Note d'application

A Single System for the Characterization of Molecular Weight Distribution and Additives in Polymers

Karl Lo, Mark Ritchie, Nobutake Sato

Waters Corporation

This is an Application Brief and does not contain a detailed Experimental section.

Abstract

This application brief demonstrates how an ACQUITY Advanced Polymer Chromatography (APC) System combined with the Waters ACQUITY UPLC Refractive Index (RI) Detector and the Waters ACQUITY QDa Mass Detector can accelerate polymer analysis accurately measuring polymer MW distribution and detecting polymer additives simultaneously, with a single system.

Benefits

Combining the benefits of the ACQUITY APC System with the ACQUITY UPLC Refractive Index (RI) Detector and the ACQUITY QDa Mass Detector yields significant laboratory efficiencies.

Introduction

The functionality of any given polymer is dependent on the base polymer structure, the molecule weight (MW) distribution, and the types and proportion of additive used during the polymerization process. Previously, polymer analysis required two chromatography systems; one to study the polymer molecular weight (MW) distribution, and another to determine the additive concentration. Conventional GPC systems typically have low resolution and long run times and have no capability to detect or measure polymer additives. While adding a mass detector to such a system can provide both qualitative and quantitative information with high sensitivity, mass detection is not generally compatible with the normal phase solvents used for MW distribution analysis. Combining the benefits of the ACQUITY APC System with the 2414 Refractive Index (RI) Detector and the ACQUITY QDa Mass Detector yields significant laboratory efficiencies.

In this study, we show how the combining an ACQUITY Advanced Polymer Chromatography (APC) System combined with a ACQUITY UPLC Refractive Index (RI) Detector and ACQUITY QDa Mass Detector can be used to simultaneously measure polymer molecular weight distribution and polymer additive detection.

Results and Discussion

An illustration of the system configuration used in the experiment is represented in Figure 1 where an ACQUITY APC System is paired with an ACQUITY UPLC Refractive Index (RI) Detector and an ACQUITY QDa Mass Detector to enable the desired results. Chromatographic analysis was performed using an isocratic elution of THF at a flow rate of 0.6 mL/min. A splitter was used to split the flow (99:1) to the ACQUITY UPLC RI Detector and ACQUITY QDa Mass Detector respectively to enable the MW measurement and additive analysis simultaneously. Post-split, a makeup flow of 5 mM ammonium formate in MeOH was applied at 0.3 mL/min on the eluent flowing to the ACQUITY QDa Mass Detector, to ensure that the eluent was both compatible with the ACQUITY QDa Mass Detector and promoted ionization of the analytes.

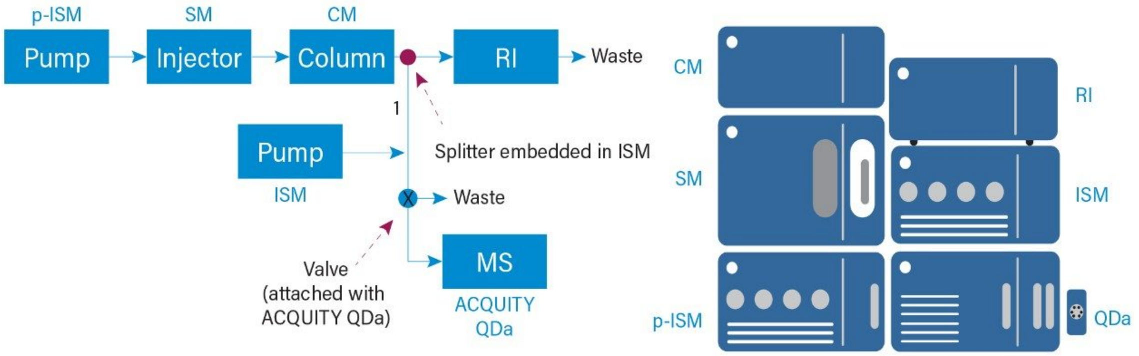


Figure 1. System configuration for the experiment. The valve is switched to waste from 1 to 7 min and then switched to the ACQUITY QDa Detector at 7 to 9 min.

For the first seven minutes of the analysis, a switching valve was used to divert the flow to the ACQUITY QDa Mass Detector to waste while the polymer was monitored by the ACQUITY UPLC RI Detector. After this, the switching valve returned flow to the ACQUITY QDa Mass Detector for additive analysis. The columns used during the analysis included the ACQUITY APC XT - Extended Temperature Column, 450Å, 2.5 µm, 4.6 mm x 150 mm, (20,000–400,000, p/n: 186007010), the ACQUITY APC XT - Extended Temperature Column, 125Å, 2.5 µm, 4.6 mm x 150 mm, (1,000– 30,000, p/n: 186007000) and the ACQUITY APC XT - Extended Temperature Column, 45Å, 1.7 µm, 4.6 mm x 150 mm, (200–5,000, p/n: 186006995). This unique combination prevented larger polymers from entering the ACQUITY QDa Mass Detector, which avoided contamination while the polymer was monitored using the ACQUITY UPLC RI Detector. The MW calibrator, additive concentration calibrator, and the samples were injected subsequently.

The chromatogram of the polymer standard used to characterize the MW distribution of the sample (ACQUITY APC Polystyrene High MW Calibration kit, p/n: 186007541) is illustrated in Figure 2. The mass range of the columns are ranged from 0.2 to 40 KDa, thus the two highest molecular weight (MW) of the standards are excluded as shown in Figure 3. The calibration curve shows good linearity with $R^2 > 0.9996$ by 3rd order of fitting. Compared to a conventional GPC system, an APC system provides higher resolution for lower MW standard (<1K) and has identifiable peaks to provide additional points at the lower MW of the calibration curve.[1] The sample used is 0.1% (w/v) polystyrene 706a (NIST) in THF and the chromatogram of the sample is shown on Figure 4a. The molecular weight distribution curve and the table in Figure 4b summarize the result of the sample. The results are comparable to the theoretical mass of polystyrene 706a and they demonstrate well the higher resolution capabilities offered by Advanced Polymer Chromatography (APC) System compared to conventional GPC.

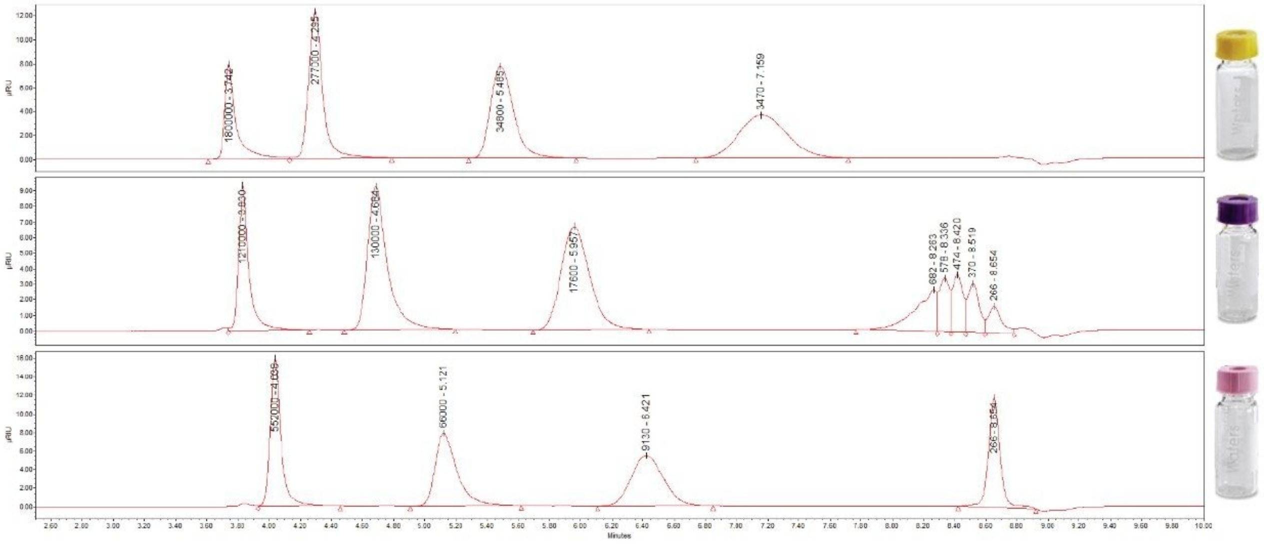


Figure 2. Chromatogram of polymer standards from the ACQUITY UPLC RI Detector.

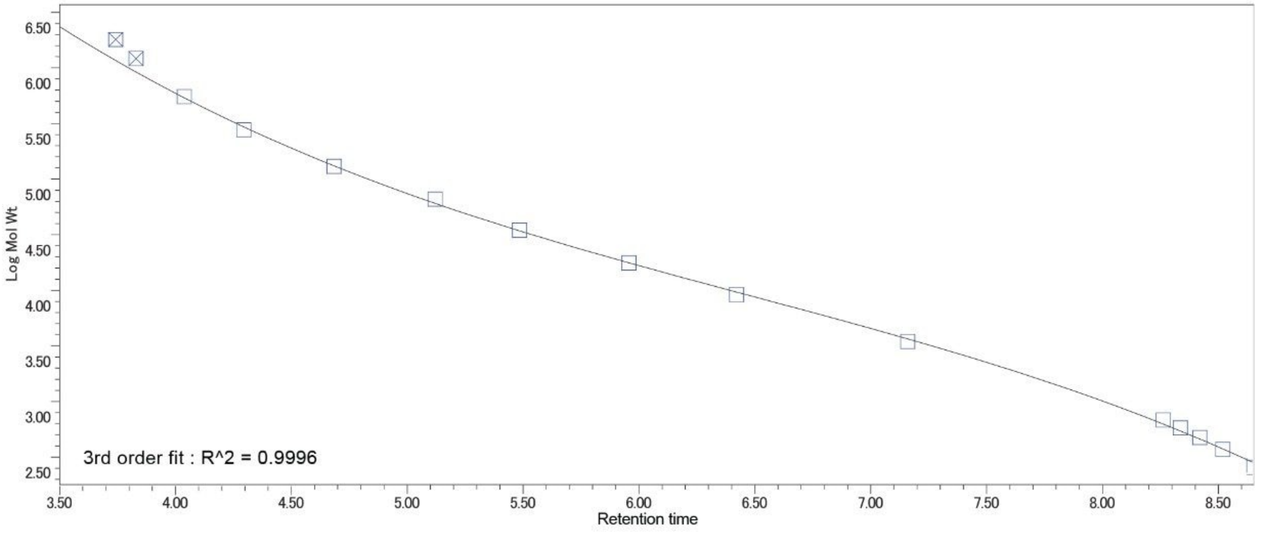
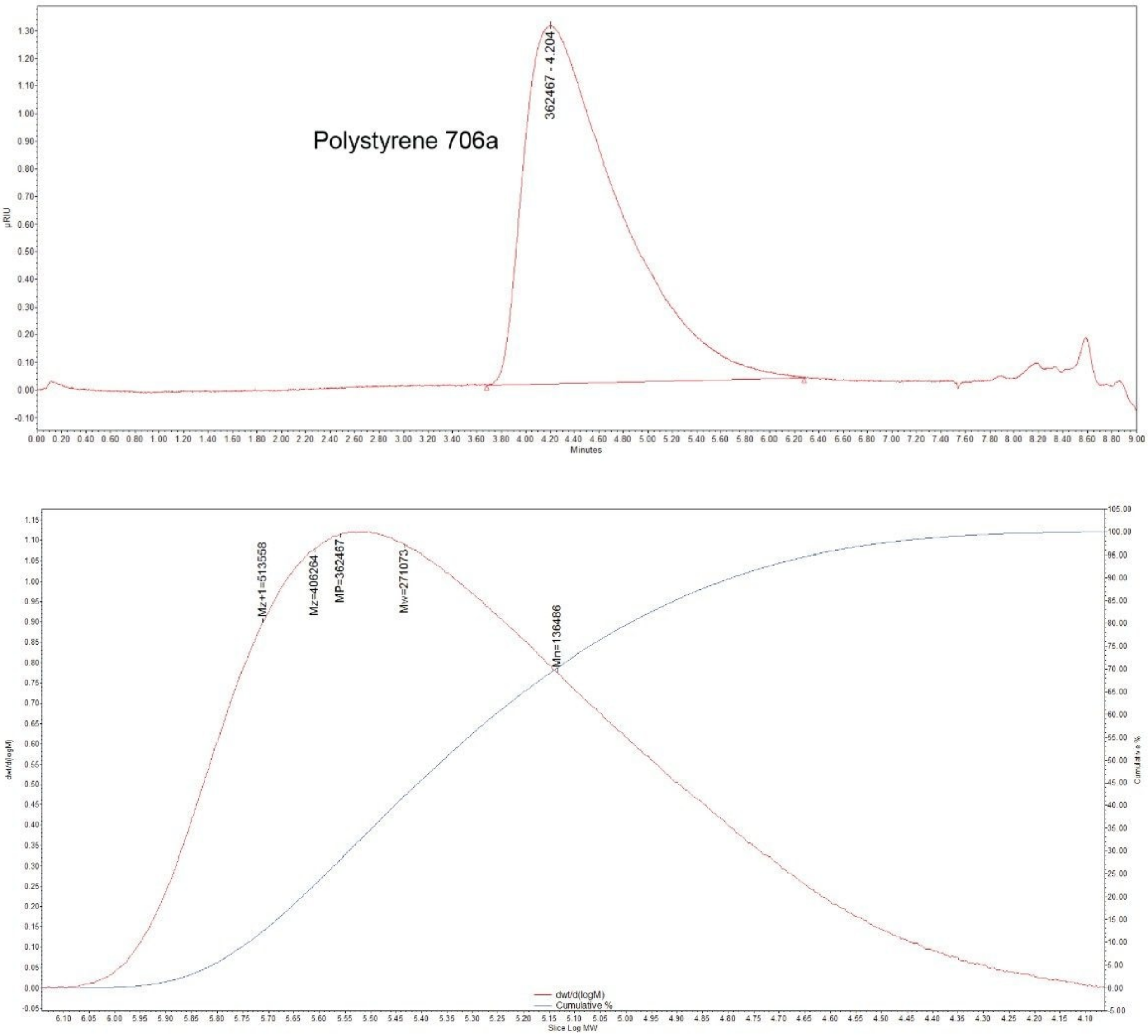


Figure 3. Chromatogram of polymer standards from the ACQUITY UPLC RI Detector.



Mn	Mw	Mp	Mz	Mz+1	Poly Dispersity Index
136,486	271,073	362,467	406,264	513,558	1.986084

Figure 4. The result of the MW analysis of sample; a) RI chromatogram of sample (Polystyrene 706a), and b) molecular weight distribution.

The additional functionality offered by combining the ACQUITY Advanced Polymer Chromatography (APC) System with the ACQUITY UPLC Refractive Index (RI) Detector and the ACQUITY QDa Mass Detector is further highlighted in Figure 5 where simultaneous analysis of the additive concentration in the polymer is shown. Different antioxidants (Irganox and Irgafos) and light stabilizers (Tinuvin) are spiked into the polymer sample and are analyzed alongside the MW of the polymer in a single injection. The ACQUITY QDa Mass Detector can run using either SIR or full scan mode for quantitative and qualitative purposes. The additives of mass 356 to 1177 Da elute after the polystyrene. Figure 6 shows the overlay SIR (M+H) chromatographs of 0.5 ppm additives spiked into 0.1% polystyrene. The additives elute in descending mass and all 8 additives are well distributed across 2 min of retention time. These results effectively demonstrate the advanced resolving power of the ACQUITY APC System on low MW compounds.

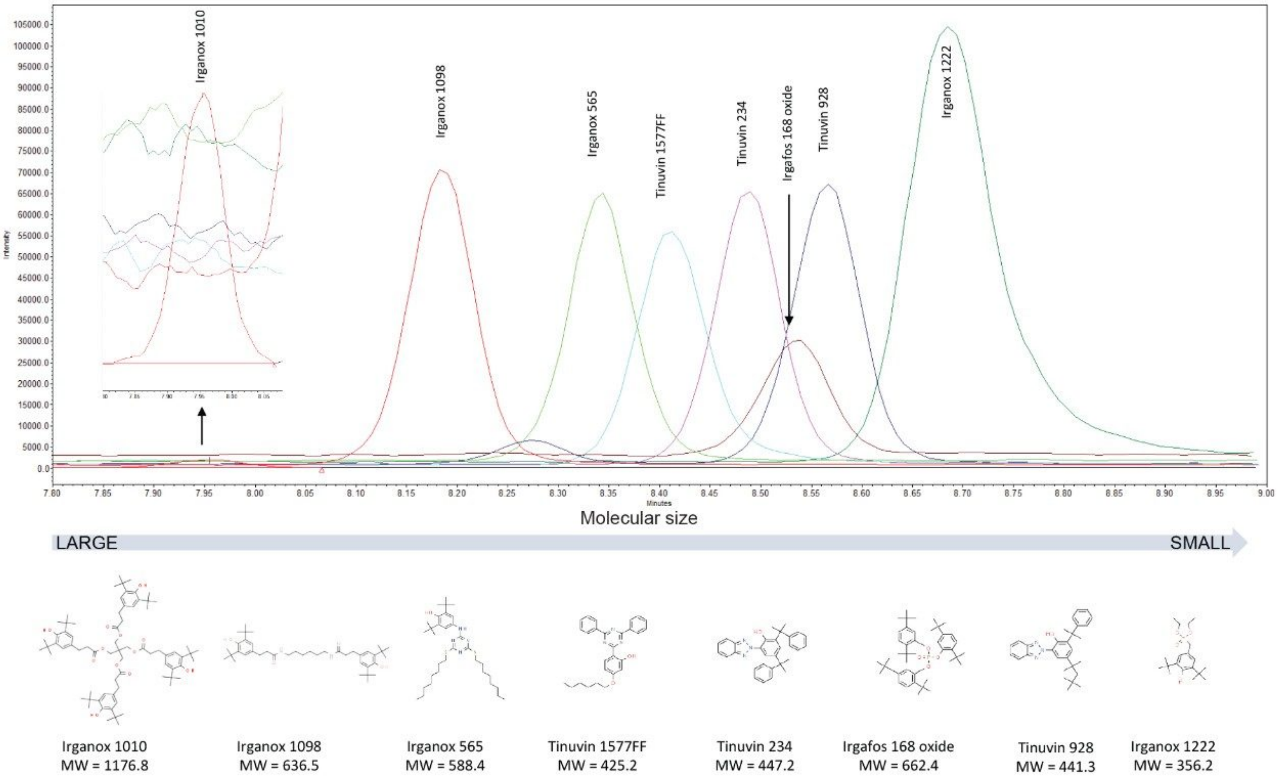
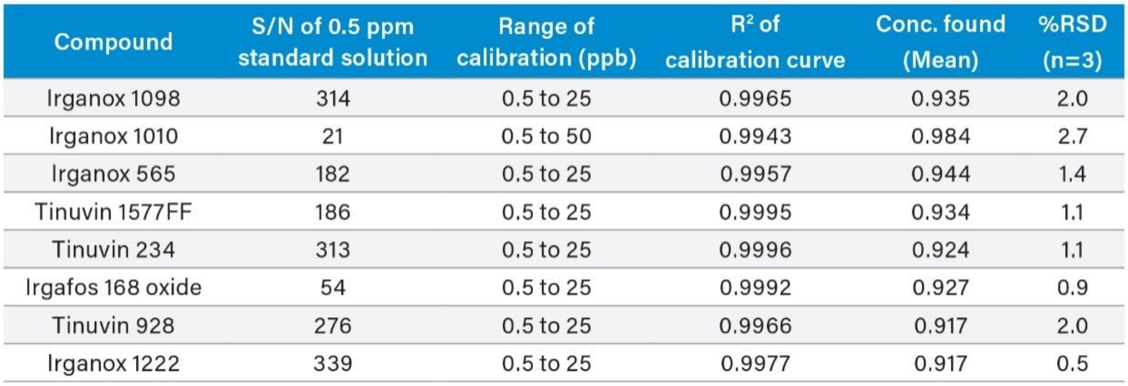


Figure 5. Overlay mass chromatographs of 0.5 ppm additive and their elution order descending according to the mass.

Table 1 summarizes the result of the quantitative analysis of the additives. Except for Irganox 1010, the standards range from 0.5 to 25 ppm with a correlation coefficient >0.993. The signal to noise ratio (S/N) for all the additives is greater than 20. The recovery of the polymer spike at 1 ppm is greater than 90% and % RSD is less than 3% for 3 replicate samples.



Compound	S/N of 0.5 ppm standard solution	Range of calibration (ppb)	R^2 of calibration curve	Conc. found (Mean)	%RSD (n=3)
Irganox 1098	314	0.5 to 25	0.9965	0.935	2.0
Irganox 1010	21	0.5 to 50	0.9943	0.984	2.7
Irganox 565	182	0.5 to 25	0.9957	0.944	1.4
Tinuvin 1577FF	186	0.5 to 25	0.9995	0.934	1.1
Tinuvin 234	313	0.5 to 25	0.9996	0.924	1.1
Irgafos 168 oxide	54	0.5 to 25	0.9992	0.927	0.9
Tinuvin 928	276	0.5 to 25	0.9966	0.917	2.0
Irganox 1222	339	0.5 to 25	0.9977	0.917	0.5

Table 1. Summary of the result from the additive analysis.

These results demonstrate the exceptional sensitivity of the ACQUITY QDa Mass Detector for additive analysis, even at less than 0.1% of additive in the polymer sample.

Conclusion

In conclusion, combining the Advanced Polymer Chromatography System with the ACQUITY UPLC Refractive Index (RI) Detector and the QDa Mass Detector is shown to be effective in accelerating analysis time by accurately and simultaneously measuring the MW and additive concentration of polymers in 9 minutes. Addition of the makeup pump and splitter were proven to provide effective split flow to both the ACQUITY UPLC Refractive Index (RI) Detector for measurement of polymer MW and to the ACQUITY QDa Mass Detector with compatible solvent. The ACQUITY APC System equipped with the advanced column technology is critical in providing higher resolving power on low MW compounds compared to conventional GPC systems. The ACQUITY QDa Mass Detector provides qualitative and quantitative information on the additives. An extra reverse phase analytical HPLC system for additive analysis is not required.

References

1. High-Speed, High-Resolution Analysis of Low Molecular Weight Polymers Using the Advanced Polymer Chromatography (APC) System. Waters Corp. U.S.A., 2013. https://www.waters.com/webassets/cms/library/docs/720004630en.pdf.

Featured Products

ACQUITY Advanced Polymer Chromatography System <https://www.waters.com/134724426>

ACQUITY QDa Mass Detector <https://www.waters.com/134761404>

ACQUITY UPLC Refractive Index Detector <https://www.waters.com/134726507>

720006818, April 2020