Polymer Characterization using Ambient and High Temperature Gel Permeation Chromatography Systems with a Dual Flow Differential Refractive Index Detector

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Objective

- To demonstrate the characterization of polymers using ambient (up to 50 ºC) and high temperature (up to 220 ºC) gel permeation chromatography (GPC) coupled to a dual flow refractive index (RI) detector.
- To make evident how the dual flow design of the RI detector significantly improves the accuracy and precision of molar mass averages and distributions of polymers determined using peak position calibration involving standards of known molar mass and chemistry.
- To highlight the multiple applications of single detector ambient and high temperature GPC for the analysis of natural and synthetic polymers.

Introduction

- Since its inception the main utility of ambient and high temperature GPC has been to extract quantitative information in the form of molar mass averages and distributions of both synthetic and biopolymers with accuracy and precision.[1]
- Ambient GPC is used for the analysis of polymers at temperatures up to 50 ºC while high temperature GPC is used for analysis of polymers up to 220 ºC.
- Synthetic polymers, as well as most natural polymers, possess a distribution of molar masses.
- The ability to accurately and precisely characterize the molar mass distribution and averages is essential as the shape and the breadth of a polymer's molar mass distribution will dictate the end-use properties of the polymer, such as hardness, tear strength, impact resistances, wear, etc.
- One of the most highly used tools for characterizing the molar mass of polymers is GPC coupled to RI detection.

Introduction

- Traditionally, molar mass averages and distributions of polymers obtained by GPC/RI are determined using peak position calibration involving polymer standards of known molar mass and chemistry.
- The repeatability and reproducibility of the molar mass averages obtained by GPC/RI are directly dependent on the baseline stability of the RI detector.
- Here we show the repeatability, reproducibility, and baseline stability of a dual flow RI detector coupled to both an ambient and high temperature GPC through the determination of molar mass averages via peak position calibration for various synthetic polymers.

Experimental

Instrumentation:

Ambient: EcoSEC® GPC System (HLC-8320) equipped with a dual flow refractive index detector and UV detector.

High Temperature: EcoSEC High Temperature GPC System (HLC-8321GPC/HT) with a dual flow refractive index detector.

Experimental Continued

A dual flow RI detector, such as that in the EcoSEC GPC System, is constructed in such a way that there are two sides:

1. a reference side, consisting of a flowing stream of pure solvent
2. the sample side, containing a flowing stream of analyte in the same solvent as in the reference side

Experimental Continued

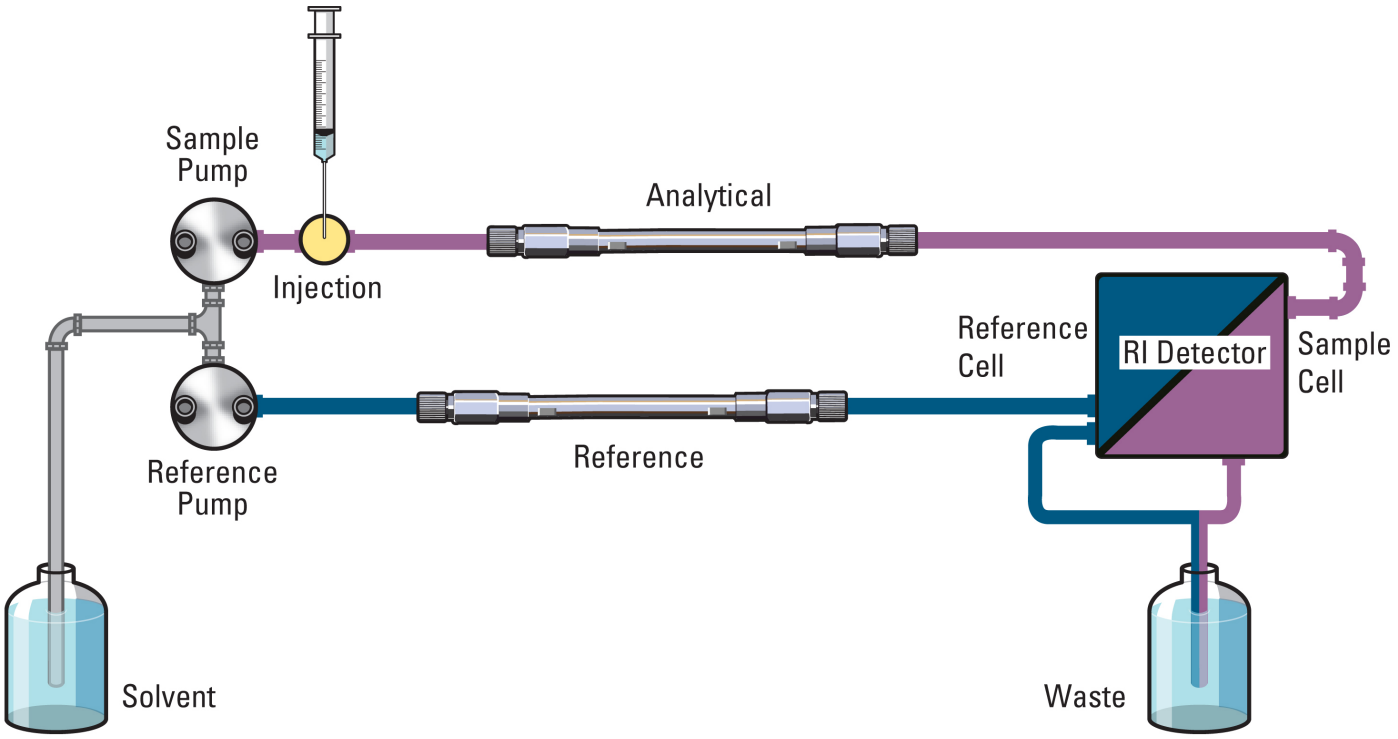


Figure 1: Depiction of the flow paths in the EcoSEC GPC Systems, showing the dual flow RI detector flow cell when the contents of the reference and sample sides have different refractive indices as each other.

Experimental Continued

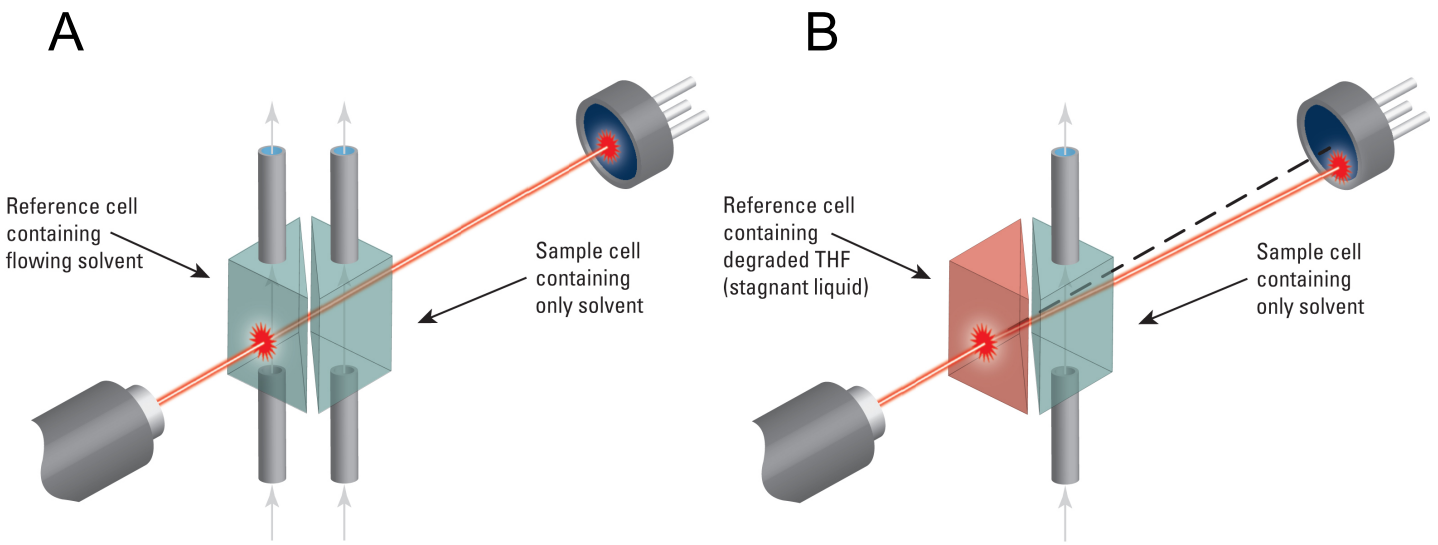


Figure 2: Depiction of a dual flow RI detector flow cell (A) and a conventional RI detector flow cell (B) showing the compensation of the changes in refractive index of the solvent over time.

Ambient Gel Permeation Chromatography

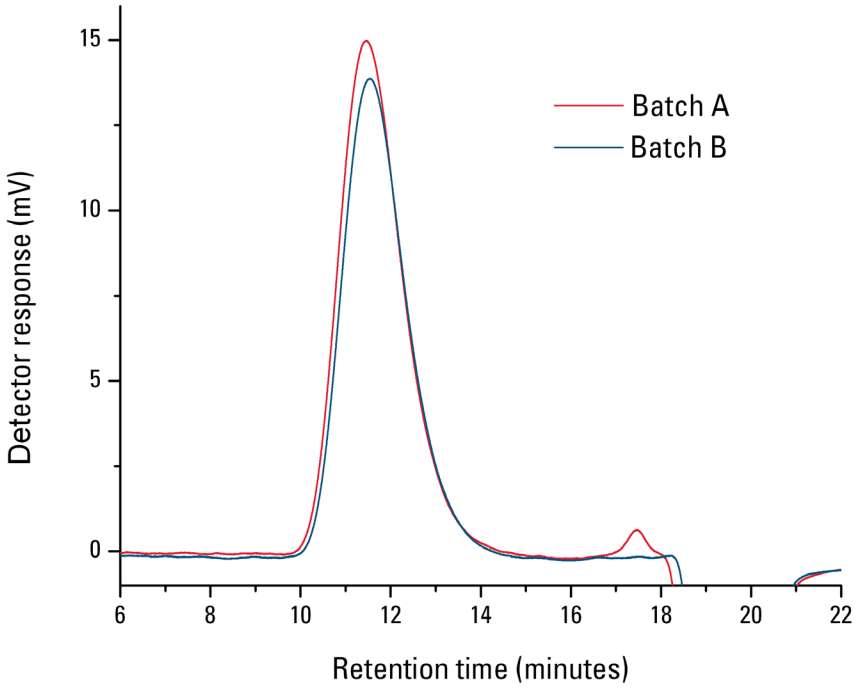
Ambient Gel Permeation Chromatography

- One of the primary focuses of the polymer and plastics industries is the ability to differentiate polymers in a sustainable and time effective manner.
- Most companies involved in the manufacturing and development of end-use products that involve polymers rely heavily on GPC.
- Throughout the polymer and plastics industries, a dual flow RI detector is used to detect differences from batch-to-batch or lot-to-lot of a given polymer, to monitor reaction processes, to determine variations in molar mass averages obtained through different synthesis routes, and to distinguish between polymers with the same chemical compositions but different end-use properties.

Lot-to-Lot Analysis

- GPC is a fast, accurate and reliable method for the comparison of different lots or batches of a given polymer.
- The GPC elution profile must remain consistent among lots in order to obtain the same end-use properties and qualities of the final product.
- An example of the nice pictorial comparison obtained by overlaying the GPC elution profile of various batches of the same product is shown in Figure 3.

Figure 3: GPC elution profiles of two different batches of a PMMA based molding resin



Column:	TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2 + TSKgel SuperHZ2500, 3 µm, 4.6 mm ID × 15 cm × 1
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detectors:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol.:	20 µL
Sample:	PMMA based molding resin

Table 1: Molar mass averages and polydispersity index of two different batches of a PMMA based molding resin

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
Batch A	6.59×10^4 $\pm 0.15 \times 10^4$[b]	1.38×10^5 $\pm 0.02 \times 10^5$	2.24×10^5 $\pm 0.01 \times 10^5$	2.11 $\pm$ 0.02
Batch B	5.90×10^4 $\pm 0.10 \times 10^4$	1.24×10^5 $\pm 0.01 \times 10^5$	2.02×10^5 $\pm 0.03 \times 10^5$	2.11 $\pm$ 0.03

[a] $PDI = M_w/M_n$ [b] Standard deviations from four injections

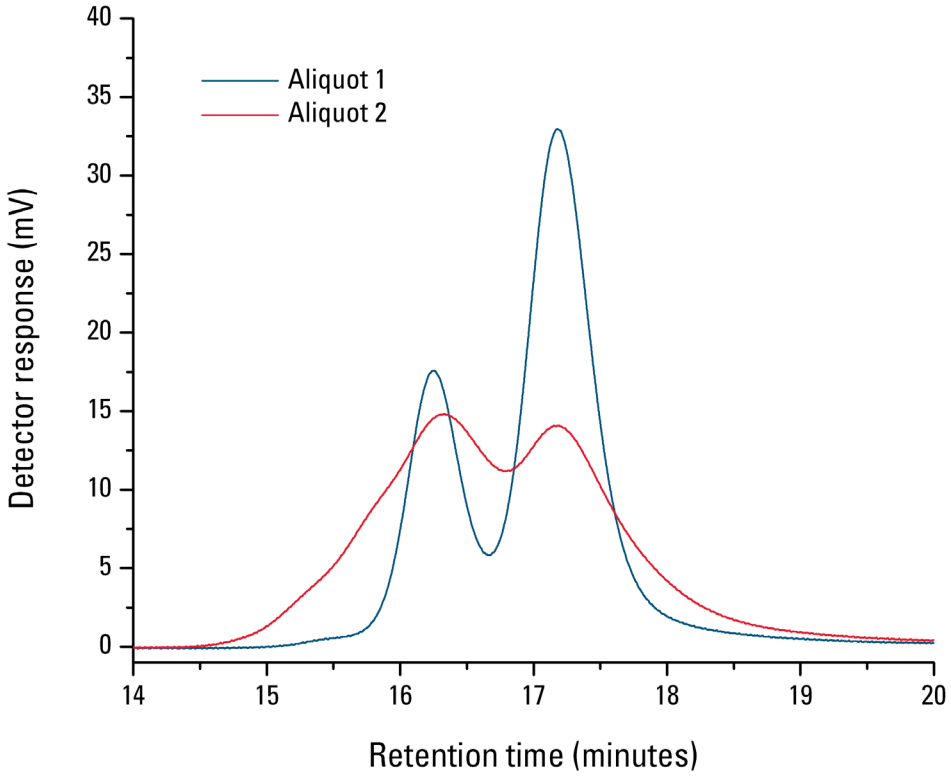
Figure 3 and Table 1: Conclusions

- Figure 3 compares the GPC elution profiles of two different batches of a PMMA based molding resin that can be used in automotive, home appliances, and electronics. Batch A extends further in the larger polymeric size, shorter retention time direction of the GPC elution profile than Batch B, an indication that the two batches differ in polymeric size.
- The slight variation in the GPC elution profile results in an approximately 10% difference in the poly(methyl methacrylate) molar mass averages between the two batches, Table 1. The difference in molar mass averages between Batch A and Batch B may or may not affect the end-use properties of a given polymer as the polydispersity index, *PDI*, remains essential constant amongst the two batches.

Synthesis Monitoring

- Synthesis monitoring using GPC not only allows for separation of polymeric material based on size but also provides information about the reactions, *e.g.,* did the reaction go to completion, is the product uniform in terms of molar mass or size, did a byproduct form, etc.
- An example of using a dual flow RI detector to monitor a reaction process is shown in Figure 4.

Figures 4: GPC elution profile of aliquots of a reaction collected thirty minutes apart



Column:	TSKgel GMHXL, 9 µm, 7.8 mm ID × 30 cm × 1
Mobile phase:	THF
Flow rate:	1.0 mL/min
Detectors:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol.:	100 µL
Sample:	synthetic rubber

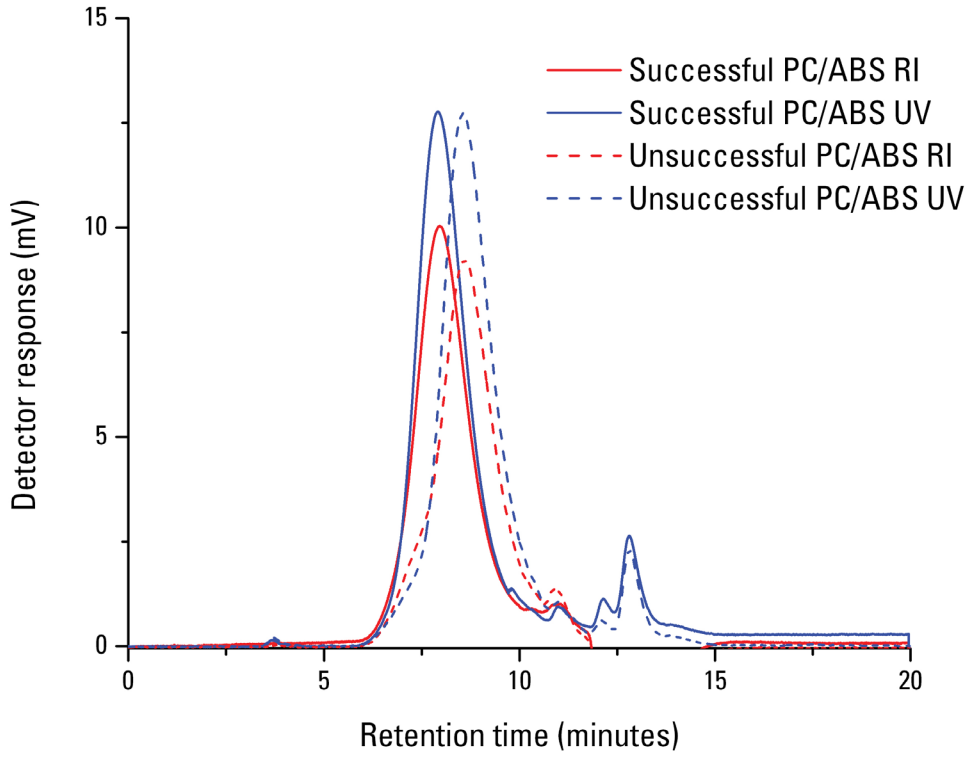
Figures 4: Conclusions

- Figure 4 shows the monitoring of a reaction process by overlaying two aliquots of a reaction collected thirty minutes apart. Each aliquot produces a different GPC elution profile which can be used to determine if the reaction process taking place is correct through a comparison process with known GPC elution profiles for various stages of the reaction.
- In general for this sample as the reaction process progresses the two individual components, indicated by the distinctive bimodal GPC elution profile of aliquot 1, blend to become one component in the final product, indicated by the decrease in the bimodality of aliquot 2.

Quality Control Procedures

- The difference between a successful and unsuccessful polymer based material can be determined by observing the difference in GPC chromatograms and molar mass distributions between the two polymers.
- Figures 5 and 6 show an example of how the EcoSEC GPC System can be used to distinguish between two batches of the same polymer. The sample labeled “successful” is a batch of polymer that performs at or above standards when used in its end-use application while the sample labeled “unsuccessful” has shown to perform below standards in the same end-use application.

Figure 5: GPC Elution Profile of Successful and Unsuccessful Polymers as Monitored by RI and UV



Column:	TSKgel SuperMultiporeHZ-M, 4.6 mm ID × 15 cm × 2
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detectors:	RI (EcoSEC GPC System) UV (EcoSEC GPC System @ 254 nm)
Temperature:	35 °C
Injection vol.:	10 µL
Sample:	polycarbonate based resin

Figure 5: Conclusions

- The shorter retention time of the successful sample indicates that the successful sample is larger in polymeric size than the unsuccessful sample; as the elution order in GPC is that of an “inverse-sieving” technique, large analytes sample a smaller pore volume than smaller analytes resulting in the larger analytes eluting from the column prior to the smaller analytes. Thus, the SEC chromatogram alone provides sufficient indication that the successful and unsuccessful samples are different from one another.

Figure 6: Overlay of Cumulative and Differential Molar Mass Distributions of Successful and Unsuccessful Polymers

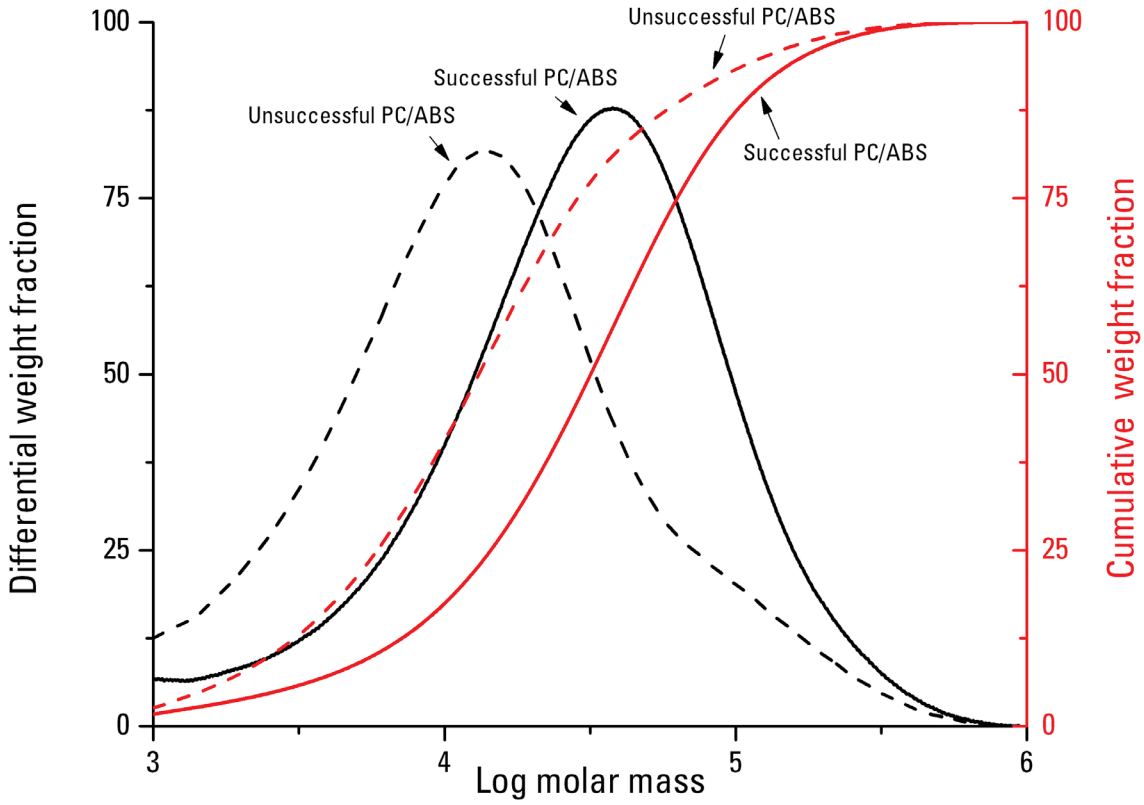


Figure 6: Conclusions

- The successful sample extends significantly further in the high molar mass direction than the unsuccessful sample, while the unsuccessful sample contains a considerably higher quantity of low molar mass species than the successful sample. The molar mass averages and distributions between the two samples differ enough to result in a successful and an unsuccessful end-use product.

High Temperature Gel Permeation Chromatography

High Temperature Gel Permeation Chromatography

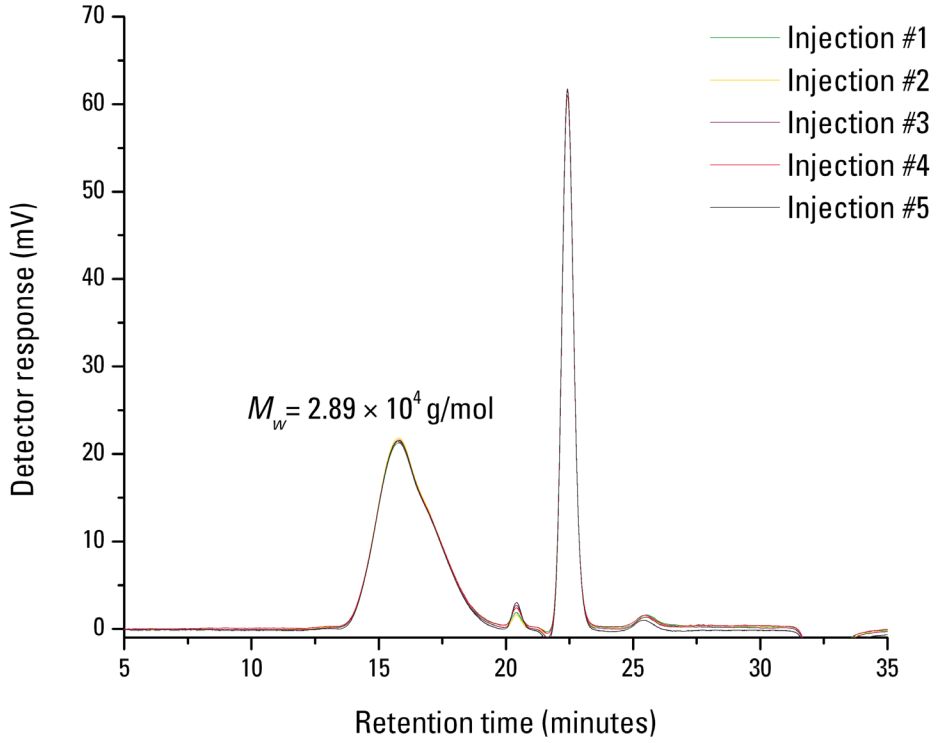
- The analysis of some polymers by GPC/RI require extremely high temperatures due to solvent compatibility and solubility issues.
- High temperature GPC is used for the same types of applications as ambient GPC.
- Peak position calibration is used to determine molar mass averages and distributions, to compare batches or lots of a given polymer, to monitor reaction processes, to determine variations in molar mass averages obtained through different synthesis routes, and to distinguish between polymers with the same chemical compositions but different end-use properties.
- GPC coupled to a dual flow RI detector for the analysis of polymers at elevated temperature has shown to increase the reliability and reproducibility of molar mass averages and distributions.

Polyethylene and Polypropylene

- Due to their ruggedness polymers such as polyethylene and polypropylene can only be analyzed by high temperature GPC.

- The end-use properties of polyethylene and polypropylene are dictated by the molar mass averages and distributions of the polymers. High temperature GPC/RI measurements provide molar mass averages and distributions via peak position calibration with polystyrene standards.

Figure 7: GPC elution profiles and molar mass averages of low density polyethylene (LDPE)

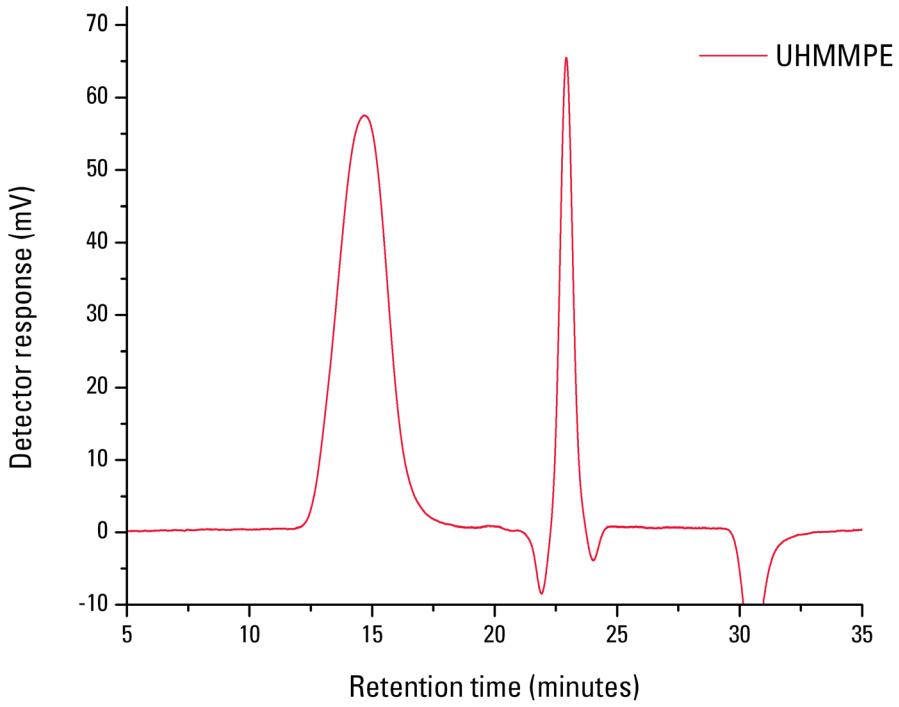


Column:	TSKgel GMHHR-H(S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	ODCB w/ 0.05% BHT
Flow rate:	1.0 mL/min
Detectors:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C
Injection vol.:	300 µL
Sample:	low density polyethylene

Figure 7: Conclusions

- Figure 7 shows the RI GPC elution profile of multiple dissolutions of the same LDPE sample obtained using the EcoSEC High Temperature GPC System. The dual flow RI detector in the EcoSEC High Temperature GPC System results in a high degree of reproducibility of retention times and molar mass determination as the coefficients of variation for the weight-average molar mass, M_w, are well below 1%.

Figure 8: GPC elution profiles and molar mass averages of ultra high molar mass polyethylene (UHMMPE)

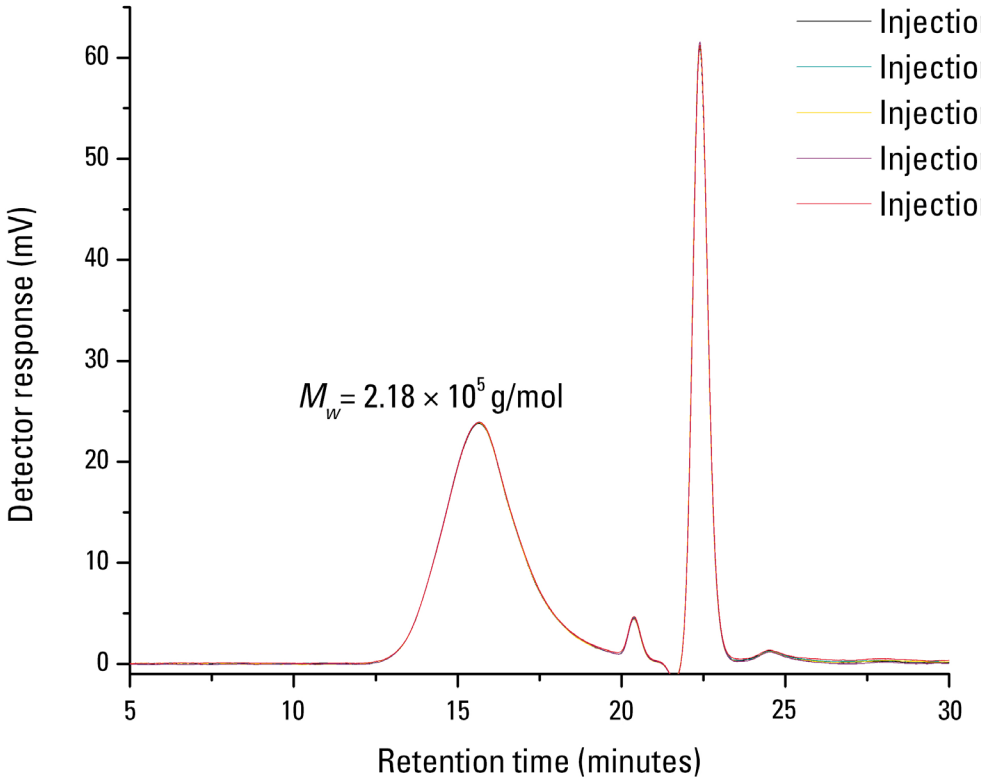


Column:	TSKgel GMHHR-H(S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	1-CN
Flow rate:	1.0 mL/min
Detectors:	RI (EcoSEC High Temperature GPC System)
Temperature:	220 °C
Injection vol.:	300 µL
Sample:	ultra high molar mass polyethylene

Figure 8: Conclusions

- The GPC elution profile obtained using the dual flow RI detector in the EcoSEC High Temperature GPC System for ultra high molar mass polyethylene is shown in Figure 8.

Figure 9: GPC Elution Profile of Polypropylene



Column:	TSKgel GMHHR-H(S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	ODCB w/0.05% BHT
Flow rate:	1.0 mL/min
Detectors:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C
Injection vol.:	300 µL
Sample:	low density polyethylene

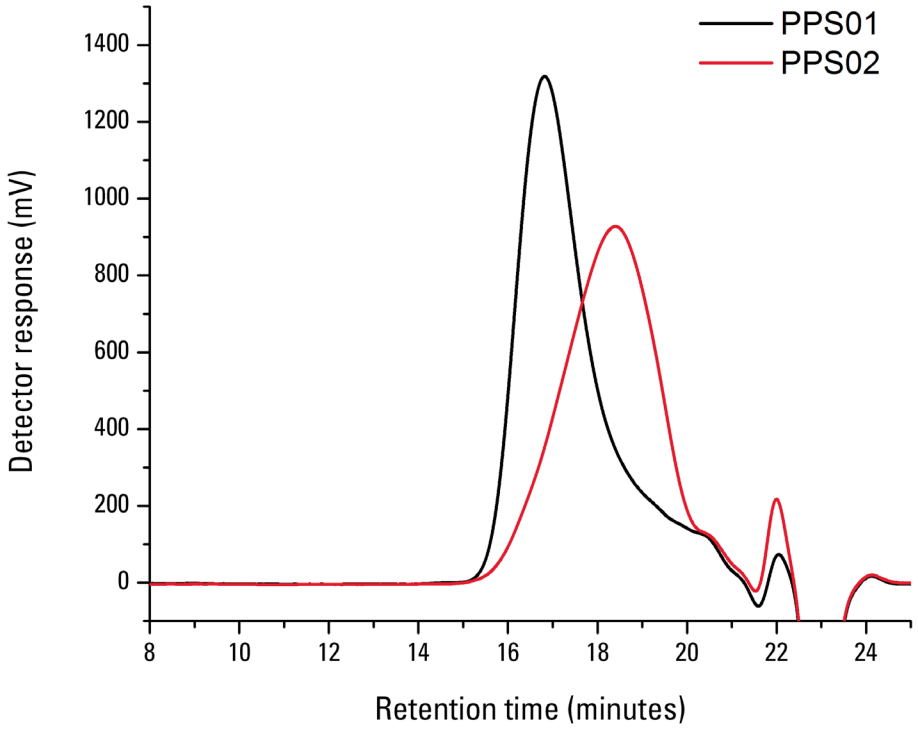
Figure 9: Conclusions

- Figure 9 shows the RI GPC elution profile of consecutive injections of a polypropylene sample obtained using the EcoSEC High Temperature GPC System. The dual flow RI detector in the EcoSEC High Temperature GPC System results in a high degree of reproducibility of retention times and molar mass determination as the coefficients of variation for the weight-average molar mass, M_w, are well below 1%.

Polyphenylene Sulfide (PPS)

- Similar to ambient GPC, high temperature GPC is a fast, accurate and reliable method for the comparison of polymers exposed to various conditions.
- For example the GPC elution profiles and molar mass averages of a virgin product and a product exposed to extreme environmental conditions can be compared to determine how the products performance may be altered due to exposure to those conditions.

Figure 10: GPC elution profiles of two PPS samples introduced to different conditions



Column:	TSKgel GMHHR-H(S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2
Mobile phase:	1-CN
Flow rate:	1.0 mL/min
Detectors:	RI (EcoSEC High Temperature GPC System)
Temperature:	220 °C
Injection vol.:	300 µL
Sample:	polyphenylene sulfide

Table 2: Molar mass averages and polydispersity index of two PPS samples introduced to different conditions

Sample	Retention time (minutes)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
PPS01	16.817	5,790	3.91×10^4	7.19×10^4	6.746
PPS02	18.413	3,176	1.62×10^4	5.54×10^4	5.106

[a] $PDI = M_w/M_n$

Figure 10 and Table 2: Conclusions

- The GPC elution profiles of the PPS polymer samples are given in Figure 10. The PPS01 sample elutes prior to the PPS02, an indication that the PPS01 sample is larger in polymeric size than the PPS02 sample, as elution order in GPC is that of an “inverse-sieving” technique. The GPC elution profiles of the PPS samples also show that PPS01 has a slightly larger molar mass distribution compared to PPS02, as the breadth of the GPC chromatogram is slightly greater for that of PPS01 than PPS02.
- From both the GPC elution profiles, Figure 10, and the molar mass averages, Table 2, that exposing the PPS sample to washing and drying results in a decrease in polymeric size and molar mass averages.

Conclusions

- The utilities of ambient and high temperature GPC are numerous as the size base mechanism of the technique and the ability to determine molar mass averages and distributions allows for various experimental goals.
- To name a few peak position calibration GPC/RI can be successfully used for synthesis monitoring, failure analysis, lot-to-lot or batch to batch variations, and exposure analysis.
- A dual flow RI detector increases the reliability and reproducibility of molar mass averages obtained using peak position calibration for both ambient and high temperature GPC.

References

[1] Striegel, A.M.; Yau, W.W.; Kirkland, J.J.; Bly, D.D. *Modern Size Exclusion Liquid Chromatography, 2nd edition;* Wiley: New York, 2009.