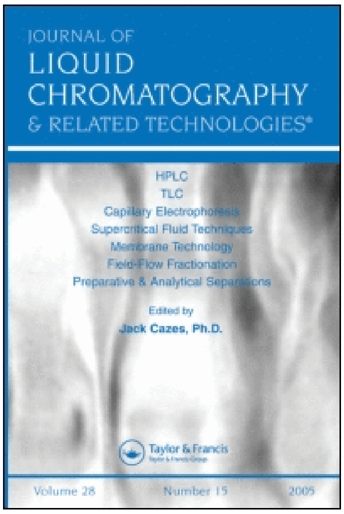

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Polymer Characterization by SEC-Viscometry: Molecular Weight (MW), Size (Rg) and Intrinsic Viscosity (IV) Distribution

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To cite this Article Yau, Wallace W. and Rementer, Stephen W.(1990) 'Polymer Characterization by SEC-Viscometry: Molecular Weight (MW), Size (Rg) and Intrinsic Viscosity (IV) Distribution', Journal of Liquid Chromatography & Related Technologies, 13: 4, 627 — 675

To link to this Article: DOI: 10.1080/01483919008051811

URL: http://dx.doi.org/10.1080/01483919008051811

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(4), 627-675 (1990)

POLYMER CHARACTERIZATION BY SEC-VISCOMETRY: MOLECULAR WEIGHT (MW), SIZE (Rg) AND INTRINSIC VISCOSITY (IV) DISTRIBUTION

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New polymer characterization capabilities have recently been added to our size exclusion chromatography (SEC) using an on-line viscosity detector. In addition to molecular weight distribution (MWD) capabilities, we now also can determine the intrinsic viscosity distribution (IVD), and the molecular size distribution, i.e., polymer radius-of-gyration, or Rg-distribution (RGD) of polymer samples. Polymer conformation and branching features can now be studied by the log(Rg) versus log(MW) results of a single SEC-viscometry experiment.

Also added to our SEC-viscometry analyses is the absolute M_n method recently proposed by J. M. Goldwasser for handling the difficult problems of determining molecular weight (MW) of copolymers and polymer blends. In this new method, the number-average molecular weight (M_n) of a complex polymer sample can be determined by SEC using an on-line viscosity detector, without the need of an on-line concentration detector.

INTRODUCTION

Background

Size exclusion chromatography (SEC) is now the generally accepted terminology to describe gel permeation chromatography (GPC) for polymer analyses in organic solvent, or gel filtration chromatography (GFC) for biopolymers in aqueous medium (1). SEC separates macromolecules according to the size of the molecule. Traditionally, an on-line concentration detector is used with a SEC instrument. Experimentally, SEC provides the concentration versus retention volume elution curve, illustrated at the top of Figure 1. What researchers would like to have, however, is the sample molecular weight distribution (MWD) curve, which is the population versus MW plot as illustrated at the bottom of Figure 1. The transformation of SEC elution curve to polymer MWD requires the calibration relationship between sample MW and SEC retention volume.

SEC-MW calibration however is a complicated matter. The calibration curves differ for different polymer types, as shown by the data in Figure 2 for the experimental SEC-MW calibration curves obtained for narrow MWD standards of four different polymer structures. For most commercial polymers, direct SEC-MW calibration is not possible because of the lack of known MW standards of narrow MWD and of the same chemical structure as the unknown samples. The alternative is the attempt to determine the polymer MW in the SEC effluent in situ by using an on-line MW-sensitive detector. One obvious possibility is the use of an on-line light scattering (LS) detector. On-line LS detectors however often have limitations in dn/dc determination and noise problems which are highly dependent on the particular polymer-solvent systems. Fortunate for SEC users and polymer scientists as a whole, it turns out that on-line viscosity detector also provides an alternative solution to the SEC-MW calibration problem. Historically, SEC-viscometry combination became attractive as an

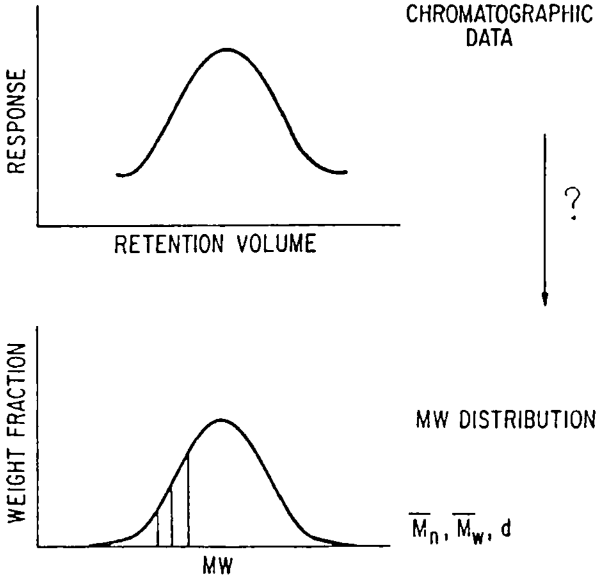


FIGURE 1. Transformation of SEC elution profile into molecular weight.

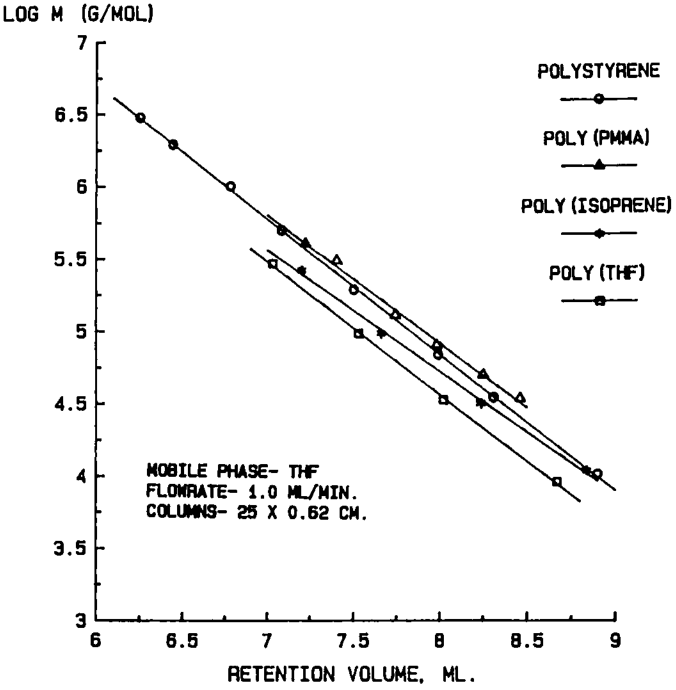


FIGURE 2. SEC molecular weight - retention volume calibration.

useful tool for SEC-MWD quantitation, only because of the existence of the unique universal calibration characteristics of the SEC separation.

Universal Calibration

Since SEC separation is based on molecular size, and the product of polymer intrinsic viscosity (IV, or [η]) times molecular weight (MW, or M) is proportional to the size of polymer molecule, Benoit has long ago predicted and proved experimentally that universal calibration exists when SEC retention is plotted against the polymer size parameter of [η] times M (2). According to basic theories in polymer science (3):

$$\text{Polymer hydrodynamic Volume (HV)} = [\eta] \bullet M \qquad (1)$$

The universal calibration curve for the four polymers shown in Figure 2 is illustrated in the right frame in Figure 3. The calibration relationship of polymer intrinsic viscosity versus SEC retention also varies from polymer to polymer, as shown in the middle frame in the figure, much like the SEC-MW calibration curves reproduced here in the left frame. The experimental data points of different polymers all fall nicely onto a single universal calibration curve when the data are plotted using the product [η] times M. In practice, an accurate universal calibration curve is typically generated using known MW standards of narrow MWD, as indicated by the arrow in Figure 3.

Once the universal calibration curve is established, one can obtain the needed SEC-MW calibration for an unknown polymer sample by using an on-line viscosity detector. Therefore, historically much attention has been devoted to develop an on-line viscometer as well as an on-line light scattering detector for SEC.

Table I is a list of commercial SEC MW-sensitive detectors available today. All these modern detectors are developed to meet the low dead-volume and high sensitivity requirement of the high performance SEC instruments for the polymer MWD analyses. There have been considerable interest in recent

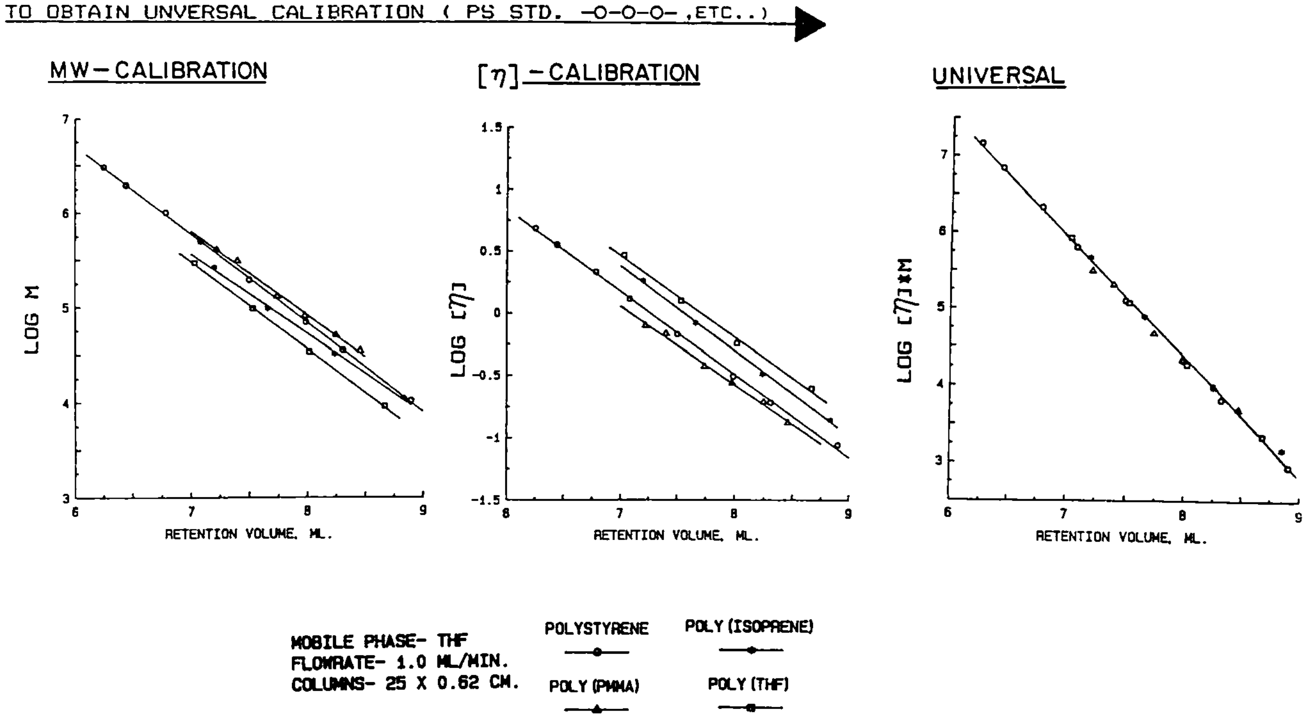


FIGURE 3. Absolute MW via universal caliobration (duPont Zorbax-PSM Trimodal columns.

Table I

SEC MW-SPECIFIC DETECTORS

Light Scattering Photometers:

- Milton Roy LDC - Chromatix KMX-6, CMX-100
  (Low Angle Laser Light Scattering, LALLS)

- Wyatt Technology - DAWN-F
  (Multiple Angle Laser Light Scattering, MALLS)

Viscometric Detectors:

- Viscotek - DV100, 200 (4 capillary bridge design)
  - Y500 (2 capillary Du Pont design)

- Waters Associates -150CV (Single capillary design)

years in exploring the next level capability of these MW-specific detectors in terms of studying molecular size distribution and polymer conformation, beyond the usual expectations of SEC-MWD analyses. The focus of this paper is on these new capabilities, especially in the SEC-viscometry combination. However, before describing the new features, let us review some of the current MWD capabilities with the SEC-viscometry technology, using the Du Pont viscometer as an example (4). The viscometer of Du Pont design is now available commercially as model Y-500 Viscometer of the Viscotek Corp.

Du Pont Viscometer

Our viscometer design utilizes two sets of capillary and pressure transducer assemblies connected in series as shown in Figure 4. The viscosity of the sample solution is measured by the pressure drop ΔP_A across the

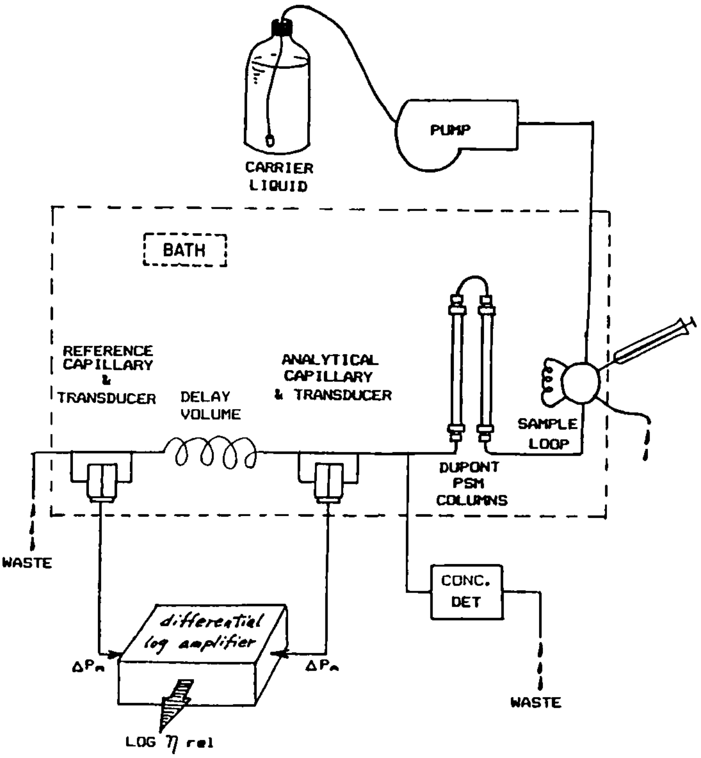


FIGURE 4. Differential pressure capillary viscometer as an in-line viscosity detector.

analytical capillary by the pressure transducer system. The second reference capillary-transducer system is added after a 5 to 10 mL. delay volume to provide the needed flow referencing. This second capillary sees the solvent while the sample liquid is flowing through the analytical capillary. The two ΔP signals are fed into a differential log-amplifier to give the direct read-out of the natural logarithmic value of the relative viscosity of the polymer solution, i.e., $\ln\eta_{rel}$. At high dilutions (C->0), the limiting value of this log signal equals to the product of sample concentration times the intrinsic viscosity of the polymer solution, see

Equation 2 below. Due to the high sensitivity of the viscometer, measurement at very low sample concentration is possible to provide for a single-point intrinsic viscosity determination capabilities.

$$\lim_{C \to 0} \ln \eta_{rel} = [\eta] \cdot C \qquad (2)$$

The high sensitivity of the viscometer is made possible by the highly effective flow-referencing scheme of eliminating the pump noises. The output of the log-amplifier gives the difference of the log of the ΔP signals; this is the same as the log of the ratio of the ΔP signals. Since the capillaries are connected in series and therefore sense exactly the same flowrate upsets, the pump flowrate noise is cancelled out in the log-amplifier output by the real time monitoring of the ratio of the two ΔP signals. The log signal is therefore insensitive to flowrate and responds only to the effect of polymer solution viscosity. The viscometer is also very insensitive to temperature fluctuations, because the two capillaries are positioned in close proximity within a temperature bath. Depending on applications, alternative configurations of our viscometer are possible, including the ones that use no delay volume, very large delay volume, or very small delay volume in the so called differential-differential mode of viscometer operation (5).

The flowrate independent feature of our SEC-viscometry system is demonstrated by the data shown in Figure 5, where the experiment was done under very large flowrate noise by intentionally disabling two of the three pistons of a Du Pont 860 reciprocating pump, leaving only one single piston to do the pumping. The figure shows the ΔP_A and the ΔP_R signals along with the log signal. The experiment was done at two flowrate levels. While the SEC elution peaks are barely visible in the noisy ΔP_A signal at the top tracing, they are, however, clearly detected in the log-amplifier signal shown at the bottom of the figure. Another exceptional feature to notice is the size of the elution peaks

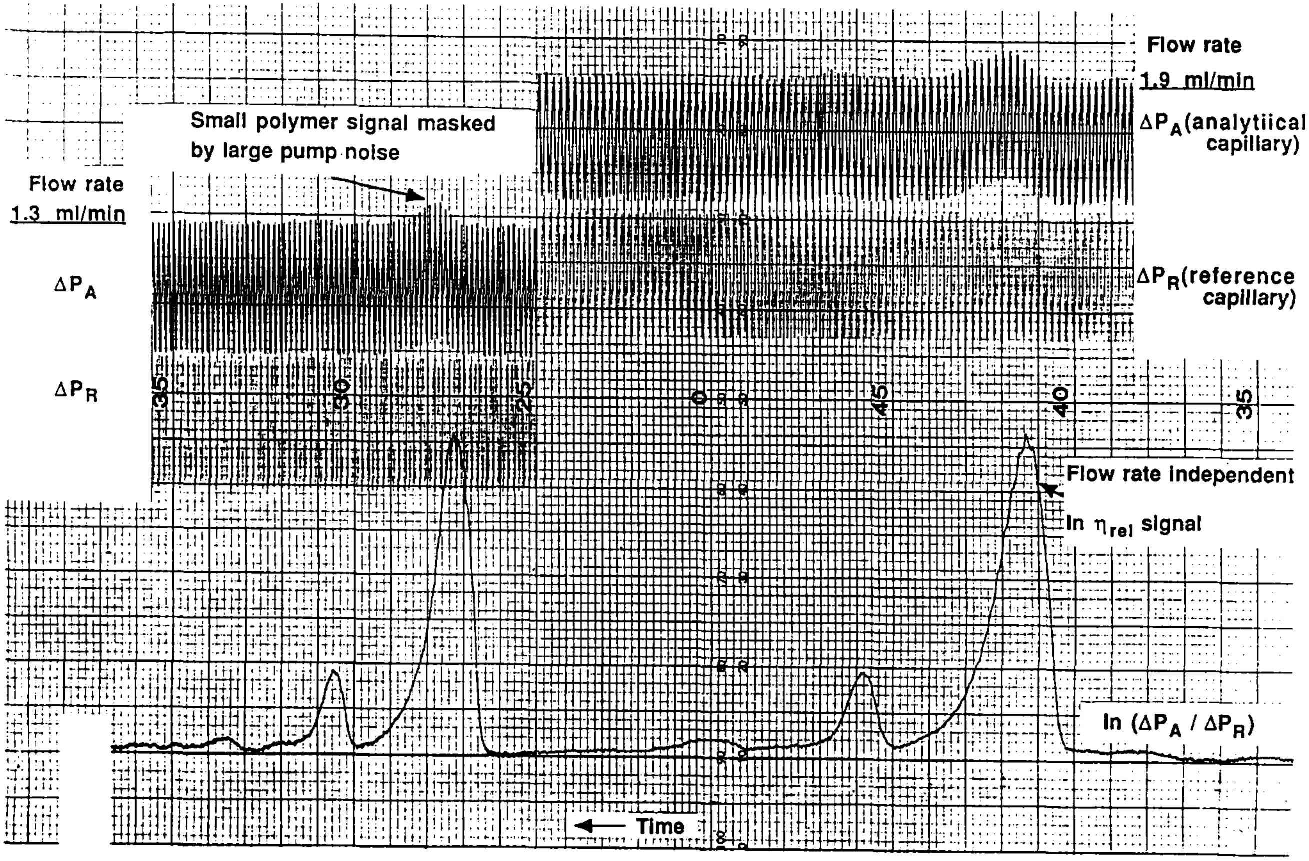


FIGURE 5. Flow rate Independent SEC-viscosity detection.

in the log tracing. The fact that the size of the elution peaks remain the same at two very different flowrates is indicative of the viscometer providing the true viscosity information of the polymer sample.

MWD by SEC-VIS

It is common for SEC-viscometry (or, SEC-VIS for short) to have dual detection capabilities including a concentration detector, which could be a differential refractometer (RI), a UV photometer, or a infrared spectrometer, etc. An example of a typical SEC-VIS elution profiles is shown in Figure 6, where the experiment was done using the Du Pont viscometer and a RI detector. Figure 6 shows the dual SEC-VIS-RI tracings for two samples: one is a broad MWD sample of polystyrene (PS), the other is a mixture of three narrow PS standards.

For the sample of three-PS mixture shown on the left part of the figure, it is obvious that the viscometer tracing is highly biased toward the earlier eluting peak which represents the higher MW component of the sample. Since the concentration of the polymer sample eluting from SEC columns is sufficiently dilute, the recorded log-amplifier signal closely approximates the product $[\eta]*C$, in accordance with Equation 2. Therefore, the intrinsic viscosity $[\eta]$ value of each of the three sample components can be determined by calculating the ratio of the relative peak heights between the viscosity and concentration detector signals.

For the broad PS sample shown on the right of Figure 6, direct $[\eta]$ determination is also possible for each SEC slice by taking ratios of the two elution curves at the corresponding retention times. By doing so point by point across the entire SEC elution curve, one can establish quantitative relationships of sample intrinsic viscosity versus the SEC retention volume. One can therefore establish a so called $[\eta]$-calibration curve of the sample to be used for the MWD calculations using the universal calibration approach.

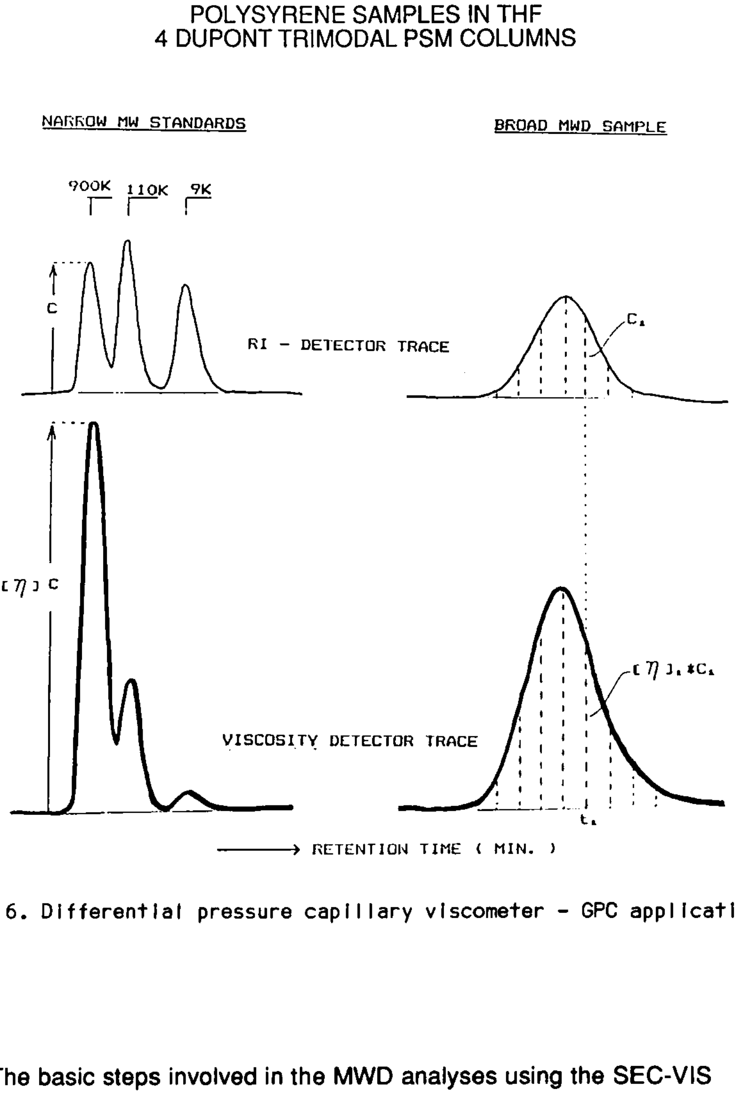


FIGURE 6. Differential pressure capillary viscometer - GPC application.

The basic steps involved in the MWD analyses using the SEC-VIS universal calibration approach can be summarized and analyzed with the help of the sketch shown in Figure 7.

The universal calibration curve of the SEC separation system has to be established first by using narrow MW standards as indicated by the top arrow pointing to the right, represented here by the calibration curves in the solid

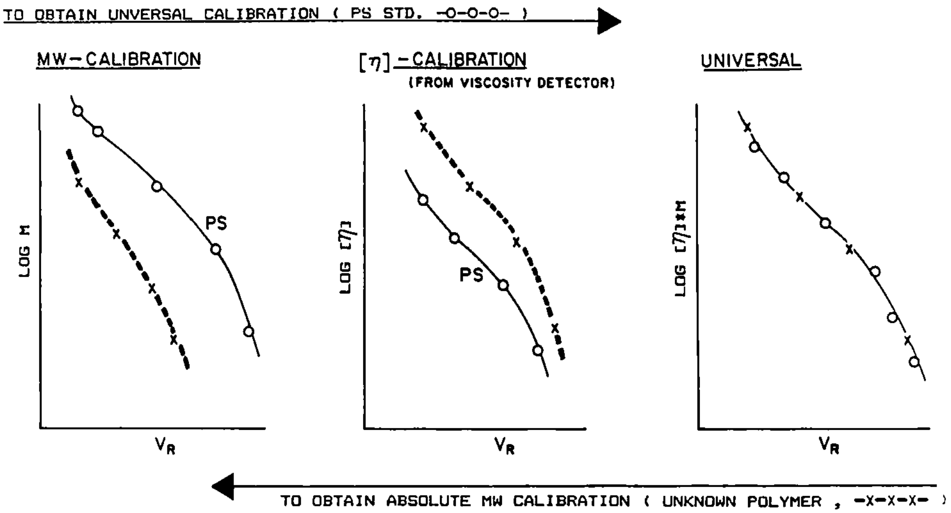


FIGURE 7. Absolute MW via Universal GPC calibration.

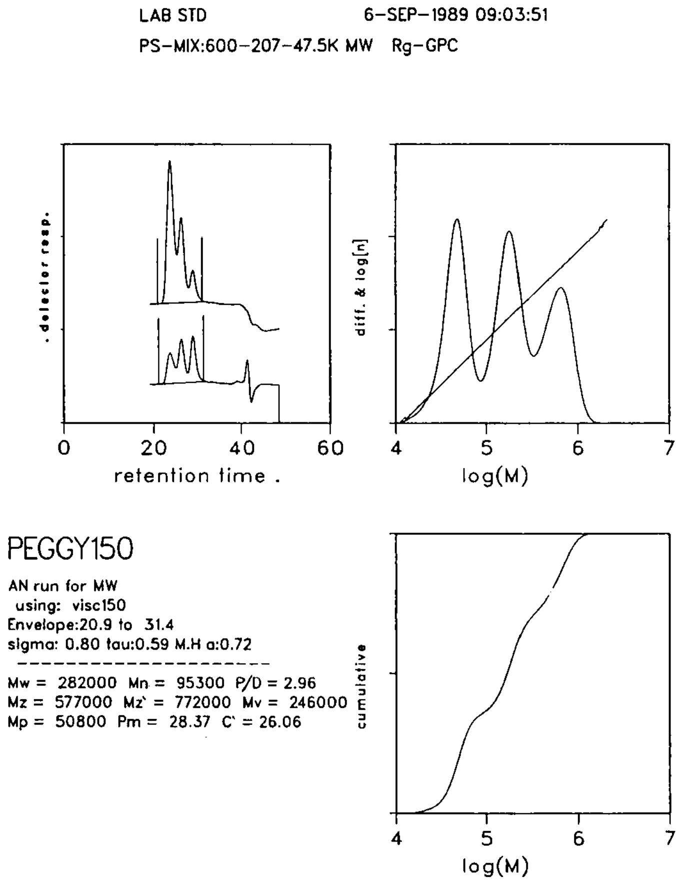
lines. Better accuracy of the resulting universal calibration is possible when more number and types of polymer standards are used for calibration. The [η] values of the narrow standards needed to establish the [η]-calibration can be obtained either off-line or by an on-line SEC viscometer. Universal calibration using broad MWD standards is not very reliable and should be used only when it is absolutely necessary. Different solvents can be used with rigid SEC packings, but may cause swelling differences of some soft SEC packings and therefore should be used with caution. Universal calibration works for separations that result from the pure size exclusion mechanism. It is therefore very important to excise the usual care of avoiding non-SEC retention complications, such as adsorption, reverse phase, ion exclusion, and ion inclusion effects.

Once the universal calibration curve is established, one can then reverse the procedure, by going from right to left following the arrow showing at the bottom of Figure 7, to obtain the MW-calibration curve of any unknown polymer X as represented here by the curve in the broken line. The MW-calibration curve is obtained literally by subtracting the [η]-calibration curve of the unknown sample from the universal calibration curve of the SEC system. An on-line sensitive viscometer is required in this procedure to establish the [η]-calibration relationship for every unknown polymer sample. The accuracy of the MW-calibration and the final MWD result for every unknown sample is affected directly by the accuracy and precision of this experimental [η]-calibration curve. In practice, one finds the viscosity calibration resulting from a broad MWD sample normally tilts away from the true [η]-calibration. The extent of this [η]-calibration mismatch is dependent on the breadth of the sample MWD and the extent of instrumental band-broadening, or so called the SEC column dispersion. Our SEC-VIS computer program corrects for the errors associated with this SEC column dispersion effect. We found that correction for SEC column dispersion is much more important in treating SEC data of an on-line MW-specific detector as compared to the case of usual SEC practices using only a concentration detector. Serious errors in SEC-MWD and polymer conformation results are likely to occur if the effect of instrumental band-broadening is not properly accounted for in the SEC-VIS methodology (6).

Before the advent of modern viscometers, the practice of SEC-MWD using universal calibration was limited strictly to off-line viscosity measurements or using the estimated values of the Mark-Houwink viscosity constants, the K and a values:

$$[\eta] = K{*}M^{a} \qquad (3)$$

Some of the K and a values are available in polymer handbooks. The typical value for a falls between 0.5 and 0.8 for polymers of the random-coil type conformation in solution. Since in most cases reliable values of Mark-Houwink constants are not available for unknown polymer samples, the universal



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AN run for MW
using: visc150
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sigma: 0.80 tau:0.59 M.H a:0.72

Mw = 282000 Mn = 95300 P/D = 2.96
Mz = 577000 Mz' = 772000 Mv = 246000
Mp = 50800 Pm = 28.37 C' = 26.06

FIGURE 8. SEC - VIS report: MWD summary.

calibration approach using viscosity constants is highly restrictive and being rapidly replaced by on-line SEC-viscometry. In fact, with an on-line viscometer the polymer viscosity exponent a can actually be determined by SEC-VIS as a parameter in studying polymer conformation.

A typical MWD report of SEC-VIS analyses is shown in Figure 8 for a mixture of three PS standards of 600000, 207000, and 47500 nominal MW in tetrahydrofuran (THF). On the upper left corner, the dual experimental elution tracings are shown, along with the cut markers and the set baselines within the window where data were selected for the MWD calculation. The bottom tracing is the RI detector response which traces out the three elution peaks of roughly equal size, reflecting nicely the fact the sample mixture was made up with equal amount of each of the three PS components. The top tracing is the viscometer response which, as expected, accentuates the early eluting high MW PS species. The differential and cumulative MWD curves are plotted on the right side of the figure. Along with the differential MWD curve, the upper right frame also shows a diagonal line resulting from the log-log plot of the intrinsic viscosity against the MW values. The slope of this line is a measure of the Mark-Houwink viscosity exponent a, the value of which is reported at the lower left corner of the figure. In this particular analysis, a value 0.72 is measured for a which is a quite reasonable value for PS in THF. Different statistical average MW values are displayed at the bottom left corner, including also the polydispersity value, the retention volume of the peak centroid and the peak maximum. Just above the MW averages, the margins of the data window and the instrumental band-broadening parameters are also printed, where the sigma and tau values represent the symmetrical and skewed band-broadening respectively (6).

NEW CAPABILITIES USING SEC-VISCOMETRY

Traditionally, all one expects to get out of the SEC viscometry and universal calibration methodology is exactly the type of the results shown in Figure 8, which is basically limited to the MWD information and the Mark-Houwink viscosity exponent. As we continue to explore the potential of the SEC-VIS technique, we became aware of several latent untapped features of the technique that can be developed into extremely useful polymer characterization tools for determining: (1) intrinsic viscosity distribution IVD, (2) Rg-distribution RGD, and (3) M_n of copolymers and polymer blends.

IVD by SEC-VIS

We have recently proposed the concept of intrinsic viscosity distribution IVD for polymer characterization. A complete IVD curve for an unknown polymer sample can be readily determined using SEC with an on-line viscometer. In fact, the IVD information has always existed in the SEC-VIS data system. When we generate the [η]-calibration curve by taking the ratio between the viscosity and the concentration detector response at every SEC elution time, we have in effect created all the IV data needed for the display of the IVD curve. According to Equation 2 and Figure 6, the intrinsic viscosity value for each SEC slice can be determined as:

$$[\eta]_i = (\ln\eta_{rel})_i / Ci \qquad (4)$$

Similar to the way that the MWD data are treated, the IVD information can be displayed as differential and cumulative IVD curves and reported in terms of various statistical IV averages and IV polydispersity ratios. It turns out that the value for the weight-average intrinsic viscosity calculated from the SEC-viscosity data is equivalent to, and directly comparable with, the laboratory IV value measured on the bulk polymer solution:

$$[\eta]_{+1} = [\eta] = \Sigma C_i [\eta]_i / \Sigma C_i \qquad (5)$$

Different symbols have been used to represent other IV averages and IV polydispersities which can be calculated using the following equations:

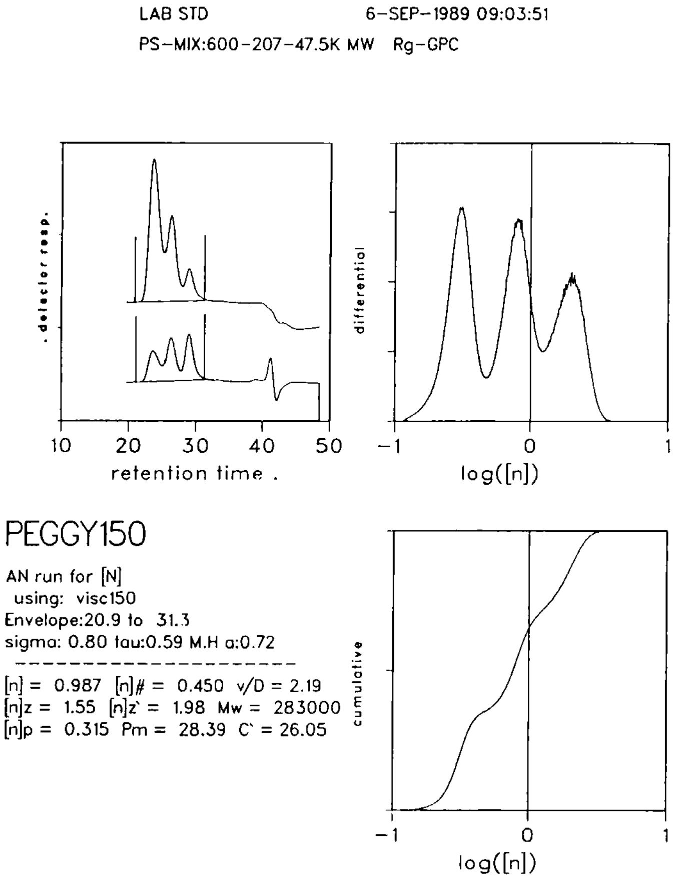
$$[\eta]_{\#} = \Sigma (C_i [\eta]_i / Mi) / \Sigma (C_i / M_i) \qquad (6)$$

$$[\eta]_0 = \Sigma C_i / \Sigma (C_i/[\eta]_i) \qquad (7)$$

$$[\eta]_{+2} = [\eta]_z = \Sigma C_i [\eta]^2 / \Sigma C_i [\eta]_i \qquad (8)$$

$$\text{Polydispersity v/D} = [\eta]_{+1} / [\eta]_{\#} \qquad (9)$$

$$\text{Polydispersity } d_{[\eta]} = [\eta]_{+1} / [\eta]_0 \qquad (10)$$



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PS-MIX:600-207-47.5K MW  Rg-GPC

PEGGY150

AN run for [N]
 using:  visc150
Envelope:20.9 to  31.3
sigma: 0.80 tau:0.59 M.H a:0.72
 ---------------------
[n] =  0.987  [n]# =  0.450  v/D = 2.19
[n]z =  1.55  [n]z` =  1.98  Mw =  283000
[n]p =  0.315  Pm =  28.39  C` = 26.05
```

FIGURE 9. SEC - VIS report: IVD summary.

A typical IVD report of SEC-VIS analyses is shown in Figure 9 for the same sample mixture and the same SEC experiment as the MWD data shown in Figure 8. Same as in Figure 8, the upper left corner shows the experimental viscometer and RI detector elution tracings. The differential and cumulative IVD curves are shown on the right side of Figure 9. The vertical line in the graphs displays the location corresponding to the IV value of 1.0 dL/g. At the lower left corner, all the IV average values are displayed, in the dL/g units. Note that, all the IV averages and the IVD curves are determined directly from the SEC-viscometry experiment. Except for the calculation of $[\eta]_{\#}$ and v/D values, where the MW information from universal calibration are required.

To appreciate the value of IVD, we need to examine why IV itself has been so important to polymer characterization. The following is a brief review of the viscosity parameters commonly used in polymer analyses. The relative viscosity (RV, or η_{rel}) of a polymer solution as defined in Equation 11 can be determined experimentally from the measured viscosity value for the polymer sample solution (η) and that of the solvent (η_o). From the RV value and the polymer sample concentration (C), the other viscosity parameters are calculated:

Relative Viscosity: $\eta_{rel} = \eta / \eta_o$ (11)

Specific Viscosity: $\eta_{sp} = \eta_{rel} - 1$ (12)

Inherent Viscosity: $\eta_{inh} = (\ln \eta_{rel}) / C$ (13)

Reduced Viscosity: $\eta_{red} = \eta_{sp} / C$ (14)

Intrinsic Viscosity: $[\eta] = \lim_{C \to 0} \eta_{inh} = \lim_{C \to 0} \eta_{red}$ (15)

where the mathematical symbol ln means natural logarithm, and lim, C→0, means the limiting value for the viscosity parameter as the sample concentration C approaches zero at infinite dilution. The term intrinsic viscosity is therefore also referred to as the limiting viscosity number.

Even though IV is determined experimentally through viscometry, the connotation of the term "intrinsic viscosity" is however very different from the usual sense of fluid viscosity. IV is a much more fundamental quantity and carries a far more reaching significance of describing the size, shape, and MW information of the polymer molecule. The IV value is well defined for a polymer sample as long as the solvent and the temperature are specified. IV is related to polymer hydrodynamic volume through Equation 1 and to polymer MW through Equation 3, often referred to as the Mark-Houwink relationship. By way of Equation 1, one can see that IV represents a measure of the molecular volume per unit mass, something like the specific volume of the polymer molecule (7). Quite appropriately, IV values are reported in the units of dL/g that is volume per unit mass.

It is clear that IV has a lot more to do with the compactness of the polymer molecule than with how viscous is the polymer solution. A good example to illustrate this distinction is to examine the effect of temperature on the measured quantities. IV is often misunderstood to be highly temperature dependent much like the viscosity of the polymer solution. This is, of course, not true. IV, being a molecular size parameter, is not greatly affected by the temperature of the solvent environment. The exception is near temperature region where polymer conformational transition takes place (12).

In industry, quality control (QC) of polymer MW in production is rarely done using MW data. Instead, viscometry is most commonly used for QC of polymer MW either in the form of IV, or RV, or the inherent viscosity. The reasons are as follows: Firstly, the viscosity parameters are themselves fundamental physical quantities that respond to polymer MW changes. Secondly, the viscosity parameters are more precisely measurable then the MW values which can be measured by either light scattering, osmometry, or SEC. Most MW techniques requires frequent calibration. No calibration is required in viscometry. Techniques that require no calibration are most attractive for production QC, so that the measured data can be universally compared, from one batch to the next, from one instrument to the next, from one month to the next, etc., and need not be concerned with any re-calibration errors.

An analogous scenario can be said about IVD and MWD. The reason that the conventional SEC-MWD technique has never made its mark in polymer

QC is because of the need of calibration and the dependency of the technique on the accurate control of experimental variables. These problems, however, disappear in the SEC-IVD analyses using an on-line viscometer. The IVD can be determined directly from SEC-VIS without any calibration, it is much more independent of SEC experimental variables. Comparing with MWD, IVD should be much less affected by column deterioration, flowrate variations, sample overloading, instrumental band-broadening and so on, and therefore more amiable for process control or QC applications. Most polymer production today relies on one viscosity parameter for QC. Whether it is IV, RV, or inherent viscosity, a single viscosity parameter can only assert its control on an average level of polymer MW. IVD used in QC can provide controls over polymer MW, polydispersity, and possibly more, through the control of the various IV average values or the IVD curve profiles.

To verify the accuracy of SEC-IVD, measurements were made on mixtures of narrow MWD polymer standards and broad MWD polymers of known characteristics. The drop-time IV values were measured on all samples by using conventional glass capillary viscometers. The drop-time IV values of the individual narrow standards were used to calculate the different IVD parameters for the sample mixture, i.e., the $[\eta]_0$, $[\eta]_{+1}$, $[\eta]_{+2}$, and $d_{[\eta]}$ values. In Table II, these calculated, or predicted, IVD values are compared with the IVD data from the SEC-VIS experiments. To test the independency of the SEC operating condition, the SEC-VIS experiments were carried out at two different flowrates: 1.04 and 1.38 mL/min. The generally good agreement of the SEC-VIS data gave the SEC-IVD the seal of approval for accuracy. The precision of all the IVD parameters obtained at two different flowrates is even more impressive. It is this high precision and insensitivity to operating variables makes IVD attractive for QC.

Table II

VERIFICATION OF INTRINSIC VISCOSITY VALUES WITH SEC

		$[\eta]_{+0}$			$[\eta]_{+1}$		$[\eta]_{+2}$		$d[\eta]$	
Polymer Sample	Flow rate mL/min	Calc.	SEC	Measured (drop-time)	Calc.	SEC	Calc.	SEC	Calc.	SEC
Polystyrene										
{87,515,1950K}	1.04	0.84	0.71	1.60	1.55	1.51	2.48	2.33	1.60	1.54
	1.38	0.84	0.98	1.60	1.55	1.52	2.48	2.10	1.60	1.38
{28,194K}	1.04	0.24	0.27	0.39	0.37	0.39	0.57	0.56	1.55	1.44
	1.38	0.24	0.28	0.39	0.37	0.40	0.57	0.57	1.55	1.42
NBS-706	1.04	-	0.59	0.93	-	0.94	-	1.14	-	1.21
	1.38	-	0.59	0.93	-	0.92	-	1.10	-	1.20
Poly (methyl methacrylate)										
{107,265,690K}	1.04	0.51	0.51	0.68	0.62	0.58	0.76	0.66	1.23	1.14
	1.38	0.51	0.55	0.68	0.62	0.63	0.76	0.72	1.23	1.14
{64,185K}	1.04	0.29	0.26	0.30	0.33	0.29	0.37	0.32	1.12	1.10
	1.38	0.29	0.25	0.30	0.33	0.28	0.37	0.32	1.12	1.14
{400,1600K}	1.04	1.06	1.08	1.21	1.27	1.24	1.54	1.52	1.21	1.23
	1.38	1.06	0.95	1.21	1.27	1.10	1.54	1.30	1.21	1.18
Lucite-40	1.04	-	0.23	0.27	-	0.26	-	0.29	-	1.12
	1.38	-	0.23	0.27	-	0.26	-	0.31	-	1.19

All $[\eta]$ values in dL/g

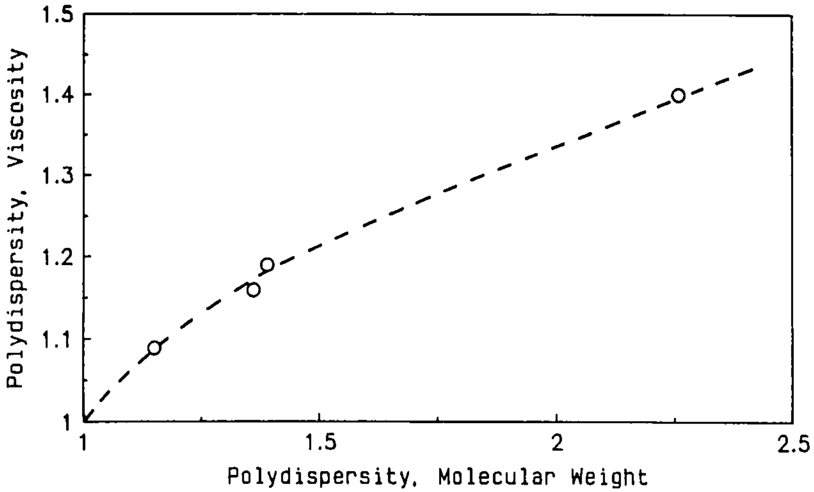


FIGURE 10. Correlation of molecular weight and viscosity polydispersity indices.

We have predicted and demonstrated that the IVD measurements are also independent of the polymer fractionation method. We showed that comparable IVD results were obtained for a particular polymer sample when either SEC or thermal field flow fractionation (TFFF) was used as the separating method for the polymer (8). In that study, we made a plot of viscosity polydispersity $d_{[\eta]}$ against the MW poly-dispersity to show there exists a good correlation of the two measurements (see Figure 10).

One final thought: this new IVD concept introduces a series of IV averages, and there is a need to determine the physical significance of these quantities. For example, does $[\eta]_z$ correlate with melt viscosity or with other rheological properties?

RGD by SEC-VIS

The ability to determine the molecular size distribution of a polymer sample is the other latent feature in the SEC-viscometry technology. Similar to the case of IVD discussed above, all the data needed to determine molecular size distribution already exist in the SEC-viscometry software using the universal calibration approach.

In the SEC-VIS analyses using the universal calibration approach, the MW as well as the IV values are already determined for the polymer molecules eluting at every SEC retention volume. One can therefore calculate polymer radius of gyration, the Rg value, at every SEC slice by using Flory-Fox and Ptitsyn-Eizner equation (9):

$$R_g = (1/\sqrt{6})([\eta]M/\Phi_0/(1-2.63\varepsilon+2.86\varepsilon^2))^{1/3} \qquad (16)$$

where Φ_0 is the Flory universal constant, equals to 2.86 x 10^{21}, and $\varepsilon = (2a-1)/3$, with a being the Mark-Houwink exponent constant which can also be obtained in the SEC-VIS universal calibration calculation. Since the product $[\eta]^*M$ that appeared in Equation 16 is what the universal calibration curve is based on, a SEC-Rg calibration curve is easily obtainable from the existing universal calibration curve through a simple mathematical transformation according to Equation 16. With a Rg calibration curve, the Rg-distribution (RGD) curves can then be calculated from the SEC concentration elution profile. Statistical averages of sample Rg values can also be calculated according to the following equations:

$$Rg_z = \Sigma C_i Rg_i^2 / \Sigma C_i Rg_i \qquad (17)$$

$$Rg_w = \Sigma C_i Rgi \; / \; \Sigma C_i \qquad (18)$$

$$Rg_{\#} = \Sigma (C_i Rg_i / M_i) / \Sigma (C_i / M_i) \qquad (19)$$

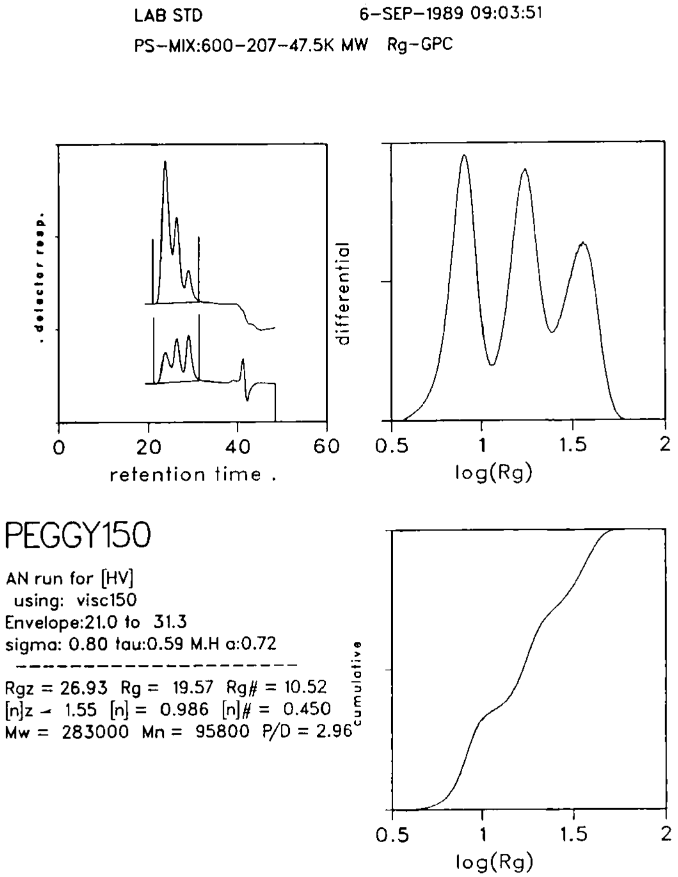
where Rg_z is expected to be directly comparable with the Rg average value determined from angular asymmetry of the light scattering measurement. In addition to the RGD curves and Rg averages, the data can also be used to estimate the exponent α of the Rg to MW relationship (12):

$$Rg \sim M^{\alpha} \qquad (20)$$

The value for α is estimated from the slope of a log-log plot of the Rg values against the MW values across the sample elution curve. The α value should equal to (1+a)/3, where a is again the Mark-Houwink exponent. For random-coil type polymers, the α value is expected to lie between 0.5 to about 0.6, depending on the chain rigidity and the goodness of the solvent.

With the addition of the RGD capability, our SEC-VIS report now offers a version that provides all key MW, IV, and Rg averages. An example of this so called HV report format is shown in Figure 11. This is the report on the SEC-VIS analyses of the same sample mixture described earlier with the MW and the IV reports in Figures 8 and 9. Again, the upper left corner of Figure 11 shows the experimental viscometer and RI detector elution tracings. The differential and cumulative RGD curves are shown on the right. At the lower left corner, the Rg averages are displayed along with the MW averages, polydispersity, and the IV average values, in the units of dL/g. The Rg values are reported in the units of nanometer, nm. Part of the SEC-VIS report also provides the detailed analyses of the individual peaks, including the Rg, $[\eta]$, MW averages and polydispersity values, as shown in Figure 12. The second line in Figure 12 lists the measured Mark-Houwink's a exponent of 0.72 and the Rg-MW exponent α value of 0.57, indicating a random-coil polymer in good solvent, as expected. The report also shows the Rg_Z values of 35, 18, 8 nm for the PS peaks of 600, 207, 47.5 K nominal MW, respectively. These Rg values are fully substantiated by careful off-line light scattering results by F. Warner of Polymer Laboratory, Amherst, Mass. (10) and independently by J. W. Jimmy Mays' data at the University of Alabama (11).

We were pleasantly surprised by the very good Rg data, especially the ability of SEC-VIS to determine the Rg value of 8 nm so precisely, since Rg values of less than 10 nm is very difficult to determine by light scattering techniques (13). We were curious to learn what is the reasonable expectation



LAB STD 6-SEP-1989 09:03:51
PS-MIX:600-207-47.5K MW Rg-GPC

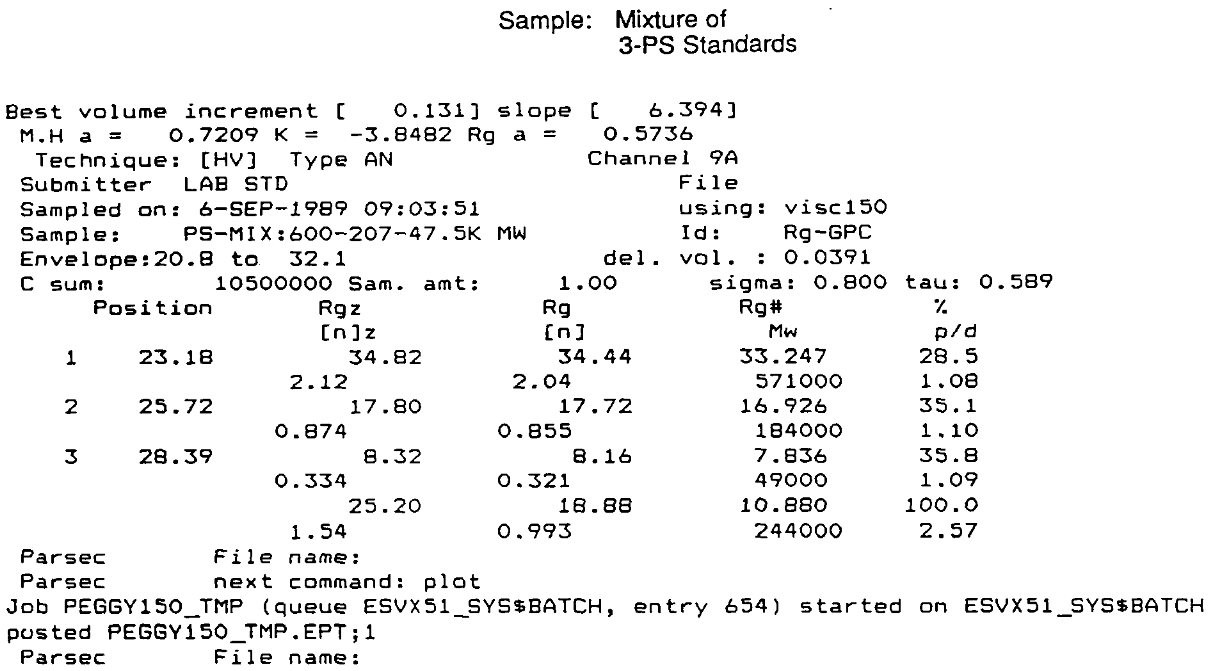
PEGGY150

AN run for [HV]
using: visc150
Envelope:21.0 to 31.3
sigma: 0.80 tau:0.59 M.H a:0.72

Rgz = 26.93 Rg = 19.57 Rg# = 10.52
[n]z ~ 1.55 [n] = 0.986 [n]# = 0.450
Mw = 283000 Mn = 95800 P/D = 2.96

FIGURE 11. SEC - VIS report: RGD summary.

about the accuracy of Rg determination by SEC-viscometry. The equation used to calculate Rg is quite simple and contains no adjustable constants (see Figure 13, where the equations were reproduced). Due to the cubic root dependence, any errors in either the MW or the [η] values will be reduced by a factor of three in the Rg calculation. For example, a 10% error in either M or [η] would lead to only 3% error in Rg. Therefore, the effect of MW or IV error on Rg would be quite



```
                                   Sample:  Mixture of
                                            3-PS Standards

Best volume increment [   0.131] slope [   6.394]
 M.H a =   0.7209 K =  -3.8482 Rg a =   0.5736
  Technique: [HV]  Type AN            Channel 9A
 Submitter  LAB STD                         File
 Sampled on: 6-SEP-1989 09:03:51            using: visc150
 Sample:    PS-MIX:600-207-47.5K MW         Id:    Rg-GPC
 Envelope:20.8 to  32.1                del. vol. : 0.0391
 C sum:       10500000 Sam. amt:     1.00      sigma: 0.800 tau: 0.589
      Position        Rgz            Rg           Rg#         %
                      [n]z           [n]           Mw         p/d
    1    23.18          34.82          34.44      33.247      28.5
                    2.12          2.04             571000     1.08
    2    25.72          17.80          17.72      16.926      35.1
                   0.874         0.855             184000     1.10
    3    28.39           8.32           8.16       7.836      35.8
                   0.334         0.321              49000     1.09
                        25.20          18.88      10.880     100.0
                    1.54         0.993             244000     2.57
 Parsec       File name:
 Parsec       next command: plot
Job PEGGY150_TMP (queue ESVX51_SYS$BATCH, entry 654) started on ESVX51_SYS$BATCH
posted PEGGY150_TMP.EPT;1
 Parsec       File name:
```

FIGURE 12. GPC - VIS results.

$$R_g = \frac{1}{\sqrt{6}}\left(\frac{M[\eta]}{\Phi}\right)^{1/3}$$ (Flory-Fox)

$$\Phi = 2.86 \times 10^{21}\left(1 - 2.63\varepsilon + 2.86\varepsilon^2\right)$$ (Ptitsyn-Eizner)

$$\varepsilon = (2a-1)/3$$

$$[\eta] = KM^a$$ (Mark-Houwink)

$$R_g \sim M^{\alpha}, \alpha = (1+a)/3$$

EXAMPLE:

M	$[\eta]$, dl/g	a, random coil	α	R_g, nm
600K	1.83	0.5 (θ - solvent)	0.5	29.7
		0.6	0.53	31.5
		0.7	0.57	33.4
		0.8 (good solvent)	0.6	35.4
207K	0.81	0.5 - 0.8	0.5 - 0.6	15.9 - 18.9
47.5K	0.26	0.5 - 0.8	0.5 - 0.6	6.7 - 7.9

(PS - THF, $[\eta] = 1.418 \times 10^{-4} M^{0.72}$)

FIGURE 13. Effect of solvation on polymer radius of gyration.

limited. Since the Ptitsyn-Eizner's Φ varies with the conditions of the solvent, we made a sample calculation to estimate the extent of solvent effect on the Rg determination of random-coil type polymers. The results are shown in Figure 13. It is again very encouraging to see that the total span of the solvent effect on Rg amounts to less than ± 10% variation. In practice, with most polymer-solvent systems having a a value around 0.7, the uncertainty in Rg could easily be less than 5%, which would compare very well with any other Rg measurements, including the modern light scattering technologies (see later section on RGD by SEC-MALLS).

Mn of Copolymers and Blends by SEC-VIS

The difficult problem of MW characterization of copolymers and polymer blends can now be handled by SEC-VIS using the computational method recently developed by J. M. Goldwasser of the office of Naval Technology (14). The inability to determine polymer concentration across the SEC elution curve has been the single limiting difficulty of analyzing copolymers or polymer blends by traditional SEC. The problem is totally obliterated by the proposed new method, where no concentration data or concentration detector is ever needed. While the method was originally developed on a Viscotek DV-100 viscometer, a bridge design using reduced viscosity notations, the following presentation is the transformed version of the method for our viscometer of two capillary design using the inherent viscosity notations.

The usual SEC-viscometry calculations using the SEC universal calibration methodology requires the use of an on-line concentration detector along with an on-line viscometer. From the detector responses, one calculates the intrinsic viscosity $[\eta]_i$ at every SEC slice, say for the i^{th} slice:

$$[\eta]_i = (\ln\eta_{rel}/C)_i \qquad (21)$$

where $\ln \eta_{rel}$ = the direct detector response of the log-amplifier output of the Du Pont viscometer. From Equation 21, one calculates MW averages of the polymer sample by way of:

$$M_n = \Sigma\, C_i / \Sigma\, (C_i/(hv/[\eta])_i) \qquad (22)$$

$$M_w = \Sigma\, C_i(hv/[\eta])_i / \Sigma C_i \qquad (23)$$

where M_n and M_w stand for the number and the weight average MW of the polymer sample respectively, and $hv = [\eta]*M$ which is the data retrievable from the universal calibration curve already established for the SEC system prior to the sample analyses. Higher order MW averages like M_n and M_w can also be calculated by using equations similar to that of Equations 22 and 23, requiring also the concentration detector signal C_i.

For the above formulations to work, the concentration detector needs to respond accurately to the polymer sample concentration across the SEC elution curve. This is normally not possible for copolymers and polymer blends using usual SEC concentration detectors. For copolymers or polymer blends, polymer composition varies across the entire SEC elution curve profile. The ability to monitor polymer concentration across the SEC elution curve is therefore impaired, because all usual SEC concentration detectors are sensitive to polymer compositional changes. Therefore, in the past, it has been nearly impossible to extract accurate MWD information for copolymers and polymer blends using conventional SEC. It has been assumed all this time that SEC-viscometry technology would suffer the same concentration detection problem. This is all changed now with the advent of the Goldwasser's method.

By rearranging, Equation 22 can be made to show that the polymer M_n value can be calculated, requiring no concentration detector data at all:

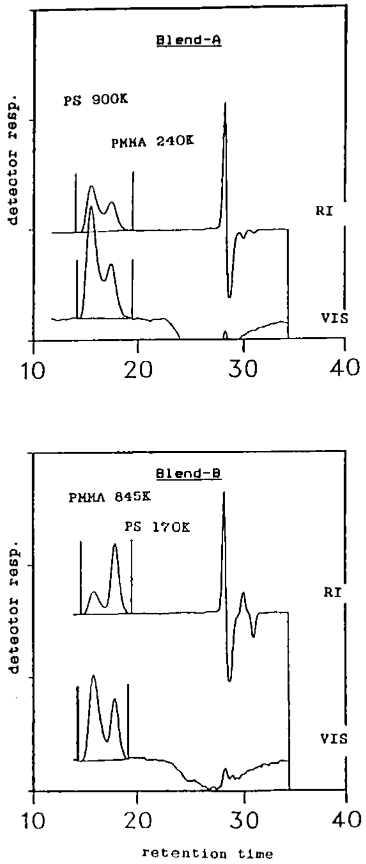
$$M_n = \Sigma\, C_i / \Sigma\, (\ln \eta_{rel} / hv)_i \qquad (24)$$

or,

$$M_n = \text{sample amount} / \Sigma\, (\ln \eta_{rel} / hv)_i \qquad (25)$$

where, again $\ln \eta_{rel}$ = the direct signal from Du Pont viscometer, and the hv data are the retrievable universal calibration data for the SEC system. The sample amount in Equation 25 can be easily determined as the product of SEC sample loop volume multiplied by the total weight concentration of the polymer in the sample solution preparation.

With this approach, the M_n value of any polymer sample can be determined by the SEC method using only a viscosity detector. This simple



Blends	NOMINAL (expected)	GOLDWASSER
A	379,000	390,500
B	265,000	283,000

$$\text{Nominal Mn} = \frac{1}{\dfrac{0.5}{M\ (PS)} + \dfrac{0.5}{M\ (PMMA)}}$$

FIGURE 14. Absolute Mn of polymer blends by SEC - VIS.

approach, however, is applicable to the measurement of the M_n value, not any of the other MW averages. This single advantage, however, is of considerable importance to polymer characterization. Many of our commercial polymers today are copolymers and polymer blends. The new method gives the SEC-VIS a very unique and important niche in characterizing copolymers and polymer blends. This M_n method can access much wider MW ranges than any existing M_n techniques, either by osmometry or end-group methods.

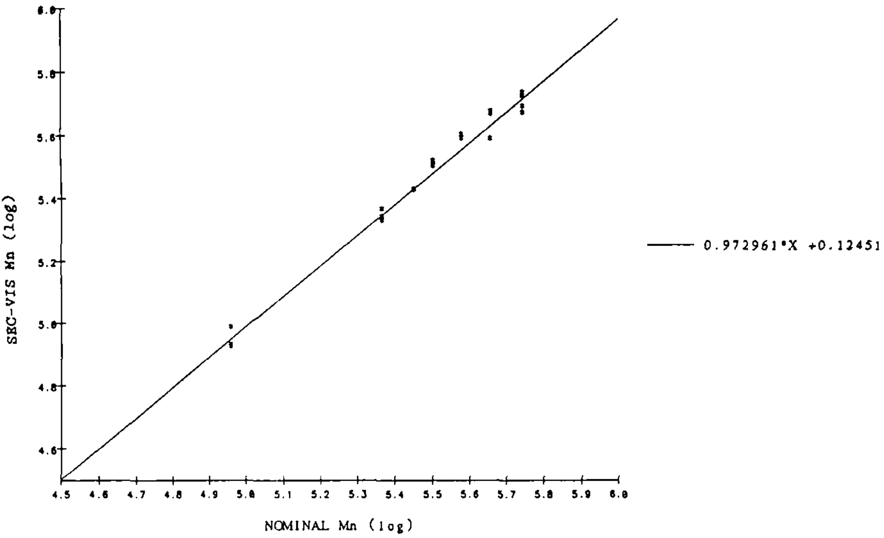


FIGURE 15. Absolute Mn determination of polymer blends (SEC - VIS with Goldwasser method).

For the purpose of demonstration, we made up several binary mixtures of the polystyrene (PS) and poly (methyl methacrylate) (PMMA) standards. These mixtures are used to simulate heterogeneous polymer blends. The expected M_n value of a sample mixture can be calculated from the known MW and weight proportions of the polymer standards constituents. Figure 14 shows the results obtained for two of these simulated polymer blend samples having a one-to-one mixing ratio between PS and PMMA. The elution curves are displayed in the figure. For each sample, the top curve is the RI tracing and the bottom curve is the viscometer response. Because of dn/dc differences, the RI detector is more sensitive to PS better than to PMMA. This is the reason why the RI tracing is highly disproportionate, even though the sample is consisted of two components of equal weight fractions. The RI signal in this case can no longer measure the polymer concentration, and therefore is of very little use.

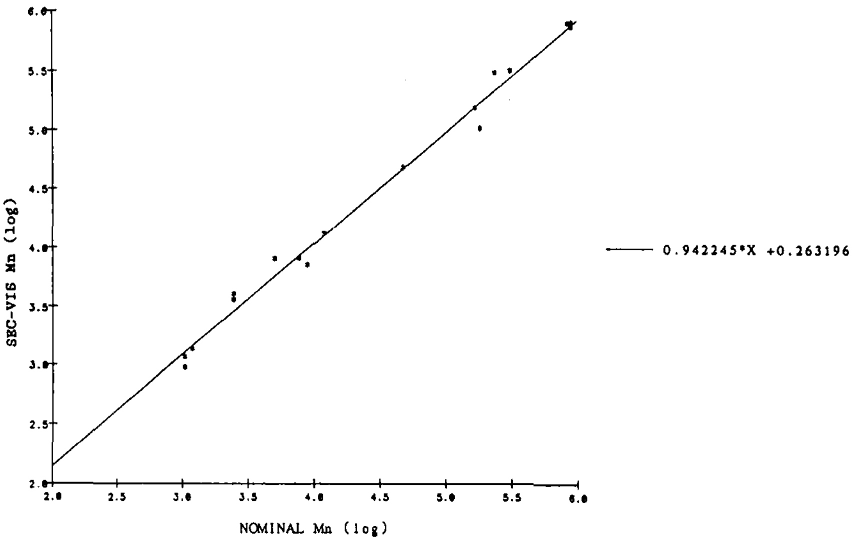


FIGURE 16. Absolute determination of PS, PMMA narrow standards (SEC - VIS with Goldwasser method).

Fortunately, the viscometer curve for each sample is still very useful that offers a way to determine the sample M_n value. On the right side of the figure, the measured M_n values are shown to agree with the expected value very well. In Figure 15, the M_n results on all the polymer blend samples are shown to correlate very well with the expected values. The standard deviation of the fit corresponds to a confidence limit of within ±5%.

One attractive feature of this SEC-VIS method of determining M_n is its wide dynamic range. The results obtained on a series of PS and PMMA standards are shown in Figure 16. Good agreement was obtained covering the MW range of 1×10^3 to 1×10^6.

How well can the new M_n method work for copolymers depends largely on how well copolymers comply with the SEC universal calibration curve. As demonstrated by Benoit, see Figure 17, a wide range of copolymers obeyed the

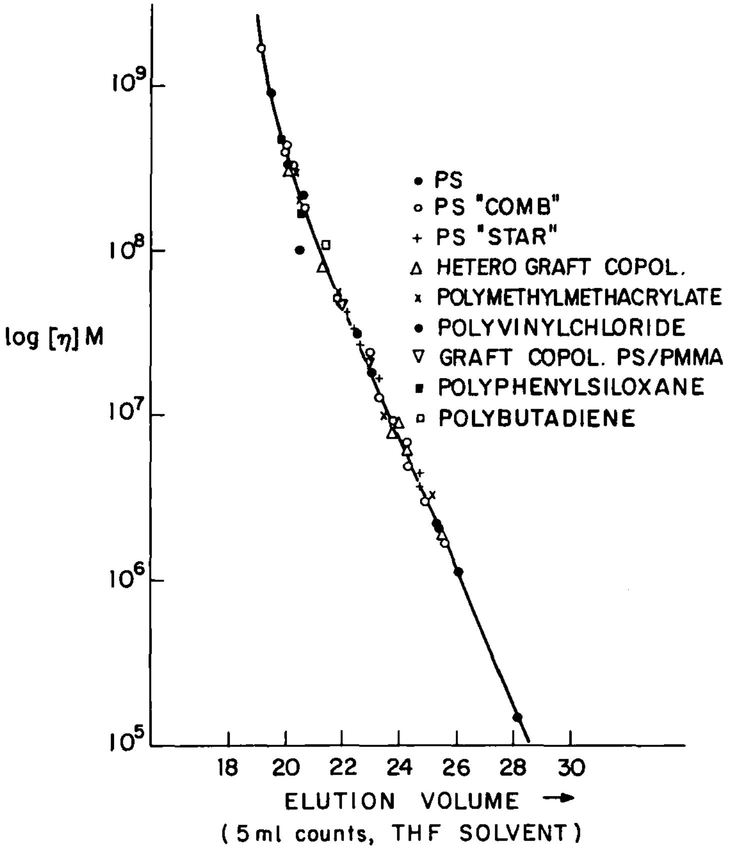


FIGURE 17. Universal calibration.

universal calibration concept (2). There may be exceptions, but in general, copolymers do seem to obey the SEC universal calibration principle quite well.

DISCUSSION

Commercial SEC Viscometers

Table III is a list of commercial viscometers that can be used as an on-line SEC viscosity detector. The main features of the viscometers are

Table III

COMPARISON OF COMMERCIALLY AVAILABLE SEC VISCOMETERS

	Waters 150CV (Integrated SEC System)	Viscotek 200 (Modular)	Viscotek 500Y (Du Pont) (Modular)
Design	Single Capillary	4-Capillary bridge	2-Capillaries in series
Cell Volume	~18μl	~50μl	~10μl
Output Signal	Flowrate Sensitive	Flowrate Sensitive	Insensitive
Flowrate Fluctuations	Sensitive	Insensitive	Insensitive
Calibration/ Accuracy	Depends on pump performance	Depends on matched capillaries	Depends on electronic adjustment
Sensitivity (S/N = 4)	-	$\sim 4 \times 10^{-5}\ \eta_{sp}$	$\sim 2\times10^{-4}\ \eta_{sp}$
Delay Volume	No	Yes	Yes

highlighted in the table. The important factors are the flowrate sensitivities. In all of these instruments, solution viscosity is measured by the pressure drop across a flow-through capillary as monitored by a differential pressure transducer. The first single capillary viscometer was proposed by A. C. Ouano nearly two decades ago (15), which was later improved by J. Lesec (16) and C. Kuo, et. al (17) and recently incorporated into the Waters 150CV SEC instrument (Waters, Milford, Mass.). Being a single capillary instrument and therefore sensitive to flowrate fluctuations, Waters viscometer is available only as an integral part of the 150CV, which has an extensive pulse dampener system built in. It is possible that constant volume pumping could be compromised by extensive pulse dampening. The potential for this problem is, of course, greatly minimized in an integrated system like 150CV which is constantly under an enclosed, temperature-controlled environment.

M. A. Haney developed a viscometer consisting of a four-capillary bridge design to compensate for flowrate fluctuation (18). Although the output of this viscometer is dependent on the flowrate level, the instrument contains an additional pressure transducer to take into account of any flowrate changes. We later developed another design, referred to as the Du Pont viscometer in this paper, that uses two capillaries in series to eliminate the flowrate problems (4). Viscometers of Haney's and Du Pont's design are now commercially available through Viscotek (Porter, Texas). Commercial viscometers of both these designs are true flow-referenced modular systems that can be adopted for use with existing SEC instruments. One distinct advantage of the Du Pont two capillary design when used as a batch viscometer is its high RV capability for QC applications. When the Du Pont and Viscotek detectors are used with a delay volume, sample analysis time is increased to allow the entire sample passing through before the next sample. If desired, this extra time to flush out the SEC sample can be avoided by way of either using a large dilution volume or the differential-differential mode of viscometer operation (5).

In principle, all the new capabilities of SEC-VIS presented earlier in this paper can be made available to all commercial viscometers. The question of how well one commercial system can perform the MWD, IVD, RGD, and Mn analyses has as much to do with the quality of the software as it is to do with the hardware. Proper account for instrumental band-broadening is absolutely one of the key important factors for getting the most out of the SEC-VIS technology. In order to evaluate the performance of viscometers, we recommend injecting a three-component polystyrene mixture of defined composition, as previously described, and compare MW, IV, and Rg average values to known values. More importantly, distortions of each of the three peaks in the display of differential MWD, IVD, and RGD curves should be examined. Computer software inadequacy can easily be determined this way. A three- component mixture is infinitely more sensitive as a probe for software flaws than a sample that shows a broad bell-shaped elution curve.

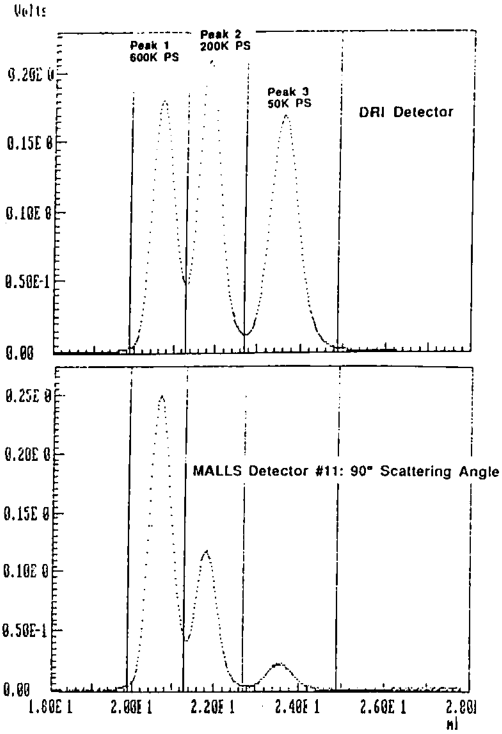
RGD by SEC-MALLS

As shown in Table I, there are two commercial on-line SEC light scattering detectors available today. One is the low-angle laser light scattering (LALLS) detector of Chromatix design, which measures the scattered light at a very small forward angle (19). Since measurements are made at very low scattering angle, the technique has the advantage of giving accurate MW values regardless of molecular size and conformation differences. The other one is the multi-angle laser LS (MALLS) detector of Wyatt Technology which measures scattered light at 18 different angles (20). One of the claimed capabilities of this instrument is its ability to determine polymer Rg-distribution when used as an on-line SEC detector.

In view of our recent work on RGD by SEC-VIS, we are very much interested in comparing these two seemingly different methods of determining polymer RGD. With this in mind, the RGD data on the same PS sample mixture were obtained by either techniques with the intend to aim for an objective comparison.

Figure 18 shows the RI response and the LS response at 90 degree scattering angle for the PS sample mixture of three narrow standards of 600, 207, and 47.5 thousand MW.

By plotting the LS signal against the scattering angles, one obtain the curves shown in Figure 19, referred to as the Debye plots (20). For each peak, a SEC slice at the peak maximum is selected to ensure the good S/N quality of the LS and RI data used in making these Debye plots. The intercepts of the Debye plot at low angle give the measure of polymer MW. The slope of the plots is proportional to the polymer mean square (MS) radius, or Rg^2. The Rg value is then calculated by taking the square root of the MS radius value. Note



Mobile Phase: Toluene
Column Set: Ultrastyragel
Sample Conc.: 0.1% of each
MALLS Cell: SF10 glass, 40μL

FIGURE 18. SEC/MALLS of a three-component PS mixture.

that Rg itself is sometimes referred to as root mean square (RMS) radius, by way of its mathematical definition. The measured Rg and MW values are printed at the top right corner of each Debye plot.

Notice that no Rg value is shown for the PS peak of 50 K MW. No estimate of Rg for this Debye plot, because this particular plot shows a slightly positive slope which would correspond to a negative value for MS radius which of course lacks any physical meaning. Therefore, no calculation of Rg is

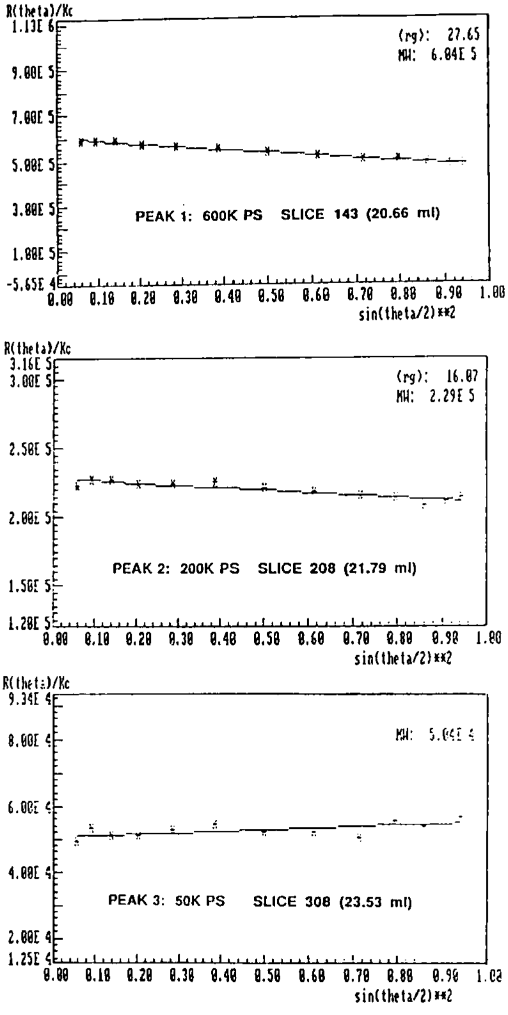


FIGURE 19. Debye plots of three-component PS mixture at peak maximum.

possible in this case. Mathematically, Rg would have to be an imaginary number resulting from taking the square root of a negative quantity. It is interesting to note, however, the individual R(theta)/Kc values for this SEC slice are reasonably consistent within ±20 % across the various scattering angles. These R/Kc values give good estimates of the intercept and the MW value. The point brought forward from the above analysis is the fact that the S/N demand for MALLS to determine MW is at one level, and the S/N demand for MALLS to determine Rg is at a level that is many times higher. What this means is that the quality of MW information by MALLS should be just that much better than the quality of the Rg information.

In comparison, see the Rg results obtained by SEC-VIS in Figures 11 through 13, SEC-VIS has no trouble to determine the Rg value of 8 nm for the 47.5K MW PS peak. The reason for the better performance displayed by SEC-VIS is not because there is a drastic S/N difference between the viscometer and the LS signal, as one can see by comparing the experimental detector responses in Figure 11 and 18. There were no excessive noise on the peak of 47.5K MW of either the viscometer or the MALLS elution curve. The difference exists in the way how these detector signals are used to determine the Rg value. In viscometry, the Rg calculation utilizes the viscometer signal directly, by way of Flory-Fox Equation shown in Figure 13. In another words, the S/N demand for viscometry to determine Rg stays at the same low level of S/N demand in determining the IV and MW value. With the appreciation of this basic difference, it become easier to understand why it is so easy to get into the negative MS radius situation in MALLS, but it is highly difficult to get into a situation even for a negative Rg in the viscometry approach. It is clear that Rg values calculated from the Flory-Fox Equation simply could not assume a negative value unless [η], or the viscometer response itself goes negative.

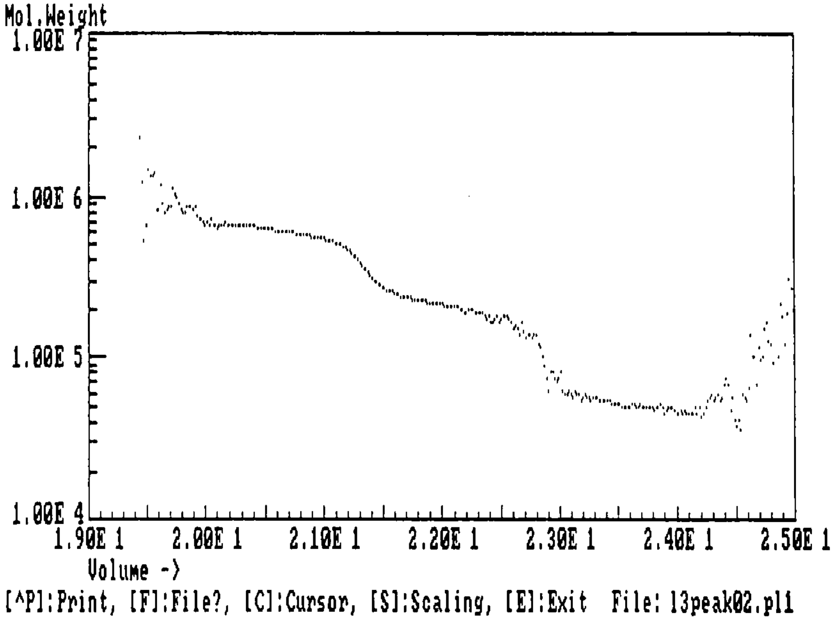


FIGURE 20. Molecular weight vs. volume.

In Figures 20 and 21, where the calculated log(MW) and log(Rg) values are plotted against the SEC retention volume. We see the MW versus V_R plot behaved quite well showing three plateaus indicating the same expected MW values are maintained across each elution peak, which is the feature expected of the narrow MWD standards. The quality of the Rg versus V_R plot however is much poorer. There are many points missing for the low MW peak at the long retention time. These missing points are caused by the problem of an incorrect slope and negative MS radius situation discussed above.

The appearance of the poor S/N problem of Rg measurement is amplified in the format of the differential RGD display as shown in Figure 22. Most of the low MW peak simply disappeared, indicating the majority of data under this peak have the problem of negative MS radius. In a sharp contrast,

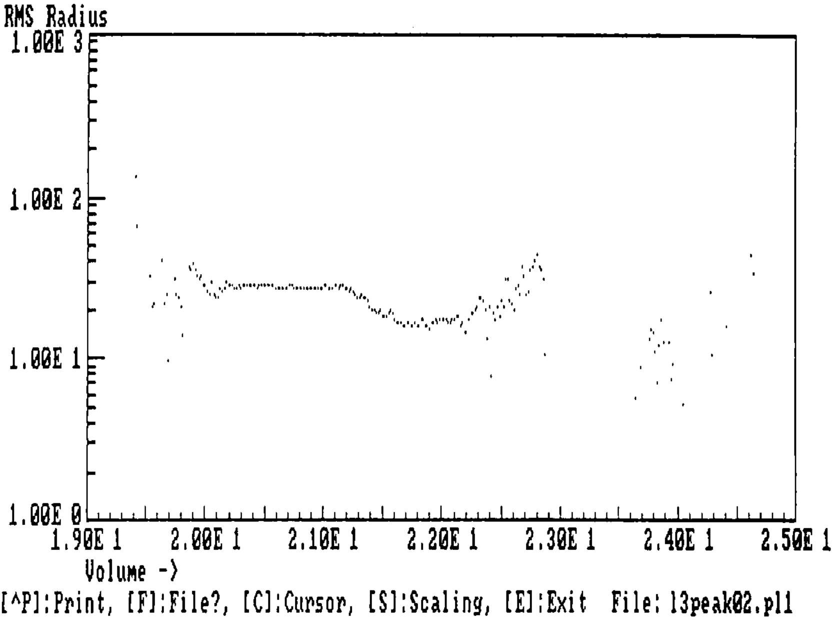


FIGURE 21. RMS radius vs. volume.

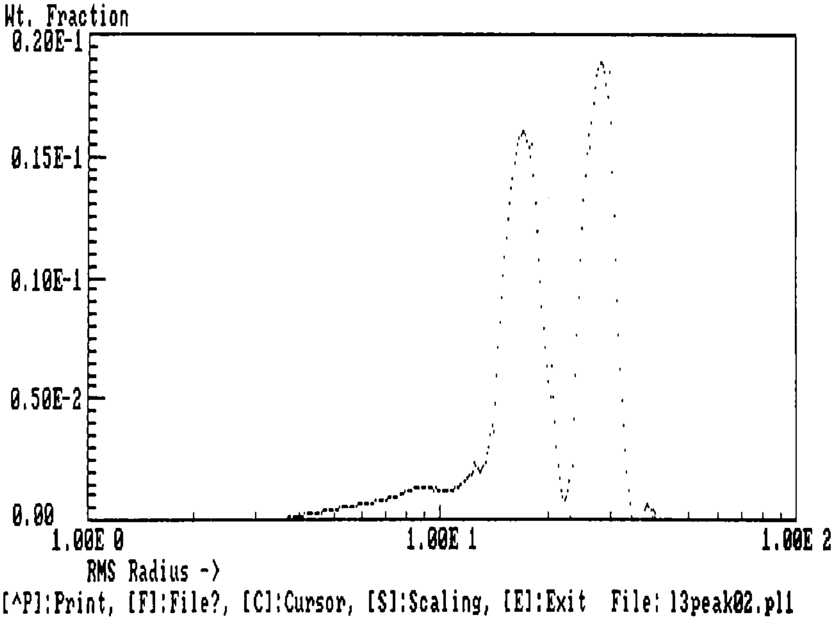


FIGURE 22. Differential RMS radius distribution.

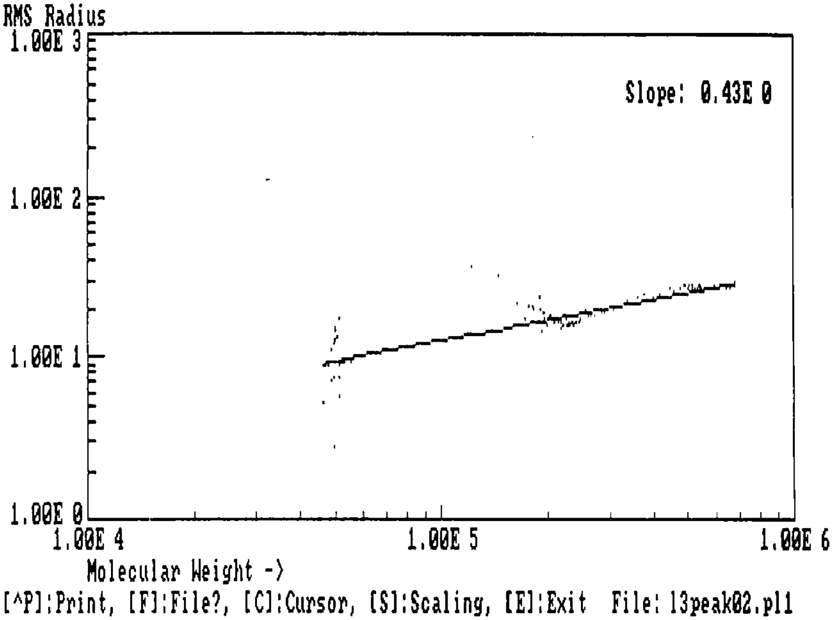


FIGURE 23. RMS radius vs. molecular weight.

the SEC-VIS approach gives very nice RGD curves for the sample mixture, see Figure 12.

Figure 23 shows the plot of log(Rg) versus log(MW). In theory, the slope of this so called polymer conformation plot should equal to the value of the exponent α in the Rg versus MW relationship of Equation 20. The data in Figure 23 provides an α value of 0.43, which is obviously in error. The value is too low, outside the expected range of 0.5 to 0.6 for random-coil type polymers (12). For PS in THF or toluene, the α value should be around 0.57. In comparison, the SEC-VIS approach estimated the α value of 0.57 accurate within ± 0.01.

Table IV shows the Rg and α results from duplicate SEC-MALLS runs. The effect of using first- or second-order fit of the Debye plot on the calculated

Table IV

DUPLICATE SEC/MALLS R_g MEASUREMENTS OF A THREE-COMPONENT PS MIXTURE

PS Peak	R_g, nm*		α (Predicted = 0.57)**	
	First-Order	Second-Order	First-Order	Second-Order
			All Peaks:	
52,000	20.3/14.0	34.9/27.5	0.17/0.28	0.30/0.01
228,000	18.7/17.6	25.4/21.0		
			Peaks 2 & 3:	
			0.44/0.49	0.33/0.39
589,000	28.0/27.6	30.1/28.7		

* From Ptitsyn-Eisner equation

$R_g =$ 8.3 for 50K

$R_g =$ 17.8 for 200K

$R_g =$ 34.8 for 600K

** $R_g \sim M^{\alpha}$

where $\alpha = (1 + a)/3$ and a is M-H exponential.

Since $a = 0.72$, $\alpha = 0.57$

Rg and α values are also included. Poor reproducibility of the results is very evident. The gross discrepancy of the α value is especially disturbing. No useful information can be derived from these α results. The Rg value for the low MW peak is grossly overestimated. The problem here is the S/N difficulty discussed before that caused massive data points rejection and faulty sample representation. The Rg value for the middle MW peak is in agreement with the expected value. For the 600 K MW peak, there is a 20 % underestimation of Rg with the first-order fit calculation. Second-order fit gives a slightly larger Rg value but precision is poorer.

To examine whether the Rg error of the 600 K MW peak is caused by the non-linearity of particle scattering function at small scattering angle, we generated a theoretical particle scattering function for a random-coil of 35 nm Rg by using the Debye' theory of P(θ) (13). As shown in Figure 24, there is indeed a likelihood that a first-order fit can easily underestimate the Rg value by 20% even at this moderate Rg level of 35 nm. The solid line in the figure shows how an accurate initial slope of the particle scattering function can be quite different from the first-order fit even though the spaced LS data points show little curvature across the span of the scattering angles.

Thus, there appears to be a narrow window in which reliable Rg values can be obtained by SEC-MALLS technology. The lower limit is approximately 10 nm, which corresponds roughly to a MW value of 100,000 PS, and the upper value is about 30 nm corresponding to 500,000 PS. For Rg>30 nm, one needs to know polymer conformation for accurate Rg determination, because particle scattering function of large particles is known to be highly dependent of particle morphology.

In summary, although LS, and therefore MALLS, may be universally recognized as the technique for accurate Rg determination, we feel the SEC-viscometry has performed well in Rg determination and offers a number of unique features.

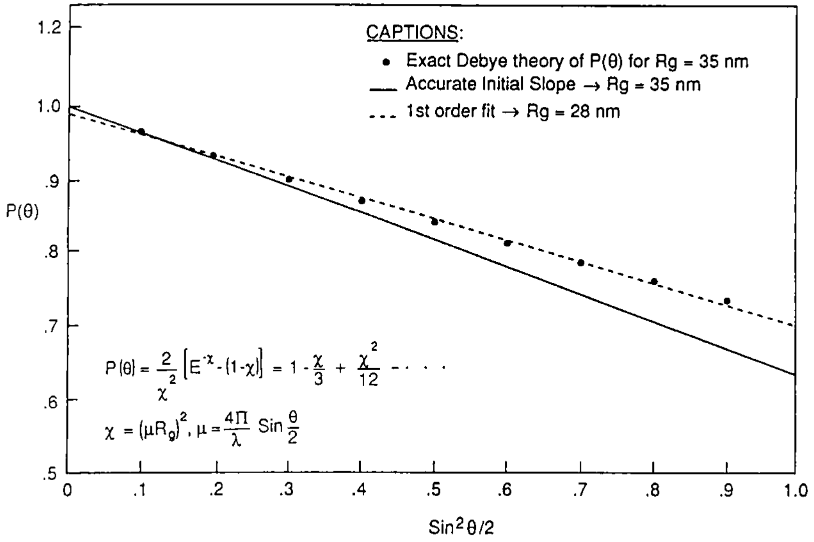


FIGURE 24. Inaccuracy of R_g MALLS with 1st order fit.

CONCLUSION

It is important to understand fundamental features about the quality of the results obtained from these different techniques. There is a natural tendency in overstating instrument capabilities involving new techniques. For new technologies, the distinctions between claimed versus actual capabilities and between potential expectations versus demonstrated performances are often difficult to make. It behooves us to recognize the confidence limits, basic assumptions and calibrations that are involved with each particular results.

General insights based on our working experience on the on-line MW-sensitive detectors are summarized in Tables V and VI. Table V lists the information content that is expected of on-line LS and viscosity detectors used with SEC. The information contents of these hyphenated SEC techniques are classified into two groups. The information listed under the "primary" category

Table V

SEC ANALYSES USING MW-SENSITIVE DETECTORS

		Information Content		
		Primary•		Secondary
SEC-LALLS	→	MWD		
-MALLS	→	MWD	⇒	RGD
-VIS	→	IVD	⇒	MWD, RGD, Copolymer M_n
SEC-VIS-LS	→	IVD, MWD, RGD	⇒	Copolymer M_n
Regular SEC	→	- - -	⇒	MWD

• High precision and accuracy, insensitive to SEC operation variables, requires no SEC-MW or universal calibration.

are results of high precision and accuracy, insensitive to SEC operation variables, and requires no SEC-MW or universal calibration. In contrast, the information listed under the "secondary" category are the less precise results or results that require SEC or universal calibration. The LS detectors provide MWD, while MALLS is also offered as a RGD detector. SEC-VIS provides direct IVD results. High quality results of MWD, RGD, and M_n values for copolymers and polymer blends can also be determined using SEC-VIS. These secondary results are derived from SEC universal calibration.

With the combination of a viscometer with LS, or with an on-line osmometer, it appears possible to obtain RGD with high precision from the

Table VI

A GENERALIZATION OF MW/SIZE-SENSITIVE SEC DETECTORS

INTENDED MEASUREMENTS / BASIC FEATURES	LALLS/MALLS	VISCOMETER
MW-Distribution(MWD).	Requires absolute LS intensity calibration	requires universal calibration
	Needs precise n, dn/dc, A_2 values	calculation parameters: k, a, k_H
	Not affected by non-exclusion effects, separation systems and expt'l variables	....
[η]-Distribution (IVD).	....	direct from experiment
	....	not affected by non-exclusion effects, separation systems & expt'l variables; specific to measuring temp. and solvent types
R_g-Distribution (RGD).	Requires LS/angle normalization, MALLS only	calculable from [η] M
Chain conformation & branching studies.	R_g vs. M plot, R_g-M exponent, MALLS only	[η] vs. M plot, Mark-Houwink [η]-M exponent; R_g vs. M plot, R_g-M exponent
Sensitivity at low MW.	limited	better
Noise/particulates, bubbles.	yes, MALLS better	least affected
Heterogeneous polymer analyses	limited	better
Process Q.C. application	MW-distribution	[η]-distribution, better precision

experimental values of intrinsic viscosity and MW across the SEC elution curve. With this approach, RGD no longer would depend on SEC universal calibration and would be insensitive to variations of SEC operating conditions. At the present time, the integrated system offers the best chance for quantitative and dependable studies of polymer conformation and polymer branching distributions. At the bottom of Table V, the regular SEC approach is given as using just a concentration detector; here of course, the MWD results are obtained via SEC-MW calibration.

Additional details of existing LS and viscosity detectors, based on our personal experience, are summarized in Table VI. Many of the entries are self explanatory and should serve as useful general references.

ACKNOWLEDGEMENT

The author wishes to express his gratitude to G. A. Smith and P. A. Ware for performing many of the SEC-VIS, MALLS, and osmometry experiments, to S. W. Rementer for developing the computer programs, and to J. J. Kirkland and H. G. Barth for their encouragement and collaboration throughout the course of this work. Special thanks are due to J. H. Foraker and B. R. Pennington for preparing this manuscript, and to H. G. Barth for providing the much needed editing of the original manuscript.

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