PII: S0032-3861(96)01043-9

Polymer Vol. 38 No. 17, pp. 4455–4468, 1997

0032-3861/97/$17.00 + 0.00

A comparison of calibration procedures for the analysis of broad molecular weight distributions using size exclusion chromatography with multiple detection

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(Received 1 May 1996; revised 11 November 1996)

A range of well characterized broad polymer standards has been analysed using size exclusion chromatography (s.e.c.), with differential refractive index, low angle laser light scattering (LALLS) and differential viscometry (DV) as on-line detection methods. This study highlights the importance of accurate and precise estimation of the inter detector delay (IDD) parameter and shows that the conventional methods of IDD measurement will lead to errors in calculation of the molecular weight (MWT) moments and also large errors in calculated Mark–Houwink–Sakurada (MHS) parameters. The method of IDD calculation suggested by Suddaby *et al.* (Suddaby, K. G., Sanayei, R. A., O'Driscoll, K. F., Rudin, A., *Makromol. Chem.*, 1993, **194**, 1965) is found to be superior, and like the earlier workers we found the IDD to be MWT sensitive for both the LALLS and DV detectors. This work shows that if the MWT dependence of IDD is ignored, then this leads to a distortion in the measured relationship between intrinsic viscosity (IV) and molecular weight. This work also highlights the shortcomings of using the MHS relationship to represent the IV–MWT relationship, and we clearly show that the Stockmayer–Fixman (SF) equation is a better relationship for s.e.c. calibration over a broader MWT range. The SF equation is also recommended, as K_θ can be readily estimated from group contribution calculations thus allowing the IV–MWT relationship to be defined with one adjustable parameter, K' (or B), which itself has a thermodynamic significance. A computer program, which adds seamlessly to existing commercial software (*PL Caliber*), has been written to implement these improved calibration methods. MHS constants, K and α, and SF constants, K' and K_θ, are reported for a number of polymers. © 1997 Elsevier Science Ltd.

(Keywords: gel permeation chromatography; size exclusion chromatography; Mark–Houwink–Sakurada)

INTRODUCTION

Size exclusion chromatography (s.e.c.) has become established as the principal method of molecular weight (MWT) analysis in many polymer laboratories. As with all instrumentation the equipment can be used as a 'black box' to provide crude numbers for comparative purposes, or if precise numbers are required then a very careful calibration procedure should be applied prior to measurement. S.e.c. is not an absolute method, and calibration is normally effected by using narrow polydispersity (PDI) poly(styrene) (PSTY) or poly(methyl methacrylate) (PMMA) standards. In these circumstances accurate MWT data can only be obtained for PSTY or PMMA unknowns, and other polymer analyses are reduced to semi-quantitative/qualitative status. In order to overcome this limitation absolute on-line detection systems have been developed by a number of manufacturers, and the use of these detection systems, viz., low angle laser light scattering (LALLS) and differential viscometry (DV), is now widespread.

For those researchers restricted to differential refractive index (DRI) analysis, the use of the universal calibration curve (UCC) together with Mark–Houwink–Sakurada (MHS) constants has provided a means to analyse their data in a quantitative fashion. Of serious concern in this instance is the wide variability in the values of MHS parameters available in the literature, which forces the researcher to make a subjective judgement in the choice of values to use. This relegates the use of the UCC with MHS parameters to semi-quantitative utility. The classical method for determining MHS parameters is to use narrow PDI polymers from either anionic synthetic origin or from fractionated broad MWT samples. The molecular weight of each fraction or sample is measured by an absolute MWT method, such as static light scattering or membrane osmometry. These MWT data are combined with intrinsic viscosity (IV) data for each sample determined via a suspended level viscometer. The data are then fitted to a linearized version of the MHS equation. As this procedure is tedious, most workers now prefer to use an on-line viscometer with s.e.c., which effectively fractionates the sample and provides IV data for each MWT 'slice'. Most commercial software packages allow calculation of MHS parameters from s.e.c.–DV, and this has led to a flood of different values in the literature for identical polymers. Our own experience showed considerable operator

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Table 1 Sample details for broad secondary standards

Polymer	Source	CAT. #	M_n	M_w	PDI
PEMA	SPP	113C	126000	340000	2.7
P(*n*-BMA)	SPP	111C	73500	320000	4.4
P(iso-BMA)	SPP	112C	140000	300000	2.1
PVC 1	SPP	038C	37400	83500	2.2
PVC 2	ARROW LAB. INC.	400-2	25500	62350	2.5
PVC 3	ARROW LAB. INC.	400-3	41000	107166	2.4
PVC 4	ARROW LAB. INC.	400-4	54000	117800	2.4
PLMA	SPP	168C	77000	113000	1.5
PMMA	Rohm & Haas	MS-1036	105000	240000	2.3
PSTY	DOW Chemical Co.	DOW	110000	260000	2.4

dependence for the determination of MHS parameters using an on-line viscometer with commercial software, and we have sought to understand the origin of this variability and to seek the best method(s) for overcoming the subjective nature of multiple-detector s.e.c. analyses. Regarding the estimation of MHS parameters we were originally puzzled that there is widespread agreement among the values reported for PSTY and PMMA, but large differences among values reported for other polymers. In the course of this work it became clear to us the strong influence that the operator can have on the data analyses, and we discuss this later in the paper. This work constitutes our attempts, which were largely successful, to ensure the objectivity of MWT data from our s.e.c. analyses. In the course of this work we developed a software program to fully implement the corrections necessary to acquire accurate and precise data from multiple detector s.e.c. equipment.

EXPERIMENTAL

Eluent

Tetrahydrofuran (THF) was refluxed on sodium metal and benzophenone until dry and then distilled. The solvent was then stabilized with 0.025% of 2,6-di-*tert*-butyl-4-methyl-phenol and filtered through a 0.02 μm pore size filter (Whatman Anodisc 47, inorganic membrane) several times and stored in the dark until required.

Broad secondary standards

Broad secondary standards were supplied by Scientific Polymer Products (SPP) and Arrow Laboratories Inc. These standards were characterized by the suppliers for their weight-average MWT (M_w) by light scattering and number-average MWT (M_n) by membrane osmometry. Specific details on the following broad samples are given in *Table 1*: poly(ethyl methacrylate) (PEMA); poly(*n*-butyl methacrylate (P(n-BMA)); poly(i-butyl methacrylate) (P(iBMA)); poly(vinyl chloride) (PVC); poly(lauryl methacrylate) (PLMA). As well as these polymers, PMMA and PSTY were supplied by Rohm and Haas and the Dow Chemical Company, and were characterized from their respective calibration curves.

S.e.c. analysis

The s.e.c. set-up comprised the following equipment: a GBC Instruments LC1120 HPLC Pump operating at room temperature; a SCL-10A Shimadzu Auto-injector with 99 position sample rack and variable injection loop facility; a column set, which consisted of a PL 5.0 micrometer bead-size guard column (50 × 7.5 mm) followed by three fixed bed size Polymer Laboratories (PL) columns (300 × 7.5 mm, 5 μm particle size with 10^6, 10^5 and 10^3 Å pore size) and an in-line filter (0.2 μm). Three detectors were connected in a series configuration; a PL DRI detector, a PL LALLS detector and a Viscotek Model 250 DV. The data were collected using two PL data capture units (DCUs), and analysed using *PL Caliber* version 6.0 g.p.c./s.e.c. software. The eluent was THF at a flow rate of 1 ml min^{-1}. Sample injection size was 150 μl in all cases. Data were collected at 1 point per second. A flow rate marker (dioctyl phthalate) was used in all runs. The volumes of the LALLS and DRI cells were 0.1 and 12 μl respectively. The tubing used throughout the system was stainless steel capillaries of 0.02 cm inner diameter with Valco nuts and ferrules making the connection between pump, injector, columns and detectors.

Calibrations

DRI detector. The DRI detector was calibrated with a PSTY narrow polydispersity index (PDI) set consisting of ten individual standards purchased from PL (1.25×10^3 to 2.95×10^6 MWT) and a further five PSTY standards purchased from Tosoh (1.8×10^4 to 2.89×10^6 MWT). A PMMA set purchased from PL (1.14×10^3 to 1.577×10^6 MWT) was used to generate a PMMA calibration curve. The supplier determined peak maxima molecular weight (M_p) was used in the generation of the calibration curves.

LALLS detector. The PL LALLS detector used throughout these analyses employed a He–Ne laser with an output of 623.8 nm and a fixed low angle of detection (5°). The detector was calibrated in the usual way by injecting narrow PDI polymers (PSTY and PMMA) and calculating the instrument parameters K_{CONC} (response factor for the concentration detector) and K^{LS} (the light scattering calibration constant). Calculations of these parameters is done by the LALLS module of the *PL Caliber* software package[1]. An initial estimate of the inter-detector delay (IDD) between the DRI and LALLS detectors was also made by measuring the time difference between peak maxima obtained from narrow PDI calibrants.

Tuning of the LALLS parameters K_{CONC} and K^{LS} was accomplished by solving equations (1) and (2) for PSTY and PMMA with known concentration, dn/dc

and M_w.

$$K_{\mathrm{CONC}} = \frac{\delta V \cdot \sum h_i^{\mathrm{conc}}}{\left(\frac{\mathrm{d}n}{\mathrm{d}c}\right) \cdot c \cdot v} \tag{1}$$

$$K^{\mathrm{LS}} = \frac{M_w \cdot K' \cdot \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2 \cdot c}{\sum h_i^{\mathrm{LS}}} \tag{2}$$

where δV is the elution volume slice interval, $\sum h_i^{\mathrm{conc}}$ is the sum of the area under the concentration chromatogram, $\sum h_i^{\mathrm{LS}}$ is the sum of the area under the LALLS chromatogram, c is the sample concentration, v is the injection volume, $\mathrm{d}n/\mathrm{d}c$ is the DRI increment of the polymer sample in solution and K' is an instrument parameter.

DV detector. Prior to analyses the viscometer bridge was carefully balanced by zeroing the inlet pressure response and ensuring that the % imbalance in the bridge (%E) was well within the acceptable tolerance level as calculated by

$$\%E = \frac{4 \cdot DP}{(IP - 2 \cdot DP)} \times 100 \tag{3}$$

where DP = differential pressure (in Pa) and IP = inlet pressure (in kPa). For all the work described herein the % error in specific viscosity was less than 0.1%.

The DV was calibrated by injecting narrow PDI standards (PSTY and PMMA) and calculating the bulk IV for each sample via equation (4). The Universal Calibration as well as the MHS and viscosity calibration can then be constructed. Also an initial estimate of the IDD between the concentration detector and the viscosity detector is made by the calibration software[1] from lag time between narrow PDI calibrant peak maxima.

$$\mathrm{IV} = \frac{1}{m} \cdot \int_0^{\infty} \eta_{\mathrm{sp}}(v)\,\mathrm{d}v \tag{4}$$

where IV = bulk intrinsic viscosity, m = mass of sample injected, v = retention volume and $h_{\mathrm{sp}}(v)$ = specific viscosity as a function of retention volume.

BASIC THEORY FOR THE ANALYSIS METHOD FOR AN UNKNOWN POLYMER

The basic theory for combining the detector responses to yield MWT data has been published extensively elsewhere and so we shall only provide basic details necessary for the general reader to understand subsequent sections of this paper.

DRI detector

The DRI (or concentration) detector signal is combined with a calibration curve which is constructed from narrow polydispersity 'standards'. By knowing an appropriate IV–MWT relationship (e.g. MHS) then the molecular weight distribution (MWD) and relevant MWT averages can be calculated.

LALLS detector

The LALLS signal is combined with the concentration signal along with the parameters K_{CONC}, K^{LS}, concentration, $\mathrm{d}n/\mathrm{d}c$, injection volume and an estimate of the IDD. This allows MWT to be calculated at each slice along the chromatogram via equation (5). Thus the MWD and appropriate MWT averages can be calculated (note: the low concentrations used in s.e.c. allow the approximation to zero of the second virial coefficient $(A_2)^2$). Errors introduced by assuming zero concentration have been studied by Prochazka and Kratochvil[3]. These errors mainly affect the low molecular weight region and hence M_n.

$$M_i = \frac{K^{\mathrm{LS}} \cdot h_i^{\mathrm{LS}} \cdot I}{K' \cdot \left(\frac{\mathrm{d}n}{\mathrm{d}c}\right)^2 \cdot c_i} \tag{5}$$

where I indicates instrument parameters, h_i^{LS} is the height of the light scattering chromatogram at each elution volume and c_i is the concentration at each elution volume. K' is an optical constant and is defined as:

$$K' = \frac{2 \cdot \pi^2 \cdot n^2 \cdot (1 + \cos^2\theta)}{\lambda^4 \cdot N_A} \tag{6}$$

where n is the solvent refractive index, θ is the scattering angle, λ is the wavelength of the incident light and N_A = Avogadro's number.

Differential viscometer detector

The differential viscometer is a 4-capillary bridge type instrument based on an analogy to a Wheatstone bridge[4]. The advantage of this instrument is that the specific viscosity (η_{specific}) is determined directly and can be calculated via equation (7):

$$\eta_{\mathrm{specific}} = \frac{4 \cdot DP}{(IP - 2 \cdot DP)} \tag{7}$$

where IP is the inlet pressure and DP is the differential pressure to the bridge. The concentration signal is then combined with the specific viscosity signal to calculate the intrinsic viscosity ($\eta_{\mathrm{intrinsic}}$) at each elution volume via equation (8).

$$\eta_{\mathrm{intrinsic}} = \frac{\eta_{\mathrm{specific,\,i}}}{c_i} \tag{8}$$

An estimate of the IDD is required to combine the outputs from the DRI and DV detectors. Finally the intrinsic viscosity as a function of elution volume chromatogram is combined with the UCC which allows MWT to be calculated at each elution volume and hence the MWD and appropriate MWT averages.

RESULTS AND DISCUSSION

IDD estimation

When detectors are placed in series rather than parallel an IDD is required. This set-up is often preferred, as a parallel arrangement requires a flow-splitter which can lead to excess broadening. In addition a consequence of split flow is a reduction of the concentration of polymer going through the individual detection systems, and therefore a corresponding reduction in the signal-to-noise ratio.

The first important point to make is that the initial estimation of the IDD performed by the commercial software package is based on matching peak maxima derived from the responses of the detectors to the narrow PDI standards. In fact what is often generated by the operator is a single IDD number based on the

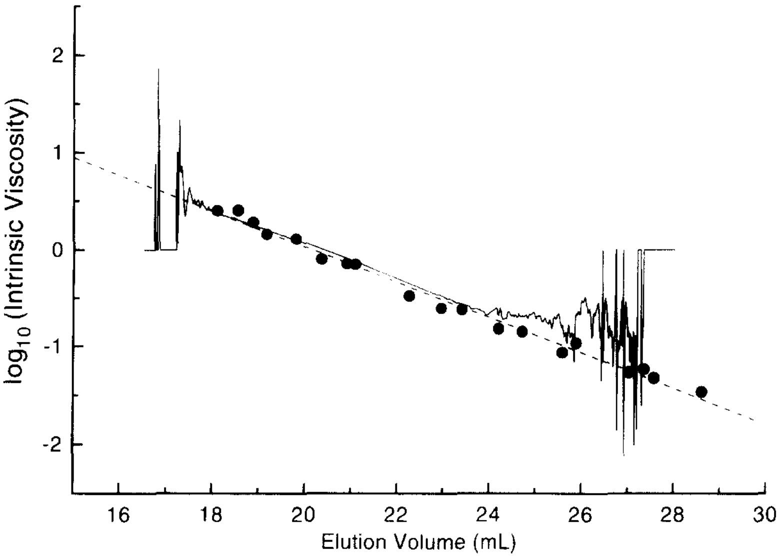

Figure 1 Optimized IDD calculation for DV detector. The dashed line (- - - -) is a first order polynomial fit to the narrow PDI calibrants (●) with an overlay of a broad PSTY from a DV analysis

arithmetical mean of several IDD estimates obtained for different molecular weight standards. This estimate is necessarily in error as the response of the detectors to a given MWT distribution is different as the detectors are inherently measuring different polymer properties.

The common understanding of the need for IDD estimation and correction is that the dead volume between the detectors must be accounted for, as this leads to a time-lag between the detector responses. As the calculation of MWT moments depends on peak 'slice' matching of the DRI (concentration) detector with the corresponding signals from either the LALLS or DV detectors, knowledge of IDD is absolutely crucial to accurate analyses. Even a small percentage error in IDD will distort the data[5,6]; typically IDD needs to be measured to a tolerance of 0.1 s or better. With this interpretation of IDD the ideal approach would be to calculate the inter-detector dead volume. However, previous attempts at this have failed, thereby suggesting that other factors need to be considered, namely, viscosity effects and different flow profiles in the various detector cells. An important point to make at this stage is that these additional factors may be dependent on the molecular weight of the polymer flowing through the tubing and cells.

As measuring the dead volume directly yields incorrect data, various procedures have been suggested to measure the *effective* dead-volume. As previously stated, it would be convenient to use narrow PDI polymers, but the small polydispersity may lead to the volume delay being overestimated[5].

Until recently the most accurate and precise technique for IDD evaluation for the Viscometer/DRI detector set is the manual search for an IDD, which successfully superimposes local IV vs retention volume for a broad polymer (PSTY or PMMA) on the plot of total IV of each narrow standard (from DV) *versus* retention volume (see *Figure 1*). A similar procedure has been found to be the best for the LALLS/DRI detector set, i.e. the IDD is manually searched until a plot of $\log_{10} M$ (for a broad polymer, PMMA or PSTY) vs retention volume superimposed on the respective polymers calibration curve (see *Figure 2*)[5,7,8].

The Suddaby–Sanayei method

Recent work by Suddaby and coworkers[9,10] has shown that the delay time between detectors in multiple detection systems is MWT sensitive. This means that the usual method of analysis, which involves accumulating the concentration detector and MWT sensitive detector and shifting them by the IDD in an attempt to overlay equivalent slices, is prone to large errors. For example, it is well documented in the literature[5,6] that the calculation of η_i is relatively insensitive to IDD, whereas the opposite is true for the estimation of the MHS K and α parameters. In an ingenious approach, Suddaby and coworkers[9,10] suggested that the MWT sensitive detectors are independently calibrated by *simulation* of the narrow PDI calibrants. Then the slices of the individual chromatograms (concentration and MWT sensitive) are 'slice'-matched through separate calibration curves.

Independent detector calibration

The signal from a concentration detector for a given 'slice' is proportional to the weight concentration of the polymer eluting through the detector, and hence

$$S_{i,\mathrm{conc}} \propto c_i \tag{9}$$

Similarly, in the case of an on-line viscometer the signal is proportional to the product of the weight concentration and intrinsic viscosity of the polymer eluting through the detector, and in the case of an on-line LALLS detector, the measured response is proportional to the weight concentration and MWT of the polymer eluting through the cell. Thus *simulation* of a DV and LALLS *signal* can be achieved by making the following transformations:

$$S_{i,\mathrm{visc}} \propto c_i \cdot [\eta_i] \tag{10}$$

$$S_{i,\mathrm{LALLS}} \propto c_i \cdot M_i \tag{11}$$

A simulated LALLS signal is shown in *Figure 3* for a narrow PDI calibrant. The analysis procedure requires that a separate independent calibration curve is generated for each detector. This is achieved by simulating each narrow PDI calibrant and using this simulated data to generate a new calibration curve. It should be stressed

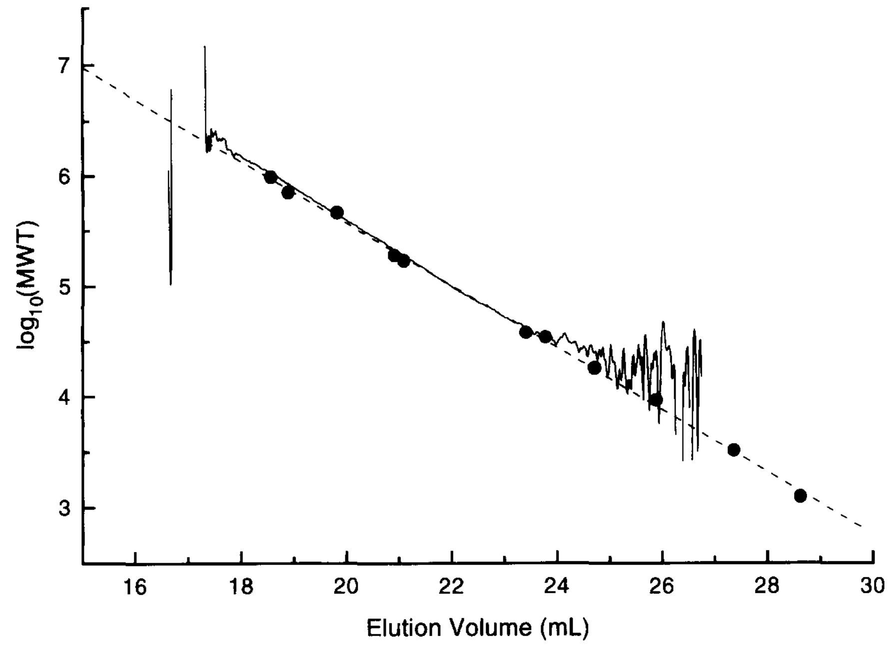

Figure 2 Optimized IDD calculation for LALLS detector. The dashed line (- - - -) is a first order polynomial fit to the narrow PDI calibrants (●) with an overlay of a broad PSTY from a LALLS analysis

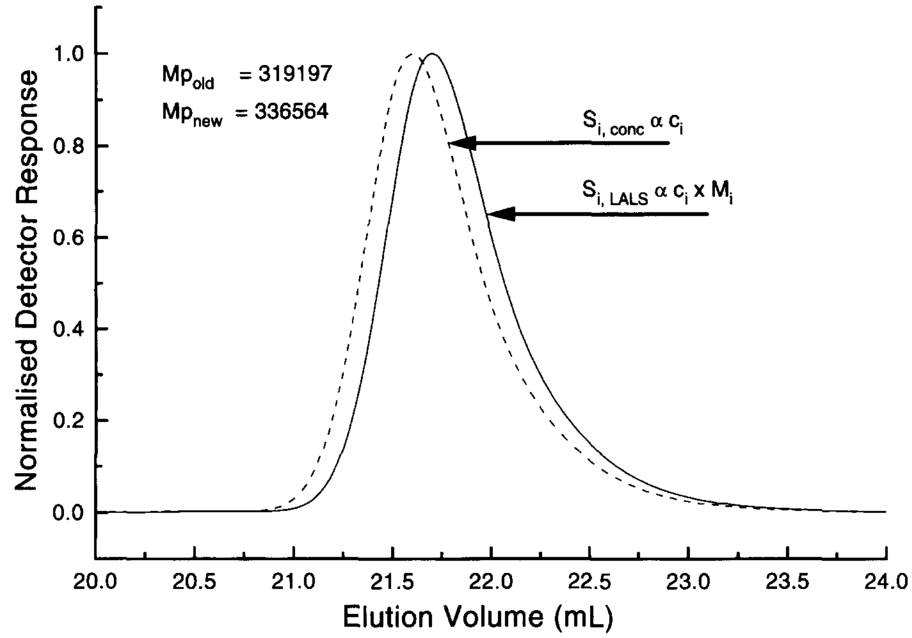

Figure 3 Comparison of responses from the concentration detector signal and the experimentally simulated LALLS response for a narrow PDI calibrant

that whilst the calibration is based on simulated chromatograms the transformations used in the procedure are firmly established, and therefore this process is fully justified on a theoretical basis.

In practice the LALLS signal can be *simulated*, using the DRI response to an injected narrow polydispersity calibrant, and equation (11) above, and a new peak maxima MWT (M_p) evaluated. This M_p is then *attributed* to the actual LALLS chromatogram trace, and so on for all the calibrants, thereby enabling a separate calibration curve to be derived for the LALLS detector. The same set of steps is performed for the DV detector, enabling a separate and independent calibration curve to be generated for this detector.

Analysis of an unknown is performed by 'slice' matching hydrodynamic volumes (HDVs) on these separate calibration curves, as shown in *Figure 4*. A computer program has been written to implement this type of analysis. This calibration method effectively obviates the need for an IDD estimation. In fact the IDD can be evaluated from the individual calibration curves, as shown in *Figure 5*. It is apparent from this analysis that the IDD is a function of molecular weight and this should be accounted for. The Suddaby–Sanayei method appears to be a superior method of calibration, as it makes no assumptions about the IDD but merely relies on molecular weight transformations which are firmly established. From *Figure 5* it is clear that both the DV

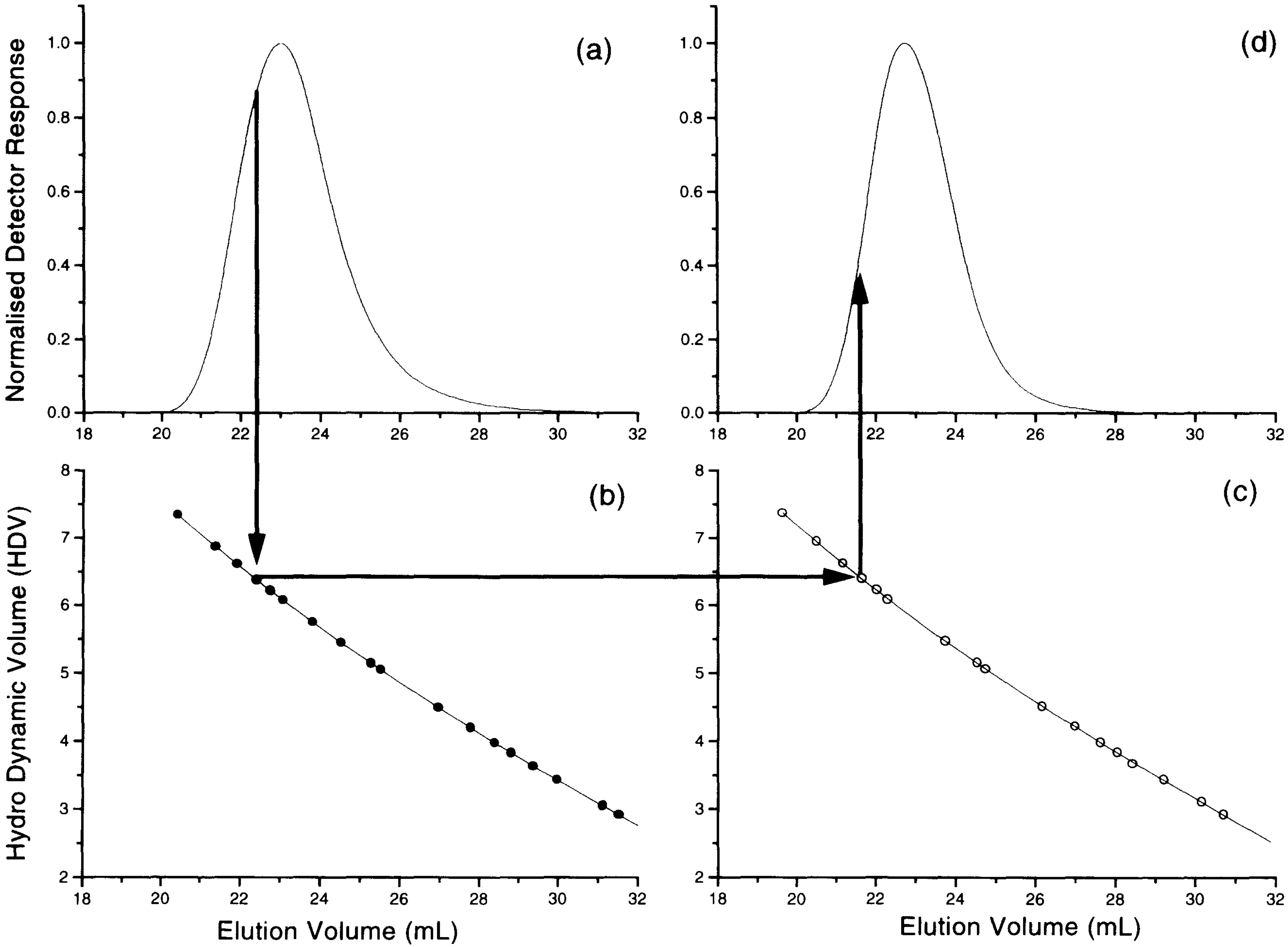

Figure 4 'Slice-matching' method of Suddaby–Sanayei *et al.* A slice is taken on the DRI response (a) and the corresponding HDV is found on the DRI calibration curve (b). The equivalent HDV is determined on the DV calibration curve (c) and then the equivalent 'slice' is matched on the DV response (d) (see text for further explanation)

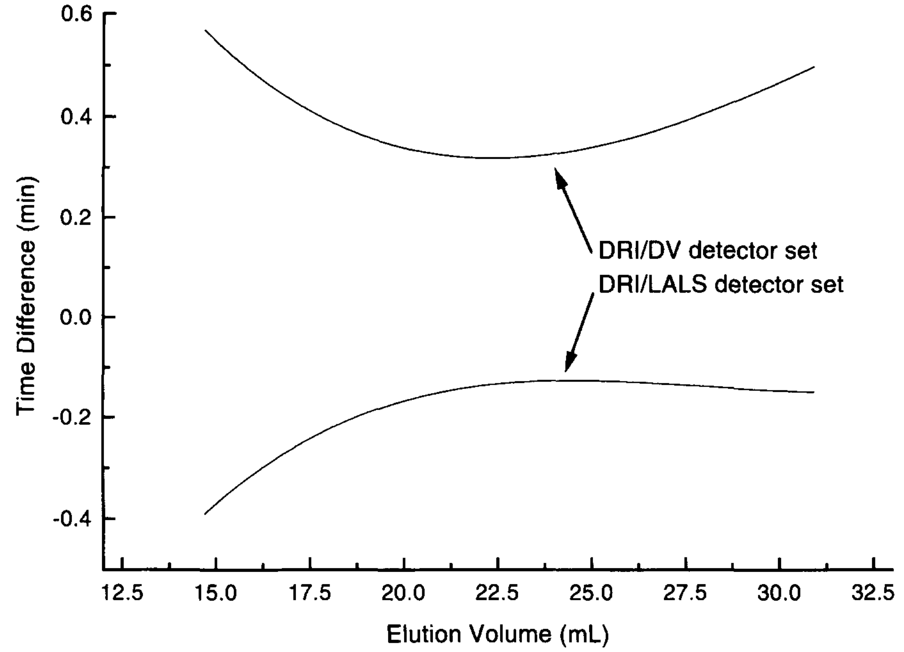

Figure 5 Time difference between separately calibrated DV/DRI detector set, and LALLS/DRI detector set

Table 2 Comparison of MWD moments for broad PSTY and PMMA from standard and Suddaby–Sanayei methods of analysis

		Analysis method				
Polymer	MWD moment	DRI	LALLS (Standard)	LALLS (Suddaby–Sanayei)	DV (Standard)	DV (Suddaby–Sanayei)
PSTY	Mn	104 569	101 672	93 521	106 076	110 720
	Mw	243 982	266 891	265 950	243 113	244 000
PMMA	Mn	104 046	107 273	97 258	100 334	105 900
	Mw	242 982	257 416	265 600	240 460	235 700

Table 3 MHS K and α parameters from standard and Suddaby–Sanayei analysis methods compared to literature and narrow PDI calibrants

		Analysis method			
Polymer	Parameter	Standard	Suddaby–Sanayei	Literature	Narrow PDI calibrants
PMMA	$K \times 10^5$ (dl g^{-1})	29.29	14.10	12.80	13.61
	α	0.627	0.692	0.697	0.687
PSTY	$K \times 10^5$ (dl g^{-1})	17.02	14.65	14.10	15.06
	α	0.694	0.705	0.700	0.704

and LALLS results will be in error if a single IDD is used in the calibration procedure.

In the subsequent discussion we will refer to the *standard* method of IDD determination, which refers to the IDD evaluated from the methodology of *Figure 1* and *Figure 2*, compared to the Suddaby–Sanayei method (IDD elimination), which is described above.

Evaluation of the calibration methods

In order to test the applicability of the new calibration procedure, we analysed a series of broad molecular weight polymer secondary standards. The data in *Table 2* show the results from analyses of broad PMMA and PSTY calibrants.

In this instance we can compare three methods of s.e.c. calibration: (1) direct comparison with a calibration curve based on narrow PDI standards; (2) the standard method of analysing using a single IDD; (3) the Suddaby–Sanayei analysis procedure. It is evident that the three methods agree to within 10%, which can be regarded as satisfactory, as the calibration methods are based on different assumptions and this may be a reflection of some uncertainty in the molecular weight assignments of the standards from commercial sources. In this instance (analysis of PMMA and/or PSTY) we would expect the best possible result for all three methods as PSTY and PMMA standards were used in the calibration procedures. These data were then used to calculate MHS values as shown in *Table 3*.

Mark–Houwink parameters derived from the Suddaby–Sanayei method give a slightly better fit to the literature values for both K and α. Similarly, *Table 4* shows a

Table 4 Evaluation of K_θ and K' parameters from standard and Suddaby–Sanayei analysis methods compared to literature and narrow PDI calibrants

Polymer	Parameter	Analysis method: Standard	Analysis method: Suddaby–Sanayei	Literature data[11]	Narrow PDI calibrants
PMMA	$K^\theta \times 10^4$	9.454	8.127	7.302	7.542
	$K' \times 10^6$	0.982	1.198	1.133	1.067
PSTY	$K^\theta \times 10^4$	9.498	8.517	8.200	10.000
	$K' \times 10^6$	2.007	2.016	1.742	1.423

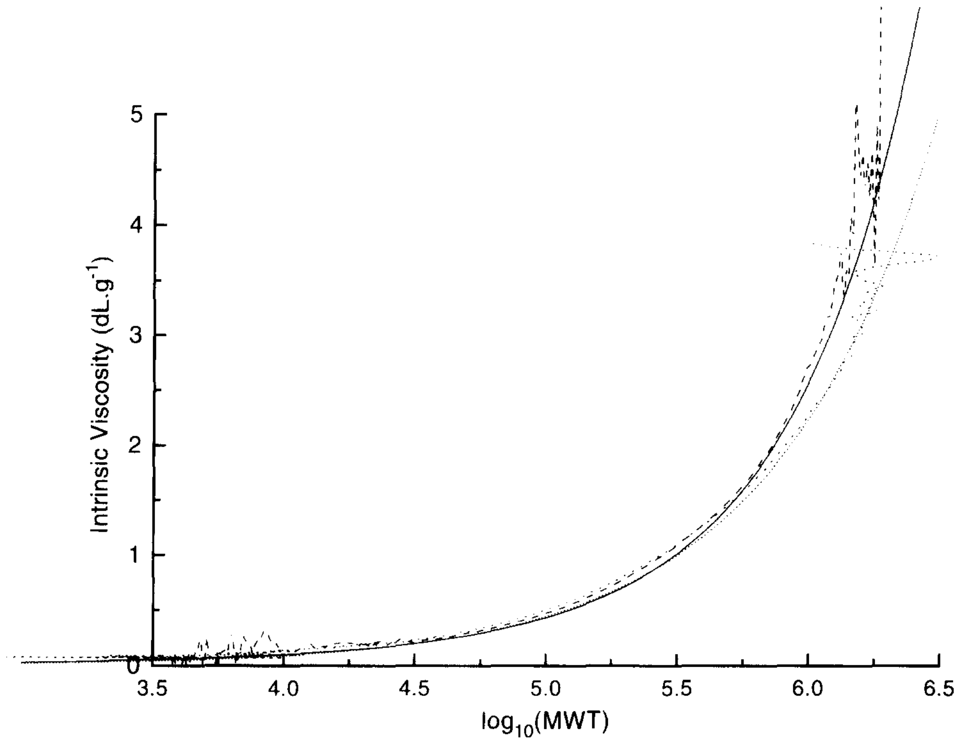

Figure 6 Overlay of polydisperse PSTY IV vs MWT calculated by the standard (······) and Suddaby–Sanayei (- - - -) methods overlaid on literature MHS (· · · · ·) and SF (——) relationships for PSTY

comparison of DV analyses for PMMA and PSTY, together with fitted SF parameters. Again the Suddaby–Sanayei method appears to be superior to the standard method of calibration with respect to the estimation of these parameters.

Viscometry results for a broad PSTY standard are shown in *Figure 6*. These data clearly show that a significant difference is obtained in the IV–MWT relationship depending on the mode of detector calibration. This difference between the methods will not only manifest itself in differences in the calculated MWT moments, but will be exacerbated in the calculation of MHS parameters as discussed in the next section.

The main application of multi-detector s.e.c. is to analyse unknown polymers where no narrow PDI standards are available. A variety of broad polymers were analysed and the results are given in *Figures 7* and *8*. These plots illustrate the differences in M_n and M_w that can be obtained using either the standard IDD or Suddaby–Sanayei approaches to calibration. A consistent feature is the underestimation of molecular weight moments using DV with the standard calibration method. The difference in calibration methods for LALLS is much less pronounced and both methods yield results within normal experimental error for the systems studied here. There is clearly more scatter for M_n, which is to be expected as M_n is highly sensitive to base line selection in the chromatograms and also baseline markers. It may also be expected that some operator dependence is possible in determining M_n, though this can be minimized with careful training.

The dn/dc of an unknown polymer can be found experimentally from the LALLS analysis by solution of equation (1) (knowing injection volume concentration and K_{conc}). A comparison of dn/dc values obtained from the LALLS analysis with those reported in the literature are in almost exact agreement, as shown in *Table 5*, providing strong corroborative evidence for the validity of the light scattering constants used in the calibration.

IV–MWT relationships

Several IV–MWT relationships have been postulated over the last 50 years. By far the most widely used

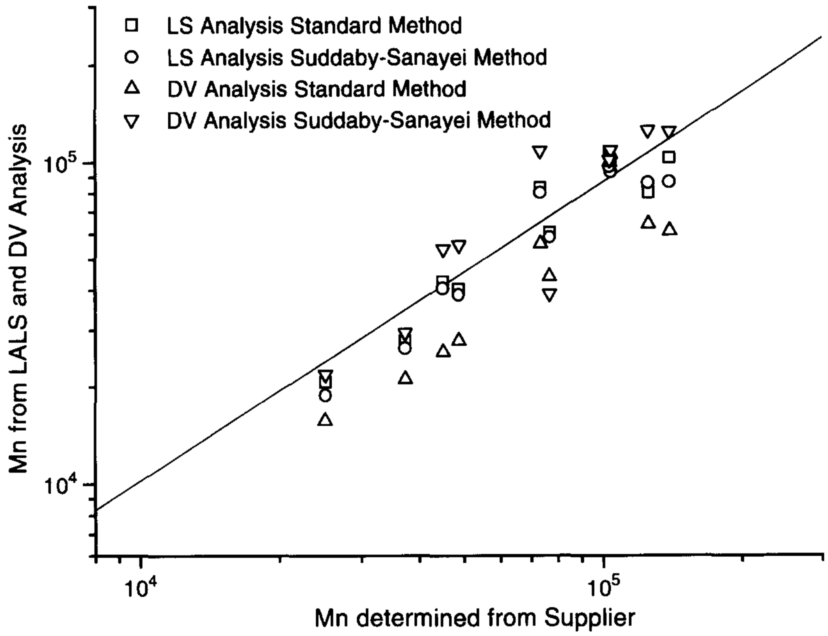

Figure 7 Comparison of supplier determined M_n vs LS and DV evaluated M_n via Suddaby–Sanayei and standard methods for broad secondary standards

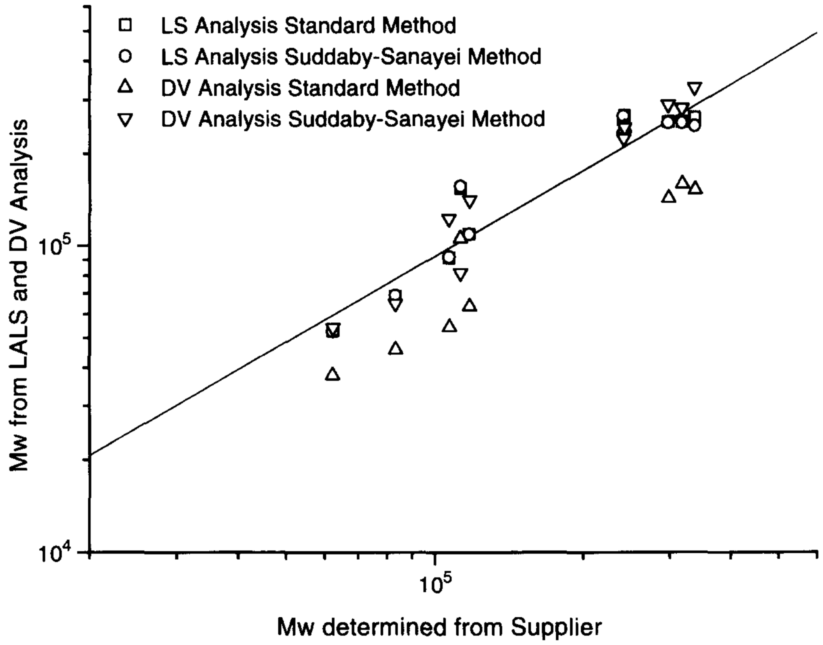

Figure 8 Comparison of supplier determined M_w vs LS and DV evaluated M_n via Suddaby–Sanayei and standard methods for broad secondary standards

expression has been the empirical relationship first proposed by Mark[13] and Houwink[14] (equation (12)), which has become widely known as the Mark–Houwink–Sakurada (MHS) equation

$$[\eta] = K \cdot M^{\alpha} \qquad (12)$$

This relationship has been widely used since its first proposal, but widely criticized due to its empirical nature and its inability to describe the region below 10^4 in MWT.

In 1963 Stockmayer and Fixman[15] proposed an alternative IV–MWT relationship, shown in equation (13).

$$[\eta] = K_{\theta} \cdot M^{1/2} + K' \cdot M \qquad (13)$$

In this equation, K_{θ} is constant for a given polymer, regardless of the solvent or temperature, and K' is a measure of the polymer–solvent interaction and thus varies with the solvent and temperature. In a θ-solvent, K' is equal to zero and the equation reduces to:

$$[\eta] = K_{\theta} \cdot M^{1/2} \qquad (14)$$

Hence K_{θ} can be defined as the ratio of the viscosity of a polymer to the square root of its MWT. The Stockmayer–Fixman (SF) equation has been shown to represent the IV–MWT relationship over a wide range of MWT, although deviation from linearity is sometimes noted in the region of large MWT[16].

The SF equation is preferable to the MHS relationship as it has a stronger thermodynamic basis, K_{θ} can be obtained via separate experiments (or can be readily estimated as shown later) and has been shown to be a better IV–MWT correlation than the MHS relationship. Throughout this paper the units used for K_θ and K' are dl mol$^{1/2}$ g$^{-3/2}$ and dl mol g^{-2} respectively.

The difference between the MHS and SF models is shown in *Figure 6*, where we overlay best-fit model curves for the MHS (· · · ·) and SF (——) models. The SF model provides a good description of the IV–MWT relationship obtained via the Suddaby–Sanayei method of calibration. In contrast, there is significant deviation from the IV–MWT data obtained using a single IDD particularly at higher molecular weights. The MHS relationship is flawed for the Suddaby–Sanayei calibration method, as it deviates at both the high and low molecular weight ranges. This is clear evidence that the use of the SF equation is preferable merely from a data fitting perspective. An additional factor in favour of the SF equation is that K_θ can be estimated either from experimental data or more usefully from group contribution theory. Values of K_θ can be predicted from the unperturbed dimensions of the polymer using the expression:

$$K_\theta = \Phi \cdot \left(\frac{\langle r_0^2 \rangle}{M} \right)^{3/2} \tag{15}$$

where Φ is Flory's constant $= 2.5 \times 10^{23}$ mol^{-1}, $\langle r_0^2 \rangle$ is the unperturbed mean end-to-end distance of the polymer coil in solution and M = MWT.

Alternatively, K_θ can be predicted from group contributions, using an additive function termed *molar intrinsic viscosity function* (J)[17,18,19] and defined as

$$J = K_\theta^{1/2} \cdot M - 4.2 \cdot Z \tag{16}$$

where J is the sum of each group multiplied by its *molar intrinsic viscosity* ($J = \sum_i n_i \times J_i$), Z is the number of backbone atoms per structural unit and M is the MWT of the repeat unit. Values for J_i are tabulated by Van Krevelen[20] and can be used to predict K_θ.

The influence of analysis method on the calculation of MHS parameters is demonstrated by the data given in *Table 6*. The different calibration methods produce significantly different MHS constants. The Suddaby–Sanayei method is far more reproducible, as evidenced by the four PVC samples. Similarly, the SF constants can be calculated from data derived from both calibration methods, as shown in *Table 7*.

In *Table 7* we also show the predicted values of $-\log K_\theta$ calculated from group contribution theory. In order to test whether it is valid to use a calculated value for K_θ and then fit the IV–MWT relationship to the SF equation with just K' as an adjustable parameter, we calculated results for well-characterized broad PMMA and a broad PSTY secondary standards using the 'reduced' SF equation (K_θ calculated from group contribution theory), the results of which are shown in *Table 8*.

In both instances (MHS and SF) we transformed the data to allow linearization of the equations, which will cause distortion of the result. Ideally non-linear regression should be used – this also has the added advantage that joint confidence intervals can be generated. The differences between linear and nonlinear regression analysis methods are illustrated in *Table 9* where we show a comparison of SF constants generated by linear and non-linear regression for broad PMMA and PSTY which have been analysed via the Suddaby–Sanayei method. These differences are significant and nonlinear regression is strongly recommended for all analyses. *Figure 9* shows a typical 95% confidence contour for these SF constants for a broad PSTY.

Elimination of operator variability

As discussed earlier in the Introduction we noted considerable operator variation when calculating MHS constants using the standard on-line method with commercial software. As narrow PDI standards are readily available for PMMA and PSTY, it is a simple procedure to use either an on-line DV or a conventional viscometer to generate the classical MHS log–log plot to

Table 5 Comparison of d*n*/d*c* between literature and LALLS analysis

	d*n*/d*c* (ml g^{-1})	
Sample ID	Literature data[12]	LALLS data
PMMA	0.086	0.085
PSTY	0.185	0.185
PEMA	0.085	0.085
P(*n*-BMA)		0.082
P(iso-BMA)		0.078
PVC 1	0.115	0.115
PVC 2	0.115	0.115
PVC 3	0.115	0.116
PVC 4	0.115	0.116
PLMA		0.072

Table 6 Comparison of MHS K and α parameters from literature and DV analysis via standard and Suddaby–Sanayei methods

	Analysis method					
	Standard		Suddaby–Sanayei		Literature values	
Sample ID	$K \times 10^5$ (dl g^{-1})	α	$K \times 10^5$ (dl g^{-1})	α	$K \times 10^5$ (dl g^{-1})	α
PEMA	14.47	0.728	7.25	0.680	15.49[21]	0.679[21]
P(*n*-BMA)	22.66	0.668	2.87	0.756	5.01[21]	0.758[21]
P(iso-BMA)	13.85	0.720	3.27	0.738	5.01[22]	0.758[22]
PVC 1	71.43	0.661	45.30	0.651	63.80[23]	0.650[23]
PVC 2	70.53	0.661	45.84	0.647	63.80[23]	0.650[23]
PVC 3	40.14	0.729	24.95	0.653	63.80[23]	0.650[23]
PVC 4	31.84	0.753	30.38	0.643	63.80[23]	0.650[23]
PLMA	20.97	0.618	6.04	0.762	5.18[22]	0.72[22]

Table 7 Tabulation of SF K_θ and K' parameters from DV analysis with comparison of standard and Suddaby–Sanayei methods, also predicted and literature values of $-\log K_\theta$

Method	Standard			Suddaby–Sanayei				
Sample ID	K_θ ($\times 10^4$)	K' ($\times 10^6$)	Experimental $-\log K_\theta$	K_θ ($\times 10^4$)	K' ($\times 10^6$)	Experimental $-\log K_\theta$	Predicted[a] $-\log K_\theta$	Literature[b] $-\log K_\theta$
PMMA	9.454	9.816	3.024	8.822	12.955	3.054	3.229	3.311
PSTY	9.497	20.067	3.022	8.859	20.014	3.052	3.075	3.202
PEMA	8.515	37.449	3.069	2.548	9.006	3.596	3.267	3.318
P(*n*-BMA)	6.317	29.558	3.199	2.731	8.540	3.563	3.310	3.469
P(iso-BMA)	8.050	29.544	3.094	2.677	7.548	3.572	3.456	—
PVC 1	18.000	113.801	2.745	14.000	38.946	2.852	2.827	2.904
PVC 2	22.000	88.606	2.657	14.000	36.445	2.844	2.827	2.904
PVC 3	19.000	134.130	2.721	12.000	9.452	2.932	2.827	2.904
PVC 4	17.000	149.750	2.769	9.249	19.489	3.033	2.827	2.904
PLMA	8.815	47.319	3.055	9.464	12.774	3.023	3.409	3.475

[a] Predicted values of K_θ come from the group contributions method outlined previously[20]
[b] Literature $-\log K_\theta$ data from ref. 23

Table 8 Implementation of group contributions method to estimate K_θ and fitting PSTY and PMMA to a SF type plot with regression for K'

Polymer	K_θ[a]	Literature K' value[b]	Fitted K' value
PMMA	5.902×10^4	1.133×10^6	2.151×10^6
PSTY	8.414×10^4	1.742×10^6	2.136×10^6

[a] K_θ determined from group contribution theory, see *Table 7*
[b] Literature values from ref. 11

Table 9 Evaluation of SF K_θ and K' parameters via linear and nonlinear regression with comparison to literature

		Suddaby–Sanayei method		
Polymer	Parameter	Linear	Nonlinear	Literature[11]
PMMA	$K_\theta \times 10^4$	8.128	7.972	7.302
	$K' \times 10^6$	1.197	1.429	1.133
PSTY	$K_\theta \times 10^4$	8.518	9.328	8.200
	$K' \times 10^6$	2.017	1.796	1.742

derive K and α. An example is shown in *Figure 10* for our narrow PDI PSTY and PMMA calibrants. In this case it is possible to get zero operator variability as the procedure does not require the operator to make any subjective judgements. It is no coincidence that there is widespread agreement in the literature for MHS constants for PMMA and PSTY. Now, if a broad polymer is analysed, the operator is confronted with a log–log plot as shown in *Figure 11*. The plot is slightly curved and the operator often chooses to omit data to optimize the linear fit; the commercial software packages allow the operator to select the molecular weight range over which the log–log correlation appears to be linear – this becomes a subjective choice. Any area of subjectivity will necessarily induce operator variability. If an IV–MWT relationship is to be implemented, then we recommend fitting the data nonlinearly to the IV–MWT distribution, and giving attention to the regions of MWT where the particular IV–MWT relationship is known to be deficient, e.g. MHS < 10^4 MWT. This is the only way

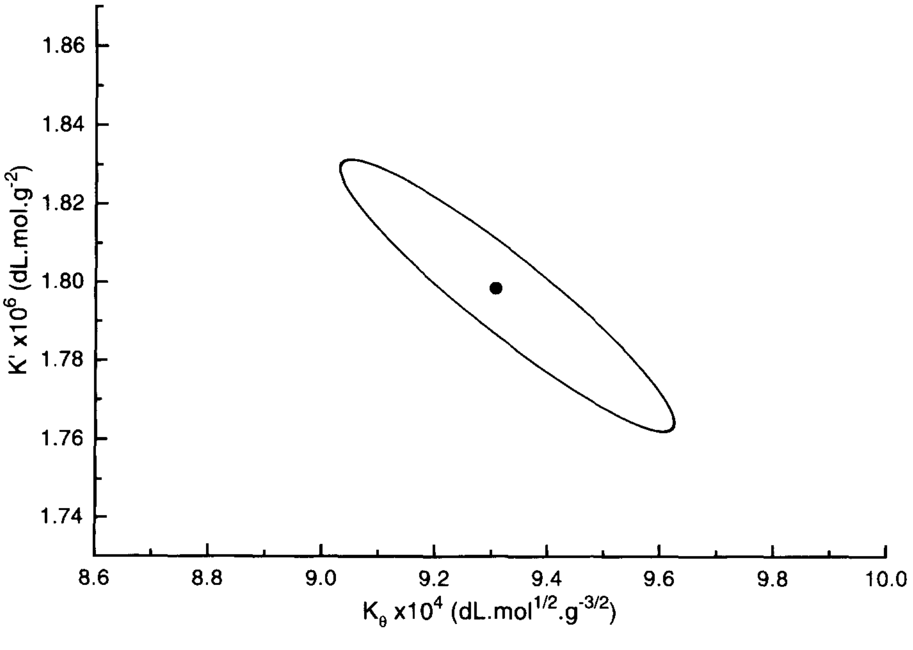

Figure 9 Ninety-five percent joint confidence region for SF K_θ and K' parameters from nonlinear regression

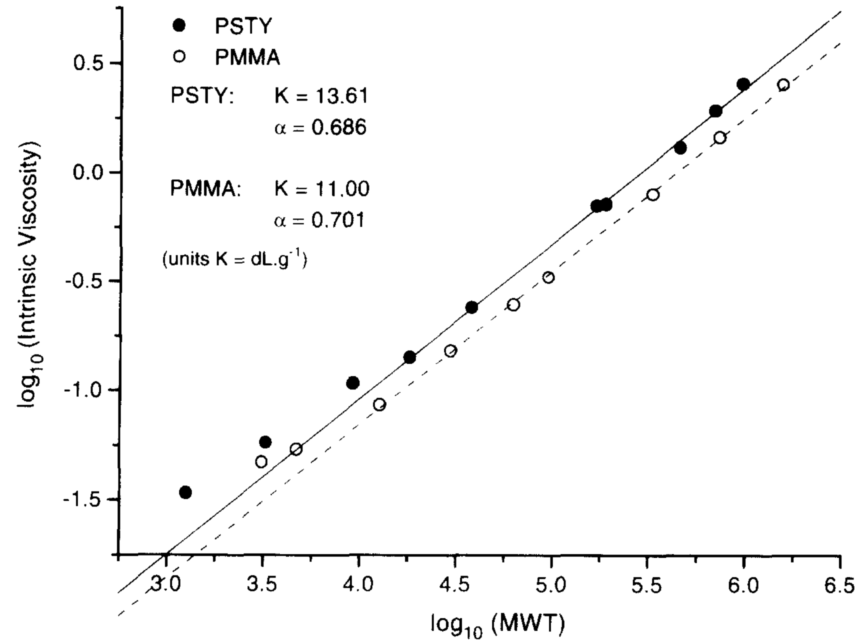

Figure 10 MHS plot for narrow PDI PSTY and PMMA calibrants (*Note* the linear fit to the data was from $<10^4$ MWT)

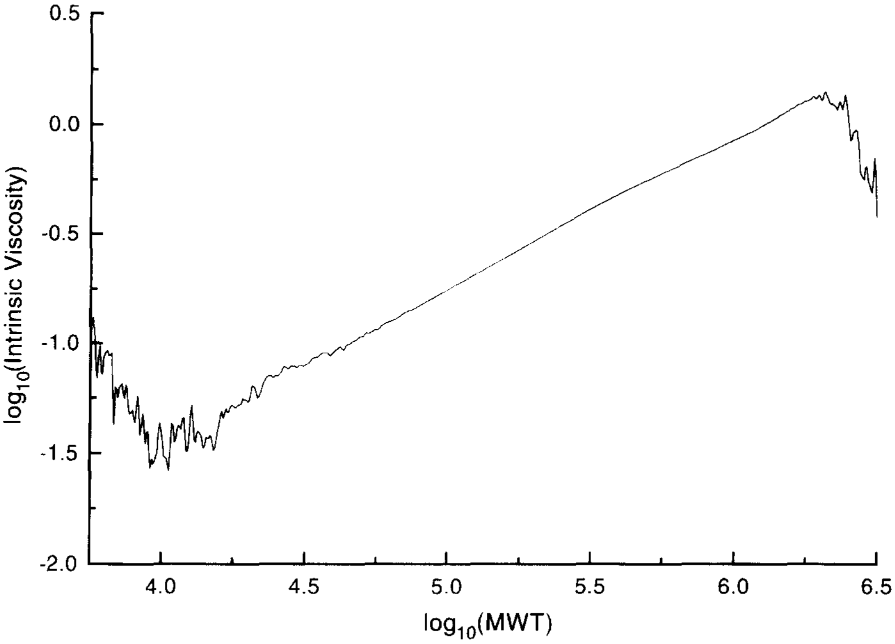

Figure 11 MHS plot for broad poly(ethyl methacrylate) secondary standard

to eliminate operator variability. This method is a far more statistically sound approach to fitting IV–MWT relationships to IV–MWT data. It should also be noted that an additional factor which leads to large variability in MHS constants is the log–log scales of linearized MHS plot. Any experimental error will be transformed by this relationship resulting in large variability in the calculated K and α.

Finally, *Figure 12* illustrates the validity of the SF equation for s.e.c. analyses (on a purely empirical basis) where we show narrow PDI PSTY calibrants plotted on an IV vs MWT scale with overlaid literature MHS and SF relationships using established constants. Also superimposed is a broad PSTY analysed via the Suddaby–Sanayei method. It can clearly be seen that the SF relationship is superior to the MHS relationship in describing the PSTY IV–MWT curve and also that the Suddaby–Sanayei method of analysis yields values for 'slice' IV that adhere to this relationship closely.

CONCLUSIONS AND RECOMMENDATIONS

In this paper we have not shown direct experimental evidence for a molecular weight dependence of IDD. However, using accepted transformations we can calibrate each detector independently, and this provides strong indirect evidence that a molecular weight dependence of IDD is real. Calibration using a single IDD estimate will result in small differences in the calculation of molecular weight moments, but large, significant differences in MHS and SF constants. This issue is significant, as previous papers dealing with this subject

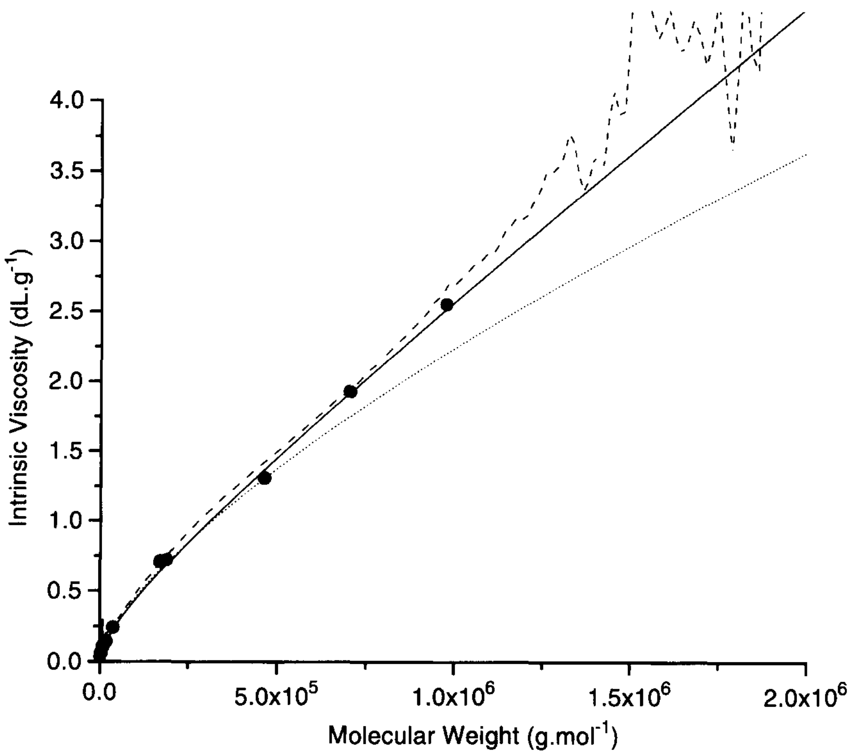

Figure 12 Plot of narrow PDI PSTY calibrants (●) and literature MHS (· · · ·) and SF (——) IV vs MWT relationships overlaid on a broad PSTY polymer analysed via the Suddaby–Sanayei (- - - -) method

have favourably compared M_n and M_w data from LALLS and DV and used this as evidence for supporting subsequently derived MHS parameters. The work reported in this paper clearly shows that congruence in molecular weight moments is not necessarily evidence for reliable MHS constants.

The SF equation provides an excellent description of the IV–MWT relationship across a wide molecular weight range as exemplified in *Figure 12*. The MHS equation is deficient in comparison. *Figure 12* is also very important as it shows that a calibration based on independent detector calibration is essential if an accurate experimental estimation of the IV–MWT relationship is to be obtained. We also show that the SF equation can be used in a reduced form with calculated K_θ values from group contribution theory. When fitting IV–MWT relationships to data the operator should be aware of the limitations of the relationship. For example a MHS fit should not extend below 10^4 MWT.

We emphasize that operator variability arises when the operator is left to make choices which involve subjective judgements. It is difficult to fully eliminate all subjectivity as base-line selection and integration ranges need to be specified. However, the reported calibration minimizes the need for the operator to make subjective judgements and hence a reduction in operator variability necessarily follows.

ACKNOWLEDGEMENT

TPD acknowledges the receipt of a grant from the Australian Research Council.

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