Correction for Interdetector Volume in Size Exclusion Chromatography (SEC)

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SYNOPSIS

In a multidetector SEC system it is necessary to match the outputs of the detectors that sense eluant concentration with those that are molecular weight dependent. There are several methods to accomplish this. The most common is to determine the interdetector volume or time difference between detectors. The difficulty with this technique is that with detector systems where the column eluent is split, the interdetector time difference varies with solution viscosity. Two new techniques were implemented on a high temperature SEC/DRI/LALLS/VISC system which take into account changes in solution viscosity due to high molecular weight polymers. Both techniques use calibration curves of hydrodynamic volume versus elution volume for the different detectors to determine the "instantaneous" time difference between the detectors as it varies with solution viscosity. Either method provides the correct interdetector time lag information. We note also that in multidetector systems the configuration of the detectors should be such as to maximize solvent flow rates through each detector and hence to minimize band broadening effects. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Technological advances in size exclusion chromatography (SEC) equipment have led to more precise and accurate polymer molecular weight analyses. The development of high resolution columns and detectors that are sensitive to different polymer properties[1-3] have increased the accuracy of analyses. The use of multiple detectors following the separation column has also made data analysis much more complex. Several pressing issues need to be considered, such as optimum configuration of the various detectors, band broadening, and correlation of data obtained from the different detectors.

Band broadening is a problem that has always plagued chromatographers. Various mathematical corrections for band broadening effects have been developed[4-7] but the most effective solution is to eliminate it physically. Equipment advances such as narrow capillary tubing, highly efficient columns, low volume fixtures, small particle size SEC gels, and low volume detector cells have reduced band broadening effects to an almost negligible level.

The most important sources of band broadening are in columns and detector cells. There is nothing that can be done physically to alleviate column band broadening, but detector orientation preceding the column can be varied to decrease band broadening. A fairly common detector system, and the one used in this work, combines a differential refractive index detector (DRI), a differential viscometer, and a low angle laser light scattering detector (LALLS). There are three different configurations (Fig. 1). Because of detector design both the DRI and the viscometer must be the last detectors in the SEC train. For this reason it is not feasible to put all three detectors in series (configuration 3). In this study band broadening effects were investigated in configuration 1 (all three detectors in parallel) and configuration 2 (the viscometer and the DRI in parallel following the LALLS).

Another major concern in multidetector systems is the correlation of data obtained from each detector. To calculate molecular weight and molecular

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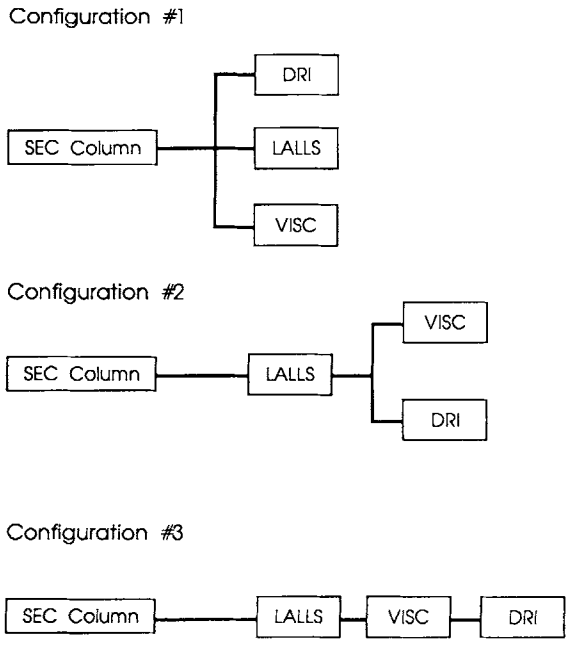

Figure 1 Possible detector configurations. Configurations 1 and 2 were investigated in this research and configuration 3 is theoretical.

weight distributions from LALLS and viscosity data the concentration of polymer in the two detectors is required. In both cases, the particular detector response is not directly related to concentration because each measures other properties of the SEC eluent (turbidity and solution viscosity, respectively). The concentration used for data analysis must come from a different detector (in this case the DRI). Several different techniques exist to correlate the data from the concentration detector to that of the other detectors. The most common method is to determine the interdetector volume or interdetector time difference by estimation[8–12] or by measuring time lags between appearances of peaks of standards in the various detectors. The major drawback of this technique is that changes in solution viscosity as a result of variations in polymer molecular weight will cause the interdetector time difference to vary if the column eluent is split between detectors. An alternate technique for detector correlation was recently published by Suddaby et al.[13] In this work calibration curves from the differential viscometer and DRI were used to correlate the data from the two detectors in an ambient temperature SEC system using polystyrene and polymethyl methacrylate (PMMA) test samples. The technique takes into account viscosity variations across the molecular weight distributions and corrects for them.

In this work, the technique described by Suddaby et al. was extended to high temperature systems and expanded to DRI/LALLS correlations using polyethylenes as test samples. The technique is compared here to the "static" interdetector volume method and one other technique, similar in nature to the one described by Suddaby et al.,[14] discussed in Results.

EXPERIMENTAL

Sample Preparation

Polystyrene standards for column calibration were dissolved in 1,2,4-trichlorobenzene (TCB) at concentrations ranging from 6.0 mg/mL for low molecular weight standards to 0.5 mg/mL for high molecular weight standards. Solutions were held at 145°C for 8 h in an oven specially designed to mix the samples on a rotating wheel.

Three linear polyethylenes (PEs) were investigated. Two were high molecular weight linear low density PE samples with broad molecular weight distributions. The third was NIST SRM 1475. All three samples were dissolved at a concentration of approximately 8 mg/mL in TCB at 160°C and rotated for 24 h prior to analysis. This treatment was required to dissolve aggregates that disrupt LALLS analyses.[15,16]

Apparatus

The SEC system consists of a high temperature gel permeation chromatograph (GPC) operating at 145°C using TCB (containing 0.1% Irganox 1010 antioxidant) as the mobile phase. A Jordi styrene–divinylbenzene linear mixed-bed column was used with a reported molecular weight range of 100–20,000,000.[17] The detector system consists of a KMX-6 LALLS (LDC Milton Roy), a Water's DRI built into the column compartment of the chromatograph, and a Model 100 differential viscometer (Viscotek). Operation of the differential viscometer is detailed in the Appendix.

All data points are reported here without smoothing. Experimental noise is recorded in the figures which follow, for the sake of accuracy in reporting. The methods for calculating molecular weight distributions are described elsewhere.[18–21] Only the methods for correlating detector data will be described here.

RESULTS AND DISCUSSION

Band Broadening

Theoretically, an arrangement with all three detectors in parallel (configuration 1, Fig. 1) would be the best configuration because the LALLS has a large detector volume (0.050 mL) that should, in theory, increase band broadening effects. Two problems exist that make configuration 2 more attractive. The first is the poor signal-to-noise ratio inherent in LALLS detectors with PE solutes in TCB. It is more desirable to boost the signal by increasing the amount of sample going through the detector (configuration 2). The second problem is the decrease in flow rate in each detector caused by splitting the flow three ways. This increases the residence time of samples in the detectors and thus increases band broadening effects.

To investigate band broadening effects in the first two detector configurations of Figure 1, the polydispersities of the narrow molecular weight polystyrene standards used for column calibration were calculated using the DRI detector and a universal calibration curve and compared to values reported by the manufacturer (Table I). The DRI detector response was used to calculate polydispersities because of the detector's low cell volume (0.010 mL). Large changes in flow rate caused by changing the detector configuration will have the smallest effect on the DRI response when compared to the LALLS and the differential viscometer, which both have larger cell volumes. It was deduced from Table I that band broadening effects from either detector configuration are negligible because calculated polydispersities are equal to or lower than reported values (no band broadening correction was applied to these estimated values).

It was found that decreasing the flow rate through a detector with a larger cell volume increased band broadening. In configuration 1, the flow split was 0.7 mL/min to the LALLS, 0.4 mL/min to the DRI, and 0.4 mL/min to the differential viscometer. In configuration 2 the flow split was 1.5 mL/min LALLS, 0.75 mL/min DRI, and 0.75 mL/min differential viscometer. This decrease in flow rate to the viscometer in configuration 1 increased calculated polydispersities (Table II). It was also possible to detect band broadening in the raw data. Figure 2 graphically shows how decreasing the flow rate to the viscometer increases band broadening. Slowing the flow rate caused the polystyrene standard (MW 22,000) to tail out of the detector. This problem was not found with a smaller cell volume detector such as the DRI. Figure 3 shows the same standard polystyrene under the same conditions as in Figure 2 using the DRI detector. The tailing observed in Figure 2 is now absent. This phenomenon would also

Table I Comparison of Polydispersity Indices Calculated Using DRI Detector with Reported PDIs

Sample Molecular Weight	PDI (Manufacturer)	PDI (Calcd) Configuration 1	PDI (Calcd) Configuration 2
580	1.14	1.09	1.08
950	1.14	1.13	1.10
1,700	1.10	1.11	1.09
3,600	1.06	1.07	1.06
5,050	1.05	1.07	1.08
9,200	1.05	1.05	1.06
11,600	1.03	1.05	1.04
22,000	1.03	1.04	1.04
28,500	1.03	1.04	1.04
47,500	1.06	1.04	1.04
68,000	1.03	1.04	1.05
90,000	1.04	1.05	1.04
165,000	1.02	1.04	1.03
207,700	1.15	1.09	1.10
475,000	1.03	1.03	1.04
950,000	1.04	1.07	1.06
1,900,000	1.05	1.09	1.08
2,750,000	1.05	1.09	1.09
4,250,000	1.07	1.11	1.10
8,000,000	1.15	1.13	1.14

Table II Comparison of PDI Calculated Using Differential Viscometer Detector with Reported PDIs

Sample Molecular Weight	PDI (Manufacturer)	PDI (Calcd) Configuration 1	PDI (Calcd) Configuration 2
580	1.14	1.14	1.09
950	1.14	1.13	1.10
1,700	1.10	1.13	1.10
3,600	1.06	1.09	1.06
5,050	1.05	1.08	1.07
9,200	1.05	1.08	1.06
11,600	1.03	1.05	1.03
22,000	1.03	1.06	1.04
28,500	1.03	1.05	1.04
47,500	1.06	1.05	1.03
68,000	1.03	1.05	1.04
90,000	1.04	1.05	1.04
165,000	1.02	1.04	1.03
207,700	1.15	1.15	1.12
475,000	1.03	1.06	1.04
950,000	1.04	1.07	1.05
1,900,000	1.05	1.10	1.08
2,750,000	1.05	1.09	1.06
4,250,000	1.07	1.11	1.09
8,000,000	1.15	1.13	1.10

occur with the LALLS detector, which has a relatively large detector cell volume. This effect can be alleviated in both the LALLS and the differential viscometer by using the detector configuration that increases flow rate to the LALLS and differential viscometer detectors. Tables I and II show that band

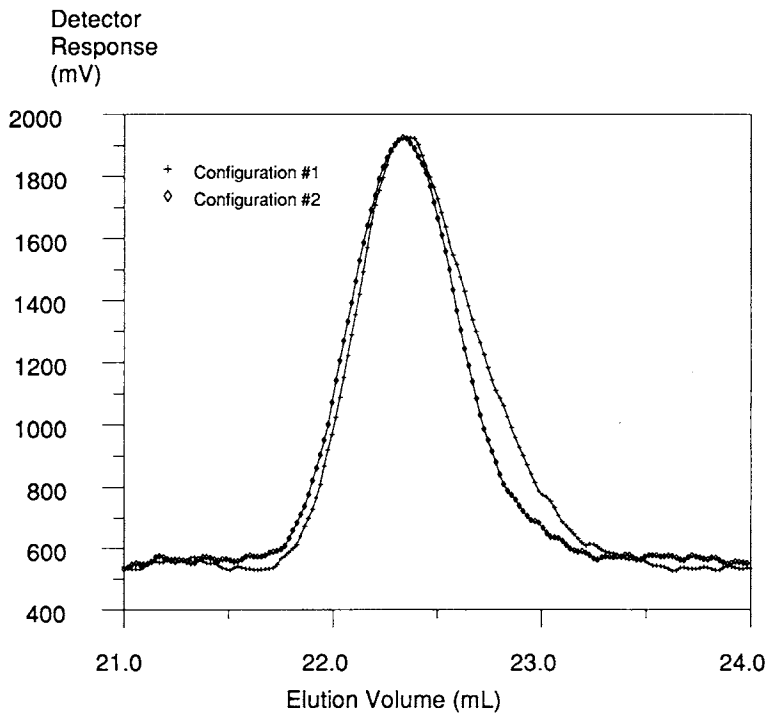

Figure 2 Differential viscometer responses for a typical polystyrene standard (MW 22,000) using detector configurations 1 and 2.

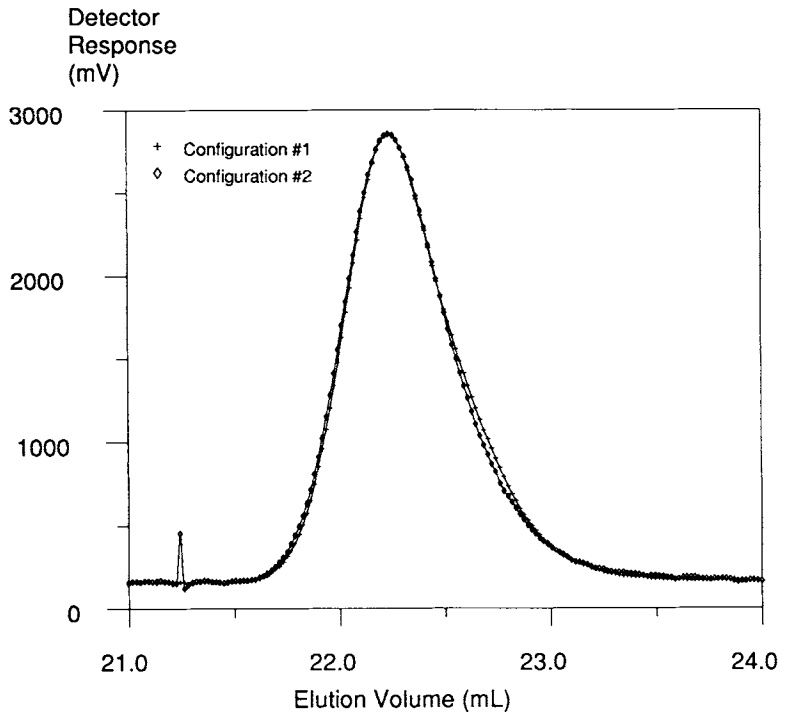

Figure 3 DRI responses for a typical polystyrene standard (MW 22,000) using detector configurations 1 and 2.

broadening in the differential viscometer and the LALLS are minimized to a negligible level with detector configuration 2 (DRI and differential viscometer preceding the LALLS).

To eliminate band broadening effects and increase detector response, configuration 2 was used in the rest of this research.

Correlation of Detector Responses

Interdetector Volume (IDV) Technique

The most common technique for correlating the response of a detector for measuring polymer concentration (DRI) to one that measures another polymer property (LALLS or differential viscometer) is to determine the IDV or time difference. A good method for determining this time difference is to select a polymer that has well-defined Mark Houwink parameters that are known to remain constant across the entire molecular weight distribution. This enables one to compare a DRI-universal calibration molecular weight distribution with the distribution obtained from the CV or LALLS. A good example is linear low density PE (LLDPE) samples. The polymer can then be analyzed using the universal calibration method[19,20] and by the method used for the detector of interest. In each of these comparisons (viscometer/DRI and LALLS/DRI) a systematic difference exists because a given polymer species will pass through each detector at a different time since injections of the samples. It is then common practice to assign an offset volume to compensate for this difference. The resulting two molecular weight distributions from the two detectors are plotted on the same graph in the form of log molecular weight versus assumed elution volume. If the time difference used to assign concentrations to corresponding LALLS or viscometer outputs is incorrect, the two distributions will have different slopes (Fig. 4) and will not overlap. In Figure 4 the time difference between the appearance of a given solute in the DRI and viscometer detectors was purposely offset by 0.50 mL. The time difference is then varied until the distribution for the detector of interest (in this case the differential viscometer) overlaps that obtained from the DRI detector that is, of course, correct for concentration (Fig. 5). To compare detector correlation techniques, the molecular weight distributions are plotted in this form (Fig. 5) because it best illustrates the accuracy of the techniques.

Two problems arise with the IDV technique. The first problem is theoretical and has no effect on the calculated molecular weight distributions. The IDV technique leads to interdetector volumes that are physically incorrect. In the case of the differential

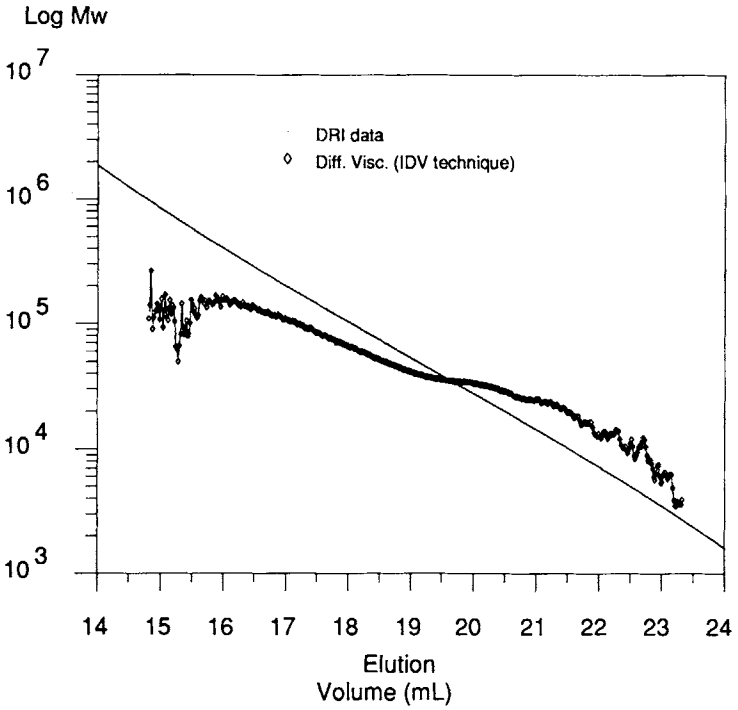

Figure 4 Log(M_w)–elution volume plots for LLDPE 1 calculated from DRI data and differential viscometer data using a detector offset of 0.50 mL.

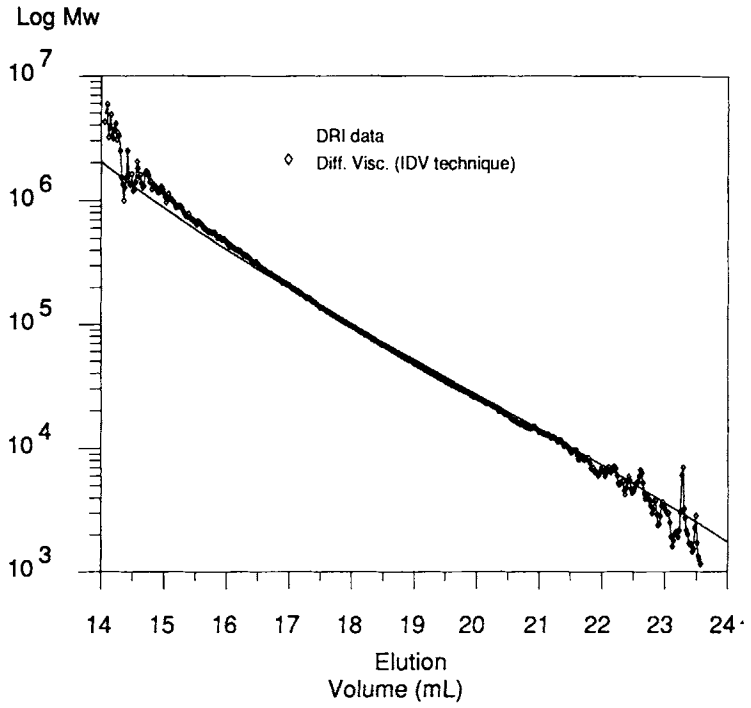

Figure 5 Log(M_w)–elution volume plots for LLDPE 1 calculated from DRI data and differential viscometer data using a detector offset of 0.12 mL.

viscometer/DRI correlation, the IDV for LLDPE 1 was found to be 0.12 mL, which is in agreement with the average IDV (0.10 mL) found from the elution volumes of the polystyrene standards. In the case of the LALLS/DRI correlation using LLDPE 1, the IDV was found to be 0.06 mL, which is very different from the average IDV (0.37 mL) found from the elution volumes of the standards. This phenomenon has been found by other researchers[11,12] and is not well understood. From an operational standpoint, however, the cause is only an academic question.

The second problem with the IDV technique is more serious and can have a large effect on calculated molecular weight distributions. This problem arises with SEC systems where the flow is split between a differential viscometer and another detector (usually the DRI). With this type of system the ID time difference will vary with solution viscosity because this can affect the relative flows through the two detectors. This variation in viscosity is reflected in a deviation from the correct molecular weight distribution. Figure 6 depicts the molecular weight-elution volume relation for the high molecular weight end of the distribution of LLDPE 1 shown in Figure 5. The detector offset is again taken to be 0.12 mL. The calculated molecular weight from the differential viscometer is higher than that calculated from the DRI alone (i.e. with a universal calibration relation) because the increase in viscosity of the eluent results in an increase in flow through the DRI detector and a decrease in flow through the differential viscometer. This results in a larger ID time difference than predicted by the IDV technique, as applied to the bulk of the species in the sample. This means that an erroneously high concentration of polymer (from the DRI data) is being used in the calculations with the differential viscometer. This leads to a lower calculated intrinsic viscosity [eq. (1)][22] and a higher calculated molecular weight [eq. (2)][23] at the same hydrodynamic volume. Here the intrinsic viscosity is conveniently calculated with the Solomon–Cuita relation[22]:

$$[\eta] = \frac{\sqrt{2}}{c}(\eta_r - 1 - \ln(\eta_r)) \tag{1}$$

and the hydrodynamic volume is related to the polymer molecular weight by[20]

$$\mathrm{HDV} = \frac{4\Pi[n]M}{9.3 \times 10^{24}}. \tag{2}$$

In eq. (1), $[\eta]$ is the intrinsic viscosity of the polymer solution in the detector cell, c is the concentration, and η_r is relative viscosity measured by the differ-

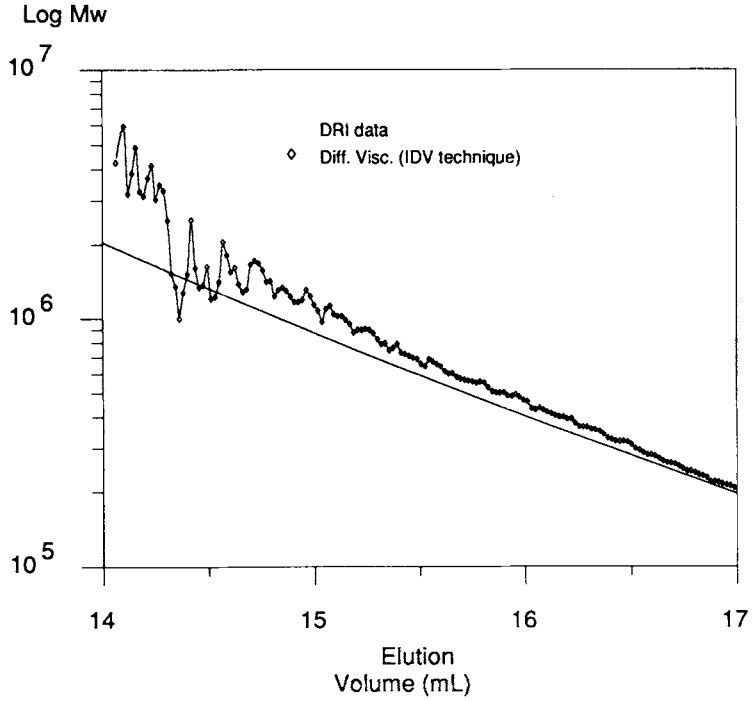

Figure 6 Log(M_w)–elution volume plots for LLDPE 1 (upper end) calculated from DRI data and differential viscometer data (IDV technique).

ential viscometer. In eq. (2), HDV is the hydrodynamic volume of the polymer coils in the DRI detector, and M is the molecular weight. Although this viscosity effect increases the time difference between the differential viscometer and the DRI, it decreases the time difference between the LALLS and the DRI for detector configuration 2. This means that an erroneously low concentration is used in the LALLS calculations [eq. (3)],[18] leading to a higher molecular weight than the true one.

$$M = \frac{R_{th}}{Kc} \tag{3}$$

where M is the molecular weight of the polymer in the LALLS cell, R_{th} is the ratio of the intensity of scattered light to initial intensity of light, K is the optical constant of the polymer (K is constant for a polymer in a specific solvent at constant temperature), and c is the concentration of polymer in solution. Shown in Figure 7 is the $\log(M_w)$ elution volume plot calculated from LALLS and DRI data for LLDPE 1 using the IDV technique to correlate the detectors. As the solution viscosity increases (high molecular end of the distribution) the molecular weight calculated from the LALLS deviates from that calculated from the DRI. In the case of the LALLS, the two plots also deviate at low molecular weights. This is believed to be due to the fact that the estimated ID time difference being used is quite different from the real, physical IDV.

Viscosity Dependent IDV (VDIDV) Techniques

The solution viscosity variation with polymer molecular weight is also reflected by the narrow molecular weight polystyrene standards used to calibrate the SEC column. The elution volume difference between the differential viscometer and the DRI detectors and also the difference between the LALLS and DRI detectors measured from the retention times of the polystyrene standards observed by each detector are shown in Figure 8. As the solution viscosity increases the ID time difference between the DRI and the differential viscometer becomes higher and in the case of the LALLS and DRI detectors the ID time difference becomes smaller due to increased flow to the DRI. Both these effects are reflected in the elution volumes for the standards observed by all three detectors.

It should be noted that, because each detector is sensitive to different features of the polymer molecular weight distribution (see below) each will sense a different molecular weight, M_p, as that of the peak elution volume in the SEC chromatogram of a narrow distribution standard polymer.[13] Therefore, the

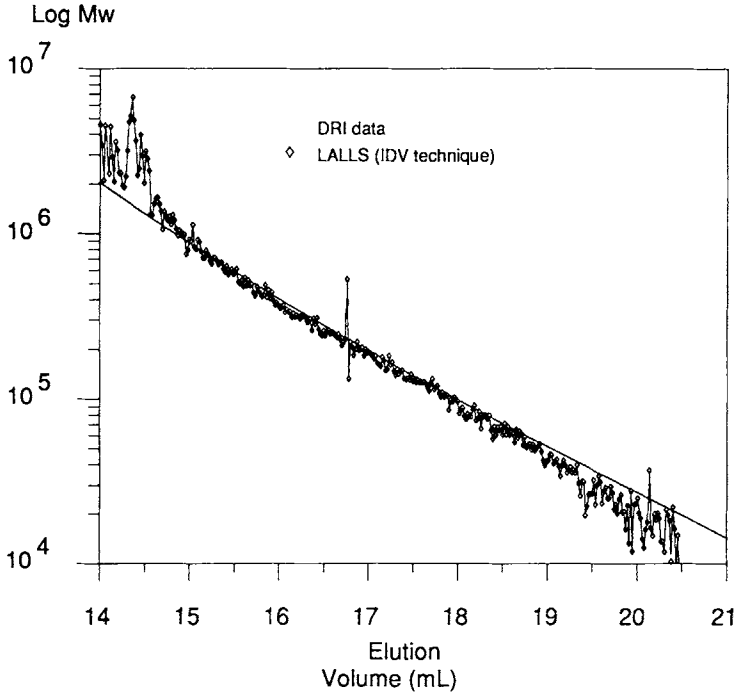

Figure 7 Log(M_w)-elution volume plots for LLDPE 1 calculated from DRI data and LALLS data (IDV technique).

calibration curves for the viscometer and LALLS were produced using the M_ps listed in Table III.

This effect can be used to correlate the detector responses based on a viscosity dependent ID time difference by using calibration curves of hydrodynamic volume versus elution volume for all three detectors. The calibration curves illustrate how the ID time differences vary as a function of hydrodynamic volume. The two viscosity dependent techniques for correlating detectors are based on the same theory. Figure 9 graphically shows how the proper concentration is found by using calibration curves from the different detectors. At a particular elution volume for the LALLS or the differential viscometer, a hydrodynamic volume is calculated from the appropriate calibration curve. This hydrodynamic volume is then used to calculate the elution volume for the DRI detector using the calibration curve from the DRI detector. The concentration of polymer going through the DRI detector at the calculated elution volume is then used in the LALLS or differential viscometer calculations. In this way the proper concentration is used by taking into account differences in solution viscosity that are dependent on the hydrodynamic volumes.

Two techniques are presented here for determination of correct detector offset volumes. The difference between them is the peak molecular weights assigned to the standards. In VDIDV technique 1 described, the peak molecular weights of standards used in the calibration curves for all three detectors

Table III Peak Molecular Weights and Polydispersities for Polystyrene Standards

M_w/M_n	M_p (DRI)	M_p (LALLS)	M_p (Diff. Visc.)
1.14	580	660	620
1.14	950	1,070	1,010
1.10	1,700	1,800	1,830
1.06	3,600	3,780	3,700
1.05	5,050	5,300	5,190
1.05	9,200	9,480	9,360
1.03	11,600	11,900	11,800
1.03	22,000	22,700	22,400
1.03	28,500	29,400	29,000
1.06	47,500	50,500	49,400
1.03	68,000	70,000	69,400
1.04	90,000	93,600	92,500
1.02	165,000	168,000	167,000
1.15	207,700	239,000	231,000
1.03	475,000	489,000	486,000
1.04	950,000	988,000	982,000
1.05	1,900,000	1,955,000	1,982,000
1.05	2,750,000	2,888,000	2,872,000
1.07	4,250,000	4,548,000	4,519,000
1.15	8,000,000	8,560,000	8,519,000

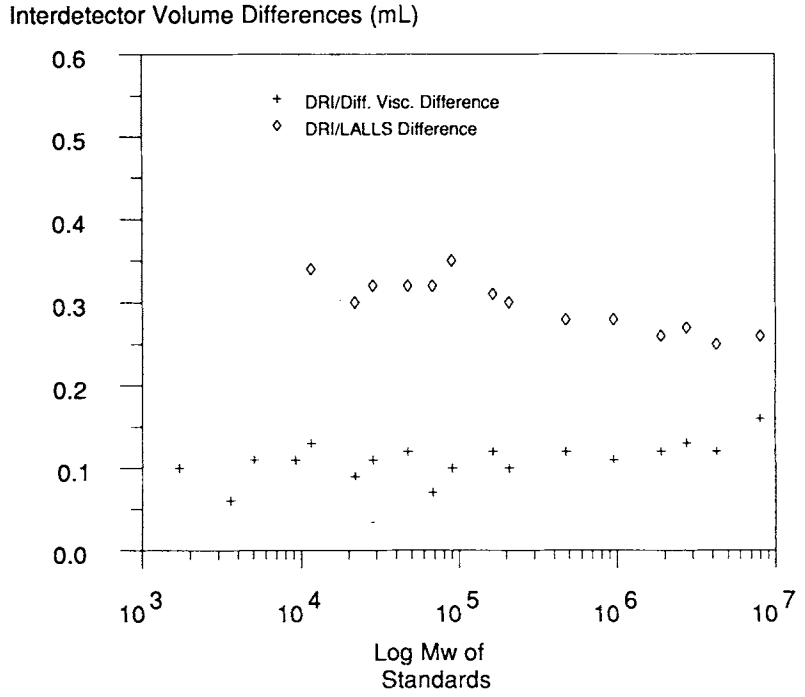

Figure 8 Differences in elution volumes for polystyrene standards using detector combinations DRI/differential viscometer and DRI/LALLS.

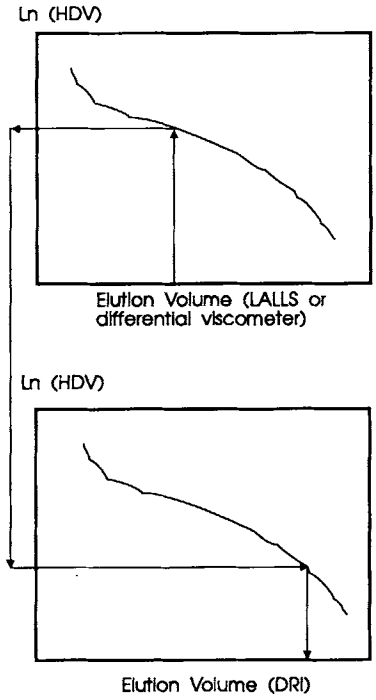

Figure 9 Operation scheme for selecting appropriate concentration values using the VDIDV technique.

are those assigned by the manufacturer of the standards. In VDIDV technique 2, the peak molecular weights used in the calibration curves are dependent on the solution property that the detector measures.[13] The method for calculating these peak molecular weights is described elsewhere[13] and depends on the standards suppliers' reported peak molecular weights and polydispersities. In brief, the responses of the three detectors of interest respond as follows to the concentration, c_i, of eluting species i:

$$S_{i,\mathrm{DRI}} \propto c_i \tag{4}$$

$$S_{i,\mathrm{visc}} \propto c_i[\eta]_i \tag{5}$$

$$S_{i,\mathrm{LALLS}} \propto c_i M_i \tag{6}$$

Here $[\eta]_i$ and M_i are the corresponding intrinsic viscosity (in the SEC solvent) and molecular weight, respectively. The values of M_p that each detector "sees" can be estimated by assuming a molecular weight distribution for the standards. Anionic polystyrenes theoretically have Poisson molecular weight distributions but assumption of a Gaussian distribution is probably closer to the characteristics of the real materials.[13] For such a distribution, eq. (7) gives the weight distribution in terms of the peak molecular weight, M_p, and the polydispersity, PDI ($=\bar{M}_w/\bar{M}_n$). The peak molecular weights for each detector are calculated using eq. (7)[13] and the appropriate proportionality of eqs. (4)–(6).

$$w(M_i) = \frac{\exp\left\{\dfrac{-(M_i - M_p)}{2\left\{\dfrac{M_p^2}{\mathrm{PDI}} - \dfrac{M_p^2}{\mathrm{PDI}^2}\right\}}\right\}}{\left\{2\pi\left\{\dfrac{M_p^2}{\mathrm{PDI}} - \dfrac{M_p^2}{\mathrm{PDI}^2}\right\}\right\}^{1/2}} \tag{7}$$

In eq. (7) PDI is the polydispersity index of the standard, M_p is the reported peak molecular weight, $w(M_i)$ is the weight fraction at each point in the distribution of the standard, and M_i is the molecular weight at each point in the distribution. The calculated peak molecular weights are listed in Table III.

Figure 10 shows molecular weight distributions for LLDPE 1 plotted in the form of log MW versus elution volume calculated from the DRI data and the differential viscometer data using the IDV technique and VDIDV technique 2. At lower molecular weights all three plots overlap but as the solution viscosity increases the distribution calculated using the IDV technique deviates from the DRI molecular weight distribution because the interdetector time lag is not the same for all solution viscosities (i.e. solute molecular weights). The molecular weight distribution calculated using VDIDV technique 2 does not deviate from that calculated from the DRI data (Fig. 11). Figure 12 shows the same plot for LLDPE 2 demonstrating that the trends are consistent between polymers.

The same trends are also found with the LALLS detector analyses. Figure 13 shows the molecular weight distributions for LLDPE 1 calculated in the same manner as Figure 10. Again it was found that the molecular weight–elution volume relation calculated using VDIDV technique 2 matches the DRI-derived relation more closely than the IDV technique. At the higher molecular weights the solution viscosity effect is compensated.

For both detectors VDIDV technique 2 works better than the conventional IDV technique. This is also reflected in the calculated molecular weight averages using all three detector correlation techniques (Table IV, LLDPE 1; Table V, LLDPE 2).

It remains to determine which VDIDV technique is more accurate. Technique 1 uses peak molecular weights supplied by the standards manufacturer and technique 2 uses peak molecular weights calculated based on detector characteristics and an assumed molecular weight distribution for polystyrene standards.[13] For both techniques, there is no discernible

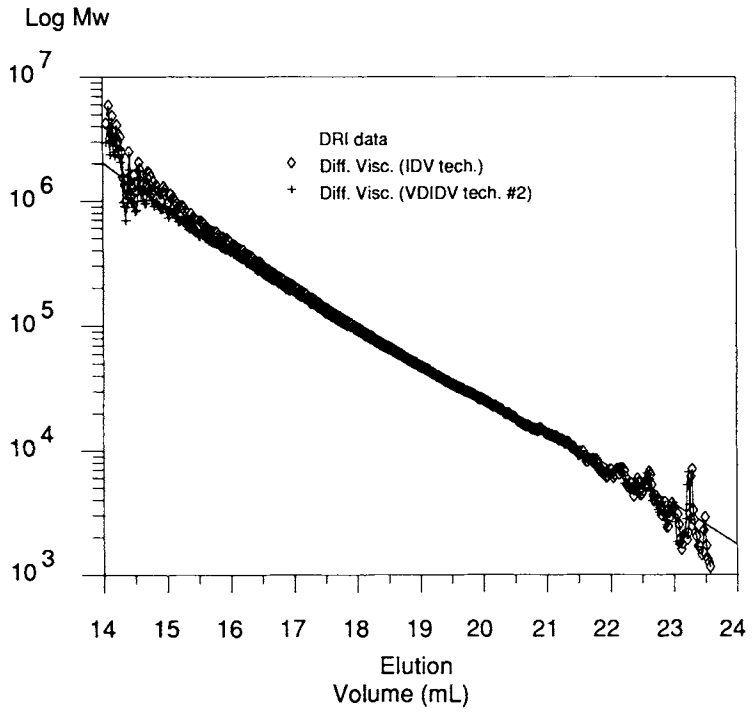

Figure 10 Log(M_w)–elution volume plots for LLDPE 1 using DRI data and differential viscometer data (IDV technique and VDIDV technique 2).

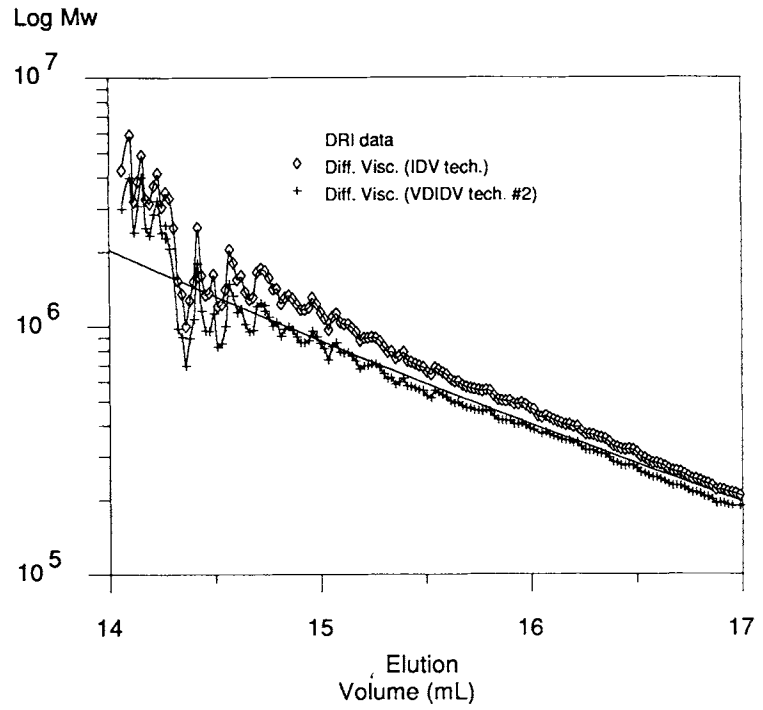

Figure 11 Log(M_w)–elution volume plots for LLDPE 1 (upper end) using DRI data and differential viscometer data (IDV technique and VDIDV technique 2).

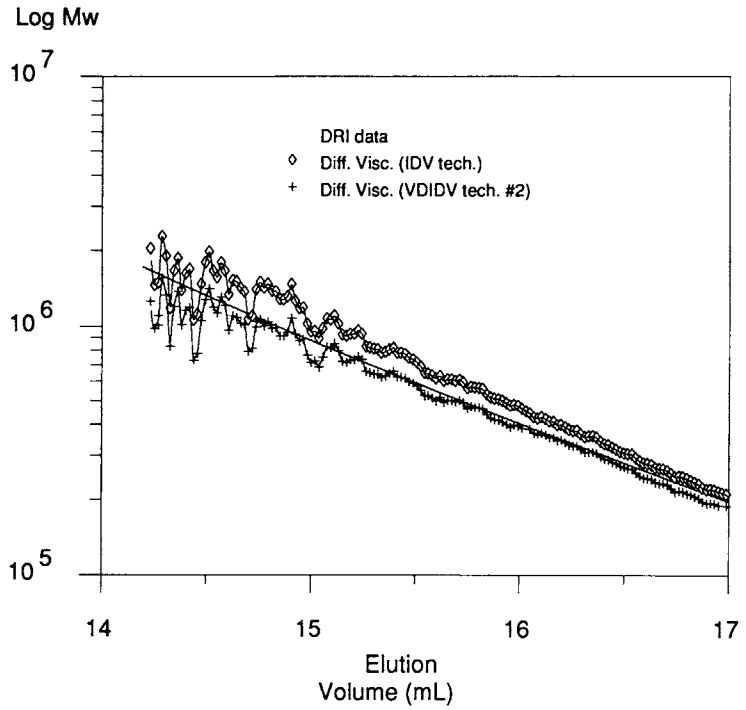

Figure 12 Log(M_w)–elution volume plots for LLDPE 2 (upper end) using DRI data and differential viscometer data (IDV technique and VDIDV technique 2).

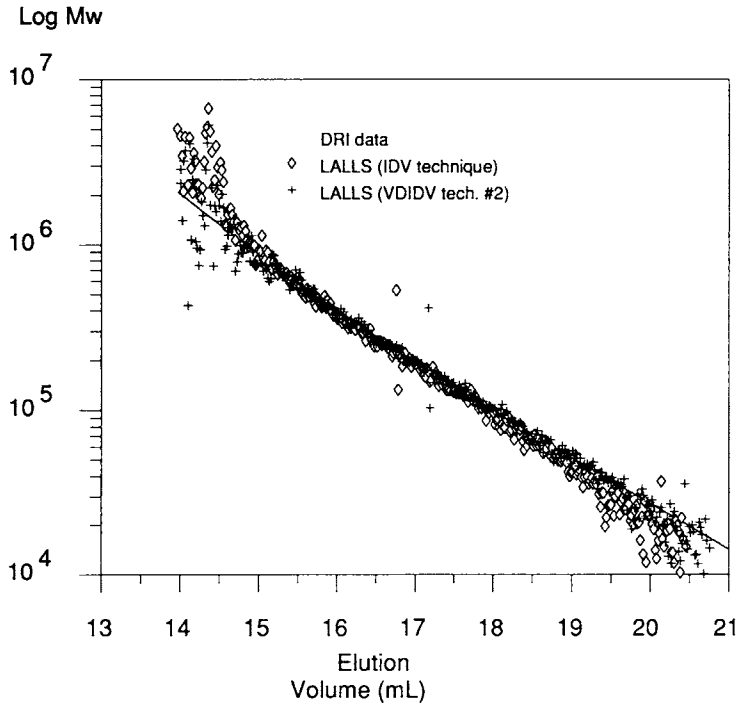

Figure 13 Log(M_w)–elution volume plots for LLDPE 2 using DRI data and LALLS data (IDV technique and VDIDV technique 2).

Table IV Molecular Weight Averages for LLDPE 1 Calculated from Data Using All Correlation Techniques

		Detector: LALLS		
Averages	DRI	LALLS (IDV)	LALLS (VDIDV 1)	LALLS (VDIDV 2)
M_n	27,100	40,100	47,400	48,500
M_w	101,000	125,200	123,000	121,300
M_z	327,000	467,000	398,000	375,200
		Detector: Diff. Visc.		
Averages	DRI	Visc. (IDV)	Visc. (VDIDV 1)	Visc. (VDIDV 2)
M_n	27,100	30,100	29,300	29,200
M_w	101,000	118,200	109,800	107,600
M_z	327,000	456,000	341,000	335,000

difference in the calculated molecular weight–elution volume relations for both the LALLS and differential viscometer detectors. Consequently, there is no significant difference in the calculated molecular weight averages (Tables IV, V).

When analyzing polymers with lower molecular weights, such as NIST SRM 1475 PE, the problem posed by high solution viscosities of higher molecular weight species is less pronounced. In the case of both detectors, solution viscosity effects are less pronounced than with higher molecular weight polymers (LLDPEs 1 and 2). The calculated molecular weight averages are listed in Table VI.

Ideally, the DRI concentration detector signal is proportional only to concentration [i.e. $S_{\mathrm{DRI}} \propto c$, eq. (4)]. The viscometer detector output scales as $cM^{0.7}$, for most polymers in common SEC solvents, and the light scattering detector signal is proportional to cM. It is expected, then, that the three different detectors will produce $\bar{M}_w$ and higher averages that rank in the order DRI < viscometer < LALLS.[24] This is what is observed with the differences between the three detectors greater for $\bar{M}_z$ than for $\bar{M}_w$. (In the case of $\bar{M}_n$, the LALLS is often too noisy and insensitive to low molecular weight species to provide good values. $\bar{M}_n$ from the DRI and viscometer generally coincide fairly well.) This order is preserved in the present results (e.g. Tables IV–VI), but it is also clear that some of the effects are attributable to detector mis-

Table V Molecular Weight Averages for LLDPE 2 Calculated from Data Using All Correlation Techniques

		Detector: LALLS		
Averages	DRI	LALLS (IDV)	LALLS (VDIDV 1)	LALLS (VDIDV 2)
M_n	26,900	39,100	45,300	46,200
M_w	103,200	131,300	129,000	122,300
M_z	325,000	471,000	387,000	368,000
		Detector: Diff. Visc.		
Averages	DRI	Visc. (IDV)	Visc. (VDIDV 1)	Visc. (VDIDV 2)
M_n	26,900	29,900	29,000	28,700
M_w	103,200	119,500	106,000	107,500
M_z	325,000	447,000	348,000	330,000

Table VI Molecular Weight Averages for NIST SRM 1475 Calculated from Data Using All Correlation Techniques

		Detector: LALLS		
Averages	DRI	LALLS (IDV)	LALLS (VDIDV 1)	LALLS (VDIDV 2)
M_n (18,310)[a]	19,500	32,000	39,300	34,500
M_w (53,070)[a]	64,200	87,600	80,900	79,600
M_z (138,000)[a]	147,700	258,000	190,700	185,300
		Detector: Diff. Visc.		
Averages	DRI	Visc. (IDV)	Visc. (VDIDV 1)	Visc. (VDIDV 2)
M_n (18,310)[a]	19,500	20,300	20,100	19,800
M_w (53,070)[a]	64,200	74,400	70,200	69,000
M_z (138,000)[a]	147,700	172,800	159,800	156,000

[a] NIST SRM 1475 vendor values.

matching that can be corrected by either VIDV method described.

CONCLUSIONS

To avoid the need for band broadening corrections in multidetector SEC systems, careful consideration must be taken when orienting detectors. A detector configuration must be chosen that will maximize solvent flow to each detector. Detectors with large cell volumes (LALLS, differential viscometer) will broaden elution profiles of standards and samples if solvent flow is too low. To achieve maximum flow in SEC systems consisting of a LALLS/DRI/differential viscometer detector array, the flow should not be split more than once. Best results were achieved by placing the LALLS first in the SEC train and splitting the flow to the DRI and the differential viscometer following the LALLS. This configuration not only minimizes band broadening effects but it also maximizes the signal-to-noise ratio in the LALLS detector response.

Correlating a detector that measures concentration (DRI) to detectors that measure other solution properties (light scattering, viscosity) is not straightforward. In a split flow detector system, solution viscosity effects play a large role in time lags between these detectors. The time difference between detectors varies in a manner that can be quantitatively measured using calibration curves of hydrodynamic volume versus elution volume generated for each detector using polystyrene standards. Two techniques of this type were presented here and compared against the traditional single-valued IDV method. The difference between the two viscosity-dependent techniques is in the peak molecular weight assigned to the standards used to generate the calibration curves. The first technique uses molecular weights reported by the supplier and the second technique used peak molecular weights calculated based on the solution properties being measured by the detector [see Results, eqs. (4)–(6)]. Both viscosity dependent techniques produced better results than the conventional IDV technique and appear to be equivalent.

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APPENDIX: DETERMINATION OF SPECIFIC VISCOSITY

The particular differential viscometer cell is a Wheatstone bridge arrangement of capillary tubing. The column eluant is split between two branches as it enters the detector and is recombined just before it leaves. One side of the branch has solvent flowing through it while the other side has the sample. A pressure transducer measures the pressure difference between the two branches (ΔP) while a second transducer measures the overall drop in pressure across the inlet and outlet of the detector (P_{in}). The

information from the transducers is used to calculate specific viscosity using eq. (A.1).

$$\eta_{sp} = \frac{4\Delta P}{P_{in} - 2\Delta P}. \quad (A.1)$$

During normal operation of the detector the inlet pressure will vary only slightly with viscosity changes in column eluant (> 2%) and a single value for P_{in} is sufficient to calculate an accurate molecular weight distribution. With highly viscous samples, P_{in} can vary up to 5% of the total inlet pressure (P_{in}) and this variation must be taken into account in eq. (A.1) to calculate specific viscosity (η_{sp}) accurately. Both pressure transducers measure pressure changes in the detector and a linear relationship exists between P_{in} and ΔP that does not vary with sample type. This linear relationship [eq. (A.2)] is used to estimate P_{in} eq. (A.1).

$$P_{in} = P_{in,initial} + 3.9\Delta P. \quad (A.2)$$

In eq. (A.2) $P_{in,initial}$ is the initial inlet pressure and the coefficient 3.9 will vary with operating conditions (temperature, solvent, and flow rate). These conditions are normally kept constant in our operation.

REFERENCES

1. T. H. Mourey and L. E. Oppenheimer, *Anal. Chem.*, **56,** 2427 (1984).
2. A. C. Ouano and W. Kaye, *J. Polym. Sci., Chem. Ed.*, **12,** 1151 (1974).
3. M. Haney, *J. Appl. Polym. Sci.*, **30,** 3037 (1985).
4. T. Ishige, S. I. Lee, and A. E. Hamielec, *J. Appl. Polym. Sci.*, **15,** 1607 (1971).
5. S. T. Balke and R. D. Patel, *ACS Symp. Ser.*, **138,** 149 (1980).
6. S. T. Balke, *Quantitative Column Liquid Chromatography, A Survey of Chemometric Methods,* Elsevier, Amsterdam, 1984.
7. R. Lew, D. Suwanda, and S. T. Balke, *J. Appl. Polym. Sci.*, **35,** 1049 (1988).
8. J. Lesec, M. Milliquant, and T. Havard, *Am. Chem. Soc.: PMSE Div. Prepr.*, **65,** 138 (1991).
9. C. Kuo, T. Provder, and M. E. Koehler, *Am. Chem. Soc.: PMSE Div. Prepr.*, **65,** 142 (1991).
10. S. T. Balke, P. Cheung, L. Jeng, R. Lew, and T. H. Mourey, *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, **48,** 259 (1991).
11. C. Kuo, T. Provder, and M. E. Koehler, *ACS Symp. Ser.*, **521,** 231 (1993).
12. T. H. Mourey and S. T. Balke, *ACS Symp. Ser.*, **521,** 180 (1993).
13. K. G. Suddaby, R. A. Sanayei, K. F. O'Driscoll, and A. Rudin, *Makromol. Chem.*, **194,** 1965 (1993).
14. K. G. Suddaby and R. A. Sanayei, private communication, 1993.
15. A. E. Hamielec, A. C. Ouano, and L. L. Nebenzahl, *J. Chromatogr.*, **1,** 527 (1978).
16. V. Grinsphun, K. F. O'Driscoll, and A. Rudin, *ACS Symp. Ser.*, **245,** 273 (1984).
17. Jordi Associates, *GPC Column Applications Notes,* Bellingham, MA, 1989.
18. Chromatix Inc. Applications Note LS-2, *Determination of MWD by combining LALLS with GPC,* 1977.
19. H. K. Mahabadi and A. Rudin, *Polym. J.*, **11,** 123 (1979).
20. A. Rudin, *The Elements of Polymer Science and Engineering,* Academic, San Diego, 1982.
21. P. J. Wang and B. S. Glassbrenner, *J. Liq. Chromatogr.*, **11,** 3321 (1988).
22. O. F. Solomon and I. Z. Ciuta, *J. Appl. Polym. Sci.*, **6,** 683 (1962).
23. Z. Grubisic, P. Remp, and H. Benoit, *J. Polym. Sci., B,* **5,** 753 (1962).
24. S. Pang and A. Rudin, *J. Appl. Polym. Sci.*, **46,** 763 (1992).

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