On the Mark–Houwink parameters for galactomannans

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Abstract

We have produced a summary plot for a number of published results for the Mark–Houwink parameters for guar and other galactomannans. Agreement between these results, collected over almost 25 years, is very good, and suggests any of the reported parameter sets discussed would be equally valid to other workers. This also implies that any values measured outside the range described should be examined very critically.
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The so-called Mark–Houwink–Sakurada equation (1), a label often truncated to just the first two of these authors, but sometimes with the name of Staudinger appended, is one of the most fundamental in the characterisation of high molecular weight polymers, relating as it does the intrinsic viscosity of a polymer, $[\eta]$, to its (usually weight average) molecular weight (molar mass), M_w

$$[\eta] = K' M_w^{\alpha} \tag{1}$$

Each of the two parameters, K' and α reflect a combination of contributions, but K' is related essentially to the intrinsic or local chain flexibility, including the orientation of the bonds to and from the constituent monosaccharides, whereas the exponent α can reflect the chain geometry, branched, sphere, rod or coil and the solvent "quality" – poor, θ or Flory, or good solvent respectively. The various values of the exponent, for example 0.5 for a linear coil like macromolecule in a θ-solvent are well known and available in any introductory textbook of polymer science (Young & Lovell, 1991).

Although values of these parameters are listed in the standard Polymer Handbook (Brandrup, Immergut, & Grulke, 2003) for a wide range of polymers and solvents, the data for carbohydrate polymers in aqueous solvents are less prevalent, and in some cases there are still disputed results. This can be seen, for example, by examining other lists of values for different carbohydrate polymers (e.g. Lapasin & Pricl, 1995).

One reason for this is that it is still by no means a trivial exercise to obtain "molecular solutions" of polysaccharides in water – some workers simply do not allow sufficient time for hydration, others use too mild conditions. As is well appreciated, hardly any "native" (as opposed to partially hydrolysed) polysaccharides dissolve readily in water – dextran may be one of these few – and both natural sample variations and the difference in hydration conditions increase the problems.

We have argued for some years (Richardson & Ross-Murphy, 1987; Robinson, Ross-Murphy, & Morris, 1982) based upon both macromolecular and semi-dilute solution rheological results, that guar gum, the most prevalent galactomannan in use, should be regarded as a model coil-like polymer. This is even though its intrinsic stiffness, as determined by chain persistence length, is significantly greater, by up to a factor 10×, than that for most synthetic coil polymers in common use (Patel, Picout, Ross-Murphy, & Harding, 2006).

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There are a considerable number of published values for the polysaccharide from guar, and a few for other galactomannans such as locust bean gum, tara and fenugreek, all of which differ in their galactose substitution pattern and degree. However, the point of this comment is to register the fact that sufficient values now exist that we can have some real confidence in the absolute values of K' and α.

Fig. 1 summarises this statement. It includes a number of published studies on guar (and as explained later for LBG and tara) and summarises them in the form of a Mark–Houwink plot.

The data have been collected over 25 years, and include the widely cited results of Robinson et al. (1982) a valuable series of measurements by Beer, Wood, and Weisz (1999) together with recent studies by a team including the current authors, for both guar (Picout, Ross-Murphy, Errington, & Harding, 2001) and tara/LBG (Picout, Ross-Murphy, Jumel, & Harding, 2002) and a careful study by Cheng, Brown, and Prud'homme (2002).

In most of these studies, M_w was measured directly by static light scattering, using either low angle or multi-angle apparatus, in some cases coupled to size exclusion chromatography (SEC) equipment. In the case of the Cheng study a neat recursive method was applied to size exclusion data without coupled scattering. Samples were prepared by a variety of methods, including the pressure-cell method (Patel et al., 2006; Picout et al., 2002) and by selective thermal and enzymatic degradation (Cheng et al., 2002). As can be seen the data cover a range of almost two decades in M_w and (the Beer data) go down close to the limit where coil-like behaviour begins to break down because there

Table 1
Mark–Houwink parameters from previously published work

α	$K'/\times10^4$/dL/g	Source
0.72	5.13	Beer et al. (1999)
0.70	6.00	Picout et al. (2001)
0.74	3.72	Picout et al. (2002)
0.72	3.80	Robinson et al. (1982)
0.747	3.04	Cheng et al. (2002)

are less than say 10 statistical segments (as calculated from the persistence length).

Also included are the authors' own Mark–Houwink parameters summarised in Table 1.

There are several points to make here, and to help justify the purpose of this short comment.

1. The data are in very reasonable agreement, and no particular datum stands out for being well outside the expected range. That said, there are some definite trends within the data sets, the early but widely cited values from Robinson and co-workers lie slightly below the other sets, while those of Beer et al. lie slightly above. In fact these two sets have identical α values (slopes), but the Beer K' is circa. 35% greater – a large difference in linear terms but not when plotted as here in 3×2 decade logarithmic coordinates. The Cheng data are well positioned, as are both of the Picout lines. We could conclude that any of the K'/α pairs would do just as well. It also suggests there is little point repeating such experiments yet again, and values which lie outside these must be re-examined very critically. It would, of course, be
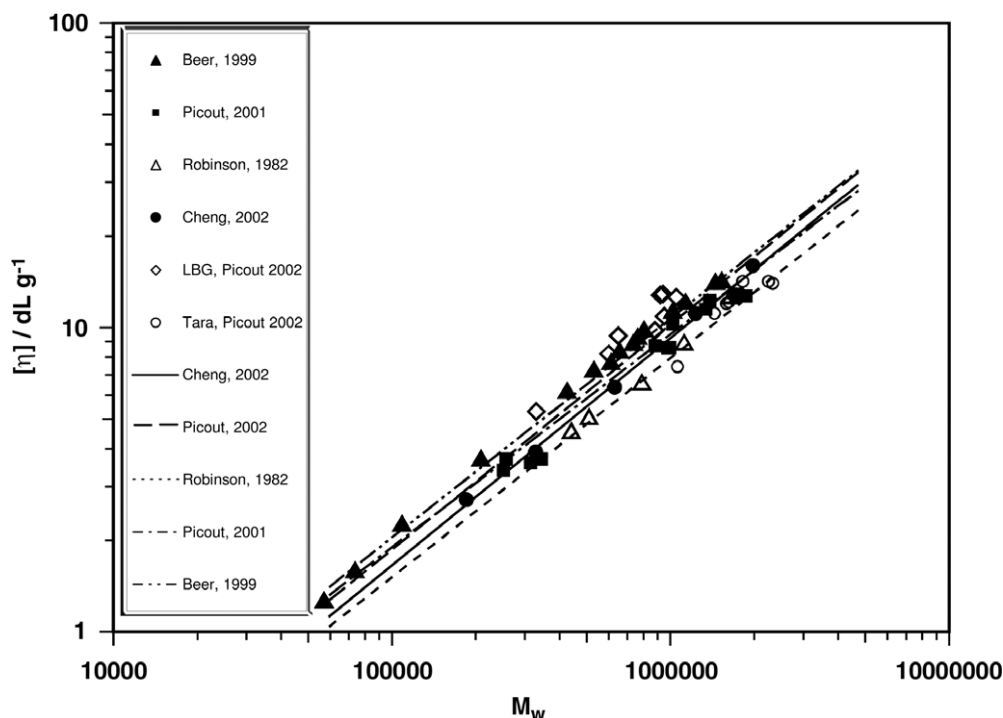

Fig. 1. Data for aqueous guar solutions (plus some for tara and LBG), from published work indicated; symbols as key.