Galactomannans are neutral polysaccharides that occur in substantial amounts in the endosperm of the seeds of some leguminous plants. Structurally they consist of a β-(1→4)-D-mannose backbone to which galactose units are attached α-(1→6). Of the number of galactomannans known, guar gum, locust bean gum (LBG), and tara gum are the most used in applications in, for example, the food, pharmaceutical, and chemical industries as thickening agents or stabilizers due mainly to the high viscosity they give at low w/w concentrations. The different galactomannans can be distinguished by their mannose-to-galactose ratio, the substitution pattern of side-chain units, and their molecular weight, the latter of which is greatly influenced by harvesting, manufacturing practices, and other factors.

While guar gum commonly has a mannose-to-galactose ratio (M/G) of ~ 2 and is usually found to have a Markov-chainlike distribution of the side-chain substituents, LBG typically has a M/G ratio of ~4 and both random, blockwise, and ordered galactose distributions are present as reported in the recent work by Duas et al. Tara gum has a M/G ratio of ~3, bridging the gap between the cold water soluble, highly galactose substituted guar and the cold water less soluble, lower substituted LBG. Here both random and blockwise distributions have been reported. In solution, tara gum shows many similar characteristics to guar and LBG. Like guar, tara gum is indeed cold water “soluble” and appears to attain a maximum viscosity in water within a few minutes. Similarly to LBG, tara gum acts in a manner described as “synergistically” with κ-carrageenan, agar, and xanthan to increase so-called gel strength and make such gels less prone to syneresis.

As we know, both the M/G ratio and the distribution pattern of the galactose units along the chain backbone are important molecular features as they affect the functional properties of the different galactomannans. Especially, as far as water solubility is concerned, the lower the degree of substitution of the galactomannan, the more difficult it is to form true (so-called molecular) solutions (i.e., when the material is fully dissolved at molecular levels). For example, LBG and tara gum tend to form aggregates in solution even more easily than does guar. This is because in low-substituted galactomannans there are long segments of unsubstituted mannans. One explanation for this is that galactose side chains promote solubility because they introduce an entropic (and perhaps steric) barrier to ordered packing of mannan chains. However, since the hydrophobic effect is itself entropic, we can regard the mannan chains to be relatively hydrophobic and the galactose units as more hydrophilic. Hence these long segments of unsubstituted mannans are deemed to be more susceptible to aggregation with other similar segments in solution.

This is not to say it is simple to prepare molecular solutions of guar. Indeed, in the first paper in this series we applied...
the technique of “pressure cell solubilization”\(^7\) using appropriate temperature, time, and pressure regimes to solutions of guar gums in order to reduce time-dependent aggregation phenomena and to achieve satisfactory dissolution at the molecular level. We found that when pressure was applied at various fixed temperatures, the intrinsic viscosity \([\eta]\) data were practically unchanged, whereas \(M_w\) data were reduced over a factor of \(~3\), showing that no degradation had occurred. This behavior was attributed to disaggregation since only \(M_w\) values were reduced. Indeed, \([\eta]\) is not very sensitive to the presence of aggregates as they are usually small in numbers and are usually compact (pseudospherical), but \(M_w\), on the contrary, is strongly affected by their presence as their size contributes largely to the light scattering intensity. A reduction in aggregates would reduce \(M_w\) without necessarily changing \([\eta]\). Besides, the light scattering data obtained were nicely reproducible and considered as reliable. By increase of the treatment temperature, under no added pressure, degradation was the behavior identified, as both \(M_w\) and \([\eta]\) were reduced significantly. This “pressure cell solubilization method” was previously applied with success on starch polysaccharides\(^7\)–\(^9\) and on a xylomucan, detarium gum.\(^10\) These previously published studies have established that the method does work, and it was proved to be very valuable in the study of guar solutions, enabling us to draw definitive conclusions on the flexibility of the guar chain backbone.\(^6\)

The same approach is used in the present investigation into two less highly substituted galactomannans (tara gum and locust bean gum) in order to obtain, together with the results of the guar study, a more general knowledge on the flexibility of galactomannan chains. The aim of the paper is to show that by using the pressure cell method, reliable light scattering data can be obtained for galactomannans. Incidentally, we found in the first paper in this series\(^6\) that the method can be used both to solubilize and to degrade the chains and that these relative contributions can be “tuned”, enabling the preparation of a number of \(M_w\) samples from a single batch of starting polymer. Physical characterization of these two galactomannans is carried out using the technique of intrinsic viscosity determination by capillary viscometry and the technique of light scattering, using both size exclusion chromatography coupled to multiangle laser light scattering (SEC-MALLS) and a more conventional, but state of the art, static and dynamic light scattering goniometer. Finally we note, because of the problems of producing molecular solutions of galactose-depleted galactomannans, there are very few reports of, for example, Mark–Houwink parameters for these systems.\(^11\) In fact it has become almost standard procedure to use the corresponding values for guar, such as those due to Robinson and co-workers, instead.\(^12\)

One aim of the present work is to establish whether this hypothesis is justified.

**Experimental Section**

**Materials.** Purified samples from commercial grade locust bean gum flour M175 supplied by Meyhall Chemicals, A.G., Kreuzlingen, Switzerland—Rhodia Group, were used in all LBG experiments. The samples were purified from the flour using an isolation procedure devised by Girhammar and Nair\(^3\) and modified by Rayment et al.\(^4\) to allow complete hydration of the gum. The moisture content of the extracted polymer was determined by incubation overnight in an oven at 103 °C to a constant weight. Freeze-drying was carried out using an Ehrist ALPHA I-5 Freeze-dryer (DAMON/IEC (UK) Ltd.), and samples were stored in a desiccatior until used. Tara gum was provided by Magenta Sales Limited, Goostrey, Cheshire, U.K., and was purified in the same way as for LBG.

**Methods.** Solutions of LBG and tara gum were prepared at 0.05 wt % by adding known weights of the freeze-dried samples to deionized water at 50 °C, containing 0.02% sodium azide as bactericide. The temperature was raised to 80 °C as dry powder was added with stirring. The heating was stopped as soon as 80 °C was reached, and the solutions were left covered overnight, with stirring, at room temperature to allow further hydration to occur.\(^15\) The solution at this stage was used as a reference material (“untreated sample”). Thirty milliliters of this solution was then added to the reaction chamber of a pressure/heating cell (HEL Ltd., Barnet, Herts, U.K.). These solutions were then subjected, under stirring, to a range of temperature and pressure conditions between 70 and 160 °C and 0–4 bar added pressure. Added pressure was applied using nitrogen gas while the reaction chamber was at a temperature of 50 °C. These conditions were applied for a range of times from 10 to 30 min. The general protocol is described in more detail in ref 6.

The treated solutions were then analyzed in various ways:

1. **Capillary Viscometry.** The intrinsic viscosity \([\eta]\) was determined using the viscosity measuring unit AVS 350 (Schott-Gerate, Hofheim, Germany), connected to a Visco-Doser AVS 20 piston buret (for automatic dilutions), to make automated measurements of the flow-through times in a capillary viscometer (Ubbelhode viscometer for dilution sequences). The viscometer was immersed in a precision water bath (transparent thermostat CT 1650, Schott-Gerate, Hofheim, Germany) to maintain the temperature at 25 ± 0.1 °C. Results were analyzed using separate Huggins and Kramer extrapolations (linear regression, 99% confidence intervals), and the final result quoted in dL/g (1 dL/g = 100 mL/g = 0.1 m³/kg).

2. **Size Exclusion Chromatography Coupled to Multiangle Laser Light Scattering (SEC-MALLS).** The size exclusion chromatography system used consisted of a Jasco HPLC pump, a guard column, and TSK G5000 and G4000 columns. An on-line degasser was used to remove gas from the eluent. A flow rate of 0.8 mL/min for the mobile phase was used at room temperature. A DAWN-DSP multiangle laser light scattering detector and an Optilab 903 refractometer (Wyatt Technologies, Santa Barbara, CA) were used for light scattering intensity and concentration detection, respectively. The mobile phase was 0.02 wt % sodium azide in distilled deionized water. One hundred microliter samples of the guar solutions were injected into the size exclusion system after filtering through 0.45 μm filters (Whatman Ltd., Maidstone, England). Repeat injections were made for each
sample. Data were captured and analyzed using the software package ASTRA (v. 4.20). Data returned are the number, weight, and z-averages for molecular weight and root-mean-square radius of gyration.

3. Static and Dynamic Light Scattering. These measurements were performed simultaneously, i.e., both in static and dynamic mode on the same photons, at 20 °C with a fully computerized ALV-5000 System comprising a compact goniometer system and a multi-τ real-time digital correlator (ALV—Laser Vertriebsgesellschaft m.b.H. Langen, Germany). The angular range applied was from 30° to 150° in steps of 10°; the duration of single measurements was typically 10 s averaged over a minimum number of three runs until a statistically significant result is obtained (ALV—Static & Dynamic Fit and Plot Program used). A He—Ne laser (λ0 = 632.8 nm) was the light source, and the scattering of toluene was used as the primary standard. The refractive index increment, dn/dc, was chosen as 0.146 mL·g⁻¹.¹⁶

Solutions used for light scattering were solutions of 0.05% (w/v) polymer (prepared as described previously and treated in the pressure cell appropriately) and serial dilutions (0.04%, 0.02%, 0.01%). These solutions were filtered three times directly into the cylindrical light scattering cuvettes (Pyrex disposable culture tubes, Corning Inc., Corning, NY) (total volume ~3 mL) using Acrodisc PF 0.8/0.2 µm syringe filters (Gelman Laboratory, Michigan, USA). All solution preparation stages were carried out in a laminar airflow cabinet to minimize contamination with dust.

Results and Discussion

Intrinsic Viscosity [η]. Samples of purified LBG and tara gum were treated in the pressure cell under different heating, time, and pressure regimes as described in Table 1. The intrinsic viscosity [η] was then determined at 25 °C for nine samples (including the “untreated” sample) of each polymer at polysaccharide concentrations ranging from 0.01 to 0.05% (w/v) so that the viscosity relative to that of the solvent (water) lies in the range 1.2 < ηi < 2.0. All data are shown in Table 1. Figures representing intrinsic viscosity plots are not illustrated here for LBG and tara gum as similar observations with guar gum in our preceding paper⁶ were made. Indeed, compared to guar under the same conditions, an increase in the treatment temperature from 70 to 160 °C, under no external pressure, and during a 10 min period of time reduces the intrinsic viscosity significantly. Samples treated at or below 100 °C, with or without added pressure, did not show any real variation in [η] values, suggesting polymer chains are stable under these conditions and not subject to depolymerization. If external pressure (i.e., 4 bar nitrogen in our experiments) is added to the reactor chamber to samples treated at any temperature above 100 °C under various time periods, the intrinsic viscosity data then determined are higher than the ones obtained under no added pressure, for the same time and temperature conditions. The pressure seems to be protecting the chains from some of the degradation effects. We do not extend here the discussion further, as this aspect has already been covered in our first paper of the series on guar gum. Suffice to say that a temperature of ~100 °C held during 10 min and an external pressure of ~4 bar served to produce samples with essentially unchanged values of [η]; guar systems were stable under the same conditions but under higher temperatures, and values of [η] did not fall as quickly as with LBG. This seems to show that guar is more resistant than LBG to heat-induced chain degradation and that perhaps the higher proportion of galactose side arms serve to protect the mannan backbone from cleavage. In this respect, tara gum samples seemed to behave more like LBG than guar.

Light Scattering. The technique of SEC-MALLS was used to determine Mw (weight-average molecular weight) and Rg (z-average root-mean-square radius of gyration) on samples of LBG. Results obtained are shown in Table 1. Similar to guar gum⁶ the Mw and Rg values for LBG followed the same pattern of observations in relation to the pressure cell treatments applied. When using SEC-MALLS for the guar samples, lower than physical exponents of Rg versus Mw (~0.4) were obtained in some of the present measurements of individual fractions. Because of this, we have less faith in the elements making up the Mw distribution than in its overall moments. Having data for Mw and [η] enabled us to plot the results for LBG in the form of a so-called Mark—Houwink—Sakurada (MHS) plot of log [η] vs log Mw, illustrated in Figure 1. The behavior observed for the MHS plot on guar gum⁶ showed that before degradation of the polymer there was a small initial horizontal region where no obvious reduction in [η] was seen but with a decrease in Mw over a factor of ~3. This does not seem to be as pronounced here for LBG, supporting the conclusion from [η] that LBG is even more susceptible to heat-induced chain degradation. Few studies on the relative sensitivity of galactomannans other than guar have appeared in the literature. However, the Mark—Houwink—Sakurada exponent obtained from the slope for the double logarithmic plot of intrinsic viscosity against Mw is found here to be 0.77 ±
0.09 for LBG. In this case the mean value is still within the range 0.5–0.8 found in the literature for a polymer chain in the so-called flexible coil conformation with excluded volume. This conformation is further supported by Figure 2, which represents the double log plot of $R_g$ against $M_w$. The Flory exponent (slope of the plot) obtained is $0.57 \pm 0.05$, which lies in the required range 0.5–0.6.

For the characterization of the tara gum samples, the technique of SEC-MALLS was not used but a goniometer based light scattering system, recently acquired, was employed instead. This was an ALV/DLS/SLS-5000 compact goniometer system designed to perform dynamic and static light scattering data simultaneously. The samples of tara gum solutions were treated under exactly the same conditions as for the LBG samples in order to get not only a physical characterization but also some elements of comparison between the two galactomannans. The relevant parameters $M_w$ and $R_g$, from the light-scattering static mode were obtained from the appropriate plots by extrapolation of the experimental data to $c = 0$ and $q^2 = 0$ using fitted polynomials. This extrapolation procedure is the basis of the classical “Zimm plot” method, illustrated here as an example in Figure 3, in this case for samples of tara gum treated in the pressure cell at 130 °C during 10 min under 4 bar added nitrogen.

Of course, this extrapolation needs to be made with care because of the problems, especially significant for water-soluble polymers, we detailed in part 1. First, the concentration dependence of scattered-light intensity does not always show linearity and the slope of this line (Figure 3) could be so high, in some cases, that it is very difficult to determine the intercept on the $K_c/R_i$ with certainty. Second, water-soluble polysaccharides, as mentioned earlier, tend to aggregate in solution and to obtain complete molecular dispersion is rather difficult. Even a tiny amount of supermolecular particles present among the individual macromolecules can distort the angular dependence of scattered light, producing a pronounced downturn in the data and leading to an overestimation for $M_w$.

In the present work, this second consideration is probably not so much an issue as we feel that the careful preparation of the samples and the pressure cell treatments applied to them under various temperature/time/pressure regimes do reduce, if not eliminate, aggregations and true molecular solutions should be obtained. As observed in Figure 3, the characteristic downturn in the data seen for incompletely dispersed solutions is not present. Further the data do not show much angular dependence which suggests the radius of gyration is significantly smaller than the incident wavelength, $\lambda_0$. All Zimm plots constructed for the nine samples of tara gum gave values of $M_w$ and $R_g$ (shown in Table 1) which were reproducible (duplicates). As with the LBG data, a MHS plot was constructed with the tara gum data (Figure 4) and the MHS exponent obtained (0.79 ± 0.12) is approximately within the bounds of the Mark–Houwink equation for linear flexible macromolecules.

Of course, with more points (nine here both for LBG and tara samples), a more reliable estimate of the MHS exponents could be possible. However, the values obtained for both

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**Figure 1.** Mark–Houwink–Sakurada plot ($\log [\eta]$ vs $\log M_w$) for LBG samples treated under various temperature, time, and pressure conditions. The $\alpha$ parameter is $0.77 \pm 0.09$. Dotted lines indicate 99% confidence intervals.

**Figure 2.** Values of $R_g$ plotted as a function of the molecular weight for the LBG data. The Flory exponent is $0.57 \pm 0.05$. Dotted lines indicate 99% confidence intervals.

**Figure 3.** Zimm plot (constructed with ALV/Static & Dynamic Fit and Plot Program) for tara gum treated at 130 °C during 10 min under 4 bar N$_2$. The $R_g$ parameter is $0.77 \pm 0.09$. Dotted lines indicate 99% confidence intervals.
having a most probable (Flory) theoretical MHS exponents are for monodisperse systems, and the polydispersity of the samples used has therefore some effect on the value of these exponents. The $M_w/M_n$ polydispersity obtained from the $M_w$ distributions for the nine LBG samples lay mainly in the range $1.3-3.0$ and was $\sim 2$ for the nine tara gum samples, which means both are close to having a most probable (Flory) $M_w$ distribution.

Figure 6 gives an example of the light scattering data, for a tara gum sample treated at $130 ^\circ C$ for 10 min under 4 bar nitrogen (corresponding Zimm plot shown in Figure 3), plotted together using the so-called Kratky plot of $u^2P(u)$ vs $u$. Here $u = qR_g$, $P(u) = R_d/R_{0=0}$ is the so-called particle scattering factor, which reflects the angular dependence of the scattered light, and $q$ is the scattering vector ($=4\pi\lambda/\sin(\theta/2)$). The different curves reflect fits to different models for the chain behavior, calculated as described in ref 18. The dimensionless parameter, $u$, measures the intramolecular probe distance relative to the incident light wavelength, and $P(u)$ can be calculated for different chain architectures. Figure 6 shows that the data obtained are very close to the linear coil model with a polydispersity of 2 (most probable or Flory distribution). Although this method of plotting is not usually that sensitive to polydispersity, it seems clear that this model fits better than that for a monodisperse distribution and that despite, the comparatively small range of wave vector (red laser light), we can also rule out the rod model. Overall this confirms the results above for the chain conformation of tara gum, with a most probable $M_w$ distribution. Kratky plots obtained for the remaining eight tara gum samples showed similar behavior.

The values of the Mark–Houwink parameters $\alpha$ and $K'$ reported in the literature for guar gums differ markedly. The very widely employed and accepted Robinson et al. $^{19}$ values of $\alpha = 0.72$ and $K' = 3.8 \times 10^{-4}$ (g/dL) are very close to the ones found by Beer and co-workers $^{20}$ ($K' = 5.13 \times 10^{-4}$ and $\alpha = 0.72$). Sharman and co-workers $^{21}$ found $\alpha = 0.8$ but with a significantly higher $K'$ and Picout et al. $^{6}$ obtained $\alpha = 0.70$ with $K' = 6 \times 10^{-4}$ (g/dL). In all these studies the polydispersity of the samples used was lower than 3 but the commercial guar samples used by Doublier and Launay $^{22}$ were highly polydisperse ($M_w/M_n > 10$) and they reported $\alpha = 0.98$ and $K' = 7.76 \times 10^{-4}$ for the Mark–Houwink parameters. Wientjes and co-workers $^{23}$ recently reported similar Mark–Houwink constants of $\alpha = 1.05$ and $K' = 6.7 \times 10^{-4}$ (L/g), although it appears to us they neglected important aspects of the solubilization process. The polydispersity and the treatment have an important influence on the value of these parameters.
In all three models there was a significant effect of log $M$ Stockmayer, and Fixman (BSF plot) in which significant differences between the intercepts ($p < 0.0005$). The value obtained for the MHS coefficient of all galactomannans combined was found to be 0.74 ± 0.01. However, from the results of galactose substitution on the mannan backbone does not seem to have a noticeable effect on the chain flexibility. To obtain a more general picture of the galactomannan chain flexibility, all data were plotted together as a MHS plot, which is shown in Figure 7. The MHS exponent was found to be $\alpha = 0.74 ± 0.01$, which is well within the boundaries of the 0.5–0.8 range for linear flexible chains. A BSF plot was also constructed (figure not shown) and an overall analysis of covariance for all data was carried out. From this analysis, significant differences were found both in the slopes and in the intercepts of the series of all data allowing no accurate calculation of the characteristic ratio and the persistence length to be obtained. However, from the results of the individual polymers, a good estimation of the characteristic ratio $9 < C_{\infty} < 16$ and the persistence length $3 < L_p < 5$ nm for galactomannan chains can be made. Although small persistence lengths are obtained, a question

### Data Analysis of Covariance

In our first paper of the series, the guar data obtained, the data from Robinson et al. and Beer et al. were all considered as one population of data. A simple regression analysis was carried out for the MHS plot ($\log [\eta]$ versus log $M_w$) giving an overall MHS coefficient of 0.70 ± 0.03. This obviously implies both slopes and intercepts of the individual sets are identical. The guar data have now been revisited, and an analysis of covariance was carried out by fitting multiple lines to the three sets of data to see if, indeed, the three series could be regarded as one population or as three different populations. This more rigorous analysis was performed using Minitab statistical software release 13.1 (Minitab Inc., Pennsylvania, USA). We found no significant differences in slopes and intercepts of the individual sets are identical. The guar gum data have been devised in order to determine the chain characteristics ratios $C_{\infty}$ and chain persistence lengths $L_p$.

<table>
<thead>
<tr>
<th>samples</th>
<th>residue $m_{g\cdot mol^{-1}}$</th>
<th>MKS exponent</th>
<th>Flory exponent</th>
<th>Burchard–Stockmayer–Fixman (BSF method)</th>
<th>Hearst method</th>
</tr>
</thead>
<tbody>
<tr>
<td>guar gum</td>
<td>267</td>
<td>0.73 ± 0.01 (SE)</td>
<td>/</td>
<td>$12.2 ± 0.8$ (SE)</td>
<td>$30 ± 1$ (SE)</td>
</tr>
<tr>
<td>tara gum</td>
<td>237</td>
<td>0.79 ± 0.12 (SE)</td>
<td>0.61 ± 0.16 (SE)</td>
<td>$12.6 ± 3$ (SE)</td>
<td>$30 ± 14$ (SE)</td>
</tr>
<tr>
<td>LBG</td>
<td>223</td>
<td>0.77 ± 0.09 (SE)</td>
<td>0.57 ± 0.05 (SE)</td>
<td>$11.8 ± 3$ (SE)</td>
<td>$33 ± 11$ (SE)</td>
</tr>
<tr>
<td>all 3 galactomannans</td>
<td></td>
<td>0.74 ± 0.01 (SE)</td>
<td>/</td>
<td>$9–16$</td>
<td>$16–44$</td>
</tr>
</tbody>
</table>

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*Guar data from Beer et al., Robinson et al., and Picout et al. All data from guar gum, tara gum, and LBG combined.*

### Evaluation of Intrinsic Chain Flexibility of Galactomannans

As discussed in our earlier paper, few methods have been devised in order to determine the chain characteristic ratio, $C_{\infty}$, and the persistence length, $L_p$, of flexible polymers. The usual plot used is that due to Burchard, Stockmayer, and Fixman (BSF plot) plotted against $M_w$. This BSF method was applied to the LBG and tara gum data (figures not shown). From these plots, the intercept $K_0$ (which corresponds to the chain in the theta state, where there is no excluded volume) was obtained, and from the MHS equation and the Flory–Fox equation, $C_{\infty}$ and then $L_p$ were calculated for both polymers. These parameters are summarized in Table 2 for the present LBG and tara gum data as well as for the guar gum data (including the data from Robinson et al. and Beer et al.) of our preceding paper. We note that from the analysis of covariance carried out on the guar gum data for the BSF plot, the characteristic ratio newly calculated is $C_{\infty} = 12.2 ± 0.8$ and the persistence length, $L_p = 3.3 ± 0.2$ nm. The values of $C_{\infty}$ and $L_p$ of the three galactomannans (guar, LBG, and tara gum) were found to be very similar showing that the degree of galactose substitution on the mannan backbone does not seem to have a noticeable effect on the chain flexibility. To obtain a more general picture of the galactomannan chain flexibility, all data were plotted together as a MHS plot, which is shown in Figure 7. The MHS exponent was found to be $\alpha = 0.74 ± 0.01$, which is well within the boundaries of the 0.5–0.8 range for linear flexible chains. A BSF plot was also constructed (figure not shown) and an overall analysis of covariance for all data was carried out. From this analysis, significant differences were found both in the slopes and in the intercepts of the series of all data allowing no accurate calculation of the characteristic ratio and the persistence length to be obtained. However, from the results of the individual polymers, a good estimation of the characteristic ratio $9 < C_{\infty} < 16$ and the persistence length $3 < L_p < 5$ nm for galactomannan chains can be made. Although small persistence lengths are obtained, a question
that arises is what if the molecular chain has large (true) persistence lengths and, in fact, involves stable intramolecular aggregation? How do we know if it is molecularly solubilized in such a case? Such a model would surely have the “shape” of an intramolecularly linked chain, which would have a different (more branched-like) chain profile. The angular dependence, shown as a Kratky plot (Figure 6), does not suggest it. There is, of course, compensation between chain stiffness and branching in the Kratky representation, but the values of the exponents encourage us to accept the simpler and more usual depiction.

A number of other plots have been proposed for hydrodynamically semiflexible polymers such as the so-called Hearst plot\(^{25}\) where \(M_w/\eta\) is plotted against \((M_w)^{1/2}\), and the characteristic ratio and the statistical segment length are extracted from the slope. The values for the above parameters, calculated from the Hearst method and analyzed with the analysis of covariance for each polymer and for all three galactomannans combined, are also shown in Table 2 for comparison. This method, sometimes used for semiflexible polymers, is in fact more appropriate for stiff polymers.

**Conclusion**

True molecular solubilization of LBG and tara gum in aqueous solution has been achieved using the pressure cell method under appropriate temperature/pressure regimes. Characterization of these two polymers by light-scattering techniques and capillary viscometry generated data, which together with our own data on guar gum\(^{6}\) and data from other authors (Robinson and co-workers,\(^ {19}\) Beer et al.\(^ {20}\)) enabled us to determine a range of values 9–16 for the characteristic ratio, \(C_w\), and 3–5 nm for the persistence length, \(L_p\), of all the different architecture galactomannan chains. On the basis of our data, and a statistical analysis thereof, the degree of galactose substitution does not have much, if any, effect on these parameters. It can be noted that typical values for the persistence length of cellulose and derivatives are between 3 and 6 nm. The \(L_p\) values for galactomannan chains lie well within this range. This seems to be attributed to their in common feature of having a \(\beta-(1-4)\)-linked O-glycosidic polymeric backbone. As we pointed out in part 1 of this series, significantly larger values have been obtained for \(\beta-(1-4)\) backboned celluloloxis chains, when polyelectrolyte chain parameters are extrapolated to “infinite” ionic strength. We believe this discrepancy is a real one but that the values obtained here, on the basis of chain geometry alone, appear to us to be both the most realistic and the most useful. As we stated previously, there are very few reliable such data for non-guar galactomannans, so the results obtained here are of general interest.

The apparent insensitivity of the persistence length \(L_p\) to substitution is slightly surprising but not inconsistent with data for differently substituted cellulose chains. The further modeling of such behavior is to be encouraged. What we can clearly conclude is that the strategy of using the MHS parameters for guar to obtained estimates of \(M_w\) for other galactomannans, originally adopted by McCleary and co-workers,\(^ {12}\) appears to be reasonable. Following his example, much work has been performed on the \(\beta\)-galactosidase treated guar samples, to produce “synthetic” LBGs.\(^ {26}\) This work suggests that examination of samples of LBG and tara which have had the backbone enzymatically cleaved would also be a fruitful exercise.

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