Estimation of Molecular Weight Averages From Intrinsic Viscosity

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Synopsis

The weight-average molecular weight is estimated by an extrapolation technique based on a linear relation between the viscosity-average molecular weight M_v and a Mark–Houwink–Sakurada constant. This method may also be used to assess the unperturbed dimensions of polymers. If the M_v data are known with high accuracy, then the straight line may be stretched to reach the number-average molecular weight confidently. The slope of the linear plot is associated with the molecular weight distribution and as such can be utilized to compute the polydispersity index.

Numerous methods have been developed for the molecular-weight determination of polymers.[1] Among them, the solution–viscosity method is perhaps the simpliest and most widely used one for the polymer characterization by far. This procedure measures the intrinsic viscosity $[\eta]$ of a polymer in a given solvent at a constant temperature. The viscosity-average molecular weight M_v is related to $[\eta]$ by the well-known Mark–Houwink–Sakurada equation given as

$$[\eta] = KM_v^a \tag{1}$$

where K and a are the empirical constants which depend solely upon the polymer–solvent combination. These constants are invariant with M_v and molecular weight distribution provided that the M_v is sufficiently high.[2] It has been shown that the values of constant a vary from 0.5 to 0.8, depending on the goodness of the solvent for flexible random polymers. Moreover, the viscosity-average and weight-average (M_w) molecular weights are defined as

$$M_v = \left(\sum_i w_i M_i^a\right)^{1/a} \tag{2}$$

$$M_w = \sum_i w_i M_i \tag{3}$$

where w_i is the weight fraction of the polymeric species with molecular weight M_i. This infers that the value of M_v approaches that of M_w in the good solvents when the values of a are close to unity. In the limit of $a = 1$, the two values merge theoretically. Also, M_v is equal to the number-average molecular weight M_n at $a = -1$. The objective of this note is to

advance a method to estimate M_w and M_n from the M_v data based on the foregoing observations.

Taylor series expansion of eq. (2) about $a = 1$ results in

$$M_v = M_w + S(a - 1) + T(a - 1)^2 + \cdots \tag{4}$$

where

$$S = \sum_i w_i M_i \ln M_i - M_w \ln M_w \tag{4a}$$

$$T = M_w \ln M_w - (1 + \ln M_w)\sum_i w_i M_i \ln M_i \tag{4b}$$

$$+ \frac{1}{2}\left[M_w(\ln M_w)^2 + \sum_i w_i M_i(\ln M_i)^2 \right]$$

However, eq. (4) can be simplified to a linear form if the second and higher power terms in $(a - 1)$ are vanishingly small, i.e.,

$$M_v = M_w + S(a - 1) \tag{5}$$

Hence a plot of M_v vs. $(a - 1)$ produces a straight line whose intercept and slope yield M_w and S, respectively. Table I demonstrates the results obtained by the linear least-squares treatment of eq. (5) for various molecular weight distribution functions.[3,4] A total of 14 systems is investigated herein. These systems are characterized by the true values of M_w and U, which is the

TABLE I
Results of M_w Obtained by Eq. (5) for Various Theoretical Models

Model	No.	$M_w \times 10^{-5}$ [a]	U	$M_w \times 10^{-5}$ [b]	$S \times 10^{-5}$	r [c]	S/M_w
Schultz	1	3.000	1.10	3.000	0.135	1.0000	0.045
	2	3.000	1.50	3.001	0.479	1.0000	0.160
	3	3.000	3.00	3.002	0.910	1.0000	0.303
	4	3.000	20.0	2.998	1.236	0.9999	0.412
	5	3.000	50.0	3.001	1.269	1.0000	0.423
	6	30.00	3.00	30.02	9.100	1.0000	0.303
Tung	7	3.000	3.00	3.001	0.779	0.9998	0.260
	8	3.000	50.0	2.998	1.225	0.9987	0.408
Flory	9	3.000	2.00	3.001	0.700	1.0000	0.233
	10	30.00	2.00	30.01	7.000	1.0000	0.233
Log-normal	11	3.000	3.00	2.972	1.400	0.9995	0.467
	12	3.000	20.0	2.961	1.610	0.9993	0.537
	13	3.000	50.0	2.733	3.334	0.9934	1.111
Multi component[d]	14	6.150	4.92	6.100	2.038	0.9974	0.331

[a] True value of M_w.

[b] Estimated value of M_w by eq. (5).

[c] Linear correlation coefficient.

[d] A three-component Schultz model with weight fractions $g_1 = 0.70$, $g_2 = 0.25$, and $g_3 = 0.05$ for fractions characterized, respectively, by $M_w = 3.0 \times 10^5$, $U = 3.0$; $M_w = 12.0 \times 10^5$, $U = 6.0$; and $M_w = 21.0 \times 10^5$, $U = 21.0$.

polydispersity index defined as the ratio of M_w and M_n. The validity of this linear relationship is substantiated by the values of linear correlation coefficient r listed in Table I. Evidently, the estimated values of M_w become more precise if the polymer samples are less polydisperse. It is discovered that the discrepancies between the true and predicted M_w values are not exceeding 1% for a large variety of hypothetical polymers covering practically all possible molecular weight distributions. A multicomponent model[5] was also studied in system 14. However, the log-normal model seems to manifest larger differences between the two M_w values as encountered in systems 12 and 13. This means that the truncation error in eq. (5) is positively noticeable in these cases. Nevertheless, in practice, the polydispersity index of a polymer sample is rarely over 20 unless the polymer is highly branched or crossedlinked. Hence eq. (5) is warrantable in most instances.

Oth and Desreux[6] have measured the intrinsic viscosities of a polystyrene sample (EF Brut) in the toluene–methanol, butanol–methanol, and chloroform–methanol mixed solvents at 25°C. Figure 1 displays a linear plot of eq. (5) for this particular sample. The independency of the parameter S upon the nature of the solvents as inferred from eq. (4a) allows the M_v data from the three different sets of mixed solvents to be combined herein. Least-squares fitting of the data reveals that $M_w = (1.53 \pm 0.03) \times 10^6$, $S = (3.56 \pm 0.90) \times 10^5$, and $r = 0.8211$. In this computation, the data points 1, 2, and 3, which are rather scattered and doubtful, have been neglected altogether. Our M_w figure agrees remarkably well with the light scattering result equal to 1.55×10^6. Rudin et al.[7] have also employed the same set of data to estimate M_w. By plotting M_v vs. a for the three polymer–solvent
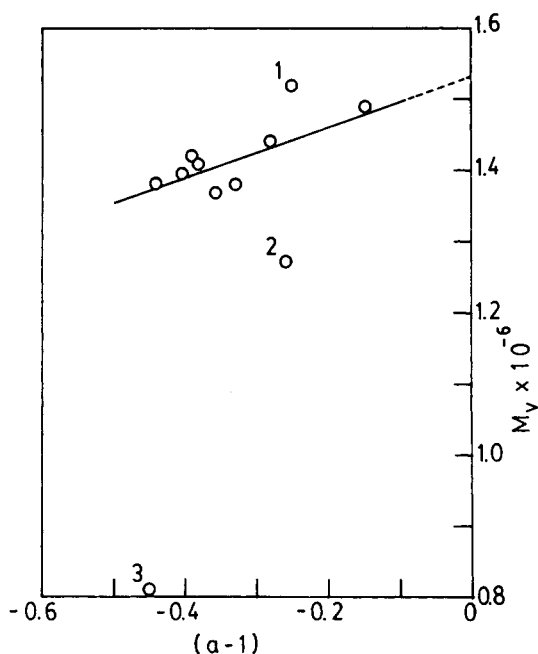

Fig. 1. Linear plot of M_v vs. $(a - 1)$ for a polystyrene sample in various mixed solvents.

pairs separately, they reported an average value of $M_w = 1.642 \times 10^6$. The two extrapolation methods are indeed different in that the present procedure involves a larger population size for analysis and thus gives rise to a more accurate and reliable result as shown in this particular case.

Table I shows that the value of ratio S/M_w increases, with increasing degree of heterogeneity measured by the parameter U. That is to say, this particular quantity is a good indication of the polydispersity of a polymer sample. In fact, using the Schultz molecular weight distribution function, it can be proved that the ratio

$$\frac{S}{M_w} = \psi(b + 2) - \ln(b + 2) \tag{6}$$

where $\psi(x)$ is the digamma function of x and

$$b = \frac{U - 2}{1 - U} \tag{6a}$$

For the sample EF Brut, eq. (6) gives $U = 1.91$, which is approximated to the most probable distribution.

Equation (5) may be used to predict the M_v under the theta condition from the viscometric data of good solvents. This would permit the unperturbed dimension of a polymer[8] to be evaluated with whole polymers instead of using sharp polymer fractions.

The attempt to extend the method to the lower moment of molecular weight distribution, viz., M_n, has met with some promising results. Applying eq. (5) to a hypothetical Schultz's sample with $M_w = 3 \times 10^5$ and $U = 3$ has yielded $M_w = 2.997 \times 10^5$, $S = 9.585 \times 10^4$, and $r = 0.9986$ for a values varying from -1 to 2. The estimated M_n is therefore equal to 1.08×10^5, which is only 8% higher than the actual value. This justifies the use of eq. (5) for estimating M_n as well if the M_v data are adequately precise and the polymer samples are not too polydisperse. Likewise, the M_n of the above polystyrene sample is found to be 8.21×10^5. Accordingly it gives $U = 1.88$ which is consistent with the value obtained from eq. (6).

Apparently, the success of this extrapolation technique rests on the accuracy of the M_v data which are computed from the values of $[\eta]$ via eq. (1). The $[\eta]$ is in turn conventionally determined by the Huggin's equation which depicts the relative viscosity of dilute polymer solution as a function of its concentration. Rosen[9] has illustrated that the uncertainties in $[\eta]$ determination leads to considerable errors in M_v. The major $[\eta]$ uncertainties are primarily due to the inaccuracy in monitoring the efflux time of the solution as well as the inherent alogrithm errors pertaining to the linear least-squares treatment of the Huggin's equation. Whereas the former may be overcome by viscometers equiped with automatic viscosity timer, the latter is ratified by some rigorous numerical analyses as proposed by Reilly et al.[10] and Nagy and co-workers.[11] Perhaps the error-in-variable method which has been successfully employed to estimate the monomer reactivity ratios of copolymerizations[12] recently may also be adopted to enhance the precision of $[\eta]$ determination. Since it is vital to know a spectrum of solvents

covering a wide range of a values, we believe that mixing of good and poor solvents would be most appropriate for the present method.

In this work, we have also used eq. (4) to estimate M_w. The results are parallel to those from eq. (5) particularly for narrow molecular weight distributions. However, in reality the experimental data may fit to eq. (4) better than to its linear version particularly when the magnitude of the $(a - 1)^2$ term is comparable to the uncertainty in M_v. Consequently, the extrapolation of the quadratic form will be less precise or erroneous, because the truly rectilinear relation between M_v and $(a - 1)$ over a limited range of $(a - 1)$ is forced to a curvilinear form. For instance, the polystyrene sample cited above quotes $M_w = 1.64 \times 10^5$ from eq. (4), which is less accurate than the estimate by eq. (5). Hence it is obvious that eq. (5) is superior to eq. (4) in estimating M_w and M_n for linear flexible random polymers.

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