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Note

On the chain flexibility of arabinoxylans and other β-(1→4) polysaccharides

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Abstract

The recent paper by Dervilly-Pinel and co-workers (*Carbohydr*. *Res*. **2001**, *330*, 365–372) presents a complete macromolecular characterisation of a series of de-esterified arabinoxylans extracted and fractionated from wheat flour. From their measurements, they were able to extract parameters related to chain flexibility, such as the Mark–Houwink exponent a and the chain persistence length. However, the estimate they obtain for the latter parameter is rather larger than would be expected, since the arabinoxylan backbone is β-(1→4) like cellulose and the galactomannans. By treating their data in an alternative, but well accepted manner, we are able to obtain a lower value of persistence length, which agrees well with estimates for this parameter for cellulose, in the literature, and our own recent measurements for a series of differently substituted galactomannans. These results suggest that the parameters obtained may be applicable to other β-(1→4) polysaccharides. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Arabinoxylan conformation; Macromolecular characterisation; Chain flexibility; Persistence length; Characteristic ratio; Galactomannans; Mark–Houwink relationship

The recent paper by Dervilly-Pinel and co-workers[1] presents a complete characterisation of a series of de-esterified arabinoxylans extracted and fractionated from wheat flour. From this they were able to extract parameters related to chain flexibility, such as the Mark–Houwink exponent a and the chain persistence length, in their notation, q (or in our notation L_p). In this they employ models familiar to workers in polymer solution characterisation.[2,3]

In the present note we re-analyse this same data using similar models, and come to slightly different conclusions from these authors. Moreover, what we are able to demonstrate by re-examining the Dervilly-Pinel data, and some recently published results of our own for a series of galactomannans, including guar,[4,5] is that the conformational behaviour of these arabinoxylans is, in fact, remarkably similar to that of the galactomannans. To many, including we suspect, these authors, this is not entirely surprising, since the geometry of the β-(1→4) polysaccharides, including cellulose, galactomannans, and the presently discussed system with a xylan backbone is known to be quite similar. However, it appears from our comparison that the similarity may be even closer than previously suggested. This allows almost universal behaviour, with consequently applicable molecular parameters, for such backbone chains to be established. It is important to point out that not all authors anticipate this. Indeed as Dervilly-Pinel and co-workers themselves point out, the high viscosity behaviour of certain arabinoxylans has been attributed by some to the presence of an extended rod-like conformation.[6] By contrast, as we describe in more detail below, we find chain persistence lengths of ~3–5 nm for all of the above backbone chains. We note that by some criteria this range of values would be regarded as semi-flexible, while to others it is relatively stiff. What is more significant however, is the number of persistence lengths (or statistical segment, Kuhn lengths) within the chain. When this becomes more than ~10 it is usually assumed that such a chain can be regarded as Gaussian. For the chains in question, this corresponds to (weight

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average) molecular weights of $> \sim 3 \times 10^4$. Since almost all commercial samples of such polysaccharides (and all the arabinoxylan samples discussed here) are significantly greater than this, they certainly behave as macroscopic coils, albeit that long range (excluded volume) interactions may perturb the dimensions from those of the paradigm 'random coil'.[2]

Mark–Houwink plot

Fig. 1 represents the data of Dervilly-Pinel and co-workers[1] for their 48 arabinoxylan fractions together with our own, and others collected data, for guar galactomannan plotted as a so-called Mark–Houwink (MH) plot.[4] In this double logarithmic plot the intrinsic viscosity $[\eta]$ is plotted versus the sample molecular weight (or more strictly, the unitless relative molecular mass). We note here that Dervilly-Pinel and co-workers prefer to plot solely against the backbone weight average M_w to eliminate perceived problems with the samples having different amounts of arabinose substitution. Their own results give a slope, *a*, of ~ 0.74. We remind readers that this is well within the range 0.5–0.8 for random coil parameters, and being towards the upper of this range, would suggest the presence of excluded volume interactions. Our recent analysis of a range of guar samples, including samples measured by ourselves, and previously published in the literature, is plotted on the same axes. We have also shown using analysis of variance, that the slopes for all these samples are statistically the same,[5] and that the 'best' value of the slope for these samples is 0.73 ± 0.01. This is, of course, effectively the same as found by Dervilly-Pinel and co-workers for the arabinoxylan samples reported above.

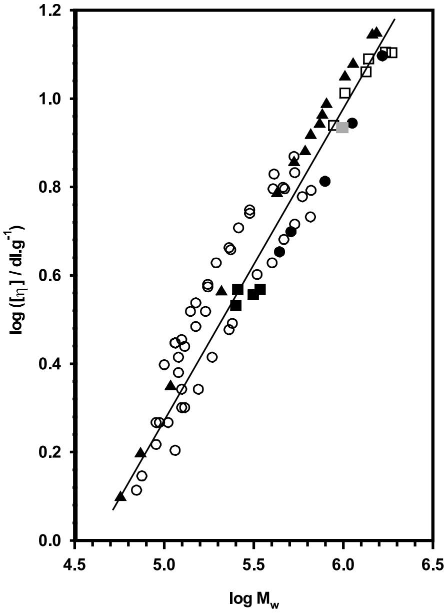

Fig. 1. Mark–Houwink plot for arabinoxylan (open circles) and guar galactomannan samples (other symbols representing various data from Picout et al. 2001).

More significantly, however, the overall MH behaviour including the K' parameter:[3,7]

$$\eta = K' M_w{}^a$$

which determine the absolute values of $[\eta]$ at any M_w is also, to all intents and purposes, the same. This appears very likely from an examination of Fig. 1, but is made clear by analysis of variance of the exponents and intercepts. Here the solid regression line is the overall slope of the regression fit, 0.706 ± 0.024 (S.E. = standard error) ($p < 10^{-3}$, degrees of freedom 77), i.e., slightly lower than the individual values, but well within statistical error limits and the overall intercept is -3.26 ± 0.14 S.E. ($p < 10^{-3}$). We note here that the slight difference in slope from that for the individual data sets is a (statistical) consequence of constraining the two curves to have the same intercept.[4]

What then has this to say about the chain flexibility? Local chain flexibility is largely (but not entirely) represented by the pre-exponential K' factor. Our own estimate of the overall persistence length of the guar samples, which closely follows initial work by one of the present authors,[8] is 3.3 ± 0.2 (S.E.) nm. This value corresponds to many of the best values for cellulose in appropriate solvents, such as that published in the early, but excellent, data of Brown and Henley and others.[9–13] This differs somewhat from that given by Dervilly-Pinel and co-workers, who find $L_p \sim 6–8$ nm.

In fact there is no doubt that all published values of L_p have to be examined carefully because of the model dependence. For example, as we noted earlier,[4] values for polyelectrolyte chains extrapolated from say the Skolnick–Fixman–Odijk model[14,15] appear significantly larger than those obtained either by the Burchard–Stockmayer–Fixman (BSF) method we employ, or simple application of geometric formulae, as used by Dervilly-Pinel and co-workers. The method of Dervilly-Pinel and co-workers assumes that the chains are in the no excluded volume limit. Overall, we feel that the latter method is inappropriate in the present case, since the Mark–Houwink slope reported is > 0.5, the Flory value, and closer to the excluded volume limit of 0.8.

We note nonetheless that there that there is a minor contradiction in this result, since the Flory mean square radius exponent (0.5 for Gaussian chains, 0.6 for excluded volume chains) is at 0.47, too low for linear polymer chains. Our own values for the guar samples is ~ 0.55. As has been noted before, lower than probable slope values are sometimes reported using the SEC-MALLS technique, and this is the most likely explanation of this minor discrepancy.

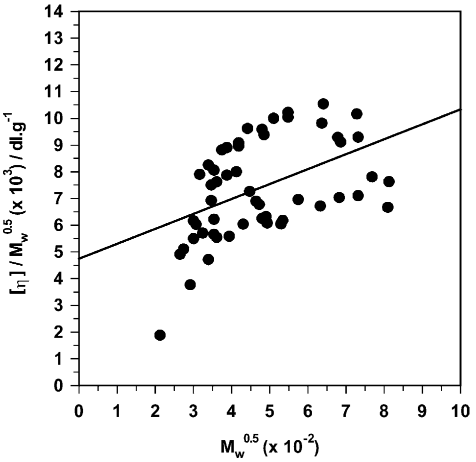

Fig. 2. Burchard–Stockmayer–Fixman plot for arabinoxylan samples. The intercept on the $[\eta]/M_w^{1/2}$ axis gives the value of K_θ.

Burchard–Stockmayer–Fixman (BSF) plot

Fig. 2 shows the corresponding BSF plot for the arabinoxylans samples. In this representation, designed to allow extrapolation of local chain parameters to the zero excluded volume limit, the data appear quite scattered. However, this is a notoriously testing procedure, and the authors probably do themselves no favours by preparing so many samples!

The best intercept from this plot is $K_\theta = 4.74 \pm 0.7$ ($\times 10^{-4}$) dl g^{-1}. From this we can calculate the chain characteristic ratio C_∞ and the persistence length L_p as below.[3]

$$C_\infty = \left(\frac{K_\theta}{\Phi}\right)^{2/3} \times \frac{m}{l^2} \quad \text{and} \quad L_p = C_\infty l/2$$

In these equations, Φ is the draining parameter 2.6×10^{26} in SI units (i.e., Kg^{-1}), l is the residue length, ~ 0.54 nm, and m is the relative residue molecular mass.

There is, of course, still some uncertainty here because, as it made clear in the original paper, although the individual fractions are narrow with respect to MW distribution, fraction to fraction they are not homogeneous with respect to the degree of arabinose substitution. The authors have chosen to normalise for this by simply using the backbone molecular weight in their notation M_wXyl. This is certainly an arguable approach, but it does make an implicit assumption that the chain flexibility parameter (e.g., the persistence length) is independent of the degree of substitution. In practice there seems no way to avoid this reasonable assumption, but we have chosen an alternative pre-averaging approach, which still approximates, albeit in a slightly different manner.

As we see from the equations above, in any final calculation of the persistence length, the residue molecular mass, m, is one of the parameters. Instead of using M_wXyl, we have evaluated m, and therefore L_p, for both extremes, and an average value of the substitution ratio $R(=\text{Ara/Xyl})$, as shown in Table 1. The range of values is 2.5–4.2 nm, and the standard error of this mean gives 3.1 ± 0.3 nm. This is around 50% of the value obtained by Dervilly-Pinel and co-workers. However, appreciating the limitations of all such extrapolation methods, it is worthy of comment that, as these workers report, 'the β-(1→4)-D-xylan chain is however more flexible than the two-fold helix of β-(1→4)-cellulose, since there is only one hydrogen bond between adjacent xylosyl residues as compared to two hydrogen bonds between adjacent glucosyl residues in cellulose'. Our recent work reports the corresponding values of the same parameter for a number of independent measurements of guar[4] and also new data for other β-(1→4)-linked galactomannans, in particular locust bean and tara gum samples,[5] to lie within the range 3–5 nm.

Finally, the one aspect of the treatment above that has been neglected is the effect of chain-length polydispersity (MW distribution). There is no doubt this will make some difference because the arabinoxylan systems are sharpened fractions, whereas the galactomannan samples, in particular, are closer to a Flory (most probable) distribution. Nevertheless, the correction (typically ∼10–30%), will not be a significant factor in making this comparison.

Analysis of the data of Dervilly-Pinel and co-workers using the classical Burchard–Stockmayer–Fixman method to eliminate the effect of chain excluded volume produces estimates of the chain persistence length of their arabinoxylans well in line with those that would be predicted on the basis of its chain conformation and

Table 1
Macromolecular parameters for arabinoxylan

$R=$ Ara/Xyl	Relative residue molecular mass m	Chain characteristic ratio C_∞ (from BSF plot)	Persistence length L_p/nm
Minimum value 0.37	181	9.3	2.5
Maximum value 1.30	305	15.6	4.2
Average value 0.70	225	11.5	3.1 ± 0.3

backbone geometry. Interestingly the Mark–Houwink plot of their data lies very close to our recent collected data for a range of galactomannans, which suggests that similar values would also be obtained for other 'simple' β-(1 → 4) polysaccharides. Even more intriguingly, it suggests the latter plot, and the parameters extracted from it, might be of more general interest and application, in other related systems.

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