

NOTES

On the Application of Fractional Moments in Determining Average Molecular Weights

INTRODUCTION

Number-, weight-, and viscosity-average molecular weights have been used to characterize polymer property. The number- and weight-average molecular weights have been obtained from gel permeation chromatography, and the viscosity-average molecular weight has been determined by intrinsic viscosity measurements with the use of the Mark-Houwink equation¹ defined as

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

where $[\eta]$ is intrinsic viscosity, M is molecular weight, and K and a are parameters determined experimentally.

Since the viscosity-average molecular weight is a piece of information which can be generated from the more general molecular weight distribution, previous workers^{2,3} have used the experimental viscosity-average molecular weight in calibrating the molecular weight distribution obtained on GPC with the use of directly integrating the differential distribution. However, when solving a set of ordinary differential equations of polymerization kinetics, it is usually a much easier task to solve for the molecular weight averages, or moments, than for the explicit molecular weight distribution itself.⁴ In this note, we demonstrate that an attempt to relate the viscosity-average molecular weight with the moments of a molecular weight distribution might be rewarding in both predicting the kinetic viscosity-average molecular weight comparable with the on-line experimental value and also leading to an efficient algorithm for the calibration of GPC data.

DIFFERENTIAL DISTRIBUTIONS FROM A SET OF MOMENTS

The molecular weight distribution function, $M(v)$, generates univariate j th moment, $\overline{M}_v^{[j]}$ of continuous chain length variable v :

$$M_v^{[j]} = \int_0^\infty (v)^j M(v) dv \quad (2)$$

A set of moments may yield its differential distribution with the expansion of either Laguerre polynomial⁴ or Hermite polynomial.⁵ Since the Laguerre polynomial has more general orthogonal property than Hermite polynomial concerning the possible fractional order of distribution variable within the integrand,

$$\int_0^\infty (x)^\alpha \exp(-x) L_n^\alpha(x) L_m^\alpha(x) dx = \frac{\Gamma(\alpha + n + 1)}{n!} \delta_{nm} \quad (3)$$

where $L_n^\alpha(x)$ is generalized Laguerre polynomial,

$$L_n^\alpha(x) = \sum_{j=0}^n (-1)^j \binom{n+\alpha}{n-j} \frac{(x)^j}{j!} \quad (4)$$

and δ_{nm} is Kronecker delta function

$$\delta_{nm} = \begin{cases} 1 & \text{for } n = m \\ 0 & \text{for } n \neq m \end{cases}$$

a normalized distribution function, $G(x)$, can be represented by a choice of Laguerre polynomial expansion as follows:

$$G(x) = \frac{(x)^\alpha \exp(-x)}{\Gamma(\alpha + 1)} \sum_{n=0}^{N_{\max}} C_n^\alpha L_n^\alpha(x) \quad (5)$$

The coefficients C_n^α can be expressed with the moments $\overline{G_x^{[j]}}$ of the normalized distribution function $G(x)$,

$$C_n^\alpha = \sum_{j=0}^n (-1)^j \frac{(\overline{G_x^{[1]}})^{\alpha!}}{\Gamma(\alpha + j + 1)} G_x^{[j]} \quad (6)$$

The free parameter α is chosen so as to provide a fast convergence of the series in eq. (5), i.e., $C_1^\alpha = C_2^\alpha = 0$, as follows:

$$\alpha = -1 + \frac{(\overline{G_x^{[1]}})^2}{\overline{G_x^{[2]}} - (\overline{G_x^{[1]}})^2} \quad (7)$$

and the normalized scaled density $G(x)$ is related to the original molecular weight distribution function $M(v)$ as follows:

$$M(v) dv = \overline{M_v^{[0]}} G(x) dx \quad (8)$$

$$v = \frac{\langle v \rangle}{\alpha + 1} x \quad (9)$$

$$\overline{M_v^{[k]}} = \overline{M_v^{[0]}} \left\{ \frac{\langle v \rangle}{\alpha + 1} \right\}^k \overline{G_x^{[k]}} \quad (10)$$

$$\langle v \rangle = \frac{\overline{M_v^{[1]}}}{\overline{M_v^{[0]}}} \quad (11)$$

Thus the, differential distribution is completely determined by a given set of integer moments.

FRACTIONAL MOMENTS

From a given set of integer moments any fractional moment can be obtained with a use of eqs. (5)–(11) as follows:

$$\begin{aligned} \overline{G_x^{[f]}} &= \int_0^\infty (x)^f G(x) dx = \frac{\Gamma(\alpha + f + 1)}{\Gamma(\alpha + 1)} \\ &+ \frac{1}{\Gamma(\alpha + 1)} \sum_{n=3}^{N_{\max}} C_n^\alpha \sum_{k=0}^n (-1)^k \frac{\Gamma(n + \alpha + 1) \Gamma(\alpha + f + k + 1)}{\Gamma(n - k + 1) \Gamma(\alpha + k + 1) \Gamma(k + 1)} \quad (12) \end{aligned}$$

More detailed derivation can be found in reference 6. This explicit representation of fractional moment from a set of integer moments can be applied in directly determining the viscosity-average molecular weight from a set of moments given.

VISCOSITY-AVERAGE MOLECULAR WEIGHT

The definition of the viscosity-average molecular weight is found⁷ as

$$\overline{M}_\mu = \left[\frac{\sum_{n=1}^{\infty} (n)^{1+a} M_n}{\sum_{n=1}^{\infty} (n) M_n} \right]^{1/a} \quad (13)$$

where \overline{M}_μ is the viscosity-average chain length, n is the length of a polymer, M_n is the number of polymers having chain length n , and a is the Mark-Houwink exponent. By making use of eq. (2), the viscosity-average molecular weight is represented in terms of the fractional moment as

$$\overline{M}_\mu = \left[\frac{\overline{M_v^{[1+a]}}}{\overline{M_v^{[1]}}} \right]^{1/a} \quad (14)$$

Thus, the viscosity-average molecular weight can be obtained by the analytic solution for the fractional moment from a set of integer moments [e.g., for a fixed, carry out solution using eq. (12)].

CONCLUDING REMARKS

The analytic expression for the viscosity-average molecular weight in terms of moments of molecular weight distribution can be applied to predict a kinetic viscosity-average molecular weight

with the moments from moment equations of polymerization kinetics. Since the intrinsic viscosity measurement is the fastest way to determine the average molecular weight of polymers, the predicted value of viscosity-average molecular weight may be easily compared with experimentally obtained values under on-line operations.

The analytic expression above can also be applied to an algorithm in calibrating gel permeation chromatography data: (1) calculate integer moments of elution volume distribution (corrected); (2) assume a value of number-average chain length (\bar{v}); (3) calculate viscosity-average molecular weight with the unscaled moments; (4) compare the calculated value with the experimental value of viscosity-average molecular weight and go to (2) until there is no deviation between the two values.

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References

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
2. M. R. Ambler, *J. Polym. Sci. Polym. Chem.*, **11**, 191 (1973).
3. M. R. Ambler, R. D. Mate, and J. R. Purdon, Jr., *J. Polym. Sci., Polym. Chem.*, **12**, 1759 (1974).
4. A. E. Hamielec and W. H. Ray, *J. Appl. Polym. Sci.*, **13**, 1319 (1969).
5. L. H. Tung, *J. Appl. Polym. Sci.*, **10**, 375 (1966).
6. K. W. Min, Ph.D. Thesis, State University of New York at Buffalo, Buffalo, New York, 1976.
7. B. Vollmert, *Polymer Chemistry*, Springer-Verlag, New York, 1975, p. 430.

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