Maximizing Performance Through
GPC Column Selection

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Column Types

▪ The factor that principally controls which type of column is selected for a GPC experiment is the solvent

▪ Many polymer dissolve in only very limited numbers of solvents

▪ The columns used must be compatible with the solvent of choice

▪ Most importantly, the size exclusion mechanism must be maintained

▪ Agilent have two main ranges of GPC column for organic solvents

▪ The properties of each range that must be considered when selecting them for an application shall be presented

What Are GPC Columns Made Of?

Silica Packings = Mechanically Stronger However Exhibit Enthalpic Properties Due to Presence of Silanols. Also Tyically Have Lower Pore Volumes

Polymeric Packings = High Pore Volume and Vendor Specific Differences in Mechanical Stability. Due to Polarity of Stationary Phase Observed Interactions are Reduced
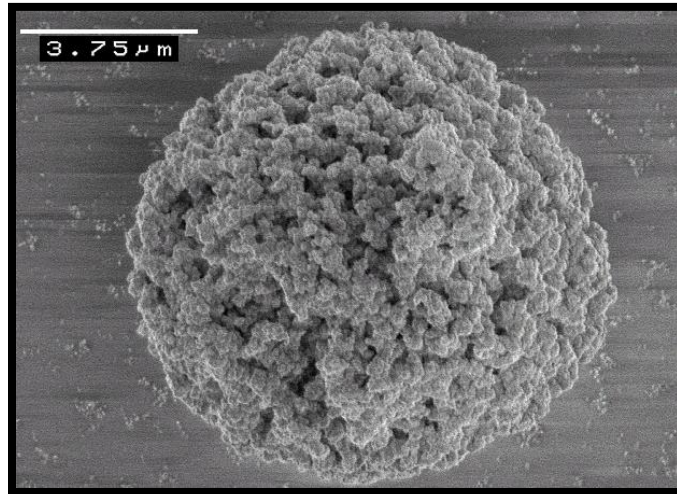
Styrene/Divinyl Benzene Columns - PLgel

PLgel is a highly crosslinked porous polystyrene/ divinylbenzene matrix which is recognized as a market leader in GPC column technology.

Manufactured and packed exclusively by Polymer Laboratories since 1976, PLgel has very special features:

- High pore volume and high efficiency for maximum resolution

- Unequalled solvent compatibility for transfers between polar and non-polar organic eluents

- Outstanding physical rigidity for extended lifetimes especially at high temperatures and in aggressive solvents

Solvent Compatibility

PLgel columns are routinely supplied in toluene*, however, they can be transferred easily and rapidly between solvents of varying polarity by the User. In organic GPC, sample to column interaction can occur occasionally and eluent modification can be used to eliminate the effects. PLgel columns are the ideal choice for these analyses, as they easily tolerate eluents in the pH range 1-14, as well as up to 10% water, in a miscible organic solvent.

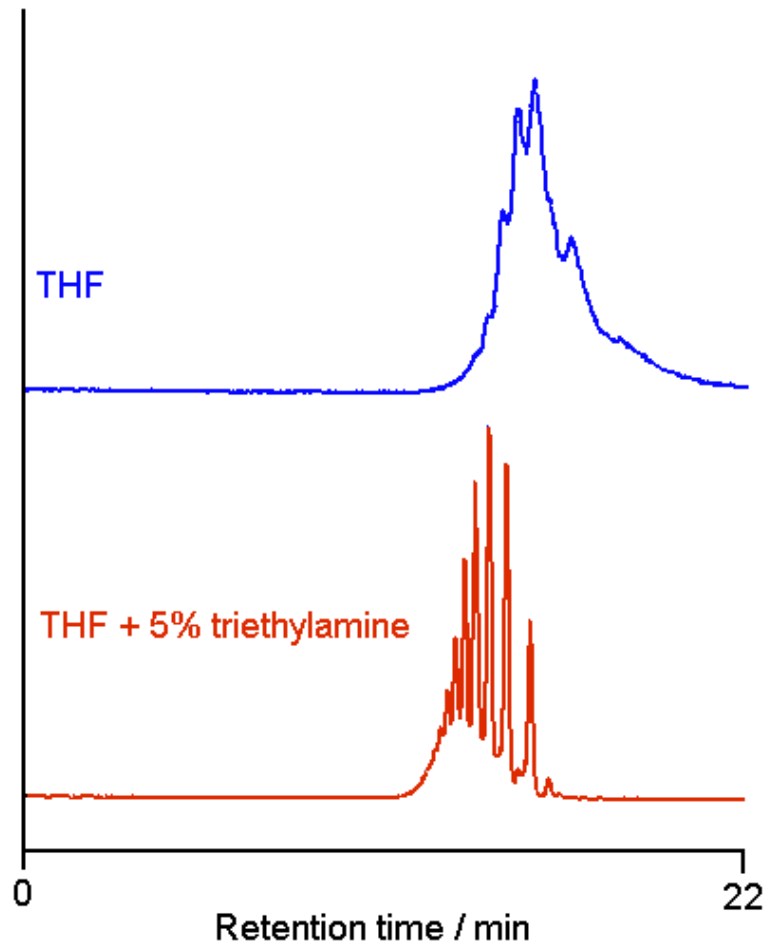## Temperature Stability to 220°C

Elevated temperature is used in GPC either to reduce eluent viscosity (eg polar solvent applications), or to maintain sample solubility (eg polyolefin applications). PLgel columns can be used at temperatures up to 220°C and operating pressures up to 150 bar (2200psi).

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PLgel Solvent Compatibility

- Columns can be used in a wide range of solvents

- Transfer between solvents is possible assuming care is taken

- The column user guide details the procedure

	Solvent Polarity	Solvent	PLgel Compatibility
Low	6.0	Perfluoralkanes	✓
	7.3	Hexane	✓
	8.2	Cyclohexane	✓
	8.9	Toluene	✓
	9.1	Ethyl acetate	✓
	9.1	Tetrahydrofuran (THF)	✓
	9.3	Chloroform	✓
	9.3	Methyl ethyl ketone (MEK)	✓
	9.7	Dichloromethane	✓
	9.8	Dichloroethane	✓
	9.9	Acetone	✓
	10.0	o-Dichlorobenzene (o-DCB)	✓
	10.0	Trichlorobenzene (TCB)	✓
	10.2	m-Cresol	✓
	10.2	o-Chlorophenol (o-CP)	✓
	10.7	Pyridine	✓
	10.8	Dimethyl acetamide (DMAc)	✓
	11.3	n-Methyl pyrolidone (NMP)	✓
	12.0	Dimethyl sulphoxide (DMSO)	✓
High	12.1	Dimethyl formamide (DMF))	✓

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Eluent Modification in Organic GPC

THF

THF + 5% triethylamine

Retention time / min

0   22

Hostavin N30

- Polymeric UV stabiliser containing secondary amine groups

Column: 2xPLgel 3μm MIXED-E
Flow Rate: 1.0ml/min
Detector: PL-ELS 1000

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PL Aquagel-OH Columns

Aqueous size exclusion chromatography (SEC) is widely used for the determination of molecular weight distributions of a variety of synthetic and naturally occurring water soluble polymers, and separations of oligomers and small molecules. The requirement to eliminate ionic and hydrophobic effects makes aqueous SEC very demanding.

The PL aquagel-OH series of columns provides a chemically and physically stable matrix for reliable aqueous SEC separations.

High Performance PL aquagel-OH Columns for Aqueous SEC

PL aquagel-OH columns are packed with macroporous copolymer beads with an extremely hydrophilic polyhydroxyl functionality.

The 'neutral' surface and the capability to operate across a wide range of eluent conditions provide for high performance analyses of analytes with neutral, ionic and hydrophobic moieties or combinations thereof.

PL aquagel-OH Features:

- pH range 2 - 10
- compatible with organic solvent, up to 50% methanol
- mechanical stability up to 140 bar (2000psi)
- low column operating pressures
- $8\mu m$ columns > 35,000 plates/m
- $15\mu m$ columns > 15,000 plates/m
- $5\mu m$ columns > 55,000 plates/m

PL aquagel-OH 8μm Analytical Columns

- PL aquagel-OH MIXED-H and M $8\mu m$ columns, high resolution over a very wide range of molecular weight, simplifying column selection and providing a versatile analytical system.

- PL aquagel-OH 30 $8\mu m$ high performance columns are ideal for relatively low molecular weight separations, combining low exclusion limits, high pore volume and high column efficiency for maximum resolution.

- PL aquagel-OH Individual Pore Size $8\mu m$ columns for high performance separations across the MW range 10,000 to >10,000,000.

PL aquagel-OH 15μm Analytical Columns

- PL aquagel-OH $15\mu m$ columns for the analysis of very high molecular weight polymers. Where molecular shear degradation is a real consideration, the larger particle size and larger frit porosity permit the analysis of high viscosity polymers in the range from 1M up to 100M.

PL aquagel-OH 5μm Analytical Columns

- In addition, Varian Polymer Laboratories has launched an ultra-high resolution PL aquagel-OH 20 $5\mu m$ column for very high resolution analyses.

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PolarGel Columns

Using its intermediate polarity surface and high mechanical stability, PolarGel-M operates with a wide range of solvents and solvent combinations. You can now analyze polar polymers that are not necessarily water soluble, and get clean chromatograms, time after time.

The PolarGel-M column has an intermediate polarity surface and high mechanical stability. It is capable of operation in a wide range of solvents and solvent combinations, greatly enhancing the ability to analyze polar polymers that are not necessarily water soluble.

PolarGel-M (300 x 7.5 mm) has the advantage of a polarity between PLgel (for organic GPC) and PL aquagel-OH (for aqueous GPC), making it suitable for applications in polar solvents and mixed solvents that fall between these systems.

Column	Particle size / µm	Resolving range (PEG/PEO in water)
PolarGel-L	8	Up to 30,000
PolarGel-M	8	Up to 2,000,000

Peak Shapes of Polar Compounds

In this example, phenol formaldehyde resin is analyzed on PolarGel-M columns and traditional styrene/divinyl benzene columns in dimethyl formamide. Both column sets perform well, but the highly polar-OH groups on the resin interact strongly with the styrene/divinyl benzene columns, resulting in an unusual peak shape with numerous shoulders and some fronting. PolarGel-M columns give a much better peak shape, clearly showing the polymeric and oligomeric regions. For highly polar materials, PolarGel-M columns are definitely superior.
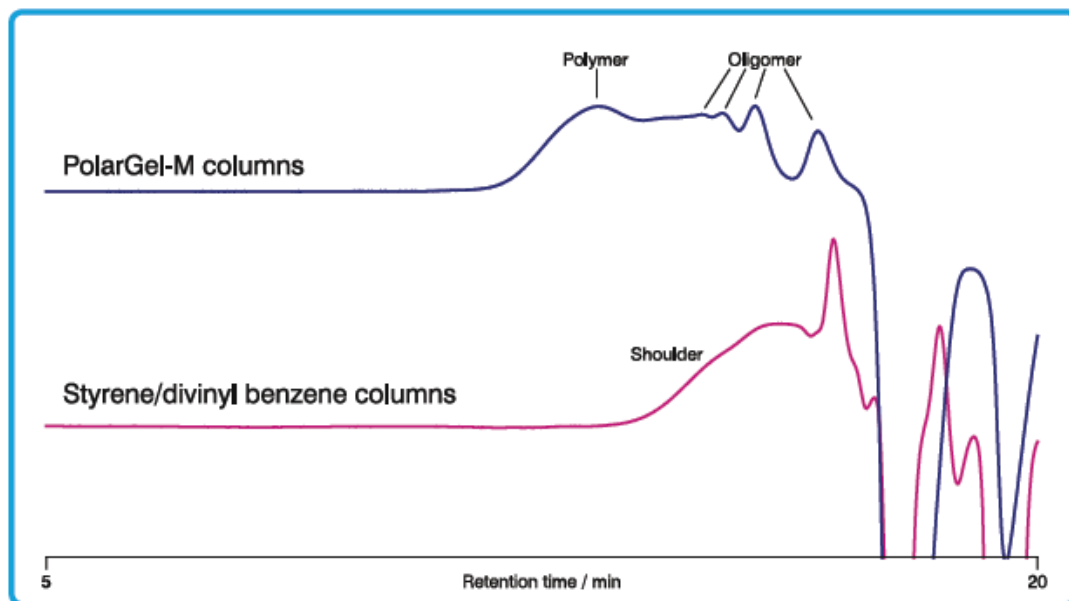
Superior polar performance from PolarGel-M.

PolarGel-M Calibrations
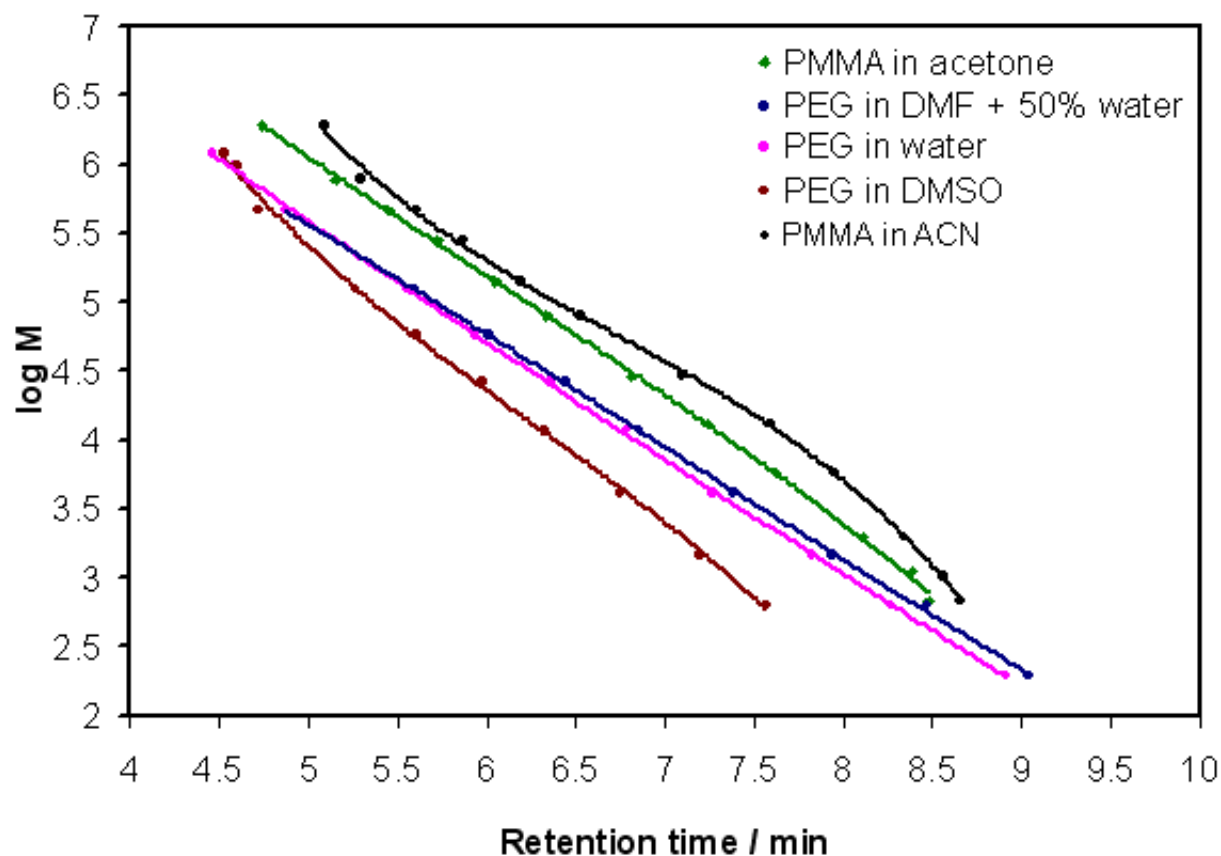
PLgel Individual Pore Size Columns

Calibration Curves

Calibrants: Polystyrene
Eluent: THF
Flow Rate: 1.0ml/min
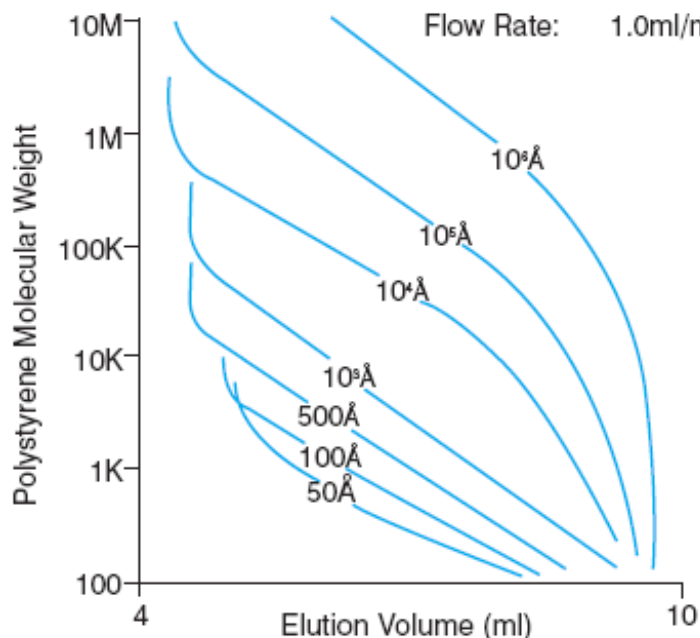
Specifications

Column Type		Effective MW Range (PS)	Guaranteed Efficiency (p/m)
PLgel 3μm	100Å	up to 4,000	>100,000
PLgel 5μm	50Å	up to 2,000	>60,000
PLgel 5μm	100Å	up to 4,000	>60,000
PLgel 5μm	500Å	500-30,000	>60,000
PLgel 5μm	10^3Å	500-60,000	>50,000
PLgel 5μm	10^4Å	10,000-600,000	>50,000
PLgel 5μm	10^5Å	60,000-2,000,000	>50,000
PLgel 10μm	50Å	up to 2,000	>35,000
PLgel 10μm	100Å	up to 4,000	>35,000
PLgel 10μm	500Å	500-30,000	>35,000
PLgel 10μm	10^3Å	500-60,000	>35,000
PLgel 10μm	10^4Å	10,000-600,000	>35,000
PLgel 10μm	10^5Å	60,000-2,000,000	>35,000
PLgel 10μm	10^6Å	600,000-10,000,000	>35,000

Determination of Column Performance
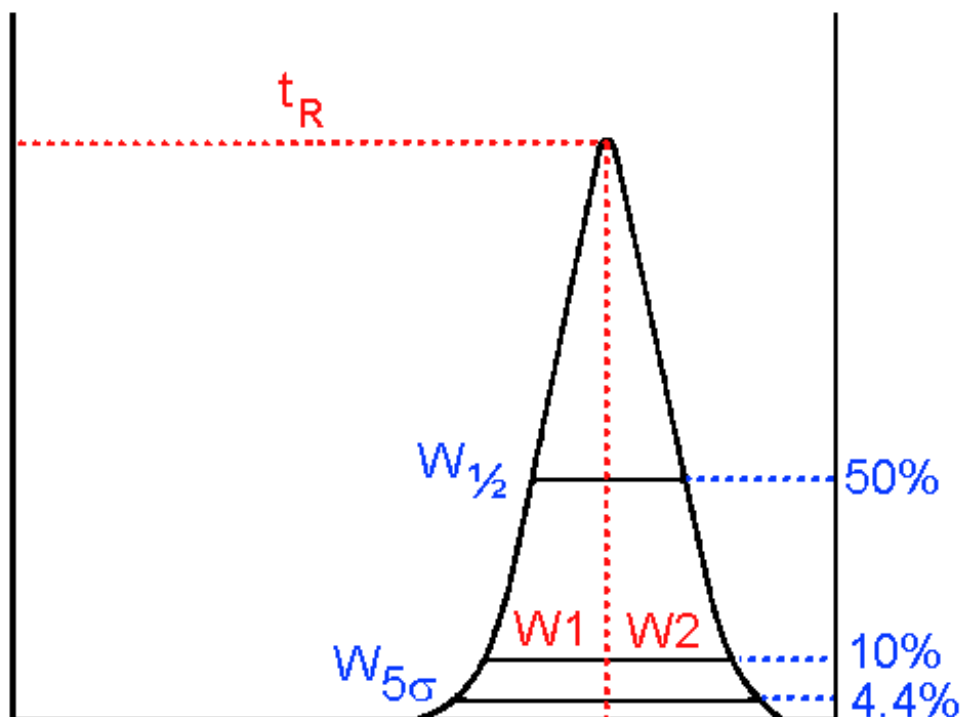
t_R = retention time

$W_{1/2}$ = peak width at 50% peak height

W_{5s} = peak width at 4.4% peak height
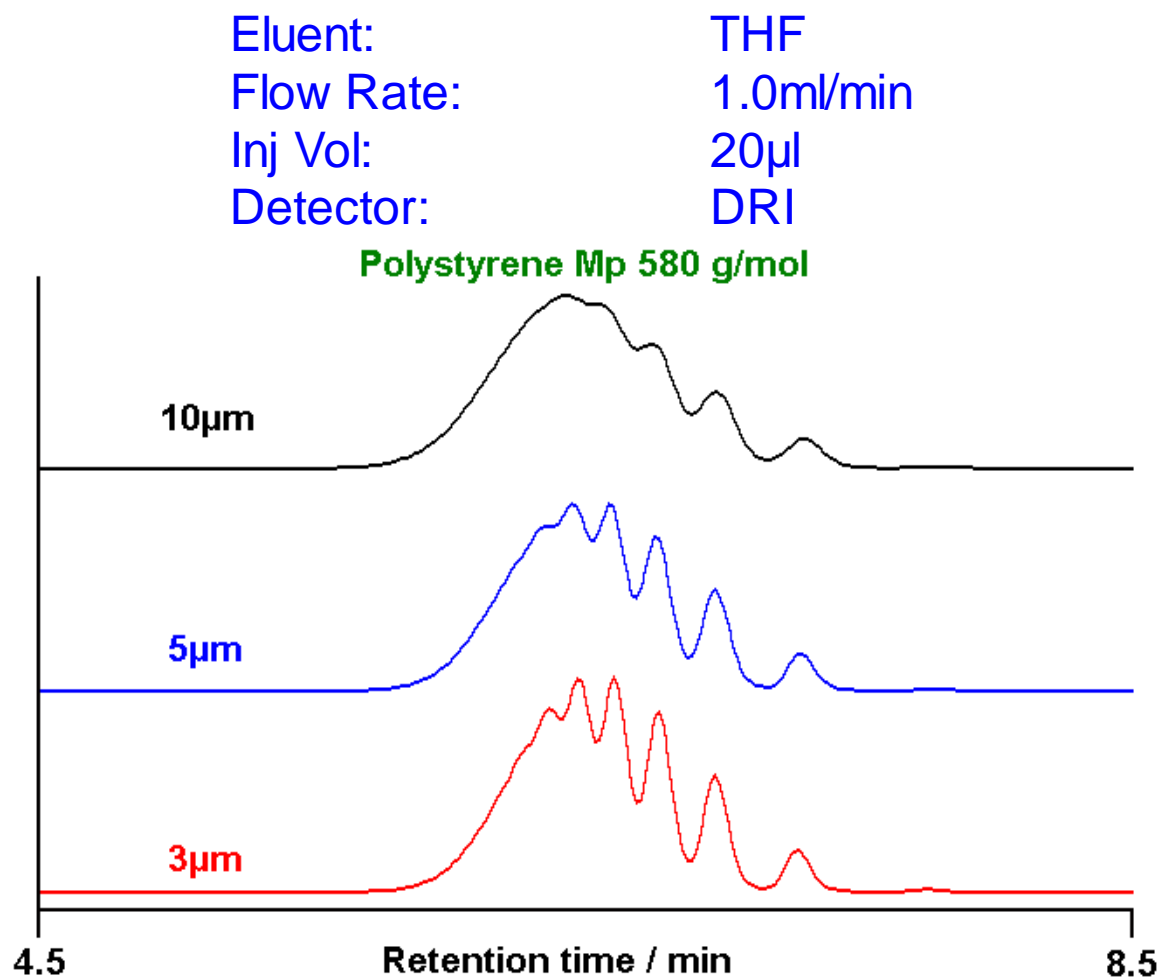
L = column length in meters

Efficiency (½ height)

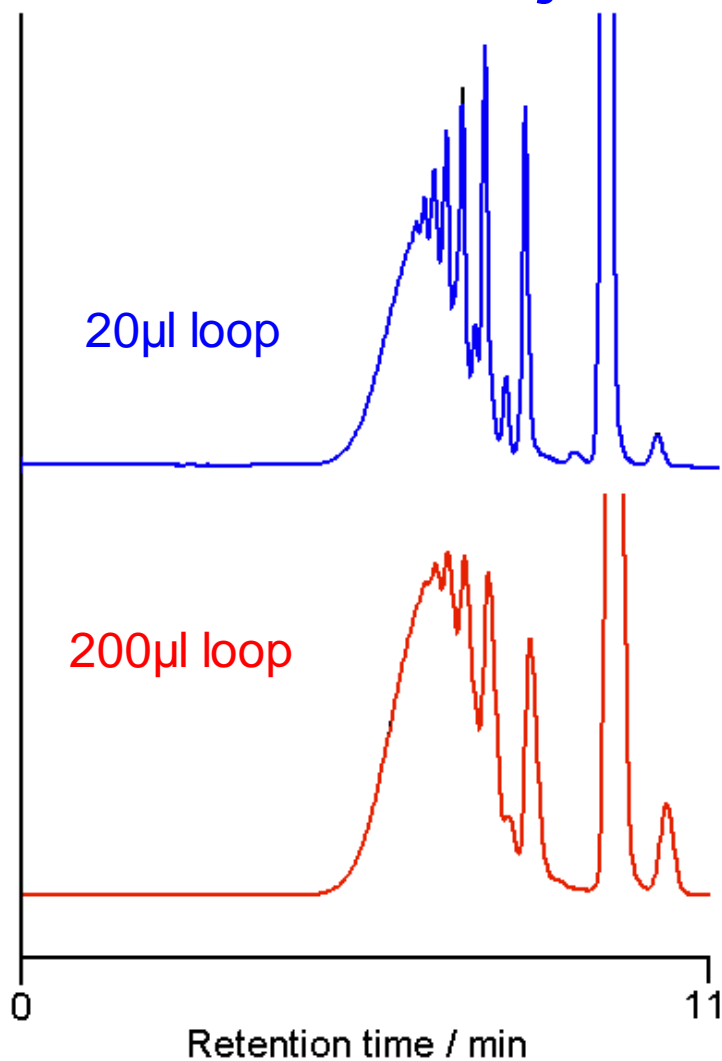$$N = \frac{5.54(t_R/W)^2}{L}$$

Plate count efficiency (5s)

$$N = \frac{25(t_R/W_{5s})^2}{L}$$

Symmetry = W_1/W_2

Effect of Particle Size on Resolution

Effect of Injector Loop Size on Resolution

20µl loop

200µl loop

0   11
Retention time / min

Column: PLgel 3µm MIXED-E
               300x7.5mm
Eluent: THF
Flow Rate: 1.0ml/min
Sample: Epikote 1001
               epoxy resin

Injection loop is a major contribution to system dead volume, use reduced injection volume and increase concentration to maintain sensitivity

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Effect of Flow Rate on Column Efficiency (1)
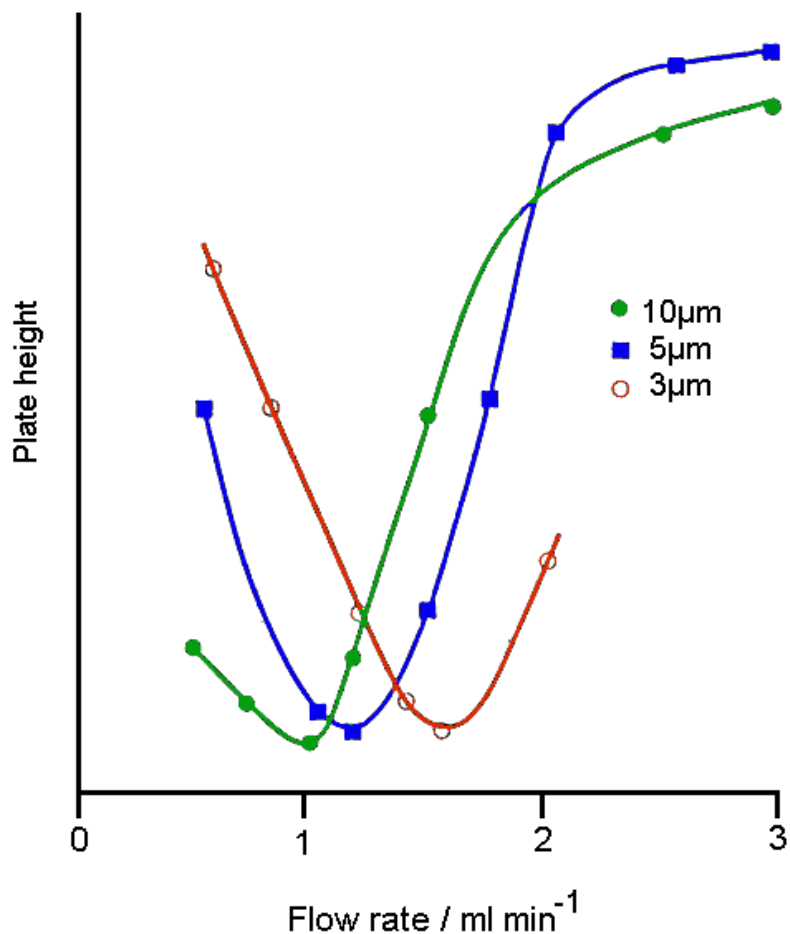
Eluent: THF
Column: PLgel 100Å
Test Probe: ODCB

Optimum flow rate for small molecule separations is around 1.0ml/min

Effect of Concentration on Peak Shape and Resolution

0.05%

0.10%

0.15%

0.20%
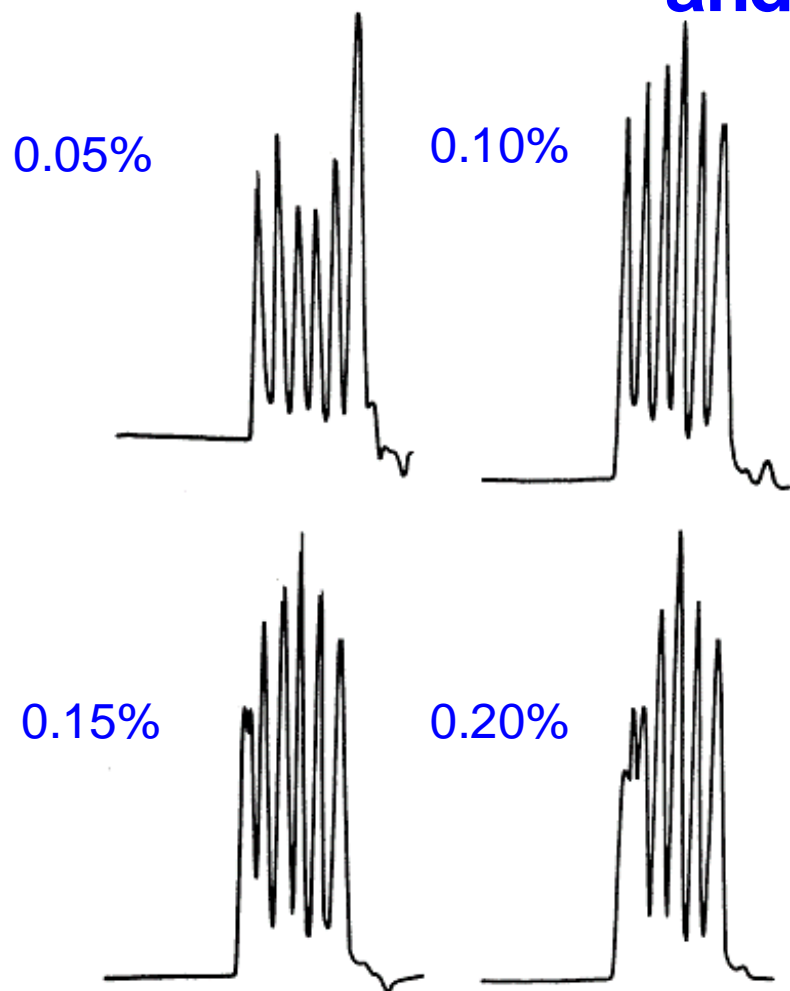
Column: PLgel 10µm MIXED-B
                    300x7.5mm
Eluent: THF
Flow Rate: 1.0ml/min
Detector: UV

Polystyrene standards
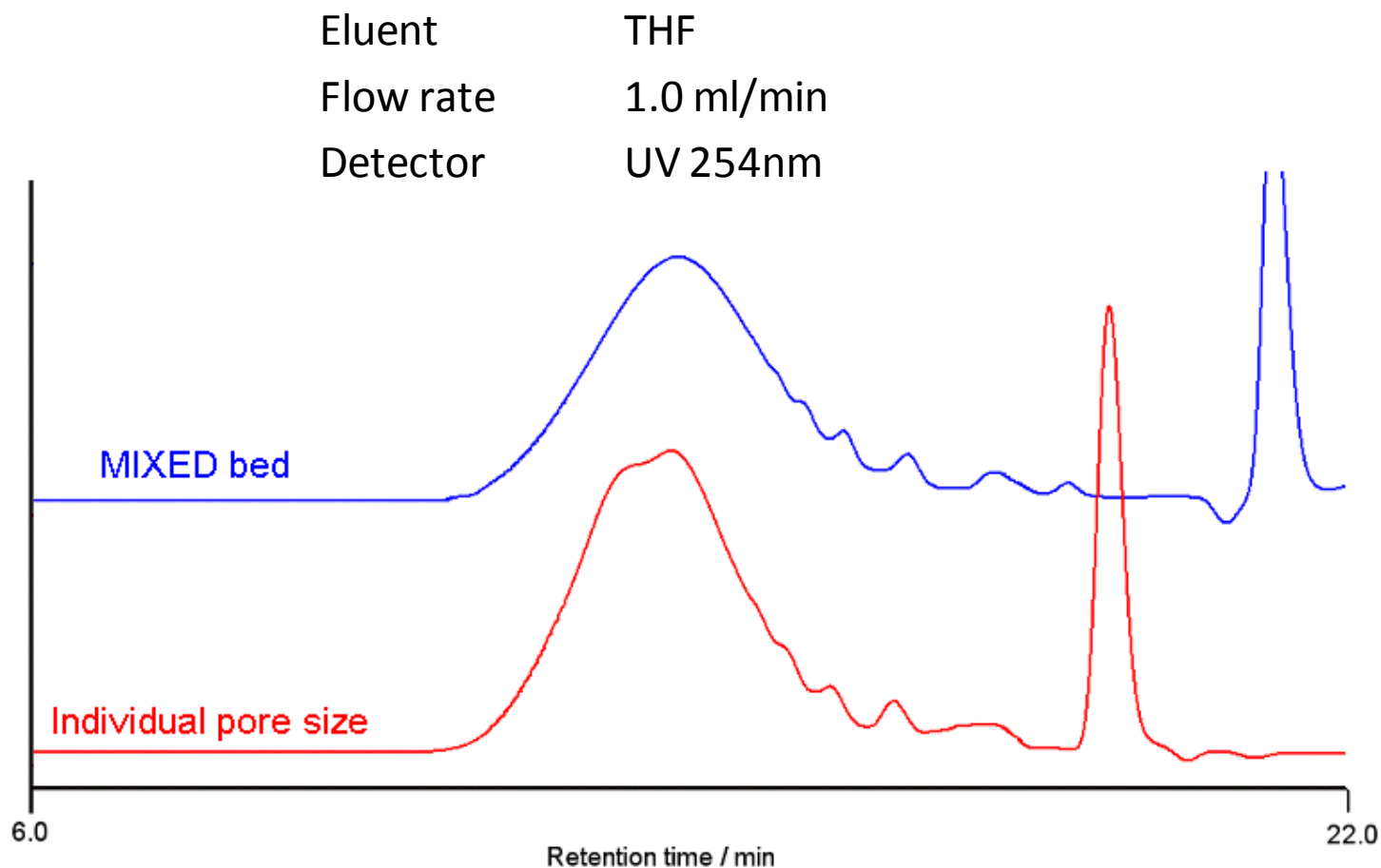1. 8,500,000   4. 34,500
2. 1,130,000   5. 5,100
3. 170,000   6. 580

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Combination of Individual Pore Size Columns

Traditional approach to increasing MW operating range of column set
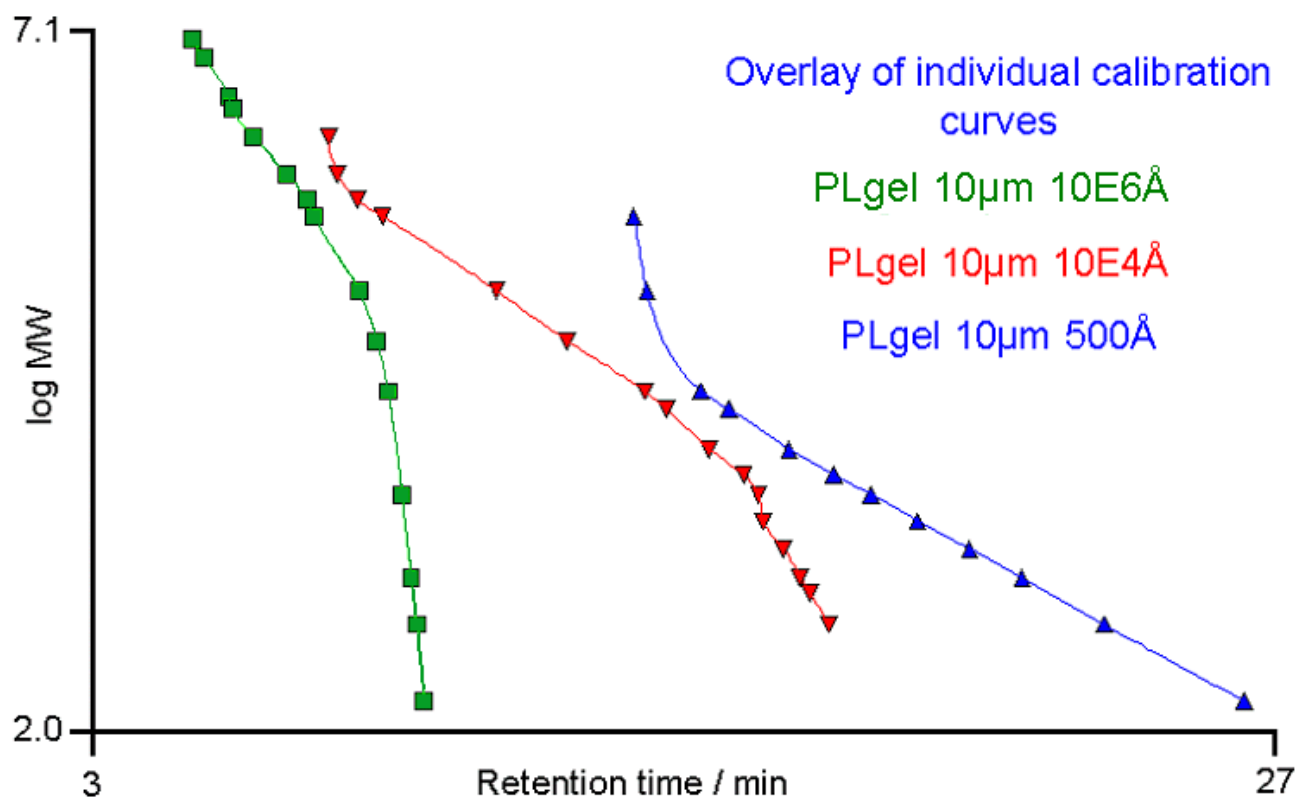
Individual Pore Size Combination Versus MIXED Gel Columns - Polydisperse Sample

PLgel MIXED Bed columns

A significant number of GPC applications involve the analysis of polydisperse materials. The modern approach to column selection is to choose PL's MIXED gel columns, where each column contains a mixture of individual pore size materials, accurately blended to cover a specified broad range of molecular weight with a linear calibration to eliminate column mismatch. As market leaders in this field, Polymer Laboratories offers a comprehensive range of MIXED gel GPC columns designed for specific application areas.

Key Advantages of PLgel MIXED Columns Include:

- Greatly simplified column selection

- Improved confidence in the accuracy and precision of calculated data

- Optimized particle size for each application area

- Reduced replacement stock

- Elimination of mismatched column sets and spurious peaks

- Simple addition of extra column(s) for greater resolution

The calibration curves are designed to be linear over a specified molecular weight range, ensuring that the same degree of resolution is achieved across the full operating range of the column.

The particle size of the packing and the porosity of a particular MIXED gel column are carefully matched to the MW range and application, thus optimizing performance and eliminating the effects of shear degradation.

Resolution in GPC is controlled by the slope of the calibration curve and the particle size of the packing material. PL has scientifically determined the minimum number of MIXED gel columns required to perform accurate MWD determinations based on specific resolution (Rsp).

Ref: "Size exclusion chromatography columns from Polymer Laboratories", in Column Handbook for Size Exclusion Chromatography, ed. Chi-san Wu, Academic Press, 1999.

PLgel MIXED Bed Calibrations

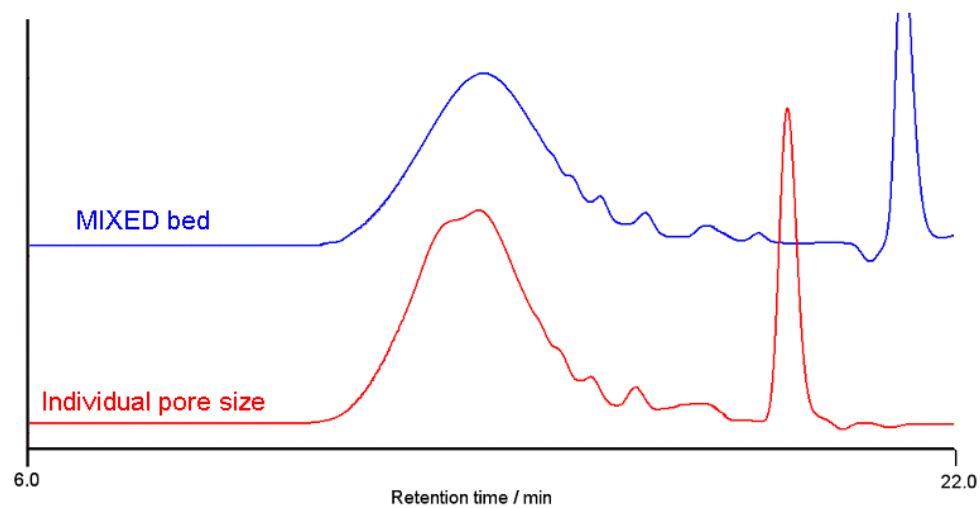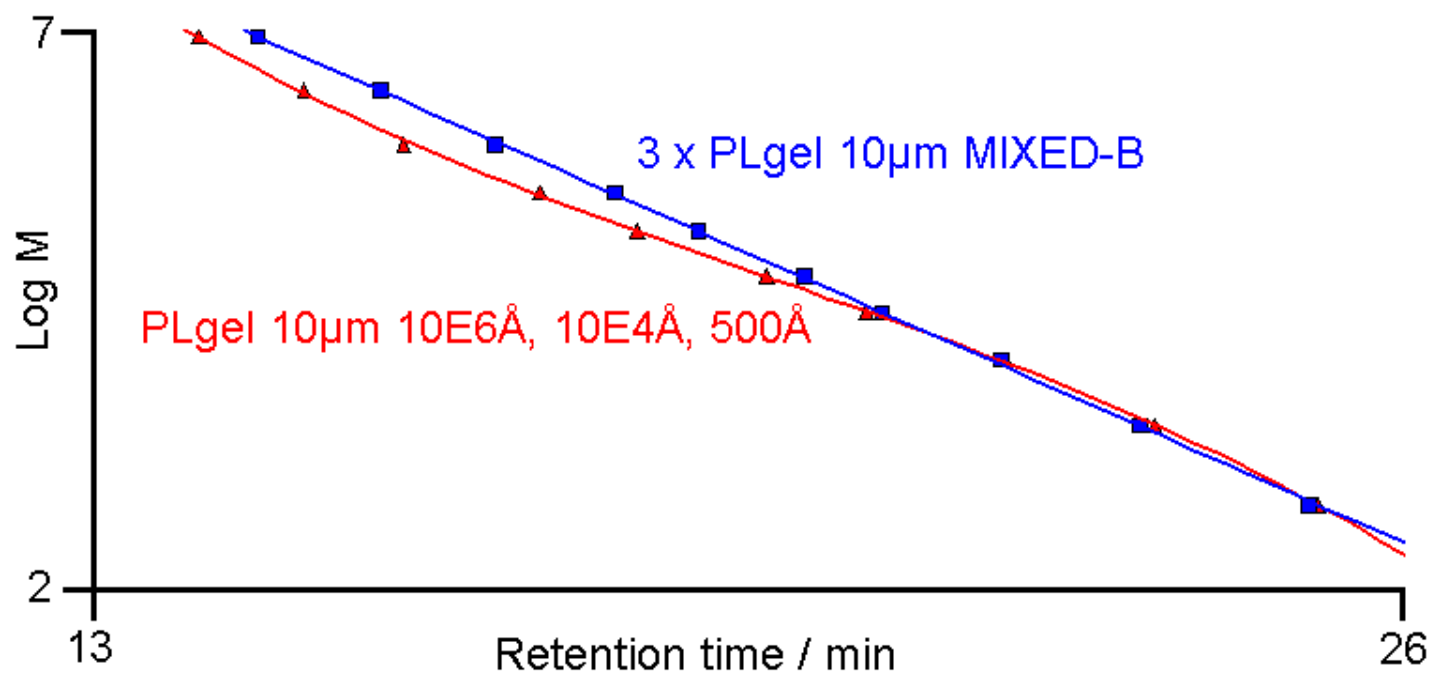## PLgel MIXED Gel

Calibration Curves

KEY
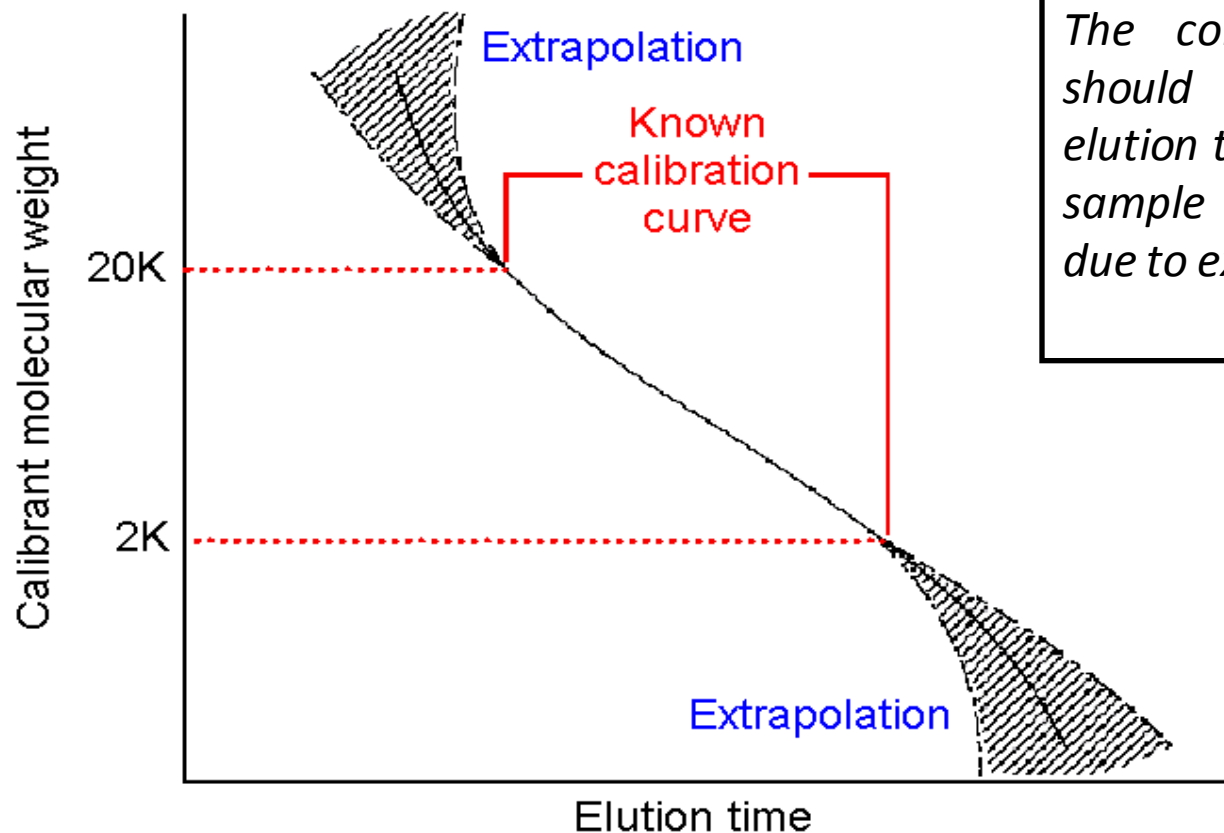- ○ 20μm MIXED-A
- ● 10μm MIXED-B
- ■ 5μm MIXED-C
- ▲ 5μm MIXED-D
- □ 3μm MIXED-E
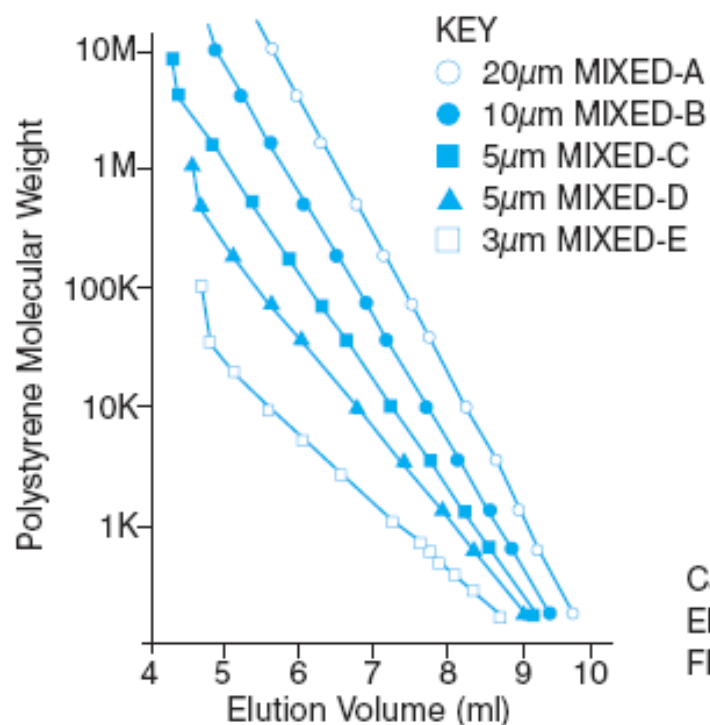
Specifications

Column Type	Linear MW Range (PS)	Guaranteed Efficiency (p/m)
PLgel 20μm MIXED-A	2,000-40,000,000	>17,000
PLgel 10μm MIXED-B	500-10,000,000	>35,000
PLgel 5μm MIXED-C	200-2,000,000	>50,000
PLgel 5μm MIXED-D	200-400,000	>50,000
PLgel 3μm MIXED-E	up to 30,000	>80,000

Calibrants: Polystyrene
Eluent: THF
Flow Rate: 1.0ml/min

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3 x PLgel 10μm MIXED-B

PLgel 10μm 10E6Å, 10E4Å, 500Å

MIXED bed

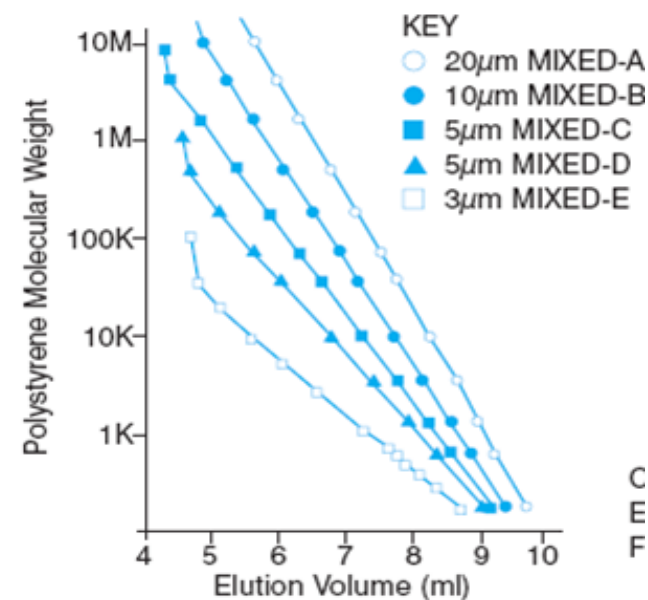Individual pore size

Errors Due to Polynomial Calibrations

The column calibration should cover the full elution time region of the sample to avoid errors due to extrapolation

Difference in Linearity
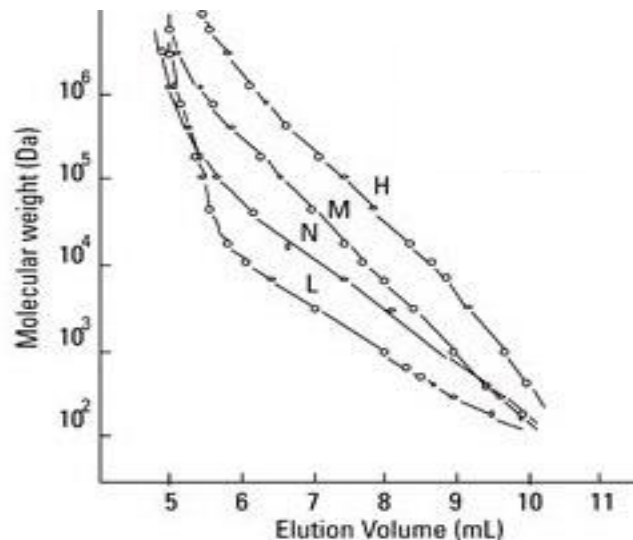
Flow Rate: 1.0mL/min
Temperature: 25°C
Detection: UV @ 254nm

Calibration Curves

KEY
○ 20μm MIXED-A
● 10μm MIXED-B
■ 5μm MIXED-C
▲ 5μm MIXED-D
□ 3μm MIXED-E

PlusPore PS/DVB Columns

The PlusPore series of columns has been specifically designed for *high resolution* GPC, and represents the very latest in GPC column technology. These novel packing materials are based on the industry standard, highly crosslinked polystyrene/divinylbenzene (PS/DVB), for the widest applicability and solvent compatibility. Each is made using a novel polymerization process to produce particles which exhibit a specific, controlled pore structure for optimum GPC performance.
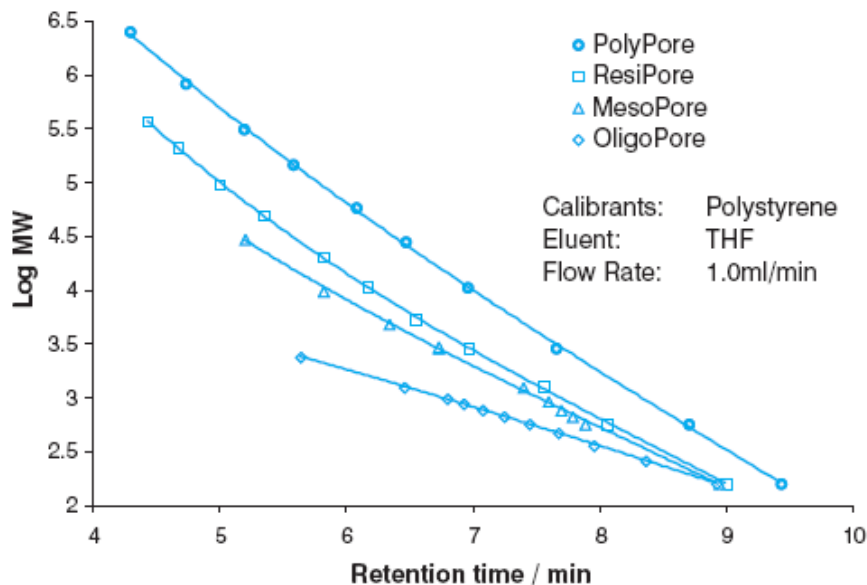
- **PolyPore** for the routine analysis of general polymers

- **ResiPore** for the analysis of resins and condensation polymers

- **MesoPore** for the analysis of prepolymers and low MW resins

- **OligoPore** for the analysis of oligomeric samples

Features and Benefits of the PlusPore Range

- High pore volume, high resolution

- Wide pore size distribution

- Optimized separation range

- Full solvent compatibility

- No MWD dislocations

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PlusPore Calibrations

PlusPore
Calibration Curves

Calibrants: Polystyrene
Eluent: THF
Flow Rate: 1.0ml/min

Specifications

	PolyPore	ResiPore	MesoPore	OligoPore
MW Operating Range	200-2,000,000	200-400,000	Up to 25,000	Up to 4,500
Nominal Particle Size	5μm	3μm	3μm	6μm
Typical Column Efficiency	>60,000 p/m	>80,000 p/m	>80,000 p/m	>55,000 p/m

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Effect of Increased Pore Volume

Columns   2xPLgel 3μm 100Å 300x7.5mm
                   2xOligoPore 300x7.5mm
Eluent   THF
Flow rate   1.0ml/min
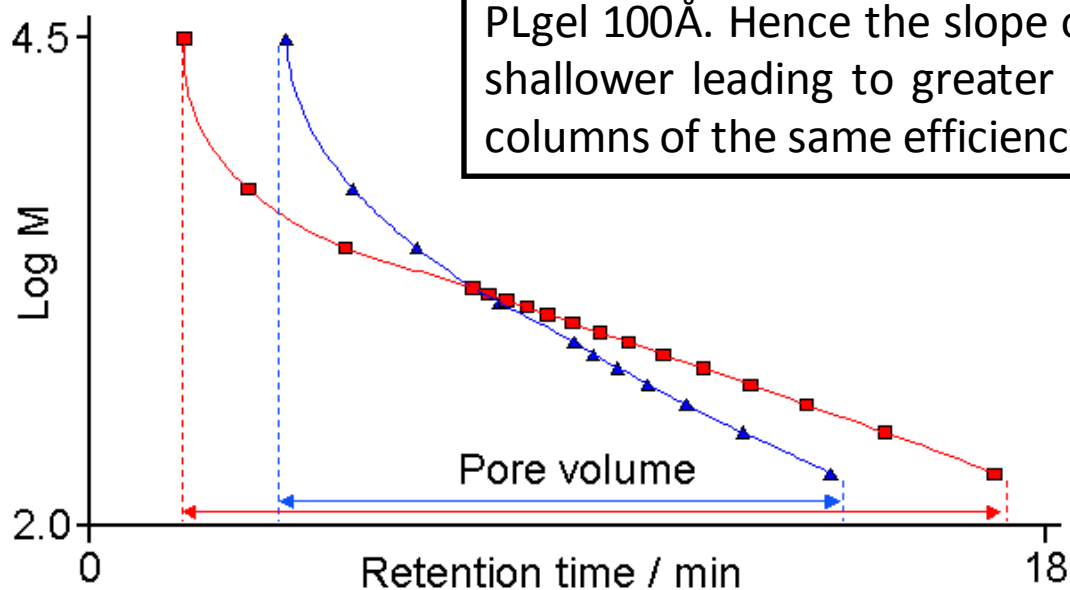
Both columns have a similar exclusion limit but OligoPore has greater pore volume than PLgel 100Å. Hence the slope of the curve is shallower leading to greater resolution for columns of the same efficiency

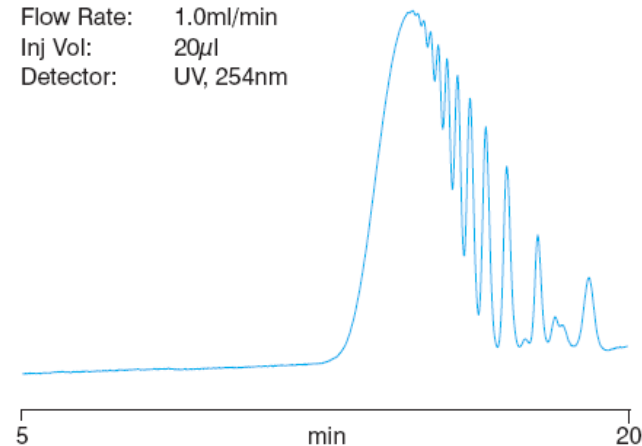# Examples of Resolution Using Pluspore Columns

Polyurethanes

Columns:	2xMesoPore, 300x7.5mm (PL1113-6325)
Eluent:	THF
Flow Rate:	1.0ml/min
Inj Vol:	20μl
Detector:	RI
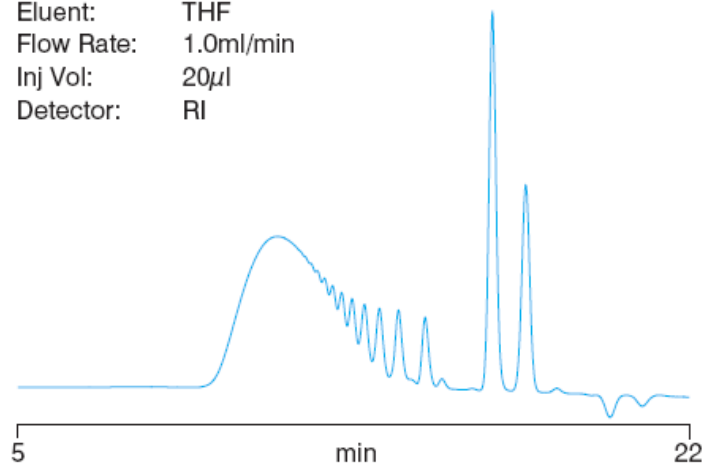
Polyester

Columns:	2xResiPore, 300x7.5mm (PL1113-6300)
Eluent:	THF
Flow Rate:	1.0ml/min
Inj Vol:	20μl
Detector:	UV, 254nm

Polystyrene Standards

Columns:	2xOligoPore, 300x7.5mm (PL1113-6520)
Eluent:	THF
Flow Rate:	1.0ml/min
Detector:	RI

1,270

580

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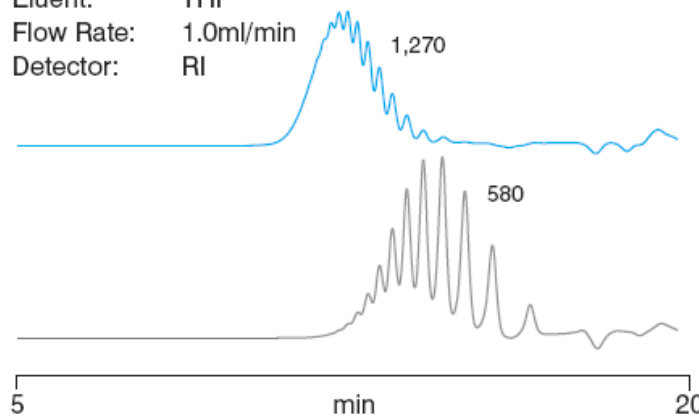
# Rapide Columns Allow For Fast Trend Analysis
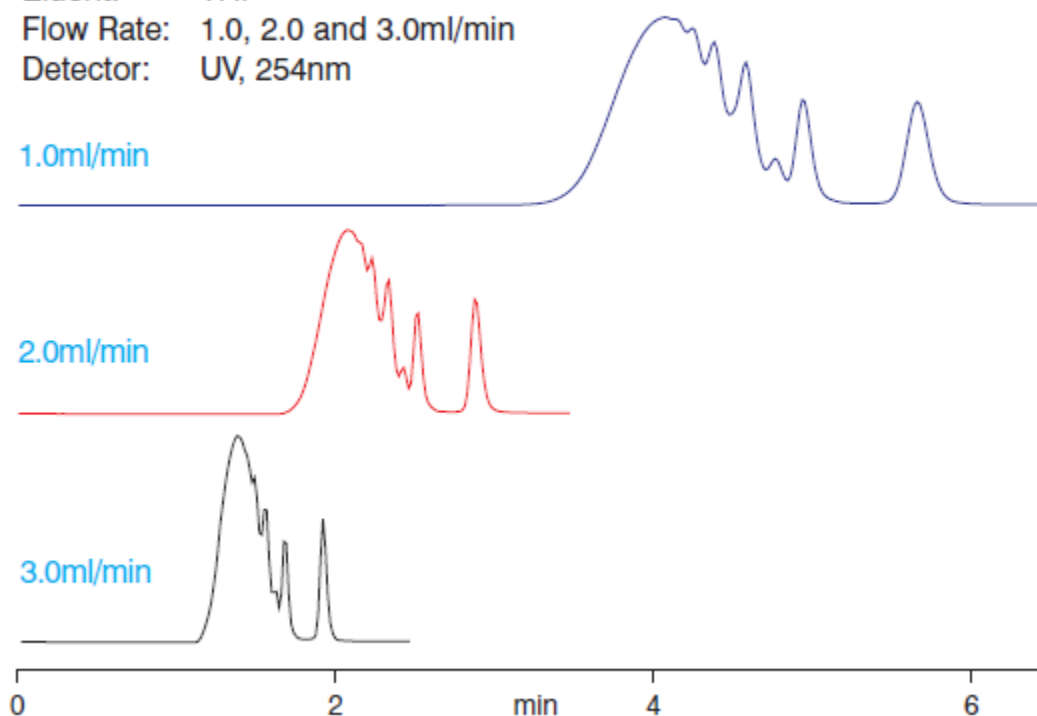
PLgel LS Columns

Polymer Laboratories has developed the PLgel LS series, a PS/DVB packing using an innovative proprietary suspension polymerization technique to virtually eliminate nano-particle leakage. A startling improvement is achieved immediately in the quality of light scattering data obtained with PLgel LS columns in place of conventional GPC columns. The light scattering chromatograms below were obtained after flushing the columns for one hour in THF at 1.0ml/min. A polystyrene standard (Mp 210,000) was injected at 1mg/ml in order to illustrate the dramatic improvement in signal to noise with the PLgel LS column.
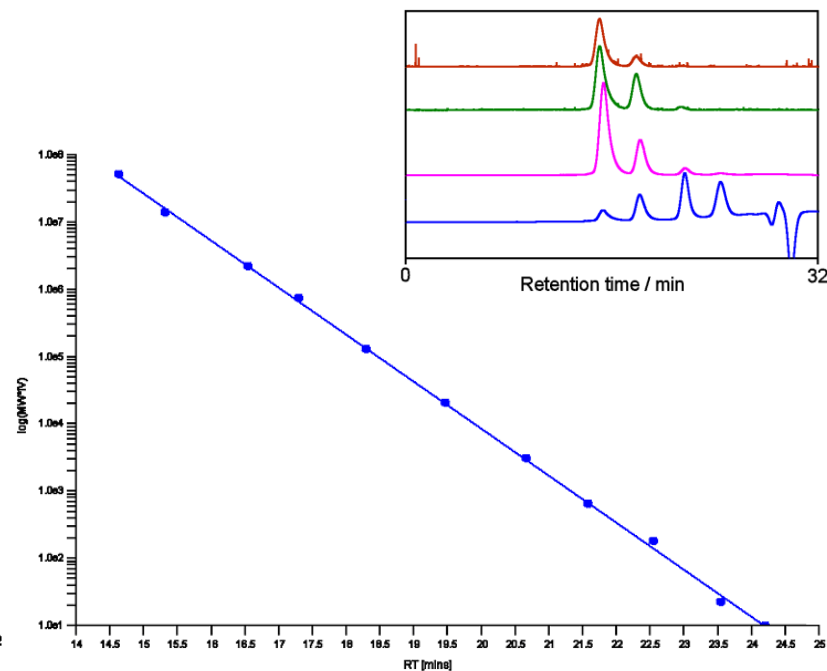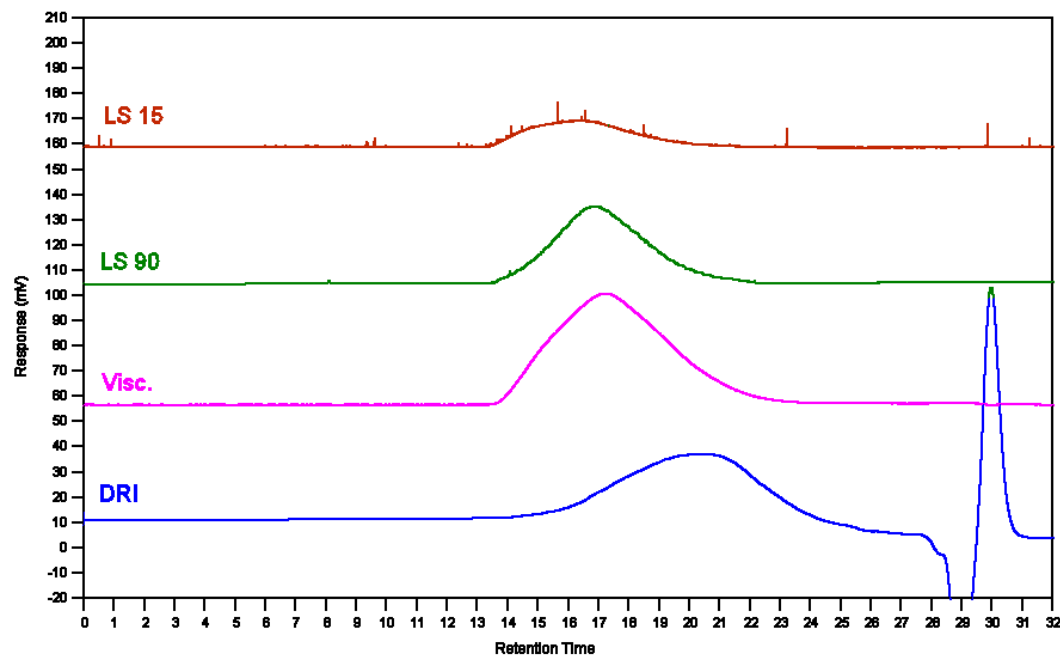
Conventional GPC Column

PLgel LS Column

Column: PLgel 10µm MIXED-B LS,
300x7.5mm (PL1110-6200LS)

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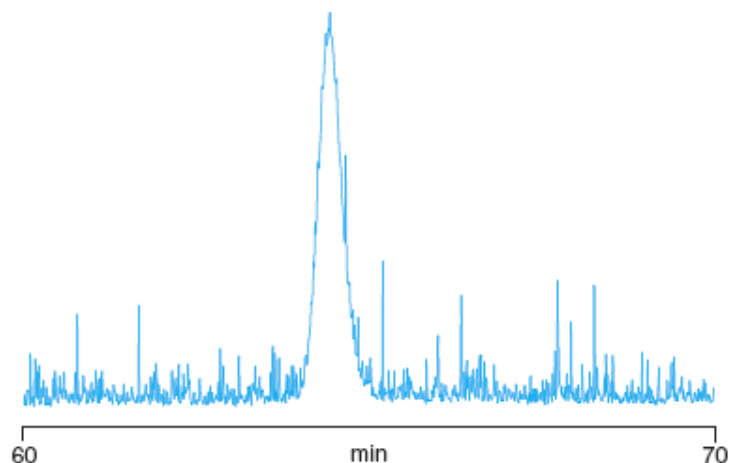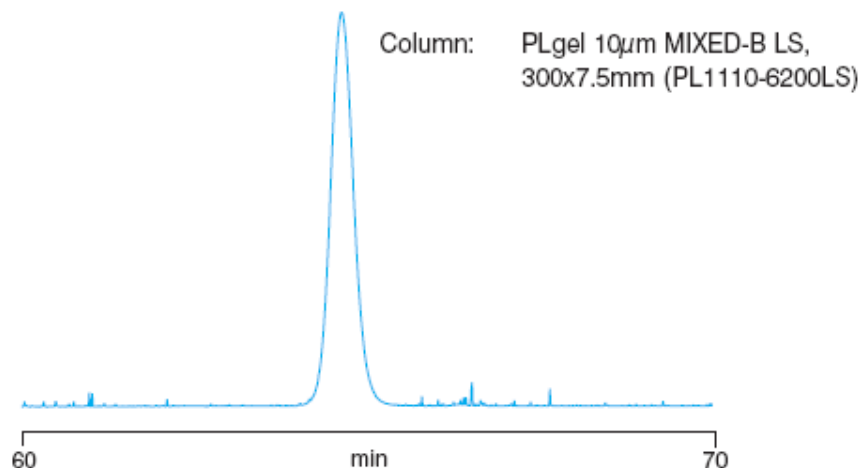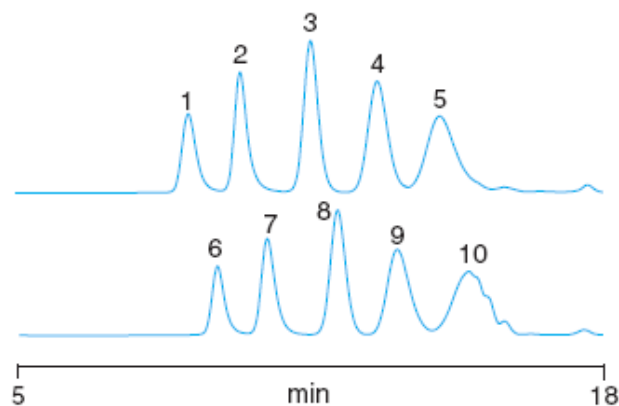
PLgel Olexis Columns

- Maximum resolution with minimum shear degradation

- The packing material is the same as the PL 'LS' product line, and so is especially suited for light scattering applications
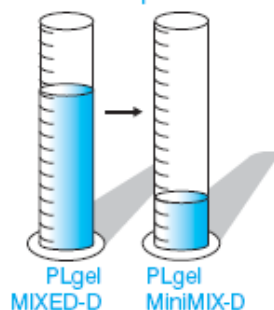
miniMIX Solvent Consumpsion

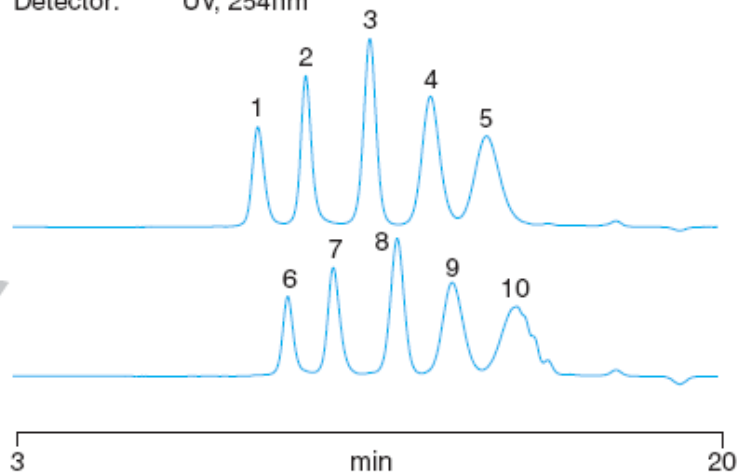## Comparison of Conventional and Narrow Bore Columns

Sample:	EasiCal PS-2
Columns:	2xPLgel 5μm MIXED-D, 300x7.5mm (PL1110-6504)
Eluent:	THF
Flow Rate:	1.0ml/min
Inj Vol:	100μl
Detector:	UV, 254nm

Sample:	EasiCal PS-2
Columns:	2xPLgel MiniMIX-D, 250x4.6mm (PL1510-5504)
Eluent:	THF
Flow Rate:	0.3ml/min
Inj Vol:	20μl
Detector:	UV, 254nm

KEY
1. 380,000
2. 96,000
3. 22,000
4. 5,050
5. 1,320
6. 156,000
7. 49,900
8. 11,600
9. 2,950
10. 580

Comparative Solvent Consumption

PLgel MIXED-D   PLgel MiniMIX-D

Comparative Preparative Separations

Applications Include
- Deformulation of competitors' products
- Sample clean-up / extraction
- Polymer fractionation

High Performance, High Capacity

PLgel Preparative columns are packed with the same rigid, high performance media as the analytical column range. The 10μm particle size provides high column efficiency (>25,000 plates/m) for optimum resolution and loading characteristics.

PLgel 25mm ID preparative columns offer more than a 10x scale up compared to PLgel 7.5mm analytical columns. In comparison with other vendors' preparative columns, PL's increased ID and column volume permit even higher loadings per injection.

| Column ID	Column Volume per 300mm Length	Minimum Scale Up
7.5mm	13	x1
19mm	85	x6
21mm	104	x8
25mm	147	x11

High Load

The large internal diameters of preparative columns, with their correspondingly larger bed volumes, mean that the injection volume can be significantly increased.

When fractionating low molecular weight materials, the sample concentration can also be significantly increased, enabling milligram quantities of very pure material to be isolated for further study. The actual loading is ultimately controlled by the sample and its molecular weight.

PLgel Preparative GPC columns are available in seven individual pore sizes and two MIXED gel types, and in column lengths of 300mm and 600mm. A Preparative Guard column (25x25mm) is also available.

Analytical Separation
Columns: 2xOligoPore, 300x7.5mm (PL1113-6520)
Eluent: THF
Flow Rate: 1.0ml/min
Loading: 0.2%, 100ml
Detector: UV
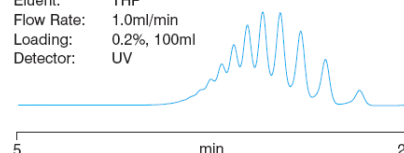
Preparative Separation
Columns: 2xOligoPore, 300x25mm (PL1513-6520)
Eluent: THF
Flow Rate: 10.0ml/min
Loading: 2.0%, 2ml
Detector: UV