EcoSEC GPC System

Engineered to deliver the following:

Superior Performance

- Baseline Stability
- Reproducibility
- Reliability

Unparalleled Versatility

- Ease of Use
- All-in-One Design

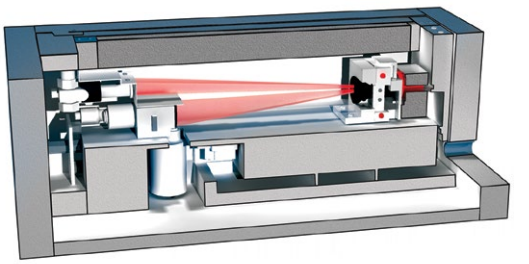
Increased Throughput

- Lower Operating Costs

Superior Performance

Unmatched Baseline Stability

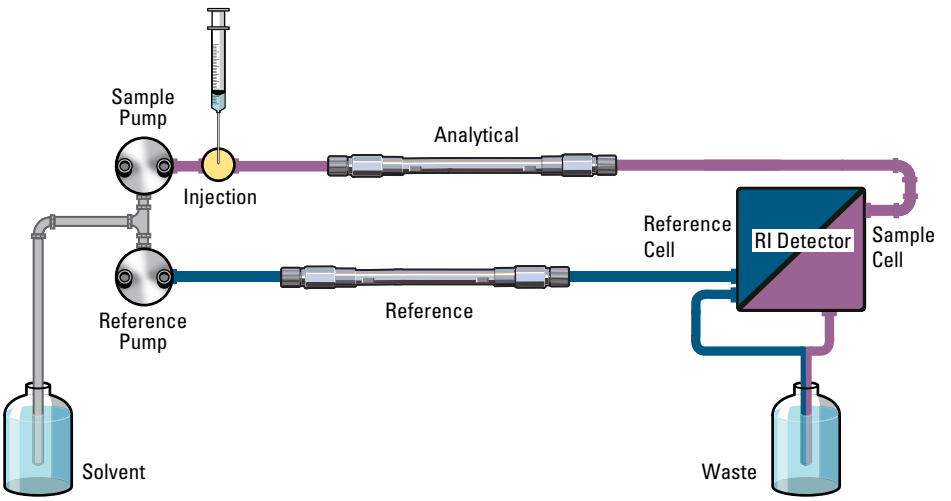
- Dual flow RI cell and pump design
- Continuous correction of RI baseline drift due to solvent instability
- Improved molar mass precision and accuracy
- Rapid baseline stability at startup



Dual Flow Pump Design

The EcoSEC 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.

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



Dual Flow Refractive Index Detector

The refractive index detector in the EcoSEC GPC System is unlike any other refractive index detector on the market due to its unique dual flow design. The EcoSEC GPC System RI flow cell is constructed in such a way that there are two sides: (1) the reference side, containing a flowing stream of pure solvent; and (2) a sample side, containing a flowing stream of analyte in the same solvent as in the reference side (Figure 2).

The unique dual flow design of the EcoSEC GPC System results in superb RI baseline stability and reduced RI baseline drift. In a conventional RI detector, over time, the refractive index of the stagnant pure solvent in the reference side will slowly change and the two photodiodes will no longer produce equal signals, thus the contents of the reference and sample sides have different refractive indices and will produce a voltage difference similar to that of an analyte in solution. For example, the refractive index of THF slowly alters over time, due to the buildup of peroxide-related compounds, resulting in baseline drift (Figure 3). The dual flow design of the RI detector in the EcoSEC GPC System compensates for the changes in refractive index of the solvent over time by continuously flowing pure solvent through the reference side of the flow cell.

Another benefit of the dual flow cell is rapid attainment of baseline stability when the instrument is first started, as purging is not required. A stable baseline can be achieved by flowing only 50 mL of solvent through the instrument. Additionally, the reference side mobile phase can be sent to waste or recycled back to the solvent bottle.

Figure 2: Depiction of dual flow RI detector in the EcoSEC GPC System, showing the compensation of the changes in refractive index of the solvent over time

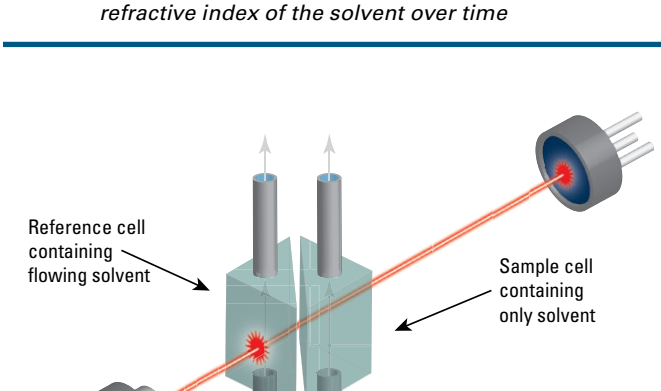
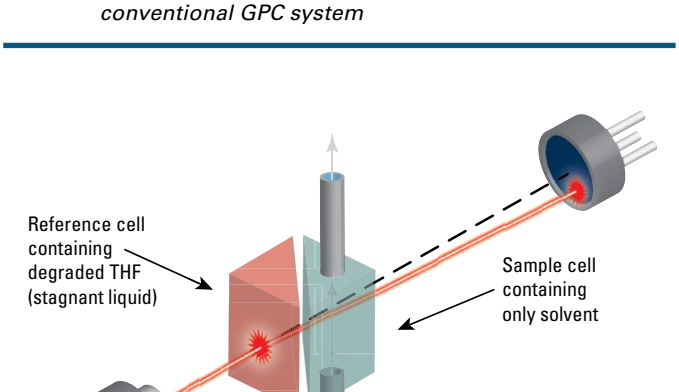


Figure 3: Depiction of RI detector flow cell showing the effects of THF degradation in the stagnant reference side of a conventional GPC system



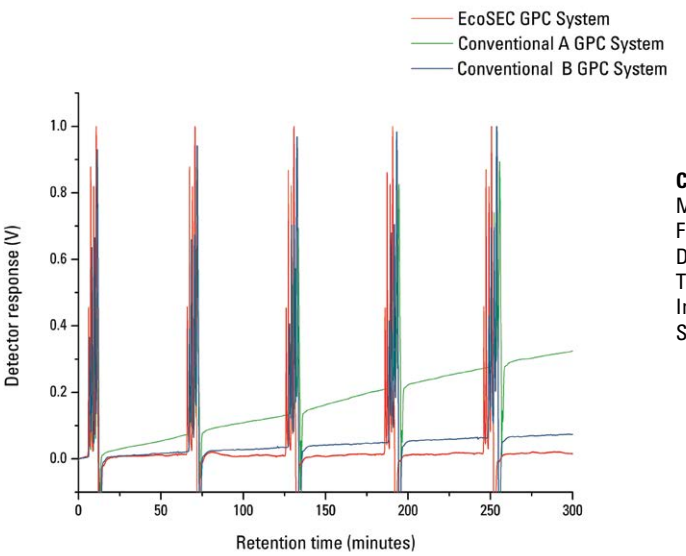
Comparison of Baseline Stability

The EcoSEC GPC System offers unmatched baseline stability because it is the only GPC system which uses a dual flow refractive index detector and temperature controlled pumps. Baseline stability is essential for the accurate calculation of polymer molar mass averages. For example, computer simulations predict a polymer with a polydispersity index (*PDI*) of 5 will have an 18% error for M_z if baseline instability leads to a 4% error in peak width determination. In addition, a 2% uncertainty in baseline height will result in a 20% error in M_z.[1]

A study was done to demonstrate the superb baseline stability of the EcoSEC GPC System compared to that of two conventional GPC systems using both 15 cm and 30 cm columns over a five hour time period. The figures below demonstrate that the EcoSEC GPC System maintains the efficiency of semi-micro columns and maintains a stable RI baseline when both conventional and semi-micro GPC columns are used.

As shown in Figures 4A and 4B, five consecutive injections of polystyrene standards with run times deliberately extended to one hour without auto zeroing the detectors between injections, resulted in an extremely stable baseline with low baseline drift on the EcoSEC GPC System and a significantly drifting baseline on the two conventional GPC systems. In comparison to the conventional GPC systems, the EcoSEC GPC System has both a lower baseline drift and a better signal to noise ratio.

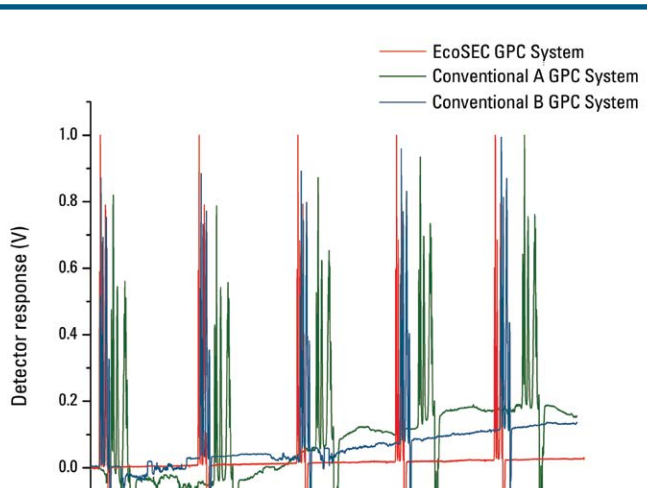
Figure 4A: Comparison of baseline drift of the dual flow refractive index detector of the EcoSEC GPC System and two conventional GPC systems using semi-micro columns



Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	polystyrene standards, PStQuick MP-M series

[1]Tcjir, W.J.; Rudin, A.; and Fyfe, C.A. Effects of data analysis on accuracy and precision of GPC results. *J. Polym. Sci. Polym. Phys. Ed.* **1982**, *20*, (8), 1443-1451.

Figure 4B: Comparison of baseline drift of the dual flow refractive index detector of the EcoSEC GPC System and two conventional GPC systems using conventional columns



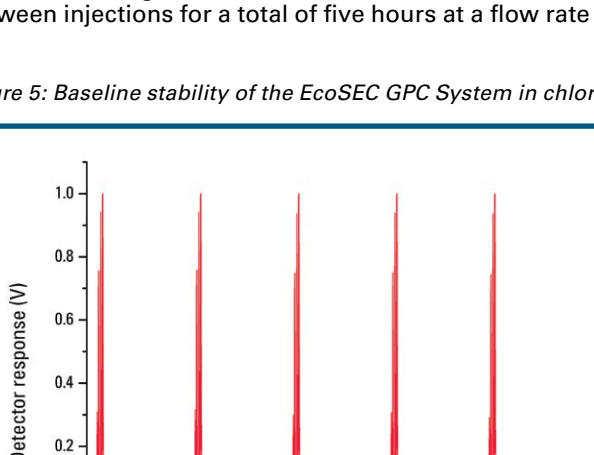
Column:	**TSKgel GMHXL-L, 5 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	THF
Flow rate:	1.0 mL/min
Detection:	RI
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	polystyrene standards, PStQuick MP-M series

Baseline Stability in Various Solvents

The EcoSEC GPC System displays an extremely stable baseline with low baseline drift when analyzing polymers in neat, mixed, and complex solvent systems.

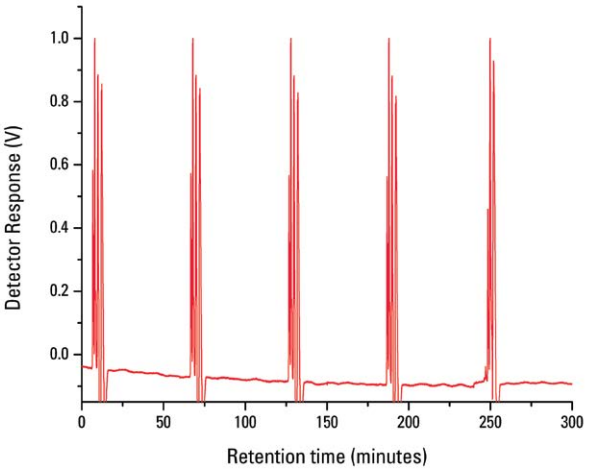
The following figures show five consecutive injections of polystyrene standards in chloroform (Figure 5), DMAc with 0.02 mol/L LiBr (Figure 6), and 95:5 Dichloromethane:HFIP with 5 mmol/L tetraethylammonium bromide (Figure 7) on semi-micro TSKgel GPC columns. The run times were deliberately extended to one hour without auto zeroing the detector between injections for a total of five hours at a flow rate of 0.35 mL/min.

Figure 5: Baseline stability of the EcoSEC GPC System in chloroform



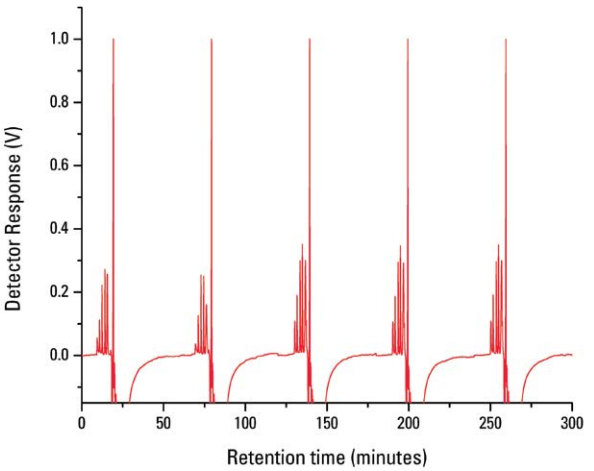
Column:	**TSKgel SuperHZM-M, 3 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	chloroform
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	polystyrene standards, PStQuick MP-M series

Figure 6: Baseline stability of the EcoSEC GPC System in DMAc with 0.02 mol/L LiBr



Column:	**TSKgel SuperHZM-M, 3 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	DMAc with 0.02 mol/L LiBr
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	polystyrene standards, PStQuick MP-M series

Figure 7: Baseline stability of the EcoSEC GPC System in 95:5 dichloromethane:HFIP with 5 mmol/L tetraethylammonium bromide



Column:	**TSKgel SuperHM-H, 3 µm, 6 mm ID × 15 cm × 2**
Mobile phase:	95:5 dichloromethane:HFIP with 5 mmol/L tetraethylammonium bromide
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	polystyrene standards, PStQuick B + PStQuick C

Comprehensive Temperature Control

Elution Time Precision

To assess the influence of environmental conditions within the laboratory on solvent flow, a study was done in which the EcoSEC GPC System and a conventional GPC system were placed in a chamber where the temperature was cycled between 23 °C and 26 °C. A series of 99 injections of polystyrene were made over a time period of ten hours. For each instrument the elution volume at peak maximum was measured; the resulting data is shown in Figures 8A and 8B below. The retention time drift of the EcoSEC GPC System was about 20% lower than that of the conventional GPC system.

The results shown demonstrate that the engineering design concepts of the EcoSEC GPC System result in a high degree of reproducibility of retention time and molar mass determination.

Figure 8A: Mobile phase delivery reproducibility of the EcoSEC GPC System with ambient temperature changes

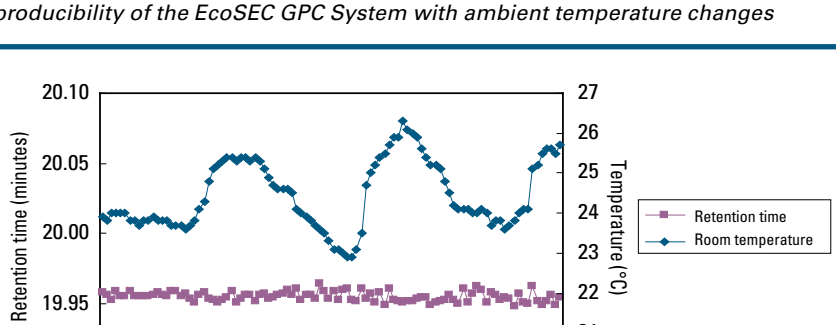
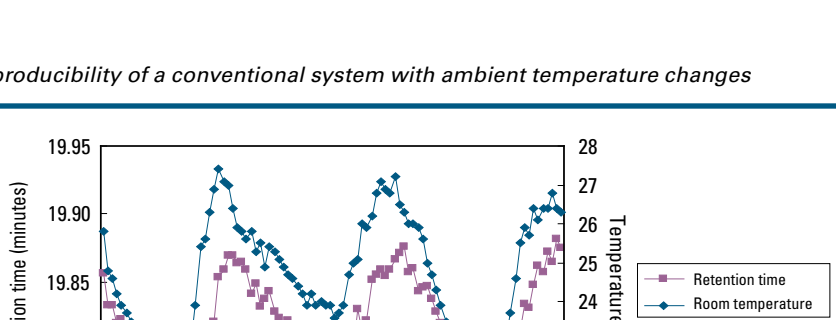


Figure 8B: Mobile phase delivery reproducibility of a conventional system with ambient temperature changes

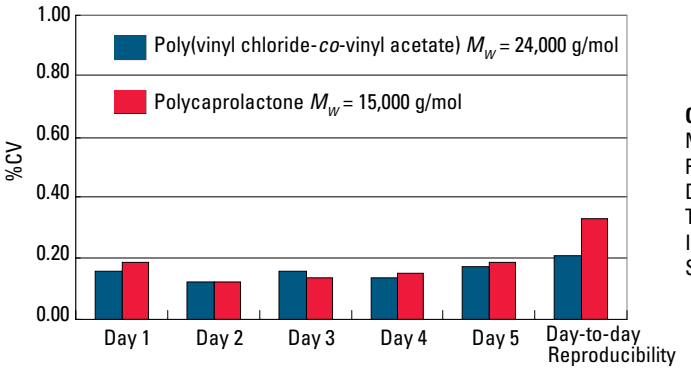


M_w Precision

Molar mass averages can be affected by changes in the environment and measuring conditions. Generally, these variations are the result of one or more factors including flow rate reproducibility, baseline drift and injection reproducibility. In addition to controlling column temperature, Tosoh engineers added temperature control for both pumps and inlet and outlet tubing on the EcoSEC GPC System to deliver top GPC analysis performance.

Figure 9 demonstrates the superiority of the EcoSEC GPC System for the determination of weight-average molar masses.

Figure 9: Reproducibility of M_w analysis

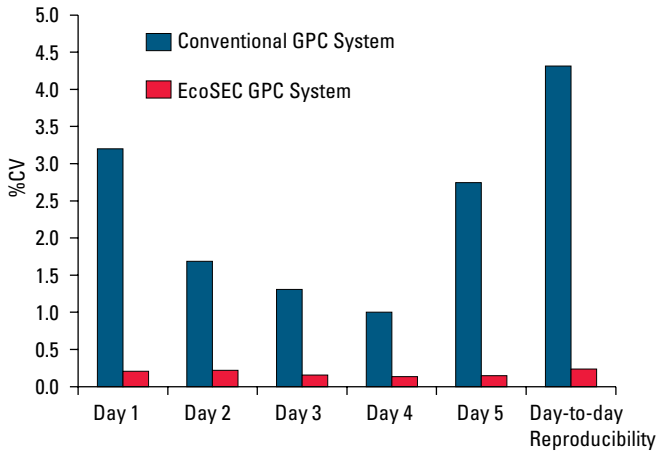


CV value less than 0.2% a day.
CV value less than 0.4% on different days.

Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	10 µL
Samples:	poly(vinyl chloride-*co*-vinyl acetate) and polycaprolactone

Figure 10 shows a comparison of M_w reproducibility for a sample injected 10 times a day for 5 days on the EcoSEC GPC System compared to a conventional GPC system. The reproducibility of the EcoSEC GPC System was superior by a factor of 3 to that of the conventional GPC system.

Figure 10: Comparing M_w reproducibility of the EcoSEC GPC System and a conventional GPC system



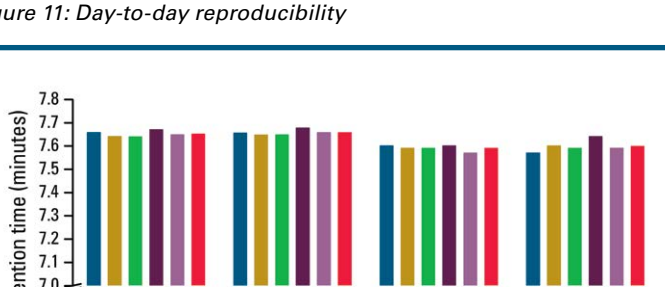
Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI
Temperature:	40 °C
Injection vol.:	10 µL
Samples:	poly(vinyl chloride-*co*-vinyl acetate)

System-to-System Reproducibility

Often measurements can be reproduced using the same equipment but results differ when an instrument from the same or another manufacturer is used. Among the system-specific factors which can influence the results of GPC analysis, fluctuations in elution time, in particular, can have a significant effect.

A study was performed using a polydisperse poly(vinyl chloride-*co*-vinyl acetate) sample run on four different EcoSEC GPC Systems by different operators to assess system reproducibility. The results are shown in Figure 11. The high precision of the EcoSEC GPC System results in minimal variation among instruments and from day-to-day.

Figure 11: Day-to-day reproducibility



Four EcoSEC GPC Systems, 4 operators,
4 column sets, 4 conditions, one location

Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	poly(vinyl chloride-*co*-vinyl acetate)

Site-to-Site Reproducibility

To test site reliability, a round-robin study was undertaken in which the same polydisperse poly(vinyl chloride-*co*-vinyl acetate) sample was run on EcoSEC GPC Systems located at four different sites. The results are displayed in Table 1.

Reproducibility from system-to-system and location-to-location is exceptional with the EcoSEC GPC System. Coefficients of variations for all molar mass averages were all well below 1%. Because of the high instrument-to-instrument reproducibility of the EcoSEC GPC System, methods developed at one location, *e.g.*, an R&D laboratory, can be reliably transferred to a second site, e.g., a QC lab at a manufacturing site, and so on.

Table 1: Site-to-site reproducibility

	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)
Site A	1.30×10^4	2.98×10^4	5.37×10^4
Site B	1.37×10^4	2.99×10^4	5.43×10^4
Site C	1.36×10^4	2.98×10^4	5.32×10^4
Site D	1.37×10^4	3.02×10^4	5.41×10^4
Average	1.37×10^4	2.99×10^4	5.38×10^4
Deviation	70	160	420
%CV	0.52	0.55	0.78

Four EcoSEC GPC Systems, 4 operators,
4 column sets, 4 conditions, 4 locations

Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	poly(vinyl chloride-*co*-vinyl acetate)

Average of values measured with each instrument (n = 10).

Column Switching Valve

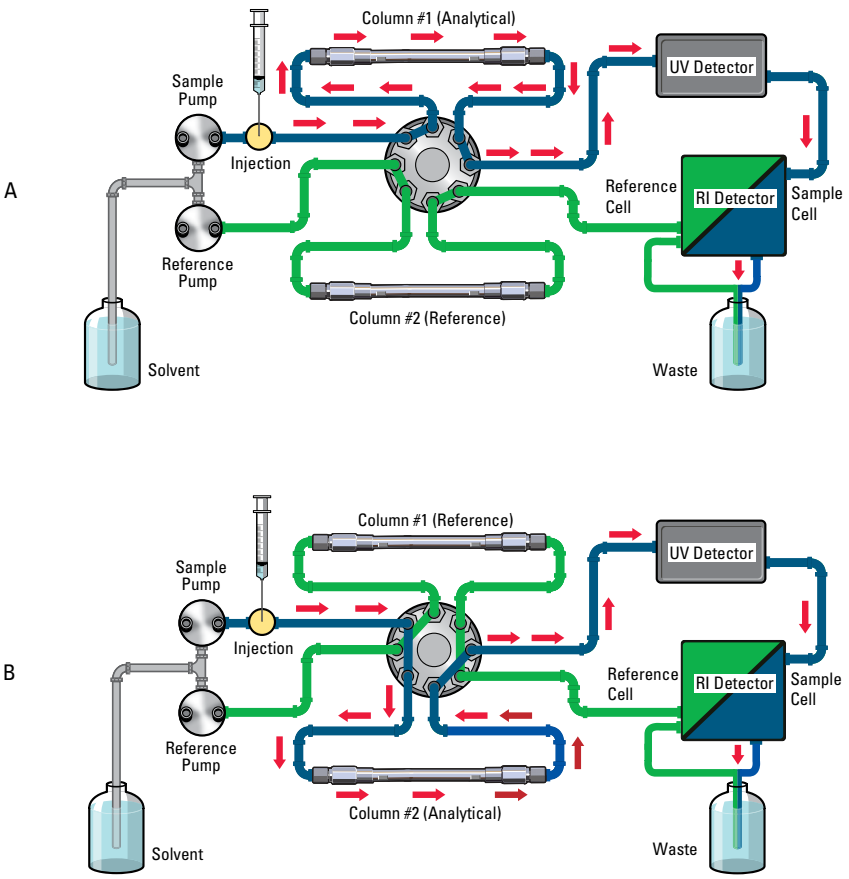
- Reduce column switching time
- Easily switch between low MM and high MM range columns
- Eliminate temperature related baseline drift following column change

Rapid Column Switching

The EcoSEC GPC System contains two pumps: a sample pump to deliver sample and solvent through the analytical column and the sample side of the RI detector flow cell and a reference pump to flow solvent (via a reference column) to the reference side of the RI detector flow cell. By installing an optional column switching valve and replacing the reference column with another analytical column, an analysis can be performed on column 1 while equilibrating column 2. After switching the valve, column 2 becomes the analytical column while column 1 will be in the flow path to the reference side of the RI detector flow cell (Figure 12).

Since the column switching valve changes column sets while the oven door remains closed and switches to an already equilibrated column set, a stable baseline is rapidly established.

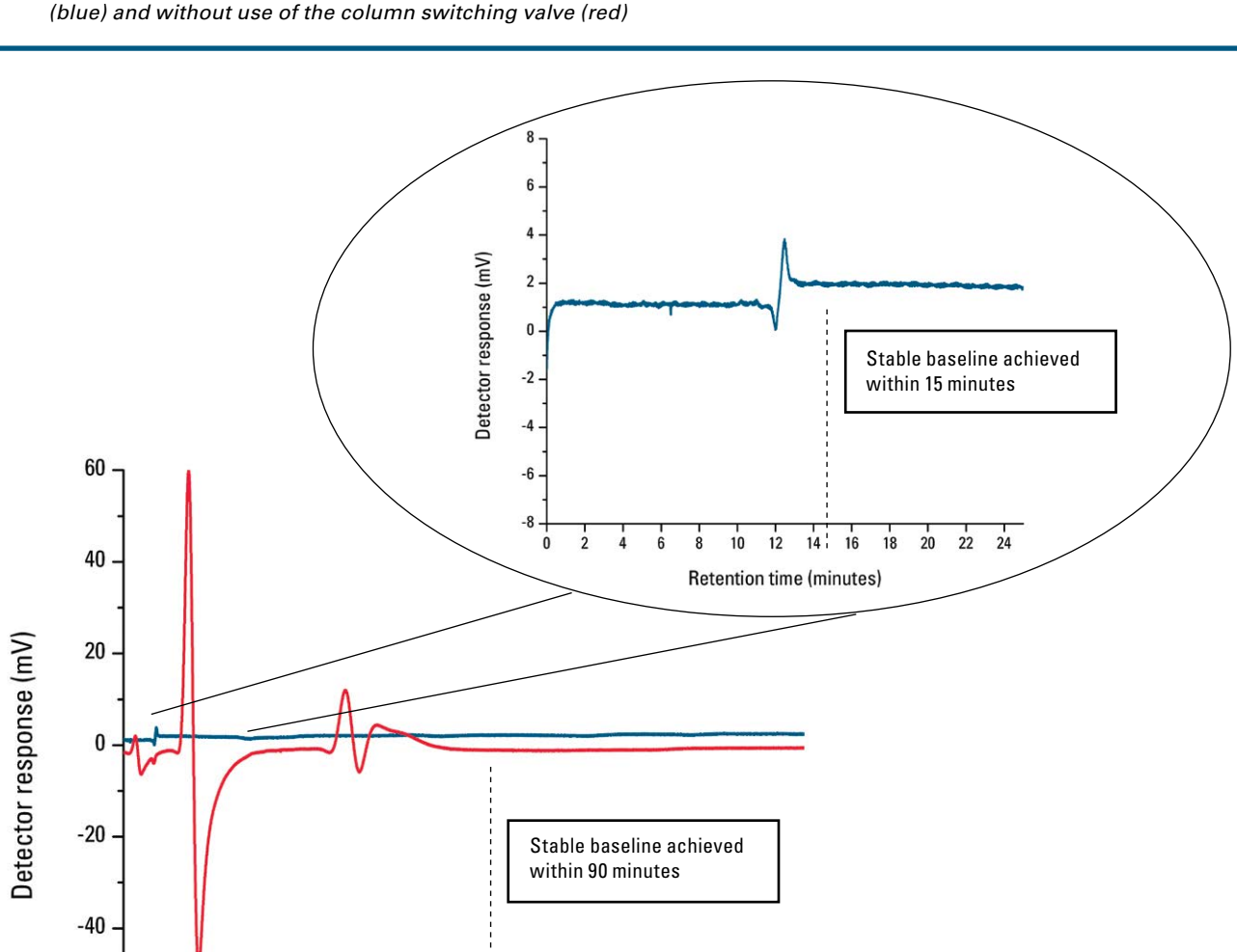
Figure 12: A: Flow path with column 1 as the analytical column B: Flow path with column 2 as the analytical column



Comparison of Time to Baseline Stability with and without the Column Switching Valve

On the EcoSEC GPC System the RI baseline is considered stabilized when the drift in signal is $1x10^{-7}$ RIU/h or less (based on THF at a flow rate of 1.0 mL/min). When a new set of columns is manually placed on the EcoSEC GPC System and the flow rate is started, the RI baseline stabilizes within 80 - 90 minutes. When a new column set is brought online using the column switching valve, the baseline stabilizes within 15 minutes. (Experimental conditions: THF, 35 °C, 0.35 mL/min, 20 min warm-up at 50% flow rate). Figure 13 clearly demonstrates the 65 - 75 minute savings in time required to reach a stable baseline when the columns are switched using the column switching valve compared to manually changing columns.

Figure 13: Overlay of refractive index detector signals during equilibration following a column change using the column switching valve (blue) and without use of the column switching valve (red)

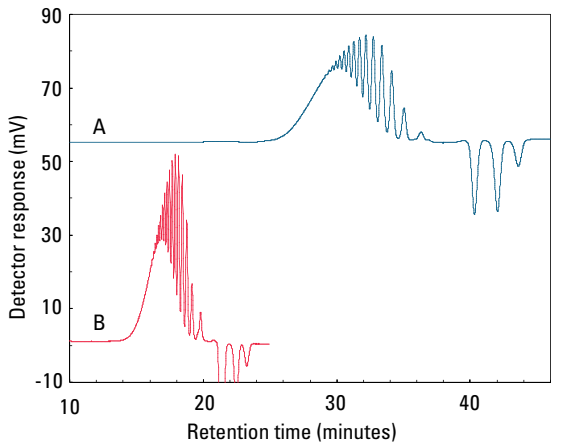


Increased Throughput and Lower Solvent Costs

Minimal extra-column band broadening is required to take full advantage of the highest efficiency GPC columns. The EcoSEC GPC System is engineered to minimize system dead volume. The semi-micro design allows the use of GPC columns with smaller ID (4.6 mm) and shorter lengths (15 cm) such as the TSKgel SuperMultiporeHZ columns. Together with a small stroke volume pump and a 2.5 µL RI flow cell, the EcoSEC GPC System allows accurate and precise molar mass measurements, particularly when benefiting from state-of-the-art column technology.

As shown in Figure 14, when run on the EcoSEC GPC System, the TSKgel SuperMultiporeHZ-N (4.6 mm ID × 15 cm) column achieves separation efficiency equivalent to that of a conventional high speed column (7.8 mm ID × 30 cm), but analysis time is reduced to half that of a conventional column and one-sixth the amount of solvent is consumed.

Figure 14: Comparing semi-micro and conventional GPC columns



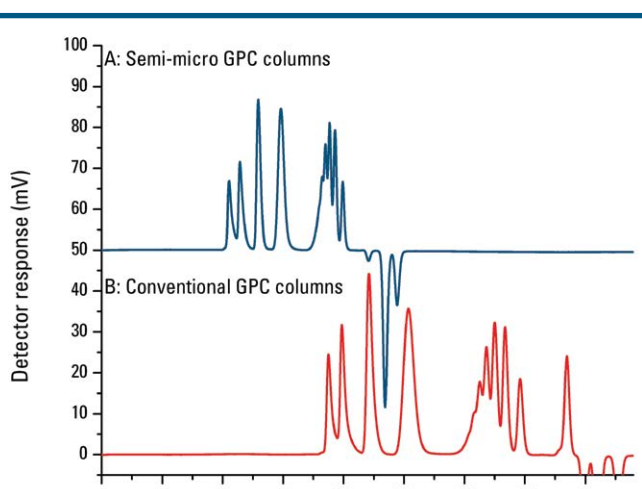
Columns:	A. Conventional columns, 7.8 mm ID × 30 cm × 4 **B. TSKgel SuperMultiporeHZ-N, 3 µm, 4.6 mm ID × 15 cm × 4**
Mobile phase:	THF
Flow rate:	A. 1.0 mL/min B. 0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	A. 50 µL B. 10 µL
Sample:	poly(teramethylene ether glycol)(PTMEG 650), 10 g/L

A comparison of chromatograms obtained from conventional and semi-micro TSKgel HXL and SuperHZ series columns are shown in Figures 15 and 16. TSKgel HXL and SuperHZ series columns have similar separation performance, solvent compatibility, stationary phase composition, and column efficiency. The differences between the two column series are particle size and column length.

A direct comparison between chromatograms obtained, under optimal operating conditions for each column length, for a mixture of polystyrene standards ranging in molar mass from 530 to 2.9 × 10^6 g/mol are shown in Figure 15. The resolution obtained via both column sets is virtually identical, the monomer, dimer, trimer, and tetramer of the lowest molar mass standard, 530 g/mol, can all be identified on both column lengths. Separation of the polystyrene standards using semi-micro GPC columns, Figure 15A, occurs in less than thirty minutes, approximately half the time required to obtain an identical separation using conventional GPC columns, Figure 15B.

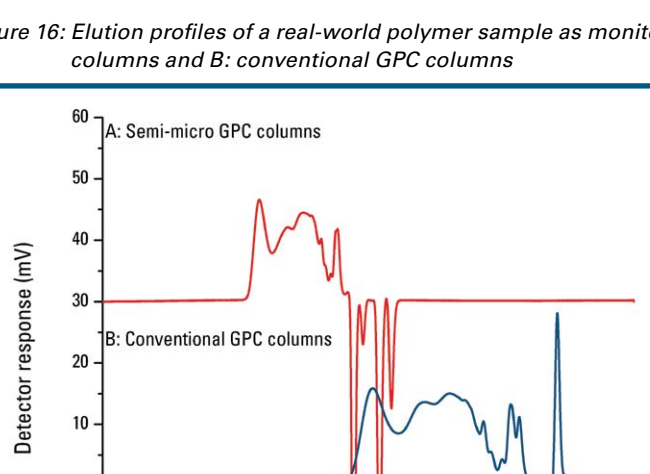
The GPC chromatogram of a real world polymer sample composed primarily of propylene glycol monomethyl ether acetate as obtained using the EcoSEC GPC System with semi-micro and conventional GPC columns was also compared. As can be seen in Figures 16A and 16B, a slight increase in resolution is observed towards the low molar mass, longer retention time region of the GPC chromatogram obtained using conventional GPC columns compared to semi-micro GPC columns. The combination of the low dead volume of the EcoSEC GPC System and the semi-micro GPC columns allowed for complete analysis in approximately 25 minutes, whereas analysis using conventional columns and the EcoSEC GPC System required an analysis times close to 45 minutes.

Figure 15: Elution profiles of polystyrene standards as monitored by RI on the EcoSEC GPC System with A: semi-micro GPC columns and B: conventional GPC columns



A Columns:	**TSKgel SuperHZ1000, SuperHZ2000, SuperHZ3000, SuperHZ4000, 3 µm, 4.6 mm ID × 15 cm**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	UV @ 248 nm, RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	30 µL
Samples:	polystyrene standards, PStQuick MP-M series
B Columns:	**TSKgel G1000HXL, G2000HXL, G3000HXL, G4000HXL, 5 µm, 7.8 mm ID × 30 cm**
Mobile phase:	THF
Flow rate:	1.0 mL/min
Detection:	UV @ 248 nm, RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	150 µL
Samples:	polystyrene standards, PStQuick MP-M series

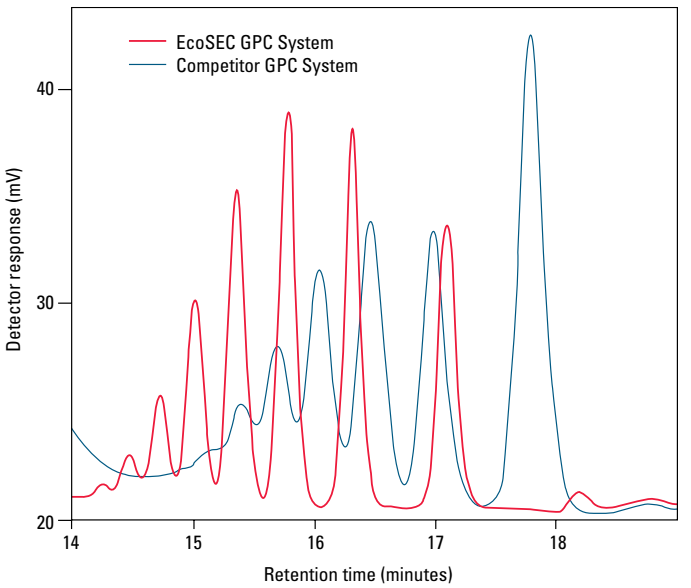
Figure 16: Elution profiles of a real-world polymer sample as monitored by RI on the EcoSEC GPC System with A: semi-micro GPC columns and B: conventional GPC columns



A Columns:	**TSKgel SuperHZ1000, SuperHZ2000, SuperHZ3000, SuperHZ4000, 3 µm, 4.6 mm ID × 15 cm**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	UV @ 248 nm, RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	30 µL
Sample:	real world polymer sample
B Columns:	**TSKgel G1000HXL, G2000HXL, G3000HXL, G4000HXL, 5 µm, 7.8 mm ID × 30 cm**
Mobile phase:	THF
Flow rate:	1.0 mL/min
Detection:	UV @ 248 nm, RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	150 µL
Sample:	real world polymer sample

Figure 17 shows an example of an oligomer (A-500) separation using four TSKgel SuperHZ2000 GPC columns in tandem on an EcoSEC GPC System and a conventional GPC system. A faster analysis and improved resolution is achieved with the EcoSEC GPC System as a result of the advanced engineering design of the system.

Figure 17: Comparison of resolution of a semi-micro column run on an EcoSEC GPC System and a conventional GPC system



Column:	**TSKgel SuperHZ2000, 3 µm, 4.6 mm ID × 15 cm × 4**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	styrene oligomer (A-500), 0.2 g/L

The combination of the EcoSEC GPC System and semi-micro columns provides significant solvent related cost savings while doubling sample throughput without compromising resolution. As shown in Table 2, the solvent related cost savings are extraordinary for samples requiring expensive solvents such as hexafluoroisopropanol.

Table 2: Annual solvent cost saving with semi-micro columns and the EcoSEC GPC System

Solvent	Competitive GPC System	EcoSEC GPC System	Savings
Chloroform ($17/L)	$1,830	$295	$1,535
DMF* ($25/L)	$2,600	$416	$2,184
NMP* ($30/L)	$3,082	$493	$2,589
THF* ($40/L)	$4,160	$666	$3,494
HFIP* ($1,000/L)	$96,493	$15,439	$81,054

* DMF: dimethylformamide; NMP: N-methylpyrrolidone; THF: tetrahyrofuran; HFIP: hexafluoroisopropanol

EcoSEC GPC System Specifications

Pump	Specification
Flow rate	0.010 to 2.000 mL/min in 0.001 mL/min steps
Accuracy	± 2%
Precision	± 0.2%
Maximum pressure	25 MPa or 3,500 psi
Safety features	Liquid supply stops if pressure rises above the upper limit or drops below the lower limit, Plunger drive count monitoring, Pan for liquid leakage
Stroke volume	7.51 µL
Auto-injector	
Injection volume	1 to 1,500 µL in 1 µL increments
Number of samples	100, 2 mL injection vials
Column Oven	
Temperature range	Ambient plus 10 °C to 60 °C
Capacity	7.8 mm ID × 30 cm × 8 columns
Accuracy	± 0.5 °C
Precision	± 0.2 °C
RI Detector	
Type	Bryce (dual flow type), Tungsten light source (1.00-1.80 RI range)
Optics	Deflection
Cell volume	2.5 µL
Cell pressure limit	0.5 MPa
Noise	2×10^{-9} RIU
Drift	1×10^{-7} RIU/h (THF, 1.0 mL/min)
Dynamic range	$\pm 2.5 \times 10^{-4}$ RIU
Temperature control	Off, 35 °C, 40 °C, 45 °C
Analog out	For connection to third party light scattering and viscometry detectors
Safety features	Leak sensor and thermal fuse for circuit block
Instrument	
Dimensions	680 (W) × 500 (D) × 550 (H) mm = 2.2′ x 1.6′ x 1.8′
Weight	95 kg = 210 lbs
Dead volume	<20 µL


EcoSEC

Unparalleled Versatility

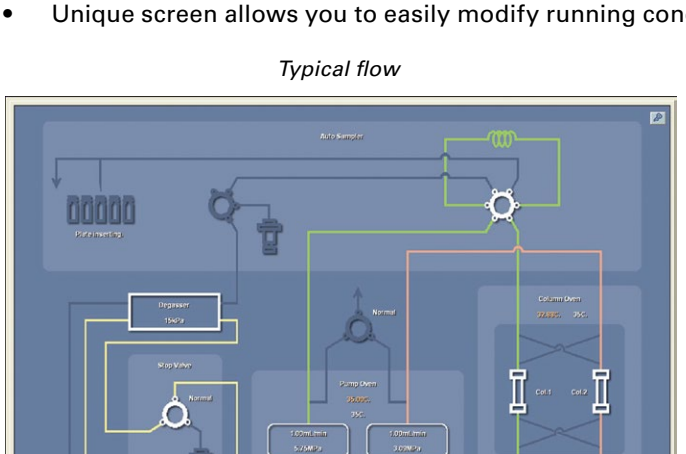
- GPC-specific EcoSEC GPC System software to simplify system control and data handling
- Controls up to 2 EcoSEC GPC Systems
- Excellent data handling and report generation
- Fully featured data handling system; analyze data from two detectors
- Start and stop system automatically
- One license for multiple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

Features include:

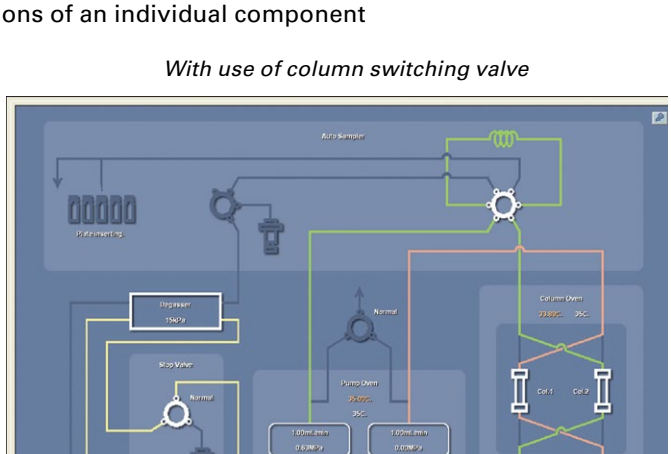
Flow Diagram

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

Typical flow

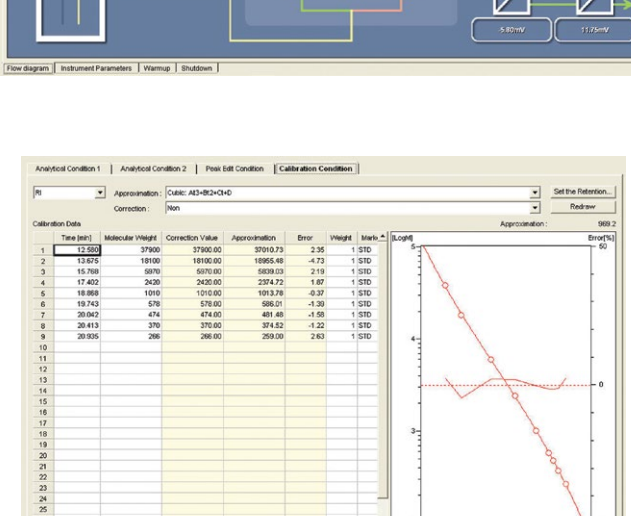


With use of column switching valve



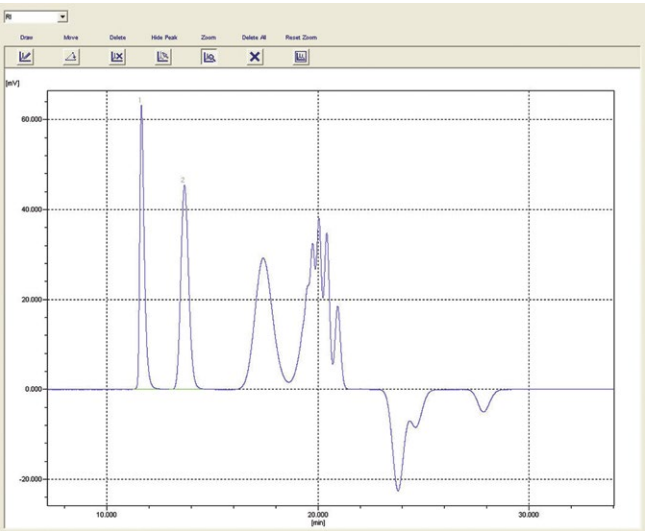
Method

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



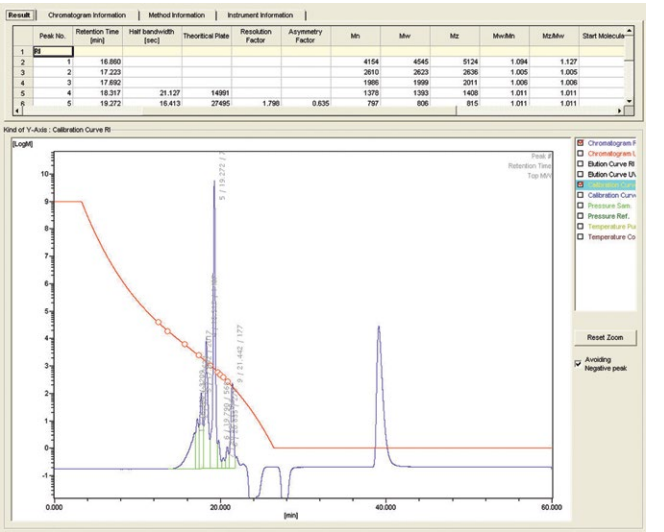
Peak Editing

- Full editing functionality including baseline setting and peak splitting using the mouse
- Automated peak editing



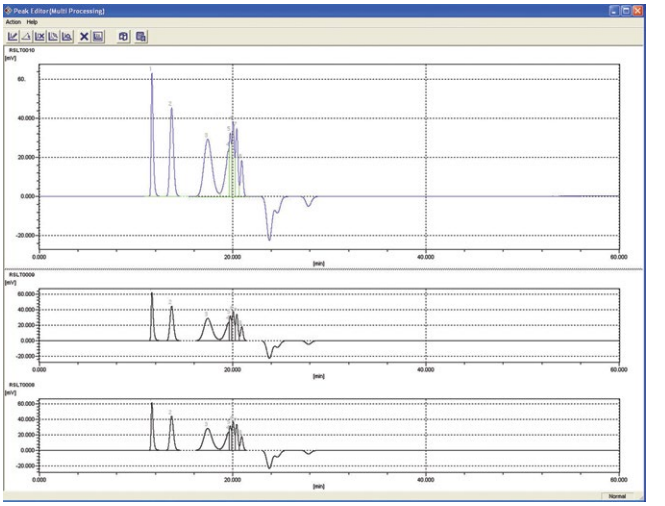
Data Management

- Allows viewing of chromatograms, elution curve, flow rate, pressure, and temperature



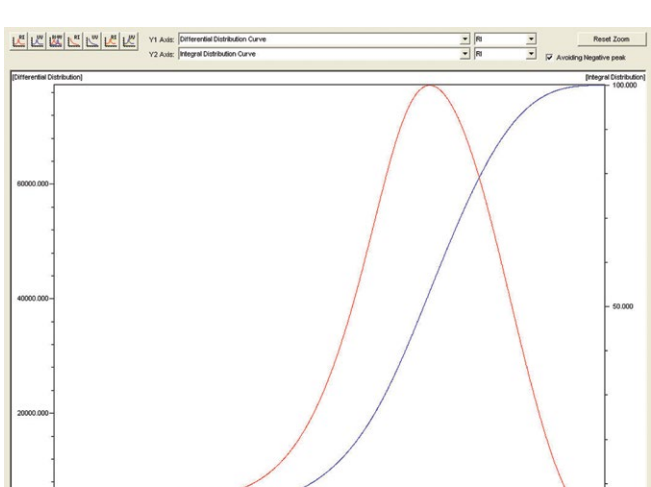
Multiprocessing Function

- Automatically applies exact set of peak detection and integration parameters to all chromatograms in a list
- Similar chromatograms are processed identically for enhanced reproducibility



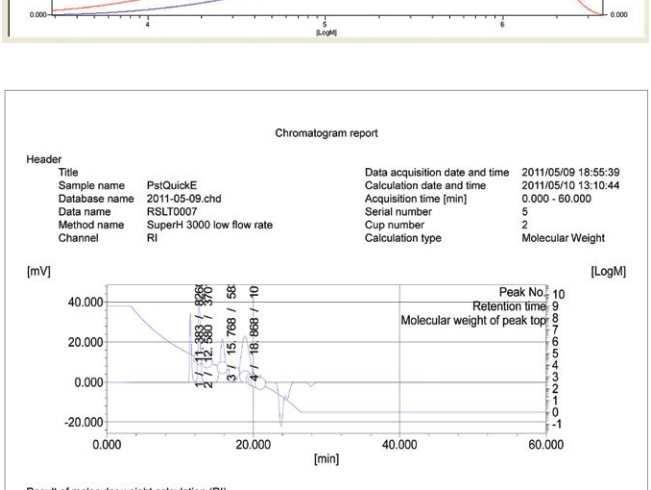
GPC Specific Quantitative Calculations

- M_n, M_w, and M_z molar mass averages
- Cumulative and differential molar mass plotting



Report Generation

- Large number of built in reports
- Customizable reports
- Easily export data into text or pdf files



Chromatogram report

Header

Title			
Sample name	PstQuickE	Data acquisition date and time	2011/05/09 18:55:39
Database name	2011-05-09.chd	Calculation date and time	2011/05/10 13:10:44
Data name	RSLT0007	Acquisition time [min]	0.000 - 60.000
Method name	SuperH 3000 low flow rate	Serial number	5
Channel	RI	Cup number	2
		Calculation type	Molecular Weight

[mV] [LogM]

40.000
20.000
0.000
-20.000
0.000
20.000
40.000
60.000
[min]
Peak No.
Retention time
Molecular weight of peak top
10
9
8
7
6
5
4
3
2
1
0
-1

Result of molecular weight calculation (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	10.902	-0.101	117,191	Mn	78,936
Peak top	11.383	34.209	82,600	Mw	79,604
Peak end	12.147	0.040	49,010	Mz	80,212
				Mz+1	80,770
				Mv	79,604
Height [mV]			34.307	Mp	82,600
Area [mV*sec]			530.161	Mz/Mw	1.008
Area% [%]			12.045	Mw/Mn	1.008
[eta]			79603.68576	Mz+1/Mw	1.015

Software Specifications

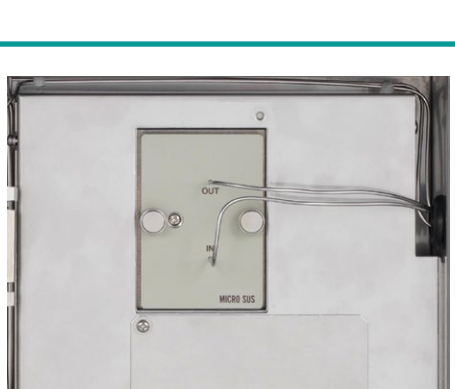
Feature	Description
Software	Provided on CD-ROM
Data acquisition	2-channel (RI,UV)/1-system USB connection
Acquisition time	0.0 to 999.9 minutes
Acquisition interval	50 ms or more (10 ms steps) Upper limit: 1000 ms
Acquisition rate	1 Hz to 20 Hz
Calibration curve approximation	• First-degree expression • 3rd-degree expression • 3rd-degree expression + hyperbola • 5th-degree expression • 7th-degree expression • 7th-degree expression (odd power) • 7th-degree expression (odd power) + hyperbola
Calibration curve correction	• Mark-Houwink • Q factor • Polymerization degree • USP
Quantitative calculation specific to GPC	• Molar mass averages (M_n, M_w, and M_z) • Polydispersity Index (*PDI*) • Cumulative/differential molar mass distributions • Concentration ratio
Special calculation function	• Internal standard correction function • Copolymer analysis • Molar mass fraction specific calculation • Calculation range specification • Lag time correction
Column test	• Theoretical plate number • Resolution • Symmetry factor • Half bandwidth
Calculation standard	• ASTM® • DIN® • USP • JIS • JP • ISO 16014 • Tosoh Standard
FDA 21 CFR Part 11	Software validation, authentication by user ID and password, log out, and audit trail
Warm up and shut down timers	• Daily • Weekly
RI and UV detector auto balance	Optional prior to injection

The standard EcoSEC GPC System consists of the following:

- EcoSEC GPC System instrument
- EcoSEC GPC Workstation Software
- Dual flow RI detector
- Optional 2-way column switching valve (see page 12)
- Optional UV detector

UV Detector

- Variable UV; 195 – 350 nm
- Semi-micro flow cell (2 µL)
- Factory installed option



The optional UV detector is variable from 195 to 350 nm and the detector flow path and electronics are optimized for the use of semi-micro columns. The volume of the flow cell is reduced to 2 µL and the shortest time constant is 0.5 seconds.

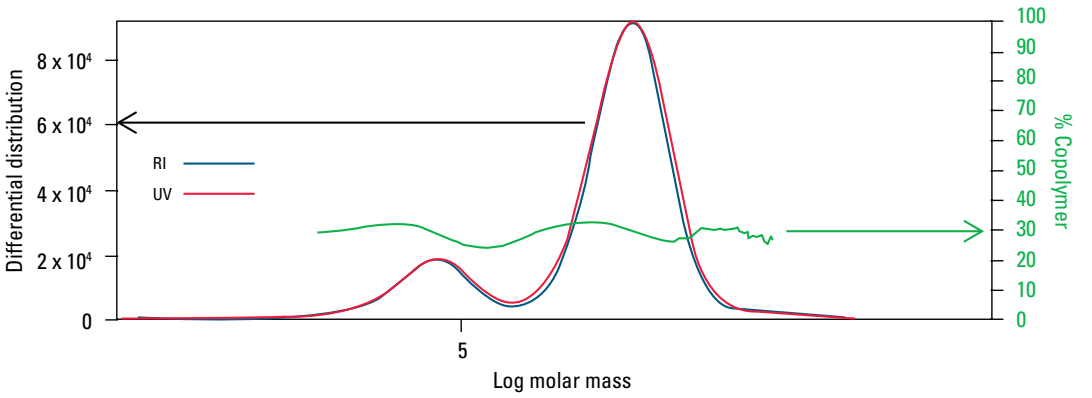
UV Detector Specifications

UV Detector	Specification
System	Dual beam, single flow cell
Light source	Deuterium lamp
Wavelength range	195 to 350 nm
Wavelength accuracy	± 2 nm
Bandwidth	8 nm
Range (FS)	0.5, 1, 2, 4 AU/1 V
Response	0.5, 1.0, 3.0 seconds
Drift	3 x 10^{-4} AU/h (254 nm, air in cell, response: 1.0 s)
Noise	2.5 x 10^{-5} AU (254 nm, air in cell, response: 1.0 s)
Flow cell volume	2 µL
Safety mechanism	Liquid leakage sensor; lighting time monitoring

Copolymer Analysis

The EcoSEC GPC System equipped with both RI and UV detectors can be used to determine the structural composition of an unknown copolymer, 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 final result is a plot of the structural composition at each molar mass. This composition curve overlaid on the chromatogram, as seen in Figure 1, can be generated using the EcoSEC GPC Workstation Software. The software allows for the creation and use of separate UV and RI specific calibration curves while correcting for the inter detector delay volume.

Figure 1: Copolymer analysis of polystyrene-b-polybutene



Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI, UV @ 254 nm (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	10 µL
Samples:	PS-*b*-PB, 0.2 wt%

Enhanced EcoSEC GPC System Analysis

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 or UV detection
- Copolymer compositional drift with RI and UV detection
- Universal calibration, intrinsic viscosity and viscometric radius with viscometry detection
- Absolute molar mass averages and radius of gyration with multi-angle light scattering (MALS) detection
- Hydrodynamic radius determination with quasi-elastic light scattering (QELS) detection

Summary of Detector Capabilities

Detector	Molar Mass Determination	Detects Most Polymers	Required For Copolymer Composition Analysis
RI	Relative	Yes	Yes
UV	Relative	No	Yes

Static Light Scattering Detectors

Detector	Measuring angle(s) (deg)	Molar Mass Range (g/mol)*	Radius of Gyration (R_G) range (nm) *
Low Angle Light Scattering (LALS)	7	$<10^3$ to $>10^7$	10 to 50 (only if combined with RALS)
Right Angle Light Scattering (RALS)	90	$<10^3$ to 10^5 (up to 10^6 if combined with viscometer)	N/A if used alone (calculated from Flory-Fox equation if combined with viscometer)
Multi Angle Light Scattering - 2 Angle	15, 90	$<10^3$ to 10^6	10 to 50
Multi Angle Light Scattering - 3 Angle	45, 90, 135	$<10^3$ to $>10^6$	10 to 50
Multi Angle Light Scattering - 7 Angle	35 to 145	$<10^3$ to $>10^6$	10 to 200
Multi Angle Light Scattering - 8 Angle	23 to 155 (solvent dependent)	$< 10^3$ to 10^7	10 to 200
Multi Angle Light Scattering - 9 Angle	28 to 156	$<10^3$ to 10^7	10 to 200
Multi Angle Light Scattering - 18 Angle	15 to 160 (solvent dependent)	$<10^3$ to $>10^7$	10 to 500
Multi Angle Light Scattering - 20 Angle	12 to 164	$<10^3$ to $>10^7$	10 to 500

**Sample dependent*

Viscometry Detectors

Detector	Split Ratio	Applicable to GPC/SEC	Obtainable Measurements
Single Capillary Viscometer	N/A	No	Relative viscosity
4-Capillary Differential Viscometer	50/50	Yes	• Intrinsic viscosity distribution • Molar mass distribution via universal calibration • Hydrodynamic radius • Mark-Houwink plots • Branching information • Conformation
4-Capillary Differential Viscometer	80/20	Yes	

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.

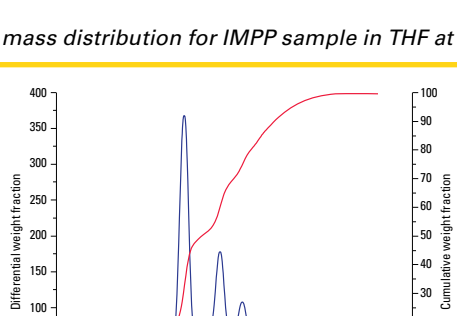
Contact us for a quote!

Molar Mass Measurements of an Isocyanate Modified Polyurethane Prepolymer in Less than 1 Hour with the EcoSEC GPC System

Isocyanates are both highly reactive and highly toxic low molar mass chemicals. One common technique used to take advantage of isocyanate reactivity while eliminating safety concerns is to synthesize polyurethane prepolymers for use in subsequent polymerizations. An EcoSEC GPC System encompassing a refractive index detector was used to perform size exclusion chromatography analysis on a isocyanate modified polyurethane prepolymer (IMPP) sample composed of 54% urethane prepolymer, 11.5% dimethyl sulfoxide (DMSO), and 34.5% 1,1,1,3,3 pentafluoropropane. The low dead volume of the EcoSEC GPC System combined with the use of semi-micro TSKgel GPC columns allowed for the successful determination in less than 30 minutes of the molar mass averages and polydispersity of the IMPP sample.

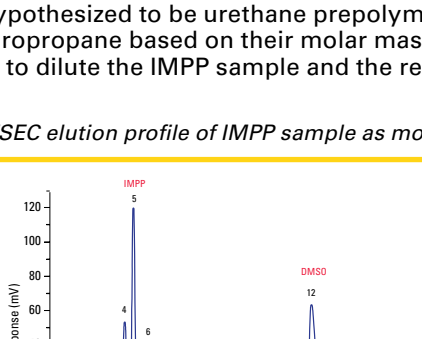
The polydispersity index, PDI = M_w/M_n, for the entire urethane prepolymer sample including 1,1,1,3,3 pentafluoropropane (peaks 1 through 9) was 2.26, while the nine individual components had PDI values ranging from 1.01 to 1.09. From the PDI values it can be concluded that collectively the sample is polydisperse with respect to molar mass but the nine visible components within the IMPP sample are virtually monodisperse with respect to molar mass. The molar mass distribution for the IMPP sample, as obtained at 0.3 mL/min, is shown in Figure 1.

Figure 1: Cumulative and differential molar mass distribution for IMPP sample in THF at 0.3 mL/min



The molar mass averages and polydispersity index of the IMPP sample was determined using a polystyrene relative calibration curve. Analysis of the IMPP was initially performed at a flow rate of 0.3 mL/min (the lowest recommended flow rate for the TSKgel SuperH3000 columns) and total analysis was achieved in 45 minutes. In order to increase the throughput of the EcoSEC GPC System the flow rate was increased to 0.6 mL/min (the highest recommended flow rate for the TSKgel SuperH3000 columns). The chromatogram of the IMPP displayed twelve distinctive peaks, as shown in Figure 2. Peaks 1 through 5 were determined to be the urethane prepolymer component of the IMPP and found to have a weight average molar mass ranging from 4,199 to 798 g/mol. The identity of peaks 6 through 9 were not confirmed but are hypothesized to be urethane prepolymer, unreactive species from the synthesis of the sample or 1,1,3,3 pentafluoropropane based on their molar mass range, M_w = 551-178 g/mol. Peaks 10 and 11 and peak 12 are due to the THF used to dilute the IMPP sample and the residual DMSO in the IMPP sample, respectively.

Figure 2. FSEC elution profile of IMPP sample as monitored by RI (blue) at 0.6 mL/min in THF at 35 °C



Column:	**TSKgel SuperH3000, 3 µm, 6.0 m ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.6 mL/min
Detection:	RI (EcoSEC GPC system)
Temperature:	35 °C
Injection vol.:	20 µL
Sample:	IMPP

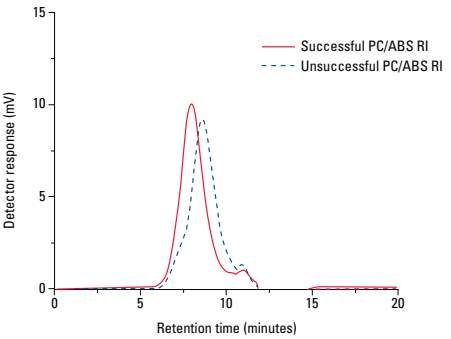
An Approach to Failure Analysis of PC/ABS Resins Used in Automobile Parts: Molar Mass Determination via Gel Permeation Chromatography

For polymeric materials the molar mass and molar mass distribution plays a vital role in the determination of mechanical, bulk, and solution properties. These properties govern polymer processing and the end-use performance of a given material[1,2]. The difference between a successful and unsuccessful polymer based material can be determined by observing the molar mass and molar mass distribution of the polymer(s) encompassing the end-use material. One polymeric material of particular interest to the automotive industry is an alloyed grade thermoplastic: polycarbonate acrylonitrile-butadiene-styrene (PC/ABS). An EcoSEC GPC System encompassing a dual flow refractive index (RI) detector was implemented to perform failure analysis on two PC/ABS automobile parts. The use of GPC for the failure analysis allowed for determination of the molar mass averages, molar mass distributions, and a comparison of successful and unsuccessful PC/ABS automobile parts.

The molar mass averages of two samples, successful and unsuccessful PC/ABS, were determined via GPC. The successful product was shown to perform up to standards while the unsuccessful product failed at some point during production or usage. The dual-detector GPC experiments provide two forms of comparison between the successful and unsuccessful PC/ABS automobile parts: GPC chromatograms and polystyrene relative molar mass averages and distributions.

The chromatograms of the successful and unsuccessful PC/ABS as monitored by the RI detector is shown in Figure 3. The successful PC/ABS sample elutes prior to the unsuccessful PC/ABS. The shorter retention time of the successful PC/ABS indicates that the successful PC/ABS sample is larger in polymeric size than the unsuccessful PC/ABS sample. Thus, the GPC chromatogram alone provides sufficient indication that the successful and unsuccessful PC/ABS samples are different from one another.

Figure 3. GPC elution profile of successful and unsuccessful PC/ABS automobile parts as monitored by RI



Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC system)
Temperature:	35 °C
Injection vol.:	10 µL
Sample:	PC/ABS at 1 g/L

The results of the experiments, in the form of polystyrene relative molar mass averages, are given in Table 1. The successful PC/ABS sample was determined to have a significantly higher number-, weight-, and z-average molar mass than the unsuccessful PC/ABS sample. The number-average molar mass, M_n, varies the greatest between the two samples, as M_n of the successful product is nearly twice that of the unsuccessful product. For PC/ABS, the molar mass averages directly influence the toughness and melt viscosity of the end-use material. Higher molar mass PC/ABS is tougher than their lower molar mass counterparts; thus, explaining one reason why the unsuccessful PC/ABS failed in the end-use material; the lower the molar mass, the weaker the end-use material.

Table 1. Molar mass averages and polydispersity index of successful and unsuccessful PC/ABS automobile parts

Sample (Detection Method)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI_a
Successful PC/ABS (RI)	$1.100 \times 10^4 \pm 335^b$	$5.199 \times 10^4 \pm 752$	$1.339 \times 10^5 \pm 3{,}072$	4.73 ± 0.08
Unsuccessful (RI)	$6{,}064 \pm 35$	$3.036 \times 10^4 \pm 260$	$1.259 \times 10^5 \pm 1{,}465$	5.01 ± 0.02

[a] PDI = M_w/M_n ; [b] Standard deviations from six injections

The use of the EcoSEC GPC System for failure analysis of PC/ABS resins used in automobile parts allowed for immediate differentiation between the successful and unsuccessful PC/ABS samples based on the GPC elution profile. This differentiation was then confirmed through observed differences in the polystyrene relative molar mass averages of the successful and unsuccessful PC/ABS samples.

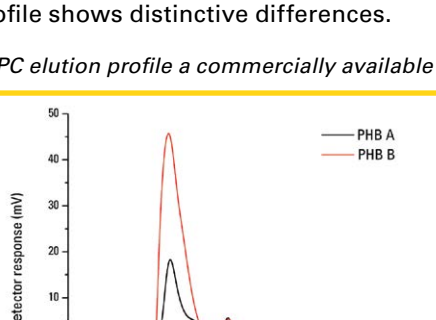
[1]Striegel, A.M.; Yau, W.W.; Kirkland, J.J.; Bly, D.D. Modern Size-Exclusion Liquid Chromatography 2nd ed; Wiley: New York, 2009.
[2]Mori, S.; Barth, H.G. Size Exclusion Chromatography; Springer: New York, 1999.

Characterization of a Plastic Alternative via Gel Permeation Chromatography: Polyhydroxybutyrate

During the past several decades there have been many promising developments of eco-friendly plastics. One promising biodegradable substitute for plastics that is not made from petroleum but from renewable resources is a biopolymer known as polyhydroxybutyrate or PHB. The use of PHB in commercial products is reliant on the development of low cost processes that produce biodegradable plastics with properties similar or superior to their petrochemical counterparts. Once a process for the production of PHB is developed, the physicochemical properties of the PHB must be characterized, as variations in properties such as the molar mass, will dictate how the biodegradable plastics performs compared to the petrochemical plastic. The chemical and thermal properties of PHB are typically analyzed using a collection of methods. The use of an EcoSEC GPC System encompassing a dual flow refractive index detector was implemented to determine the molar mass averages and molar mass distribution of two PHB polymers produced from different processes (commercially available and homemade).

The GPC chromatograms of the commercially available and the homemade PHB samples as monitored by the RI detector are shown in Figure 4. The commercially available PHB sample (PHB A) elutes prior to the homemade PHB sample (PHB B). The slightly shorter retention time of the PHB A sample indicates that the commercially available PHB is larger in polymeric size than the homemade PHB; 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 column prior to the smaller analytes. In addition to variations in elution time amongst the two samples, the shape of the GPC elution profile shows distinctive differences.

Figure 4. GPC elution profile a commercially available PHB sample (PHB A) and a homemade PHB sample (PHB B) as monitored by RI



Column:	**TSKgel SuperHZM-M, 3 & 5 µm, 4.6 mm ID × 15 cm × 2**
Mobile phase:	Chloroform
Flow rate:	0.30 mL/min
Detection:	RI (EcoSEC GPC system)
Temperature:	35 °C
Injection vol.:	25 µL
Sample:	polyhydroxybutyrate (PHB) at 1g/L

The molar mass averages, M_n , M_w , and M_z, as determined via a polystyrene RI calibration curve are given in Table 2. The molar mass averages of the commercial available PHB (PHB A) and the homemade PHB (PHB B) are in agreement with the variations seen in the GPC elution profile, as the molar mass averages for PHB A are slightly less than those of PHB B. The polydispersity of the commercially available PHB, PHB A, is nearly double that of homemade PHB, PHB B, PDI=8.744 and PDI=4.863 for PHB A and PHB B, respectively (Table 2). The ability to determine variations in the molar mass averages and molar mass distributions of PHB is essential, as it can affect the thermoplasticity and biodegradability of the plastic.

Table 2. Molar mass averages and polydispersity index of a commercially available PHB sample (PHB A) and a homemade PHB sample (PHB B)

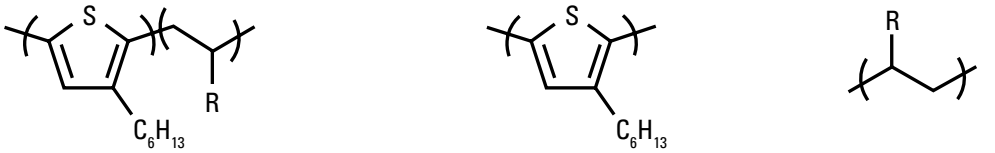
Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI_a
PHB A	$8.22 \times 10^4 \pm 0.49^b \times 10^4$	$7.17 \times 10^5 \pm 0.01 \times 10^5$	$1.44 \times 10^6 \pm 0.01 \times 10^6$	8.74 ± 0.38
PHB B	$2.15 \times 10^5 \pm 0.14 \times 10^5$	$1.04 \times 10^6 \pm 0.01 \times 10^6$	$2.00 \times 10^6 \pm 0.01 \times 10^6$	4.86 ± 0.30

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

Analysis of gradient copolymers using the EcoSEC GPC System

Gradient sequence copolymers are novel materials which have provoked interest due to their unique properties compared to their random, alternating and block equivalents. Unlike block copolymers which have an abrupt change in sequence, gradient sequence copolymers exhibit a gradual change in co-monomer composition from one type of monomer to another. An example of a gradient copolymer is poly(3-hexylthiophene-b-[1-hexane]), Figure 5, which is composed of poly(3-hexylthiophene) and poly(1-hexene).

Figure 5. Example of a gradient copolymer



poly(3-hexylthiophene-b-[1-hexene]) poly(3-hexylthiophene) poly(1-hexene)

The ability to characterize the molar mass averages and distributions of a π-conjugated gradient copolymer is critical for designing polymer blends as molar mass averages and distributions affect the phase separation of polymer blends. An EcoSEC GPC System housing a dual flow refractive index detector was used to perform gel permeation chromatography analysis on poly(3- hexylthiophene-b-[1-hexane]), poly(3-hexylthiophene) and poly(1-hexene). The GPC elution profiles and molar mass averages of the copolymer and homopolymer were obtained in less than fifteen minutes with the use of the EcoSEC GPC System and TSKgel semi-micro GPC columns, thus providing a fast and reliable method for the analysis of copolymers.

The GPC chromatograms of the copolymer, poly(3-hexylthiophene-b-[1-hexane]), and the two homopolymers, poly(3-hexylthiophene) and poly(1-hexene) are shown in Figures 6-8, respectively The copolymer, poly(3-hexylthiophene-b-[1-hexane]), displays a distinctive bimodal distribution while the two homopolymers have a mono-modal distribution. By comparing the retention times of the RI detector response for the three samples the later eluting species seen in Figure 6 has the same retention time as the homopolymer, poly(3-hexylthiophene), in Figure 7. The early eluting species seen in Figure 6 elutes later than that of the other homopolymer, poly(1-hexene) (Figure 8), an indication that the later elution species in Figure 6 is that of the copolymer. The copolymer elutes prior to the homopolymers is an indication that the copolymer is larger in polymeric size than the homopolymers.

Through the comparison of the GPC elution profiles and the molar mass averages of the copolymer, poly(3-hexylthiophene-b-[1-hexane]), and the two homopolymers, poly(3-hexylthiophene) and poly(1-hexene) it can be concluded that the copolymer sample, poly(3-hexylthiophene-b-[1-hexane]), contains copolymer and excess amounts of one of the homopolymers, poly(3-hexylthiophene).

Figure 6. GPC elution profile of the copolymer, poly(3-hexylthiophene-b-[1-hexane], as monitored by the RI (blue) and UV (red)

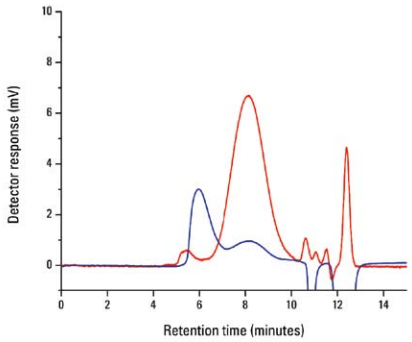


Figure 7. GPC elution profile of homopolymer, poly(3-hexylthiophene), as monitored by the RI (blue) and UV (red)

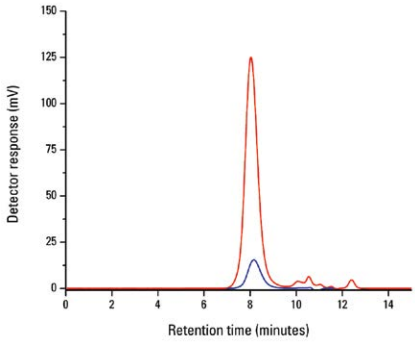
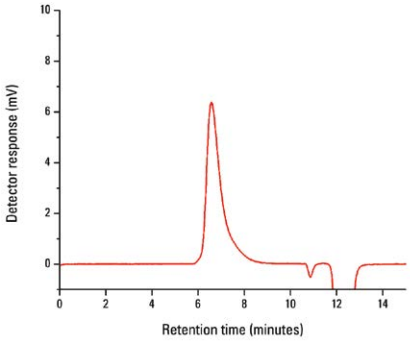


Figure 8. GPC elution profile of homopolymer, poly(1-hexene), as monitored by the RI



Columns:	**TSKgel SuperMultipore × 2 + TSKgel mixed bed x2**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC system)
	UV (EcoSEC GPC system @ 254 and 350 nm)
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	poly(3-hexylthiophene-b-[1-hexane])

Renewable-Based Thermoplastic Polyurethanes

The demand for renewable or bio-based polymers continues to rise exponentially as manufacturers within the automotive, footwear, carpet, and furniture sectors seek to sell more sustainable products. One group of polymers gaining a great deal of interest is thermoplastic polyurethanes or TPUs. A TPU is an elastomer that resembles rubber in consistency and feel but by nature has outstanding abrasion resistance, great low temperature flexibility, resistance to oil, and a high threshold for support weight, in addition to being very bondable, durable, paintable, and impact resistant. The specific end-use properties, such as tensile strength, elongation, conductivity, chemical resistance, and toughness, depends on macromolecular properties such as molar mass, branching, degree of crosslinking, and polymeric size.

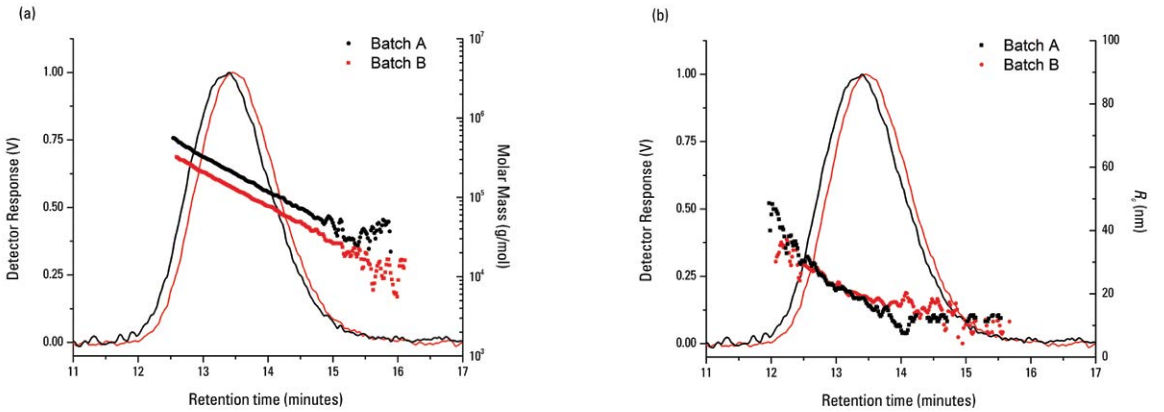
Two different batches of TPUs were characterized based on molar mass and polymeric size using the EcoSEC GPC System coupled to a multi-angle light scattering detector (MALS). The GPC elution profiles of the two samples are shown in Figures 9A and 9B. TPU Batch B elutes after TPU Batch A, indicating that TPU Batch B is slightly smaller in size compared to TPU Batch A.

The size comparison can be done quantitatively as the addition of a MALS detector to the EcoSEC GPC System permits for the determination of a polymeric sizing parameter, the root-mean-square radius or radius of gyration, R_G. Figure 9B shows the R_G distributions as plotted across the GPC elution profile: both curves overlay and the size of the TPUs decreases as a function of increasing retention time, as expected in a size exclusion mechanism. Although the average radius of gyration for both TPUs, A and B, were identical, R_G = 20 nm, the left end of the curves in Figure 9B shows that TPU Batch A does contain slightly more of large polymer species than TPU Batch B.

The molar mass distributions of the two different batches of TPUs were also plotted across the GPC elution profile, Figure 9A. The absolute weight average molar mass, M_w, is slightly higher for A than B, 1.64 × 10^5 and 1.42 × 10^5 g/mol, respectively. From Figure 9A it can be noticed that for any given retention time – and thus polymer size – TPU Batch A has a higher molar mass than TPU Batch B. This shows that the two TPUs have a different structure or conformation in the solvent.

In conclusion, the higher molar mass average of TPU Batch A is not only due to the presence of a small amount of larger species in the distribution, but also to a denser structure or conformation in solution, as compared to TPU Batch B.

Figure 9: Thermoplastic polyurethanes



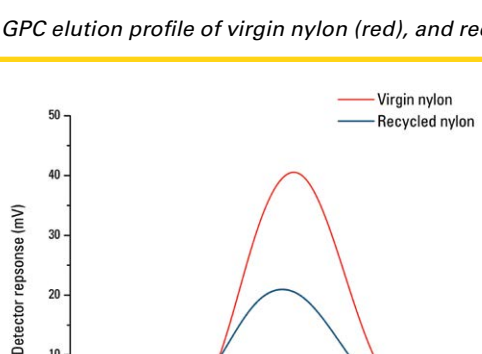
Column:	**TSKgel GMH$_{HR}$-H, mixed bed, 7.8 mm ID × 30 cm × 2**
Mobile phase:	DMF with 0.01% LiBr
Flow rate:	1.0 mL/min
Detectors:	RI (EcoSEC GPC System), MALS (Wyatt DAWN® 8+)
Temperature:	50 °C
Injection vol.:	100 µL
Sample:	thermoplastic polyurethanes

Environmentally Friendly Analysis of Nylon

Green initiatives are continuously approaching the polymer science discipline from all sides as companies are not only interested in greener products and additives but greener and more cost effective synthesis and characterization methods. One class of polymers that is of high interest is polyamides, more specifically nylons, as these plastics are common materials in everyday life which produce large quantities of environmental contaminates.[3] It is critical to be able to characterize virgin and recycled nylon as the recycling process of nylon can result in the reduction of physical-mechanical properties as well as changes in morphology resulting in different end-use properties. A greener and more cost effective method for the characterization of the molar mass averages and distributions of nylon in hexafluoroisopropanol (HFIP) was employed by using an EcoSEC GPC System and semi-micro GPC columns. The combination of the low dead volume of the EcoSEC GPC System and semi-micro GPC columns provides significant solvent related costs while doubling sample throughput without compromising resolution.

The GPC experiments provide two forms of comparison between the virgin and recycled nylon samples: GPC chromatograms and poly(methyl methacrylate) (PMMA) relative molar mass averages and molar mass distributions. The GPC elution profiles of the virgin and recycled nylon as monitored by the RI detector are shown in Figure 10. The virgin nylon elutes after the recycled nylon. The longer retention time of the virgin nylon indicates that the virgin material is slightly smaller in polymeric size compared to the recycled material: as elution order in GPC is that of an "inverse-sieving" technique, smaller analytes elute after the larger analytes.

Figure 10: GPC elution profile of virgin nylon (red), and recycled nylon (blue) as monitored by RI



Column:	**TSKgel SuperAWM-H, 9 µm, 6.0 mm ID × 15 cm × 2**
Mobile phase:	HFIP
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	40 °C
Injection vol.:	20 µL
Samples:	virgin and recycled nylon

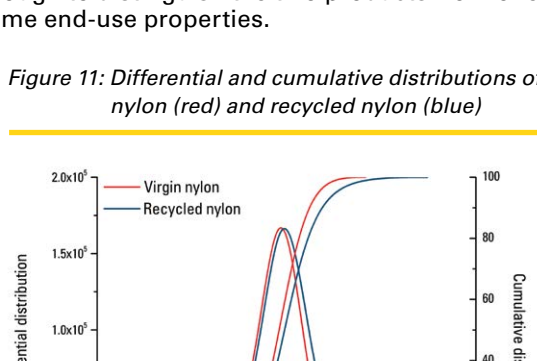
The molar mass averages and polydispersity index, *PDI*, as determined via a PMMA RI calibration curve are given in Table 3. A comparison of the molar mass averages and molar mass distribution, Figure 11, of the virgin nylon material with the recycled nylon material reveals an increase in the molar mass averages and breadth of the distribution curve of the recycled nylon compared to the molar mass averages of the virgin nylon. The molar mass averages and distributions of the virgin and recycled nylon samples obtained by GPC are different enough to distinguish the two products from one another but similar enough to both create successful products with the same end-use properties.

Table 3: Molar mass averages and polydispersity index of nylon samples via RI

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	*PDI*[a]
Virgin nylon	1.22×10^4 ± 46[b]	1.71×10^4 ± 75	2.29×10^4 ± 346	1.41 ± 0.01
Recycled nylon	1.33×10^4 ± 438	2.17×10^4 ± 210	3.93×10^4 ± 1,105	1.62 ± 0.05

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

Figure 11: Differential and cumulative distributions of nylon (red) and recycled nylon (blue)



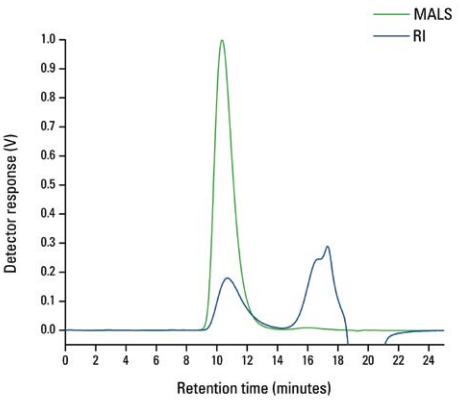
[3]Crespo, J.E; Parres, E.; Peydro, M.A.; Navarro, R. *Polym. Eng. Sci.*, **2013**, 53, 679-688.

Additives and Fillers in Commercial Polymers

Small quantities of additives and fillers are embedded in most commercial polymers in order to obtain certain desirable end-use properties. Typically additives and fillers are added to commercial polymers to improve compatibility of dissimilar elastomers, mixing, processing and surface tack, extrusion rates, appearance, and reinforcement. Commercial polymers can contain a wide variety of additives and fillers, some of which can easily be removed from the commercial polymer through filtering while others may require a separation method such as GPC. The ability to separate a commercial polymer from the various additives and fillers is necessary when analyzing the molar mass averages and distributions of a polymer as the additives and fillers can skew the molar mass averages and distributions.

An EcoSEC GPC System with a dual flow RI detector coupled to a multi-angle light scattering detector (MALS) was used to separate and identify the presence of an additive in a commercial rubber sample. Figure 12 shows the overlay of the GPC traces from the RI and MALS detectors. The RI detector shows two baseline resolved peaks while the MALS detector shows a single peak. The later eluting species, present only in the RI detector, are indicative of the additive, as materials polymeric in nature would be detectable by both the MALS and RI detectors. Additives are generally molecules low in molar mass and approaching the detection limit of the MALS detector (~1,000 g/mol) but present at a fairly high concentration, thus detectable by the concentration sensitive detector.

Figure 12: GPC elution profile of a rubber sample with additives as monitored by RI (blue) and MALS (green)



Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID × 15 cm × 3**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System), MALS (Wyatt DAWN 8+)
Temperature:	35 °C
Injection vol.:	30 µL
Sample:	rubber

The baseline separation of the rubber from the additive allows for the determination of the polystyrene relative molar mass averages of both species and the absolute molar mass averages of the rubber, Table 4. The polystyrene relative and absolute molar mass averages obtained for the rubber are not expected to match, as the polystyrene relative values are dependent on the chemistry and architecture of the sample and standards. The dual detector GPC set-up allows for the identification of the presence of an additive and determination of the molar mass averages of both the rubber and additive within the commercial polymer sample.

Table 4: Molar mass averages and polydispersity index of a rubber sample and additive via RI and MALS

Sample (Detection Method)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
Rubber (RI)	$1.33 \times 10^5 \pm 0.02^b \times 10^5$	$3.10 \times 10^5 \pm 0.02 \times 10^5$	$4.80 \times 10^5 \pm 0.03 \times 10^5$	2.33 ± 0.01
Additive (RI)	455 ± 6	$1.06 \times 10^3 \pm 0.01 \times 10^3$	$2.42 \times 10^3 \pm 0.04 \times 10^3$	2.33 ± 0.02
Rubber (MALS)	$3.98 \times 10^5 \pm 0.39 \times 10^5$	$7.34 \times 10^5 \pm 0.21 \times 10^5$	$1.08 \times 10^6 \pm 0.21 \times 10^5$	1.849 ± 0.126

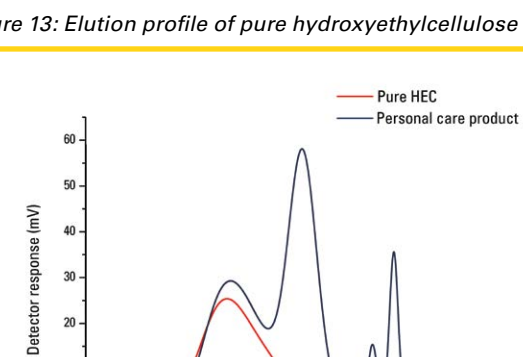
[a] $PDI = M_w/M_n$; [b] Standard deviations from four injections

Polymers in Personal Care Products

Cosmetic and personal care companies are interested in the ability to characterize one of the most highly used non-ionic, water soluble polymers in their formulations, hydroxyethylcellulose (HEC). HEC is derived from cellulose and used in products such as shampoos, body washes, shower gels, and eye drops as it has the ability to thicken solutions and reduce the amount of suds or foam they form. The characterization of pure HEC and HEC within a personal care product was performed utilizing the EcoSEC GPC System with an internal dual flow RI detector and semi-micro columns for polymer analysis in an aqueous mobile phase.

The chromatograms of the pure HEC and the HEC within a personal care product, as monitored by the RI detector, are shown in Figure 13. The elution profile of the pure HEC displays the presence of one species while the personal care product displays a distinctive bimodal distribution in the location of the pure HEC as well as two additional components in the low molar mass region of the chromatogram. The bimodal distribution in the HEC region of the chromatogram for the personal care product could be a result of either two completely different polymer species in the product or the presence of two distinctive size (molar mass) distributions of HEC in the product with the lower molar mass portion of the HEC being present at a higher concentration than the high molar mass portion. The two later eluting species in the chromatogram for the personal care product are two additional components of the product that are significantly smaller in size than the main polymeric components of the product.

Figure 13: Elution profile of pure hydroxyethylcellulose and hydroxyethylcellulose in a personal care product



Column:	**TSKgel SuperMultiporePW-H, 8 µm, 4.6 mm ID × 15 cm × 3**
Mobile phase:	H_2O with 0.1 mol/L $NaNO_3$ and 0.02% NaN_3
Flow rate:	0.50 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol.:	25 µL
Sample:	hydroxyethylcellulose

The polyethylene oxide and polyethylene glycol RI relative molar mass averages of the pure HEC and the HEC within a personal care product are given in Table 5. The molar mass averages for the HEC within the personal care product were shown to vary from that of the pure HEC when the molar mass averages of both components in the HEC region of the chromatogram for the personal care product were determined collectively and separately. The molar mass distribution of the pure HEC and the HEC region of the personal care product indicate a polydisperse polymer as *PDI*=9.82 and *PDI*=12.64 (collectively) or *PDI*= 2.27 and 1.59 (separately), respectively.

Table 5: Molar mass averages and polydispersity index of pure hydroxyethylcellulose and hydroxyethylcellulose in a personal care product

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	*PDI*[a]
Pure HEC	$1.50 \times 10^5 \pm 0.04$[b] $\times 10^5$	$1.47 \times 10^6 \pm 0.01 \times 10^6$	$5.93 \times 10^6 \pm 0.01 \times 10^6$	9.82 ± 0.20
HEC in a personal care product (collectively)	$4.67 \times 10^4 \pm 0.01 \times 10^4$	$5.89 \times 10^5 \pm 0.02 \times 10^5$	$2.78 \times 10^6 \pm 0.06 \times 10^6$	12.61 ± 0.03
HEC in a personal care product (separately)	$5.21 \times 10^5 \pm 0.06 \times 10^5$ $2.69 \times 10^4 \pm 0.07 \times 10^4$	$1.12 \times 10^6 \pm 0.04 \times 10^6$ $4.32 \times 10^4 \pm 0.09 \times 10^4$	$2.47 \times 10^5 \pm 0.16 \times 10^5$ $6.38 \times 10^4 \pm 0.01 \times 10^4$	2.29 ± 0.01 1.61 ± 0.23

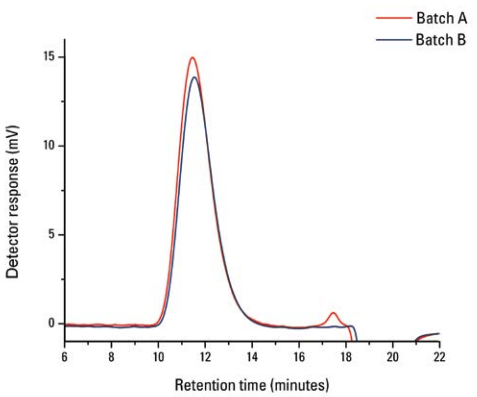
[a] $PDI = M_w/M_n$; [b] Standard deviations from four injections

Utilities of GPC in Industry

One of the primary focuses of the polymer and plastics industries is the ability to differentiate polymers in a sustainable and time effective manner. Currently GPC methods are being used to distinguish polymers based on molar mass or hydrodynamic volume (size) in solution, as GPC is a fast, reliable, and robust method for polymer characterization. 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, the EcoSEC GPC System 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, to name a few.

Some of the utilities of the EcoSEC GPC System in the polymer and plastics industries are shown in Figures 14-16. Figure 14 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 6. 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 essentially constant amongst the two batches.

Figure 14: GPC elution profiles of two different batches of a PMMA based molding resin



Columns:	**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
Detection:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol.:	20 µL
Sample:	PMMA based molding resin

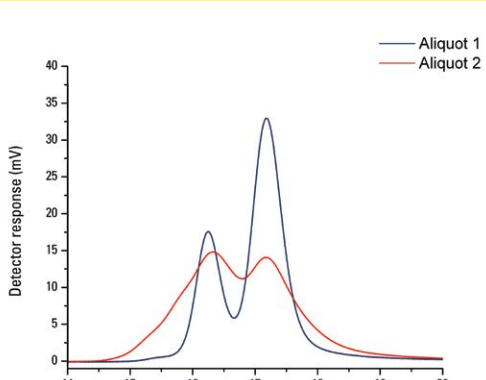
Table 6: Molar mass averages and polydispersity index of two different batches of a PMMA based molding resin

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

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

An example of using the EcoSEC GPC System to monitor a reaction process is shown in Figure 15 by overlaying 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.

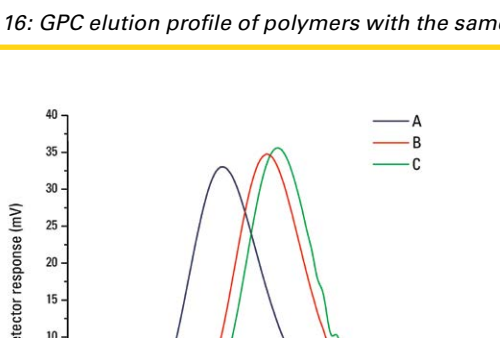
Figure 15: GPC elution profile of aliquots of a reaction collected thirty minutes apart



Column:	**TSKgel GMHXL, 9 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	THF
Flow rate:	1.0 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol.:	100 µL
Sample:	synthetic rubber

The use of the EcoSEC GPC System to distinguish between polymers obtained through different synthesis routes with the same chemical composition but different end-use properties is shown in Figure 16. The GPC elution profile for three polyimide samples shows a variation in retention time, thus also in the molar mass averages, Table 7. While these three polyimide samples are composed of the same chemical composition, the samples are shown to have different end-use properties due to differences in their molar mass averages and molar mass distributions.

Figure 16: GPC elution profile of polymers with the same chemical composition but different end-use properties



Column:	**TSKgel GMHXL, 9 µm, 7.8 mm ID × 30 cm × 2**
Mobile phase:	DMF with 0.02 mol/L LiBr
Flow rate:	1.0 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol.:	100 µL
Sample:	polyimides

Table 7: Molar mass averages and polydispersity index of polymers with the same chemical composition but different end-use properties

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
A	$3.98 \times 10^4 \pm 0.01^b \times 10^4$	$6.47 \times 10^4 \pm 0.01 \times 10^4$	$8.98 \times 10^4 \pm 0.01 \times 10^4$	1.62 ± 0.02
B	$1.86 \times 10^4 \pm 0.01 \times 10^4$	$2.87 \times 10^4 \pm 0.01 \times 10^4$	$3.95 \times 10^4 \pm 0.01 \times 10^4$	1.54 ± 0.01
C	$1.53 \times 10^4 \pm 0.01 \times 10^4$	$2.34 \times 10^4 \pm 0.01 \times 10^4$	$3.20 \times 10^4 \pm 0.01 \times 10^4$	1.52 ± 0.01

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

Polymer-Based Therapeutics

Polymer–based drug and gene delivery systems began to emerge from the laboratory benches about 30 years ago as a promising therapeutic strategy for treatment of devastating human diseases. Polymeric materials are useful for solving drug delivery problems as they are relatively large compared to low molar mass drugs, and when combined with these drugs they can augment the drug's performance and change their bioavailability.[4] The use of synthetic polymers in therapeutics is continuously growing, thus increasing the need for a method to characterize the molar mass averages and molar mass distributions of these polymers as variations in molar mass averages and molar mass distributions can affect aspects of the therapeutic such as in vitro binding activity and biodegradation.[5] The molar mass averages and molar mass distributions of a polymer being used in therapeutics is critical for designing an effective polymer-based therapeutic and is most commonly characterized using GPC.

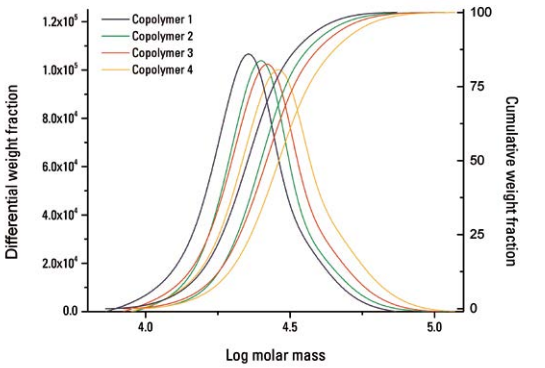
The EcoSEC GPC System was used to determine the molar mass averages and distributions of four block copolymers intended to be used in polymer-based drug or gene delivery systems. The polystyrene relative molar mass averages, M_n, M_w, and M_z, are given in Table 8. The variation of the molar mass averages for the four block copolymers may be great enough to affect the role the polymer plays in the polymer-based therapeutic within the body. For example, the molar mass of the polymer can influence the biodegradation of synthetic polymer in the body, thus resulting in the production of lower molar mass polymer that has different biological effects. In addition to the molar mass averages, the molar mass distribution can also influence various properties of therapeutics. The molar mass distributions of the four block copolymers are compared in Figure 17.

Table 8: Molar mass averages and polydispersity index of four block copolymers for use in a polymer-based therapeutic

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
Copolymer 1	2.09×10^4 $\pm 0.01^b \times 10^4$	2.38×10^4 $\pm 0.01 \times 10^4$	2.70×10^4 $\pm 0.01 \times 10^4$	1.13 ± 0.01
Copolymer 2	2.38×10^4 $\pm 0.01 \times 10^4$	2.64×10^4 $\pm 0.01 \times 10^4$	2.93×10^4 $\pm 0.01 \times 10^4$	1.11 ± 0.01
Copolymer 3	2.48×10^4 $\pm 0.01 \times 10^4$	2.81×10^4 $\pm 0.01 \times 10^4$	3.22×10^4 $\pm 0.01 \times 10^4$	1.14 ± 0.01
Copolymer 4	2.74×10^4 $\pm 0.01 \times 10^4$	3.10×10^4 $\pm 0.01 \times 10^4$	3.55×10^4 $\pm 0.01 \times 10^4$	1.14 ± 0.01

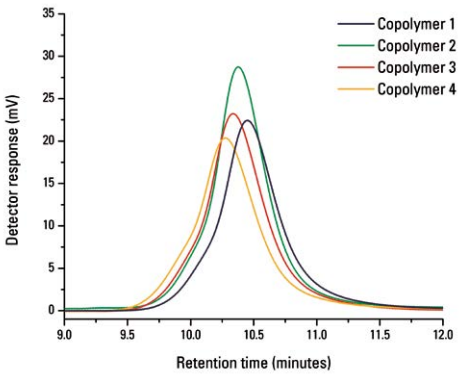
[a] $PDI = M_w/M_n$; [b] Standard deviations from four injections

Figure 17: Overlay of cumulative and differential molar mass distribution of four block copolymers for use in a polymer-based therapeutic



Information regarding the differences between the four block copolymers for use in a polymer-based therapeutic can be seen by comparing their GPC elution profiles, Figure 18. The shift in GPC retention time amongst the four block copolymers indicates a variation in polymeric size between the block copolymers, as elution order in GPC is that of an "inversing-sieving" technique, large analytes sample a smaller pore volume than smaller analytes resulting in the larger analytes eluting from the column prior the smaller analytes. Variations in polymeric size within a polymer-based therapeutic can dramatically affect its behavior within a biological system.

Figure 18: GPC elution profile of four block copolymers for use in a polymer-based therapeutic



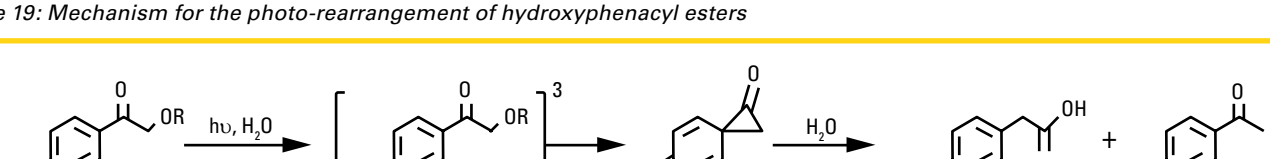
Columns:	**TSKgel SuperHZ4000, 3 µm, 4.6 mm ID × 15 cm + TSKgel SuperHZ3000, 3 µm, 4.6 mm ID × 15 cm + TSKgel SuperHZ2000, 3 µm, 4.6 mm ID × 15 cm**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol.:	10 µL
Sample:	block copolymer

[4]Kabanov, A.V.; Okano, T. Challenges in Polymer Therapeutics. In *Polymer Drugs in the Clinical Stage: Advantages and Prospects*, Volume 519; Maeda, H.; Kabanov, A.V.; Kataoka, K., Okano, T. eds.; Academic Press: New York, 2003; pp 1-20.

Photodegradable Polymer Degradation Analysis

Due to the need for polymers that are both photodegradable and biodegradable, Dr. Abraham Joy and his colleagues at the University of Akron have developed polycarbonate materials based on the alkoxyphenacyl photoactive moiety.[6] This new class of polymers is mechanically robust, biodegradable, and stable to high temperatures in the absence of light with potential applications in controlled drug release devices, ocular implants, and dermal patches. Upon radiation, the photoactive moiety undergoes a Favorski type of rearrangement, resulting in two major products, the phenylacetic acid derivative and the reduced acetophenone (Figure 19).[7]

Figure 19: Mechanism for the photo-rearrangement of hydroxyphenacyl esters



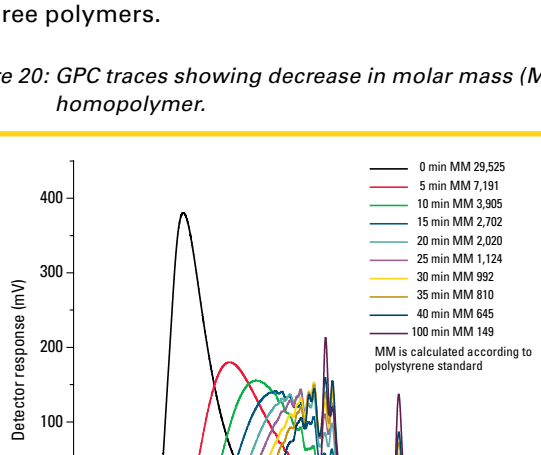
The EcoSEC GPC System was used to determine the polystyrene relative molar mass averages, M_n and M_w, and the polydispersity index, *PDI*, of an alkoxyphenacyl-based polycarbonate homopolymer, 5% PEG copolymer, and 10% PEG copolymer, all given in Table 10. The *PDI*s of the 5% and 10% PEG copolymer are smaller than the *PDI* of the homopolymer because the PEG copolymer samples were fractioned twice and the homopolymer was fractioned only once.

Table 10: Molar mass distributions and polydispersity index for homopolymer and copolymers

Composition	M_n (g/mol)	M_w (g/mol)	*PDI*
Homopolymer	1.29×10^4	2.95×10^4	2.3
5% PEG	2.27×10^4	2.63×10^4	1.2
10% PEG	8,810	1.04×10^4	1.2

Photodegradation of the homopolymer and copolymers was investigated by irradiation of the polymers in chloroform in a Rayonet reactor at 300 nm. Figure 20 shows GPC traces indicating time-dependent degradation with a 75% reduction in average molar mass within 5 minutes of irradiation. Subsequent analysis (data not shown) shows similar degradation for all three polymers.

Figure 20: GPC traces showing decrease in molar mass (M_w) with increasing radiation time for the alkoxyphenacyl-based polycarbonate homopolymer.



Columns:	**TSKgel SuperH3000, 3 µm, 6.0 mm ID x 15 cm x 2 + TSKgel SuperH4000, 3 µm, 6.0 mm ID x 15 cm x 1**
Mobile phase:	chloroform
Flow rate:	0.38 mL/min
Detection:	UV (EcoSEC GPC System @ 278 nm)
Temperature:	40 °C
Injection vol.:	10 µL
Sample:	alkoxyphenacyl polycarbonate homopolymer, 1 - 2 mg/mL

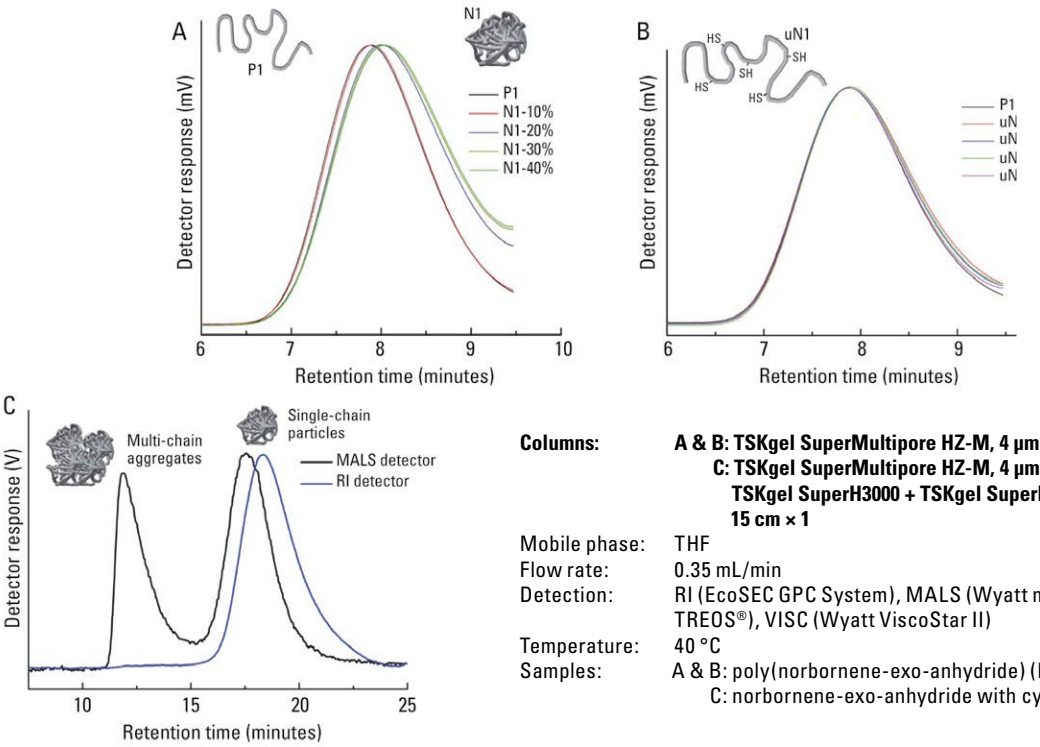
[6]Sun, S.; Chamsaz, E. A.; Joy, A. *Macro Lett.*, **2012**, 1 (10), 1184–1188.
[7]Givens, R. S.; Heger, D.; Hellrung, B.; Kamdzhilov, Y.; Mac, M.; Conrad, P. G.; Cope, E.; Lee, J. I.; Mata-Segreda, J. F.; Schowen, R. L.; Wirz, J. J. *Am. Chem. Soc.* **2008**, 130, 3307-3309.

Single-chain Polymer Nanoparticles

Dr. Erik Berda's research group at the University of New Hampshire is working on the fabrication and characterization of single-chain polymer nanoparticles (SCNPs) that can reversibly undergo a coil to particle transition via formation and cleavage of intramolecular disulfide cross-links.[8] In their initial studies Dr. Berda's group synthesized poly(norbornene-exo-anhydride) (P1), via ROMP using third generation Grubbs catalyst as an initiator and controlled the degree of collapse that occurs during nanoparticle (N1) formation by varying the amount of difunctional cross-linker added. The coil to particle transition was then characterized using the EcoSEC GPC System with dual flow RI via polystyrene relative molar mass averages. Figure 21A shows a series of GPC traces for P1 and its corresponding N1 after various extents of intramolecular cross-linking. As expected, an increase in GPC retention time is observed as the intramolecular cross-linking reaction progresses. This is due to a decrease in hydrodynamic volume that occurs as the coil collapses. Once the folding of the chains into SCNP was confirmed via the GPC retention times, dithiotheritol was introduced to unfold the N1 back to their original conformation. The transition from particle to coil was also confirmed via decreased GPC retention time, signifying an increase in hydrodynamic volume, Figure 21B.

To complement their initial studies Dr. Berda's group synthesized a second polymer, norbornene-exo-anhydride with cyclooctadiene (COD) (P2), to characterize via triple-detector GPC. For the characterization of P2, the EcoSEC GPC System with dual flow RI was coupled to multi-angle light scattering (MALS) and differential viscometry (VISC). The effectiveness of the triple-detector GPC system was highlighted by determining the difference between single-chain and multi-chain behavior. Figure 21C shows an overlay of the MALS and RI traces when the intra-molecular cross-linking reaction was extended with a slight excess of the cross-linker to encourage intermolecular coupling. The RI detector shows a single peak that can be attributed to single-chain particles, while the MALS detector shows two peaks of nearly equal intensity. The later eluting MALS peak corresponds to the single-chain particles while the early eluting peak is that of multi-chain aggregates, which are present at a negligible concentration as indicated by the RI detector. For this particular sample analysis, single-detector GPC would not have revealed the presence of the larger aggregates.

Figure 21: Single-chain polymer nanoparticles



Columns: **A & B: TSKgel SuperMultipore HZ-M, 4 µm, 4.6 mm ID × 15 cm × 2**
C: TSKgel SuperMultipore HZ-M, 4 µm, 4.6 mm ID × 15 cm × 2 + TSKgel SuperH3000 + TSKgel SuperH4000, 3 µm, 4.6 mm ID × 15 cm × 1
Mobile phase: THF
Flow rate: 0.35 mL/min
Detection: RI (EcoSEC GPC System), MALS (Wyatt miniDAWN™ TREOS®), VISC (Wyatt ViscoStar II)
Temperature: 40 °C
Samples: A & B: poly(norbornene-exo-anhydride) (P1)
C: norbornene-exo-anhydride with cyclooctadiene

[8]Tuten, B.T.; Chao, D.; Lyon C.K.; Berda, E.B. *Polym. Chem.* **2012**, 3, 3068-3071.

HFIP Reproducibility

Dr. Li Jia and co-workers at the University of Akron are investigating different synthetic routes for the formation of polypeptoids with alternating block structures. Highly reproducible data is needed to obtain subtle molar mass distribution trends from the various synthetic routes. The EcoSEC GPC System and a set of TSKgel mixed bed columns were used successfully to obtain high quality molar mass distribution (MMD) data of a series of Dr. Jia's block poly-ß-alkylalanoids with hexafluoroisopropanol (HFIP) as the mobile phase in under 15 minutes.

As shown in Table 11, percent standard deviations are more than 10x lower than values previously reported for polyamides in HFIP.[9] Percent relative standard deviation of the polydispersity index (*PDI*) ranged from 0.1 to 0.5%, permitting one to report *PDI*s within three significant figures. The high precision of the EcoSEC GPC System allows for the detailed study of polymerization reactions.

Table 11: Averaged values from three consecutive injections and the percent relative standard deviations

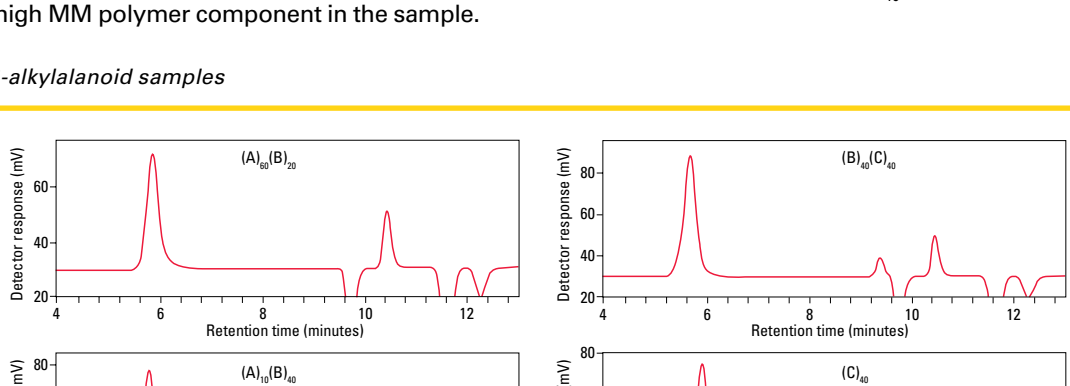
Sample[a]	M_n[b] (g/mol)		M_w[b] (g/mol)		*PDI*[b]	
		Rel std dev		Rel std dev		Rel std dev
$(A)_{10}(B)_{40}$	$2.65 \times 10^4 \pm 10$	0.04%	$3.03 \times 10^4 \pm 30$	0.11%	1.14 ± 0.01	0.09%
$(A)_{60}(B)_{20}$	$3.33 \times 10^4 \pm 170$	0.52%	$4.07 \times 10^4 \pm 28$	0.07%	1.22 ± 0.01	0.50%
$(A)_{40}(B)_{40}$	$4.87 \times 10^4 \pm 220$	0.45%	$6.09 \times 10^4 \pm 160$	0.26%	1.25 ± 0.01	0.10%
$(C)_{40}$	$3.01 \times 10^4 \pm 50$	0.18%	$3.64 \times 10^4 \pm 140$	0.37%	1.21 ± 0.01	0.39%

[a] Block lengths were determined by Dr. Jia from independent measurements. Chemical composition of blocks A, B and C will be published by L. Jia.

[b] Molar mass data were obtained from a PMMA calibration curve. Molar mass averages given in the table are averages of three sequential injections per sample. Based on block lengths, MMD are significantly overestimated.

Sample chromatograms from 4 selected poly-ß-alkylalanoid samples run on an EcoSEC GPC System using two TSKgel GMHHR-M, 5 µm, 4.6 mm ID × 15 cm columns are shown in Figure 22. Sample profiles display very little tailing and no baseline drift, allowing for highly precise data not available with conventional systems. All samples, with the exception of $(C)_{40}$, contain almost symmetrical, narrow polymer profiles eluting around 6 minutes. The shoulder seen in $(C)_{40}$ is indicative of another population of a high MM polymer component in the sample.

Figure 22: Poly-ß-alkylalanoid samples



Column: **TSKgel GMHHR-M, 5 µm, 4.6 mm ID × 15 cm × 2 packed in HFIP**
Mobile phase: HFIP containing 5 mmol/L sodium trifluoroacetate
Flow rate: 0.35 mL/min
Detection: RI (EcoSEC GPC System)
Temperature: 40 °C
Injection vol.: 10 µL
Samples: selection of poly-ß-alkylalanoid samples

[9]Robert, E. C.; Bruessau, R.; Dubois, J.; Jacques, B.; Meijerink, N.; Nguyen, T. Q.; Niehaus, D. E.; Tobisch, W. A. *Pure Appl. Chem.* **2004**, 76, 2009–2025.

Analysis of Styrene and Isoprene Block Copolymers

Dr. Jimmy Mays' group from the Department of Chemistry at the University of Tennessee, Knoxville, is synthesizing and characterizing the bulk morphology of fluorinated and sulfonated block copolymers. Well-defined block copolymers of sulfonated polystyrene-*b*-fluorinated polyisoprene (*s*PS-*b*-*f*PI), Figure 23, were synthesized by anionic polymerization followed by fluorination and sulfonation.[10] The EcoSEC GPC System, equipped with TSKgel SuperMultiporeHZ columns, was then used to determine the number-average molar mass, M_n, and the polydispersity index, *PDI*, of *s*PS-*b*-*f*PI, as well as that of the precursor polymer (PS-*b*-PI), Table 12. As seen in Figure 24, complete analysis of *s*PS-*b*-*f*PI was obtained in less than 10 minutes with excellent resolution using the EcoSEC GPC System.

Figure 23: Structure of sulfonated polystyrene-b-fluorinated polyisoprene (sPS-b-fPI)

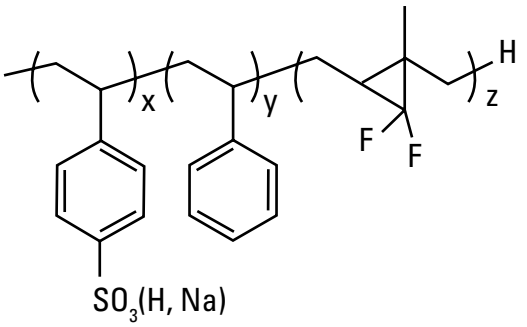
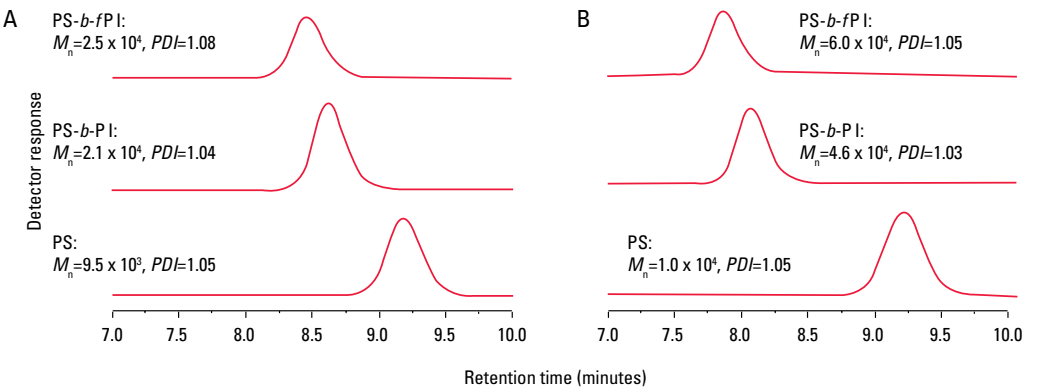


Table 12: Number-average molar mass, M_n, and the polydispersity index (PDI) of sPS-b-fPI and the precursor polymer (PS-b-PI)

	PS-*b*-PI		*s*PS-*b*-fPI	
Series[a]	M_n (g/mol)	*PDI*	M_n (g/mol)	*PDI*
1	2.1 x 10^4	1.04	2.5 x 10^4	1.08
2	4.6 x 10^4	1.03	6.0 x 10^4	1.05

[a] series 1 in acid form; series 2 in Na form

Figure 24: Sulfonated polystyrene-b-fluorinated polyisoprene precursor samples



Column:	**TSKgel SuperMultiporeHZ-M, 4 µm, 4.6 mm ID x 15 cm**
Mobile phase:	THF
Flow rate:	0.35 mL/min
Detection:	RI (EcoSEC GPC System)
Temperature:	35 °C
Injection vol:	20 µL
Samples:	A. series 1, table 12 B. series 2, table 12

[10]Wang, X.; Hong, K.; Baskaran, D.; Goswami, M.; Sumpter, B.; Mays, J. *Soft Matter*, **2011**, 7, 7960.