

Estimation of Mark-Houwink-Sakurada Constants Using Polydisperse Polymers

Although the solution-viscosity method provides a simple approach to characterize the molecular weight of a polymer sample, it is a relative method which hinges on the Mark-Houwink-Sakurada (MHS) equation given as

$$[\eta] = KM_v^a \quad (1)$$

where the intrinsic viscosity $[\eta]$ for a particular polymer solution is related to the viscosity-average molecular weight M_v . Here the MHS constants K and a are established by analyzing either the viscosity data of standard samples of narrow molecular weight distribution or the gel permeation chromatography (GPC) results of whole polymers.¹⁻³ The former is the conventional technique, but it is more tedious than the latter which depends utterly on the measurements of two polymer samples of broad molecular weight distribution. This note reports a reliable route to these constants by regression analysis of the relevant experimental data from a number of unfractionated polymer samples.

It has been shown that M_v is a linear function of constant⁴ a given as

$$M_v = M_w + (\sum_i w_i M_i \ln M_i - M_w \ln M_w)(a - 1) \quad (2)$$

where M_w is the weight-average molecular weight and w_i is the weight fraction of the i th polymeric species of molecular weight M_i . Combining eqs. (1) and (2) leads to

$$\ln[\eta] + C = \ln K + a \ln M_w \quad (3)$$

where C is a correction factor arising from the heterogeneity of the polymer expressed as

$$C = -a \left[1 + \left(\frac{\sum_i w_i M_i \ln M_i}{M_w} - \ln M_w \right) (a - 1) \right] \quad (4)$$

Equation (3) may be processed by iterative technique. First by taking the factor C as zero, a plot of the lhs of the equation versus $\ln M_w$ will yield a straight line whose intercept and slope are equal to the first approximations of $\ln K$ and a , respectively. The value of a is then substituted into eq. (4) to compute C , which allows the above linear plot to be repeated resulting in the second approximation of a . Hence successive approximations of a are obtained likewise until the iteration converges to a root of a .

If eq. (2) is valid for long-range extrapolation to $a = -1$ where M_v is equal to the number-average molecular weight M_n , then⁴

$$C = -a \ln \left[1 - \frac{1}{2}(1 - a)(1 - 1/U) \right] \quad (5)$$

where

$$U = M_w/M_n \quad (6)$$

However, the summation term in eq. (4) may also be calculated directly from the GPC chromatogram provided that the MHS constants for the GPC solvent are known or predetermined as explained below.

According to the universal calibration of GPC, the elution volume is a function of J_i defined as

$$J_i = [\eta]_i M_i \quad (7)$$

where the subscript i is for the i th polymeric species. Substitution of eq. (7) into eq. (3) yields

$$\ln[\eta] + D = \frac{1}{(1+a)} \ln K + a \ln \sum_i w_i J_i^{1/(1+a)} \quad (8)$$

where

$$D = -\alpha' \ln \left[1 + \left(\frac{1}{1+\alpha'} \frac{\sum_i w_i J_i^{-1/(1+\alpha')} \ln J_i}{\sum_i w_i J_i^{1/(1+\alpha')}} - \ln \sum_i w_i J_i^{1/(1+\alpha')} \right) (\alpha' - 1) \right] \quad (9)$$

Equation (8) is written in an approximate form to facilitate the iterative process. Here the lhs of the equation is plotted versus $\ln \sum_i w_i J_i^{1/(1+\alpha')}$, where α' is an approximation of a . The best estimates of constants K and a for a particular GPC solvent are finally derived by exactly the same manner as above-outlined for eq. (3). Since good solvent is always employed in the GPC studies, the iteration of eq. (8) may be conveniently initiated by setting $\alpha' = 0.70$.

Dobbin et al.² have performed the $[\eta]$ and GPC measurements on three commercial poly(methyl methacrylate) samples in various solvents. These data are employed for the present proposes by using eqs. (3) and (5). In this work eq. (3) is treated by the linear least-squares method. Our results shown in Table I are in fact marginally closer to the literature values resulted from the well-fractionated samples² than those quoted by the above workers using the GPC method for both systems 1 and 2. The values of correlation coefficient r also listed in the table support the linear relationship of eq. (3).

Based on the assumption that the GPC chromatogram follows a Gaussian distribution function, Wu et al.³ have estimated the MHS constants for poly(stearyl methacrylate) (PSMA) in tetrahydrofuran (THF) with results displayed in Table I. It is found that comparable results are achieved by applying the present regression analysis to the same system.

However, if the factor U is neglected altogether in the calculations inconsistent results on the MHS constants are inevitable particularly for whole polymers. This is illustrated by the work of Ali and Raina⁵ who have studied the dilute solution behavior of poly(vinylidene fluoride) (PVLF) with U varying from 1.34 to 1.62 in N,N -dimethylacetamide (DMA) at 125°C. They plotted $\ln[\eta]$ vs. $\ln M_w$ to obtain the MHS constants. The differences between these figures

TABLE I
Mark-Houwink-Sakurada Constants for Polymers

No.	System	U	$K \times 10^4$ (dL/g)	a	r
1	PMMA in THF at 25°C	2.13	1.48	0.677	1.0000
		-2.81	(1.99) ^a	(0.660) ^a	
2	PMMA in CHCl ₃ at 25°C	2.13	1.07	0.733	1.0000
		-2.81	(1.47)	(0.714)	
3	PSMA in THF at 30°C	1.28	0.579	0.708	0.9973
		-1.59	(0.54-1.00)	(0.66-0.71)	
4	PVLF in DMA at 125°C	1.34	0.259	0.718	1.0000
		-1.62	(0.178)	(0.740)	

^a The values in parentheses are quoted from the original references.

and those produced by the present algorithm are indeed noticeable as evidenced in Table I. This means that the polydispersity factor C in eq. (3) is playing an important role in estimating the MHS constants particularly for polydisperse polymers.

Clearly, if the factor U is constant for a series of samples, then it can be incorporated into the constant K in eq. (3). Under this situation $\ln[\eta]$ is linearly dependent on $\ln M_w$ and the factor C is actually corresponding to the polymolecularity correction factor elaborated by Bareiss.⁶

The present method is a rapid process in that it takes no more than three iterations to resolve the MHS constants in all the instances investigated herein. Hence it is handy to use and particularly useful when fractionated polymers are not available. In addition, the crucial molecular parameters M_w and U are experimentally accessible by either the light scattering, osmotic pressure, and other absolute methods, or GPC measurement. If the values of K and a for the GPC solvent are unknown, the applicability of the procedure is upheld by invoking eq. (8) instead. We thus have formulated a reliable, practical, and adaptable approach to estimate the MHS constants.

References

1. A. R. Weiss and E. Cohen-Ginsberg, *J. Polym. Sci., Part B*, **7**, 379 (1969).
2. C. J. B. Dobbin, A. Rudin, and M. F. Tchir, *J. Appl. Polym. Sci.*, **27**, 1081 (1982).
3. Z. Wu, M. Song, N. Nadjichristidis, and L. J. Fetters, *Macromolecules*, **14**, 1591 (1981).
4. K. K. Chee, *J. Appl. Polym. Sci.*, to appear.
5. S. Ali and A. K. Raina, *Makromol. Chem.*, **179**, 2925 (1978).
6. R. E. Bareiss, in "Polymer Handbook, 2nd ed., J. Brandrup and E. H. Immergut, Ed., Wiley, New York, 1975.

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