Simple, Fast and High Throughput Copolymer Analysis Using the EcoSEC® GPC System

Introduction

Synthetic copolymers, composed of at least two components, are commonly synthesized in the polymer industry in order to obtain more desirable properties than those of each individual polymer. Both molecular weight (MW) and structural composition of copolymers are critical to their mechanical, electrical and thermal properties.

Gel permeation chromatography (GPC) is a fundamental characterization tool to obtain MW/MWD (molecular weight distribution) information for homopolymers, which are composed of one component. A calibration curve, constructed from the retention times of a series of monodisperse polymer standard samples with known MWs, is then used to calculate the MW of an unknown sample. The calculated MW is called the relative MW compared to the standard samples, which are usually polystyrene (PS) in GPC.

In the case of copolymers, the chemical heterogeneity adds a layer of complexity. MW and chemical composition may be different even when the samples elute at the same retention time, since the molecules are separated by size instead of MW. Also, at least two concentration-sensitive detectors must be employed to determine the chemical composition distribution, for example refractive index (RI) and ultraviolet (UV) detectors. In this case applicable copolymers must consist of one UV visible component, while the other component does not have a UV chromophore.

In this report, we demonstrate a simple, fast method using an EcoSEC GPC System for the high throughput data analysis of copolymers on a daily basis.

Objective

To demonstrate the use of the EcoSEC GPC System for the analysis of the class of copolymers containing a UV active and a non-UV active component.

Materials and Methods

Instrumentation: EcoSEC GPC System (Tosoh Bioscience)
Data Processing: EcoSEC-WS (Tosoh Bioscience)

Columns - Tosoh Bioscience:
TSKgel® SuperMultiporeHZ-M, 4.6mm ID x 15cm
TSKgel SuperMPHZ-M Guard, 4.6mm ID x 2cm
TSKgel SuperH-RC, 6.0mm ID x 15cm (reference column)

Standards and Materials:
PStQuickMP-M, consisting of A-500, A-5000, F-10, F-80 (Tosoh)
Poly(styrene-co-butadiene) [P(S-B)] (Sigma-Aldrich)
Polystyrene-block-polybutadiene-block-polystyrene [PS-PB-PS] (Sigma-Aldrich)
Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene [PS-P(E-B)-PS1] (Sigma-Aldrich)
Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene [PS-P(E-B)-PS2] (Sigma-Aldrich)

Detection: RI and UV at 254nm
Temperature: 40°C
Flow rate: 0.35mL/min
Sample volume: 10µL
Mobile phase: THF, containing about 0.025% butylated hydroxytoluene as a preservative (Fisher Chemical)

The EcoSEC GPC System was used with both RI and UV detectors. The column set consisted of a TSKgel SuperMPHZ-M guard column in series with two TSKgel SuperMultiporeHZ-M columns. The average molecular weights and wt% styrene composition of all copolymers were reported by the supplier; they are listed in *Table 1*. In these copolymers, the styrene component is UV visible while the ethylene, butylene or butadiene component cannot be detected by UV. Multiple (6) injections were made for each sample.

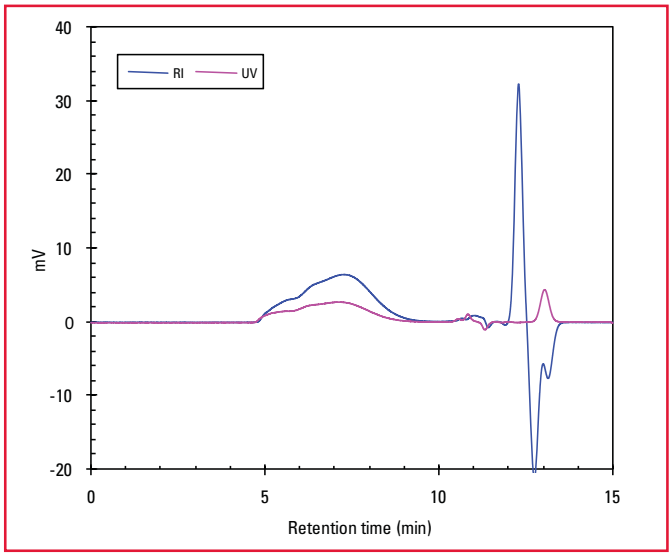
Table 1. Copolymer samples with their Mw and %styrene reported from manufacturer.

Sample code	Average Mw (g/mol)	% styrene
P(S-B)	N/A	45%
PS-PB-PS	140,000	30%
PS-P(E-B)-PS1	118,000	N/A
PS-P(E-B)-PS2	89,000	N/A

Results and Discussion

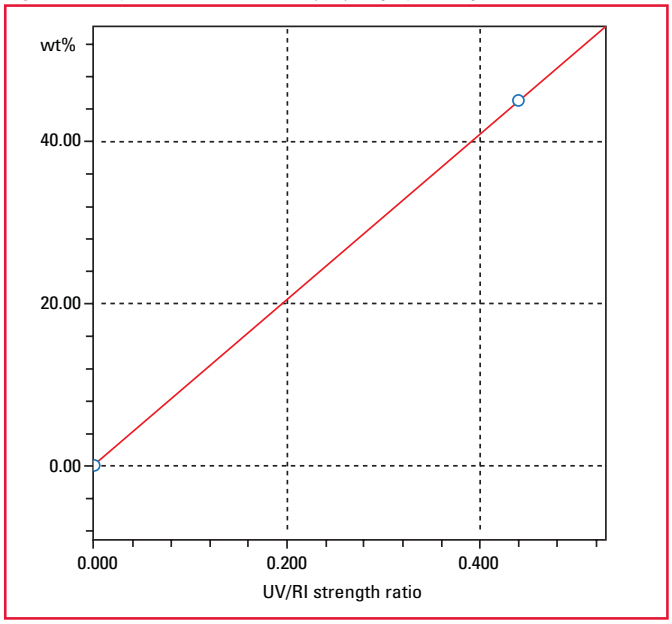
To determine the structural composition of the copolymers at each molecular weight, we made a calibration curve from at least one of the copolymers with a known composition percentage. In this study, we used P(S-B) to generate the calibration curve. From the chromatograms of P(S-B) shown in *Figure 1*, the analyzed data on the EcoSEC WS software provided areas of the peaks in both RI and UV signals.

Figure 1. Chromatograms (RI and UV) of P(S-B) at a concentration of 1mg/mL on TSKgel SuperMultiporeHZ-M columns.



The analyzed result of P(S-B) copolymer was $5.5x10^5$g/mol, with a polydispersity index of 3.17. The calculated area ratio of UV/RI was 0.44. The calibration curve can be generated from two points, from two copolymers with known composition percentages. Also, a one-point calibration curve going through the origin is acceptable. *Figure 2* shows the one-point calibration curve generated from the P(S-B) copolymer.

Figure 2. One-point calibration curve of P(S-B) weight percentage versus UV/RI area ratio.



Since the UV detector precedes the RI detector in the EcoSEC GPC System, an inter-detector lag time between UV and RI detectors is required to shift and overlay two chromatograms. Once this is achieved, the copolymer percent composition can be obtained at each elution time based on this one-point calibration and displayed as the composition curve overlaid on the chromatogram. When combined with the Multi Processing feature in the Peak Editing mode of the EcoSEC WS software, which allows the simultaneous analysis of data from multiple injections, the user now has a simple and fast method to analyze high throughput copolymer data on a daily basis.

Figure 3. Differential distribution and structural composition of three copolymers samples (A) PS-PB-PS, (B) PS-P(E-B)-PS1, (C) PS-P(E-B)-PS2 determined on an EcoSEC GPC System.

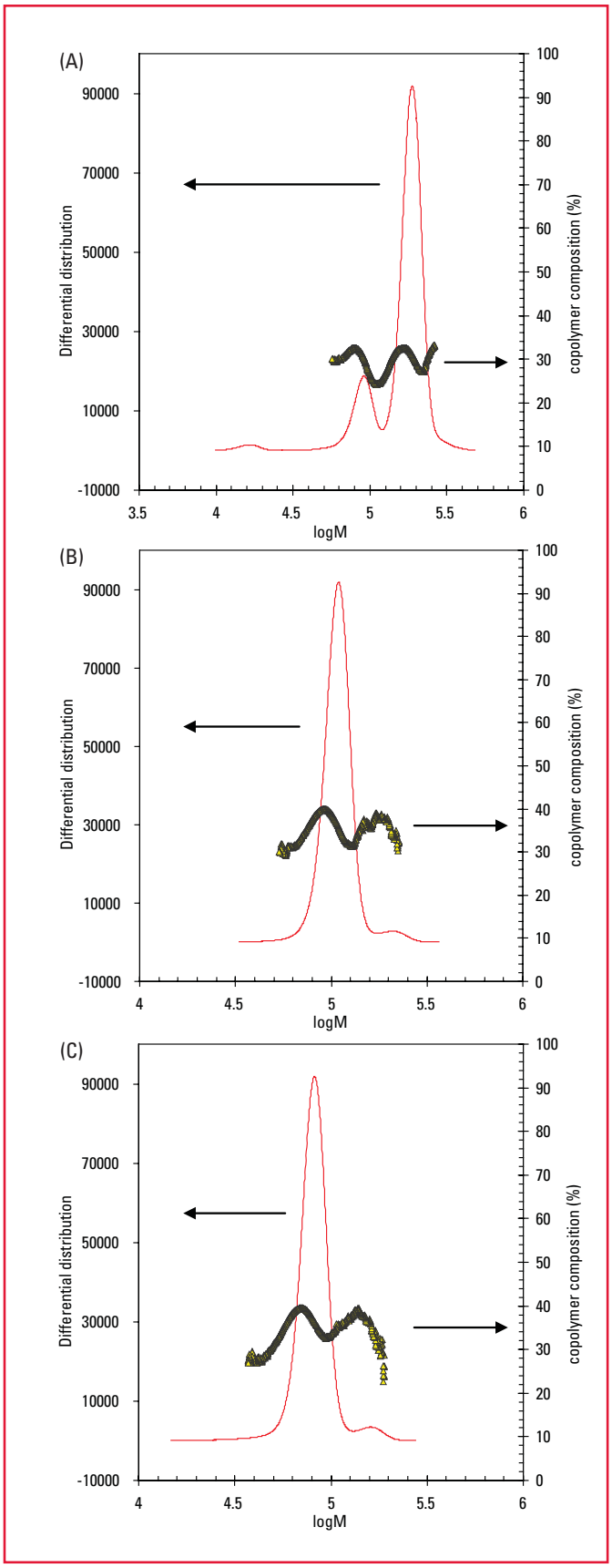


Figure 3 shows the copolymer composition of the other three samples: (A) PS-PB-PS, (B) PS-P(E-B)-PS1, and (C) PS-P(E-B)-PS2. The average composition can be calculated directly from UV/RI ratios, which are (A) 29.7%, (B) 35.2%, (C) 34.3% for these three copolymers respectively. The established result of 29.7% for PS-PB-PS was very close to the manufacturer's reported value of 30 wt%. The structural composition at each MW is illustrated in *Figure 3* and can be reported in a tabulated format in the EcoSEC WS software. The two largest peaks in each chromatogram are within the included volume of the columns.

Conclusions

The EcoSEC GPC System, equipped with both RI and UV detectors, can be used to determine copolymer composition, in which the copolymer contains one UV visible and one non-UV visible component. At least one copolymer of known composition must be available to create a copolymer calibration curve. The structural composition of an unknown copolymer sample can be obtained in the EcoSEC WS software by analyzing that sample's RI and UV chromatograms. The final result is a plot of the molecular weight distribution as a function of the copolymer composition at each molecular weight.

In addition, the data from multiple injections can be analyzed simultaneously using the Multi Processing feature in the EcoSEC WS software. In summary, copolymer analysis using the EcoSEC GPC System can be done in a simple and fast way, which is most beneficial in a high throughput analysis setting.

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