Use of Continuous Viscometer and Light Scattering Detectors in Characterization of Polyolefins: Comparisons of Data from Individual and Combined Detectors

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SYNOPSIS

Molecular weights of polyethylenes have been characterized using differential refractometer (DRI), continuous viscometer (CV), and low-angle laser light (LALLS) detection. In normal operation with the latter two detectors, the DRI is also employed as a concentration detector. The intrinsic viscosity of the whole polymer can be derived from the CV without use of a DRI concentration detector. If one calibrates the size exclusion chromatography (SEC) columns using the CV detector, it is possible to use this universal calibration relation and the CV detector to calculate number average molecular weight (M_n) of the polymer. Weight average molecular weight (M_w) of the sample can be calculated using data from the LALLS alone, without reference to the DRI. These variations of the analysis were tested and the advantages and limitations of the different detectors were compared using standard reference polyethylene samples in solution in 1,2,4-trichlorobenzene at 145°C.

INTRODUCTION

To assure efficient separation by size exclusion chromatography (SEC), the concentration of the injected polymer should be kept low. This is a fundamental requirement to enable the polymer coils to occupy independent hydrodynamic domains.[1,2] In practice, the concentration of the polymer solution injected should not exceed about one half of the reciprocal of its intrinsic viscosity. Consequently, if a polymer sample has an intrinsic viscosity of 2 dL/g the maximum concentration that should be injected is 0.25 g/dL (0.25% by wt.). An intrinsic viscosity of 2 dL/g generally characterizes high-molecular-weight tails of broad distribution polymers.

In normal SEC, a polymer sample may be diluted by a factor of about 200 during its flow through columns to the detectors. As a result, if the injected polymer sample has an intrinsic viscosity of 2 dL/g the eluent concentration at the detectors is only 12.5 ppm. Ideally, one should use a fluorescence or ultraviolet detector at such low concentrations. These detectors are not generally usable in SEC, however, and a less sensitive differential refractive index detector (DRI) is usually employed as a concentration detector.

Small changes in solvent composition and particularly in temperature may mask the DRI signals generated by very low concentrations of polymer. This is especially noticeable in high-temperature SEC analyses, which must be used with semicrystalline polyolefins. As a result, many commercial polyolefins of interest have broad molecular weight distributions in which the high-molecular-weight tails may not be detected by the DRI.

Low-angle laser light scattering (LALLS)[3] and continuous viscometer (CV) detectors[4] have advantages over the DRI in being more sensitive to low concentrations of high-molecular-weight species. In addition, both LALLS and CV can be used to analyze polymers that contain long branches, for which universal calibration with a DRI detector is not valid.

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Here, we compare polyethylene analyses using DRI, CV, and LALLS detection. In normal operation with the latter two detectors, the DRI is also employed as a concentration detector. We test a method to derive the intrinsic viscosity of the whole polymer without use of a DRI concentration detector.

If one calibrates the SEC columns using the CV detector, it is possible to use this universal calibration relation and the CV detector alone to calculate the number average molecular weight of the polymer. This is the Goldwasser technique,[5] which has the unique advantage also of applicability to mixtures and copolymers in which the composition may vary with molecular weight. M_n data from this method are compared to those from analyses of the "entire" molecular weight distribution.

As a further comparison, M_w of the sample is calculated using data from the LALLS alone, without reference to the DRI concentration detector. M_w from SEC is compared with that obtained by light scattering analyses of the whole polymer sample.

EXPERIMENTAL

Instruments

The SEC system used in this study (Fig. 1) consisted of a high-temperature chromatograph equipped with a DRI, LDC/Milton Roy KMX-6 LALLS, Viscotek™ Model 100 CV detector, an Erma Optical Works Ltd (Tokyo) ERC-3510 on-line degasser, a Molytek thermopulse flowmeter, and a set of Jordi columns that comprised a mixed bed column and a 1000-Å linear column. The experiments were run with a flowrate of 1.5 mL/min at 145°C.

The LALLS photometer with a high-temperature flow-through cell was serially connected with the column. Scattering intensity data were collected using a 6–7° annulus with a 6328-Å wave length He-Ne laser. The DRI and CV detectors were connected in parallel to the LALLS detector. The ratio of the flow volumes between the DRI and CV lines was approximately 50:50. A flowmeter was connected in series with the DRI to monitor the instantaneous flowrate between the branches during the experimental runs. Polymer concentration in the eluent was monitored with the DRI detector. The mobile phase was filtered through an on-line 0.5-μm tetrafluoroethylene filter just before the LALLS cell.

The value of (dn/dc) for the polyethylenes were determined independently with a LDC/Milton Roy KMX-16 differential refractometer. This value was found to be -0.091 cm^3/g.

Using a software package developed in our laboratory, the analog data from all three detectors were collected and digitized through a Cyborg A/D interface. Collected data were processed with an Apple Macintosh computer with our software package.

Materials and Sample Preparation

All solutions for analysis were prepared in filtered 1,2,4-trichlorobenzene (TCB), the same solvent used as the SEC eluent. Polymer solutions were prepared by dissolving known quantities of polyethylenes and diluting to the desired volume with the filtered TCB solvent. Dissolution of PE samples was achieved by rotating the samples at 160°C for 16–24 h. To prevent oxidative degradation of LDPE, 0.1 wt % antioxidant (Irganox 1010) was added. The mixed bed SEC column was calibrated using 30 polystyrene standard samples with molecular weights ranging from 580–15,000,000.

Complete dissolution of the polymers were assumed to have been achieved when the LALLS detector trace was free of spikes.[6] Higher-molecular-weight linear polyethylenes may require longer dissolution times than those used in this study. Noise in any of the signals was not suppressed electronically and the calculated molecular weight distribution curves were not smoothed.

Theory and Calculation

Intrinsic Viscosity Measurement

The specific viscosity, η_{sp}, chromatogram of a polymer sample sample can be related to the intrinsic viscosity of the polymer sample, $[\nu]$, using the following rationale. The intrinsic viscosity is defined as the limiting ratio of the specific viscosity when the polymer concentration approaches zero.[7]

$$[\eta] = \lim_{c \to 0} \frac{\eta - \eta_0}{c\eta_0} = \lim_{c \to 0} \frac{\delta P - \delta P_0}{c\delta P_0} \qquad (1)$$

Here, η and η_0 are the viscosities, respectively, of the polymer solution with concentration, c, and the solvent. δP and δP_0 are the pressures recorded in the solution and solvent legs of the viscometer.[4] For very dilute polymer concentrations, such as those existing in SEC, eq. (1) can be closely approximated by

$$[\eta] = \frac{\delta P - \delta P_0}{c\delta P_0} \qquad (2)$$

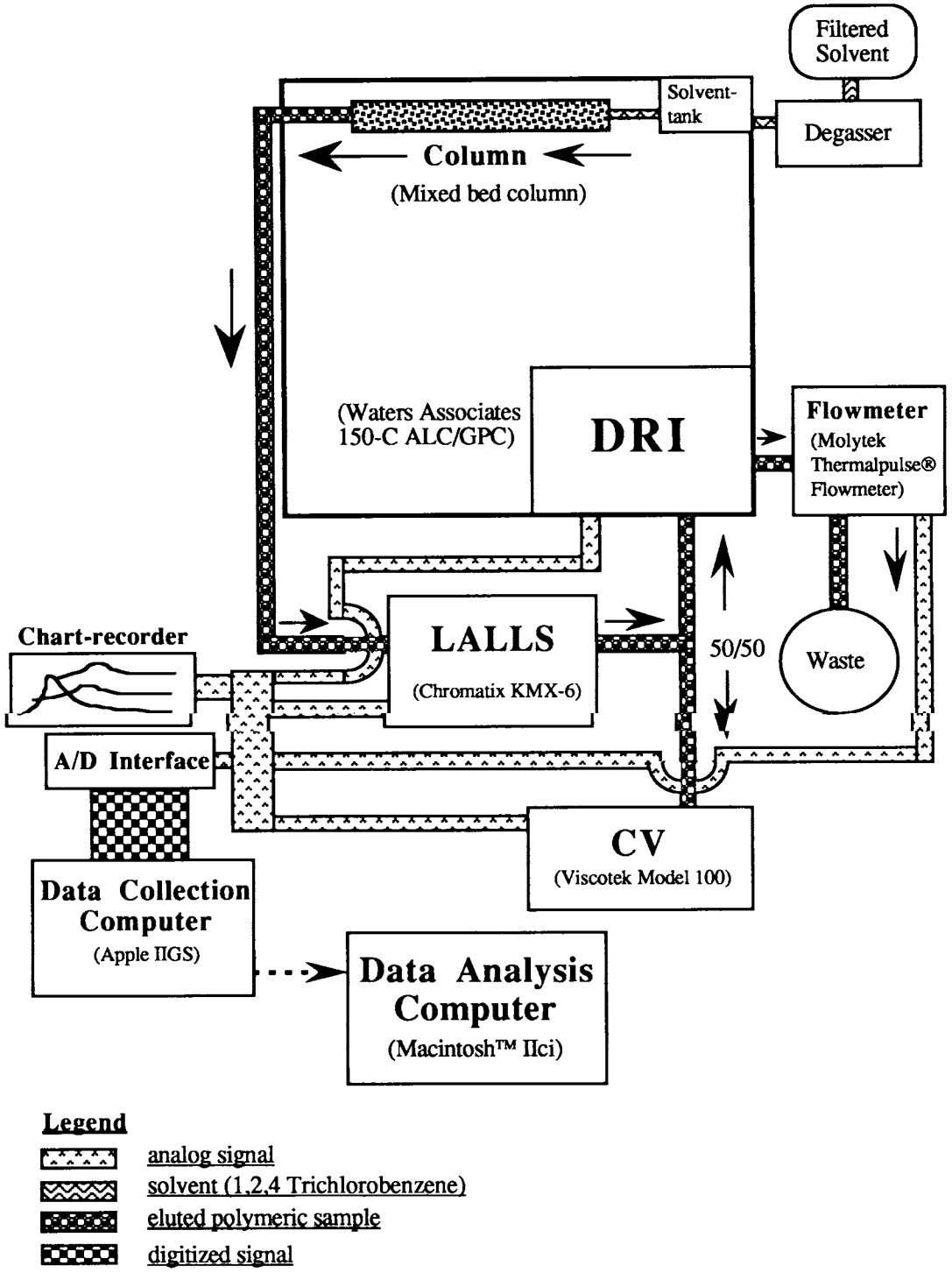

Figure 1 Schematic of apparatus.

The specific viscosity of random coil polymer molecules in dilute solution can also be expressed by the Einstein relationship[8]:

$$\frac{\delta P - \delta P_0}{\delta P_0} = \frac{\eta - \eta_0}{\eta_0} = \omega\Phi \qquad (3)$$

In eq. (3), Φ is the volume fraction of polymer existing in solution and ω is the shape factor for random coils. Combination of eqs. (1) and (3) gives

$$[\eta] = \frac{\omega\Phi}{c} \qquad (4)$$

The volume fraction of polymer in all the eluent that flows through the column, Φ, is equal to the volume due to polymer, V_p, divided by the total elution volume, V_e. The total elution volume is the fluid volume that passed through the SEC columns. This is the volume collected from starting point "s" of the eluted peak to ending point "e" of the peak on a typical chromatogram as shown in Figure 2.

$$\Phi = \frac{V_p}{V_e} \tag{5}$$

But, these volumes are equal to the sum of the incremental volumes taken at each point on the chromatogram starting at point s and ending point e. If Φ_i and δVei are the incremental volume fraction of polymer and the change in elution volume, respectively, on the chromatogram, then

$$V_p = \sum \Phi_i \delta V_{ei} \tag{6}$$

$$V_e = \sum \delta V_{ei} \tag{7}$$

Consequently, eq. (5) can be rearranged to

$$\Phi = \frac{\sum \Phi_i \, \delta V_{ei}}{\sum \delta V_{ei}} \tag{8}$$

Combining eqs. (4) and (8) gives

$$[\eta] = \frac{k \sum \Phi_i \, \delta V_{ei}}{c \sum \delta V_{ei}} \tag{9}$$

Assuming no polymer is lost in the packing by absorption or entrapment, then the polymer concentration, c, is the total mass of polymer injected, m, divided by the total elution volume, $\sum \delta V_{ei}$. Thus

$$c = \frac{m}{\sum \delta V_{ei}} \tag{10}$$

Combining eqs. (9) and (10) eliminates $c \sum \delta V_{ei}$ and gives

$$[\eta] = \frac{k \sum \Phi_i \, \delta V_{ei}}{m} \tag{11}$$

By using eq. (3), the volume fraction of polymer, Φ_i, at increment i can be expressed in terms of solution and solvent pressures:

$$\Phi_i = \frac{\delta P_i - \delta P_{0i}}{\omega \delta P_{0i}} = \frac{\eta_{spi}}{\omega} \tag{12}$$

Elimination of Φ_i and ω is obtained by combining eqs. (11) and (12). The sample intrinsic viscosity then becomes

$$[\eta] = \frac{\sum (\eta_{spi} \delta V_{ei})}{m} \tag{13}$$

The summation term in eq. (13) is simply the area under the eluted sample peak within the specific viscosity chromatogram envelope measured by the CV detector.

Number Average Molecular Weight M_n Calculation[7]

If the SEC columns are calibrated by using the CV detector, then at any elution volume, V_{ei}, the corresponding hydrodynamic volume, V_{hi}, can be obtained from the predetermined calibration curve:

$$V_{hi} \propto [\eta]_i M_i \tag{14}$$

where M_i is really M_{ni}.

By using the Rudin model,[9,10] eq. (14) can be expressed as

$$V_{hi} = \frac{4\pi[\eta]_i M_i}{3\phi''} \tag{15}$$

where ϕ'' is Flory's "universal" constant[11] = 3.1×10^{24} (with $[\eta]$ in cm^3/g).

At any elution volume, V_{ei}, the intrinsic viscosity of the ith species can calculated from eq. (13):

$$w_i[\eta]_i = \frac{\eta_{spi} \delta V_{ei}}{m} \tag{16}$$

Dividing eq. (15) by (16), we have

$$\frac{V_{hi}}{n_{spi} \delta V_{ei}/m} = \frac{4\pi[\eta]_i M_i}{3\phi'' wi[\eta]_i} = \frac{4\pi M_i}{3\phi'' w_i} \tag{17}$$

Therefore, combining eqs. (16) and (17) the number average molecular M_n can be calculated based upon the data obtained from the CV detector and the calibration curve alone:

$$M_n = \frac{3\phi'' m}{4\pi \delta V_{ei}} \frac{1}{\sum \frac{\eta_{spi}}{V_{hi}}} \tag{18}$$

Weight Average Molecular Weight M_w Calculation

The absolute molecular weight of the macromolecules in the ith elution volume increment in the

LALLS chromatogram can be calculated from the following equation:

$$\frac{Kc_i}{R_{\theta i}} = \frac{1}{M_i} + 2A_{2,i}c_i \qquad (19)$$

where M_i is really M_{wi}, $R_{\theta i}$ is the excess Rayleigh factor calculated directly from the LALLS detector data, c_i is the sample concentration of the polymeric species that appeared at elution V_{ei}, K is a polymer solution optical constant, and $A_{2,i}$ is the second virial coefficient. A_2 is a weak inverse function of molecular weight. At the dilute concentration condition in the SEC effluent, the second term in eq. (19) can be neglected so that

$$\frac{Kc_i}{R_{\theta i}} = \frac{1}{M_{wi}} \qquad (20)$$

The concentration c_i can be expressed as

$$c_i = \frac{w_i m}{\delta V_{ei}} \qquad (21)$$

where m is the injected mass of the sample, V_{ei} is the elution volume of the ith increment, and w_i is the weight fraction corresponding of the sample. Substituting eq. (21) into (20),

$$M_{wi} = \frac{R_{\theta i \delta} V_{ei}}{w_i K m} \qquad (22)$$

Since

$$M_w = \sum w_i M_{wi} \qquad (23)$$

Therefore, the weight average molecular of the sample can calculated from the combination of eqs. (22) and (23):

$$M_w = \frac{\delta V_{ei}}{Km} \sum R_{\theta i} \qquad (24)$$

without using the DRI as a concentration detector. (This equation assumes implicitly that the specific refractive index increment, dn/dc, is independent of polymer molecular weight or composition. It is reasonable for olefin copolymers but not for other copolymers or mixtures.)

RESULTS AND DISCUSSION

Table I lists calculated intrinsic viscosities of several polymer standards based upon data from the CV detector and eq. (13). Good agreements exist between the literature values and calculated measurements.

Table I Intrinsic Viscosity Measurements of NBS 1475, NBS 1476, and a Broad Distribution Polystyrene Sample

Sample	IV g/dL[a]	IV g/dL[b]	IV g/dL[c]
NBS 1475	1.011	1.011	1.009
NBS 1476	0.933	0.985	0.968
Polystyrene[d]	—	0.837	0.844

[a] NBS reported values.
[b] Measurement obtained by using CV data and eq. (13).
[c] Measurement obtained by using CV data and eq. (25).
[d] Broad distribution commercial sample.

The DRI signal is proportional to the concentration, c, of the polymer in the eluent. The LALLS signal is proportional to cM, where M is the molecular weight of the eluting species. Also, the CV signal scales as $cM^{0.7}$ for most polymer solutions of interest in SEC. (The proportionality is to $cM^{0.5}$ in theta solutions.) These features give advantages to CV and LALLS detectors over DRI detectors when dealing with high-molecular-weight polymers. These differences are already shown in Figure 2, which records the normalized DRI, CV, and LALLS traces of low-density polyethylene standard material National Bureau of Standards (NBS) 1476. These results are presented without any signal smoothing. Recall that the molecular weights of the eluting species decrease from left to right in this plot since the abscissa is in units of elution volume.

It can be seen here that the LALLS signal is the noisiest of these. This is inherent in the techniques since LALLS will be sensitive to the presence of dust, dirt, or large species of any type. (The LALLS peak is particularly noisy at its peak in this chromatogram. Noise at the peak here is adventitious.) Also, the LALLS detector is the only one that reveals the bimodality of the molecular weight distribution of this polymer.

No concentration detector, such as DRI, is required to determine the concentration of polymer in the eluent when using eq. (13) to measure total sample intrinsic viscosity. Prior to this, on-line CV detectors have been used with DRI detectors to determine both the concentration and intrinsic viscosities at each point along a SEC chromatogram.[4,12-17] The weight averaged sum of these intrinsic viscosities at each point is equal to the sample intrinsic viscosity.

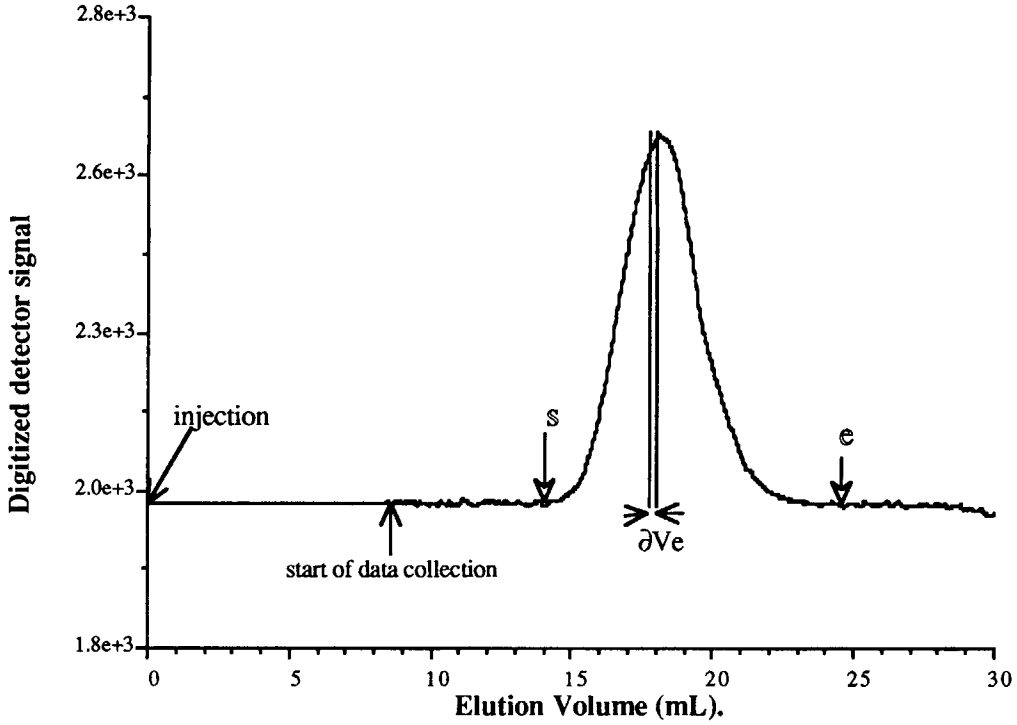

Figure 2 Typical SEC chromatogram.

$$[\eta] = \frac{\sum w_i[\eta]_i}{\sum w_i} \qquad (25)$$

In eq. (25), $[\eta]$ is the intrinsic viscosity of the whole sample, w_i is the weight concentration of the polymer in the ith elution volume, and $[\eta]_i$ is the intrinsic viscosity of the sample in the same volume increment. Table I shows the comparison of the total intrinsic viscosities for several polymers calculated using eq. (13), as well as eq. (25), to sum the individual intrinsic viscosities along the chromato-

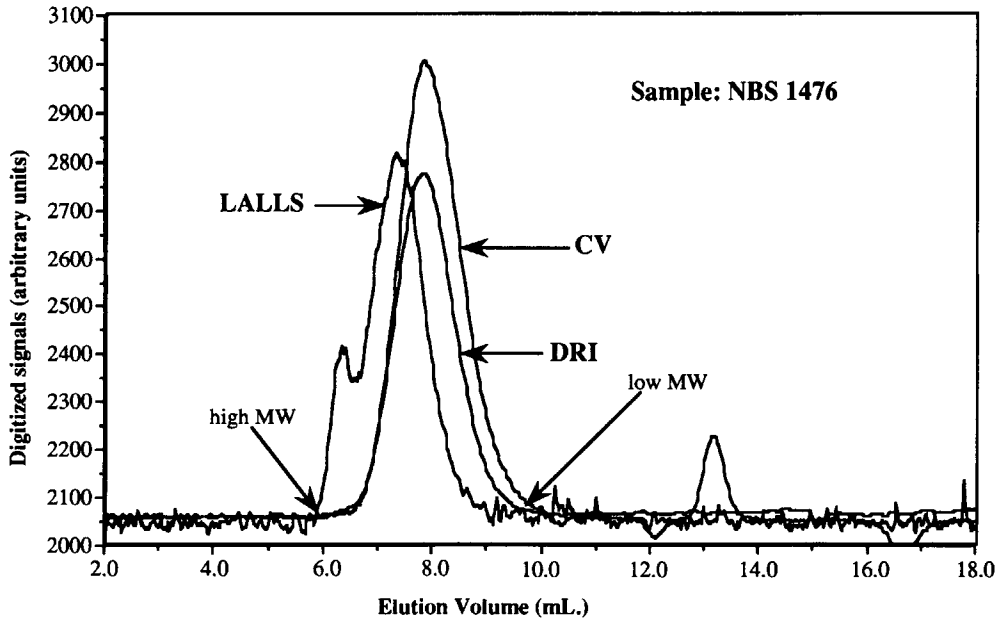

Figure 3 Normalized raw data traces and SEC signals of NBS SRM 1476.

grams. Good agreement exists between the two reported intrinsic viscosity values. The greatest discrepancy is for sample NBS 1476, which shows a higher $[\eta]$ using eq. (13) than eq. (25). This reflects the presence of high-molecular-weight species that are detected by the CV detector, but not the DRI, as shown in Figure 3 of the raw SEC chromatograms.

It is suggested that a good general practice would involve routine calculations of $[\eta]$ using both eqs. (13) and (25). Any significant difference between the two values suggests the existence of high-molecular-weight species in low concentrations such that the DRI has failed to record their presence. This indicates that the measured molecular weight distribution has been truncated at the high molecular end.

One advantage in calculating individual intrinsic viscosities along a SEC chromatogram [i.e., using the method implied in eq. (25)] is that Mark–Houwink K and a values can be determined from the $[\eta]$-M calibration curve. This is achieved by using the Mark–Houwink–Sakurada relation [eq. (26)] and plotting the log of molecular weight vs. the corresponding log of intrinsic viscosity throughout the chromatogram:

$$[\eta] = KM_v^a \tag{26}$$

In applying eq. (26) here, the assumption has been that each eluted fraction has a narrow and uniform molecular weight distribution.[18] Therefore, it is valid to assume that the value of $M_n \approx M_w \approx M_v$ without serious error. Figure 4 shows the Mark–Houwink plots for the linear polyethylene (NBS SRM 1475) and the branched polyethylene (NBS 1476) used.

Some useful features of this plot include the calculation of K and a, of course. These values are $K = 0.596$ ml/g, $a = 0.69$, from the NBS 1475 plot. In addition, we note that the NBS 1476 plot lies below the NBS 1475 line. This is to be expected since LDPE 1476 contains long branches and its hydrodynamic volume is less at a given molecular weight than that of the linear homolog 1475. It can be seen also that the NBS 1476 data are not linear, indicating that branching character is not uniform with molecular weight and that long branching is least at higher molecular weights.

Another useful feature of these Mark–Houwink plots lies in their sensitivity to noise in the chromatograms. Clearly, here the NBS 1475 data become quite noisy at molecular weights < 6000 and $> 200{,}000$. These uncertainties in the tails of the molecular weight distributions are not as readily discernable from the raw chromatograms or the molecular weight distribution plots.

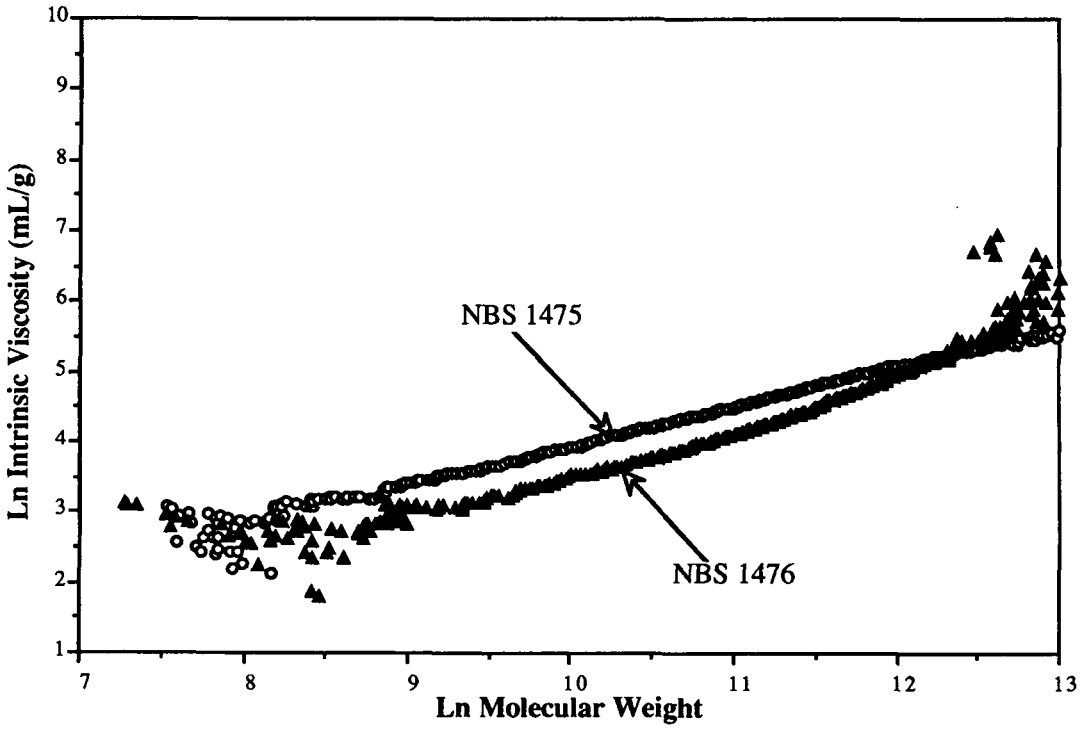

Figure 4 Log–log plot of intrinsic viscosities vs. molecular weights for NBS 1475 and 1476.

Table II Molecular Weight Averages of NBS 1475 and 1476 Polyethylenes and a Broad Distribution Polystyrene

			CV			LALLS		
Sample	M_n	M_w	M_n	M_w	M_z	M_n	M_w	M_z
NBS 1475	18,000[a]	53,000[a]	19,200	50,600	120,800	11,300	52,800	311,400
			18,800[b]				59,000[c]	
NBS 1476	28,000[d]	100,400[d]	40,100	101,500	278,100	38,400	100,300	1,536,200
			36,200[b]				102,800[c]	
Polystyrene[e]	—	—	74,000	359,700	947,700	113,800	358,700	988,200
			68,000[b]				360,100[c]	

[a] NBS certified value.
[b] Measurement obtained by using CV data using eq. (18).
[c] Measurement obtained by using LALLS data using eq. (24).
[d] Ref. 21.
[e] Broad distribution sample.

There have been a number of reports on measurement of molecular weight averages of NBS 1476 standard reference material branched polyethylene.[19-23] All results indicated that M_w measured by SEC in combination with a LALLS–DRI detector system is significantly lower than its true value, which is measured by light scattering analyses of solutions of the whole polymer. It has been suggested[24] that this resulted from the lack of sensitivity of the concentration detector (DRI) in monitoring the concentration of the high-molecular-weight species present. In Table II, we compare M_w from LALLS–DRI data as usual, with M_w obtained from the LALLS alone, using the method of eq. (24). It can be seen that the latter technique does not produce results that are significantly different from the more conventional calculation method.

Measurements of M_w of NBS 1476 using light scattering of the whole polymer samples have produced values of about 220,000.[23,25,26] This has been

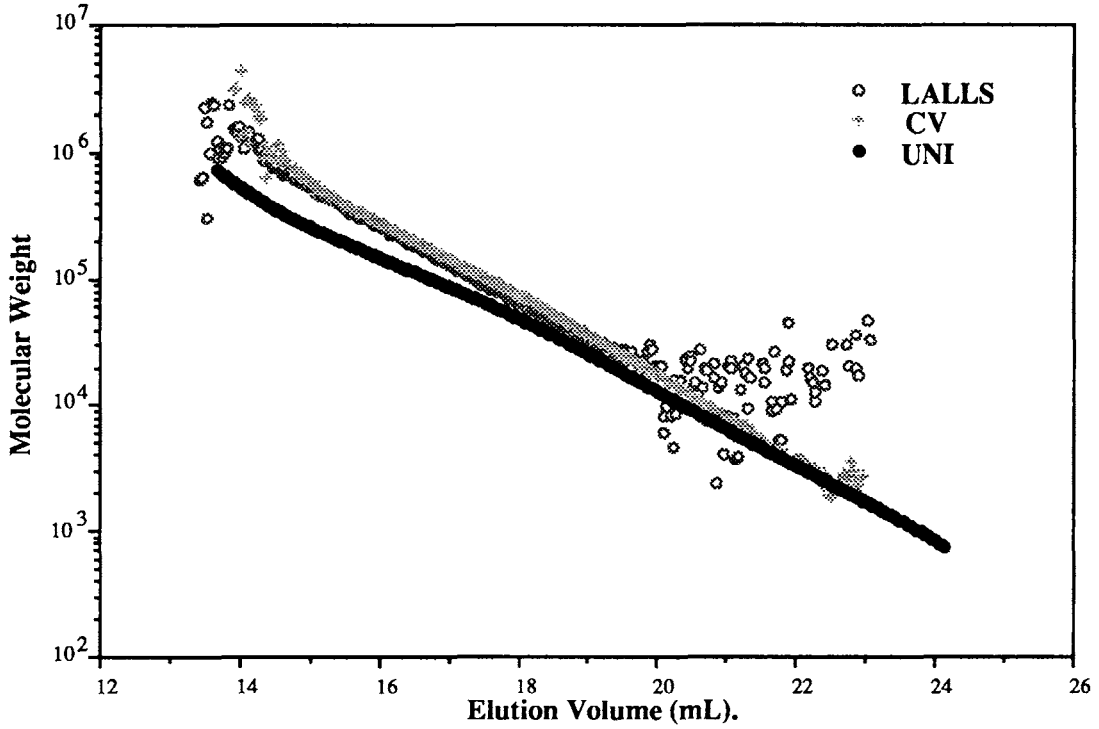

Figure 5 Molecular weights vs. elution volumes: NBS 1476.

attributed to the presence of high-molecular-weight species that become too diluted on passage through the SEC columns to be observed even by the LALLS detector.[25] It could also be considered that the difference noted could reflect the failure of the DRI detector to sense high-molecular-weight species in low concentrations. While this is undoubtedly a factor, the data in Table II show that use of eq. (24) with LALLS input alone still does not change M_w significantly from that obtained with the conventional LALLS–DRI method. It can be concluded that the original explanation as a dilution effect[25] is valid.

Figure 5 shows the elution volume-molecular weight measurements for NBS 1476 using the three different detectors. The continuous viscometer data coincide fairly well with the LALLS results line. (Note that the molecular weight axis is on a logarithmic scale.) The universal calibration line has quite a different slope. This can be attributed to the presence of long-chain branching in this sample. At low elution volumes, LALLS and CV report higher molecular weights than those estimated from universal calibration.

Figure 6 shows differential and cumulative molecular weight distributions of NBS 1476, as measured by CV and LALLS techniques. Evidently, the two coincide fairly well at higher molecular weights but LALLS data deteriorate at molecular weights less than the peak value. Note also that the LALLS trace only accounts for 90% of the distribution, i.e., the LALLS overlaps only 90% of the DRI concentration envelope. At lower molecular weights, the DRI indicates a finite concentration, while the LALLS trace is too faint or noisy to assign a nonzero corresponding molecular weight. At higher molecular weights, the LALLS shows a signal but the DRI indicates zero concentration. The LALLS molecular weight distribution in Figure 6 does not show the bimodal distribution that is evident in the raw data (Fig. 2). This is because the DRI indicates zero concentration at elution volumes where the high-molecular-weight peak occurs.

Figure 7 shows differential and cumulative molecular weight distributions for NBS 1475. Again, the LALLS signal is unacceptably noisy at molecular weights < 30,000. The LALLS detects the high-molecular-weight tail better than the CV, however. Since NBS 1475 has a lower molecular weight than NBS 1476, the cumulative distribution from the LALLS signal encompasses more of the sample in the former case.

A useful feature of the LALLS trace, which is not shown in the data presented to this point, is its usefulness to detect the presence of large (undissolved?)

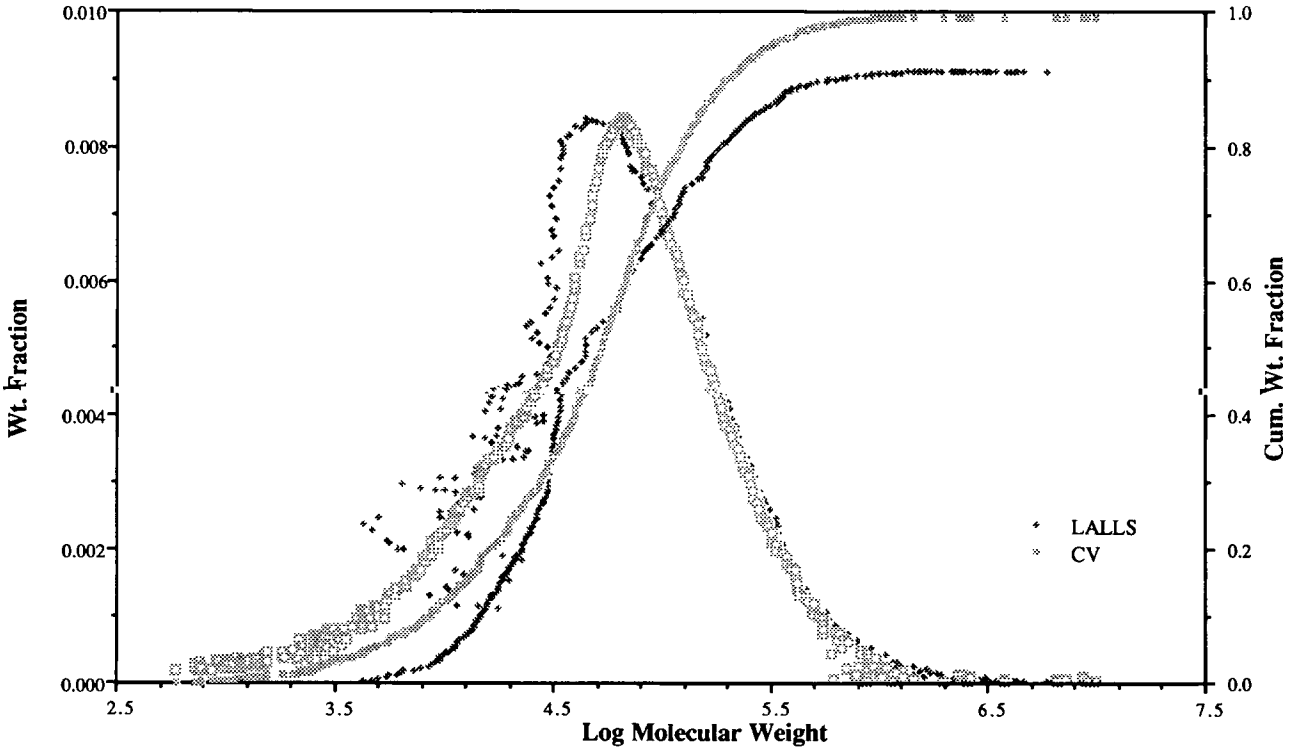

Figure 6 Differential (left axis) and cumulative molecular weight distributions for NBS 1476.

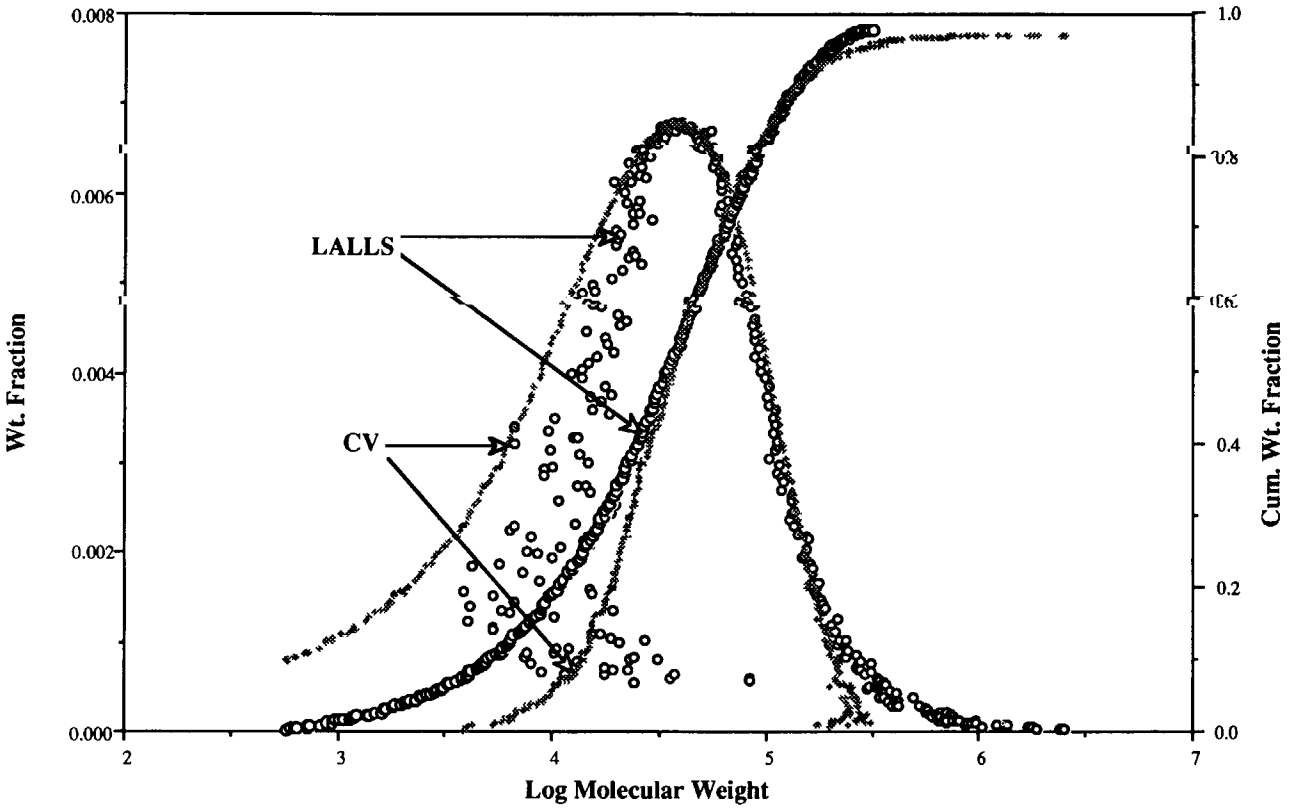

Figure 7 Differential (left axis) and cumulative molecular weight distributions for NBS 1475.

polymer or column debris in the eluent.[6] The other detectors are not sensitive to these artifacts, the presence of which might affect the accuracy of the analysis.

Note that these molecular weight curves are presented without curve smoothing. Resorting to this procedure would present a more attractive picture but would obscure the uncertainties and limitations of the data.

CONCLUSIONS

Molecular weight distributions are measured in SEC analyses using a universal calibration technique, with a DRI detector alone or along with direct measurement of the sizes of eluting species, with CV or LALLS molecular-weight-sensitive instruments. The various detectors are not equally sensitive and accurate in different molecular weight regions. The analysis technique is easily adapted to the advantages of the different detectors and to check the accuracy of the particular analysis.

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