focus on
Chromatography

High-Speed, High-Resolution Analysis of Low Molecular Weight Polymers Using the Advanced Polymer Chromatography (APC) System

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Gel permeation chromatography (GPC) is a well-established, informative method for characterising polymers. However, while a great amount of information can be obtained using this technique, there are inherent limitations to this type of analysis. Columns are frequently styrene-divinylbenzene based and require proper conditioning as well as operation under low back pressures to ensure long-term stability. Particles are typically larger (≥5µm) and resolution is often compromised as a result. Smaller particle (<5µm) columns are commercially available and improve the speed of GPC separations, but the speed is limited by their inherently low maximum operating pressures. In addition, the large system volumes of conventional GPC instrumentation require the use of large diameter columns to mitigate the system bandspreading, which can lead to a deterioration in resolution. Waters ACQUITY Advanced Polymer Chromatography (APC) System combines sub 3-µm hybrid particle columns, enhanced system stability, and the capability of accurate flow rates at higher pressures. Additionally, the low overall system dispersion can significantly affect resolution, especially for low molecular weight oligomers. Improved resolution in low molecular weight oligomer separations with shortened runtimes enables rapid monitoring of polymer process development, earlier detection of new polymeric species, and altogether faster commercialisation of new polymer products.

In this application note, separations using the ACQUITY APC System will be compared to conventional GPC separations. Faster analysis, improved resolution, and the beneficial effect on calibration of low molecular weight oligomers using a low-dispersion system with sub 3-µm hybrid particle technology columns will be illustrated. The combination of these technologies allows more robust and precise determination of molecular weight parameters for low molecular weight polymer samples. Earlier identification of even subtle changes in a polymer can significantly speed up the development of polymers for chemical and biomaterial applications.

Results and Discussion

To properly characterise polymers using SEC, it is important to generate a calibration curve using appropriate standards to establish the separation range with the columns being used. With long conventional GPC run times of up to one hour (or more), analyses of standards and samples can be quite time-consuming. Since the data generated for samples will be compared against the calibrated standards to determine molecular weight, the accuracy of the standard results is paramount in order to obtain accurate results for the polymer sample. In addition to the long run times inherent in GPC, the large extra-column volume of conventional GPC systems can result in peak bandspreading, reducing the resolution and thus accuracy of the calibration points. The lower dispersion ACQUITY APC System, delivers less bandspreading and the narrow standard peaks are much sharper, compared to the conventional GPC system, as shown in *Figure 1*. Additionally, combining the low-dispersion of the APC System with robust sub 3-µm APC Column Technology that supports higher flow rate and backpressures also improves resolution for the 1K polystyrene standard, and provides a five-fold reduction in analysis time.

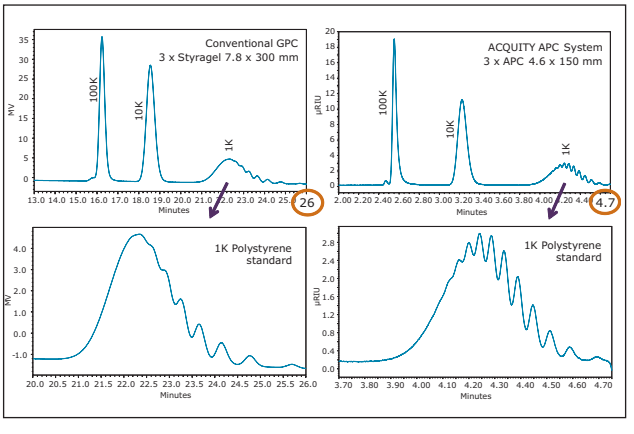

Figure 1. A comparison of run times and resolution for polystyrene standards (Mp: 100K, 10K, and 1K) on a conventional GPC system and the ACQUITY APC System.

Experimental

Alliance GPC System Conditions

Detection: 2414 RI
RI flow cell: 35°C
Mobile phase: THF
Flow rate: 1mL/min
Columns: Styragel 4e, 2 and 0.5, 7.8 x 300 mm (3 in series)
Column temp: 35 °C
Sample diluent: THF
Injection volume: 20µL

ACQUITY APC System Conditions

Detection: ACQUITY RI
RI flow cell: 35°C
Mobile phase: THF
Flow rate: 1mL/min
Columns: ACQUITY APC XT 200 Å and two 45 Å, 4.6 x 150mm (3 columns in series)
Column temp: 35°C
Sample diluent: THF
Injection volume: 20µL

Data management

Empower 3 CDS

Samples

Waters Polystyrene Standards (100K, 10K, and 1000K) at 1mg/mL
Epoxy resin at 2mg/mL

The improved resolution delivered by the APC System results in additional identifiable peak molecular weights for the 1K polystyrene standard. Using molecular weight information that may be determined from the standard supplier or from measurements of the standard using external methods, the additional points can then be added to the calibration curve, shown in *Figure 2*, adding confidence to the sample results calculated relative to this curve.

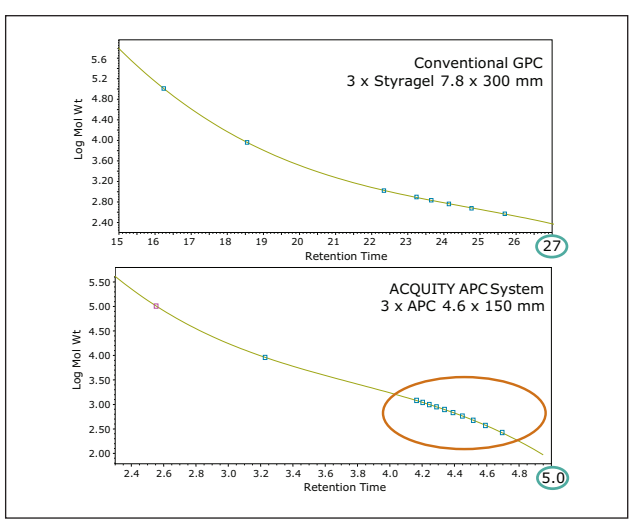

Figure 2. More points on the calibration curve for polystyrene standards (100K, 10K, and 1K) using the ACQUITY APC System, due to improved resolution of the 1K low molecular weight standard.

Typically, a series of standards are run to obtain the points in the calibration curve. With conventional GPC, the equilibration, preparation and analysis of each standard can take hours to days. As a result, the calibration may not be done frequently and results may be based on an 'old' calibration. With the ACQUITY APC System, equilibration is much faster due to the low system dwell volume and the run times are much shorter due to the use of smaller particles at higher flow velocity. Shortened run times allow the equilibration and calibration to be easily completed within one hour. Finally, with the additional resolution, fewer standards may need to be prepared and injected to obtain a robust curve that can be used for calibration.

When a sample is analysed, the greater robustness of the calibration allows for higher confidence in the molecular weight determinations of the low molecular weight oligomers. The analysis of an epoxy resin sample relative to polystyrene calibration standards is shown in *Figure 3*. The result shows resolution of oligomers with a run time of less than five minutes using three ACQUITY APC XT 4.6 x 150 mm Columns in series.

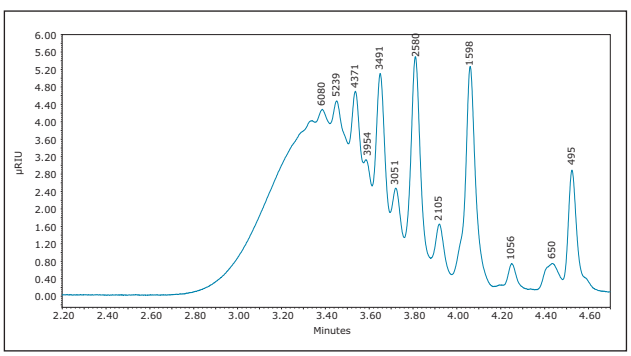

Figure 3. An epoxy resin sample in THF using three ACQUITY APC XT 4.6 x 150mm columns in series with ACQUITY RI detection. Resolution of low molecular weight oligomers (shown by peak molecular weights) was achieved in less than five minutes.

The fast run times with APC can benefit reaction monitoring in process development. Increased resolution can facilitate faster identification of changes to the polymer that may occur in synthesis applications or degradation studies. Earlier detection of process changes by monitoring various molecular weights can provide a better understanding of the polymers and expected properties. This can facilitate the development of new polymers and lead to more rapid commercialisation.

Conclusions

The Advanced Polymer Chromatography System provides significant improvements over conventional GPC systems due to lower dispersion in the system and higher backpressure capabilities that allow the use of smaller, hybrid particles. By combining the APC System with advancements in column technology, improved resolution of low molecular weight oligomers is also realised, compared to conventional GPC. APC performance benefits include more robust calibrations, which are essential in generating accurate measurements for polymer characterisation. The combination of speed and resolution improvements for low molecular weight polymers allows quick, reliable characterisation of polymers in the development process, which can facilitate fast-tracking of new polymers to market.