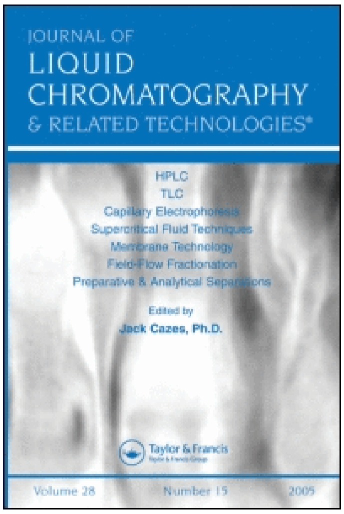

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AN EXPERIMENTAL EVALUATION OF A NEW COMMERCIAL VISCOMETRIC DETECTOR FOR SIZE-EXCLUSION CHROMATOGRAPHY (SEC) USING LINEAR AND BRANCHED POLYMERS

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ABSTRACT

Herein are reported some findings on the application of a new type of continuous automatic viscometer, in parallel with a differential refractometer, as a detector system for SEC. A universal calibration is required for the instrument and two methods of construction are applicable. The first is the customary peak-position calibration using polymer standards of narrow molecular-weight distribution and the second uses a single broad standard of known $\overline{M}_w$ and $\overline{M}_n$. The two types of calibration are shown to give nearly-identical values of molecular weight when used to process chromatograms obtained from various linear homopolymer standards of varying chemical composition. These values compare favourably with those quoted by the suppliers of the polymer standards. One of the more powerful features of this instrumentation, namely its potential for estimating accurate molecular weights of branched polymers, is demonstrated by analysis of a series of branched polyvinylacetates prepared by a conventional bulk, free-radical polymerisation procedure. The calculation of the degree of chain branching is discussed. Another particular feature of the viscometer detector, its ability to indicate the presence of low concentrations of high-molecular-weight impurity in polymer samples, is also shown.

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INTRODUCTION

Since its discovery in 1959 (1) and first application to synthetic organic polymers in 1964 (2), SEC has become the most widely used technique for routine characterisation of polymer molecular weights (MW) and molecular-weight distributions (MWD), as attested by the volume of publications which have appeared over the last twenty years. The basic technique and applications are well covered in books and reviews, eg. refs. 3-5. The major advantages of SEC over classical techniques (light scattering, osmometry, ultracentrifugation) are speed, simplicity of operation and reproducibility. A major drawback, however, in the case where a single detector (commonly a differential refractometer, DRI) is used to monitor column effluent, is the need for a calibration of the instrument, which reduces SEC to a secondary technique of polymer characterisation. Despite considerable experimental drawbacks and high costs, the idea of continuously monitoring the MW of the effluent as well as the concentration has proven attractive and powerful instrumentation has appeared over the past decade. Use of both an MW and a concentration detector in tandem provides data that can be used to make absolute MW calibrations.

The two techniques which have so far been applied to MW detection in SEC are low angle laser light scattering photometry (LALLSP) and viscometry (VISC). The earliest flow-through, light-scattering sample cell using a laser light source was described in 1966 by Cantow et al. (6). Pioneering work on a more useable system was done in the mid seventies by Ouano et al. (see eg. ref. 7) which led to the commercialisation of a reliable instrument, the KMX-6 and more recently the KMX-100, by the Chromatix Corporation. The earliest VISC detectors (8-10) in use sampled effluent discontinuously by successively charging a series of Ubbelohde-type viscometers. The first instrument which continuously measured viscosity, by monitoring the pressure drop across a capillary containing the column effluent, was described by

Ouano (11) in 1972. The main problem with this design was a noisy signal due to extreme sensitivity of the pressure transducer in the flow cell to variations in solvent flow rate. Only recently has this problem been overcome. The Viscotek Model 100 instrument, which is a capillary-bridge viscometer, became commercialised in 1985 (12-14) and has a much improved signal-to-noise ratio. The purpose of the present work was an evaluation of this instrument. To this end a universal (hydrodynamic-volume) calibration (15) for our SEC system was constructed using well-characterised, narrow-as well as broad-MWD polystryrene (PS) and polymethylmethacrylate (PMMA) standards from commercial sources. The customary method for constructing a universal calibration is to determine MWs and intrinsic viscosities, $[\eta]$, for the polymers in question, chromatograph them on a suitable SEC system to obtain their retention volumes, V_R, then plot V_R against log $[\eta]M$. Separate determination of $[\eta]$ is not necessary when the Viscotek detector is employed in tandem with a suitable concentration detector, in our case a DRI. The Viscotek continuously monitors the pressure drop across a capillary tube which is proportional to the specific viscosity, η_{sp}, of the fluid flowing through it. Since the approximation

$$\eta_{sp} = [\eta]\, c \tag{1}$$

is valid at the low polymer concentrations in SEC effluents and since we know c from the DRI detector response, then for any volume increment ΔV in a chromatogram.

$$[\eta]\,(\Delta V) = \eta_{sp}\,(\Delta V)/c\,(\Delta V) \tag{2}$$

We can thus obtain $[\eta]$ for a slice of the chromatogram as narrow as we wish, or for the whole polymer. The only information required independently of our SEC system is the molecular weights of our calibration standards. This represents a significant advance over the previous situation in which $[\eta]$ had either to be determined in a separate experiment or through use of the Mark-Houwink parameters, K and a, if available from the literature.

Having obtained a suitable calibration for our system, the next step was to chromatograph a number of polymers of different chemical types having known MWs, namely polyvinylchloride (PVC), polysulphone, broad-MWD PMMA and both linear and branched polyvinylacetates (PVAc), on the VISC/DRI system, to compare the absolute MWs with those calculated from the instrumental data. Finally, some experiments were performed which demonstrate the utility of the VISC in detecting small amounts of high MW "impurity" in polymer samples.

EXPERIMENTAL

The majority of polymer samples examined in this work were of commercial origin. The suppliers' MW data were assumed to be accurate. Data pertaining to these polymers are given in Table 1.

Some PVAc samples examined in this study were synthesised in our laboratories at McMaster by a method which had been previously shown to yield products with extensive long-chain branching (LCB) (16). Freshly-distilled vinyl acetate monomer, to which was added 2,2'-azobis (2-methylpropionitrile) (AIBN) initiator at 1.02×10^{-4} mol. dm^{-3}, was pipetted into glass ampoules. These were plunged into liquid N_2 to freeze the monomer, attached to a vacuum line and evacuated for approx. 15 seconds, then sealed using a blowtorch. Polymerisation was started by immersing the ampoles in an oil bath at 100 ± 1°C. Six sets of ampoules were removed at various intervals between 900 and 6300 seconds reaction time in the hope of obtaining polymer samples of varying MWs and degrees of branching. In each case the ampoules were quenched in liquid nitrogen then broken open and a small quantity of 1-4-dioxane added to dissolve the polymer. After dissolution was complete, which took up to two days under ambient conditions, diethyl ether was added to the polymer solution in a flask immersed in iced water to bring about

TABLE 1
Data Pertaining to Linear Polymers of Commercial Origin Used in This Study.

Sample Identification	Supplier and Lot number	$\overline{M}_w$ /10^3gmol^{-1}	$\overline{M}_n$ /10^3gmol^{-1}	c* mg/ml
PS Narrow 2070	PC-61222	2.07	1.79	1.73
" 3970	PC-61110	3.97	3.57	1.69
" 8770	PC-80314	8.77	-	1.71
" 18100	PC-41220	18.1	15.1	1.66
" 46500	PC-30908	46.5	46.3	0.81
" 114K	GY-S-8	114	108	0.33
" 168K	PC-30126	168	164	0.42
" 262K	PC-50124	262	258	0.47
" 402K	PC-00507	402	395	0.32
" 599K	PC-30121	599	585	0.42
" 940K	PC-80323	940	925	0.27
" 1560K	PC-50329	1560	1495	0.41
" 1894K	PC-50724	1894	1790	0.36
" 2817K	WA-14B	2817	2300	0.34
PS Broad Dow 1683	Dow 1683	250	100	2.29
" 321K	SPP	321	84.6	2.60
PMMA Narrow 7670	PC-PM5-1	8.01	6.96	2.0
" 27K	PC-PM5-2	27.0	24.3	0.46
" 49K	PC-PM5-3	49.0	40.0	0.81
" 107K	PC-PM5-5	107	107	0.54
" 240K	PC-PM3-5	240	266	0.30
" 330K	PC-PM5-9	330	295	0.63
" 400K	PC-PM5-10	400	360	0.22
" 840K	PC-PM5-12	840	750	0.30
PMMA Broad 33K	PS-06	33.3	13.7	2.62
" 93K	PS-09	93.3	46.4	1.54
" 490K	PS-08	490	119.2	1.59
" 699K	PS-16215	699	213	0.49
Polysulphone	SPP-01	67.0	20.4	3.25
PVC 77K	SPP-02	77.3	39.6	1.47
" 122K	SPP-03	122	57.3	1.85
" 193K	SPP-04	194	86.3	1.67
PVAc 125K	SPP-05	125	52.7	2.75
" 195K	SPP-06	195	63.6	2.06
" 237K	SPP-07	237	89.9	2.01

Note:

c* denotes concentration of sample injected into VISC/DRI SEC system.

Suppliers:

PC denotes Pressure Chemical Co., Pittsburgh, Pa.
GY denotes Goodyear Tyre and Rubber Co., Akron, Oh.
WA denotes Waters Associates, Milford, Ma.
PS denotes Polysciences, Warrington, Pa
SPP denotes Scientific Polymer Products, Ontario, N.Y.

precipitation of the polymer. The product was finally melt evacuated at 130°C under high vacuum to constant weight.

An absolute value of $\overline{M_w}$ for each of these branched PVAcs was obtained from light-scattering measurements. In each case five polymer solutions were made up in tetrahydrofuran (THF) solvent and a Chromatix KMX-6 LALLSP instrument was employed to measure the intensity of light scattered from these solutions at 7° to the incident laser beam. A Chromatix KMX-16 laser differential refractometer was used to determine the refractive index increments, dn/dc, of the polymer solutions under ambient conditions.

Values of 0.0455 and 0.0528 $cm^3\ g^{-1}$ were obtained respectively for the samples of lowest (900s) and highest (6300s) conversions. These are close to the value of 0.05 obtained for the same system by Atkinson and Dietz (17) who examined linear PVAcs, albeit using polarised light of wavelength $\lambda = 546$ nm as opposed to our laser light source of $\lambda = 633$ nm. Atkinson and Dietz also reported no significant variation of dn/dc with molar mass in the range $3 \times 10^4 - 1.5 \times 10^5\ g\ mol^{-1}$, so it was decided to use the value 0.05 $cm^3\ g^{-1}$ in each of our customary plots of Kc/R_θ against c to obtain $\overline{M_w}$.

In order to demonstrate whether or not the PVAcs we had synthesised were branched it was decided to perform some measurements using an SEC instrument with a single DRI detector. The instrumentation comprised a Waters Associates ALC-150 automated liquid chromatograph fitted with five Toyo Soda H Gel columns designated 1000, 2500, 3000, 4000 and 6000. THF was pumped at 1.0 cm^3/min through the system which was kept at 30°C. The columns were calibrated with a kit of ten narrow-MWD linear PS standards from the Toyo Soda Co. Our PVAcs were then chromatographed on the same instrument (sample concentrations ≃ 1 mg/ml). The Mark-Houwink constants for linear polystyrene in THF at 25°C (15), $K_1 = 1.50$

$\times$ 10^{-2} cm^3 g^{-1}, $a_1 = 0.70$ and for linear PVAc in THF at 35°C (17), $K_2 = 1.56 \times 10^{-2}$ cm^3 g^{-1}, $a_2 = 0.708$ were employed to obtain estimates of MW for our PVAcs based on their peak retention volumes. This was performed assuming validity of the universal ($[\eta]M$) calibration procedure, ie. at any V_R

$$[\eta]_1 M_1 = [\eta]_2 M_2 \tag{3}$$

$$\text{so} \log M_2 = \log(K_1/K_2) + ((a_1 + 1)\log M_1)/(a_2 + 1) \tag{4}$$

The instrument which formed the basis of this investigation, an SEC with a dual VISC/DRI detector system, is now briefly described, together with basic operational information. Degassed UV grade THF was pumped through the system at 1.5 cm^3/min by a Waters Associates Model 6000 A pump. Two Modchrom mixed-bed columns, each 7.8 mm × 30 cm, packed with porous particles of nominal diameter 5 μm (similar to μ-Styragel), were maintained at 50°C in a Waters TCM column oven. Samples were applied by means of a Rheodyne 7125 six-port injector equipped with a 100 μl sample loop. The two detectors, fitted in parallel, were a Knauer LED (DRI), operating at 21-22°C and a Viscotek Model 100 (VISC) operating at 30°C. Data acquisition and analysis were performed on an IBM XT computer using an ASYST – UNICAL 2.04 software system as supplied with the Viscotek instrument.

The experimental plan for this SEC system was as follows. First, calibration was achieved using a single broad standard PS of known $\overline{M_n}$, $\overline{M_w}$ and $[\eta]$ ie. Dow 1683. Knowledge of $[\eta]$ allows one to set the instrument parameters for the VISC, the most important being the differential pressure transducer (DPT) sensitivity. This was accomplished by setting an initial value for the instrument parameters and establishing a calibration using the Dow 1683 chromatograms by supplying the known values of $\overline{M_w}$ and $\overline{M_n}$. The same chromatogram was then analysed using the newly-established calibration to give back $\overline{M_w}$, $\overline{M_n}$ and $[\eta]$. This latter step was repeated as often as necessary, each time entering a modified value of DPT sensitivity, until the correct value of [η] was obtained. (N.B. in our work the optimum value of DPT sens. was 1.30. This gave [η] = 0.841 dl/g which is exactly the value quoted by the supplier). Next, peak-position calibrations were established using linear, narrow-MWD PS and PMMA standards. A comparison of separately the broad PS, narrow PS and narrow PMMA calibrations was then made by comparing values of MW calculated using each one from chromatograms of selected known samples.

Secondly, a series of linear, well-characterised polymers (PVCs, PMMAs, PVAcs and polysulphone) were chromatographed and their MWs by SEC compared with those quoted by the supplier.

Thirdly, we examined the branched PVAcs, mentioned earlier. A comparison was made of the three sets of MW data calculated from the LALLS, the SEC-DRI system and the SEC-dual VISC/DRI system.

Finally, we sought to demonstrate the efficiency of the VISC detector in measuring small quantities of high-MW impurities in polymer samples. This was done by chromatographing solutions of the three PS blends made from PS Narrow 2817 K and PS Narrow 168 K with small, successively increasing weight fractions of the former.

RESULTS AND DISCUSSION

a) Calibration

Figure 1 shows the (linear) calibration established using the Dow 1683 broad PS standard. Figure 2 shows the calibration established using 14 narrow-MWD PS standards together on the same plot with data for the 8 narrow-MWD PMMAs. In constructing these two calibrations, values of [η] and peak V_R were determined by the instrument. The MWs chosen were $\overline{M}_w$s, from the suppliers (Table 1). Clearly the PMMA data fit very well on the PS curve in fig. 2, which is intuitively satisfying.

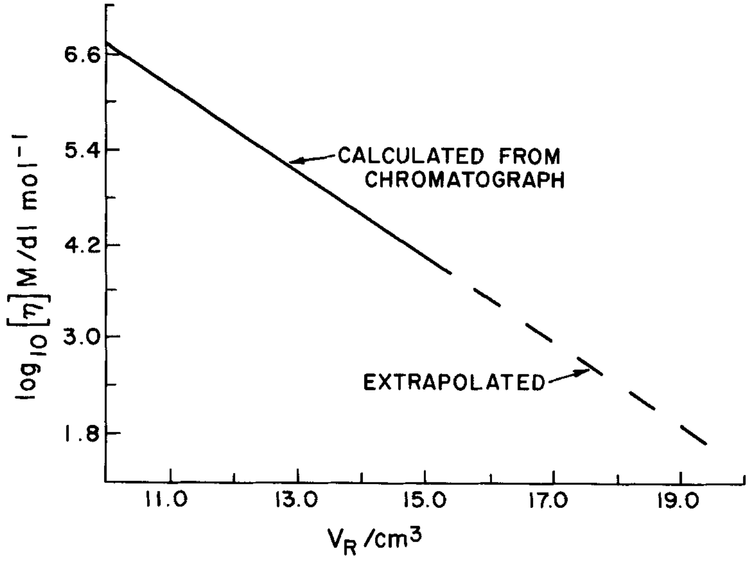

Figure 1 Universal calibration curve established using a single broad-MWD PS standard of known $\overline{M_w}$ and $\overline{M_n}$.

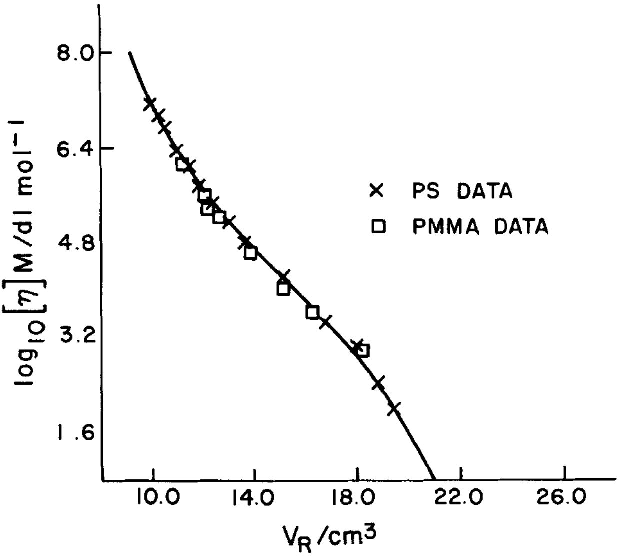

Figure 2 Universal calibration curves established using a series of narrow-MWD PS and PMMA standards.

TABLE 2

Comparison of MW Data from Supplies with Those Calculated from the Three Types of Calibration Established for the VSIC/DRI SEC.

Sample	$\overline{M_w}$ $/10^3 g mol^{-1}$	$\overline{M_n}$ $/10^3 g mol^{-1}$	Calibration
Dow 1683	251.9	101.3	PS broad
broad	248.5	97.8	PS narrow
standard	247.0	118.4	PMMA narrow
	(250.0)	(100.0)	(Suppliers' value)
PS 321K	295.6	111.3	PS broad
broad	332.1	128.1	PS narrow
standard	301.2	129.4	PMMA narrow
	(321.0)	(84.6)	(Suppliers' value)
PMMA 33K	36.8	15.7	PS broad
narrow	36.7	19.3	PS narrow
standard	38.0	20.9	PMMA narrow
	(33.3)	(13.7)	(Suppliers' value)

Table 2 gives a comparison of the values of $\overline{M_w}$ and $\overline{M_n}$ calculated from the VISC/DRI chromatrograms of three standards using the three calibrations described above. The two PS calibrations in particular give excellent agreement with the Dow 1683 data. $\overline{M_w}$ values are within 10% of those quoted for both PS 321K and PMMA 33K although the $\overline{M_n}$ values are in somewhat greater disagreement. This discrepancy is discussed later.

Figure 3 is illustrative of the type of errors which could be incurred if one attempted to use a single narrow-MWD standard to calibrate an SEC instrument. Fig. 3(a) is an intrinsic-viscosity plot calculated from the DRI and VISC responses for

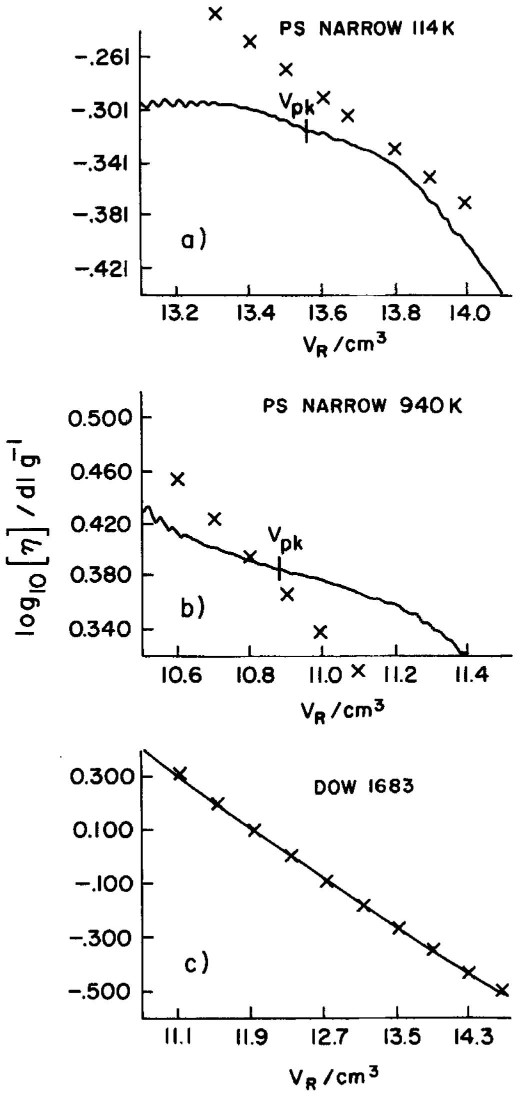

Figure 3 Intrinsic-viscosity plots for the polystyrene standards a) PS Narrow 114K, b) PS Narrow 940K and c) Dow 1683 (broad).

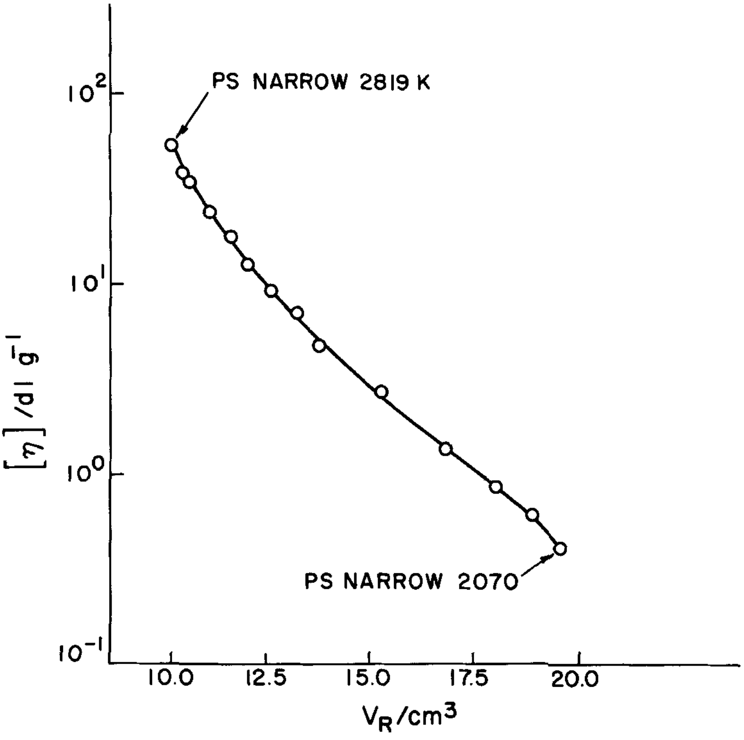

Figure 4 "Ideal" intrinsic viscosity vs. peak V_R plot, constructed from narrow-MWD PS standard data.

PS Narrow 114K. Plotted on the same graph is a portion of the $[\eta]$ versus V_R curve constructed from the $[\eta]$ and peak V_R values of the narrow-MWD PS standards given by the VISC/DRI system, which we call the "ideal" curve (see fig. 4). Fig. 3(b) is a similar plot for PS Narrow 940K. Although the value of $[\eta]$ around the peak V_R is close to the ideal value, departure from ideality occurs very rapidly as one moves away from the peak in both cases. This is a result of peak-broadening effects which are most marked for narrow-MWD polymers. Even though the chromatograms were corrected for broadening, an entirely satisfactory algorithm for dispersion correction has yet to be devised owing to the complexity of the transport phenomena within SEC columns giving rise to the broadened peaks. Fig. 3(c) is the intrinsic-viscosity plot for the Dow 1683 broad PS standard. The curve is the actual plot and the data points are taken from the "ideal" curve. Agreement between the two sets of data is very good, which is validification of the single-broad-standard calibration method. Owing to the actual width of the MWD in such standards, the errors incurred in applying peak-broadening corrections are relatively much smaller than is the case for narrow-MWD polymers.

b) Linear Polymer Standards

The suppliers' values of $\overline{M_w}$ and $\overline{M_n}$ for linear PVC, PMMA, PVAc and polysulphone samples are given in Table 3, together with those calculated from VISC/DRI chromatographic data using the narrow PS calibration. Once again the calculated $\overline{M_w}$ values are generally in very good agreement with the quoted ones, whilst the $\overline{M_n}$ values are somewhat at variance. There are two possible reasons for the latter. One is the reliability of the quoted $\overline{M_n}$ values. Some of these were themselves calculated from other SEC data with the concomitant pitfalls. The second and possibly more important factor is the fact that the current Viscotek-supplied software uses constant values of σ (the Gaussian broadening parameter) and τ (the skewing factor) in correcting peaks for broadening. It is well known (see, eg. ref. 4), however, that these parameters do vary with V_R. This is illustrated in figure 5 for our SEC system where values of σ and τ, as calculated from the VISC/DRI chromatograms, for eleven of the narrow PS standards are plotted as a function of peak V_R. The peak-broadening correction routine in the ASYST-UNICAL 2.04 software accepts only a single value of either of these parameters and recommends the use of those obtained from the narrowest standard; in our case PS Narrow 262K.

TABLE 3

Comparison of MW Data from Suppliers with Those Calculated from the Narrow-PS Calibration for Linear PVCs, PMMAs, PVAcs and Polysulphone.

	Sample	$\overline{M}_w/10^3 gmol^{-1}$		$\overline{M}_n/10^3 gmol^{-1}$	
PVC	77K	71	(77)	33	(40)
	122K	82	(122)	45	(57)
	193K	175	(193)	81	(86)
PMMA	33K	37	(33)	19	(14)
	93K	102	(93)	65	(46)
	490K	521	(490)	233	(119)
	699K	695	(699)	264	(213)
PVAc	124K	125	(124)	51	(64)
	194K	218	(194)	91	(53)
	237K	242	(237)	72	(90)
Polysulphone		67	(67)	32	(20)

Figures in brackets refer to suppliers' quoted values.

c) Branched PVAcs

Table 4 gives the values of $\overline{M}_w$ for the six samples calculated from the LALLSP data, the Waters ALC-150 chromatographic data (using Mark-Houwink parameters for linear PS and linear PVAc) and from the VISC/DRI SEC system. Considering the LALLSP data alone the increase in $\overline{M}_w$ with conversion is in accord with previously-published data (16,18) and is bound up with the kinetics of bulk, free-radical VAc polymerisation (18). Comparison of the $\overline{M}_p$ values (MWs calculated at the peak V_R) from the ALC-150 instrument with the $\overline{M}_w$s from LALLSP shows a consistent, sizeable underestimate in each case for the chromatographic data. That

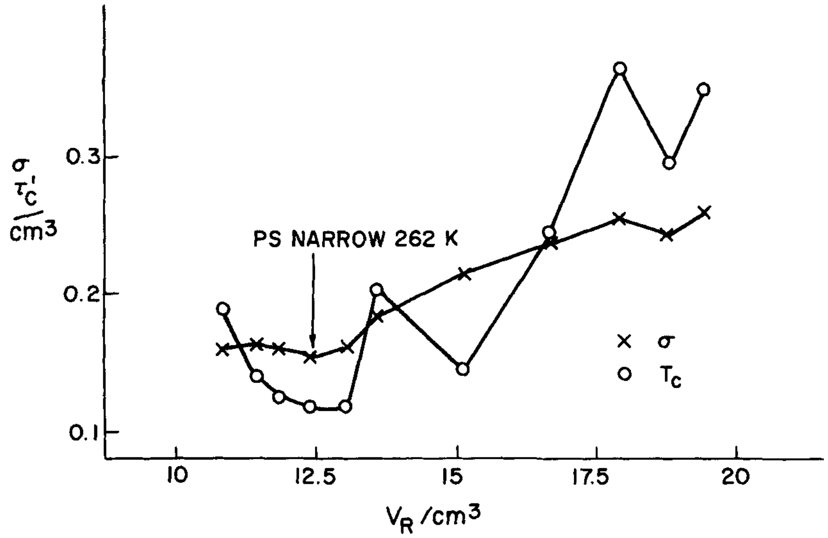

Figure 5 The variation of the peak-broadening parameters, σ and τ, against V_R for eleven narrow-MWD PS standards.

TABLE 4

Value of $\overline{M_w}$ for branched PVAcs calculated using one absolute technique (LALLSP) and two SEC instruments (DRI and dual VISC/DRI).

PVAc Identification	MWs/10^3 g mol^{-1}				
	$\overline{M_p}$ (Waters A(C – 150)		$\overline{M_w}$(LALLSP)	$\overline{M_w}$ (VISC/DRI)	
900	270	(– 18%)	328	402	(+ 23%)
1900	270	(– 34%)	411	434	(+ 1%)
3600	279	(– 31%)	406	422	(+ 4%)
4500	279	(– 42%)	482	436	(-10%)
5400	321	(– 33%)	479	456	(– 4%)
6300	396	(-37%)	628	539	(– 14%)

Percentages in brackets refer to discrepancy between chromatographic and absolute (LALLSP) $\overline{M_w}$ data.

the use of Mark-Houwink constants for linear PVAc gives rise to such underestimates is good evidence that the polymers are in fact branched. Branched polymers have more compact conformations and hence lower intrinsic viscosities than their linear analogues. Substitution of a value of $[\eta]_2$ which assumes linearity in equation 3 will then lead to too low a value of M_2 if the polymer happens to be branched. The values of $\overline{M_w}$ calculated from the VISC/DRI data, where $[\eta]$ is measured directly for each whole-polymer sample, branched or unbranched, compare much more favourably with the LALLSP values.

No attempt was made to calculate actual degrees of branching for those PVAcs in the present work. The computational scheme for so doing is quite straightforward, but the exact meaning of such estimates is open to question owing to the many assumptions, valid and invalid, required to derive a quantitative estimate of branching from SEC and viscometric data.

The experimental quantity from which information concerning branching is derived is g', the ratio of intrinsic viscosities of branched (subscript br) and linear (subscript l) isomers;

$$g' = [\eta]_{br} / [\eta]_l \tag{5}$$

We need further to infer from g' an estimate of g_0 the ratio of unperturbed radii of branched and linear isomers:

$$g_o = < r_g^2 >_{br}^{1/2} / < r_g^2 >_l^{1/2} \tag{6}$$

Relations between g′ and g_0 are semi empirical and approximate (19,20). It is assumed that g' is independent of solvent conditions and that a theta solvent for a linear polymer is also a theta solvent for its branched analogues. Neither of these assumptions is well founded (19). In practical applications, exponential relations between g' and g_0 of the form

$$g' = g_0^k \tag{7}$$

have been proposed. For example, a well-studied branched polymer is low-density polyethylene (LDPE), for which k = 1.2 has proven satisfactory (21-23). The number, n, of branches per macromolecule is obtained through one of the Zimm-Stockmayer relationships (24), an example of which is given below:

$$g_0 = \left[\left(1 + n/7\right)^{1/2} + 4n/9\pi\right]^{-1/2} \tag{8}$$

In outline, a method of calculating n using the VISC/DRI system is as follows. First, one should establish a universal calibration for the instrument. Second, obtain chromatograms for the branched polymer, together with a value of $[\eta]_{br}$. M_{br} is calculated directly from the universal calibration. An estimate of $[\eta]_l$ is then obtained using a suitable Mark-Houwink relationship and we now have sufficient information to calculate g' and hence n through equations 5-8. The great advantage of the VISC/DRI system over earlier methods of determining branching by SEC and off-line viscometric measurements is that it is possible to measure $[\eta]_{br}$ across the chromatograms in slices as small as we desire. This means that we could examine how branching varies with MW across a given sample, as well as obtaining the average value of n for the whole polymer.

d) Detection of Small Amounts of High-MW Impurities

The dual chromatograms for the three blends of PS Narrow 2817 K and PS Narrow 168 K are shown in fig. 6. Estimates of the amount of high-MW material calculated separately from the DRI and from the VISC detector responses are shown alongside each dual chromatogram, together with the amount actually weighed in to the sample vial. Clearly, there is a substantial difference between the amounts

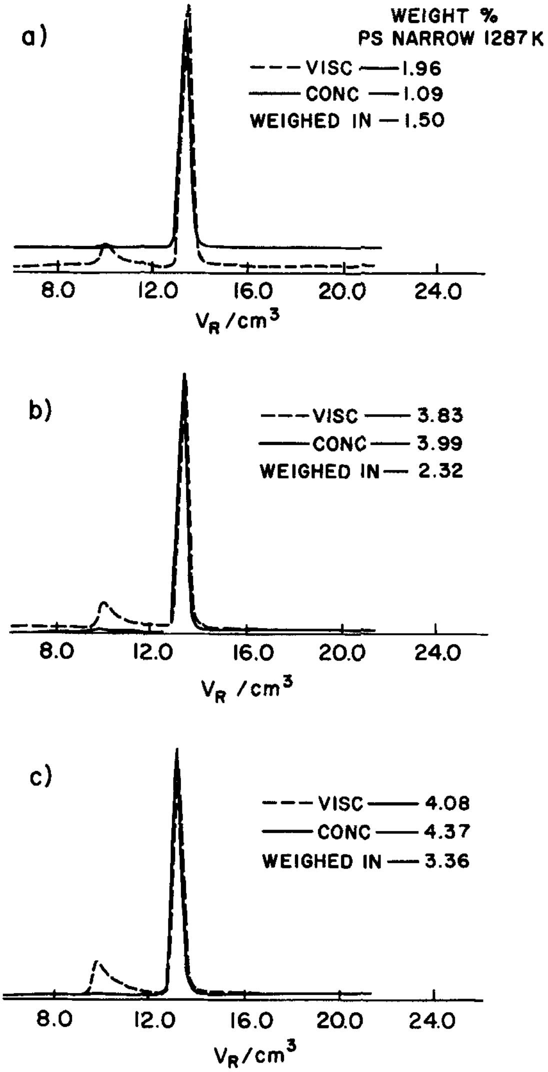

Figure 6 Dual chromatograms obtained from polystyrene blends of PS Narrow 2817K and PS Narrow 168K.

calculated from the detector responses and those obtained by direct weighing. A number of reasons for this are possible, the most important being the method of calculation. For a DRI response, at any V_R, the chromatogram height $H_{DRI}(V)$ is proportional to the concentration c(V). Hence, for the volume interval ΔV

$$c_{DRI}(\Delta V) = \left(\sum_{\Delta V} H_{DRI}(V) / \sum_{\text{all } V} H_{DRI}(V) \right) \times \text{Total c}, \tag{9}$$

For a VISC response H_{VISC} (V) is proportional to the specific viscosity, η_{sp} (V), i.e. is proportional to [η] (V) c(V). Hence

$$c_{VISC}(\Delta V) = \left(\sum_{\Delta V} (H_{VISC}(V)/[\eta](V)) / \sum_{\text{all } V} (H_{VISC}(V)/[\eta](V)) \right) \times \text{Total c}, \tag{10}$$

Values of [η] (V) were obtained directly from the curve shown in fig. 4. All our calculations were performed manually by taking approximately 40 raw chromatogram heights from across the entire sample. Greater accuracy would be achieved using a computer with a proper integration routine (based, eg., on Simpson Rule) which takes every chromatogram height.

Whatever numerical errors are incurred in calculating percentage concentrations from detector responses, it is clear from fig. 6 that the viscometer detector gives a much better qualitative indication of the presence of high-MW species in a sample than the DRI. This is particularly noticeable in fig. 6a where the presence of 1.5% high-MW polymer is barely discernible from noise in the DRI trace, whilst a substantial peak is obtained from the VISC.

It is noteworthy that the VISC detector would not be particularly useful in the detection of microgel, i.e. high-MW cross-linked impurity in polymer samples. Microgels have very low viscosities, despite their high MWs, owing to their compact, spherical conformations. We can illustrate this with reference to a specific example. A series of polystyrene-co-divinylbenzene microgels containing approximately 5%

cross-linking agent were prepared by Booth et al. (25). Subsequent intrinsic-viscosity determinations revealed that the microgels had intrinsic viscosities which were approximately one-thirtieth the values obtained for linear polystyrenes of equivalent MW.

SUMMARY

The present work has been concerned with the evaluation of an SEC system with dual detectors; a DRI coupled with a new type of differential viscometer. The system was calibrated with both narrow-and broad-MWD polymer standards and the accuracy of each type of universal calibration checked by chromatographing various linear, well-characterised polymers. Good agreement was obtained between the quoted $\overline{M_w}$ values and those calculated from the chromatograms. $\overline{M_n}$ values were at somewhat greater variance. Several possible reasons for this were discussed. Some branched PVAcs were synthesised and characterised by an absolute technique, LALLSP. Values of $\overline{M_w}$ obtained from the VISC/DRI system were in very good agreement with the absolute data, which gives further validification to the universal-calibration method of Benoit, et al. (15) and illustrates the power of this new SEC system as a rapid, reliable technique of characterising branched polymers.

Finally, we have demonstrated the utility of the viscometer in detecting small amounts of high-MW impurity in polymer samples.

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