

## Estimation of $M_w$ from Dilute Solution Viscosity

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### Synopsis

The viscosity-average molecular weight,  $M_v$ , of a polymer is given operationally through its limiting viscosity number  $[\eta]$  and the Mark-Houwink equation  $[\eta] = KM_v^\alpha$ , where  $K$  and  $\alpha$  are empirical constants. If  $[\eta]$  is measured under different conditions,  $\alpha$  and  $M_v$  will vary for the same sample.  $M_v^\alpha$  is the  $\alpha$ -order moment about the origin of the differential weight distribution of the polymer. Practically, the results of a series of  $M_v$  measurements on the same polymer are equivalent to a cluster of fractional moments of the weight distribution, with orders between 0.55 and 0.80. It is shown that the first moment of this distribution,  $M_w$ , may be estimated reliably by a straight-line plot of  $M_v$  against  $\alpha$  extrapolated to  $\alpha$  equals 1. This simple expedient is effective although there are probably no molecular weight distributions in which the relation is strictly linear and there are no mathematical distributions for which the  $\alpha$ th root of the  $\alpha$ th moment is a linear function of  $\alpha$  for all  $\alpha$ . The deviation from linearity is small enough, however, that the real curve can be represented by a straight line over a short range of  $\alpha$ . Thus,  $M_w$  can be measured accurately, but  $M_n$ ,  $M_z$ , or the breadth of the distribution is not accessible by this method. Experimental and literature examples show that the precision of  $M_w$  estimated by this method compares well with that of primary methods for measuring this molecular weight average. If a linear relationship is observed with reliable  $\alpha$  values, this appears to be a sufficient condition for estimation of a valid  $M_w$ .

### INTRODUCTION

The viscosity-average molecular weight,  $M_v$ , of a polymer is defined operationally through its limiting viscosity number,  $[\eta]$ . Experimentally,  $[\eta]$  depends on the polymer type, solvent, and temperature and is related to  $M_v$  through the Mark-Houwink expression:

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

Here  $K$  and  $\alpha$  are empirical constants which depend on the particular system, but are independent of the value of  $M_v$  and the peculiarities of the molecular weight distribution. There are reasons<sup>1,2</sup> to expect that these constants may not be valid over a very wide range of molecular weights, for a particular polymer. Nevertheless, the Mark-Houwink equation is known from experience to apply to many polymer-solvent combinations and the measurement of  $M_v$  is a convenient, reliable procedure if  $K$  and  $\alpha$  have

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been determined with calibration samples that span a sufficiently wide molecular weight range.

If the limiting viscosity number of a polymer is measured in different solvents or at different temperatures, the exponents  $\alpha$  will vary and so will the corresponding viscosity-average molecular weights. This paper describes the use of this variation to estimate the weight-average molecular weight of the polymer.

### Background

Several ingenious attempts have been made to extend solution viscosity measurements beyond the immediate evaluation of  $M_v$ . They are reviewed briefly below, as experience with these proposals is useful in judging the merits of the present method.

In 1959, Onyon<sup>3</sup> and Frisch and Lundberg<sup>4</sup> suggested that an index of the breadth of the molecular weight distribution could be obtained from the ratio of viscosity-average molecular weights in two solvents. The polydispersity index chosen for comparison, was the Schulz parameter, which is usually taken as  $M_w/M_n$ , or  $M_w/M_n - 1$ . This widely used parameter is related to the breadth of the number distribution and may be converted to the standard deviation,  $S_n$ , of this distribution by

$$\frac{S_n^2}{M_n^2} = \frac{M_w}{M_n} - 1. \quad (2)$$

In a subsequent paper, Lundberg, Hellman, and Frisch<sup>5</sup> reported solution viscosity measurements on several polymers, from which it was concluded that the proposed viscometric polydispersity index was useful for characterizing whole polymers. The method is, of course, restricted to polymers for which the Mark-Houwink constants can be determined independently and excludes those in which the degree of branching may vary significantly from that in the calibration samples.

This proposal has been criticized by Breitenbach<sup>6</sup> and by Koningsveld and Tuijnman<sup>7</sup> because the limited accuracy of viscometric methods and the restricted range of  $\alpha$  values make it difficult to estimate polydispersity accurately. The latter authors point out that a plot of  $[\eta]$  against  $M_n$  (if this datum is available) is a more sensitive indicator of distribution breadth than the viscometric index.

Herdan<sup>8</sup> has suggested the use of  $M_v$ , alone or preferably in combination with one or more integral molecular weight averages, to estimate the shape of the cumulative distribution, using the Markoff inequality. The Markoff inequality estimates the most conservative distribution consistent with the available data, and this cannot be a very good substitute for the real distribution unless a large number of molecular weight averages are given. Herdan's suggestion would appear, however, to represent a more efficient use of the data than the practice of quoting bald averages.

### Statement of the Problem

The viscosity-average molecular weight is defined with reference to the parent molecular weight distribution as

$$M_v = [\sum w_i M_i^\alpha]^{1/\alpha} = \left[ \frac{{}_n U'_{\alpha+1}}{{}_n U'_1} \right]^{1/\alpha} = [{}_w U'_\alpha]^{1/\alpha} \quad (3)$$

where  $w_i$  is the weight fraction of polymeric species with molecular weight  $M_i$ ,  $U'$  is a moment of the distribution about the origin, the subscripts  $n$  and  $w$  refer to the number and weight distributions, respectively, and the subscripts  $\alpha$ ,  $\alpha + 1$ , and 1 are moment orders. In this case  $\alpha$  is also equal to the Mark-Houwink exponent in eq. (1).

When  $\alpha = 1$ ,  $M_v$  coincides with the weight-average molecular weight,  $M_w$ . It is not possible in practice, however, to measure  $M_w$  directly by viscometric means. According to the theory of Flory and Fox,<sup>9</sup> the limits of  $\alpha$  for a nondraining flexible polymer lie between 0.5 and 0.8. Although more recent theoretical studies suggest that the upper limit may be as high as 1.0 for polar polymers in good solvents,<sup>2</sup> the great majority of Mark-Houwink exponents for synthetic polymers do in fact lie in the range predicted. The lower limit, 0.5, is characteristic of the Flory theta conditions, where the polymer is on the verge of precipitating. This is hardly convenient for routine measurements, so that practically the range of accessible  $\alpha$  values lies between about 0.55 and 0.80.

Because of this restricted range and the limits of accuracy of viscometric methods it is possible to measure four, or perhaps five, distinct  $M_v$  values by changing conditions to vary  $\alpha$ . From eq. (3) one may derive a corresponding number of fractional moments about the origin of the weight distribution. The closest integral moment is the first moment, which equals  $M_w$  for a normalized distribution. We have chosen to attempt to estimate this value from the viscometric data. This differs from the work cited above in that we have not tried to relate the experimental data to  $M_n$  (equal to  $({}_w U'_0 / {}_w U'_{-1})$ , in terms of moments of the weight distribution) or to the breadth of the number distribution. This choice avoids a long-range extrapolation with attendant inaccuracies. The problem then resolves into an estimate of the first moment of the differential weight distribution from a cluster of fractional moments with orders between 0.55 and 0.80.

### Estimation of $M_w$

The problem stated above is solved simply. Evidence presented below shows that the plot of  $[{}_w U'_\alpha]^{1/\alpha}$  ( $M_v$ ) against  $\alpha$  can be represented reasonably by a straight line. Extrapolation of this line to  $\alpha = 1$  yields  ${}_w U'_1$  ( $M_w$ ) with a precision which appears to be comparable to that of light scattering measurements of this parameter.<sup>10</sup>

This simple expedient is without complete theoretical foundation. In fact, there are probably no molecular weight distributions in which the relation is strictly linear and there are no mathematical distributions for

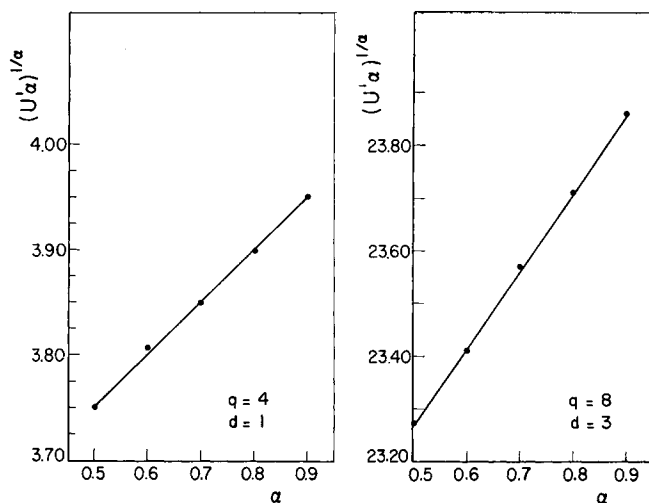


Fig. 1. Schulz distribution.

which  $(U'_\alpha)^{1/\alpha}$  is a linear function of  $\alpha$  for all  $\alpha$ . The deviation from linearity is small enough, however, that the real curve can be represented by a straight line over a short range of  $\alpha$ .

As an example, we consider the Schulz distribution in the form

$$w(M) = \frac{M^{q-1} \cdot e^{-M/d}}{d^q \Gamma(q)} \quad (4)$$

where  $w(M)$  is the weight fraction with molecular weight  $M$ , and  $q$  and  $d$  are scaling constants. Table I lists  $[U'_\alpha]^{1/\alpha}$  for  $\alpha$  between 0.5 and 0.9, at two sets of  $q$  and  $d$ . These data are plotted in Figure 1, where it can be seen that the relationship between  $[U'_\alpha]^{1/\alpha}$  and  $\alpha$  is very close to linear over this short range of  $\alpha$ . Extension of this procedure to estimate  $M_n$   $\left[ \frac{wU'_0}{wU'_{-1}} \right]$  or  $M_z$   $\left[ \frac{wU'_2}{wU'_1} \right]$  is not possible because the relationship is no longer linear in the ranges  $-1 \leq \alpha \leq 0.5$  and  $1 \leq \alpha \leq 2$ . It should be noted that the Schulz distribution function has been introduced here only to illustrate the proposed method. No implication is intended that actual distributions must conform to this function to be amenable to the present technique nor that polymers are described very well by this distribution.

TABLE I  
Fractional Moments of Schulz Distribution

Scaling constants	$[U'_\alpha]^{1/\alpha}$				
	$\alpha = 0.5$	$\alpha = 0.6$	$\alpha = 0.7$	$\alpha = 0.8$	$\alpha = 0.9$
$q = 4, d = 1$	3.751	3.807	3.850	3.900	3.951
$q = 8, d = 3$	23.27	23.41	23.57	23.71	23.86

If a number of whole polymers are combined,  $M_w$  of the mixture will be determined by the weight fraction of each component. The same dependence is shown by the limiting viscosity number of the mixture, since this parameter is the weight average of the limiting viscosity numbers of the components.<sup>11</sup> Thus, if  $M_w$  of each component can be estimated by the present linear extrapolation method, their combination will not upset this relationship.

### EXPERIMENTAL

Four commercial polystyrenes were examined by the proposed method. The  $M_w$  values for these polymers did not differ greatly, and it was of interest to see how precisely this molecular weight average could be estimated from viscometric data measured without unusual precautions.

The molecular weight distribution of each sample was determined from gel permeation chromatography elution curves. A Waters Model 200 chromatograph was used, with polystyrene gel packings of stated pore sizes  $10^7$ ,  $10^5$ ,  $10^4$ , and  $10^3$  Å. Chromatograms were run in tetrahydrofuran at 25°C, with solutions of 0.25 g polymer in 100 ml solvent. Distribution

TABLE II  
Molecular Weight Parameters of Polystyrenes<sup>a</sup>

	K1	K2	D8	K3
$M_n$	86,400	99,400	130,500	103,500
$M_w$	240,900	280,600	315,900	335,000
$M_z$	559,200	563,000	601,100	725,800
$M_{z+1}$	912,800	833,900	892,000	1,069,000
Number Distribution				
Standard deviation, $S_n$	$1.16 \times 10^5$	$1.34 \times 10^5$	$1.56 \times 10^5$	$1.55 \times 10^5$
Skewness, $B_n$	4.89	3.87	3.48	4.48
Kurtosis, $K_n$	38.36	22.33	18.38	29.03
$S_n/M_n$	1.34	1.35	1.20	1.50
Weight Distribution				
Standard deviation, $S_w$	$2.77 \times 10^5$	$2.82 \times 10^5$	$3.00 \times 10^5$	$3.62 \times 10^5$
Skewness, $B_w$	2.52	1.92	1.94	1.92
Kurtosis, $K_w$	7.96	4.58	4.54	4.14
$S_w/M_w$	1.15	1.00	0.95	1.08

<sup>a</sup> Symbols and terms are defined in the text.

parameters were computed from the elution curves both without correction for imperfect resolution and using Tung's Hermite polynomial method<sup>12</sup> to estimate this correction. Both methods of computation yielded values of  $M_w$  which agreed closely, but the resolution correction appeared to over-emphasize the low molecular weight end in the more highly skewed polymers.  $M_n$  values for the more highly skewed polymers, K1, K2, and K3, differed significantly by the two methods. The uncorrected data seemed to be more consistent with differences observed in the melt viscosities of these polymers, and these are the figures which are quoted here.

Table II lists parameters of the molecular weight distributions of the four polystyrenes. The standard deviation of the number or weight distribution,  $S_n$  or  $S_w$ , is the square root of the second moment of the differential distribution about its mean. Equation (2) expresses  $S_n$  in terms of  $M_w$  and  $M_n$ . A similar equation, in  $M_z$  and  $M_w$ , applies to  $S_w$ . The skewness of each distribution is estimated from the third moment about the mean. The skewness parameters,  $B_n$  and  $B_w$ , are normalized on the breadth of the distribution by dividing this third moment by the cube of the standard deviation. In terms of molecular weight averages,  $B_n$  and  $B_w$  are given by

$$B_n = \frac{(M_z M_w M_n - 3M_n^2 M_w + 2M_n^3)}{(M_w M_n - M_n^2)^{3/2}} \quad (5)$$

$$B_w = \frac{(M_{z+1} M_z M_w - 3M_w^2 M_z + 2M_w^3)}{(M_z M_w - M_w^2)^{3/2}} \quad (6)$$

The kurtosis parameters,  $K_n$  and  $K_w$ , are relative measures of the "peakedness" of the differential number and weight distribution, respectively. That is, they reflect the relative steepness of the differential distribution curve in the neighborhood of the mode. The parameter is usually defined by

$$K = (U_4/S^4) - 3 \quad (7)$$

where  $U_4$  (without a prime superscript) is the fourth moment of the appropriate distribution about the mean,  $S^4$  is the fourth power of the corresponding standard deviation, and the number 3 is the value of  $U_4/S^4$  for a normal distribution. Application of the statistical shift-of-origin rule to eq. (7) produces the following expressions for  $K_n$  and  $K_w$  in terms of molecular weight averages:

$$K_n = \frac{(M_{z+1} M_z M_w M_n - 4M_z M_w M_n^2 + 6M_w M_n^3 - 3M_n^4)}{(M_w M_n - M_n^2)^2} - 3 \quad (8)$$

$$K_w = \frac{(M_{z+2} M_{z+1} M_z M_w - 4M_{z+1} M_z M_w^2 + 6M_z M_w^3 - 3M_w^4)}{(M_z M_w - M_w^2)^2} - 3 \quad (9)$$

The background to these statistical parameters is given in statistics textbooks<sup>13</sup> and review articles.<sup>14</sup>

Viscometric measurements were made in Ubbelohde dilution viscometers. The solvent efflux times were between 100 and 200 sec and the ratio of solvent/solution efflux times did not exceed 1.7. Solvents were reagent grade and were used without purification. Limiting viscosity numbers were calculated conventionally from linear least-squares fits to  $c$  (concentration) against  $(1/c)$  ( $\ln t/t_0$ ) and  $(1/c)$  ( $t/t_0 - 1$ ), where  $t_0$  and  $t$  are the respective solvent and solution efflux times. The values reported are the means of these extrapolations, which coincided well. The conditions and results of these measurements are listed in Table III.

TABLE III  
 Viscometric Data of Polystyrenes

	K1	K2	D8	K3
Tetralin, 25°C				
$\alpha = 0.75$ (ref. 5)				
$[\eta]$ , dl/g	0.785	0.876	—	—
$M_v$	203,300	235,300	—	—
Toluene, 34°C				
$\alpha = 0.72$ (ref. 15)				
$[\eta]$ , dl/g	0.761	0.847	0.990	0.958
$M_v$	203,000	235,000	292,000	279,000
Toluene, 25°C				
$\alpha = 0.69$ (ref. 16)				
$[\eta]$ , dl/g	0.7239	0.862	0.966	—
$M_v$	181,900	234,400	276,300	—
Methyl ethyl ketone/ methanol (97.5/2.5), 25°C				
$\alpha = 0.62$ (ref. 17)				
$[\eta]$ , dl/g	0.416	0.472	0.543	0.471
$M_v$	187,300	229,200	288,000	229,000
Methyl ethyl ketone, 25°C				
$\alpha = 0.58$ (ref. 16)				
$[\eta]$ , dl/g	0.417	0.493	0.563	0.492
$M_v$	167,100	223,100	280,000	222,200

Figure 2 shows the plot of  $M_v$  against  $\alpha$  for each polymer and the least-squares line through each set of points. There is some scatter, but none of the patterns suggests anything other than a linear relationship. Table IV compares measured and estimated  $M_w$  values. The measured and calculated  $M_w$  values agree to within 9% of the former figure for polystyrenes

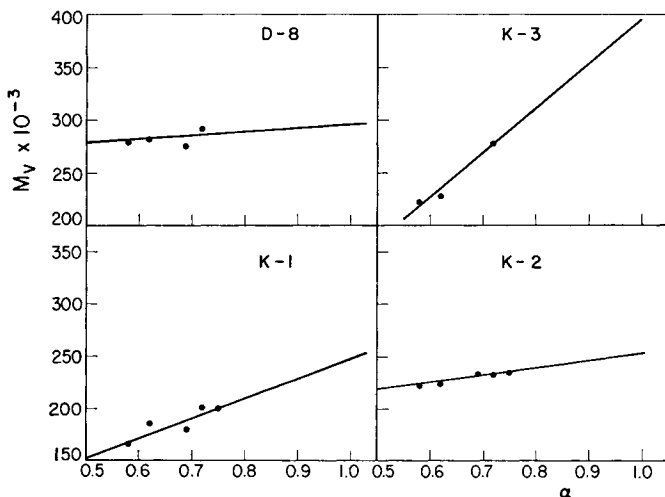

 Fig. 2. Estimate of  $M_w$  of commercial polystyrenes K1, K2, D8, and K3.

TABLE IV  
Measured and Estimated  $M_w$  of Polystyrenes

	K1	K2	D8	K3
$M_w$ (measured)	240,900	280,600	315,900	335,000
$M_w$ (estimated)	250,600	254,500	295,700	396,000
Slope of least-squares line (Fig. 2) $\times 10^{-3}$	189.2	70.3	33.5	424

K1, K2, and D8. The discrepancy is 18% of the measured value for sample K3, to which the fewest  $M_w$  data apply. The estimations rank the polymers in the correct order despite the occasional inversion of order of  $M_w$  measured in a particular solvent (compare D8 and K3). These results illustrate the value of obtaining as many distinct  $M_w$  figures as possible. There is no evidence in these data that the viscometric method is appreciably less sensitive than primary methods for measuring  $M_w$ .

Previous workers<sup>4</sup> have been forced to try to relate viscometric measurements to the breadth of the number distribution because data were not available to estimate the breadth of the differential weight distribution. Intuitively, however, one would expect differences in limiting viscosity number or related parameters to be more responsive to the influence of the weight distribution. The data for our four polystyrenes hint at this dependence, but the evidence is hardly compelling and the following observations are recorded to stimulate further study rather than to suggest that a firm relationship has been established. The slopes of the linear least-squares lines in Figure 2 are recorded in Table IV. A plot of these slopes against the corresponding coefficient of variation of the weight distribution,  $S_w/M_w$ , is steeply linear for polymers K1, K2, and D8. The correlation does not hold for polymer K3, for which  $M_w$  and probably the least-squares slope have been overestimated. No such relation is clearly evident between these slopes and  $S_n/M_n$ .

A correlation between the slopes of the least-squares lines and the breadth of the weight or number distributions is consistent with the properties of the Schulz distribution. Details are omitted here, since the connections between a mathematical distribution and a polymer of undetermined distribution is of little a priori value. The relative sensitivity of this slope to the weight or number distribution is determined by the accuracy and nature of the viscometric technique rather than by the nature of the appropriate mathematical distribution function.

### Literature Values

The proposed method was applied to the few studies we could locate in which  $M_w$  and a number of  $M_n$  values are recorded for the same polydisperse sample. The data of Lundberg, Hellman, and Frisch<sup>5</sup> are particularly useful in this respect. These measurements are summarized in Table V, along with  $M_w$  figures calculated by a linear least-square fit to  $M_n - \alpha$ .



TABLE V  
Data of Lundberg, Hellman, and Frisch<sup>5</sup>

Polymer <sup>a</sup>	Solvent	Temp, °C	$\alpha$	$M_v$ $\times 10^{-6}$	$M_w$ (meas.) $\times 10^{-6}$	$M_w$ (calc.) $\times 10^{-6}$
PMMA I	benzene	25	0.76	0.98	1.79	1.57
	toluene	25	0.73	0.86		
	ethyl acetate	20	0.64	0.74		
	butanone-isopropanol	23	0.55	0.42		
	acetonitrile	30	0.50	1.12		
PMMA II	benzene	30	0.76	2.81	3.25	3.71
	acetone	30	0.71	2.62		
PS I	tetralin	25	0.75	0.93	1.25	1.45
	toluene	25	0.69	0.82		
	butanone	25	0.58	0.58		
PS II	tetralin	25	0.75	0.23	0.239	0.250
	toluene	25	0.69	0.21		
	butanone	25	0.58	0.21		

<sup>a</sup> Polymer nomenclature is that of the cited authors.<sup>5</sup>

The agreement can be seen to be reasonably good, with the worst case being that of poly(methyl methacrylate) PMMA II, for which only two  $M_w$  values are given. We have not used these authors' data for poly(isopropenyl acetate) because the measured  $M_v$  figures are higher than the reported  $M_w$ . Similarly, the acetonitrile  $M_v$  datum for PMMA I in Table V is obviously unreliable and was not used to compute  $M_w$ .

Oth and Desreux<sup>17</sup> record  $M_v$  figures for one sample of polystyrene in three binary solvent combinations.  $M_w$  for this polymer (EF Brut) is given as  $1.55 \times 10^6$ , from light scattering. The viscometric data of these

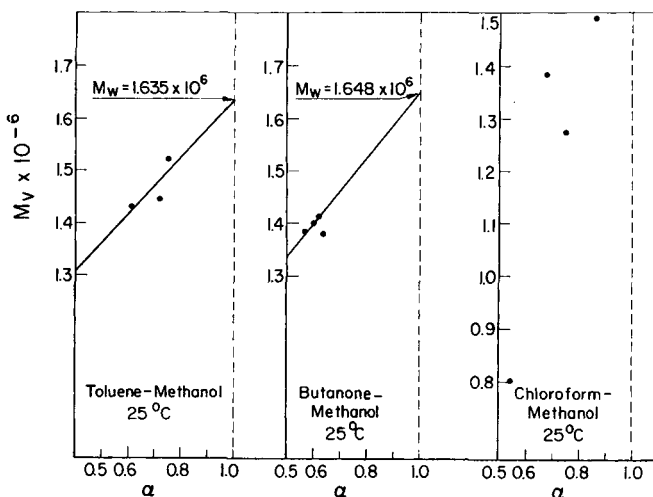


Fig. 3. Polystyrene EF Brut.<sup>17</sup>

authors are plotted in Figure 3, with least-squares lines through the experimental points. Toluene-methanol and butanone-methanol systems yield estimated  $M_w$  values of  $1.64 \times 10^6$  and  $1.65 \times 10^6$ , respectively. One datum in the latter system has been neglected because it is evidently off the line. The  $M_n$  data for chloroform-methanol, also shown in Figure 3, are so badly scattered that a linear fit is not worthwhile.

Stivala, Valles, and Levi<sup>18</sup> report three  $M_n$  figures for a sample of poly-(butene-1) with  $M_w$  270,000. A linear fit to the  $M_n$  figures yields an estimated  $M_w$  of 410,000. This discrepancy may perhaps be excused by noting that the reported  $M_w$  is less than either of the two highest  $M_n$  figures, which should correspond to lower moments of the weight distribution.

### CONCLUSIONS

While all the examples available seem to exhibit a linear relationship between  $M_n$  and  $\alpha$ , it is not unlikely that there may be polymers which do not. We do not suggest that the proposed method will be universally applicable. It seems reasonable to assume, however, that if a linear relationship is observed with reliable  $\alpha$  values, this is a sufficient condition for estimation of a valid  $M_w$ . In doubtful cases it may be advisable to quote confidence limits on  $M_w$  from conventional statistical methods assuming a linear relationship and no error in  $\alpha$ .

The same precautions which apply to determination of  $M_n$  are, of course, necessary in estimating  $M_w$ . The Mark-Houwink equation must be known to apply in the molecular weight range of interest. The constants are preferably determined against  $M_w$  of sharp fractions and the unknown and calibration samples should have the same degree of branching.

It is of interest also to compare  $M_w$  values estimated by the present method with those which would be given by the practice of simply equating  $M_n$  to  $M_w$ . In some cases, where the slope of the least-squares line is shallow, there is evidently little gain from the new technique. Examples are K2 and D8. In other cases, however, the  $M_n$  value at the highest recorded  $\alpha$  value is a very poor estimate of  $M_w$ . The data for PMMA I, PMMA II, and EF Brut in methanol-butanone are striking examples. Thus the present method appears to be considerably more reliable in its application to polymers with unknown molecular weight distributions.

The authors wish to thank the National Research Council of Canada for financial aid, R. Y.-M. Huang for use of gel permeation apparatus and computer program, and K. K. Chee for several of the limiting viscosity number determinations. This report is based on a paper presented at the Fifteenth Canadian High Polymer Forum, Kingston, Canada, 1969.

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Received May 5, 1969