EcoSEC High Temperature GPC System

Engineered to deliver the following:

Superior Performance

- Baseline Stability
- Reproducibility
- Reliability

Unparalleled Versatility

- Ease of Use
- All-in-One Design

Thermal Stability

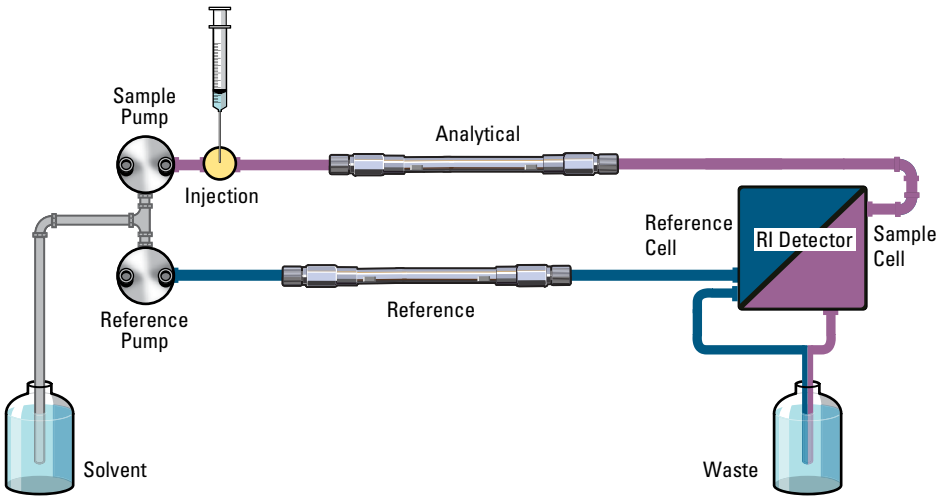
- Heated Solvent Holder
- Complete Thermal Precision

Superior Performance

Baseline Stability

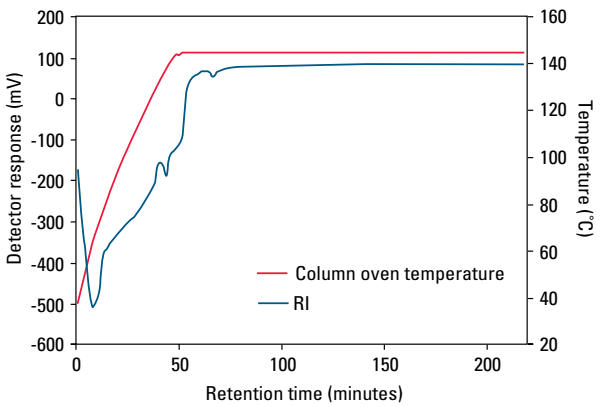
Incorporated into the design of our two pump delivery system is 40+ years experience in engineering. The EcoSEC High Temperature GPC System has a unique dual flow design which includes the use of two pumps. Figure 1 demonstrates the flow paths of the sample and reference pumps. The sample pump flows solvent from the solvent reservoir through the following system components in sequence: autosampler, analytical column, sample side of RI detector cell, and waste container. The solvent flows via the reference pump from the solvent reservoir through a reference column, the reference side of the RI detector cell, and then the waste container. The entire flow system is temperature controlled to eliminate the effects of fluctuations in ambient temperature.

Figure 1: Flow paths of sample and reference pumps in the EcoSEC High Temperature GPC System



On the EcoSEC High Temperature GPC System the RI baseline is considered stabilized when the drift in the signal is 3.0×10^{-7} RIU/h or less. When a new set of columns is manually placed on the EcoSEC High Temperature GPC System and the flow rate and temperature controls are started, the RI baseline stabilizes within 3 hours. Figure 2 demonstrates the equilibration time from start-up of the EcoSEC High Temperature GPC System in orthodichlorobenzene (ODCB).

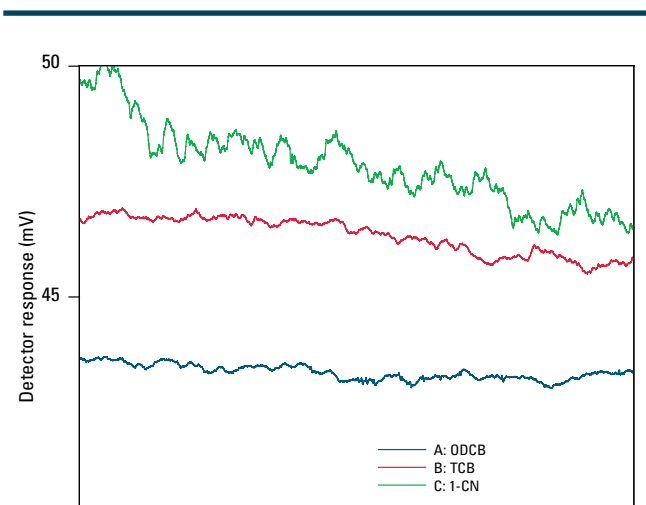
Figure 2: Refractive index detector signal during equilibration of the EcoSEC High Temperature GPC System



Column:	**TSKgel GMH$_{HR}$-H (S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	ODCB with 0.05% BHT
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C

Advanced engineering, along with complete temperature control and a dual flow RI detector, means rock steady baselines in even the most challenging solvents and temperatures. The RI baselines as obtained for three commonly used high temperature GPC solvents: Trichlorobenzene (TCB) at 145 °C, orthodichlorobenzene (ODCB) at 145 °C and 1-chloronaphthalene (1-CN) at 210 °C are shown in Figure 3. The RI baseline drift for all three solvents is less than 1 mV/h.

Figure 3: Baseline drift of the dual flow refractive index detector of the EcoSEC High Temperature GPC System for TCB, ODCB, and 1-CN



Column: **TSKgel GMH$_{HR}$-H (S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase: A: ODBC
B: TCB
C: 1-CN
Flow rate: 1.0 mL/min
Detector: RI (EcoSEC High Temperature GPC System)
Temperature: A and B: 145 °C
C: 210 °C

The unmatched baseline stability of the dual flow RI detector in the EcoSEC High Temperature GPC System is also shown in Table 1 through the drift, fluctuation, and noise obtained when ODCB at 145 °C, TCB at 145 °C, 1-CN at 210 °C, and THF at 40 °C are used as the mobile phase.

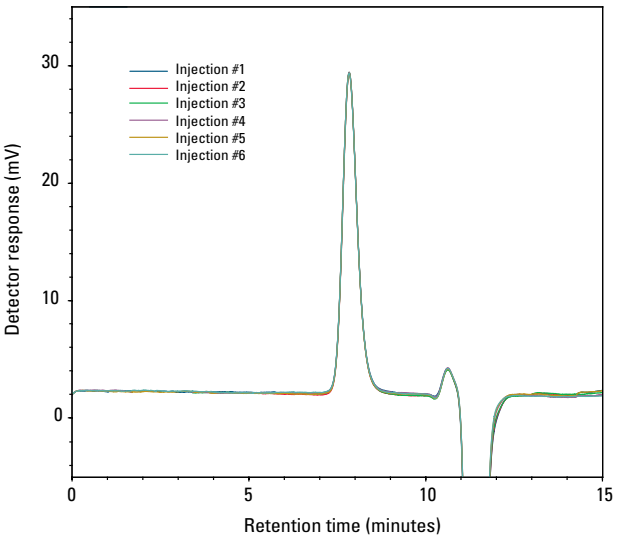
Table 1: Baseline drift, fluctuation and noise of the EcoSEC High Temperature GPC System in ODCB, TCB, 1-CN, and THF

Solvent (temperature)	Drift (mV/h)	Fluctuation (mV)	Noise (mV)
ODCB (145 °C)	-0.41	0.54	0.044
TCB (145 °C)	-1.30	0.69	0.046
1-CN (210 °C)	-0.91	1.61	0.098
THF (40 °C)	-0.35	0.23	0.022

Reproducibility

The dual flow design of the RI detector and the temperature controlled pumps of the EcoSEC High Temperature GPC System deliver precise flow rates at all temperatures, even when changes in environmental conditions occur, thus producing reproducible results sample after sample, day after day. The intraday and day-to-day reproducibility of the EcoSEC High Temperature GPC System are shown in Figure 4.

Figure 4: GPC elution profile of intraday reproducibility of the EcoSEC High Temperature GPC System



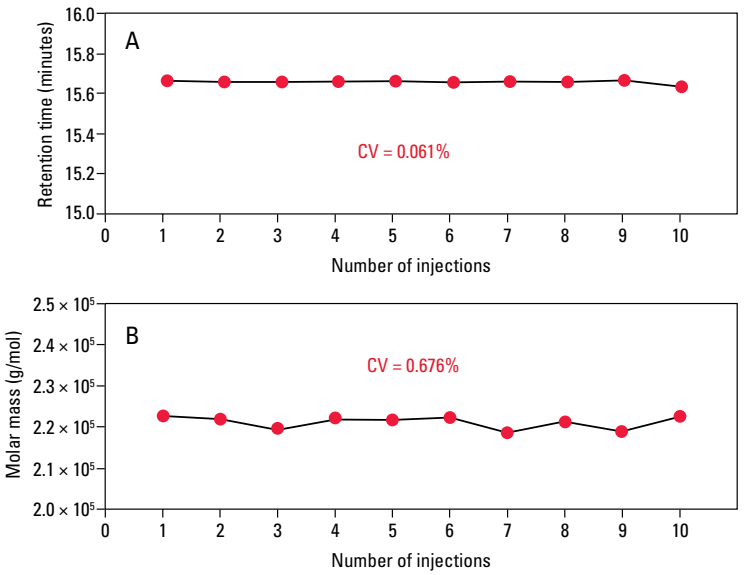
Reproducibility (intraday, n=6)
R.T.: CV 0.017%
Area: CV 0.42%

Reproducibility (day to day, n=5)
R.T.: CV 0.047%
Area: CV 0.71%

Column:	**TSKgel GMH$_{HR}$-H (S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	ODCB with 0.05% BHT
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C
Injection vol.:	300 µL
Sample:	polystyrene (F-20), 0.02%

The engineering design concepts of the EcoSEC High Temperature GPC System result in a high degree of reproducibility of retention times (Figure 5A) and molar mass determinations (Figure 5B). The coefficients of variation for retention time and weight-average molar mass, M_w, are well below 1% for successive injections.

Figure 5A and 5B: A: Intraday retention time reproducibility, B: Intraday weight-average molar mass reproducibility



Column:	**TSKgel GMH$_{HR}$-H (S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	ODCB with 0.05% BHT
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	145 °C
Injection vol.:	300 µL
Sample:	polypropylene

EcoSEC High Temperature GPC System Workstation Software

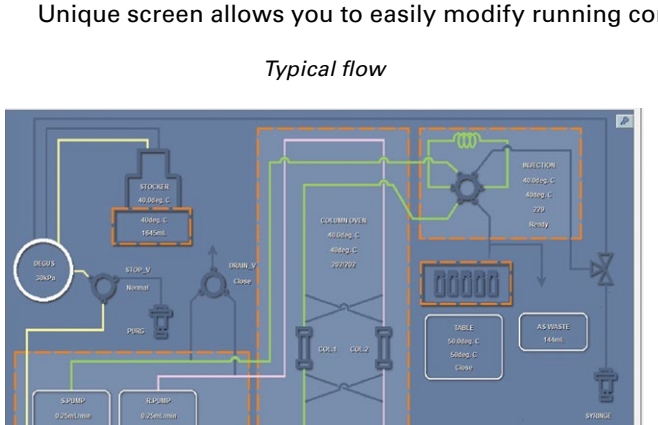
- GPC-specific EcoSEC High Temperature GPC System software to simplify system control and data handling
- Controls up to 2 EcoSEC High Temperature GPC Systems
- Excellent data handling and report generation
- Fully featured data handling system; analyze data from two detectors
- Start and stop system automatically
- One license for multiple locations

Features include:

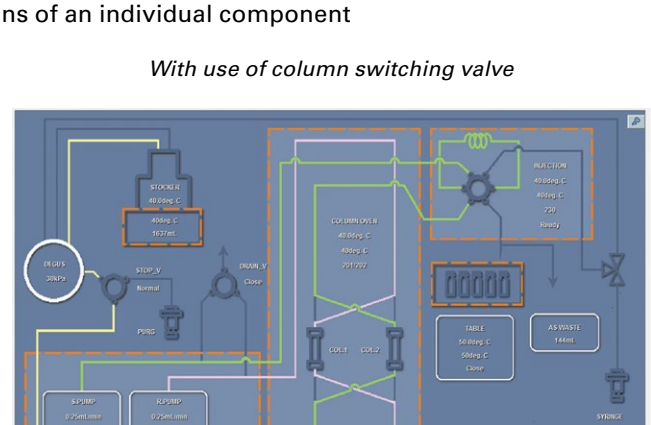
Flow Diagram

- Unique screen allows you to easily modify running conditions of an individual component

Typical flow

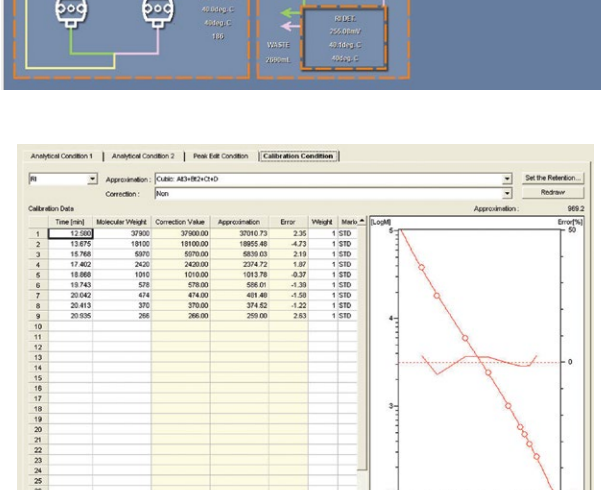


With use of column switching valve



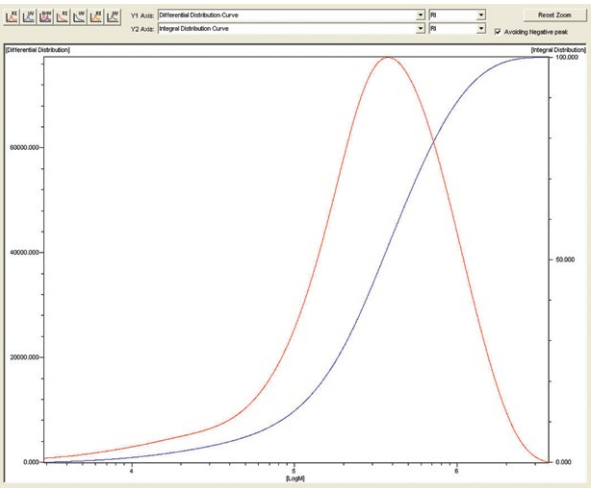
Method

- All parameters for data acquisition and peak integration, including baseline operations, are saved in the template method
- One click switching between calibration curves



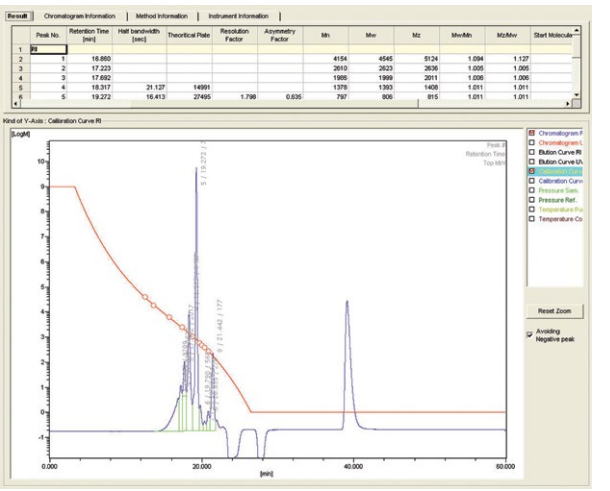
GPC Specific Quantitative Calculations

- M_n, M_w, and M_z molar mass averages
- Cumulative and differential molar mass plotting
- Polydispersity index (*PDI*) values



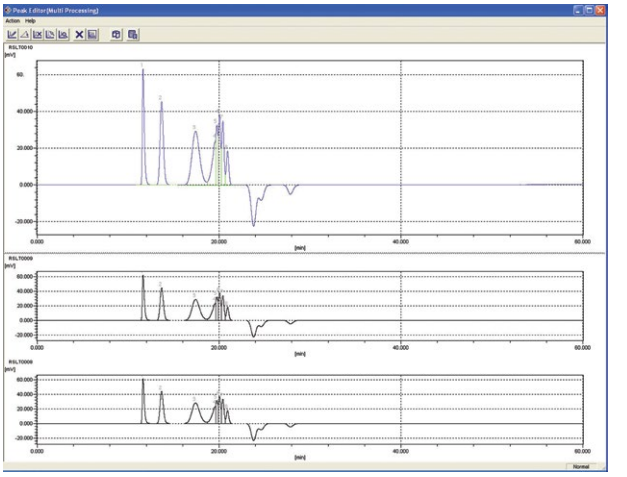
Data Management and Report Generation

- Allows viewing of chromatograms, elution, curve, flow rate, pressure, and temperature.
- Large number of built in reports
- Fully customizable reports
- Easily export data into text or pdf files.



Peak Editing and Multiprocessing Function

- Full editing functionality including baseline setting and peak splitting using the mouse
- Automatic peak editing
- Automatic application of peak detection and integration parameters to multiple chromatograms of the same sample using the multiprocessing function; resulting in identical processing for similar chromatograms for enhanced reproducibility.



Please see software specifications on page 26.

Enhanced EcoSEC GPC System Analysis: External Detectors and Accessories

The addition of multiple detection methods to the EcoSEC GPC System allows for the characterization of a variety of polymer properties. A multi-detector GPC set up can be used to determine:

- Polystyrene relative molar mass averages based on RI
- Branching, universal calibration, intrinsic viscosity, and hydrodynamic radius with viscometry detection
- Absolute molar mass averages and radius of gyration with multi-angle light scattering (MALS) detection

Sample Prep System

- Sample shaker 10 - 100 RPM
- 24 vial capacity
- Aluminum heated block
- 40 - 220 °C

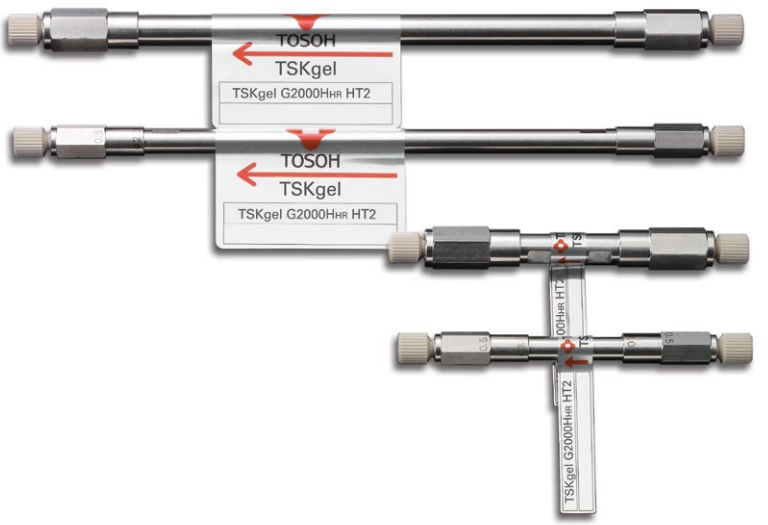
Column Switching Valve

- Easily change between 2 column sets
- Equipped above column oven
- Manual switching
- Position is recognized by software

Tosoh Bioscience can tailor a system to meet your application needs.

Does your analysis require additional detectors beyond RI and UV?
The EcoSEC GPC System provides easy and effortless connectivity when using multi-detector configurations. We offer external light scattering and viscometry detectors.

Contact us for a quote!


TOSOH
TSKgel
TSKgel G2000HHR HT2
TOSOH
TSKgel
TSKgel G2000HHR HT2

Polypropylene: Random Copolymer

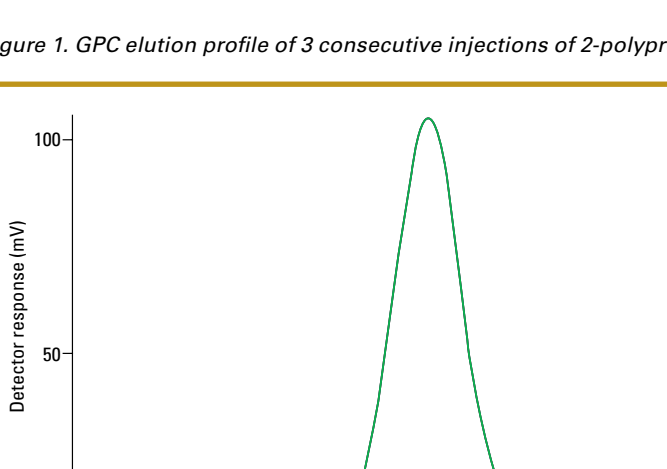
The polypropylene market is one of the largest most versatile polymer markets today, with over 50 million tons produced annually and sold into a wide variety of household and industrial applications. In the home, polypropylene can be found in everything from audio speakers to carpets and automotive components. Industrially, polypropylene is essential in living hinges, RF capacitors, medical devices, and contact lens molding.

The variety of products in which polypropylene is present require versatility in mechanical, thermal and chemical properties. For this reason, depending upon the application, three major categories of polypropylene exist: homopolymer, block copolymer and random copolymer. While homopolymer is the general purpose grade of polypropylene, block copolymers that usually containing 5-15% ethylene exhibit enhanced impact resistance. Random copolymers containing 1-7% ethylene are more malleable and crystal clear. For these reasons, random copolymers are often used in medical applications and contact lens production.

The molar mass averages and polydispersity of two polypropylene random copolymer samples via refractive index (RI) detection using the EcoSEC High Temperature GPC System and TSKgel columns were determined. The number, weight and z-average molar mass values (M_n, M_w, and M_z) and polydispersity index, *PDI*, were calculated for polypropylene equivalents via EcoSEC Workstation software by applying Mark-Houwink constants. The obtained values are given in Tables 1 and 2.

The enhanced thermal, flow rate, and dual flow RI detector stability of the EcoSEC High Temperature GPC System in combination with the excellent resolving power of the TSKgel GMH$_{HR}$-H (20) HT2 high temperature GPC columns produce reliable and highly reproducible data for two polypropylene random copolymer samples analyzed in triplicate (Figures 1 and 2). Very low variation in sample retention and superb baseline stability are observed when overlaying three consecutive RI injections of each sample.

Figure 1. GPC elution profile of 3 consecutive injections of 2-polypropylene random copolymer sample #1 as monitored by RI

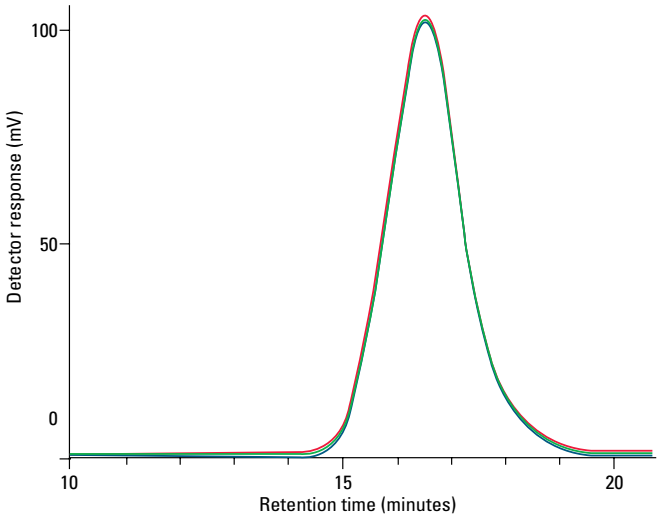


Column:	**TSKgel GMH$_{HR}$-H (20) HT2, 20 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	trichlorobenzene [butylated hydroxyl toluene (BHT) added, 200 ppm]
Flow rate:	1 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Sample:	polypropylene random copolymer

Table 1. Molar mass averages and polydispersity index of 2-polypropylene random copolymer sample #1 via RI

Injection Number	Retention Time (min)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI (M_w / M_n)
1	16.532	54,380	145,630	286,074	2.678
2	16.527	54,153	145,548	289,290	2.688
3	16.548	54,027	145,195	286,331	2.687
Average	16.537	54,187	145,458	287,232	2.684
Standard Deviation	0.011	179	231	1787	0.005
CV%	0.066	0.330	0.159	0.620	0.200

Figure 2. GPC elution profile of 3 consecutive injections of 2-polypropylene random copolymer sample #2 as monitored by RI.



Column: **TSKgel GMH$_{HR}$-H (20) HT2, 20 µm, 7.8 mm ID × 30 cm x 2**
Mobile phase: trichlorobenzene [butylated hydroxyl toluene (BHT) added, 200ppm]
Flow rate: 1 mL/min
Detector: RI (EcoSEC High Temperature GPC System)
Sample: polypropylene random copolymer

Table 2. Molar mass averages and polydispersity index of 2-polypropylene random copolymer sample #2 via RI

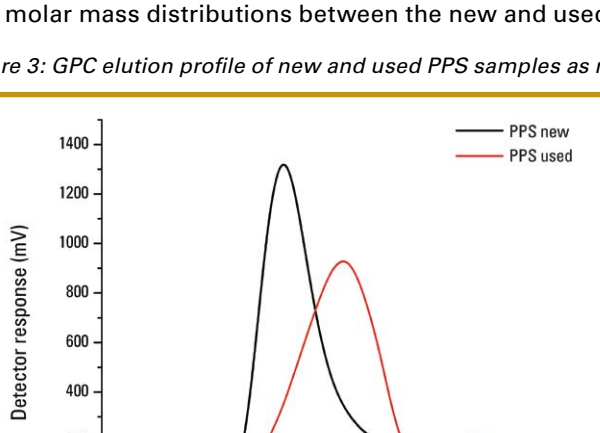
Injection Number	Retention Time (min)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI (M_w / M_n)
1	16.532	52,396	145,040	292,193	2.768
2	16.532	52,519	145,298	292,904	2.767
3	16.533	54,427	145,729	291,369	2.677
Average	16.532	53,114	145,356	292,155	2.737
Standard Deviation	0.001	1139	348	768	0.052
CV%	0.004	2.14	0.24	0.26	1.90

Polyphenylene Sulfide

Polyphenylene Sulfide (PPS) has attracted a considerable amount of interest in the polymer industry due to its high tensile strength, good dimensional stability, flame resistance, and excellent stability in organic liquids. PPS is virtually insoluble in most organic solvents at ambient temperatures and thus can only be characterized in the solid state or by using elevated temperatures. The limited solubility of PPS makes it very difficult to determine macromolecular properties, such as molar mass and molar mass distribution, that play a vital role in the determination of mechanical, bulk and solution properties of the processing and end-use properties of a given material. Traditionally, PPS has been characterized by infrared spectrometry and thermal analysis methods. One method which can also be used to characterize PPS is high temperature GPC as PPS is soluble in 1-chloronaphthanlene (1-CN) at extremely elevated temperatures (> 200 °C). 1-CN is a difficult solvent to use for analytical experiments as the solvent ambers over time and can cause havoc for detection methods such as RI. GPC analysis of PPS in 1-CN for the determination of molar mass averages and molar mass distributions is possible using the EcoSEC High Temperature GPC System due to the unique dual flow refractive index detector.

A new and a used PPS sample were compared for failure investigation through their GPC elution profiles, Figure 3, and their polystyrene relative molar mass averages, Table 3. As seen in Figure 3, the new PPS sample eluted prior to the used PPS sample. The shorter retention time of the new PPS sample indicated that the new PPS sample was larger in polymeric size than the used PPS sample, as the elution order in GPC is that of an "inverse-sieving" technique, larger analytes sample a smaller pore volume than smaller analytes resulting in the larger analytes eluting from the GPC column prior the smaller analytes. As seen in Table 3, the new PPS sample was determined to have a higher number-, weight-, and *z*-average molar mass and greater polydispersity index, *PDI*, than the used PPS sample. The approximately 20 to 50% decrease in the molar mass averages and 25% increase in *PDI* observed between the new PPS and the used PPS is potentially enough evidence to determine that after a predetermined amount of time the end-use product(s) made with this PPS sample will begin to fail or will no longer be able to perform up to standards. The use of GPC/RI for the failure investigation of PPS allows for immediate differentiation between the new and used PPS samples based on the GPC/RI elution profile, which was then confirmed through differences in the polystyrene relative molar mass averages and molar mass distributions between the new and used PPS samples.

Figure 3: GPC elution profile of new and used PPS samples as monitored by RI



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

Table 3: Molar mass averages and polydispersity index of new and used PPS samples via GPC/RI

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	*PDI*[a]
PPS new	5,790	3.91×10^4	7.19×10^4	6.74
PPS used	3,176	1.62×10^4	5.54×10^4	5.10

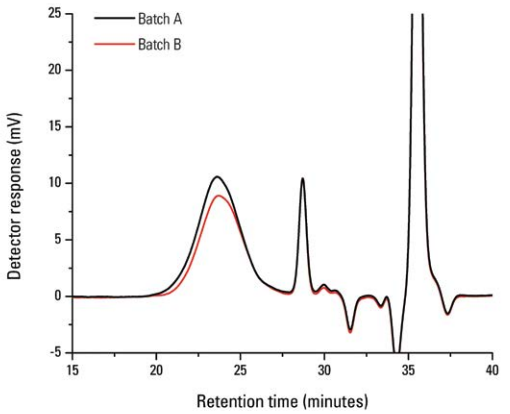
[a] $PDI = M_w/M_n$

Polyethylene

One of the most common plastics and commercially available polymers on the market is polyethylene. Polyethylene in general describes a huge family of resins obtained by the polymerization of ethylene gas. Polyethylene is available in a range of flexibilities and properties depending on the production process. Properties of polyethylene such as toughness, hardness, and clarity can be regulated by altering the molar mass averages, comonomer type, and comonomer content. Most polyethylene resins for commercial products are fabricated by controlling the molar mass average, molar mass distribution and branching characteristics. The molar mass averages and molar mass distributions of polyethylene can be determined using the EcoSEC High Temperature GPC System.

High temperature GPC experiments provide two forms of comparison between the two difference batches of polyethylene samples: GPC chromatograms and polystyrene relative molar mass averages and molar mass distributions. Figure 4 shows the GPC elution profiles as monitored by the RI detector in the EcoSEC High Temperature GPC system for the difference batches of polyethylene. 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 slightly in polymeric size, as elution order in GPC is that of an "inverse-sieving" technique, as smaller analytes elute after larger analytes.

Figure 4: GPC elution profile of two batches of polyethylene as monitored by RI



Column:	**TSKgel GMH$_{HR}$-H (S) HT2, 13 µm, 7.8 mm ID × 30 cm × 3**
Mobile phase:	ODCB with 0.05% BHT
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	135 °C
Injection vol.:	300 µL
Sample:	polyethylene

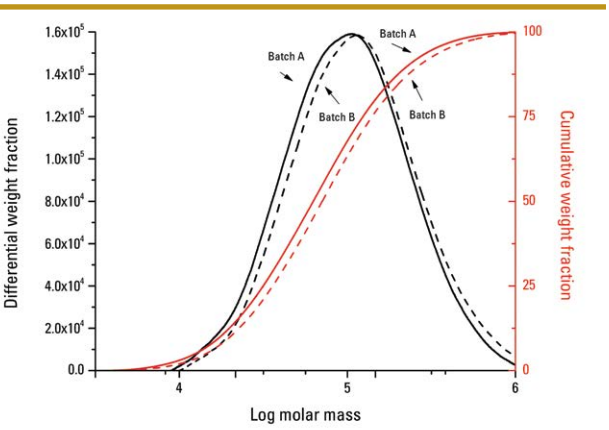
The molar mass averages and polydispersity index, *PDI*, as determined by the polystyrene RI calibration curve are given in Table 4. A comparison of the molar mass averages and molar mass distribution, Figure 5, of the two different batches of polyethylene reveals an approximately 10 to 15% difference in the polystyrene molar mass averages and distributions between the two batches. The molar mass averages and distributions of the two different batches of polyethylene obtained by high temperature GPC are different enough to distinguish the two batches from one another but may be similar enough to both create a successful commercial plastic with the same end-use properties.

Table 4: Molar mass averages and polydispersity index of two batches of polyethylene via GPC/RI

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
Batch A	4.48×10^4 ± 364[b]	1.18×10^5 ± 790	2.95×10^5 ±1,821	2.64 ± 0.06
Batch B	3.66×10^4 ± 135	1.03×10^5 ± 124	2.64×10^5 ± 2,806	2.80 ± 0.01

[a] $PDI = M_w/M_n$

Figure 5: Overlay of cumulative and differential molar mass distribution of two batches of polyethylene



Polythiophene

Conducting polymers, such as polythiophenes, have been widely investigated over the past several decades due to their potential industrial applications based on their conductivity and organic light-emitting capability. To date polythiophenes have been used in the development of electronics, energy storage batteries, photochromic devices and nonlinear optical devices. The heavy focus on synthesis of conducting polymers facilitates the need for characterization methods. Among the methods employed for the characterization of the intermediates and final conducting polymers are FT-IR, NMR, GPC, and microscopy. Some conducting polymers have limited solubility thus require the use of high temperature GPC for determination of the molar mass averages and molar mass distributions. Similar to other polymers, the molar mass averages and molar mass distributions of conducting polymers play a role in determining the end-use properties of the applications for which the polymer is used.

The molar mass averages and molar mass distributions of two conducting polymers similar to polythiophene were determined using the EcoSEC High Temperature GPC System. The polystyrene relative molar mass averages, M_n, M_w, and M_z, are given in Table 5. The variation between the molar mass averages of the two conducting polymers may be enough to change the conductivity of the polymers, thus their end-use applications. In addition to the molar mass averages, the molar mass distribution can also influence various properties of conducting polymers. The molar mass distributions of the two conducting polymers are compared in Figure 6. The molar mass distribution of polymer A is significantly larger than that of polymer B.

Information regarding the difference between the two conducting polymers can be seen by comparing their GPC elution profiles, Figure 7. The shift in GPC retention time amongst the two conducting polymers indicates a variation in polymeric size between the two conducting polymers, as elution order in GPC is that of an "inverse-sieving" technique, large analytes sample a smaller pore volume than smaller analytes resulting in larger analytes eluting from the GPC column prior to the smaller analytes. Based on the GPC elution profile, polymer A is significantly larger in polymeric size than polymer B.

Table 5: Molar mass averages and polydispersity index of two conducting polymer sammples via GPC/RI

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)
Polymer A	$2.58 \times 10^4 \pm 0.01 \times 10^4$[a]	$6.51 \times 10^4 \pm 0.02 \times 10^4$	$1.34 \times 10^5 \pm 0.03 \times 10^5$
Polymer B	$9.39 \times 10^3 \pm 0.01$[a] $\times 10^3$	$1.26 \times 10^4 \pm 0.04 \times 10^4$	$1.60 \times 10^4 \pm 0.01 \times 10^4$

[a] Standard deviation from two injections

Figure 6: Overlay of cumulative and differential molar mass distribution of two conducting polymer samples

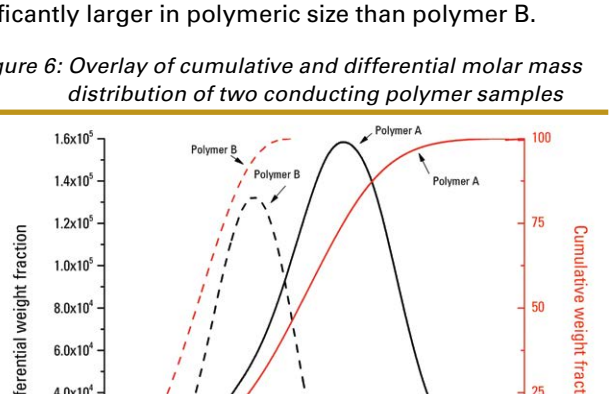
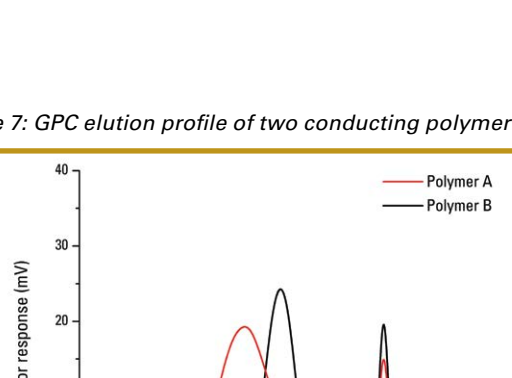


Figure 7: GPC elution profile of two conducting polymer samples as monitored by RI



Column:	**TSKgel GMH$_{HR}$-H (S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	TCB
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	135 °C
Injection vol.:	300 µL
Sample:	polythiophene

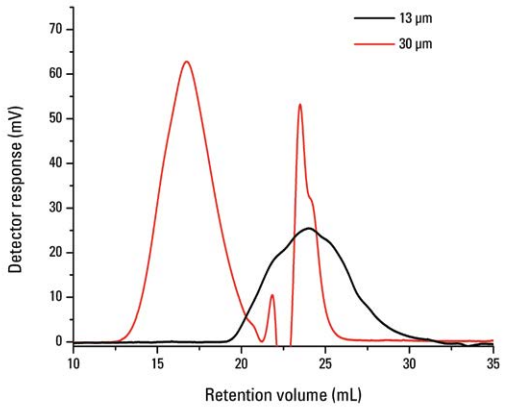
High Molar Mass Polymers

High temperature GPC is a common and important technique used for the characterization of polyolefins. GPC analysis of polyolefins can be difficult as those containing over 10% ethylene and polypropylene monomers have limited solubility due to their characteristically high strength and toughness that results from their high crystallinity. In addition to the limited solubility of most polyolefins, high molar mass polyolefins, such as ultra-high molar mass polyethylene (UHMMPE) present their own subset of issues when being analyzed by GPC. High molar mass polyethylenes are extremely long polymer chains with a molar mass greater than 2×10^6 g/mol. Polymers greater than a million in molar mass have been shown to experience on-column flow induced degradation when analyzed by GPC. To decrease the amount of degradation that occurs when UHMMPE samples are analyzed by high temperature GPC and thus obtain the most accurate molar mass averages and molar mass distributions, GPC columns packed with larger size particles with large pores are ideal.

An EcoSEC High Temperature GPC System with a dual flow refractive index detector was used in conjunction with 13 µm and 30 µm TSKgel high temperature GPC columns to determine the molar mass averages and distributions of a UHMMPE. Figure 8 show the GPC elution profiles obtained on both column sets. The shape of the GPC elution profile varies between the two column sets. The elution profile obtained using the 13 µm high temperature GPC column has a shoulder in the high molar mass region (the molar mass region most likely affected by on-column flow induced degradation) while the elution profile obtained using the 30 µm high temperature GPC column does not.

The polystyrene RI relative molar mass averages of the UHMMPE obtained using two different high temperature GPC column sets are given in Table 6. The molar mass averages obtained using the 13 µm high temperature GPC columns are significantly smaller than those obtained using the 30 µm high temperature GPC columns. The sample degradation is more prevalent in the high molar mass region of the sample as the *z*-average molar mass is two orders of magnitude greater when analysis is performed on the 30 µm high temperature GPC columns. The molar mass distribution of the UHMMPE obtained by both high temperature GPC column sets indicate an extremely polydisperse polymer. The use of 30 µm high temperature GPC columns provides a better representation of the polystyrene relative molar mass averages as the larger size particles and pores decrease the amount of degradation experienced by UHMMPE.

Figure 8: GPC elution profile of UHMMPE samples as monitored by RI with 13 µm and 30 µm TSKgel high temperature GPC columns



Column:	**TSKgel GMH$_{HR}$-H (S) HT2, 13 µm, 7.8 mm ID × 30 cm × 2 + TSKgel G2000H$_{HR}$(20) HT2, 20 µm, 7.8 mm ID × 30 cm TSKgel GMH$_{HR}$-H (30) HT2, 30 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	TCB
Flow rate:	1.0 mL/min
Detector:	RI (EcoSEC High Temperature GPC System)
Temperature:	135 °C
Injection vol.:	300 µL
Sample:	polyethylene

Table 6: Molar mass averages and polydispersity index of UHMMPE samples via RI with 13 µm and 30 µm TSKgel high temperature GPC columns

Column (particle size)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
13 µm	2.23×10^4	5.76×10^5	4.41×10^6	25.75
30 µm	9.21×10^4	7.74×10^6	2.55×10^8	84.07

[a] $PDI = M_w/M_n$