A CRITICAL EVALUATION OF MOLECULAR-WEIGHT-SENSITIVE DETECTORS FOR SIZE EXCLUSION CHROMATOGRAPHY

Howard G. Barth and Wallace W. Yau
Central Research & Development Department
E. I. du Pont de Nemours & Company
Experimental Station
P.O. Box 80228
Wilmington, Delaware 19880-0228

Molecular-weight-sensitive detectors for size exclusion chromatography have added a new dimension to the information content that can be obtained from an SEC separation. The primary data that can be obtained from light scattering measurements is the molecular weight distribution. With the use of multi-angle measurements, the radius of gyration can also be determined directly provided that the signal-to-noise ratio is sufficiently high and the size of the polymer is greater than approximately 10 nm. For viscometers, the primary information that can be obtained is intrinsic viscosity; however, this data can be converted to molecular weight by using the Mark-Houwink constants of the sample or by employing universal calibration. Furthermore, by utilizing the Flory-Fox equation, molecular size information can also be obtained readily from viscometric data. These detectors also have the potential of providing molecular conformation and branching information of a polymer as a function of molecular weight as well as the Mark-Houwink constants.

INTRODUCTION

The commercial availability of online molecular-weight-sensitive detectors for size exclusion chromatography (SEC) has greatly increased the information content that can be obtained from an SEC experiment. By coupling these detectors to an SEC column, one can not only measure the statistical average molecular weights and the molecular weight distribution of a polymer, but, depending on the detector being employed, molecular size and conformation, branching index, and Mark-Houwink constants can also be determined.

In this paper, we will examine the principles, applicability, and limitations of commercially available low-angle and multi-angle laser light scattering photometers, and capillary viscometers.
LASER LIGHT SCATTERING

Theory

When light interacts with a molecular, it induces a temporary dipole moment that oscillates in phase with the incident beam. In effect, the molecule acts as an antenna and radiates light in all directions. This is referred to as Rayleigh scattering. The light scattering behavior of a polymer in solution, using vertically polarized light as the incident beam, is described by the Rayleigh equation (1):

\[
\frac{I_\theta}{I_0 V} = \frac{4\pi n^2}{\lambda_o r^2 N} \frac{(dn)^2}{(dc)} \frac{c}{[M_w P(\theta)]^{-1} + 2A_2c}
\]  

(1)

where \(I_0\) is the intensity of the incident beam, \(I_\theta/V\) is the light scattering intensity per unit volume, \(n\) is the refractive index of the medium, \(\lambda_o\) is the wavelength of light in vacuum, \(r\) is the distance from the scatterer to the detector, \(N\) is Avogadro's number, \(dn/dc\) is the specific refractive index increment, \(c\) is the polymer concentration, \(M_w\) is the weight-average molecular weight, and \(A_2\) is the second virial coefficient. \(P(\theta)\) is the particle scattering function, which depends on the geometry and the size of the macromolecule with respect to the wavelength of the incident beam. At low angles, the inverse function of \(P(\theta)\) is

\[
P(\theta)^{-1} = 1 + \frac{16\pi^2 \langle r^2 \rangle_z}{3\lambda_o^2} \sin^2 \frac{\theta}{2} + \text{higher terms}
\]  

(2)
where $<r^2>_z$ is the z-average of the mean-square radius of gyration. The value of the radius of gyration, $<r^2>^{1/2}$ is related to the average dimensions of a polymer in solution and is defined as the square root of the weight average of the square distances of all mass elements from the center of mass of a macromolecule.

Equation 1 can be simplified by defining a reduced scattering term, $R_\theta$, also known as the Rayleigh factor, which is simply the intensity of scattered light of a given material per unit volume at defined $\theta$, $r$, and $I_0$:

$$R_\theta = \frac{I_\theta r^2}{I_0 V}$$

(3)

To further simplify equation 1, an optical constant, $K$, is defined that can be measured independently of the light scattering experiment:

$$K = \frac{4\pi n^2}{\lambda_0^2} \left( \frac{dn}{dc} \right)^2$$

(4)

Because we are interested in the scattering intensity from the polymer, the scattering contribution caused by the solvent must be subtracted from the solution:

$$\overline{R}_\theta = R_{\theta, \text{solv}} - R_{\theta, \text{solv}}$$

where $\overline{R}_\theta$ is called the excess Rayleigh factor. Substituting equations 3-5 into equation 1, we arrive at

$$\frac{Kc}{\overline{R}_\theta} = \frac{1}{M_w P(\theta)} + 2 A_2 c$$

(5)
In an online SEC measurement, the polymer concentration is sufficiently low so that the second virial coefficient term in equation 5 can be neglected. If needed, $A_2$ can be determined in a repeat SEC experiment with light scattering measurements with two or more sample concentrations.

With low-angle laser light scattering photometry (LALLS), in which $R_\theta$ is measured at a low angle ($<7^\circ$) using coherent, monochromatic light, $\sin^2 (\theta/2)$ becomes close to 0, $P(\theta)$ and $P(\theta)^{-1}$ approach unity. Thus, equation 5 becomes

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_2c$$

(6)

However, because the angular dependency of light scattering intensity is not used, information regarding molecular size is not available.

When LALLS is used as an online SEC detector, a concentration sensitive detector is placed in series. At each elution volume increment, both $R_\theta$ and $c$ are determined and the molecular weight calculated at each volume increment using equation 6. Assuming perfect chromatographic resolution, the molecular weight distribution and statistical average molecular weights can be calculated (2, 3):

$$M_x = \frac{\Sigma c_i M_i^x}{\Sigma c_i M_i^{x-1}}$$

(7)

where $c_i$ is the concentration, and $M_i$ is the molecular weight at a given incremental elution volume. If $x = 0$, $M_x = M_n$ (number-average molecular weight); if $x = 1$, $M_x = M_w$ (weight-average molecular weight); if $x = 2$, $M_x = M_z$ (z-average molecular weight); and if $x = 3$, $M_x = M_{z+1}$ ([$z + 1$]-average molecular weight).
Because of imperfect resolution, a weight-average molecular weight is actually measured at each elution volume increment so that equation 7 becomes

$$M_x = \frac{\sum c_i M_{wi}^x}{\sum c_i M_{wi}^{x-1}}$$  \hspace{1cm} (8)

and, as a result, $M_n$ and $M_z$ are usually overestimated unless band broadening corrections are made.

If $R_e/Kc$ (Debye plot) is plotted versus $\sin^2(\theta/2)$ at low polymer concentration (limit as $c \to 0$), the molecular weight can be determined from the reciprocal of the intercept, and the mean-square radius of gyration can be determined from the initial slope, $k$ (in Debye plot, $k = (-1) \times$ measured slope):

$$<r^2>_z = \frac{3k\lambda_o^2}{M_w 16\pi \eta^2}$$  \hspace{1cm} (9)

This is the basis of multi-angle laser light scattering, commonly referred to as MALLS (4-6). Thus, at each elution volume increment,

$$<r^2>_z^{1/2}$$ as well as $M_w$ (M and $<r^2>^{1/2}$ for perfect resolution) can be obtained.

To accurately determine molecular size, the signal-to-noise ratio of the measurement must be sufficiently large to extract $<r^2>^{1/2}$ from the slope (eq. 9). Radius-of-gyration measurements below approximately 10 - 20 nm (1) are difficult to determine reliably. In SEC, the low sample concentration reaching the detector imposes a further constraint on this limit. Since the particle scattering function is a power series, of which only the first term is shown in equation 2, the initial slope needs to be determined accurately at low angles or accurately extrapolated from higher angles. As the molecular weight
is increased, higher-order fits are needed to obtain reliable radius-of-gyration measurements (1, 7).

**Instrumentation**

Table 1 summarizes the characteristics of commercially available LALLS and MALLS photometers for SEC. The major difference between the LALLS units is that the KMX-6 and CMX-100 are calibrated from geometric considerations (8-10), while the LS-800 is calibrated with a known molecular weight polymer standard (11,12).

The Dawn model F MALLS unit consists of 18 photodiodes spaced out around the flow cell, of which the output of up to 15 can be measured simultaneously. The instrument (90° diode) is first calibrated using either a polymer standard or solvents of known Rayleigh ratios. The remaining diodes are then normalized to the calibrated diode using a polymer standard of known molecular size (6). If the size is well below 10 nm, the photodiode responses are normalized such that the slope of $R_g/Kc$ versus $\sin^2(\theta/2)$ is equal to zero.

**Evaluation**

The unique feature of MALLS is its potential for giving molecular size information, as well as molecular weight data. In view of this, the Dawn F MALLS instrument (Wyatt Technology, Santa Barbara, Calif.) was evaluated using a mixture of three polystyrene standards as a test mixture. An experimental cell, designed and constructed at Du Pont, was used in place of the commercial cell. The experimental cell had a cylindrical cross-section to reduce stray light for increased signal-to-noise. The data were analyzed using Astra 1.05 software (Wyatt Technology).
Experimental. The polystyrene standards were from Pressure Chemical (Pittsburgh, Penn.) and had the following nominal molecular weights: 50K, 200K, and 600K. The injected mixture consisted of equal amounts of each standard and 100 µL of a 2.5 mg/mL solution was injected into a column set comprising of a Zorbax bimodal column set. Toluene was used as the mobile phase at a flow rate of 1 mL/min. The instrument was calibrated by best fitting the nominal MW values of each component in the above PS mixture, and the photodiodes were normalized to a low-molecular-weight polystyrene standard. A Waters 410 DRI was used as a concentration-sensitive detector.

Results and Discussion. Figure 1 shows the MALLS output of the injected mixture. As expected, the signal intensity of the MALLS detector is related to both concentration and molecular weight (equation 5). The Debye plots (\(\bar{R}_g/Kc\) vs. \(\sin^2(\theta/2)\)) of slices at the peak maximum are given in Figure 2, along with the corresponding molecular weights and radii of gyration. Because the slope of the 50K polystyrene was close to zero and the signal-to-noise ratio of this slice was poor, a reliable molecular size was not possible; however, the molecular weight values were in agreement to predicted values.

Molecular weight versus elution volume is given in Figure 3. Except for the ends of the distribution, in which the low signal-to-noise ratio is responsible for the scatter of data, there is a smooth transition of molecular weight across the chromatogram. (Please note that no band broadening corrections were available for the software used.) A comparison of weight-average molecular weights obtained by SEC/MALLS to manufacturer's values is given in Table 2.

Figure 4 is the radius of gyration versus elution volume plot. As indicated, the only results with any precision were obtained for the 600K and
may be the 200K polystyrene standards. Table 3 shows the radius-of-gyration results using first-order fits of the Debye plots. For reference, the predicted values from the Ptitsyn-Eizner extension of the Flory-Fox equation are also given in the table (13,14).

These trends can be explained by examining the particle scattering function (equation 2). Higher-order terms are needed in this equation if the radius of gyration is greater than approximately 30 nm (14); however, a higher order fit demands a greater signal-to-noise ratio to accurately define the initial slope.

A convenient method to determine the reliability of radius-of-gyration results is to compute the exponent, \( \alpha \), in the following power-law function:

\[
<r^2> \propto M^\alpha
\]

and compare this result to a predicted value in which \( \alpha = (1 + a)/3 \), where \( a \) is the exponent in the Mark-Houwink relation ([\( \eta \]) = KM^a). Since \( a = 0.72 \), the predicted value of \( \alpha \) for polystyrene in toluene should be close to 0.57. In addition, from offline light scattering measurement of polystyrene in toluene, an \( \alpha \) value of 0.586 has been found (15). As indicated in Table 3, these values are underestimated. In fact, the theoretical value of a random coil at theta conditions is 0.5.

Based on these and other results (14), there appears to be a window in which reliable radius of gyration values can be obtained using MALLS as an on-line SEC detector. Even though the particle scattering function becomes independent of particle shape as the angle of scattering approaches zero (16), in order to obtain reliable size information a very high signal-to-noise ratio is needed at higher angles for reliable extrapolation.
Useful size information by extrapolation requires the use of low angle light scattering measurements with extreme degree of signal-to-noise performance. Based on our data, reliable low-angle data were not available for online SEC/MALLS measurements because of excessive stray light and refraction complications at low angle forward scattering. In SEC, this often is a serious constraint because of limited sample concentration that can be injected and because of peak dispersion caused by instrumental band broadening and sample polydispersity.

For our test mixture, which simulates a polydisperse sample, the lower size limit that can be determined from SEC/MALLS is approximately 10 nm which corresponds to a molecular weight of 100,000 g/mol for polystyrene. The upper limit is dictated by the signal-to-noise ratios of the concentration and MALLS detectors, and the curve-fitting routines that are used for data analysis of the Rayleigh equation. For our studies presented in this paper using an early version of Wyatt software, the upper limit was found to be approximately 30 nm for polystyrene. This corresponds to a molecular weight of 500,000.

To obtain more reliable molecular size data, we recommend that software needs to be used that incorporates higher order curve-fitting routines in which the order of fit can be adjusted across the molecular weight distribution. For the lower molecular-weight-end of the distribution, extrapolation of equation 11 to the low-molecular-weight region should prove valuable.
VISCOMETERS

Theory

As compared to light scattering, the theory and instrumentation involved with online viscometric measurements is much simpler. The column eluate passes through a capillary tube at constant flow rate and temperature. By dividing the pressure drop across the capillary tube of the eluent, \( \Delta P \), by the pressure drop of the mobile phase, \( \Delta P_o \), the relative viscosity of the eluting polymer, \( \eta_{rel} \), can be measured:

\[
\eta_{rel} = \frac{\Delta P}{\Delta P_o}
\]  

(11)

By the use of the intrinsic or inherent viscosity equations,

\[
[\eta] = \left( \frac{\ln \eta_{rel}}{c} \right)_{c \to 0} = \left( \frac{\eta_{rel}^{-1}}{c} \right)_{c \to 0}
\]  

(12)

and knowing the polymer concentration at each elution volume increment, the intrinsic viscosity can be determined:

\[
[\eta] = \left( \frac{\ln(\Delta P/\Delta P_o)}{c} \right)_{c \to 0} = \left( \frac{(\Delta P/\Delta P_o)^{-1}}{c} \right)_{c \to 0}
\]  

(13)

If the Mark-Houwink constants of the polymer being analyzed are accurately known, then the molecular weight can be determined at each elution volume increment. If these constants are not known, then universal calibration is used to calculate molecular weight at each elution volume increment i:
Here subscript 1 represents the standard used to construct the universal calibration curve. By using equation 7, average molecular weights can be determined. It should be noted, however, that only the molecular weight of the standards need to be known, since their intrinsic viscosities are determined by the online viscometer. As in the case of light scattering detectors, band broadening corrections should be taken into account (17).

Since, in a typical SEC experiment, polymer concentrations are sufficiently low, there is usually no need to extrapolate equation 13 to zero concentration (17, 18).

Instrumentation

Three types of capillary viscometer configurations have been reported: single-capillary design (18-20), four-capillary bridge (21,22), and a two-capillary series configuration (17). The single-capillary design of Lesec (18) has been incorporated into the Waters 150C high temperature GPC system (Waters Chromatography Division, Milford, Mass.) and is now commercially available. The viscometer of bridge design is commercialized by Viscotek. The referenced-capillary differential viscometer of Yau (17), referred to as the Du Pont viscometer in this paper, has been licensed to Viscotek (Porter, Texas) and is currently being marketed as a batch (offline) viscometer. An online version will be introduced in the future.

Table 4 lists the characteristics of these viscometer designs. Since the single-capillary configuration is sensitive to flowrate fluctuations, the Waters 150CV unit consists of special pulsation dampeners and is available only as an integrated GPC unit. The other two designs are referenced
configurations, so that flowrate fluctuations are canceled out, and are not a major concern in the operation of these detectors. As a result, they are modular units and can be used with any high-quality HPLC pumping system. Although the output of the Viscotek viscometer is dependent on the flowrate level, it contains an additional pressure transducer to take into account the flowrate of the HPLC system. When the Du Pont and Viscotek detectors are used with a delay coil, analysis time using these referenced viscometers is increased, that is, the entire sample has to pass through the viscometer before the next injection can be made. This is not the case for the single-capillary design of the Waters 150CV. The extra time to flush out the GPC sample can be avoided, however, when these flow-referenced viscometers are used that contain large-sample dilution delay coils.

**Evaluation**

**Experimental.** Polystyrene test mixture was the same as described for the MALLS study. A reference-capillary differential viscometer (17) and a Waters 401 DRI were used in series. The column set was four Du Pont PSM biomodal columns. Tetrahydrofuran was used as the mobile phase at 1 mL/min. The injection volume was 200 µL. Universal calibration was accomplished using a series of polystyrene standards. The software that was employed, which also contained band broadening corrections, was developed inhouse by Yau and Rementer (14).

**Results and Discussion.** Weight-average molecular weights of the polystyrene peaks in the test mixture are shown in Table 5 along with manufacturer's values. As indicated, there was excellent agreement with values measured on individual samples.
Radius of gyration results, determined using the Ptitsyn-Eizner extension of the Flory-Fox equation, are given in Table 6. As indicated, the exponent of equation 10 is 0.57, very close to the expected value of 0.57 and an experimental value of 0.596 obtained from offline light scattering measurements (15).

**COMPARISON OF LIGHT SCATTERING AND VISCOSITY SEC DETECTORS**

Table 7 is an intercomparison of the applications and limitations of light scattering and viscometric detectors for SEC. The output from light scattering is an absolute measurement of molecular weight, and as a result, is independent on the separation mechanism. For light scattering, precise values of $dn/dc$ and $n$ are required. Intrinsic viscometry can also be used in an interactive HPLC mode provided that Mark-Houwink constants of the polymer being analyzed are accurately known. If not, the universal calibration needs to be employed, which is dependent on the separation mechanism.

An intrinsic viscosity distribution can be obtained directly from a viscometer, and is independent of the separation mechanism and flowrate variations (14, 23). Because of this, the intrinsic viscosity distribution concept holds great promise for process control, in which the stringent requirements of stable flowrate and column calibration, which are often times difficult to meet, can be relaxed (14).

Although limited molecular size data can be obtained from MALLS, the use of viscometry, at this time, appears to be a more accurate and precise method, especially for lower molecular weight components. From a knowledge of molecular size versus molecular weight, conformational information can also be obtained. By the use of universal calibration, viscometry can be used to obtain Mark-Houwink constants, as well as the
branching index as a function of molecular weight. It may also be possible to employ light scattering with universal calibration to obtain intrinsic viscosity. Such an approach has been reported by Cotts (24).

One of the unique features of viscometry with universal calibration is that molecular weight data can be obtained from chemically heterogeneous polymers. This is possible for light scattering only if the dn/dc values are known as a function of composition and molecular weight. This requirement of dn/dc for light scattering is not easily met in practice.

The sensitivity of the viscometer is much greater for low-molecular-weight components than light scattering; for high-molecular weight components, the converse is true.

LALLS detectors behave essentially as particle counters, and are therefore highly sensitive to particulates in the column eluate, caused either by particulates in the mobile phase or debris from the column packing. As a result, mobile phase filtration and column conditioning are required. In some instances, online filters are installed between the column and detector. MALLS, however, is much less sensitive to particulates since light scattering intensity from low angles of measurement, which scatter more light from particles than higher angles, can be selectively dropped from calculations. Care needs to be exercised, however, in MALLS when low angle data are dropped. The accuracy of the MW intercept by angular extrapolation suffers if there are not enough low angle data. Viscometers, however, are significantly less sensitive to particulates than LS.
CONCLUSIONS

Light scattering and viscometers offer different modes of detection, and therefore, have distinct advantages and limitations. However, these characteristics are not only inherent in the detectors themselves, but are also highly dependent on the software employed. The future of these detectors lies not only with instrumentation improvements, but also with the incorporation of features in the software to maximize information content and minimize errors. Finally, the use of both light scattering and viscosity detectors in series gives us the best of both worlds, in which, for example, polymer conformation and branching, can be more accurately determined independent of experimental variables than with either alone.
REFERENCES


### COMMERCIAL SEC-LIGHT SCATTERING PHOTOMETERS

<table>
<thead>
<tr>
<th></th>
<th>KMX6*</th>
<th>CMX-100*</th>
<th>LS-8**</th>
<th>Dawn Model F***</th>
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<tbody>
<tr>
<td><strong>Cell Volume</strong></td>
<td>10 μL</td>
<td>10.5 μL</td>
<td>30 μL</td>
<td>33 μL</td>
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<tr>
<td><strong>Scattering Volume</strong></td>
<td>35 nL</td>
<td>40 nL</td>
<td>100 nL</td>
<td>250 nL</td>
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<tr>
<td><strong>Angle</strong></td>
<td>2-3°</td>
<td>5.1-6.1°</td>
<td>5°</td>
<td><em>Simultaneously monitors 18 angles.</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td><em>Scattering angle depends on solvent, e.g., toluene,</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(\theta = 12) to 152°; for THF: (\theta = 3) to 160°.</td>
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<td></td>
<td>3-4°</td>
<td></td>
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<td></td>
<td>3-7°</td>
<td></td>
<td></td>
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<td></td>
<td>4.5-5.5°</td>
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<td></td>
<td>6-7°</td>
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<tr>
<td></td>
<td>90°</td>
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<td></td>
<td>175°</td>
<td></td>
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</tbody>
</table>

* LDC Division/Milton Roy Corporation  
** Tosoh Corporation  
*** Wyatt Technology
Table 2

SEC/MALLS $M_W$ MEASUREMENTS OF A THREE-COMPONENT PS MIXTURE

<table>
<thead>
<tr>
<th>SEC/MALLS*</th>
<th>LALLS**</th>
<th>SEC**</th>
</tr>
</thead>
<tbody>
<tr>
<td>50,400</td>
<td>47,500</td>
<td>47,900</td>
</tr>
<tr>
<td>204,000</td>
<td>216,000</td>
<td>208,000</td>
</tr>
<tr>
<td>619,000</td>
<td>591,000</td>
<td>573,000</td>
</tr>
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</table>

* Determined in mixture of all three PS samples.

** Supplied by Pressure Chemicals, determined from individual samples.
Table 3

SEC/MALLS \( R_g \) MEASUREMENTS OF A THREE-COMPONENT PS MIXTURE

<table>
<thead>
<tr>
<th>PS Peak</th>
<th>( R_g, \text{nm}^* )</th>
<th>( \alpha ) (Predicted = 0.57)**</th>
</tr>
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<tr>
<td>50,400</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>204,000</td>
<td>19</td>
<td>All data: 0.35</td>
</tr>
<tr>
<td>619,000</td>
<td>30</td>
<td>200K/600K data: 0.40</td>
</tr>
</tbody>
</table>

* From Ptitsyn-Eisner equation (see Table 6):

\[
R_g = 8.2 \text{ for } 50K \\
R_g = 17.2 \text{ for } 200K \\
R_g = 34.4 \text{ for } 600K
\]

** \( R_g \sim M^\alpha \)

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

Since \( a = 0.72 \), \( \alpha = 0.57 \)
<table>
<thead>
<tr>
<th></th>
<th>Waters 150CV (Integrated SEC System)</th>
<th>Viscotek 200 (Modular)</th>
<th>Viscotek 500Y (Du Pont) (Modular)</th>
</tr>
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<tbody>
<tr>
<td>Design</td>
<td>Single Capillary</td>
<td>4-Capillary bridge</td>
<td>2-Capillaries in series</td>
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<tr>
<td>Cell Volume</td>
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<td>Output Signal</td>
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<td>Insensitive</td>
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<td>Sensitive</td>
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<td>Fluctuations</td>
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<td>Calibration/Accuracy</td>
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<td>Depends on matched capillaries</td>
<td>Depends on electronic adjustment</td>
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<td>Sensitivity</td>
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<td>~ 4 x 10^{-5} η_{sp}</td>
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<tr>
<td>Delay Volume</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
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</tbody>
</table>
### TABLE 5

**SEC/VISCOSITY M_W MEASUREMENTS OF A THREE-COMPONENT PS MIXTURE**

<table>
<thead>
<tr>
<th>SEC/Viscosity</th>
<th>LALLS*</th>
<th>SEC*</th>
</tr>
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<tbody>
<tr>
<td>49,000</td>
<td>47,500</td>
<td>47,900</td>
</tr>
<tr>
<td>184,000</td>
<td>216,000</td>
<td>208,000</td>
</tr>
<tr>
<td>571,000</td>
<td>591,000</td>
<td>573,000</td>
</tr>
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</table>

Supplied by Pressure Chemicals, determined from individual samples.
### SEC/VISCOSITY $R_g$ MEASUREMENTS OF A THREE-COMPONENT PS MIXTURE

<table>
<thead>
<tr>
<th>PS Peak</th>
<th>$R_g^*, \text{nm}$</th>
<th>$\alpha^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>49,000</td>
<td>8.2</td>
<td>0.57</td>
</tr>
<tr>
<td>184,000</td>
<td>17.2</td>
<td></td>
</tr>
<tr>
<td>571,000</td>
<td>34.4</td>
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</table>

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

where $\Phi = 2.86 \times 10^{21} (1-2.63\varepsilon + 2.86\varepsilon^2)$, $\varepsilon = (2a - 1)/3$, and $a$ is the Mark-Houwink exponent.

** $R_g \sim M^\alpha$, where $\alpha = (1 + a)/3$.

Since $a = 0.72$, $\alpha = 0.57$
# Table 7: Comparison of Online LS vs. Viscosity Detectors

<table>
<thead>
<tr>
<th>Parameter</th>
<th>LALLS/MALLS</th>
<th>Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWD (MWD Absolute Measurement)</td>
<td>Need precise n, dn/dc, A2 values</td>
<td>Relative Measurement</td>
</tr>
<tr>
<td></td>
<td>Indep. of separation mechanism</td>
<td>Need univ. calib. or a and K values</td>
</tr>
<tr>
<td>[η] Dist.</td>
<td>Indirect from univ. calib.</td>
<td>Direct; Indep. of separation mechanism</td>
</tr>
<tr>
<td>Rg</td>
<td>Direct from MALLS but range is limited</td>
<td>Indirect from univ. calib.</td>
</tr>
<tr>
<td>Chain Conformation</td>
<td>MALLS: Rg vs. M plot but range is limited</td>
<td>[η] vs. M plot (Mark-Houwink constants can be obtained)</td>
</tr>
<tr>
<td></td>
<td>[η] vs. M plot via univ. calibration</td>
<td>Rg vs. M plot</td>
</tr>
<tr>
<td>Branching</td>
<td>Direct from MALLS Indirect from LALLS</td>
<td>Indirect from univ. calib.</td>
</tr>
<tr>
<td>Analysis of Heterogeneous Polymers</td>
<td>Limited because of dn/dc uncertainty</td>
<td>Directly applicable with univ. calib.</td>
</tr>
<tr>
<td>Lower M. Wt. Detectability</td>
<td>2,000 g/mol, depending on dn/dc and polydispersity</td>
<td>As low as 300-400 g/mol has been reported.</td>
</tr>
<tr>
<td>Response to Particle Contamination</td>
<td>LALLS: Highly sensitive MALLS: Less sensitive</td>
<td>Insensitive</td>
</tr>
</tbody>
</table>
FIG. 1 - SEC/MALLS (Wyatt Technology) Output from Channel 10 (90°)
(Zorbax Bimodal Column Set; 100 uL injection; 2.5 mg/mL)
EXPERIMENTAL CELL

FIG. 2 -
Debye Plot of Three-Component Mixture (PS 47.5/207K/600K)
Data Taken at Peak Maximum
(Zorbax Bimodal Column Set; 100 uL injection; 2.5 mg/mL)
FIG. 3 - Molecular Weight vs. Elution Volume of Three-Component PS Mixture Using MALLS
FIG. 4 - Rg vs. Elution Volume of a Three-Component Mixture (PS 47.5K/207K/600K) Using a DuPont Experimental Cell