Full Characterization of Polymers Using the ACQUITY Advanced Polymer Chromatography (APC) System with Multi-Detection

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APPLICATION BENEFITS

The ACQUITY™ APC™ System employs high efficiency separation columns and a low dispersion flow path, resulting in:

- High resolution analysis
- Shorter analysis times
- Reduced solvent consumption
- Reduced sample concentration

WATERS SOLUTIONS

ACQUITY Advanced Polymer Chromatography™ (APC) System

ACQUITY APC XT Columns

KEYWORDS

Size Exclusion Chromatography, SEC, Ultra High-Performance Liquid Chromatography, UHPLC, GPC, polystyrene, PS1478 and PS706a, polyvinylchloride, PVC, polycarbonate

INTRODUCTION

In recent years, new developments in the area of Size Exclusion Chromatography (SEC) have resulted in the introduction of Ultra High-Performance Liquid Chromatography (UHPLC) for polymer applications. Waters™ ACQUITY Advanced Polymer Chromatography (APC) is a breakthrough technology that is able to provide SEC analyses of polymeric materials with enhanced resolution and speed than conventional SEC. The APC System employs Refractive Index (RI) and Ultraviolet PDA (UV) to generate relative molecular weight information versus conventional calibration techniques that use elution volume/retention times.

Similar improvements have been made to advanced GPC/SEC technologies such as viscometers and light scattering detectors to make them compatible with APC. Malvern Panalytical recently introduced a version of the OMNISEC REVEAL advanced detector unit that through a collaboration with Waters has been optimized for integrated use under APC conditions.

In this application note, the analyses of several polymers by ACQUITY APC combined with the OMNISEC REVEAL are presented and discussed.

Figure 1. ACQUITY APC System with OMNISEC REVEAL.

EXPERIMENTAL

Sample description

Two NIST polystyrene (PS) standards, PS1478 and PS706a, a broad polyvinylchloride (PVC) and a broad polycarbonate (PC)

LC conditions

LC system:	ACQUITY APC
Detection:	OMNISEC REVEAL with RI, LS (RALS 90° angle, LALS 7° angle), and IV detectors
Vials:	Waters vials with pre-slit septa
Column	ACQUITY APC XT, 150 mm, 900 Å, 450 Å, and 200 Å, in series
Column temp.:	35 °C
Sample temp.:	35 °C
Injection volume:	20 µL
Flow rate:	1.0 mL/min
Mobile phase:	THF (unstabilized)

Data management

ACQUITY APC operation: Standalone ACQUITY Console Software

OMNISEC operation, data collection, and processing: Malvern Panalytical OMNISEC software

RESULTS AND DISCUSSION

NIST POLYSTYRENE STANDARDS

A chromatogram for the NIST PS1478 polystyrene narrow molecular weight standard is shown in Figure 2. Also shown in Figure 2 is the Log molecular weight, Log intrinsic viscosity (IV), and Log hydrodynamic radius (Rh). Figure 3 shows the chromatogram for the NIST PS706a polystyrene broad molecular weight standard. Also shown in Figure 3 is the Log Mw, Log IV, and Log Rh.

Both chromatograms demonstrated excellent detector response with low sample loadings.

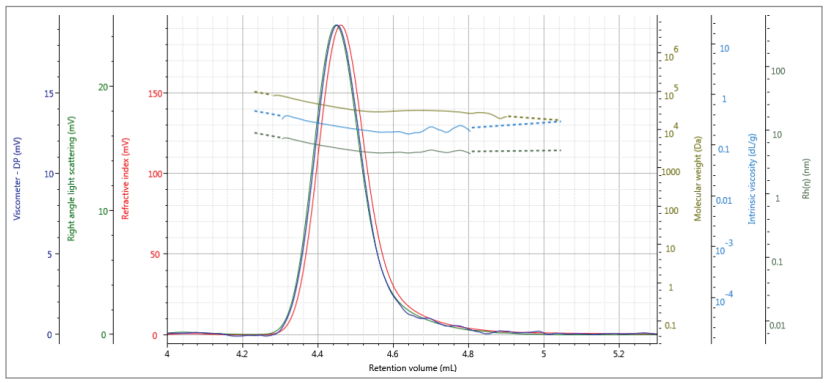

Figure 2. RI, RALS, and DP chromatograms obtained from a PS1478 NIST standard. 10 µL injection volume, 2.5 mg/mL concentration. Log Mw, IV, and Rh are also shown.

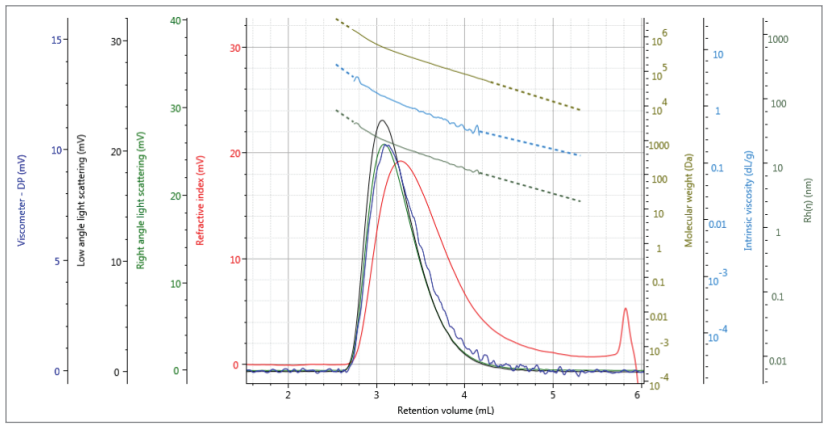

Figure 3. RI, RALS, LALS, and DP chromatograms obtained for a PS706a NIST standard. 5 µL injection volume, 2 mg/mL concentration. Log Mw, IV, and Rh are also shown.

Table 1 shows the quantitative results obtained from the OMNISEC-REVEAL. The absolute molecular weights were calculated directly from Right Angle Light Scattering (RALS) and Low Angle Light Scattering (LALS). In addition, the viscometer provides the ability to calculate the size and structural information about the polymers. The values of molecular weight, dispersity (Mw/Mn), intrinsic viscosity (IV), hydrodynamic radius (Rh), and the Mark-Houwink plot, and log K parameters were all consistent with the values expected. The calculated values of PS706a and PS1478 matched the NIST certified Mw values of 285±0.23K g/mol and 37.4±0.26K g/mol respectively, illustrating excellent precision and accuracy.

Table 1. Molecular weight, size, and structure results for PS1478 and PS706a.

Parameters	Samples	
	PS1478	PS706a
Retention volume (mL)	4.47	3.28
Mn (g/mol)	35,790	11,600
Mw (g/mol)	37,360	286,700
Mz (g/mol)	39,120	479,300
Mw/Mn	1.044	2.57
IVw (dL/g)	0.2322	0.9394
Rhw (nm)	5.144	15.34
Rgw (nm)	N/A	15.42
M-H a	0.7239	0.6534
M-H log K (dL/g)	-3.943	-3.534

POLYCARBONATE AND POLYVINYLCHLORIDE

Samples of polycarbonate (PC) and polyvinylchloride (PVC) were dissolved in the mobile phase and injected into the ACQUITY APC-OMNISEC REVEAL system. Figure 4 shows the chromatogram obtained for PC, and Figure 5 that for PVC. As with the NIST samples, both chromatograms show excellent detector response with low sample loadings.

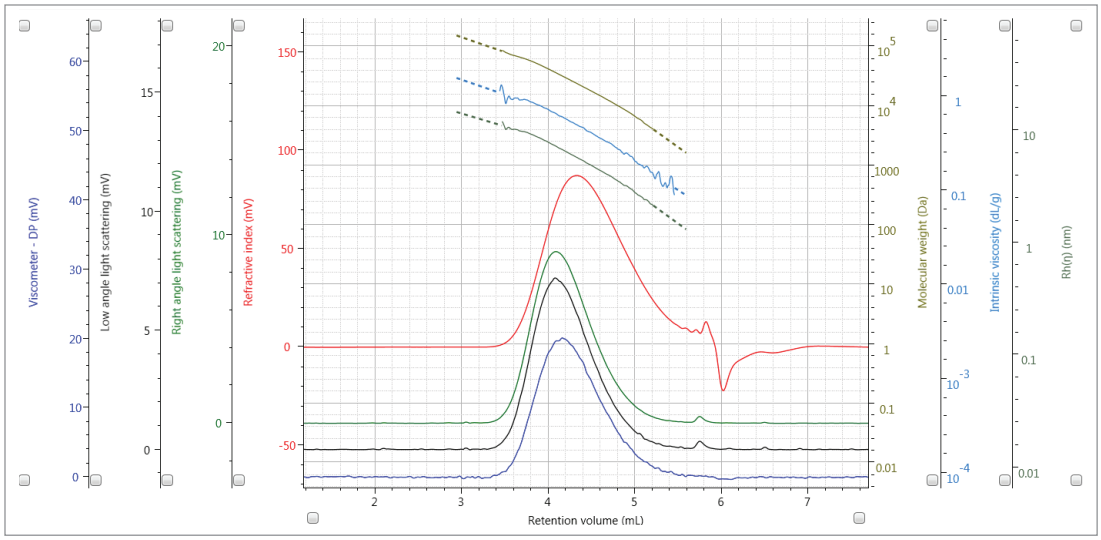

Figure 4. Representative RI, RALS, LALS, and DP chromatograms with molecular weight, IV, and Rh distributions of polycarbonate (PC). 10-µL injection volume, 3 mg/mL concentration. Log Mw, IV, and Rh are also shown.

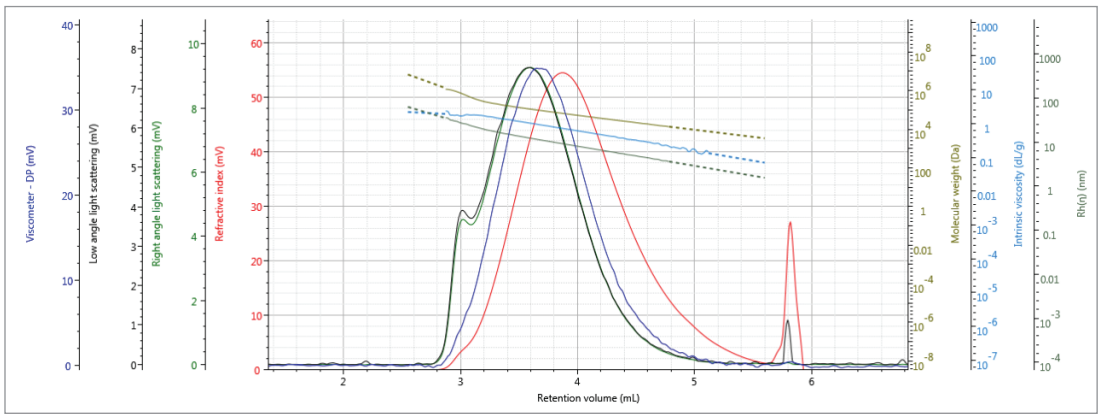

Figure 5. Representative RI, RALS, LALS, and DP chromatograms with molecular weight, IV, and Rh distributions of polyvinylchloride (PVC). 10-µL injection volume, 3 mg/mL concentration. Log Mw, IV, and Rh are also shown.

Table 2 shows the results obtained for PC and PVC by the ACQUITY APC-OMNISEC REVEAL system. The quantitative data obtained align with the expected results obtained previously using traditional GPC.

An overlay of the Mw distributions for duplicate injections of PC, PVC, and PS706a is shown in Figure 6. Figure 6 also demonstrates that the three samples (PC, PVC, and PS) have very different molecular weight distribution plots, with the PS sample shifted toward the high Mw region and PC toward the low Mw region.

The results in Table 1 and 2 show the average values for IV and Rh for the different polymers. These values can be used to make broad structural comparisons between samples, but to get a complete picture of the structure it is necessary to use a Mark-Houwink plot to look at the IV distribution across the entire Mw range.

The Mark-Houwink plot in Figure 7 shows the structural comparison between the three different samples, PC, PVC, and PS706a. This plot shows the Log Mw plotted against the Log IV and allows structural differences between the samples to be clearly identified. PS is lowest on the plot indicating it has a lower IV than PC and PVC at comparable Mws. A lower IV is indicative of a higher molecular density and suggests a more compact configuration. PC has the highest IV value indicating it has the most open configuration.

PVC has a density falling between PC and PS. In addition to this the IV of PVC deviates from a linear behavior, with decreasing IV values in the high Mw region. This indicates the presence of branching at higher molecular weights. It would have not been possible to obtain this insight into the polymer's architecture without the use of a viscometer.

Table 2. Molecular weight, size, and structure results for PC and PVC samples.

Parameters	Samples	
	PC	PVC
Retention Volume (mL)	4.34	3.87
Mn (g/mol)	12,220	39,750
Mw (g/mol)	23,060	84,460
Mz (g/mol)	33,650	268,600
Mw/Mn	1.886	2.124
IVw (dL/g)	0.4545	0.7351
Rhw (nm)	5.272	9.283
Rgw (nm)	N/C	N/C
M-H a	0.667	0.7063
M-H log K (dL/g)	-3.323	-3.566

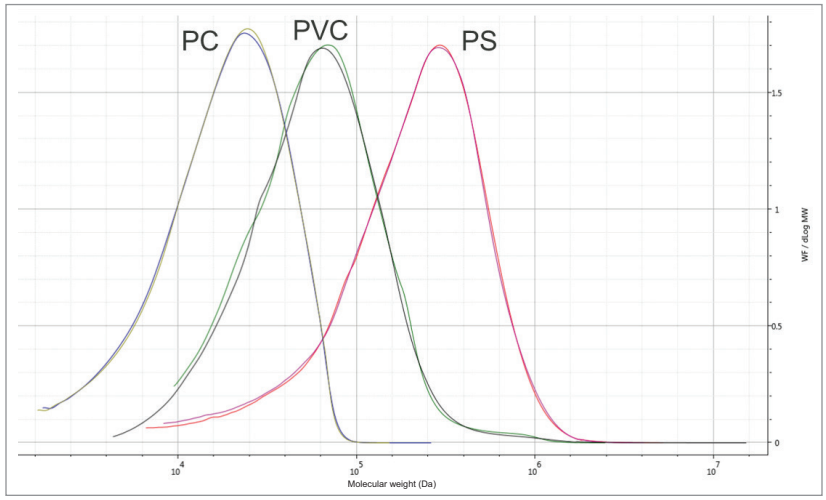

Figure 6. Overlay of duplicate molecular weight distributions of PC, PVC, and PS.

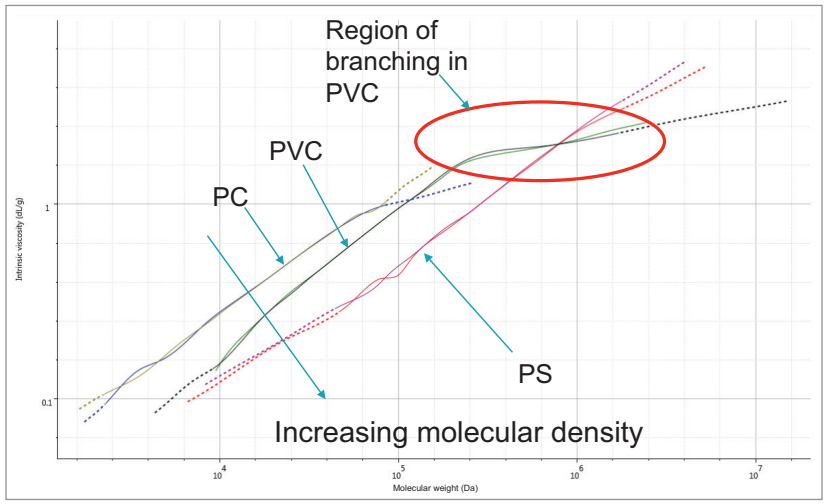

Figure 7. Mark-Houwink plots of PC, PVC, and PS overlaid and compared to show structural differences.

CONCLUSIONS

The combination of the ACQUITY APC System with the OMNISEC REVEAL multi-detector system provides high quality, high-resolution and rapid sample analysis. The presence of the highly sensitive LS and RI detectors and the viscometer in the OMNISEC REVEAL system allowed for the calculation of absolute molecular weight, hydrodynamic radius, and structure of the materials. Two NIST polystyrene standards were correctly characterized using the system as well as PC and PVC samples. A structural comparison was performed using the Mark-Houwink plot with differences between samples observed and regions of branching within PVC identified.

A comparison of the polymer characteristics was performed which would not have been possible using only a conventional calibration system. Accurate molecular weights and structural information can only be attained using a multi-detection platform, such as ACQUITY APC and OMNISEC REVEAL. The unique combination of ACQUITY APC separations with Malvern Panalytical's advanced detectors offers greater resolving power with full sample characterization.

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