# Direct estimation of the true Mark–Houwink–Sakurada parameters from gel permeation chromatography, intrinsic viscosity and one average of molecular weight

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A method is described for the simultaneous determination of the true constants in the Mark–Houwink viscosity equation and the absolute calibration of gel permeation chromatography data. In this method, polydisperse samples can be used. The experimental data required on each sample are its gel permeation chromatogram, its intrinsic viscosity and one average of molecular weight, $\bar{M}_w$ or $\bar{M}_n$. The method does not require any calibration curve for another polymer (e.g. polystyrene monodisperse standards). The method is applied to the system poly(*N*-vinyl-3,6-dibromocarbazole) in tetrahydrofuran at 25°C. The procedure may be especially useful in those cases in which, due to the existence of secondary exclusion mechanisms resulting from polymer–stationary phase or polymer–solvent interactions, the hydrodynamic volume universal calibration concept is not valid.

**(Keywords: intrinsic viscosity; gel permeation chromatography calibration; Mark–Houwink constants; polydisperse samples; poly(*N*-vinyl-3,6-dibromocarbazole)**

## INTRODUCTION

Gel permeation chromatography (g.p.c.) has been presented in the recent past as a non-time-consuming technique for obtaining a complete characterization of the molecular weight distribution (*MWD*) of a macromolecular polydisperse sample. However, it seems to be subject to a series of limitations, especially when very precise values of molecular weight averages are required: (a) It is a secondary method. (b) For polymers for which narrow *MWD* standards are unavailable, it is necessary to convert a primary g.p.c. calibration into a secondary calibration for the second polymer. Unfortunately, this may lead to the wrong results if the separation does not take place on the basis of molecular size alone, if the polymer molecules are not present as random coils in solution, or if some of the well known non-exclusion effects are operative. (c) Instrumental broadening is important for narrow *MWD* standards.

To generate a universal calibration plot in g.p.c., the hydrodynamic volume is generally used. There are a series of criteria for establishing which average of $V_h$ (hydrodynamic volume) can be used in each particular case[1–3]. If the sample has a very narrow *MWD*, any measured average of the molecular weight can be adequate to calculate $V_h$. However, such a type of standard is often not available.

If there are no narrow *MWD* standards of the polymer under study and interaction exists between the polymer and the stationary phase, universal calibration may be obtained using the Mark–Houwink constants $K$ and $a$. These constants are in fact needed in order to use the $V_h$ procedure[4,5]. At present it is not clear how universal calibration curves must be constructed through their respective Mark–Houwink constants.

If we plot $\log [\eta]M$ ($[\eta]M = V_h$, $M$ selected by one of the criteria already proposed in the literature) as a function of elution volume, $V_e$, measured at the peak of the chromatogram in the usual manner, then we are neglecting differences between the molecular weight of the species eluting at the peak and the true viscometric molecular weight, or between $V_e$(peak) and the true elution volume, which corresponds to the measured limiting viscosity number $[\eta]$.

The difficulties in assigning the true values of $[\eta]$, $M$ and $V_e$, which should be used jointly for a proper universal calibration plot, are solved by profitable use of g.p.c. on samples having polydisperse *MWD* and then studying the non-exclusion effects very often found besides the size exclusion mechanism.

One of the easiest ways to estimate the average molecular weight of a sample is to measure $[\eta]$ of the sample in a given solvent at a given temperature, and to

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calculate its viscosity-average molecular weight, $\bar{M}_v$, through the Mark–Houwink equation:

$$[\eta] = K\bar{M}_v{}^a \tag{1}$$

where $K$ and $a$ are constants in a given solvent at fixed temperature. $\bar{M}_v$ is defined by:

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

where $w_i$ and $M_i$ are the weight fraction and molecular weight, respectively, of the $i$th polymer species.

The constants $K$ and $a$ must be determined empirically by comparison of $[\eta]$ of several fractions with their molecular weight determined by one of the absolute methods ($\bar{M}_n$ by membrane osmometry, or $\bar{M}_w$ by light scattering).

Viscosity-average molecular weights, $M_v$, may be calculated by iteration or successive approximations starting with the Mark–Houwink exponent $a$ derived from the experimental plot of either $\log[\eta]$ vs. $\log \bar{M}_n$ or $\log[\eta]$ vs. $\log \bar{M}_w$, and assuming a given *MWD* for each of the samples. Thus, for a sample with a normal *MWD*, the viscosity-average molecular weight is obtained by means of[6]:

$$\bar{M}_v = (a+1)(\bar{M}_w/2) - (a-1)(\bar{M}_n/2) \tag{3}$$

and for a log-normal *MWD*[7]:

$$\bar{M}_v = \bar{M}_w(\bar{M}_w/\bar{M}_n)^{(a-1)/2} \tag{4}$$

The iteration is finished when the calculated values of $K$ and $a$ agree with the test ones entered in the respective iteration. However, this procedure is subject to restrictions such as the adequacy of the functions used to describe the *MWD*s of the fractions employed.

It does not seem always to be realized that the constants of equation (1) are very sensitive to differences in *MWD* among the fractions being used and that these distributions should be the same[8] or very similar. Moore[9] has reviewed critically the possible sources of error in establishing adequate Mark–Houwink relationships by classical methods.

G.p.c. may provide a much more convenient route to $K$ and $a$. Many of the g.p.c. methods used to obtain $K$ and $a$ have been based on the universal calibration principle, or its transformations[10–27]. Some methods use data furnished by the coupling of g.p.c. to automatic viscometry[28–32]. G.p.c. methods normally used hitherto to obtain Mark–Houwink constants [10–32] appear, however, to be as unreliable as the classical ones.

The method described in the present paper uses a combination of g.p.c. data, intrinsic viscosity measurements, and one (or more) average(s) of molecular weight. Apart from its own usefulness and reliability, the values of $K$ and $a$ may then be used to construct a universal calibration curve[4] suitable for any *MWD* of some other samples of the same particular polymer. It may also be of especial utility to study partial separation effects by non-exclusion mechanisms in g.p.c.[33]

## EXPERIMENTAL

### *Materials*

The synthesis, fractionation and characterization of the ten fractions of poly(*N*-vinyl-3,6-dibromocarbazole) PVK-3,6-$Br_2$) used in the present study have been reported elsewhere[34,35]. The values of the weight-average molecular weight, $\bar{M}_w$, and number-average molecular weight, $\bar{M}_n$ are shown in *Table 1*.

### *Viscometric measurements*

Details of the limiting viscosity number $[\eta]$ determination have also been reported[36]. Solvent flow times in THF exceeded 160 s and no kinetic energy corrections were made. At least four or five flow time measurements were made at each of the four concentrations and a mean deviation less than 0.2 s from the mean value was desirable. Limiting viscosity numbers were estimated by the simultaneous extrapolation of $\eta_{sp}/c$ and $(1/c)\ln\eta_{red}$ vs. concentration plots to infinite dilution according to the Huggins[37] and Kraemer[38] equations. Data on $[\eta]$ are given in *Table 1*.

### *Gel permeation chromatography*

G.p.c. experiments were performed at 25°C with THF as eluant using a Waters Associates model 200 gel permeation chromatograph. THF employed as the solvent was distilled from copper(I) chloride and potassium hydroxide. A series arrangement of five polystyrene gel columns, with nominal exclusion sizes (in Å) of $10^7$, $10^6$, $10^5$, $10^4$ and $3\times10^3$ (Waters designation), was used. Elutions were conducted with a flow rate of 1 ml min$^{-1}$. Elution volumes (counts) were calculated from the initial point of injection to the appearance of the peak height

**Table 1** Averages of molecular weight, intrinsic viscosity in tetrahydrofuran at 25°C and gel permeation chromatography data for poly(*N*-vinyl-3,6-dibromocarbazole) (PVK-3,6-$Br_2$) fractions in tetrahydrofuran at 25°C utilizing columns packed with crosslinked polystyrene gel

| Fraction | $\bar{M}_n$(exp) $\times10^{-3}$ | $\bar{M}_n$(calc) $\times10^{-3}$ | $\bar{M}_w$(exp) $\times10^{-3}$ | $\bar{M}_w$(calc) $\times10^{-3}$ | $\frac{\bar{M}_w\text{(calc)}}{\bar{M}_n\text{(calc)}}$ | $\bar{M}_v\times10^{-3}$ | $[\bar{\eta}]$(exp) (ml g$^{-1}$) | $[\bar{\eta}]$(calc) (ml g$^{-1}$) | $V_e$(peak) (counts) |
|---|---|---|---|---|---|---|---|---|---|
| F-3 | – | 392 | 602 | 475 | 1.21 | 634 | 57.2 | 44.0 | 31.6 |
| F-4 | – | 376 | 492 | 461 | 1.23 | 500 | 47.0 | 42.9 | 32.0 |
| F-5 | 284 | 223 | 333 | 325 | 1.46 | 314 | 32.0 | 31.8 | 32.8 |
| F-6 | – | 250 | 303 | 348 | 1.39 | 272 | 28.4 | 33.6 | 32.9 |
| F-7 | 203 | 197 | 285 | 283 | 1.43 | 274 | 28.6 | 28.2 | 33.0 |
| F-8 | 175 | 186 | 208 | 248 | 1.34 | 206 | 22.6 | 25.5 | 33.8 |
| F-9 | 142 | 125 | 166 | 155 | 1.23 | 150 | 17.4 | 17.4 | 34.9 |
| F-10 | 96.6 | 93.9 | 129 | 107 | 1.14 | 114 | 13.8 | 13.0 | 35.8 |
| F-11 | 63.0 | 70.1 | 78.0 | 80.3 | 1.14 | 84 | 10.7 | 10.2 | 36.7 |
| F-12 | 39.5 | 43.5 | 48.0 | 49.4 | 1.13 | 48 | 6.8 | 6.9 | 37.8 |

maximum of the gel permeation chromatograms. Polymer concentrations were 0.2–0.3 w/v, all the polymer in the sample loop being injected. An injection time of 120 s for sample solutions was used. Some characteristic chromatograms are given in *Figure 1*.

### *Automatic capillary viscometry*

The capillary viscometer[28] was connected on-line behind the siphon and thermostated to 25°C ± 0.005°C. The flow time of an exactly defined amount of pure THF between two photocells was about 100 s.

Polymer concentration $c_i$ for fraction $i$ from the siphon has been determined by means of the following expression:

$$c_i = (m/v) \int_{v_{i-1}-v_d}^{v_i - v_d} F(V)\,\mathrm{d}V \Bigg/ \int_{-\infty}^{\infty} F(V)\,\mathrm{d}V \qquad (5)$$

where $F(V)$ is the gel chromatogram curve of the polymer sample, $c_i$ is the concentration, $m$ is the mass of the polymer injected ($m$ = polymer concentration in the solution injected × injection loop volume), $v$ is the volume of the siphon, $v_{i-1}$ and $v_i$ are the initial and final eluant volumes of the $i$th fraction, and $v_d$ is the dead volume of the connecting capillary between the refractometric cell and the siphon. The intrinsic viscosity of the individual fraction $[\eta]_i$ could then be calculated with an error less than 2% by the infinite dilution equation

$$[\eta]_i = (t_i - t_s)/t_s c_i$$

in which $t_s$ is the flow time for pure solvent and $t_i$ is the flow time for count $i$. Likewise, the intrinsic viscosity of the whole sample $[\eta]$ is obtained as a weight average from

$$[\eta] = \sum_i w_i [\eta]_i$$

Moreover, the measured value of $[\eta]$ for the whole sample does agree with the value calculated from the values of $w_i$ and $[\eta]_i$ for each of the subfractions.

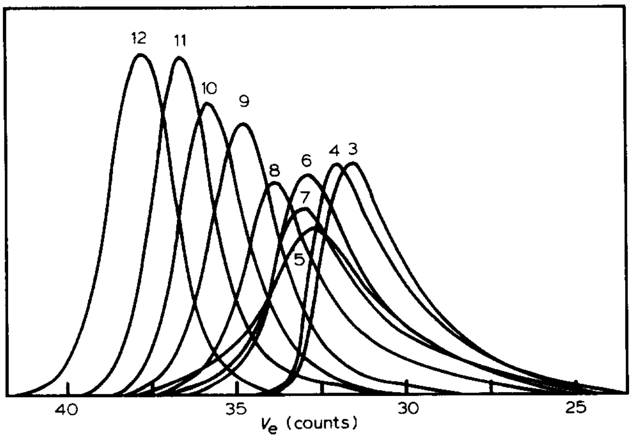

**Figure 1** G.p.c. chromatograms shown as a function of the differential refractometric signal Δ*RI* vs. volume of elution (1 count = 5.32 ml) of ten fractions of poly(*N*-vinyl-3,6-dibromocarbazole) (PVK-3,6-$Br_2$) in tetrahydrofuran at 25°C. Other experimental conditions are indicated in the text (see Experimental section)

## THEORY AND NUMERICAL TREATMENT

### *Calibration curve for molecular weight*

In a previous paper some of the present authors[41] have used a method to analyse g.p.c. data by means of a nonlinear calibration of log $M$ vs. elution volume at the peak, $V_e$(peak), using an iterative computer method applicable to polydisperse samples. It was very useful to test the validity of the universal g.p.c. calibration of log $V_h$ ($V_h$ = hydrodynamic volume) vs. $V_e$(peak).

This method and the procedures developed can be extended without any difficulties to the establishment of true Mark–Houwink equation parameters $K$ and $a$, as well as to the resolution of some other problems related to the combination of g.p.c. and dilute solution properties of polymers.

The determination of true $K$ and $a$ parameters will be dealt with in the next subsection. We explain here the g.p.c. calibration problem first, because it is needed as input into the calculation of $K$ and $a$.

In the present investigation, two different approaches to obtain the $\log M = f(V)$ calibration curve have been chosen. One is that proposed by Szewczyk[42] and the other by McCrackin[43]. Both include nonlinear effects. In both cases the equation sought is of the form:

$$\log M = \sum_{k=0}^{n} A_k V^k = A_0 + A_1 V + A_2 V^2 + \ \ldots\ A_n V^n \qquad (6)$$

where $M$, $V$, $A_0, A_1, \ldots, A_n$ represent the molecular weight of an ideally monodisperse species, its elution volume and polynomial coefficients, respectively. The experimental data for $M$ and $V$ are the elution volume at the peak, $V_e$(peak), of each of the fractions and their corresponding average molecular weight, $\bar{M}$. In our case, as $\bar{M}$ we may use $\bar{M}_n$ determined by membrane osmometry, or $\bar{M}_w$ determined by light scattering. $A_0$, $A_1$, $A_2$, ..., $A_n$ in equation (6) are unknown coefficients chosen to produce the least root-mean-squared relative deviation ($\sigma$) between the calculated and experimental values of $M$ for the set of fractions used in the calibration. If $n$ is the total number of fractions, $\sigma$ is defined by:

$$\sigma = \left[\frac{1}{n}\sum_{i=1}^{n}\left(1 - \frac{\bar{M}_i(\text{calc})}{\bar{M}_i(\text{exp})}\right)^2\right]^{1/2} \qquad (7)$$

and $\sigma$ should be a minimum.

The calculated values of the averages $\bar{M}_i$ are obtained from the g.p.c. chromatograms of the fractions. Calling $H_i$ the normalized chromatogram of the $i$th fraction, we have:

$$\bar{M}_{n,i}(\text{calc}) = \left(\int_0^{\infty} \frac{H_i(V)}{M(V)}\,\mathrm{d}V\right)^{-1} \qquad (8)$$

$$\bar{M}_{w,i}(\text{calc}) = \int_0^{\infty} H_i(V) M(V)\,\mathrm{d}V \qquad (9)$$

In the method proposed by Szewczyk[42], the minimum deviation is sought by an iterative procedure. The experimental $\bar{M}_i$ and $V_{e,i}$ values are used as trial values and least-squares regression is applied repeatedly in a cyclic way until a minimum $\sigma$ is reached. Details about the previous application of this method to another polymer can be found elsewhere[41].

In the method of McCrackin[43] (method I in his paper), extremum conditions with respect to $A_0$, $A_1$, $A_2$,... are imposed and the resulting equations are then solved for the coefficients. The extremum conditions are $\partial\sigma/\partial A_l=0$ ($l=0, 1, 2,\ldots$). For $l=0$, it is found that:

$$10^{A_0}=\left(\sum_{i=1}^{n}\frac{S_i^0}{\bar{M}_i}\right)\left[\sum_{i=1}^{n}\left(\frac{S_i^0}{\bar{M}_i}\right)^2\right]^{-1} \tag{10}$$

where $\bar{M}_i$ is the experimental value of the average $\bar{M}_i=\bar{M}_i(\mathrm{exp})$, and $S_i^0$ has the following meaning. Let us define a general $S_i^l$, where $l$ can be $l=0, 1, 2,\ldots$. Depending on the type of average being used in the calibration, $S_i^l$ has a different expression. If the $\bar{M}_i$ values are weight averages ($\bar{M}_{w,i}$), then:

$$S_i^l=\int_0^\infty H_i(V)10^{A_1V+A_2V^2+\cdots}V^l\,\mathrm{d}V \tag{11}$$

but, if the $\bar{M}_i$ values are number averages ($\bar{M}_{n,i}$), then:

$$S_i^l=\left(\int_0^\infty H_i(V)10^{-(A_1V+A_2V^2+\ldots)}V^l\,\mathrm{d}V\right)^{-1} \tag{12}$$

$A_0$ is the only coefficient that can be written explicitly. The other coefficients ($A_1$, $A_2$,...) are given implicitly in the equations that result from the extremum conditions for $l=1, l=2,\ldots$. The form of such equations also depends on the type of average $\bar{M}_i$ being used. If they are $\bar{M}_w$, then:

$$10^{A_0}=\left(\sum_{i=1}^{n}\frac{S_i^l}{\bar{M}_i}\right)\left(\sum_{i=1}^{n}\frac{S_i^0S_i^l}{\bar{M}_i^2}\right)^{-1} \tag{13}$$

and if they are $\bar{M}_n$, then:

$$10^{A_0}=\left(\sum_{i=1}^{n}\frac{(S_i^0)^2}{S_i^l\bar{M}_i}\right)\left(\sum_{i=1}^{n}\frac{(S_i^0)^3}{S_i^l\bar{M}_i^2}\right)^{-1} \tag{14}$$

There is one such pair of equations for every value of $l$ ($l=1, 2, \ldots$). In fact, equations (13) and (14) can be generalized to cover $l=0$ also, since equation (10) is a particular case of both equations (13) and (14).

In our application of this method to determine $A_1$, $A_2$,..., we follow a procedure somewhat modified with respect to that originally described by McCrakin[43]. The modification consists on minimizing $\sigma$ (equation (7)) as a function of $A_1$, $A_2$,... (equation (6)) by using a minimization routine. Thus, for each trial set $\{A_1, A_2, \ldots\}$, equations (11) or (12) is used to compute $S_i^0$; then $A_0$ is calculated with equation (10); substitution of $A_0$, $A_1$, $A_2$,... into equation (6) and of the calculated $\bar{M}$ into equation (7) gives the deviation $\sigma$ for that particular set. The procedure is then repeated, treating $A_1$, $A_2$,... as independent variables, until a minimum for $\sigma$ is attained.

We have applied both the methods of Szewczyk[42] and of McCrackin[43] (modified) to our data of $V_e$(peak), $\bar{M}_n$ and $\bar{M}_w$. The degree of the polynomial in $V$ tested (equation (6)) has been the usual linear ($l=0, 1$) and also quadratic ($l=0, 1, 2$). The results of the calculation are as follows.

In *Table 2* we show the results obtained with the ten fractions studied here using their $\bar{M}_w$ values as average molecular weights for the calibration. We can see that the methods of Szewczyk[42] and of McCrackin[43] lead to essentially the same results. It is also evident that, in either method, no significant improvement is achieved by use of a second-degree polynomial instead of the linear calibration. The results shown in *Table 2* for the method of Szewczyk[42] correspond to three iterations. After three iterations the value of $\sigma$ reached is very close to that obtained by the method of McCrackin[43]. For higher iterations, some small oscillations occur.

For several of the fractions studied here, we have determined both $\bar{M}_n$ and $\bar{M}_w$. Therefore, we can check the sensitivity of the calibration curve to the kind of average being used. For this study we consider the six consecutive fractions (F-7 through F-12) whose $\bar{M}_n$ and $\bar{M}_w$ values are known. With two different molecular weight averages available for each fraction, we can gauge the goodness of the calibration by two different $\sigma$ values, one referred to $\bar{M}_w$ and the other referred to $\bar{M}_n$. The results obtained applying the method of McCrackin[43] to the six consecutive fractions with known $\bar{M}_n$ and $\bar{M}_w$ are shown in *Table 3*. We can see that the results obtained using $\bar{M}_n$ or $\bar{M}_w$ as average molecular weight of the fractions are very similar. The calibration curve is not significantly dependent on the type of average being used.

In *Figure 2* we show the calibration curve determined with all ten fractions compared with the experimental values of $\bar{M}_n$ and $\bar{M}_w$ against $V_e$(peak).

### *Viscosity calibration and Mark–Houwink–Sakurada parameters*

To determine the viscosity equation $[\eta]=KM^a$ or the Mark–Houwink–Sakurada constants $K$ and $a$, using fractions of finite polydispersity, poses a problem similar to the g.p.c. calibration. The analogy between both kinds of problems can be established by writing:

$$\log[\eta]=\log K+a\log M \tag{15}$$

where $[\eta]$ and $M$ refer to strictly monodisperse values. We then define the average value of $[\eta]$ for the $i$th fraction,

**Table 2** G.p.c. calibration (ten fractions; average molecular weight $\bar{M}_w$)

| Case | Degree of polynomial (equation (6)) | Method | $\sigma$ (equation (7)) | Parameters of equation (6) $A_0$ | $A_1$ | $A_2$ |
|---|---|---|---|---|---|---|
| 1 | 1 | McCrackin | 0.121 | 9.651 | −0.13136 | – |
| 2 | 1 | Szewczyk | 0.127 | 9.813 | −0.13608 | – |
| 3 | 2 | McCrackin | 0.120 | 7.480 | 0.00070 | −0.001988 |
| 4 | 2 | Szewczyk | 0.130 | 11.310 | −0.22791 | 0.001394 |

**Table 3** Comparison between g.p.c. calibrations using $\bar{M}_n$ or $\bar{M}_w$ (six fractions; method of McCrackin)

| Case | Degree of polynomial (equation (6)) | Average molecular weight used | $\sigma(\bar{M}_w)$ | $\sigma(\bar{M}_n)$ | $\frac{1}{2}[\sigma(\bar{M}_w)+\sigma(\bar{M}_n)]$ | $A_0$ | $A_1$ | $A_2$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | $\bar{M}_w$ | 0.114 | 0.121 | 0.118 | 9.533 | −0.12798 | – |
| 2 | 1 | $\bar{M}_n$ | 0.200 | 0.075 | 0.137 | 10.381 | −0.15206 | – |
| 3 | 2 | $\bar{M}_w$ | 0.089 | 0.076 | 0.082 | 1.084 | 0.37303 | −0.007376 |
| 4 | 2 | $\bar{M}_n$ | 0.099 | 0.063 | 0.081 | 1.047 | 0.37358 | −0.007376 |

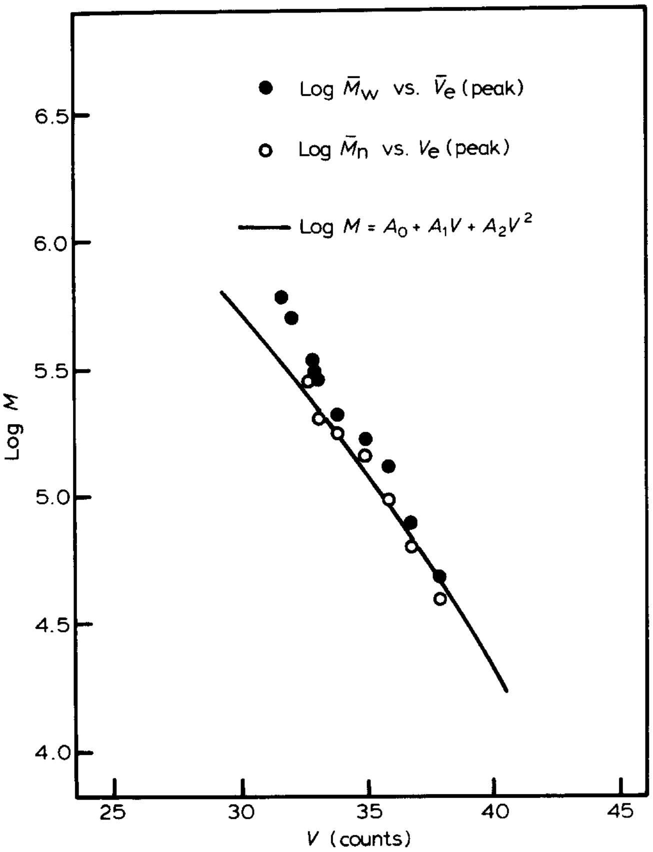

**Figure 2** G.p.c. calibration curve on a semilogarithmic scale for the PVK-3,6-Br$_2$ fractions: full circles are experimental results of the log $\bar{M}_w$ (experimentally measured by light scattering) vs. elution volume at the peak $V_e$(peak); open circles are experimental results of log $\bar{M}_n$ (experimentally measured by membrane osmometry) vs. elution volume at the peak $V_e$(peak); full curve is calibration curve log$M$ vs. $V$ fitted to the experimental results with a second-degree polynomial (see *Table 2*, case 3)

$[\bar{\eta}]_i$, and calculate it from the normalized chromatogram of that fraction, $H_i$, as:

$$[\bar{\eta}]_i(\text{calc}) = \int_0^\infty H_i(V)K[M(V)]^a \mathrm{d}V \qquad (16)$$

Parallel to equation (7) we may also define a root-mean-square deviation, $\sigma'$:

$$\sigma' = \left[\frac{1}{n}\sum_{i=1}^{n}\left(1 - \frac{[\bar{\eta}]_i(\text{calc})}{[\bar{\eta}]_i(\text{exp})}\right)^2\right]^{1/2} \qquad (17)$$

where $[\bar{\eta}]_i$(exp) is the experimentally determined intrinsic viscosity of fraction $i$.

The problem of determining the viscosity equation is to obtain the values of coefficients log$K$ and $a$ in equation (15) that produce the least $\sigma'$. To solve this problem we can use the same numerical methods devised to obtain the calibration curve in g.p.c. Since in the calculation of $[\bar{\eta}]_i$(calc) we need $M(V)$, our procedure to determine the viscosity equation is as follows:

(i) From the experimental data for $\bar{M}$ vs. $V_e$ and the chromatograms $H(V)$, we determine the g.p.c. calibration curve $M(V)$ yielding the least $\sigma$.

(ii) Then, with this calibration curve, we use the experimental data for $[\bar{\eta}]$ vs. $\bar{M}$ and the chromatograms $H(V)$ to determine $K$ and $a$ giving the least $\sigma'$.

The results thus obtained are shown in *Table 4*. These results are for the method of McCrackin. The method is applied twice: first to $M$ vs. $V_e$ to determine $M(V)$, and then to $[\bar{\eta}]$ vs. $M$ to determine $K$ and $a$. The results obtained applying the method of Szewczyk, also twice, are very similar to those shown.

Comparing rows 1 and 2 of *Table 4* we can see that the Mark–Houwink–Sakurada constants are insensitive to the degree of the polynomial used as calibration curve in g.p.c. Comparing rows 4 and 5 of *Table 4* we can see that $K$ and $a$ are also insensitive to the type of average molecular weight ($\bar{M}_n$ or $\bar{M}_w$) used for the fractions.

It should be noted that the choice of $\bar{M}_n$ or $\bar{M}_w$ is maintained through steps (i) and (ii) of the procedure described above. That is, the same type of average is used to determine the g.p.c. calibration and the Mark–Houwink–Sakurada equation.

In *Figure 3* we represent the Mark–Houwink–Sakurada equation determined with all ten or only six fractions compared with the experimental results of $[\bar{\eta}]$ against $\bar{M}_n$ and $\bar{M}_w$. The full straight line on *Figure 3* can be drawn with values for Mark–Houwink–Sakurada parameters $K$ and $a$ given in *Table 4*, either for cases 1 or 2, since they yield almost identical sets of values for $K$ and $a$ (i.e. degree of polynomial 1 or 2, average molecular weight $\bar{M}_w$, and ten fractions for the fitting), or for case 3( i.e. degree of polynomial 1, average molecular weight $\bar{M}_w$, and six fractions for the fitting). All this indicates the non-sensitivity of the type of polynomial and number of fractions selected in the search for $K$ and $a$.

It may be of interest to question whether the intrinsic viscosities of the subfractions within a fraction follow the same viscosity equation as the fractions themselves. The answer is no. In *Figure 4* we show a typical example of the variation of log$[\eta]_{i,k}$ vs. log$M(V_{i,k})$ (subfraction $k$ within fraction $i$), compared with the Mark–Houwink–Sakurada equation drawn in *Figure 3*. The results shown in *Figure 4* are for fraction F-7, but they are representative of the general behaviour displayed by most of the fractions. In general, in our case, log$[\eta]_{i,k}$ is a curved function of log$M(V_{i,k})$ with an upward trend for the few last and early eluting subfractions. The same upward curvature and some other trends have been observed in the current literature. Thus, we observe upward curvature in the

**Table 4** Constants $K$ and $a$ of the Mark–Houwink–Sakurada equation: $[\eta]=K\bar{M}_v^a$

| Case | Degree of polynomial in g.p.c. calibration | Average molecular weights used in g.p.c. calibration and in MHS equation | Fractions used | $\sigma'$ (equation (17)) | $K\times10^3$ ($cm^3\,g^{-1}$) | $a$ |
|---|---|---|---|---|---|---|
| 1 | 1 | $\bar{M}_w$ | 10 | 0.106 | 0.910 | 0.827 |
| 2 | 2 | $\bar{M}_w$ | 10 | 0.108 | 0.947 | 0.823 |
| 3 | 1 | $\bar{M}_w$ | 6 | 0.061 | 0.969 | 0.822 |
| 4 | 2 | $\bar{M}_w$ | 6 | 0.051 | 1.214 | 0.802 |
| 5 | 2 | $\bar{M}_n$ | 6 | 0.051 | 1.210 | 0.805 |

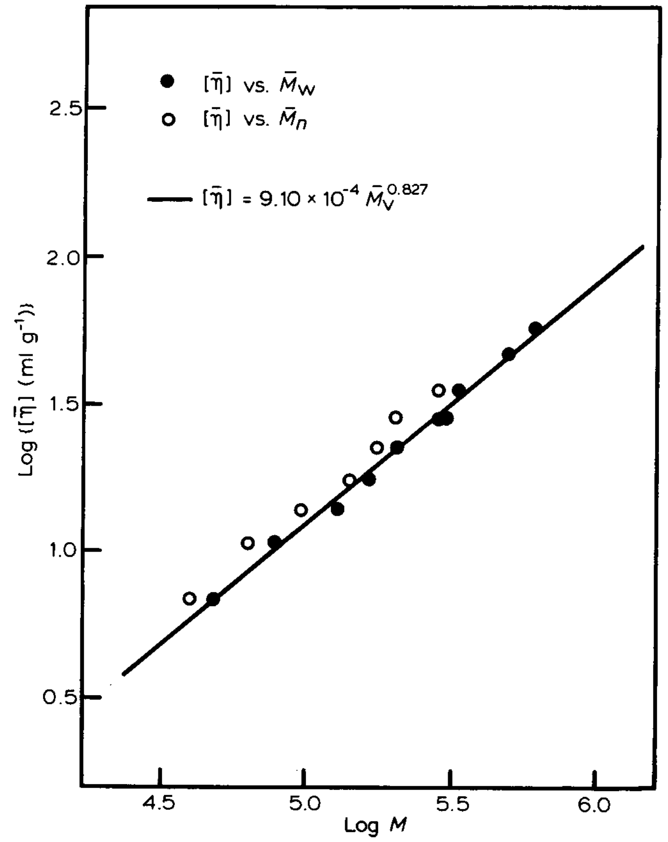

**Figure 3** Mark–Houwink–Sakurada relationships for PVK-3,6-$Br_2$ in THF at 25°C (log–log coordinates). Intrinsic viscosities $[\bar{\eta}]$ represent values measured by conventional viscometry. Full circles are intrinsic viscosities $[\bar{\eta}]$ plotted against weight-average molecular weights $\bar{M}_w$ measured by light scattering. Open circles are intrinsic viscosities $[\bar{\eta}]$ plotted against number-average molecular weights $\bar{M}_n$ measured by membrane osmometry. Full straight line is calibration line constructed on the basis of the Mark–Houwink–Sakurada constants estimated in the present work (see *Table 4*, case 1)

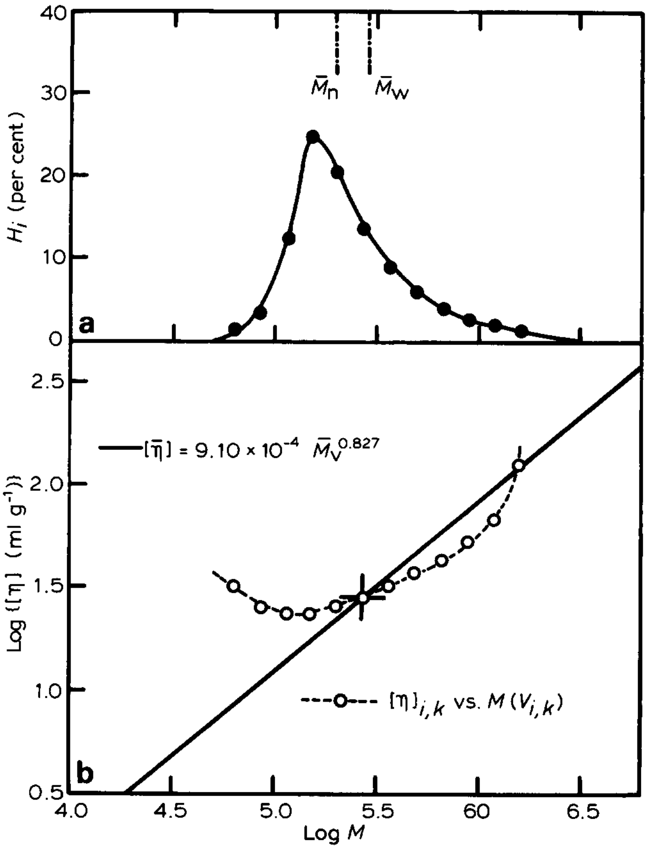

**Figure 4** (a) Normalized differential distribution plot for fraction F-7 of PVK-3,6-$Br_2$ determined from g.p.c. fractionation. (b) Calibration line (———) constructed on the basis of the Mark–Houwink–Sakurada constants estimated in the present work (see *Table 4*, case 1), and distribution of intrinsic viscosities $[\eta]_{i,k}$ as a function of $M(V_{i,k})$ for subfractions from fraction F-7 (-- ○ --). Intrinsic viscosities measured by automatic capillary viscometry. The cross represents the actual value of $[\bar{\eta}]$ for fraction F-7 measured by conventional viscometry

results of Peureux and Lochon[21] (their Table 2) for PS in tetrahydrofuran at 50°C.

A possible source of error may be that in dealing with extremely dilute solutions anomalous viscosity behaviour may occur. Various explanations have been suggested for such anomalous viscosity behaviour, some associated with the polymer itself[44,45] and others arising from the experimental technique of intrinsic viscosity[46–48]. Both effects may be present here.

On top of the representation $\log[\eta]_{i,k}$ vs. $\log M(V_{i,k})$ of *Figure 4*, we have added the plot of $H_i$ vs. $\log M(V_{i,k})$ to show the relative weights of the subfractions and appreciate which are the most important in determining the average $[\bar{\eta}]_i$ of the whole fraction. The actual experimental value, $[\bar{\eta}]_i$(exp), measured by conventional viscometry, is denoted by a cross in *Figure 4*. $\bar{M}_n$ and $\bar{M}_w$ are also shown on the same plot for comparative purposes only.

Grübisic-Gallot *et al.*[28] have obtained acceptable agreement between parameters $K$ and $a$ obtained by classical viscometry on narrow *MWD* samples of PS, when results for the middle subfractions only are considered and those for tail and head subfractions are disregarded.

The direct relationship between intrinsic viscosities and elution volume may also be useful. Making use of equation (6) for the case $n=1$ and substituting into equation (15), we obtain:

$$\log[\eta]=(\log K+aA_0)+aA_1V \qquad (18)$$

From the g.p.c. and $K$ vs. $a$ calibrations (case 1 in *Tables 2* and *4*: $A_0=9.651$, $A_1=0.13136$, $K=9.10\times10^{-4}$ cm$^3$ g$^{-1}$, $a=0.827$) we get:

$$\log[\eta]=4.94-0.108V \qquad (19)$$

In *Figure 5* we show this equation (19) as a broken line. The filled circles represent the experimental $\log[\bar{\eta}]$ vs. $V_e$(peak) ($[\bar{\eta}]$ measured by conventional viscometry). It may be seen that all the points lie almost in a straight line with little scatter, but this line does not agree with the calibration expressed by equation (19) (broken line). The reason for this discrepancy is that $V_e$(peak) is not a good representation of the viscometric average.

When the viscosity-average volume of elution, $\bar{V}_v$, defined in equation (14) of ref. 33 and calculated with the use of the g.p.c. chromatograms, is used instead of $V_e$(peak), then the resulting plot $\log[\bar{\eta}]$ vs. $\bar{V}_v$ of the experimental points, drawn as half-filled circles in *Figure 5*, lies on the calibration curve. In other words, $V$ in equation (19) is equivalent to $\bar{V}_v$ for a heterodisperse sample or fraction.

It is clear, then, that not using the correct volume of elution may lead to serious errors in establishing good correlation between $\log[\eta]$, $\log M$, or $\log[\eta]M$ (universal calibration) vs. elution volume.

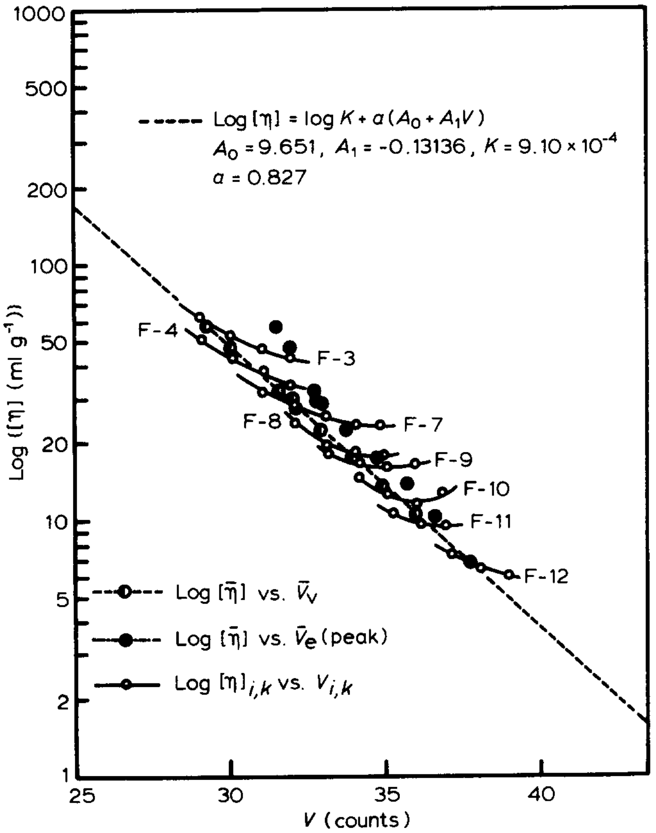

**Figure 5** The broken line represents $\log[\eta]$ vs. $V$ (counts) constructed by means of equation (18) using parameters from *Table 2*, case 1, and *Table 4*, case 1. The open circles show $\log[\eta]_{i,k}$ as a function of the volume of elution $V_{i,k}$(counts) for selected subfractions (see the text) from eight fractions of PVK-3,6-Br$_2$ in tetrahydrofuran at 25°C. The $[\eta]_{i,k}$ have been measured by automatic capillary viscometry. The full circles are experimental results of $\log[\bar{\eta}]$ vs. volume of elution at the peak $V_e$(peak). Intrinsic viscosities determined by conventional viscometry in THF at 25°C. The half-filled circles are experimental results of $\log[\bar{\eta}]$ vs. their viscosity-average volume of elution $\bar{V}_v$(counts). Intrinsic viscosity determined by conventional viscometry in THF at 25°C

It is also of interest to compare these results with those from automatic capillary viscometry done on the subfractions belonging to each one of the fractions. By plotting $\log[\eta]_{i,k}$ vs. the respective elution volume $V_{i,k}$ (open circles in *Figure 5*), we find an anomalous dependence similar to that shown for $\log[\eta]$ vs. $\log M$ in *Figure 4*. In *Figure 5* data for fractions F-5 and F-6 are omitted for the sake of clarity. Also, subfractions amounting to less than 10% of the total fraction are not represented. The full curves of *Figure 5* are drawn joining subfractions from the same fraction.

As in *Figure 4*, the subfractions with the highest weight of each fraction lie almost on our calibration curve given by equation (19). But the whole set of subfractions belonging to a given fraction does not follow the Mark–Houwink equation. This is also clearly seen in that subfractions having the same $M(V)$ but belonging to different fractions have widely different values of $[\eta]$.

The same characteristic dependence between $\log[\eta]_{i,k}$ and $V_{i,k}$ for subfractions has been found by other authors[49–51]. Brüssau[52] has found some anomalous effects when coupling g.p.c. effluent to automatic capillary viscometer. He could not obtain agreement between calibration curves derived by plotting $\log[\eta]_{i,k}$ vs. $V_{i,k}$ for all the subfractions and those for the fraction measured by classical viscometry. Janča and Kolínský[51] and Janča and Pokorný[53] attributed this to inadequate resolution of their g.p.c. separation systems.

Mencer and Grübisic-Gallot[50] have discussed the dependence of intrinsic viscosity on elution volume in the same terms as those used to explain the non-universality of the universal calibration in the case of chemically modified silica, i.e. by the presence of some preferential interactions between polymer, solvent and active sites on the gel.

Holt *et al.*[54], in studying the system cellulose trinitrate/ethyl acetate on styragel columns, have shown that the concentration of the injected samples exerts a strong influence on the dependence between intrinsic viscosity and elution volume, and Soeteman *et al.*[55] have analysed how the intrinsic viscosity is related to the elution volume taking into account dispersion.

## CONCLUDING REMARKS

The method proposed here is based on knowledge of the actual molecular weight distribution of each fraction by means of its respective chromatogram and on the direct g.p.c. calibration. This method should, in principle, lead to more accurate values for $K$ and $a$ than other more elementary methods, which are based either on the assumption of a given theoretical form for the *MWD* of the samples or on the validity of the universal calibration concept.

The improvement gained by applying the present numerical procedure should be larger when the samples to be characterized have different polydispersities because of their different molecular weight distributions. However, this does not apply to the samples used here in the experimental work, since all of them came from the same fractionation batch, they give chromatograms of similar shape and their $\bar{M}_w/\bar{M}_n$ values are not very different. In order to test the limits of applicability of the numerical method, samples with different as well as with broader *MWD*s would be required.

Therefore, with our experimental data for PVK-3,6-$Br_2$ fractions, almost the same results for $K$ and $a$ can be obtained using a classical method, such as the one given by Schulz *et al.*[6] But this is not always the case, and in general the characteristics of the fractions employed to establish the Mark–Houwink equation may differ in some extent from one another. Since the method proposed here is relatively simple and does not demand excessive primary data, its application as a general procedure to establish the Mark–Houwink constants of any polymer–solvent system at different temperatures seems justified.

A practical application of the present method to the g.p.c. technique could be as follows. Once the $K$ and $a$ parameters have been firmly established, the data of intrinsic viscosity can be used to determine the true g.p.c. universal calibration plot, with which to determine *MWD* characteristics of some other samples, or to analyse the non-exclusion phenomena which take place in some g.p.c. systems.

Our method of determining $K$ and $a$ is not restricted to only one average of molecular weight for the fractions. With polydisperse samples or fractions, the calibration can be done using more than one average property for each of the samples employed.

Thus, the experimental $[\bar{\eta}]_i$ values can also be used as an average property together with some other available information such as $\bar{M}_{n,i}$ and/or $\bar{M}_{w,i}$. Under these circumstances, the calibrating equation is determined to produce the least sum of relative root-mean-squared deviations for all the averages used, namely:

$$\sigma(\bar{M}_n)+\sigma(\bar{M}_w)+\sigma'([\bar{\eta}]) \qquad (20)$$

as has been suggested by Belenkii and Vilenchik[56].

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