

Expanding the GPC/SEC Experiment Beyond Conventional Limits using Viscometry and Light Scattering Detection

Application Note

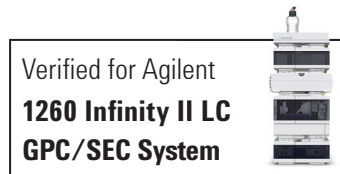
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Abstract

The Agilent 1260 Infinity Multi-Detector GPC/SEC System is a powerful tool for polymer characterization. The signals from a concentration sensitive detector such as refractive index (RI) or ultra-violet (UV) coupled with light scattering and viscometry can be used to determine the absolute molecular weight, size, and shape of the polymer in solution. This Application Note shows the value of the technique applied to the analysis of three very structurally different materials and illustrates the advantages of using multi-detection GPC/SEC to study a range of polymers.



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Introduction

GPC/SEC is an essential tool for the analysis of polymers, providing information required to understand how a polymer will process and perform. When using a concentration detector such as RI, the process is known as Conventional GPC/SEC. The chromatographic mechanism separates by the size of the polymer coil in solution, and is useful to determine the distribution of component chain lengths within a given sample. The information obtained can be increased considerably by adding viscometry and light scattering detection to create a multi-detector system. High performance modules are required to control temperature and maintain precise flow rates to ensure reproducible results. As with any chromatographic system, minimal band-broadening is critical to ensure data integrity is maintained.

This Application Note highlights the advantages multi-detection brings to the GPC/SEC experiment with a range of polymer examples.

Experimental

Instrumentation

The Agilent 1260 Infinity Multi-Detector GPC/SEC System used in the experiments consisted of the following individual modules:

1. Agilent 1260 Infinity Standard Degasser (G1322A)
2. Agilent 1260 Infinity Isocratic Pump (G1310B)
3. Agilent 1260 Infinity Standard Autosampler (G1329B)
4. Agilent 1260 Infinity Thermostatted Column Compartment (G1316A)
5. Agilent 1260 Infinity GPC/SEC Multi-Detector Suite (G7800A)
6. Agilent 1260 Infinity MDS RID (G7801A)
7. Agilent 1260 Infinity MDS Viscometer (G7802A)

8. Agilent 1260 Infinity MDS Light Scattering (G7803A)

Software

All instrument control, data collection and data analysis was performed with the Agilent GPC/SEC Software CDS consisting of:

- Agilent GPC/SEC Software (G7850AA)
- Agilent GPC/SEC Multi-Detector Upgrade (G7852AA)
- Agilent GPC/SEC Instrument Control (G7854AA)

Column Set and Calibrants

- 3 × PLgel 10 µm Mixed-B, 300 × 7.5 mm (PL1110-6100)

- PS nominal Mp 100 k (PL2013-5001)
- EasiVial PS-H 4 mL (PL2010-0200)

Reagents, samples, and materials

All chemicals and reagents were of HPLC grade and passed through a 0.22 µm filter prior to use. Samples were prepared by dissolution over a 16 hour period with gentle agitation in the eluent at the concentrations stated in Table 1.

Chromatographic parameters

GPC/SEC parameters used with the 1260 Infinity Multi-Detector GPC/SEC System are shown in Table 2.

Table 1. Sample preparation details.

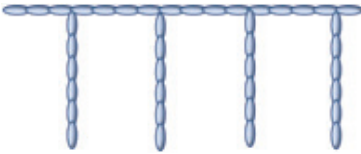
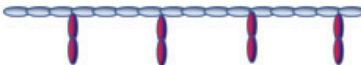

Sample type	Structure	Concentration (mg/mL)
Polyacrylate comb		2.020
Synthetic rubber		1.300
Polymethacrylate homopolymer		1.107

Table 2. Chromatographic parameters used for GPC/SEC.

Parameters	Conditions
Eluent	Tetrahydrofuran (stabilized with 250 ppm BHT)
TCC Temperature	35 °C
Detectors temperature	35 °C
Injection Volume	100 µL
Flow Rate	1.0 mL/min
Stop Time	35 minutes
Post Time	12 minutes
Detection	Refractive Index at 660 nm Viscometer Inlet Pressure Viscometer Differential Pressure Light Scattering 15 ° at 660 nm Light Scattering 90 ° at 660 nm

Results and Discussion

The polymer samples were analyzed using multiple methods to highlight the differences between the different techniques. Stable baselines and excellent signal-to-noise (S/N) were achieved by precise temperature control for the column oven and each individual detector (Figure 1).

System calibration

The system was first calibrated using a narrow dispersity polystyrene calibrant of 113,000 g/mol, dispersity 1.03 (Figure 2). This single standard determines essential detector constants and calculates the inter-detector delay (IDD) between the detectors, which are connected in series.

The unique small volume flow cell designs result in market-leading low dispersion technology, minimizing the band-broadening commonly seen when employing multiple detectors. This is clearly illustrated in the separation of the narrow polystyrene standard (Figure 2).

Molecular weight comparisons

In Conventional GPC/SEC, the molecular weight results are relative to the standards used to generate the column calibration. For further information on Conventional GPC, refer to the Agilent primer¹.

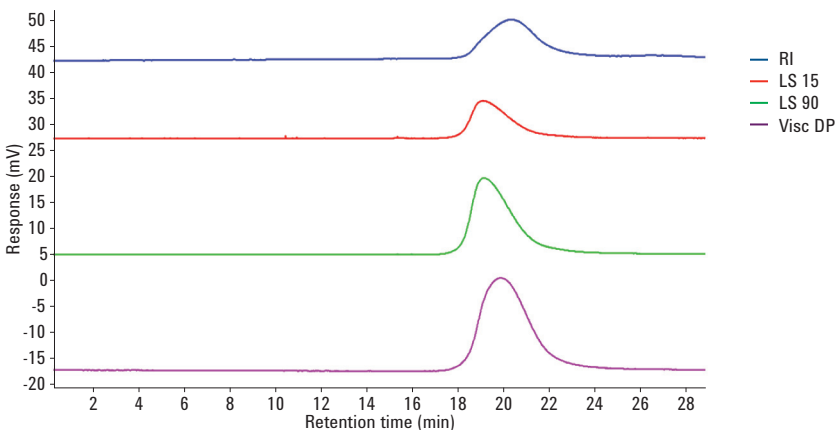


Figure 1. Raw data chromatogram for the polymethacrylate sample.

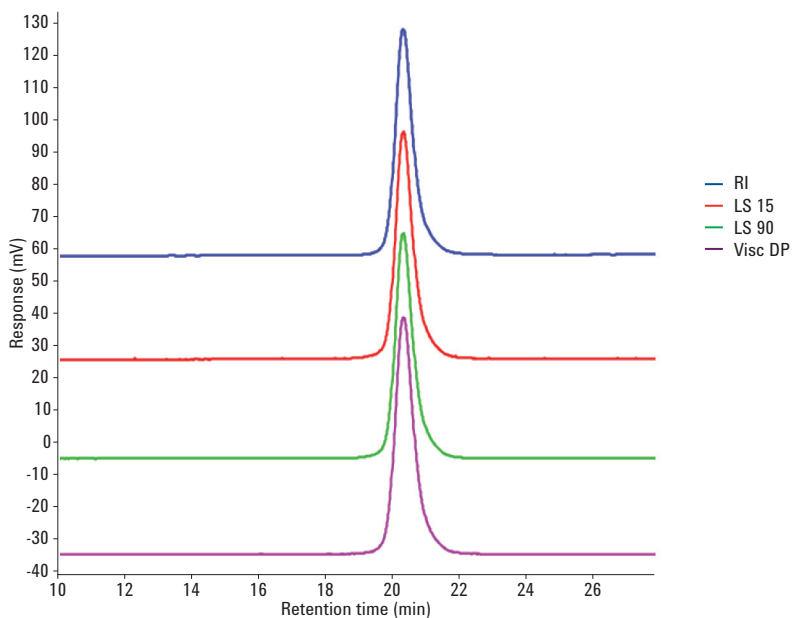


Figure 2. Chromatogram showing normalized responses for all detectors highlighting low dispersion and excellent S/N.

Conventional GPC

In conventional GPC, the concentration detector response alone is used, usually a refractive index detector. A calibration curve is generated using narrow calibrants, in which the apex of the peak, M_p , is related to the retention time, as in Figure 3. Polystyrene EasiVials, PS-H vials were used in this study which with the Mixed-bed column technology creates a first order calibration curve.

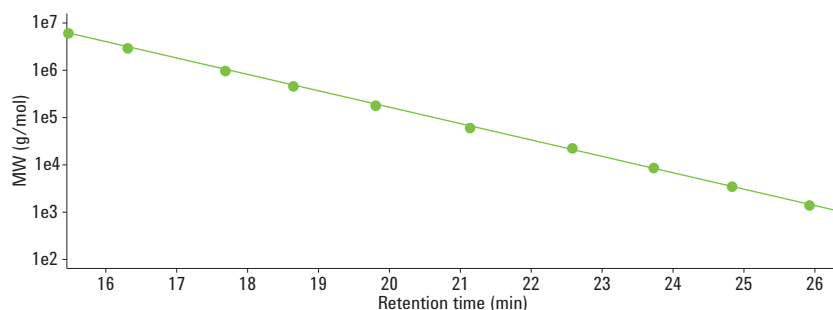


Figure 3. Conventional calibration curve.

GPC/SEC viscometry

A viscometer measures the solution viscosity of materials as they elute from the column, this property is used to determine molecular weights using the Universal Calibration. This is an approach that permits the calculation of accurate molecular weights regardless of the chemistry of the standards employed in the calibration.

The same polystyrene EasiVial-H standards were used to generate a Universal column calibration (Figure 4).

GPC light scattering

By measuring the Raleigh scattering, molecular weights are determined from first principles negating the requirement for a column calibration. Importantly, by simultaneously measuring at more than one angle, angular dependence is overcome. For further information on multi-detector GPC, refer to the Agilent primer².

Table 3. Conventional calibration data.

Retention time (min)	MW	log MW	Percent error	Residual
15.50	6,035,000	6.78	1.77	0.008
16.32	3,053,000	6.48	-0.95	-0.004
17.70	990,500	6.00	-2.76	-0.012
18.65	473,600	5.68	-0.42	-0.002
19.83	184,900	5.27	0.30	0.001
21.17	60,450	4.78	-4.83	-0.020
22.60	21,810	4.34	7.82	0.035
23.73	8,450	3.93	4.01	0.018
24.83	3,370	3.53	0.26	0.001
25.97	1,280	3.11	-5.94	-0.025

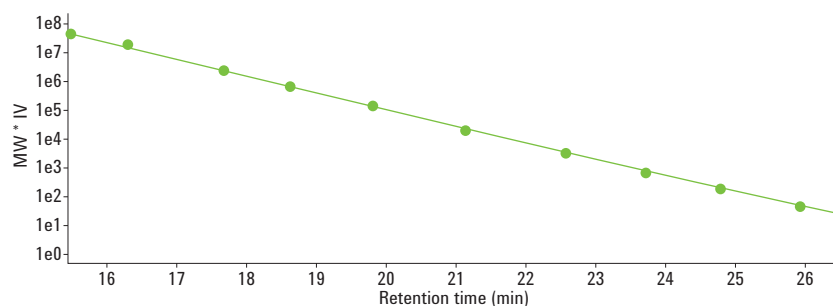


Figure 4. Universal calibration curve.

Table 4. Universal calibration data.

Retention time (min)	MW	IV	log(MW × IV)	Percent error	Residual
15.50	6,035,000	6.252	7.58	-2.90	-0.012
16.32	3,053,000	4.655	7.15	5.60	0.025
17.70	990,500	2.033	6.30	-5.56	-0.023
18.65	473,600	1.279	5.78	2.84	0.013
19.83	184,900	0.654	5.08	2.51	0.011
21.17	60,450	0.299	4.26	-7.14	-0.030
22.60	21,810	0.140	3.49	5.87	0.026
23.73	8,450	0.076	2.81	-3.46	-0.015
24.83	3,370	0.051	2.24	2.28	0.010
25.97	1,280	0.034	1.64	-0.99	-0.004

Molecular weight comparison

The samples were analyzed using three different calculation methods. The first applies a conventional column calibration which was generated using narrow distribution polystyrene standards. The second utilizes a viscometer detector to generate a “Universal calibration” from the same set of polymer standards. The third method uses a light scattering detector, which does not require a column calibration. The results calculated using the three different methods are, as expected, quite different as can be seen in Table 5. The main reason being that polymers of differing chemistry and topology have different sizes when in solution. Because the polystyrene calibrant is structurally different from the polymer being characterized, for a given molecular weight the two polymers have a different size in solution. As the GPC/SEC mechanism separates by hydrodynamic volume, not molecular weight, the retention time for a given molecular weight of synthetic rubber for example, is quite different than for a polystyrene standard of the same molecular weight. The effect can be quite dramatic, for example, synthetic rubber in THF forms a much larger coil in solution to that of the equivalent molecular weight polystyrene, resulting in calculated molecular weights of almost twice the actual true value.

By introducing a viscometer and using the intrinsic viscosity to determine the universal calibration curve, chemical and structural differences between the polystyrene standard and the sample of interest are compensated for. The calculated molecular weights are no longer relative, providing much more accurate results. When using light scattering, the detector response is directly proportional to the molecular weight, and is considered to give an absolute, accurate, measurement of molecular weight, without the need to calibrate the columns.

Table 5. Molecular weight results from the different analysis methods.

Sample	Conventional calibration		Universal calibration		Light scattering	
	Mn	Mw	Mn	Mw	Mn	Mw
Polyacrylate comb	105,800	234,700	57,600	142,800	61,300	132,300
Synthetic rubber	251,000	604,800	148,300	373,600	154,700	382,900
Polymethacrylate homopolymer	53,100	131,500	67,100	170,500	74,000	188,900

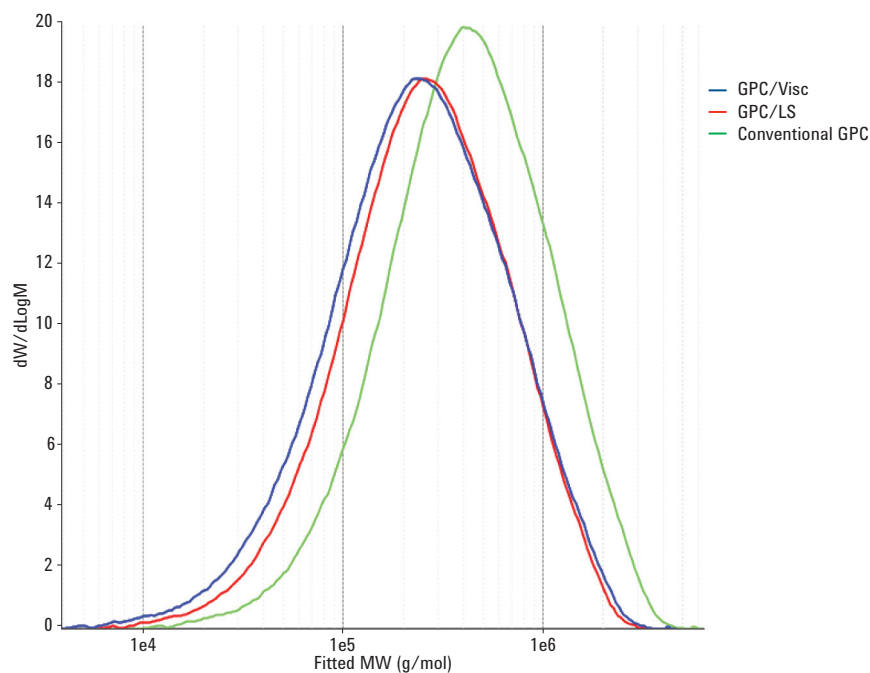


Figure 5. Overlaid molecular weight distribution plots for the synthetic rubber.

It is not only chemistry that has an effect on the hydrodynamic size, for example certain types of polymer have extended side chains (also known as branching). One such example being a polyacrylate graft polymer, where a large relative difference is observed between molecular weights calculated using conventional GPC and using light scattering and/or viscometry. The Agilent GPC Software contains powerful sub routines to be able to identify and quantify these branched polymer structures³. The results for a polymethacrylate homopolymer show less of a difference in molecular weight between the different calculation methods. This is because, when dissolved in THF, it has only a slightly smaller hydrodynamic volume than that of polystyrene standard of the same molecular weight.

Results and Discussion

Advanced detectors increase the power of the experiment and allow determination of other useful parameters of the polymer in solution which conventional GPC cannot provide.

Molecular size

The molecular size can be determined by using advanced detection. The viscometer measures the intrinsic viscosity of a polymer, which is directly related to the hydrodynamic radius, R_h . Light scattering directly determines a different size measurement, the radius of gyration, R_g . This measurement requires that data from two angles (15 and 90 degrees) is

collected simultaneously and the polymer is large enough to observe an angular dependence (above approximately 10 nm). This difference between R_h and R_g can be observed by comparing the conformation plots for a sample of synthetic rubber, shown in Figure 6. The size measurement determined using light scattering begins at approximately 200,000 g/mol, which is the molecular weight at which angular dependence is first observed for this sample. However, as the molecular distribution extends down to lower molecular weights the viscometer has a larger range for this particular sample, since the detector response simply relies on a change in solution viscosity.

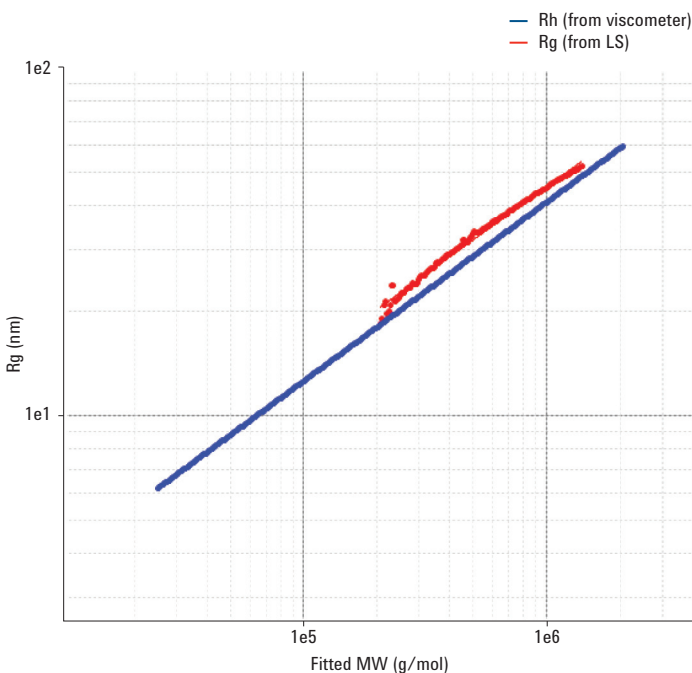


Figure 6. Conformation plot for synthetic rubber.

Molecular shape

The slope of the conformation plot provides information on the shape of the polymer in solution. When using a viscometer a similar plot, the Mark-Houwink plot (Figure 7) is generated by plotting the intrinsic viscosity against the molecular weight.

This plot illustrates the differences in conformation of the different types of polymer. The polyacrylate has an alpha (slope) of 0.59, whereas the synthetic rubber and polymethacrylate have alphas of 0.63 and 0.64 respectively. A value of 0.7 suggests the polymer is behaving like a random coil in a good solvent whereas 0.5 suggests a tightly coiled polymer. The offset is related to the density of the polymer which is quite different for the polymethacrylate, which indicates a much denser coiling in solution compared to the other two polymers.

GPC triple detection

This technique uses all of the available detectors to provide a comprehensive understanding of the polymer through GPC/SEC. The RI detector provides accurate concentration information and polymer profile, the light scattering detector provides an accurate molecular weight and size, and the viscometer provides information on conformation and size across the molecular weight range.

Conclusion

GPC/SEC is a unique, important technique to help understand how polymers will behave during processing and their physical properties under application as a finished product. The Conventional column calibration has limitations which can be addressed by using light scattering and/or viscometry. These advanced detectors also further the ability to detect subtle but significant differences between sets of polymers.

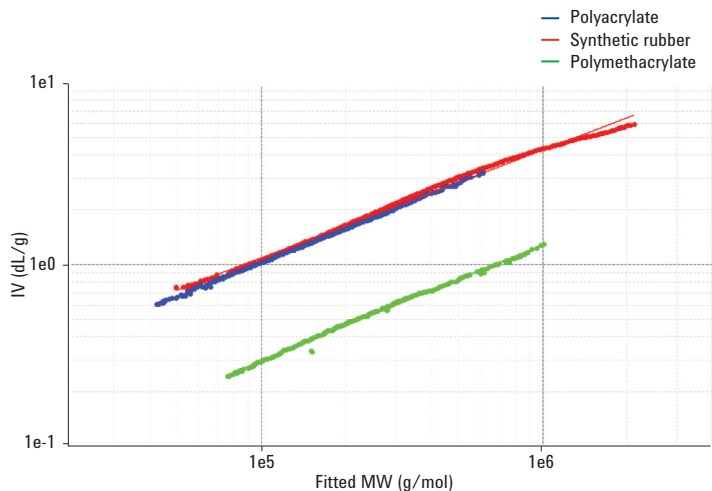


Figure 7. Mark-Houwink plot showing all samples overlaid.

Molecular weight results from GPC/SEC can be quite different depending on the method used in the calculations. Concentration only data, for example just a RI or UV, are relative to the standards used to generate the column calibration and therefore the molecular weight results are often not accurate. The advanced detectors are sensitive to molecular weight and overcome the relative nature of GPC. Through the use of the Universal Calibration, a viscometer provides this by producing molecular weights independent of the calibrants used. The most accurate molecular weight data is determined using a light scattering detector, which responds directly to molecular weight and therefore requires no column calibration.

The advantages of advanced detectors is not limited to just more accurate molecular weights. Molecular sizes can be calculated from both viscometry and Light Scattering detection, each having its own strengths. The light scattering detector directly calculates the size

but a viscometer has a lower operating range. The shape, or conformation of the polymer can also be determined, a crucial parameter to understand how a polymer behaves in solution.

The Agilent 1260 Infinity Multi-Detector GPC/SEC System can have any combination of RI, UV, light scattering and viscometry to expand the GPC/SEC experiment beyond conventional limits. The efficiency of separation is maintained with low dead volume detectors which exhibit excellent signal-to-noise and stable baselines for confidence in analysis.

References

1. "An Introduction to GPC/SEC", Agilent publication, 5990-6969EN.
2. "An Introduction to Multi-Detector GPC/SEC", Agilent publication, 5990-7196EN.
3. "Analysis of Star Polymers Using the Agilent 1260 Infinity Multi-Detector GPC/SEC System", Agilent Application Note 5991-2887EN.

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