

SIMULTANEOUS CHARACTERIZATION OF MOLECULAR WEIGHT DISTRIBUTION AND MASS SPECTRUM ANALYSIS OF ADDITIVES IN POLYMERS IN UNDER 9-MINUTES

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INTRODUCTION

Abstract

This application demonstrates how an ultra-high performance size exclusion chromatograph (UHPSEC) coupled to a combination of refractive index (RI) and single quadrupole mass spectrometry (MS) detections can accelerate polymer analysis by accurately measuring polymer molecular weight (MW) distribution and detecting polymer additives simultaneously with a single system.

Benefits

Combining the benefits of the UHPSEC with the RI and the MS yields significant laboratory efficiencies and confidence in results.

Introduction

The functionality of any given polymer is dependent on the base polymer structure, the MW distribution, and the types and amount of additive used during the polymerization process. Previously, polymer analysis required two chromatography systems; one to study the polymer MW distribution, and another to determine the additive concentration. Conventional SEC systems typically deliver low resolution and long run times and have no capability to detect or quantify 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 UHPSEC with the RI and the MS yields significant laboratory efficiencies.

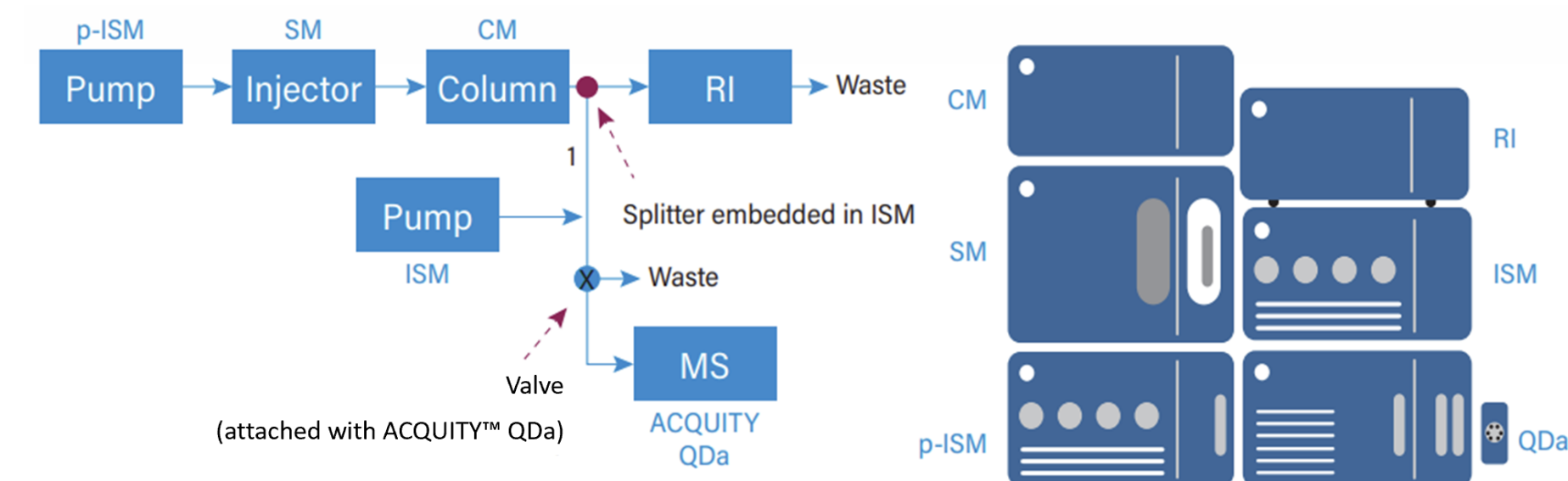


Figure 1. System configuration for the experiment: Column Manager (CM), Sample Manager (SM), polymer Isocratic Solvent Manager (p-ISM). The valve is switched to waste from 1 to 7 min and then switched to the MS detector at 7 to 9 min.

Goal

This analytical study demonstrates the advantages offered by combining a UHPSEC with the RI and the MS can be used to simultaneously measure polymer molecular weight distribution and polymer additive detection.

METHODS

An illustration of the system configuration used in the experiment is represented in Figure 1, where a UHPSEC (Waters ACQUITY™ Advanced Polymer Chromatography™ (APC) system) is coupled to an RI and single quad mass detector (ACQUITY QDa™) modified with hexane/THF kit to enable the desired results. Chromatographic analysis was performed using an isocratic elution of THF and 0.6 mL/min. A splitter was used to split the flow (99:1) to the RI and QDa respectively enabling the molecular weight measurement and additive analysis simultaneously. Post-split, a makeup flow of 5 mM ammonium formate in methanol (MeOH) was applied at 0.3 mL/min on the eluent flowing to the QDa ensuring the eluent was both compatible with the mass detector and promoted ionization of the analytes.

For the first seven minutes of the analysis, a switching valve was used to divert the flow of the QDa to waste while the polymer was monitored by the RI. After the first seven minutes, the switching valve returned flow to the QDa for additive analysis.

The unique combination of switching valve procedure and ACQUITY APC™ XT column bank prevented larger polymers from entering the QDa, while the polymer was monitored by the RI. The MW calibrator, additive concentration calibrator, and the samples were injected subsequently.

The polymer standards used to characterize the MW distribution were polystyrene. The mass range of the columns is from 0.2 to 400 KDa. The calibration curve had good linearity with $R^2 > 0.9996$ by 3rd order fit. Compared to a conventional GPC system, an APC system provided higher resolution for lower MW standard (<1K) and had identifiable peaks to provide additional points at the lower MW of the calibration curve.¹

The sample used was 0.1% (w/v) polystyrene 706a (NIST) in THF and the chromatogram of the sample is shown on Figure 2a. The MW distribution curve and the table in Figure 2b summarizes the result of the sample. The results are comparable to the theoretical mass of polystyrene 706a and they demonstrate shorter run time capabilities offered by the APC system compared to conventional SEC.

Different antioxidants (Irganox® and Irgafos®) and light stabilizers (Tinuvin®) were spiked into the polymer sample and analyzed alongside the MW of the polymer in a single injection. The QDa can run in two acquisition modes, specifically single ion reaction (SIR) or full scan for quantitative and qualitative purposes. The masses of the additives (356 to 1177 m/z) elute after the polystyrene polymer. Figure 3 shows the overlay SIR $[(M+H)^+]$ chromatographs of 0.5 ppm (ng/ μ L) additives spiked into 0.1% polystyrene. The additives elute in descending mass and all eight additives are well distributed across 2 minutes of retention time. These results effectively demonstrate the advanced resolving power of the APC system on low MW compounds.

Table 1 summarizes the result of the quantitative analysis of the additives. The standards range from 0.5 to 25 ppm with a correlation coefficient >0.994 . 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. These results demonstrate the exceptional sensitivity and reproducibility of the QDa for additive analysis, even at less than 0.1% of additive in the polymer sample.

DISCUSSION AND RESULTS

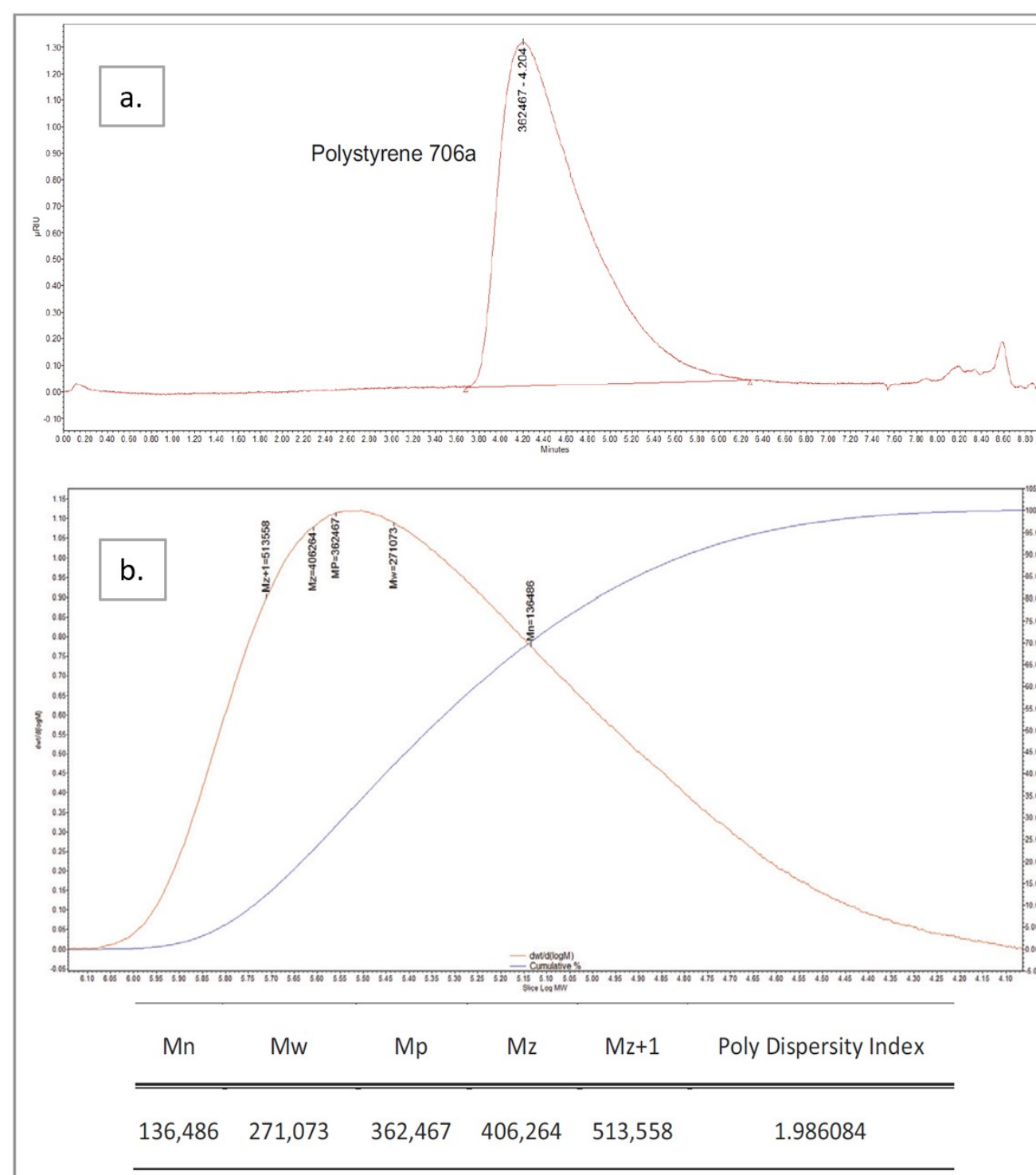


Figure 2. The result of the MW analysis of sample; a) RI chromatogram of sample (Polystyrene 706a), and b) molecular weight distribution.

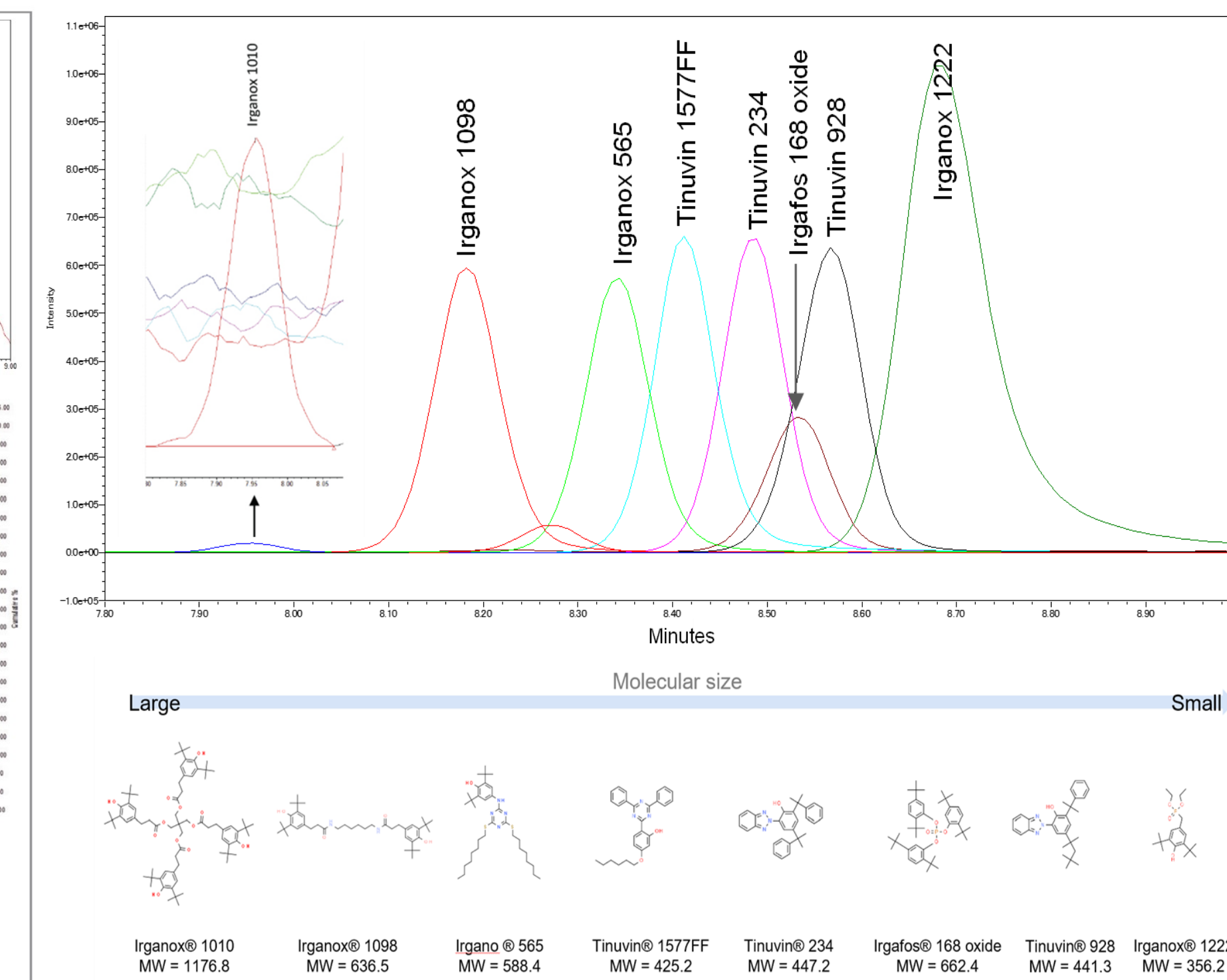


Figure 3. Overlay mass chromatograms of 0.5 ppm additive and their elution order descending according to the mass.

Compound	Range of calibration (ppb)	R ² (cal. curve)	Mean Conc. Found (ppb)	%RSD (n=3)
Irganox® 1098	0.50 to 25	0.9965	0.935	2.0
Irganox® 1010	0.50 to 25	0.9943	0.984	2.7
Irganox® 565	0.50 to 25	0.9957	0.944	1.4
Tinuvin® 1577FF	0.50 to 25	0.9995	0.934	1.1
Tinuvin® 234	0.50 to 25	0.9996	0.924	1.1
Irgafos® 168 oxide	0.50 to 25	0.9992	0.927	0.9
Tinuvin® 928	0.50 to 25	0.9966	0.917	2.0
Irganox® 1222	0.50 to 25	0.9977	0.917	0.5

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

CONCLUSION

- Combining UHPSEC with RI and MS accelerates analysis time by simultaneously measuring MW and additive concentration of polymers in 9-minutes.
- Addition of a makeup pump and splitter effectively split flow to both the RI and mass detector with compatible solvents to each.
- The APC system equipped with advanced column technology ensures high-resolution for low MW compounds compared to conventional SEC systems.
- The QDa allows for qualitative and quantitative information of the additives without the need for a secondary LC system for reverse phase analysis.

References

- 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>.