GPC/SEC
An essential tool for polymer analysis

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26th March 2013

Introduction to Polymers

Where are they found?

Analysis of engineering polymers by GPC/SEC

Application Compendium

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Engineering Polymers

Biodegradable polymers - analysis of biodegradable polymers by GPC/SEC

Application compendium

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Biodegradable Polymers

Analysis of elastomers by GPC/SEC

Application compendium

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Elastomers

Resins

Low molecular weight resins - Analysis of low molecular weight resins and prepolymers by GPC/SEC

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Polyolefins

Analysis of polyolefins by GPC/SEC

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Analysis of food additives by GPC/SEC

Application compendium

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Food

Excipients

Excipient analysis by GPC/SEC and other LC techniques

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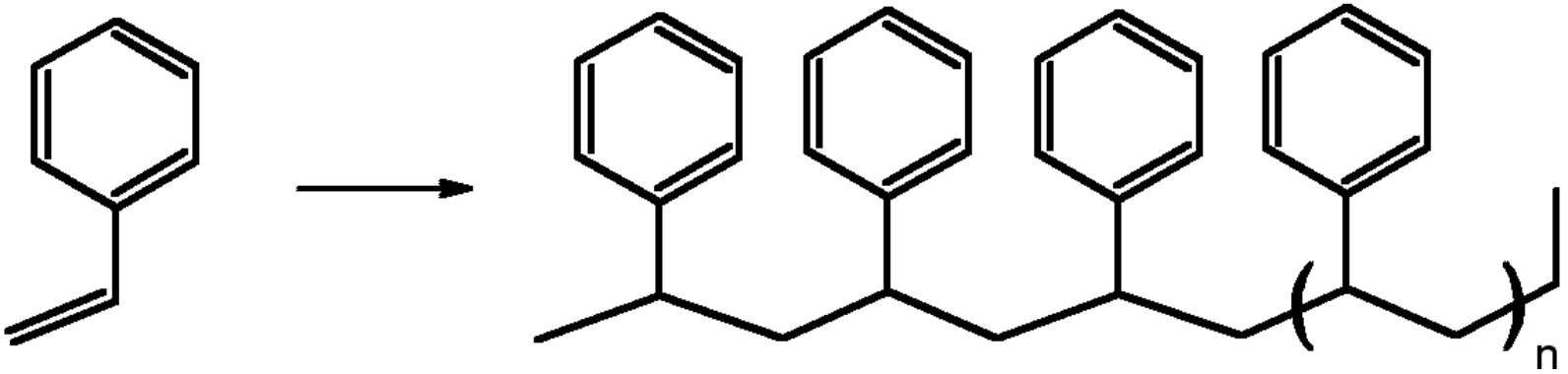
Molecular Weight

The molecular weight of a polymer is a way of describing how long the polymer chains are

Each monomer has a molecular weight (often called the formula weight)

Adding the monomers together to make polymers increases the molecular weight

The longer the chains, the higher the molecular weight



Effect of Molecular Weight

For example, let's look at hydrocarbons

Very short chain hydrocarbons are the predominant component of petrol – liquid at room temperature

Longer chain hydrocarbons are present in various waxes such as candle wax – soft, pliable and easy to melt

Polyethylene is a very long chain hydrocarbon – tough, strong and very resistant to heat and solvents

Polymer Molecular Weight Distributions

Samples of synthetic polymers *always* contain polymer chains with a range of chain lengths

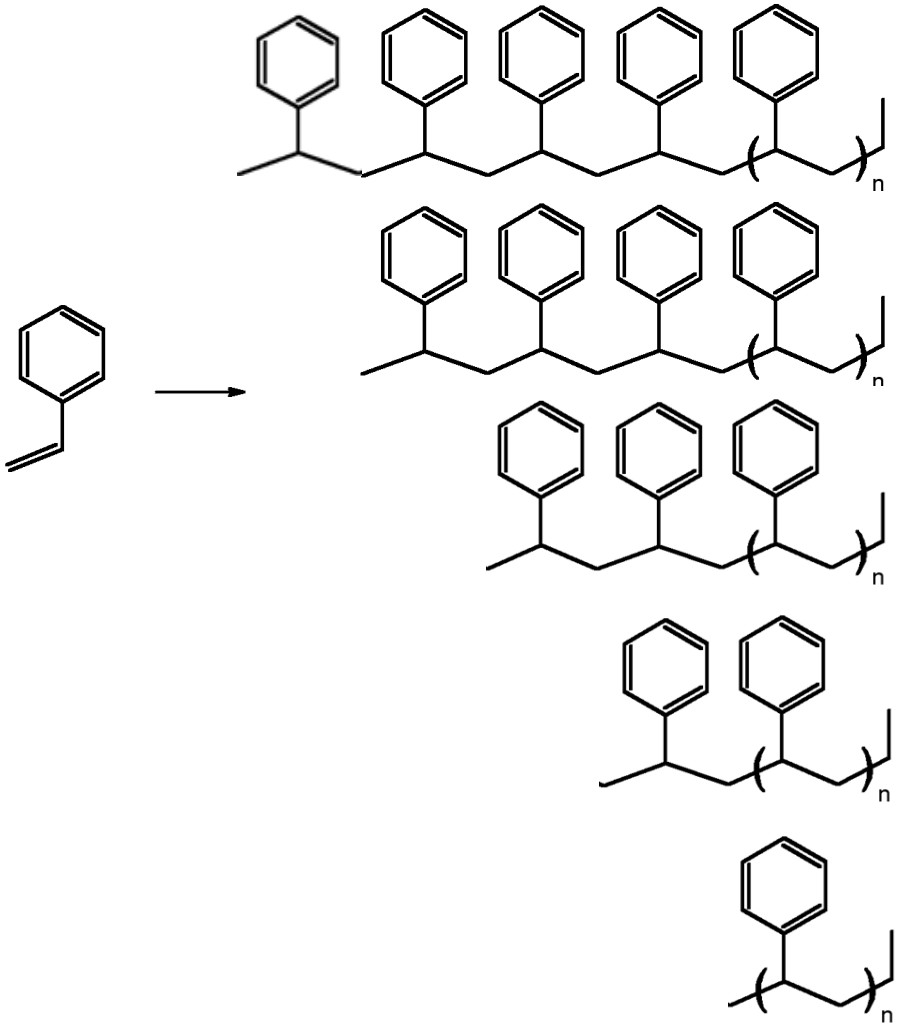
One way to describe the length of the polymer chains is in terms of an average molecular weight, i.e the average of all the chain lengths in the sample

HOWEVER….

Different samples of the same polymer can have the same average chain length but very different distributions of chain lengths depending on the method of production

In polymer science it is the molecular weight *distribution* that is important

Molecular Weight Distribution



6%

12%

70%

10%

2%

What is my Molecular Weight?

Molecular Weight Averages

NMR measures Mn

Light scattering measures Mw

Osmometry measures Mz

GPC measures *distribution*

Shape of Distributions

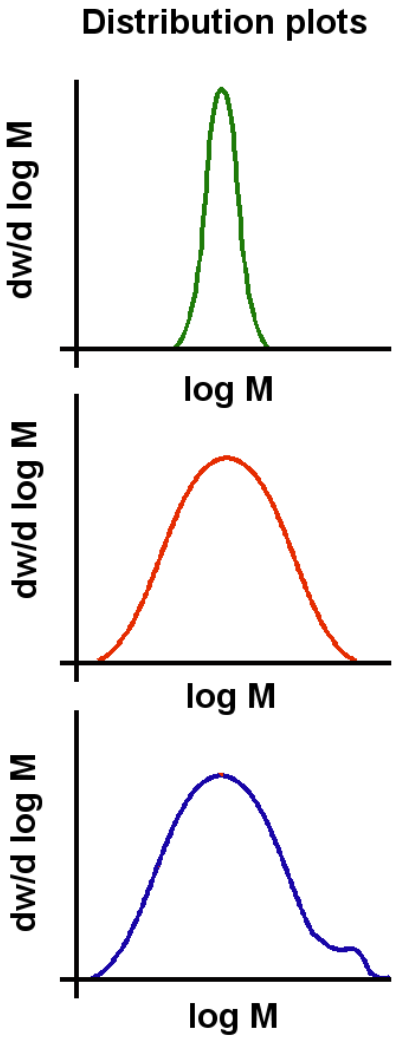
Even for the same type of polymer, each of these distributions will describe a polymer that behaves differently.

The Mn or Mw might be identical for all plots.

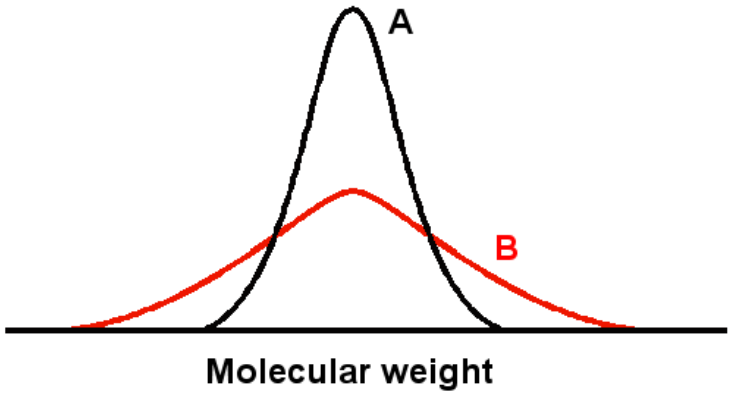
The red and green plots are for low and high polydispersity materials

The blue plot shows a high polydispersity material with a additional high molecular weight component

Describing these distributions is not easily, especially if they are complex



Effect of Polydispersity on a Polymer



As the broadness of the distribution decreases the strength and toughness of the polymer increases

However as the broadness of the distribution decreases the polymer becomes more difficult to process

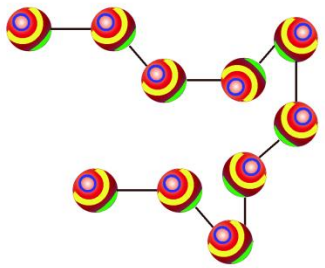
GPC provides key information to predict the processability and material properties of a polymer

	Strength	Toughness	Brittleness	Melt viscosity	Chemical resistance	Solubility
Increasing Mw	+	+	+	+	+	-
Increasing distribution	+	-	-	-	-	-

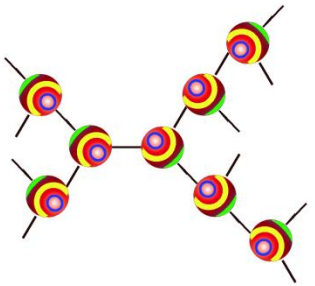
Variations in Polymers

There are a variety of ways to alter properties

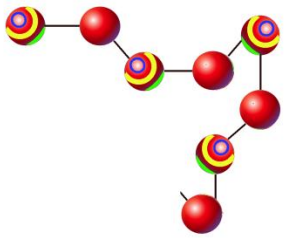
- Chemical Structure of Monomer Unit



- 3D Structure



- Different Monomer Units
- Length of polymer chains



- Distribution of polymer chain lengths

Introduction to GPC/SEC

GPC Separation Mechanism

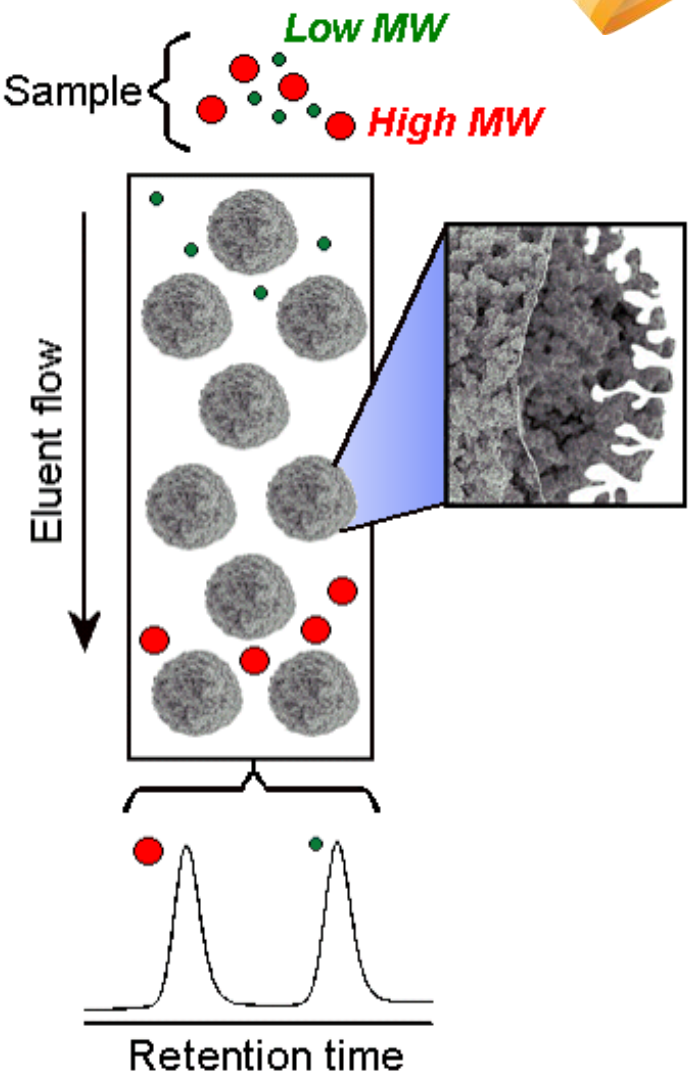
The established technique to measure the distribution of chain lengths is

Gel Permeation Chromatography, **GPC**

also known as

Size Exclusion Chromatography, **SEC**

Separation based on size of the polymer in solution (hydrodynamic volume) only.



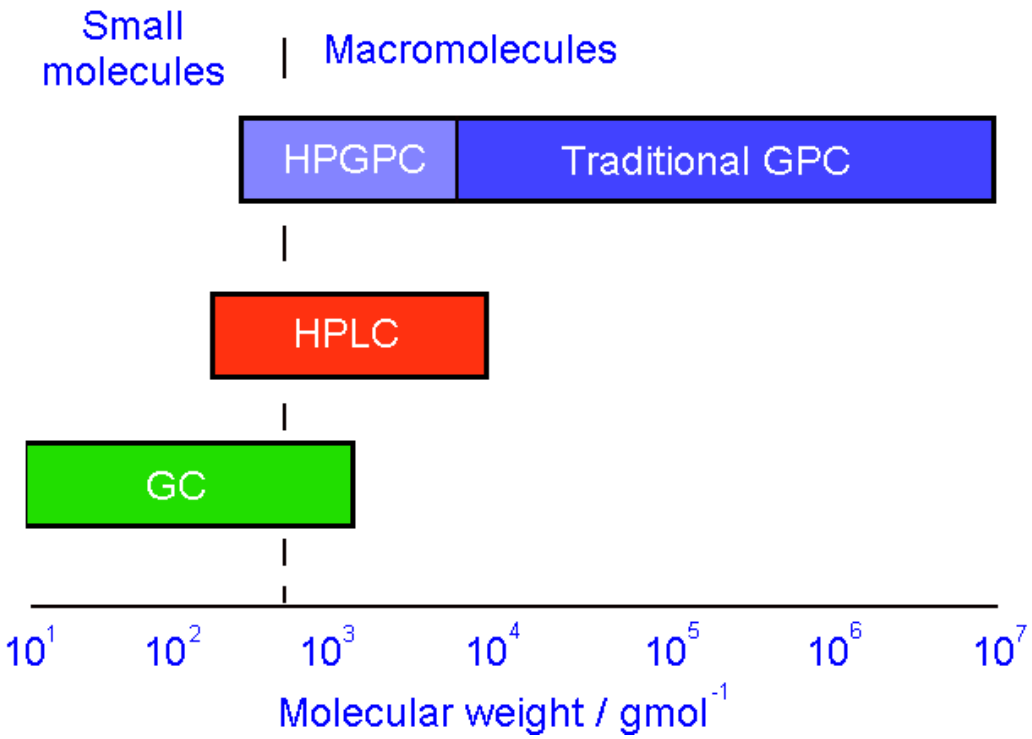
Introduction to GPC/SEC

GPC Separation Mechanism

Types of Chromatography

Interactive adsorption, partition, ion exchange, etc

Non-interactive GPC, SEC, GFC



GPC/SEC compared to HPLC

Isocratic elution, often single solvent systems

Typically uses organic eluents, not ACN, MeOH, IPA

Typically lower sample concentrations (0.1 – 0.2%)

Typically larger injection volumes (20 – 200 µl)

Primary use is to measure molecular weight distribution

Resolution provided by **non-interactive** mechanism

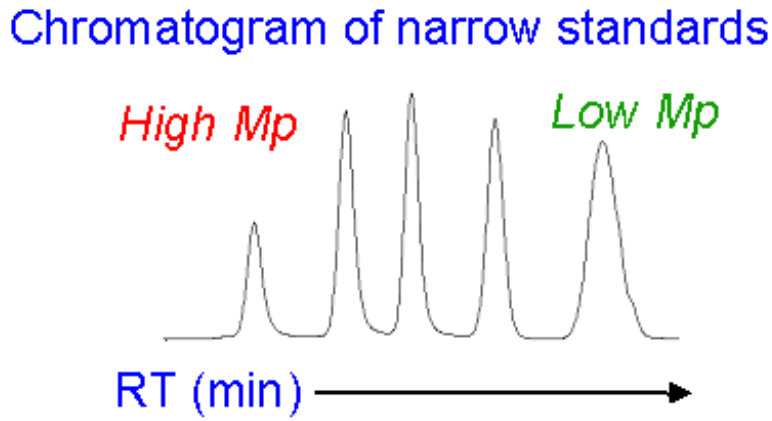
Larger columns (300 x 7.5 mm industry standard)

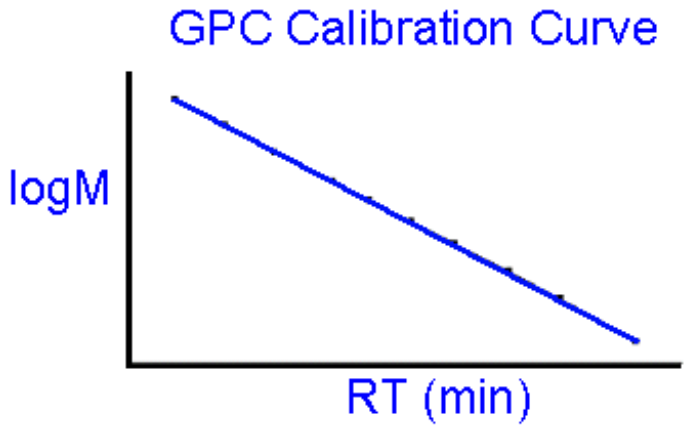
Use of multiple columns in series (2 – 4)

Conventional GPC

Generating molecular weights

- Calibrate the column with a set of polymer standards
- Plot retention time (RT) versus peak log molecular weight (logM)
- Calibration is used to generate molecular weights of unknowns
- **BUT** Molecular Weights are only **equivalent** to the Standards used
- So a Polystyrene calibration will give Polystyrene equivalent molecular weights for all samples analysed.





Molecular Weight Averages by GPC

INFINITELY BETTER TECHNOLOGIES

Number average $Mn = \frac{\Sigma Ni\,Mi}{\Sigma Ni}$

Mn can be correlative with polymer colligative properties, e.g. freezing point depression

Weight average $Mw = \frac{\Sigma Ni\,Mi^{2}}{\Sigma Ni\,Mi}$

Mw may be correlated with properties such as melt viscosity

Z average $Mz = \frac{\Sigma Ni\,Mi^{3}}{\Sigma Ni\,Mi^{2}}$

Mz may be correlated with properties such as toughness

Polydispersity, $d = \frac{Mw}{Mn}$

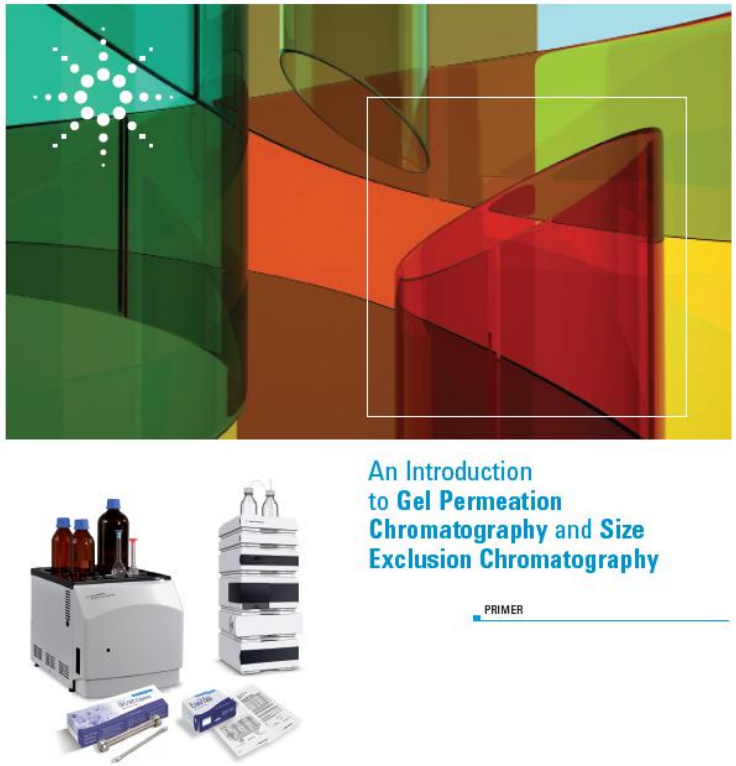
Polydispersity characterises the shape of the distribution

Introduction to GPC/SEC

GPC Separation Mechanism

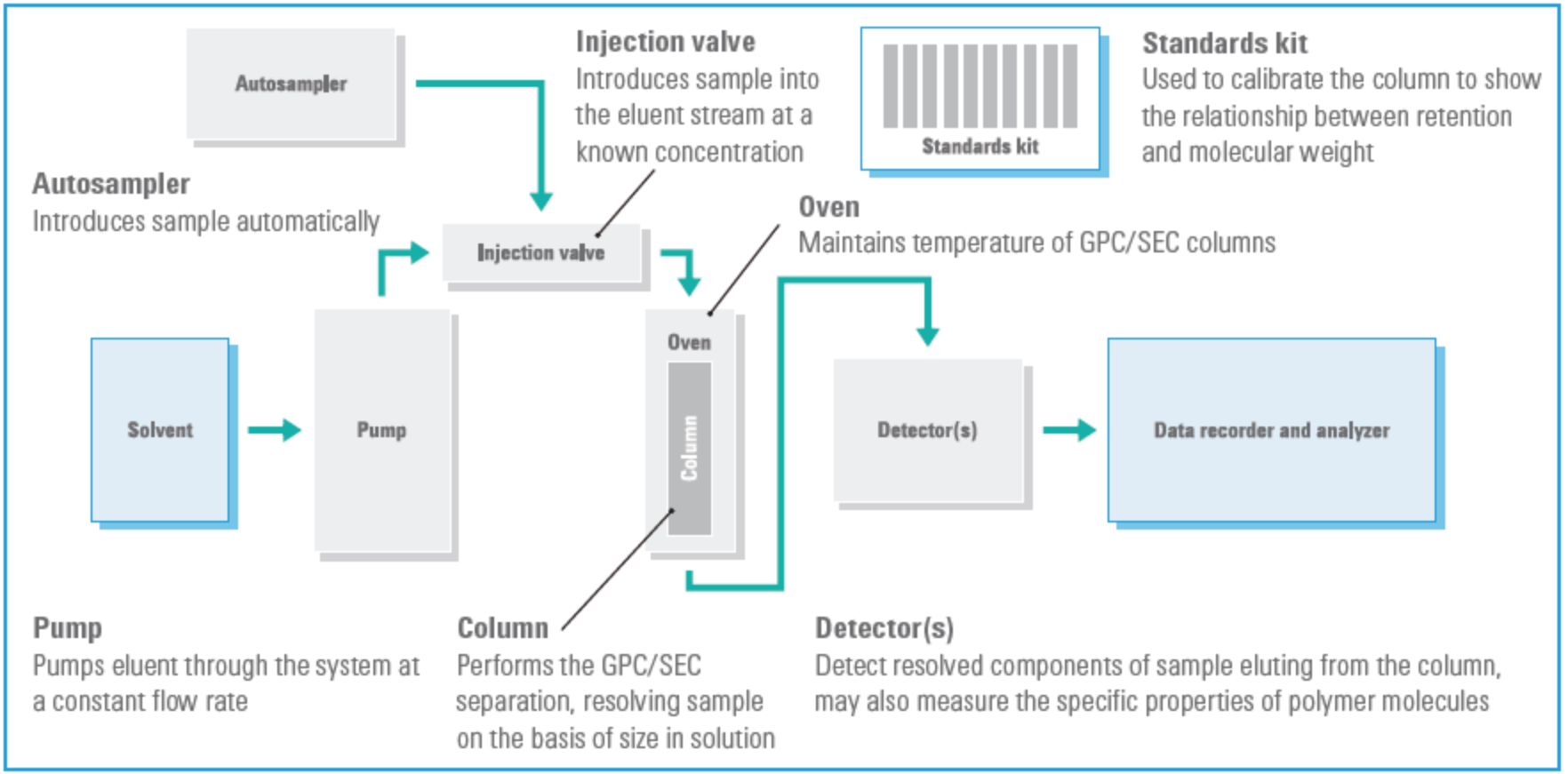
To learn more about Conventional GPC please ask your local Account Manager for the

Introduction to GPC Primer



A Typical GPC/SEC System

Components of a GPC/SEC system



Columns

For polymer applications using organic solvents

PLgel series

- Covers all molecular weight ranges
- high pore volume
- high efficiency
- maximize resolution

Unequalled solvent compatibility

- easy transfer between polar and non polar eluents
- outstanding physical rigidity
- provides extended lifetimes that minimize downtime

Available in a range of column dimensions, mini-bore to prep

Columns

For polymer applications using aqueous solvents

PL aquagel-OH series

Available with mixed and individual pore sizes, and 5, 8 and 15 µm particle sizes, to cover a very wide range of molecular weights.

- chemically and physically stable
- “neutral” surface
- high performance analyses
- neutral, ionic & hydrophobic moieties

Available in a range of column dimensions, mini-bore to prep

Polymer Standards

Ideal reference materials

- generate accurate, reliable GPC/SEC column calibrations
- highest quality polymer standards
- extremely narrow polydispersity
- widest molecular weight range commercially available

Comprehensive range

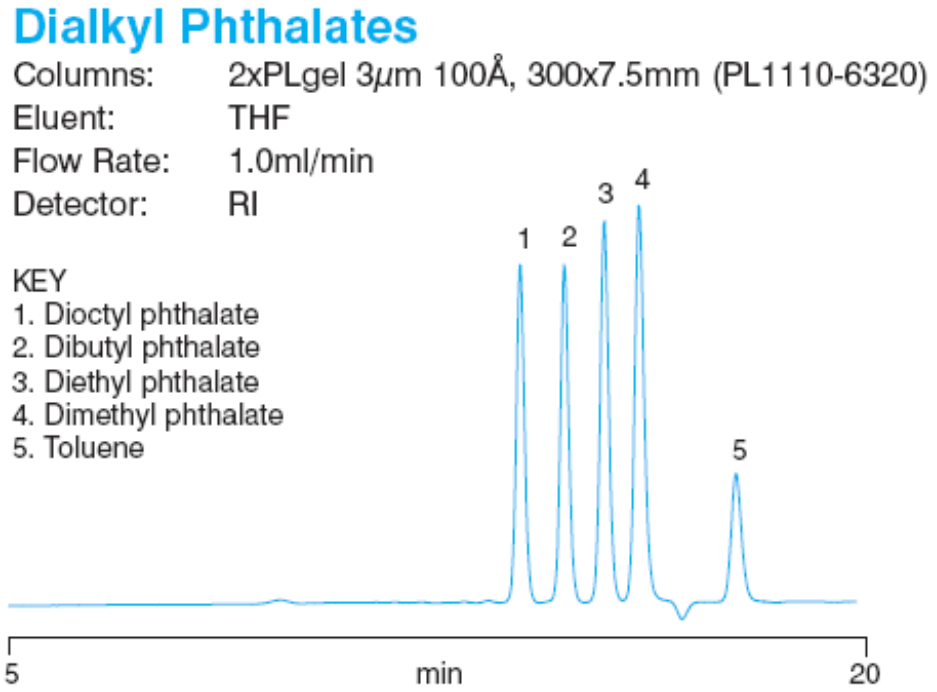
- EasiVial
- EasiCal
- Traditional calibration kits
- Covers all molecular weight ranges
- Organic & aqueous GPC/SEC applications.

Scope of GPC

Application Range

GPC can be applied to an extremely broad range of polymers

- Wide range of solvents employed
  - – Organic – Polar – Aqueous
- Wide range of operating temperatures
- Wide range of molecular weights



Scope of GPC

Application Range

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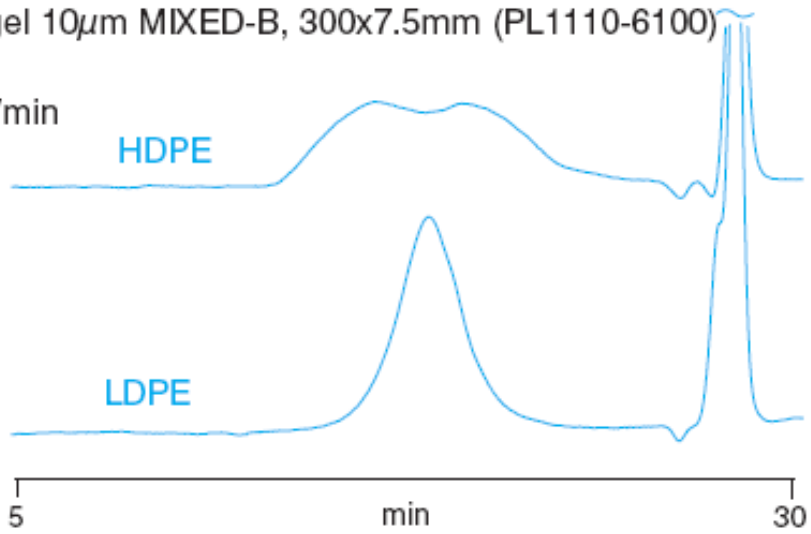
- Wide range of molecular weights

Polyethylenes

Columns:	3xPLgel 10µm MIXED-B, 300x7.5mm (PL1110-6100)
Eluent:	TCB
Flow Rate:	1.0ml/min
Temp:	160°C
Detector:	RI



Agilent GPC/SEC Software

The fastest, easiest way to complete your GPC Workflow

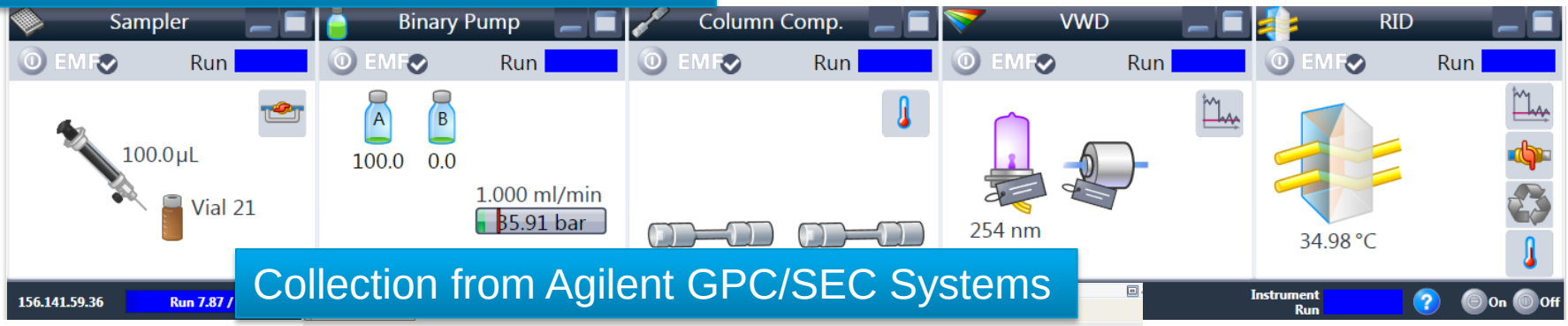
Simplifies and facilitates your GPC/SEC process

- Everything required for GPC/SEC in a single package

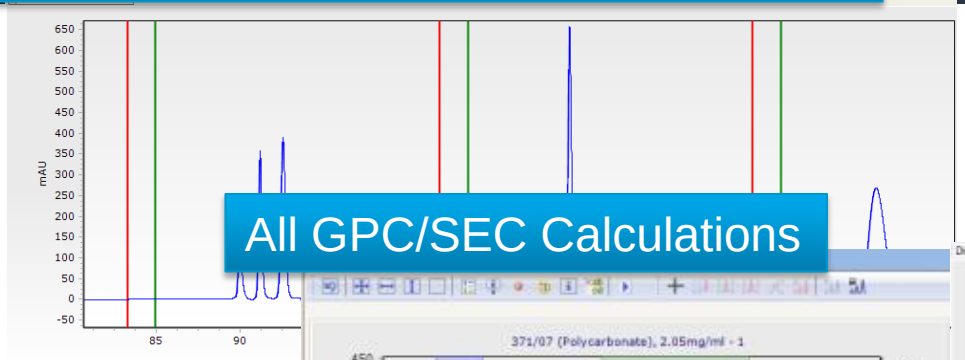
Agilent GPC/SEC Software

Single solution for all your GPC/SEC Requirements

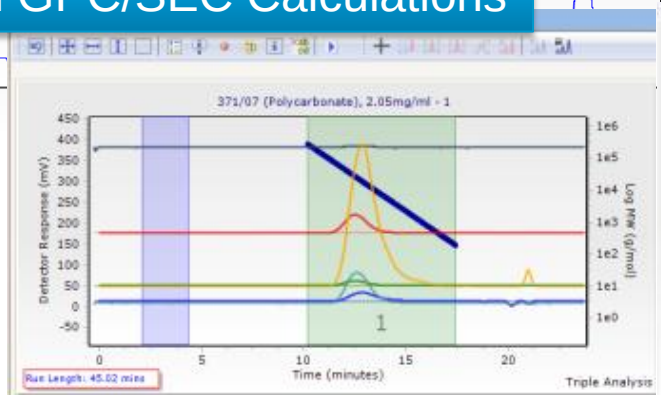
Control of Agilent GPC/SEC Systems

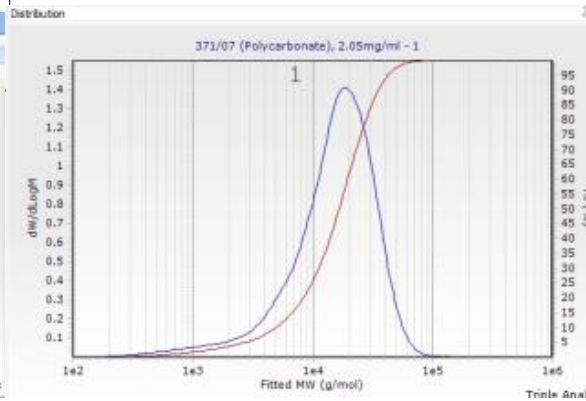


Collection from Agilent GPC/SEC Systems



All GPC/SEC Calculations

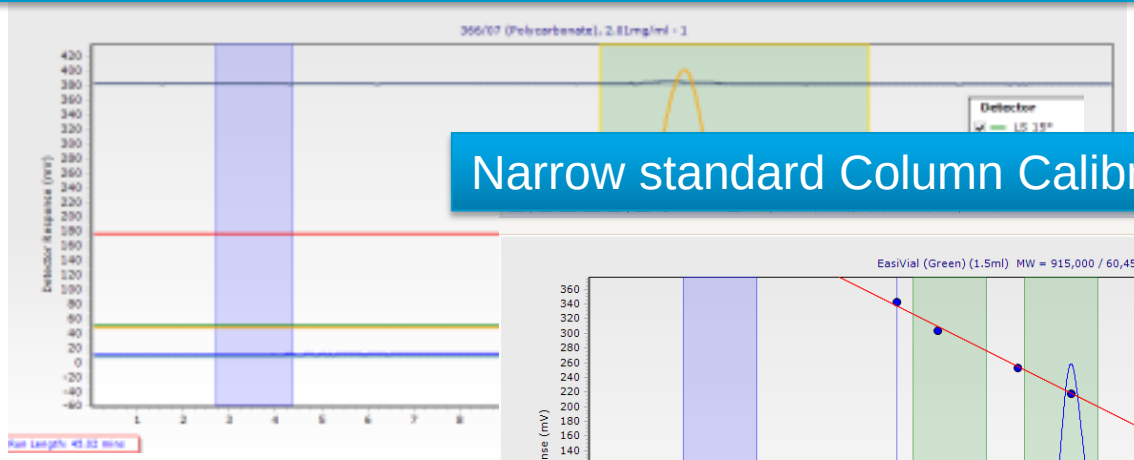




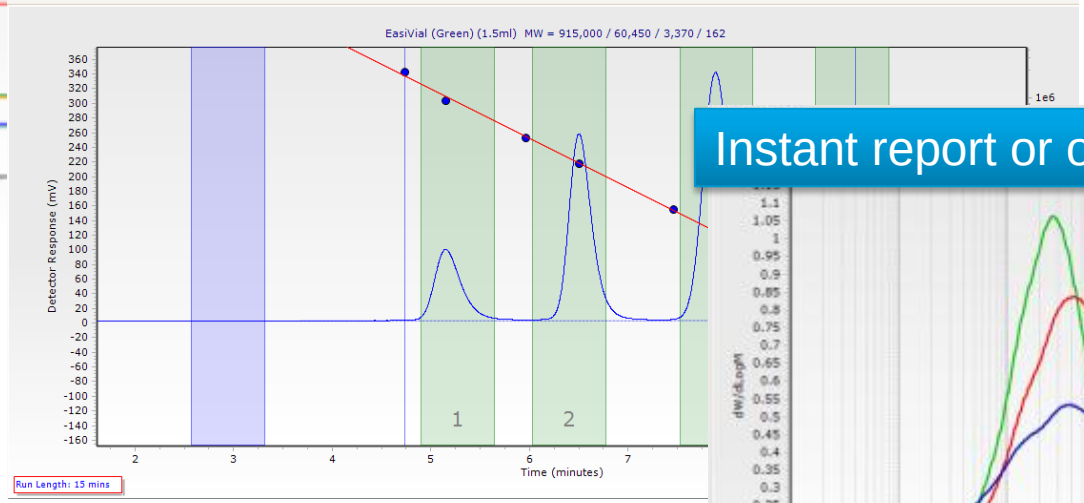
Agilent GPC/SEC Software

Fast and Easy GPC/SEC

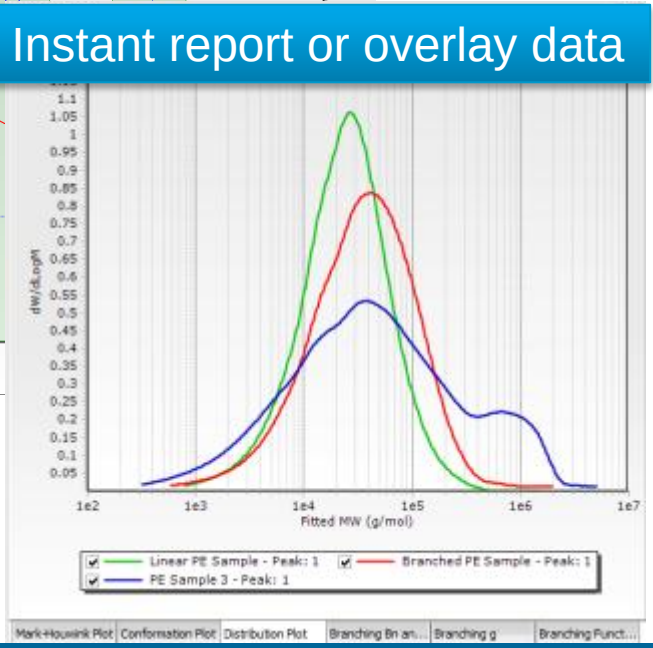
Baselines / integration regions added with single click



Narrow standard Column Calibrations easily created



Instant report or overlay data



Testing of material batches

Analysis of poly(styrene/butadiene) copolymers

Background:

A poly(styrene/butadiene) block copolymer mimics the properties of natural rubber.

Characteristics provided by:

- hard polystyrene chains surrounded by
- a network of rubbery polybutadiene

which provides strength and flexibility over a large temperature range.

Problem:

New batch of material is failing rheology testing

- Synthetic method to produce the copolymer has not changed
- End properties of the polymer significantly different to previous batches of the same material.

Solution:

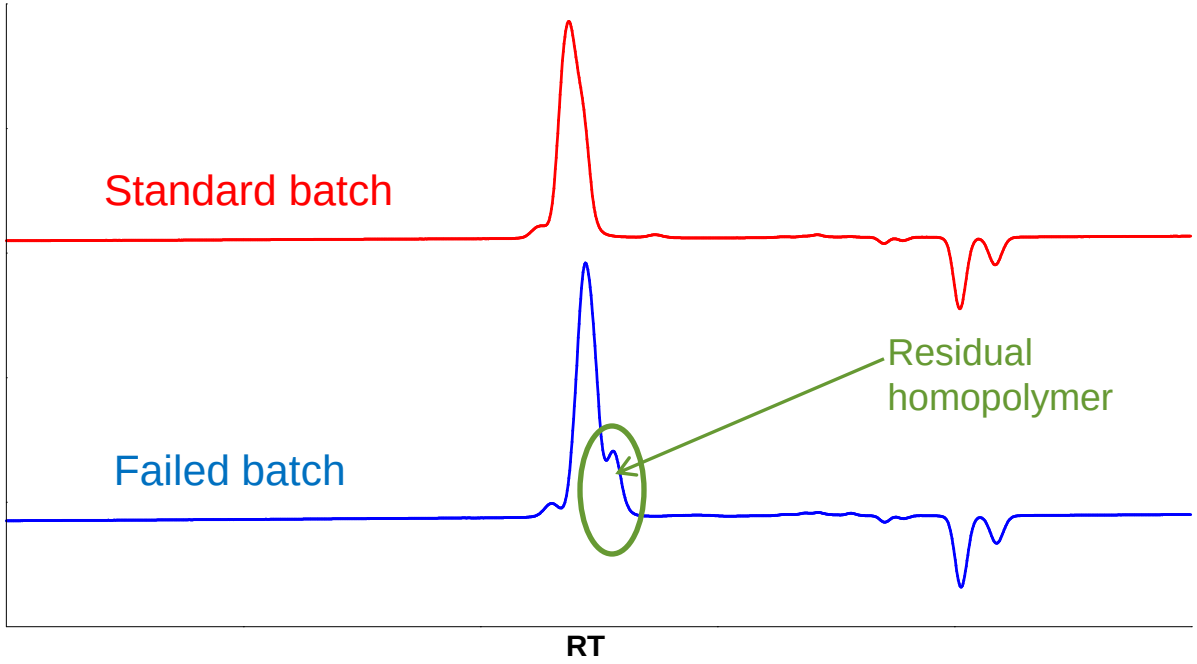
Investigate molecular weight distribution using GPC

Testing of material batches

Analysis of poly(styrene/butadiene) copolymers

The GPC chromatogram shows evidence of low molecular weight material within the failed batch.

System : 1260 Infinity GPC System
Columns : 2 x PLgel 5µm MIXED-D
Temperature : 40 °C
Eluent : THF

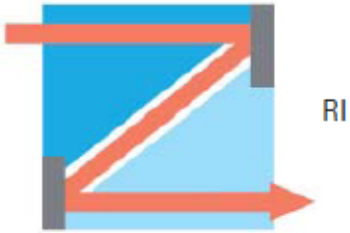


This was attributed to residual homopolymer from the synthesis which was imparting different characteristics to that of the desired copolymer.

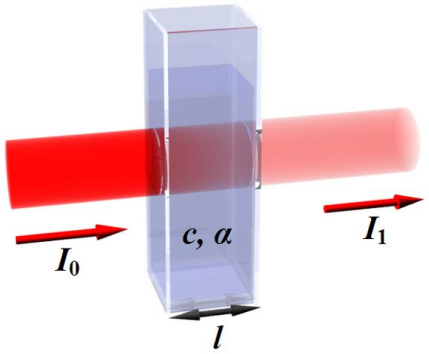
With the problem identified the cause was discovered and rectified.

Increasing the information from GPC/SEC

Most common detectors for GPC/SEC are *concentration* detectors:



RID



UV / DAD

<u>Evaporative</u> LSD

These provide information on the amount of polymer eluting from the column at any given time.

Increasing the information from GPC/SEC

There are two common *molecular weight sensitive* detectors.

Viscometer

Static Light Scattering Detector

These not only respond to the amount of polymer eluting but provide direct information on properties of the polymer relating to molecular weight.

Increasing the information from GPC/SEC

GPC/SEC provides critical information for the polymer chemist:

Distribution of chain lengths

(Relative molecular weights)

Further parameters can be determined by employing advanced detectors

The molecular **weight** (accurate or absolute)

The polymer's **size**

The polymer's **shape**

Can be used to investigate polymer **branching**

Polysaccharides

Investigation into structure

Complex polymers constructed from various sugar units.

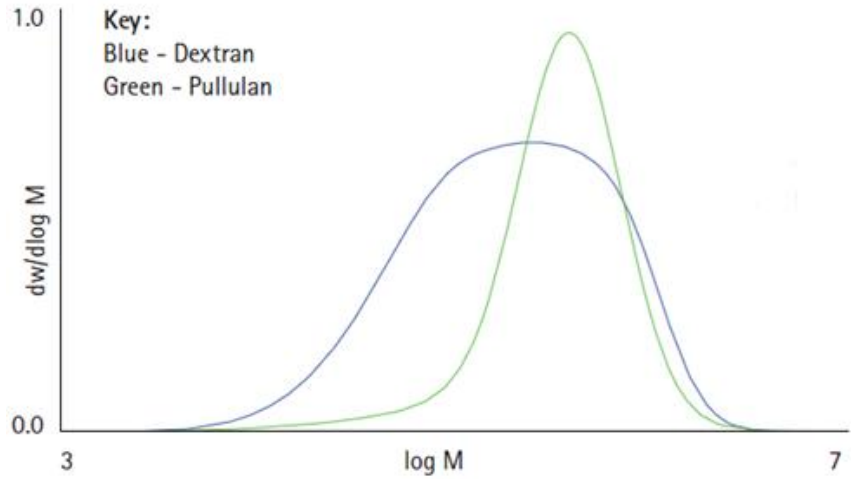
Wide range of polysaccharides with large structural difference depending on source.

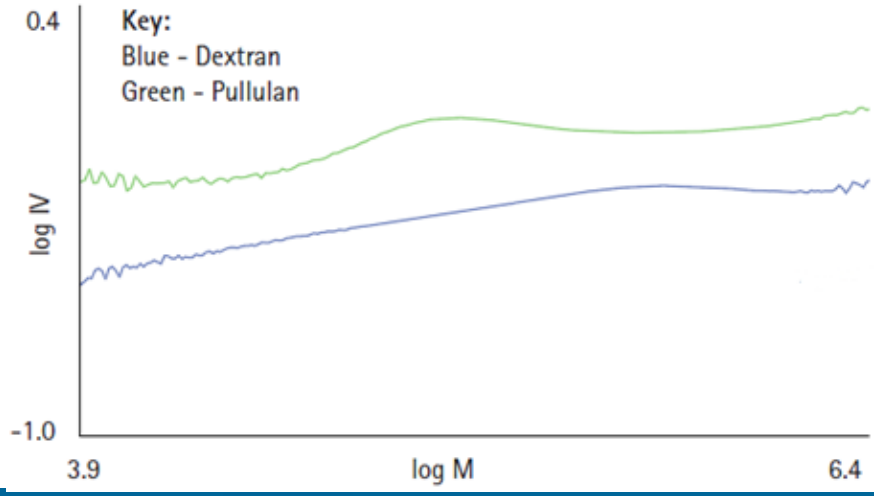
Pullulan, produced from starch by the action of a fungus, is composed of maltotriose units and has a linear structure.

Dextran, manufactured from sucrose by bacterial action has a highly branched structure.

Investigating their structure is of great interest for determining their properties and therefore end use application.

Light Scattering & Viscometry are employed to highlight molecular weight and structural differences





Summary

GPC/SEC is an indispensable analytical tool for the analysis of

- Polymers
- Polymer Additives

Applicable in a wide range of solvents allowing almost all commercial polymers to be analysed

The critical and often unique information attained is the population of polymer chain lengths in any given sample

The GPC/SEC experiment can be expanded to further investigate polymer properties – more on this later

Thanks for Listening

Any Questions

COMPREHENSIVELY BETTER POLYMER ANALYSIS

From research to quality control, each of your challenges in polymer characterization requires a unique approach. No matter which state-of-the-art solution you prefer Agilent Technologies delivers proven answers. Experience the versatility, performance, and confidence that come with 35 years of GPC/SEC engineering excellence from Agilent Technologies—the Polymer Analysis People.

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REPRODUCIBLE
Agilent 1260 Infinity GPC

ACCURATE
Agilent 1260 Infinity MDS GPC

DEDICATED
Agilent PL-GPC 50

POWERFUL
Agilent PL-GPC 220

EXTENSIVE
Agilent GPC/SEC Columns and Calibrants

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	Analysis of elastomers by GPC/SEC	5990-6866EN
	Biodegradable polymers	5990-6920EN
	Low molecular weight resins and prepolymers	5990-6845EN
	Excipient analysis	5990-7771EN
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	A guide to multi-detector GPC	5990-7196EN
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	1260 Infinity Multi-GPC/SEC System	5990-9921EN
	Agilent PL-GPC 50	5990-9937EN
	Agilent PL-GPC 220	5990-9926EN
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	GPC/SEC standards	5990-7996EN
Selection guide	Quick guide for selecting columns and standards for GPC/SEC	5990-6868EN

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