrady.[21] Monte Carlo simulation techniques have also been proposed to investigate branching effects and recombination in polymer degradation.[22−24] An equation predicting time evolution of the concentration of selected range of polymer molecular weights has also been suggested.[25] In this paper, however, we focus on the discrete model of Basedow et al.[6] because it lends itself more easily to combination with experimental data and has been used successfully to predict changes in molecular weight distributions, for example, in depolymerization of DNA molecules.[9]

Modes of Chain Scission. To obtain the rate constants, k_i, and $k_{i,j}$, three specific cases are considered to account for different possible modes of chain scission.

(i) Random Scission. For this mode, scission occurs with equal probability at any site along the chain; therefore, $k_{i,j} = k$.

(ii) Central Scission. Here, the molecules are split only at the midpoint of the chain. The rate constants can be expressed as

i odd: $k_{i,j} = 1$ for $j = (i-1)/2$; $k_{i,j} = 0$ for $j \neq (i-1)/2$

i even: $k_{i,j} = 1$ for $j = (i/2)$; $k_{i,j} = 0$ for $j \neq i/2$

(iii) Gaussian Scission. The probability of chain scission is assumed to follow a Gaussian distribution about the chain midpoint.[26] Thus

$$k_{i,j} = \frac{1}{\sqrt{2\pi}\sigma_i} \exp\left(-\frac{(j - i/2)^2}{2\sigma_i^2}\right)$$

Here σ_i is the standard deviation and was set at $0.2i$. For these three cases, k_i, the sum of $k_{i,j}$ is directly proportional to i, the chain length.

Computational Procedure. By a method due to Ballauf and Wolf,[27] the system of differential equations is transformed to an eigenvalue problem and solved using vector algebra technique. Making the assignments

$$d\vec{n}/dt = \begin{pmatrix} dn_1/dt \\ ... \\ dn_i/dt \\ ... \\ dn_r/dt \end{pmatrix} \qquad \vec{n} = \begin{pmatrix} n_1 \\ ... \\ n_i \\ ... \\ n_r \end{pmatrix}$$

eq 1 can be rewritten as

$$d\vec{n}/dt = A\vec{n} \quad (2)$$

where A is a coefficient matrix such that eq 1 is satisfied for $i = 1$ to r

$$A = \begin{pmatrix} 0 & k_{2,1} + k_{2,1} & k_{3,1} + k_{3,2} & ... & \\ 0 & -k_{2,1} & k_{3,2} + k_{3,1} & ... & \\ 0 & 0 & \sum_{j=1}^{2} k_{3,j} & ... & k + k \\ 0 & 0 & 0 & . & .. \\ 0 & 0 & 0 & 0 & \sum_{j=1}^{r-1} k_{r,j} \end{pmatrix}$$

Matrix A is upper triangular in nature, making eq 2 amenable to computer-aided iterative calculations. The input to the computer program includes the initial molecular weight distribution, which was supplied from GPC data, and values for matrix A elements, which were determined using the specific scission models listed in the previous section. The program provides a resultant number fraction of molecules with molecular weight M, $f_n(M)$ as a function of time t. This number fraction is converted to a weight fraction, $f_w(M)$, and finally, the molecular weight distribution is plotted as $g_w(\log M)$ vs $\log M$, the relation between g_w and f_w being[9]

$$f_w(M)\, dM = f_w(M)[dM/d(\log M)]\, d(\log M) = g_w(\log M)\, d(\log M)$$

Actual computations were performed on a Sun-Sparc workstation by a program written to run on Matlab, a software by The Mathworks, Inc., Natick, MA. Because of restrictions on computer memory, the largest molecule was assumed to consist of 1000 subunits; as a result, each subunit consisted of approximately 20 monomers. Additional simulations were performed using 200, 500, and 2000 subunits to a molecule to ensure that the results did not depend with the number of subunits.

3. Materials and Experimental Methods

Materials. Food grade guar galactomannan (Jaguar 6003, Rhone-Poulenc, NJ) was purified through Soxhlet extraction with ethanol.[28] Hydrocolloid dispersions were prepared by dispersing purified guar powder in a sodium phosphate buffer.[15] Subsequently, solutions were centrifuged at 20000*g* for 1.5 h to remove suspended impurities and obtain a clear solution. Enzymatic guar degradation was performed using a purified endo-β-mannanase (from *Aspergillus niger*) obtained commercially from Megazyme Corp. (Ireland). Product Information from the manufacturer reveals this enzyme to have zero specific activity (0.000 U/mg of protein) on a pNP-β-mannosidase substrate (that mimics the ends of a guar chain). This clearly indicates that the endo-β-mannanase enzyme used in this study has no ability to cause chain scission from the polymer chain ends, thereby eliminating any misinterpretation of the chain scission data, as discussed later. The degradation was performed on 1% (w/v) guar solutions at 25 °C. For GPC calibration, eight pullulan standards were obtained from Shodex Corp., Japan (ranging from molecular weights of 5200 to 1.6 million). Solutions were prepared in deionized water (Millipore, Bedford, MA) as prescribed by company literature. For sonication, 25 mL of a 1% guar solution was taken in a polypropylene conical that was immersed in an ice bath. Ultrasonic irradiation was carried out with a sonicator (XL 2020, Heat Systems-Ultrasonics, Farmingdale, NY) for up to 30 min (30 repetitions of 60-s pulses with 4 min equilibration time between pulses).

GPC Measurements. Molecular weight averages and molecular weight distributions (MWD) were determined by GPC on a bank of Waters columns (Ultrahydrogel 2000, 500 and 120). A guard column (Ultrahydrogel Guard Column, Waters) was used ahead of the column bank. A Shimadzu HPLC system with RID-6A differential refractive index detector was used. The eluant was water containing 0.1 M sodium nitrate and 5×10^{-3} M sodium azide; the flow rate was 0.8 mL/min; temperature was 45 °C. All degraded guar samples were diluted to 0.05% (w/v) (to eliminate viscous spreading in the column) and filtered through a 0.45 μm filter prior to analysis. The bank of columns was calibrated using the pullulan standards. The MW distributions thus obtained were checked for skewing and symmetrical spreading using ASTM method D3536−91. Both effects were found to be negligible. A Universal Calibration procedure (hydrodynamic volume correction) was applied to calculate absolute guar molecular weight distributions from raw chromatogram data.[15] The molecular weight averages were calculated by numerical integration of the MW distribution curve. The reproducibility in the MW averages was within ±2%.

Viscosity Measurements. Guar solutions, degraded by enzyme or ultrasonication to different extents, were tested on a stress controlled rheometer (DSR), Rheometrics, Piscataway, NJ). Steady stress viscosity measurements were made using a couette geometry with inner bob and outer cup radii of 14.75 and 16.0 mm, respectively, and a bob length of 44.25 mm. For all samples, Newtonian behavior was observed with viscosity independent of shear stress, at low shear stresses ($\sim$<1 dyn/cm^2). At higher stresses, guar solutions displayed shear thinning; i.e., the viscosity decreased with increasing shear stress. The viscosity in the Newtonian region (also termed as zero-shear viscosity) was used to compare samples degraded to different extents.

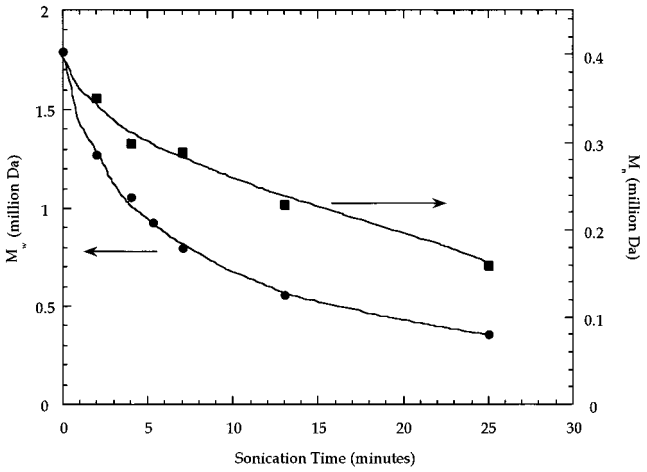

Figure 1. Number- (M_n) and weight-average (M_w) molecular weights of a guar solution (1% w/v) during sonication.

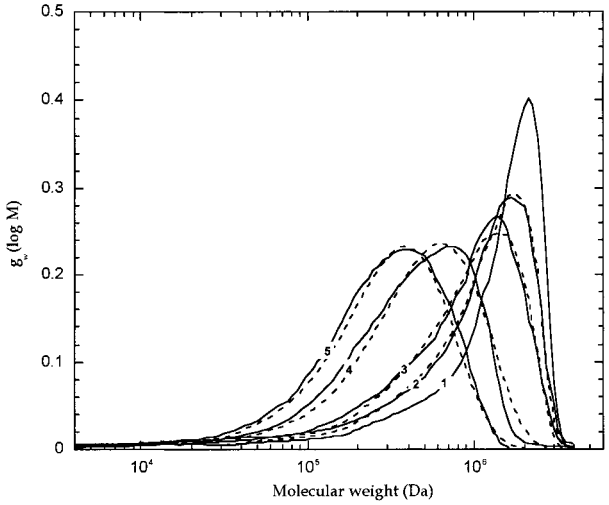

Figure 2. Comparison of measured and simulated molecular weight distribution of guar solution during ultrasonication. Solid curves refer to GPC measurements whereas broken curves correspond to random scission model predictions. Numbers on curves relate to ultrasonication time in minutes: 1 (0), 2 (1), 3 (4), 4 (13), and 5 (25).

4. Results and Discussion

Figure 1 shows changes in weight-average molecular weight, M_w, and number-average molecular weight, M_n, as a function of sonication time. As expected, guar molecular weight decreases continuously with increasing sonication time. The reduction in molecular weight is rapid for short sonication times and slower for subsequently longer sonication time periods. The kinetics of molecular weight reduction are consistent with those observed for sonication of other systems, such as polystyrene in toluene[26] and nucleic acids in aqueous solution.[9] Figure 2 compares the experimentally observed molecular weight distributions with model predictions for ultrasonication of guar via random hydrolysis. The solid lines indicate experimental data while the broken lines represent best fits for the model. We find that the random mode of chain scission, where all bonds are equally susceptible to breakage, fits the data well for all sonication times. Predictions of the MWD for Gaussian and central chain scission are shown in Figure 3, parts a and b, respectively. The Gaussian mode of chain scission predicts distributions that are narrower than experimentally observed while central

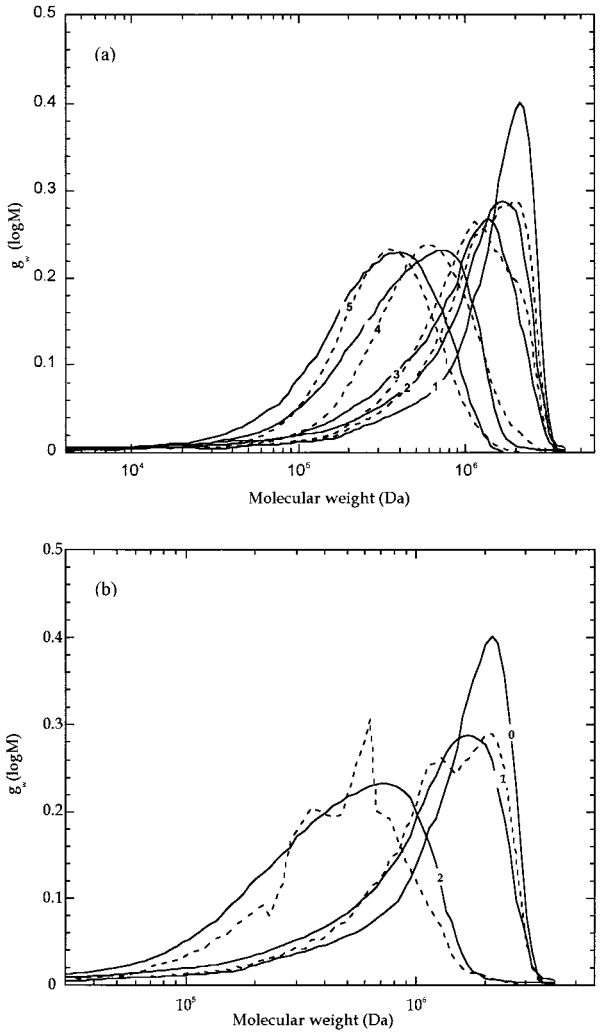

Figure 3. Measured and simulated molecular weight distributions of guar solutions subjected to sonication. Solid curves correspond to GPC measurements. (a) Broken curve represents Gaussian scission model predictions. Number on curves refer to time of sonication in minutes: 1 (0), 2 (1), 3 (4), 4 (13), and 5 (25); (b) Broken curves corresponds to central scission model prediction. Sonication times in minutes: 0 (0), 1 (1), 2 (13).

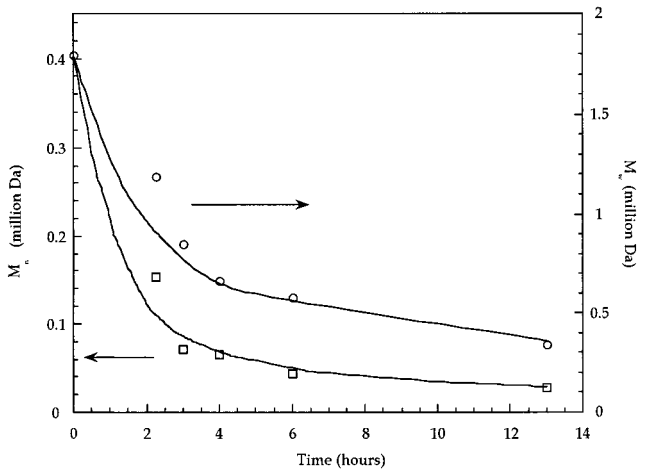

Figure 4. Number- (M_n) and weight-average (M_w) molecular weights of a guar solution (1% w/v) during enzymatic hydrolysis. An enzyme concentration of 0.83 units/mL of 1% guar solution was used.

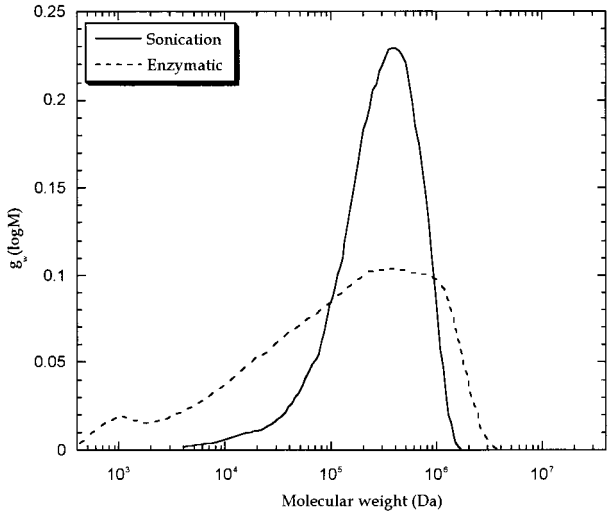

Figure 5. Comparison of representative molecular weight distributions of guar solutions (1% w/v) degraded to approximately the same molecular weight (M_w) using sonication (solid lines) and enzymatic hydrolysis (dashed line).

scission predicts the development of a bimodal distribution at short times thereby suggesting that both these modes of chain scission can be ruled out for sonication of guar. It is interesting to note that several previous studies have found chains to break preferentially near the center upon ultrasonication (polystyrene in toluene;[26] dextran in water[29]), resulting in bimodal molecular weight distributions. The fact that guar chains follow an almost random degradation suggests that the modes of chain scission may be strongly influenced by features specific to the polymer molecule under study.

Figure 4 shows changes in the molecular weight averages, M_w, and M_n, for enzymatic degradation of guar. Similar to the trends in ultrasonication, both averages show a rapid decrease at short times and slower reduction at longer times. An interesting difference is that while for sonication, the reduction in M_w was faster than that in M_n, the reverse trend is observed for enzymatic degradation (reduction in M_n faster than that in M_w). Figure 5 compares the molecular weight distribution of guar solutions degraded to approximately the same weight-average molecular weight by the two methods. The enzymatically degraded guar ($M_w = 0.4$ million, 13 h hydrolysis time) shows a much broader distribution of chain sizes than the sonicated guar ($M_w = 0.36$ million after 25 min of ultrasound radiation). The differences in the distributions can be quantified by comparing the polydispersity index ($\equiv M_w/M_n$) for the two methods of guar degradation and is illustrated in Figure 6. The polydispersity for enzymatically degraded guar increases rapidly with the degree of scission, S, defined as ($M_w(0)/M_w(t) - 1$) with values greater than 10 being observed after $S = 1$. This is in contrast with the sonication process where a narrowing of molecular weight distributions is observed, with polydispersity values close to 2 being observed after high degrees of chain scission. Thus, the differences in the mechanisms of degradation by sonication and enzymatic action produce profound differences in the size distributions of the guar molecules.

Figure 7 shows the evolution of molecular weight distributions for enzymatically hydrolyzed guar. In addition to a significant broadening, there is also a low molecular weight peak (MW $\sim$ 1000) that develops with increasing degradation time periods. Figure 8 compares the experimental observations with the model predictions. For the sake of clarity, predictions are shown only

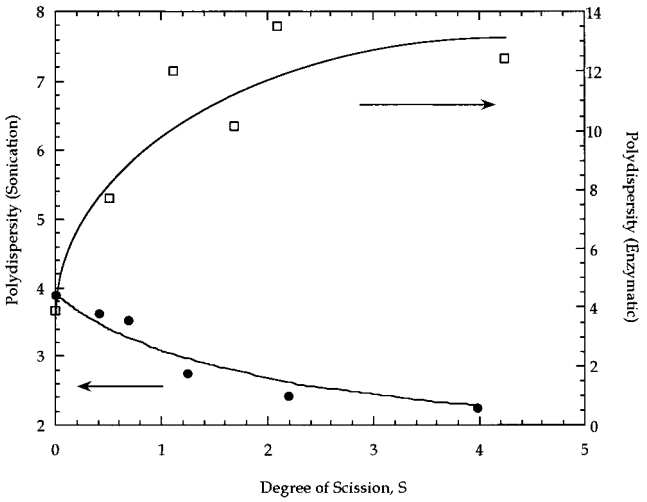

Figure 6. Changes in the polydispersity index (M_w/M_n) of guar solutions as a function of the degree of chain scission [$\{M_w(0)/M_w(t)\} - 1$] during enzymatic hydrolysis and sonication.

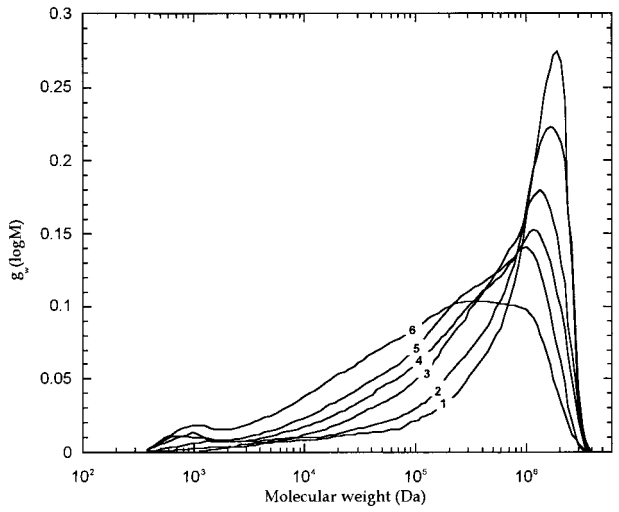

Figure 7. Evolution of the molecular weight distribution of guar solutions during enzymatic hydrolysis. Hydrolysis time in hours: 1(0), 2(2), 3(3), 4(4), 5(6), 6(13).

for one particular extent of degradation (6 h). Clearly, the model fails to account for either the broadening or the development of the low molecular weight peak for all three modes of scission considered, viz. random, Gaussian, and central. Since the model is based on a single scission pathway, it seems that enzymatic guar degradation may not be occurring by the single scission pathway. [The possibility that the enzyme is also acting as an "exo" enzyme (exo-β-mannosidase) and cleaving chain ends to produce the small molecular weight fractions can be ruled out. This is because the endo-β-mannanase enzyme used in this study exhibits zero (0.0000 U/mg of protein) specific activity toward a pNP-β-mannosidase substrate (that mimics the ends of a guar chain).] Thus, the possible degradation pathway is the multiple chain type, where the enzyme can effect several secondary cleavages on one of the fragments formed by the initial scission. A result of this pathway is the accumulation of significant amount of small oligosaccharides. The development of the low molecular weight peak observed in the experimentally measured distributions (Figure 7) with increasing degradation times may thus be indicative of the presence of a multiple attack pathway. In addition, the polydispersity

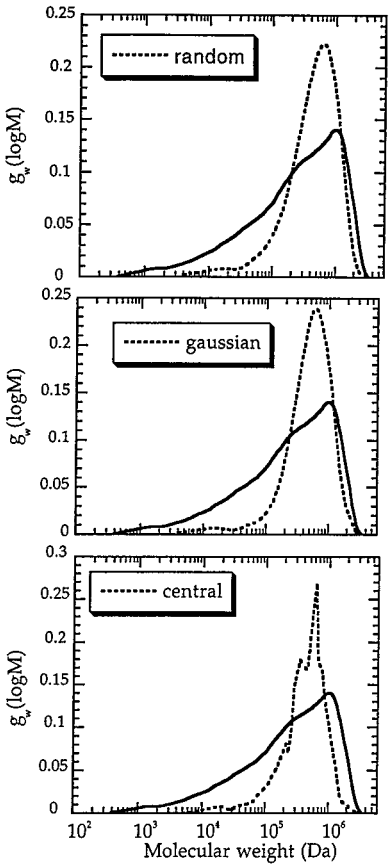

Figure 8. Comparison of measured and simulated molecular weight distributions of a guar solution following enzymatic hydrolysis for 6 h. Solid curves represent GPC measurements; broken curves correspond to various scission model predictions.

ratio should increase upon degradation since the small sugars formed reduce M_n but do not affect M_w. A mathematical analysis[30] has shown that the polydispersity should increase and reach an asymptotic limit at long degradation times. Indeed, this trend is observed for enzymatic guar degradation (Figure 6). Thus, there is evidence to suggest that the degradation may follow a multiple attack pathway. Ongoing work is focused on adapting the multiple scission pathway to predict the evolution of molecular weight distribution upon enzymatic degradation.

Finally, since guar is primarily utilized as a rheology modifier in most of its applications, it is of interest to examine the relationship between molecular structure and steady shear viscosity of guar solutions degraded by the two different methods. Figure 9 compares the zero shear viscosity, η_0, of guar solutions degraded by enzymatic and ultrasound action, as a function of the number-average molecular weight, M_n, and the weight-average molecular weight, M_w. For the same M_n, an enzymatically degraded guar solution displays a much higher viscosity than sonicated guar solution (Figure 9a). In contrast, when the zero-shear viscosity is plotted as a function of M_w, the viscosity-molecular weight relation for enzymatic degradation is very similar to that of sonicated guar (Figure 9b) even though there is a significant difference in the polydispersity ratios for the two sets of guar samples (>10 for enzymatic degradation; ~ 2 for ultrasonication). This seems to be in disagreement with the observation that polydisperse polymer systems show higher zero shear viscosity as compared to systems with narrower molecular weight

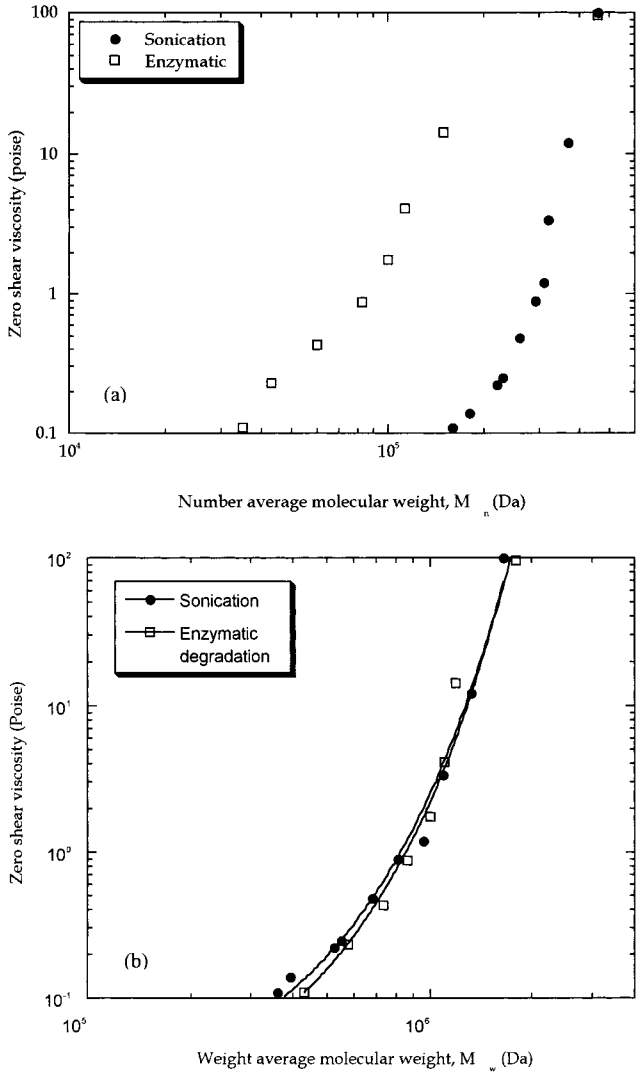

Figure 9. Zero shear viscosity of guar solutions degraded by sonication and enzymatic hydrolysis, plotted as a function of (a) number-average, M_n, and (b) weight-average, M_w, molecular weights.

distributions.[31] We suggest that the effects of polydispersity are largest when it increases from 1 to 2, and a further increase does not affect the zero shear viscosity significantly. So, in the range of interest, the zero shear viscosity of polydisperse guar solutions can be adequately described by the weight-average molecular weight, M_w.

5. Conclusions

Ultrasonic and enzymatic degradation behavior of guar galactomannan are compared through molecular weight measurements and computer simulation. Both degradation processes lead to a rapid decrease in molecular weight at short degradation times and a slower rate subsequently. However, the resulting molecular weight distributions are strikingly dissimilar. Ultrasonication of guar leads to a narrowing of the molecular weight distribution while enzymatic hydrolysis broadens the distribution significantly. The mechanistics of chain scission were investigated by modeling different modes of degradation. Random chain hydrolysis, with all bonds having an equal probability of being cleaved, predicted molecular weight distributions which compared well with those measured experimentally for sonicated guar. For enzymatic degradation, however, the distributions were not in accord with any of the different modes of chain scission tested, viz. random, Gaussian, or central. These results suggest that the single scission model is not applicable for enzymatic degradation of guar. The development of a low molecular weight peak and the rise in polydispersity to an asymptotic value suggest that multiple chain attack may be the operating pathway for enzymatic hydrolysis. Plots of zero shear viscosity, η_0, vs M_w, were very similar for the two systems despite the large differences in polydispersity. We infer that for polydisperse systems, the steady shear rheological properties are not very sensitive to the molecular weight distribution and can be adequately described by M_w.

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References and Notes

(1) Singh, M.; Roy, A. R.; Vasudevan, P. *Biomaterials* **1982**, *3*, 16.
(2) Tayal, A.; Kelly, R. M.; Khan, S. A. *Soc. Pet. Eng. J.* **1997**, *2* (2), 204.
(3) Rollings, J. *Carbohydr. Polym.* **1985**, *5*, 37.
(4) Kuhn, W. *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 1503.
(5) Simha, R. *J. Appl. Phys.* **1941**, *12*, 569.
(6) Basedow, A. M.; Ebert, K. H.; Ederer, H. J. *Macromolecules* **1978**, *11*, 774.
(7) Pytela, J.; Jakes, J.; Rypachek, F. *Int. J. Biol. Macromol.* **1994**, *16*, 15.
(8) Rypacek, F. *Polym. Degrad. Stab.* **1998**, *59*, 345−351.
(9) Tanigawa, M.; Suzuto, M.; Fukudome, K.; Yamaoka, K. *Macromolecules* **1996**, *29*, 7418.
(10) Nguyen, T. Q.; Kausch, H. H. *Int. J. Polym. Anal. Charact.* **1998**, *4*, 447.
(11) Painter, T. J.; Gonzalez, J. J.; Hemmer, P. C. *Carbohydr. Res.* **1979**, *69*, 217.
(12) McCleary, B.; Clark, A.; Dea, I.; Rees, D. *Carbohydr. Res.* **1985**, *139*, 237.
(13) Brant, D. A.; Ed. *Solution properties of polysaccharides*; ACS Symposium Series 150; American Chemical Society: Washington DC, 1981.
(14) Shay, G. D. In *Polymers in aqueous media: Performance through association*; Glass, J. E., Ed.; ACS Symposium Series 223; American Chemical Society: Washington, DC, 1989; Chapter 25, p 457.
(15) Tayal, A.; Kelly, R. M.; Khan, S. A. *Macromolecules* **1999**, *32*, 294.
(16) Tayal, A.; Pai, V. B.; Khan, S. A. *Macromolecules* **1999**, *32*, 5567.
(17) Doulah, M. S. *J. Appl. Polym. Sci.* **1978**, *22*, 1735.
(18) Tabata, M.; Sohma, J. *Chem. Phys. Lett.* **1980**, *73*, 178.
(19) Azhari, R.; Lotan, N. *J. Mater. Sci. Lett.* **1991**, *10*, 243.
(20) Vink, H. *Makromol. Chem.* **1963**, *67*, 105.
(21) Ziff, R. M.; McGrady, E. D. *J. Phys. A: Math. Gen.* **1985**, *18*, 3027.
(22) Tobita, H. *Macromolecules* **1996**, *29*, 3010.
(23) Nakatani, H. *Biopolymers* **1996**, *39*, 665.
(24) Emsley, A. M.; Heywood, R. J. *Polym. Degrad. Stab.* **1995**, *49*, 145.
(25) Sendra, J. M.; Carbonell, J. V. *Biotechnol. Bioeng.* **1998**, *57*, 387.
(26) Glynn, P. A. R.; van der Hoff B. M. E. *J. Macromol. Sci.—Chem.* **1973**, *A7*, 1695.
(27) Ballauff, M.; Wolf, B. A. *Macromolecules* **1981**, *14*, 654.
(28) Whitcomb, P. J.; Gutowski, J.; Howland, W. W. *J. Appl. Polym. Sci.* **1980**, *25*, 2815.
(29) Basedow, A. M.; Ebert K. H. *Makromol. Chem.* **1975**, *176*, 745.
(30) Banks, W.; Greenwood C. T. *Carbohydr. Res.* **1977**, *57*, 301.
(31) Ferry, J. D. *Viscoelastic properties of polymers*, 3rd ed.; Wiley: New York, 1980.

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