An Introductions to Advanced GPC Solutions

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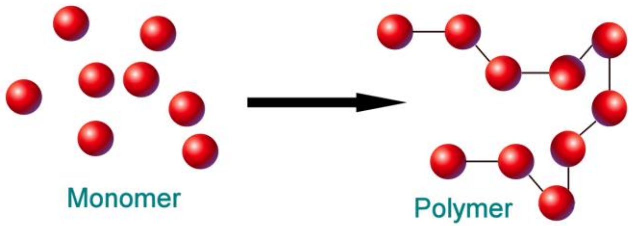
Introduction to Polymers

Polymers are long chain molecules produced by linking small repeat units (monomers) together

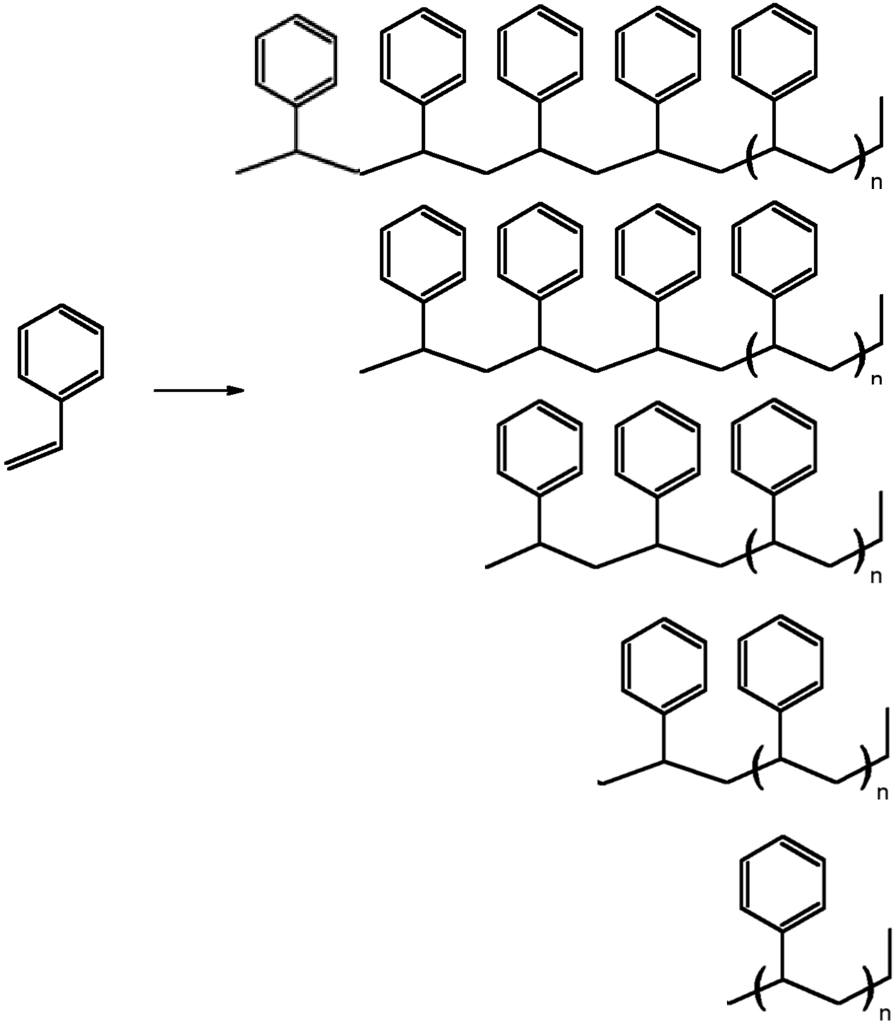
Very different physical properties are attained compared to the monomers, dependent on the length of the polymer chains

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

- Strength
- Toughness
- Brittleness
- Melt Viscosity
- Chemical Resistance
- Solubility



Distribution of Polymer Chain Lengths
Conventional GPC



6%

12%

70%

10%

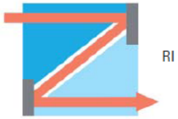
2%

There will usually be a large range of chain lengths in a polymer material.

The GPC technique is used to measure this *distribution* of chain lengths

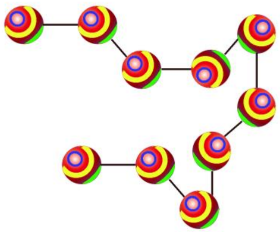
Characterization of Polymers

There are a variety of characteristics that influence polymer behaviour and performance. Some of the most important can be investigated using GPC and FTIR

- **Distribution** of Polymer Chain Lengths -- GPC 

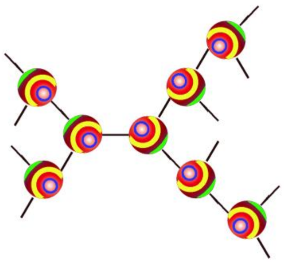
DRI

  (conventional GPC -- relative molecular weight)



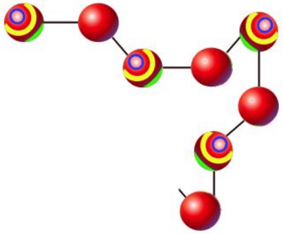
- Molecular Weight – Length of Chains -- GPC

- Polymer Structure – Branching -- GPC



- Different Monomer Units -- FTIR

- Chemical Structure of Monomer Unit -- FTIR



What is a GPC/SEC System?

- A simple isocratic LC system fitted with a GPC/SEC column is a GPC/SEC system!
- Mode of separation only difference to other HPLC methods
- Specialist detectors can be used to determine properties of the samples investigated
- Special GPC/SEC software required to perform analysis

Liquid Chromatograph → **GPC/SEC Column** → **Detectors, Data Acquisition and Processing**

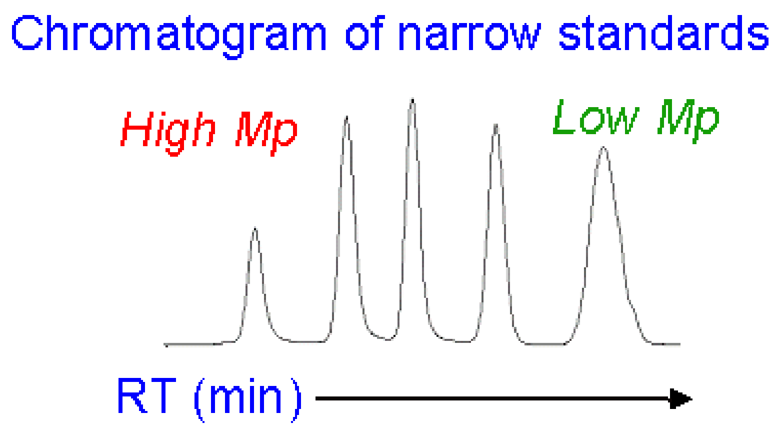
Simple isocratic system
Provides solvent flow

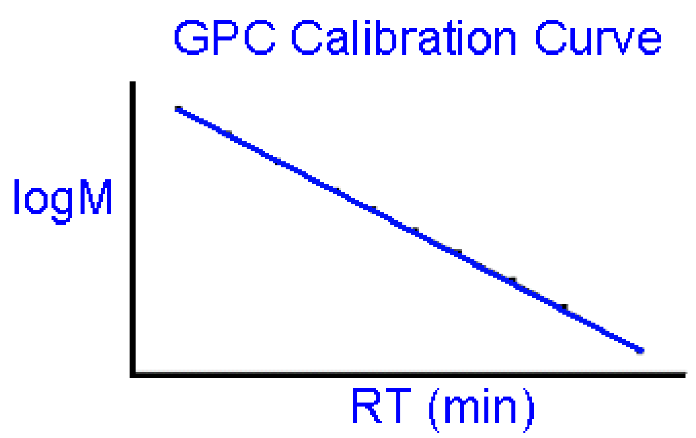
Column separates sample
Into components

Detectors measure the properties of eluted sample, data system provides analysis

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 from Conventional GPC

Mn	- *number average molecular weight*
Mw	- *weight average molecular weight*
Mz	- *z average molecular weight*
Mz+1	- *z+1 average molecular weight*
Mp	- *peak molecular weight*
Mw/Mn	- *polydispersity by GPC*

A typical GPC Case Study
Testing of material batches – QC Troubleshooting

Background:

A poly(styrene/butadiene) block copolymer is a high performance synthetic rubber.

Characteristics provided by:

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

which provides strength and flexibility over a large temperature range

Perfect for tyre manufacturers – Dunlop, Goodyear, Hankook, Firestone …….

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.

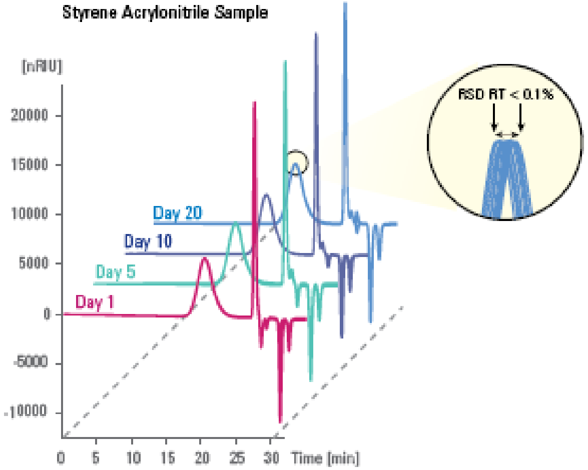
Solution:

Investigate molecular weight distribution using GPC

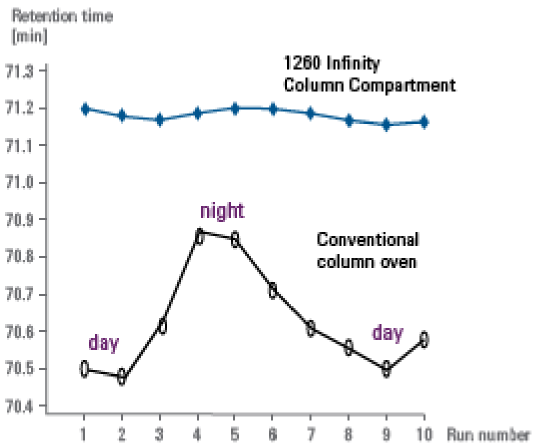
Instrument Requirement
GPC/SEC System

Precise and reproducible GPC

- Pump, Injector, Column Oven, Detector (RI)
- Flow rate precision & temperature stability
- Instrument, Software, Columns and Standards



This overlay of 10 consecutive runs per day over 20 days shows the remarkable daily and day-to-day precision of retention times. The average RSD for retention times is 0.035%.



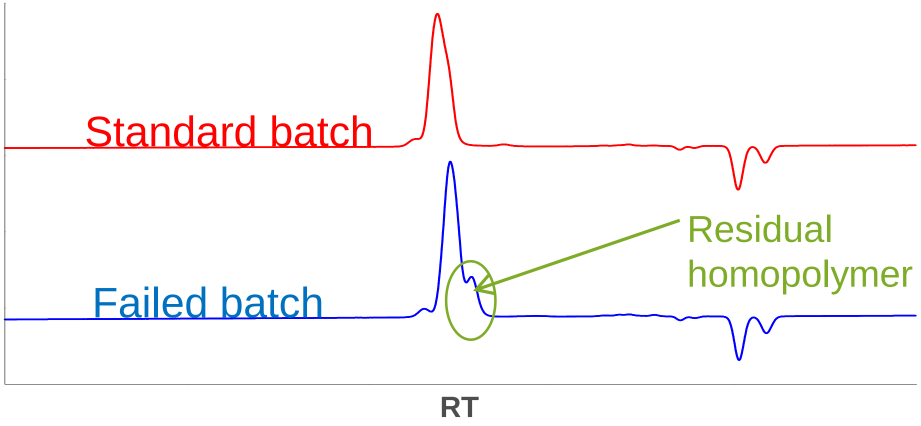
The 1260 Infinity Column Compartment exhibits superior temperature stability and is unaffected by overnight temperature variations often encountered in laboratories.

Testing of material batches

Analysis of synthetic rubber

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

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



Molecular weight averages can be calculated to give a numerical comparison

With the problem identified the cause was discovered and rectified.

Agilent Infinity GPC System is used to troubleshoot a production problem and improve manufacturing consistency when used as part of the QC process.

How do we improve our Polymer Analysis?

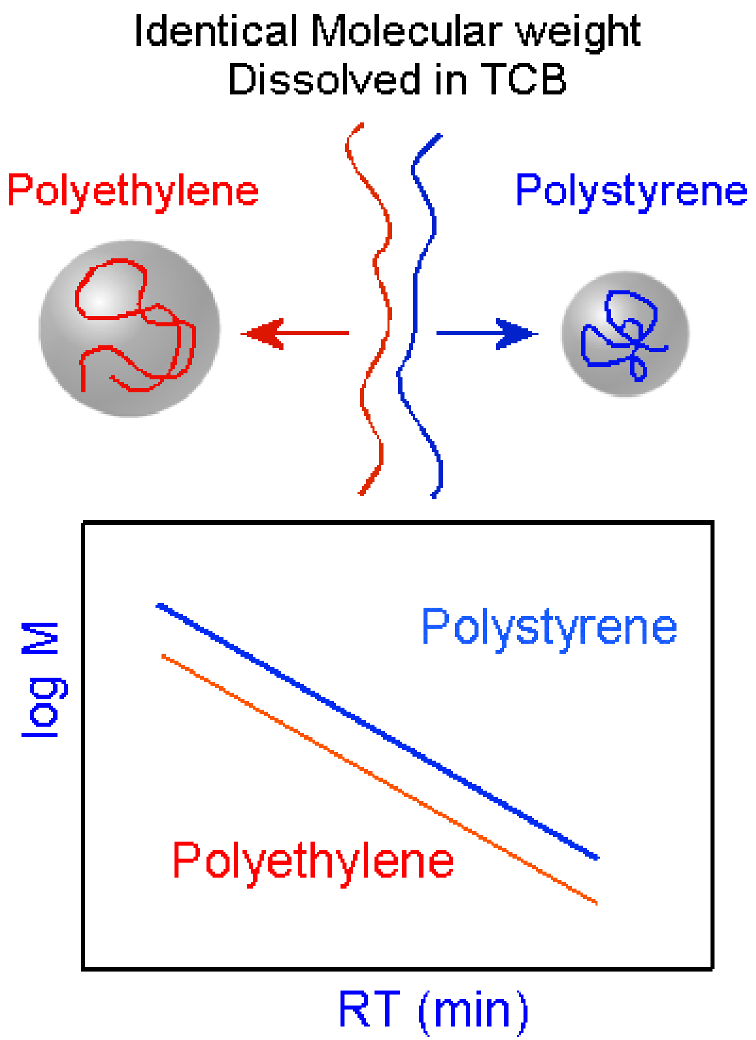
Molecular weight sensitive detectors for GPC

Molecular weights calculated from conventional GPC will be relative to the standards only

This is because two polymers of different chemistries will interact differently with a particular solvent

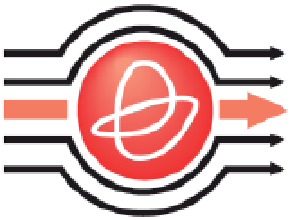
At any molecular weight, the two polymers will have different sizes in solution

To improve our calculated molecular weights we add molecular weight sensitive detectors to our GPC system



How do we improve our Polymer Analysis?
Molecular weight sensitive detectors for GPC

- **Viscometer** detector
  - Response proportional to the intrinsic viscosity (IV) of the polymer
  - Generate **accurate molecular weight** for polymers using the ***Universal Calibration*** principle
  - Determination of **Branching**
  - Conformation of polymer



- **Dual angle light scattering (LS)** detector
  - Response directly proportional to molecular weight (Mw) of the polymer – **‘Absolute Molecular Weight’**
  - Scattered light measured at more than one angle permits determination of **Radius of gyration (Rg)** – a key piece of information for Polymer Chemists
  - Determination of **Branching**
  - No column calibration required

1260 Infinity GPC/SEC Multi Detector Suite

Advanced detection for Absolute Accuracy

Information Rich

- Accurately heated (ambient to 60 °C) advanced detector modules:
  - Refractive Index
  - Viscometer
  - Dual Angle Light Scattering

Low Dispersion

- Industry leading detector flow cell technology

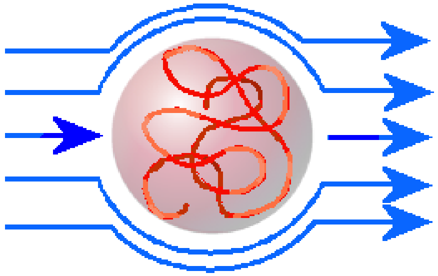
Agilent GPC/SEC Software

- Single software solution

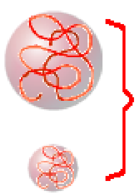
Molecular Weights

Using a Viscometry Detector

The IV of the standards is used to generate a *Universal Calibration.* By measuring the viscosity response of the samples, ‘true’ molecular weights independent of the standards used for the column calibration are calculated.

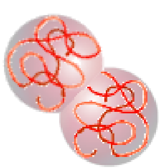


Polymer coil disrupts laminar flow of solvent

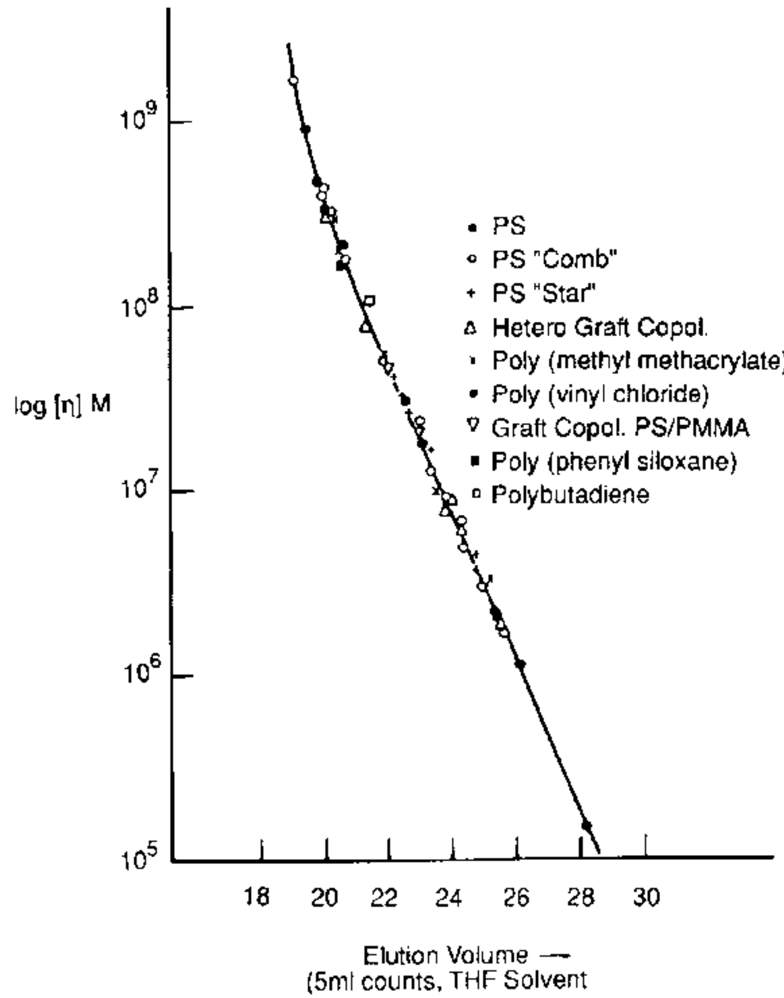


The smaller the coil (i.e. lower MW), the lower the viscosity

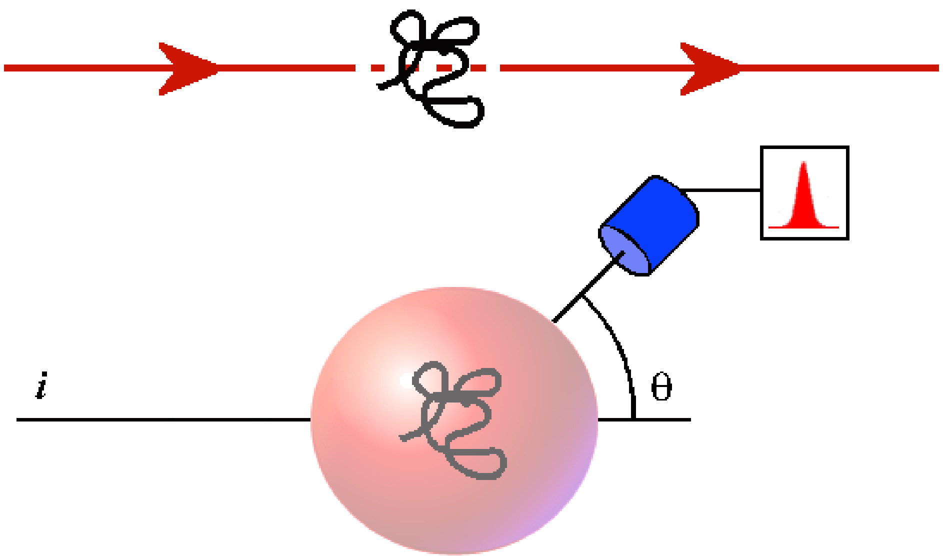
Intrinsic viscosity is a property of the isolated coil in solution as the concentration tends to zero



The greater the concentration, the greater the viscosity



Molecular Weights
Using a Light Scattering Detector



Excess scattered light from a sample in solution is directly proportional to molecular weight (Mw).

$$R(\theta) = C\,M\,(dn/dc)^2\,P(\theta)\,K(\theta)$$

Absolute determination

No reliance on column calibration so 'absolute' molecular weights are calculated

Characterization of Polymers

There are a variety of characteristics that influence polymer behaviour and performance. Some of the most important can be investigated using GPC and FTIR

- **Distribution** of Polymer Chain Lengths -- GPC

  (conventional GPC -- relative molecular weight)

- Molecular Weight – **Length** of Chains -- GPC

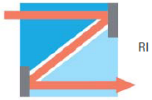
  (true, absolute molecular weight)

- **Polymer Structure** – Branching -- Mw -- GPC

  (shape and size of polymer)

- Different Monomer Units -- FTIR

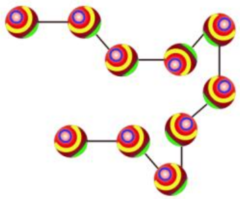
- Chemical Structure of Monomer Unit -- FTIR

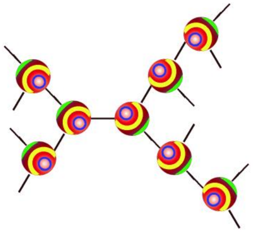


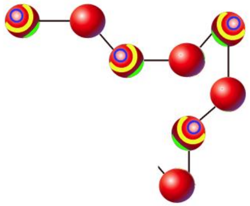
DRI

Light Scattering

Viscosity



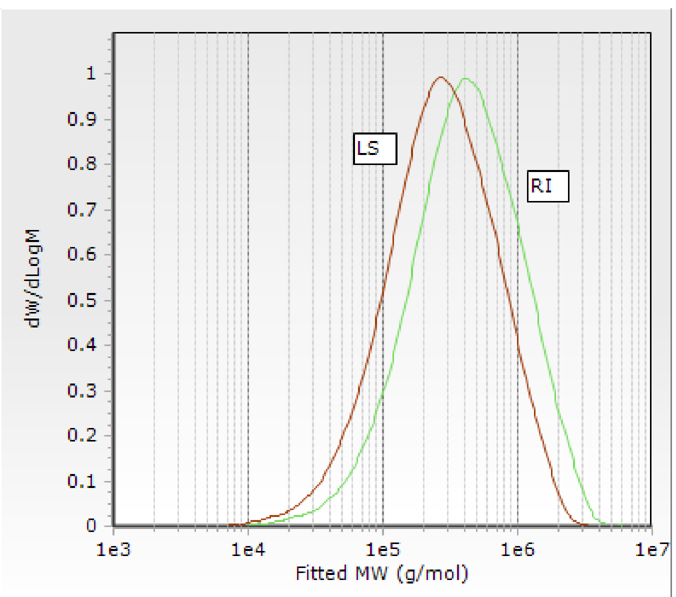




Length of polymer chains (Mw)

To measure ‘true’ Molecular Weights rather than relative ones generated from conventional GPC, we can use an advanced detector which directly measures the Mw of the polymer chains

A Light Scattering detector will produce a response directly proportional to the Molecular Weight (Mw) of the polymer.



Sample	Conventional Calibration		Light Scattering	
	Mn	Mw	Mn	Mw
Synthetic rubber	251000	604800	154700	382900

In this example the true Mw of the Synthetic Rubber is actually 37% smaller than that calculated through conventional GPC

Advanced GPC Case Studies

Analysis of polycarbonates

- Polycarbonates are thermoplastic polymers with excellent optical and impact resistant properties
- Common applications in everyday life are, sunglasses, CD's, headlights.

Conventional GPC only gives you 'comparative' molecular weights

Using a viscometer detector in the you can calculate 'true' molecular weights using a 'Universal Calibration'

True Molecular Weights

Analysis of polycarbonates

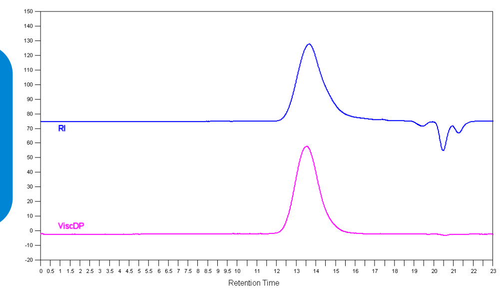
- Convert ‘conventional’ GPC with an RI detector to ‘advanced’ GPC with the addition of a Viscometer
- Two detectors = true molecular weights

RI

PS Equivalent Mw
Mw = 61273
Mn = 21666
Mz = 99350

RI + Visc

True Mol Wt
Mw = 37815
Mn = 11376
Mz = 64712



These advanced detectors can be added to <u>any</u> HPLC/GPC and achieve ‘information rich’ GPC...

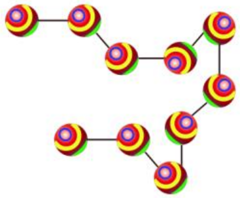
Characterization of Polymers

There are a variety of characteristics that influence polymer behaviour and performance. Some of the most important can be investigated using GPC and FTIR

- **Distribution** of Polymer Chain Lengths -- GPC

  (conventional GPC -- relative molecular weight)

DRI



- Molecular Weight – **Length** of Chains -- GPC

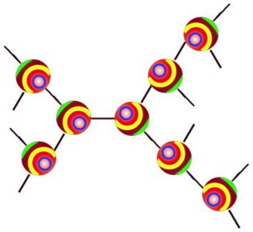
  (true, absolute molecular weight)

Light Scattering

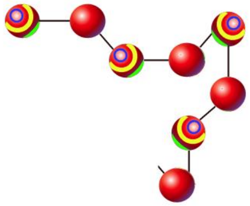
- **Polymer Structure** – Branching -- Mw -- GPC

  (shape and size of polymer)

Viscosity



- Different Monomer Units -- FTIR



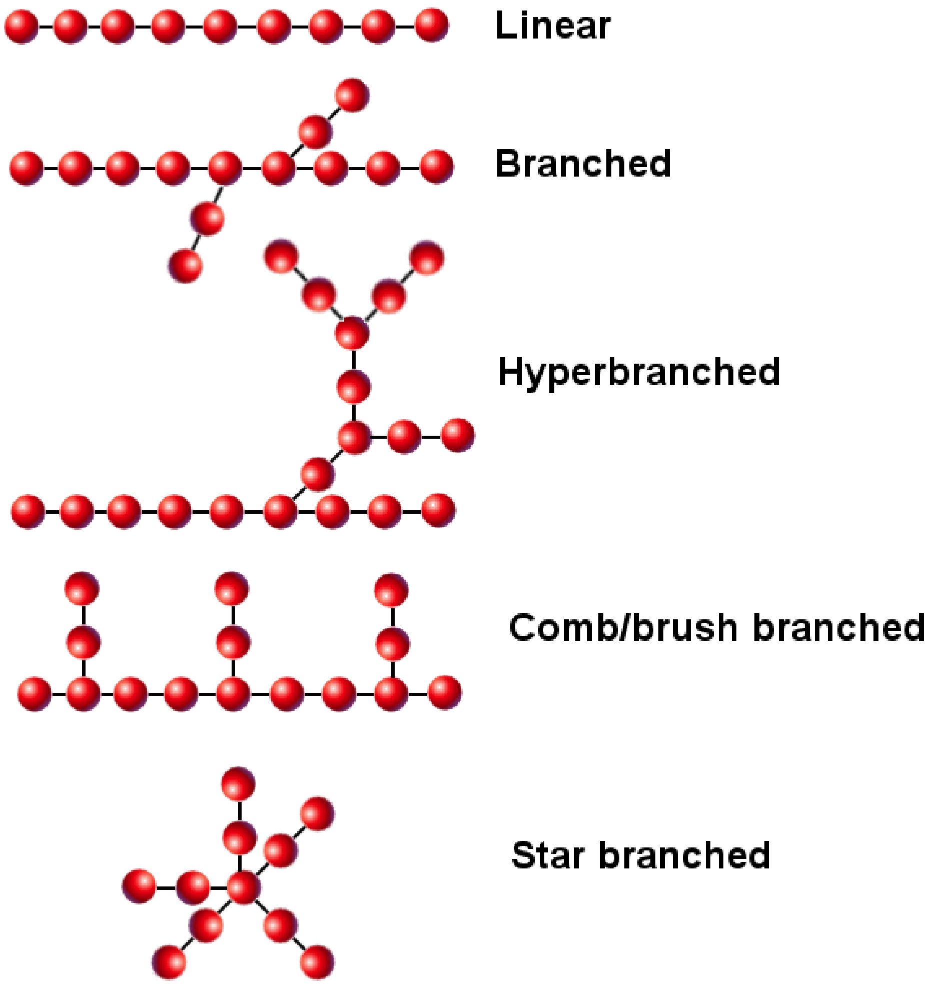
- Chemical Structure of Monomer Unit -- FTIR

Polymer Structure -- Branching

Polymers may have a wide variety of branching structures depending on how they have been made or modified

The branching can be further defined by the length of the branch into long chain or short chain branching

Long chain branching affects the size and density of polymer molecules and is easier to measure by GPC.



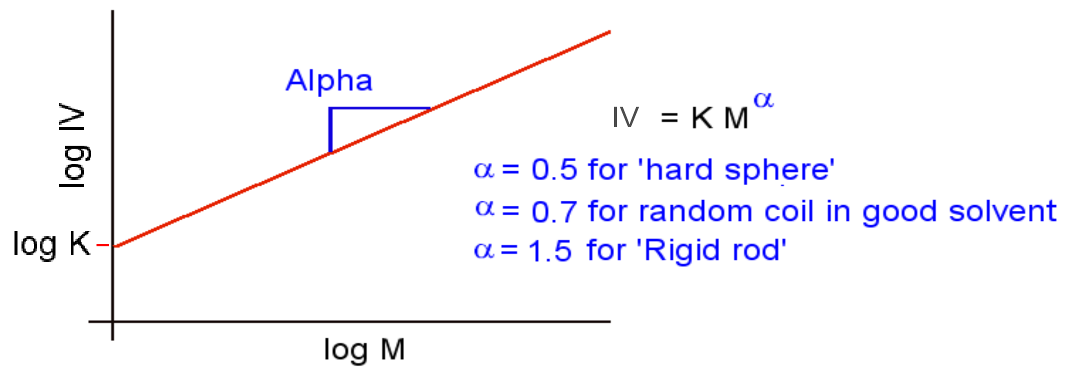
Polymer Structure -- Branching

So, rather than being linear chains, many polymers have a more complex branched structure.If we use a detector that measures a different property of the polymer in solution, we extract more information about this polymer structure.

A viscometer responds directly to the intrinsic viscosity (IV) of the polymer.

Using this response we can generate a *Mark-Houwink Plot* which relates the viscosity of the polymer to molecular weight

The slope of this plot can also indicate the shape of the polymer.



Linear homopolymers have linear slopes

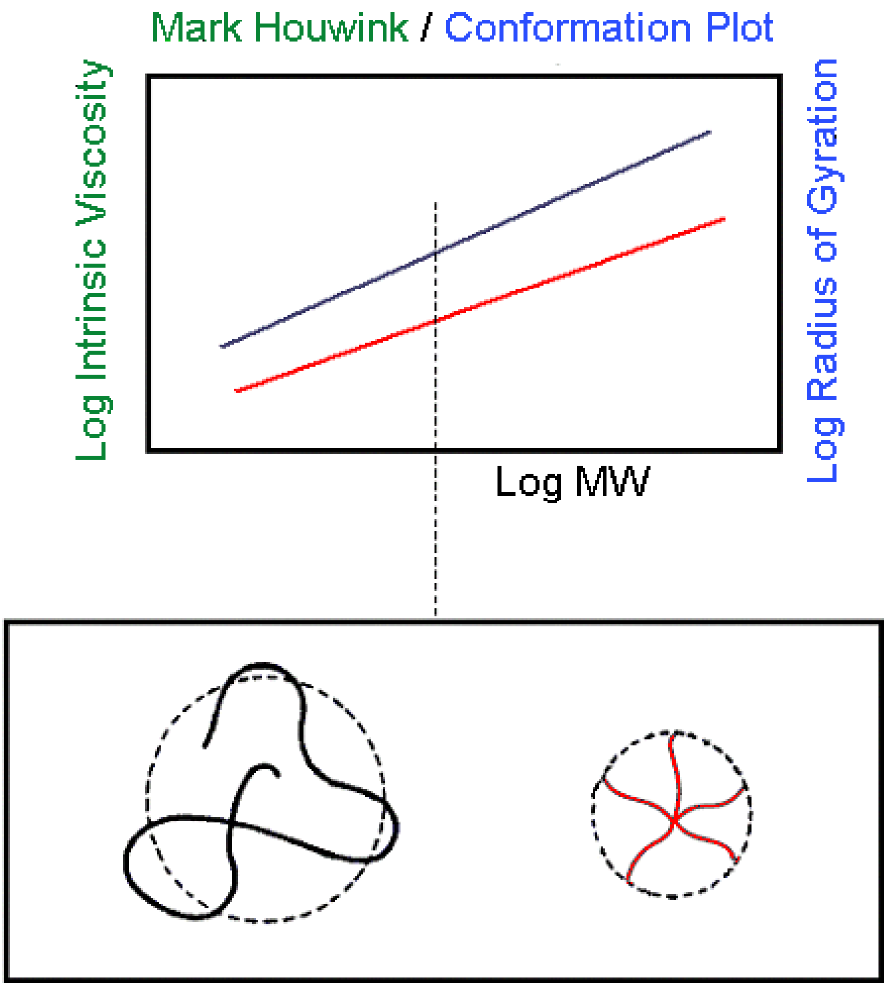
Using Viscometry and Light Scattering

Determination of Branching

Linear versus **branched** polymers

We can compare Mark Houwink plots of linear and branched polymers. The **branched** molecule will have a smaller hydrodynamic volume and Radius of Gyration compared to a **linear** molecule

This information can be very useful when looking for evidence of branching in apparently similar polymers

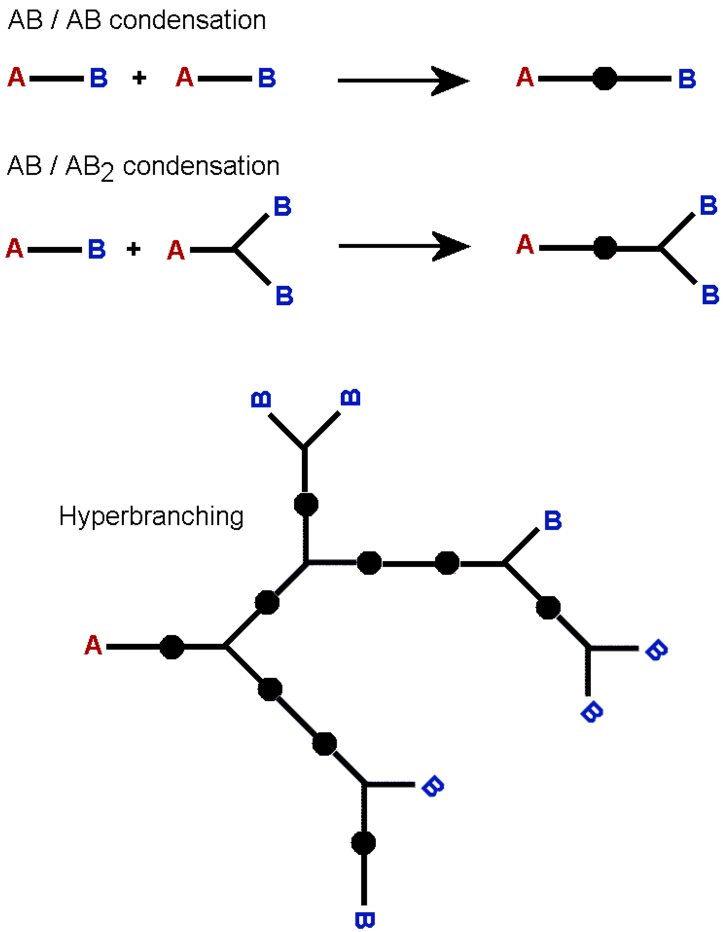


Hyperbranched Polyesters

Effect of Branching on IV

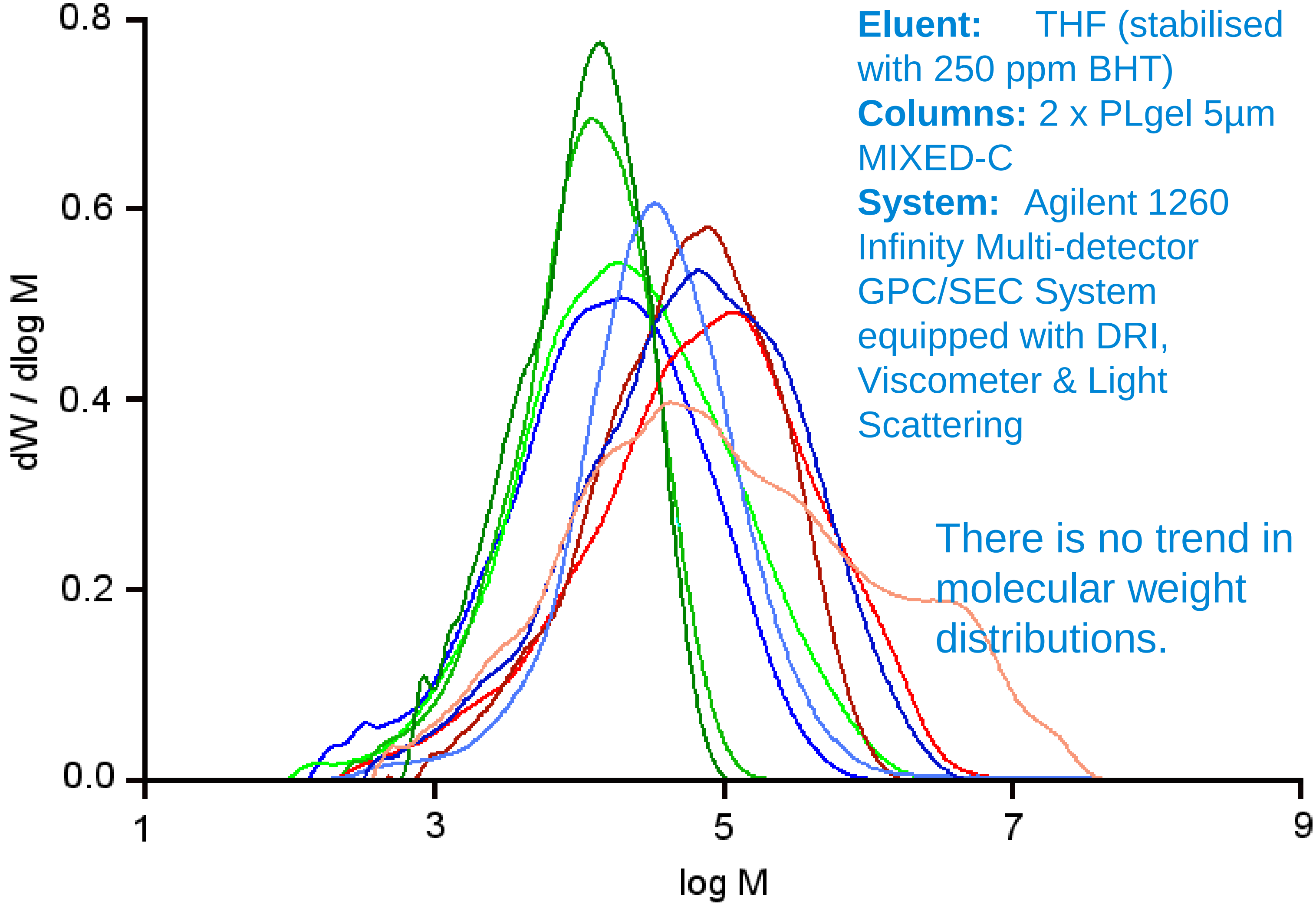
Hyperbranched polyesters have been found to contribute to improved physical, chemical and mechanical properties

- Polyester AB/AB_2 polymers produced by the condensation of A and B end groups
- Branching introduced by the addition of AB_2 monomers into the reaction
- A Hyperbranched polymer structure is formed
- Different chain length AB_2 monomers can be used to vary the 'compactness' of the polymer molecule in solution



Hyperbranched Polyesters

Molecular Weight Distributions

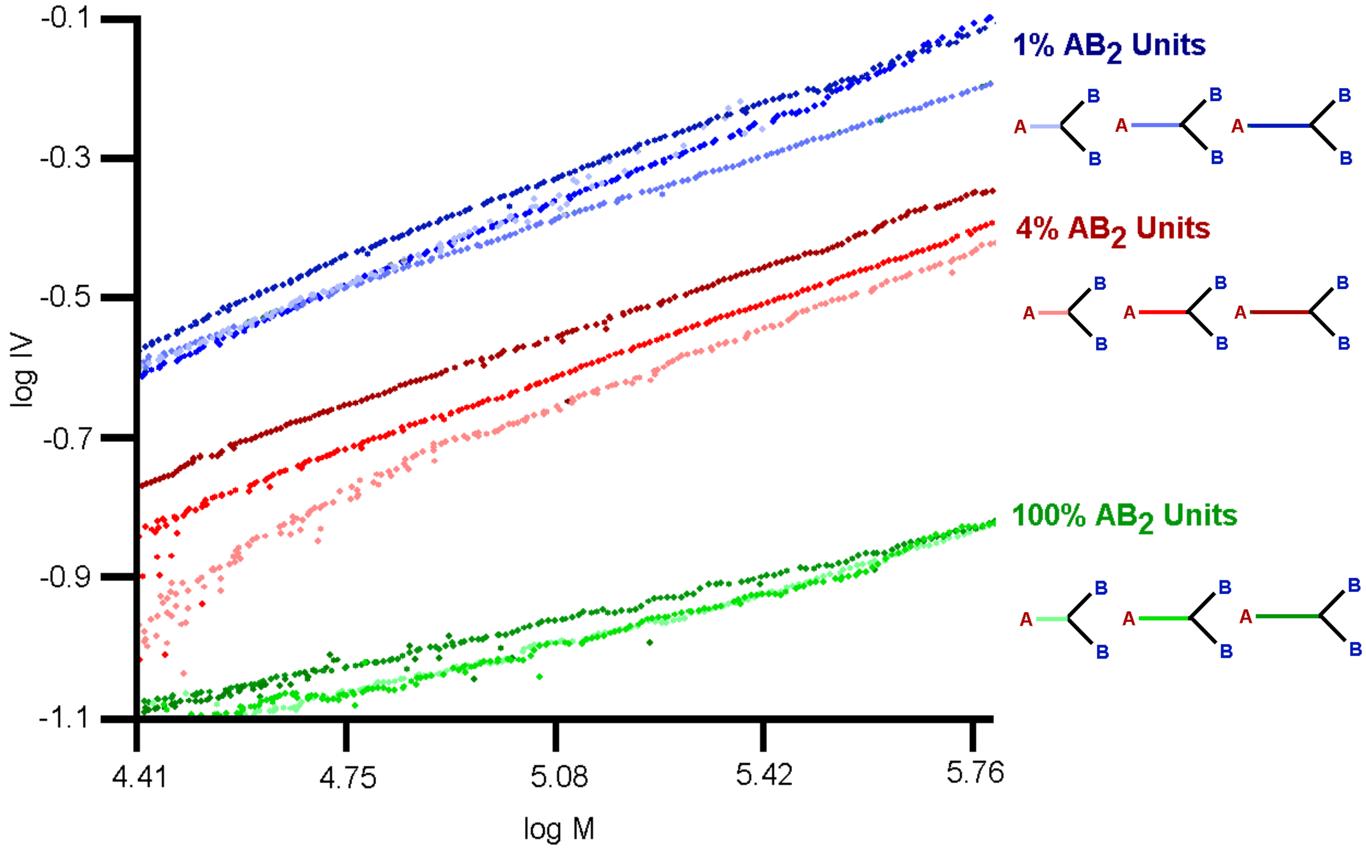


Eluent: THF (stabilised with 250 ppm BHT)
Columns: 2 x PLgel 5µm MIXED-C
System: Agilent 1260 Infinity Multi-detector GPC/SEC System equipped with DRI, Viscometer & Light Scattering

There is no trend in molecular weight distributions.

Hyperbranched Polyesters

Mark-Houwink Plots



Clear trend in Mark-Houwink plots

Increased branching/decreased molecular size leads to a decrease in IV

Expanding Conventional GPC/SEC

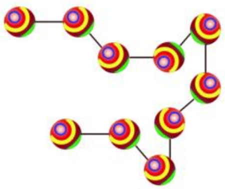
Viscometer and Light Scattering Detectors

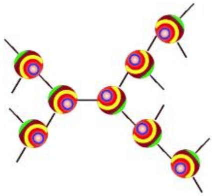
Viscometers and Light Scattering detectors are powerful detectors to expand the capabilities of Conventional GPC/SEC – expanding distribution only information to determining accurate molecular weights, size, shape and structure of the polymer.

GPC/SEC Technique	Molecular Weight	Molecular Size	Information
Conventional (RI or UV)	Relative to standards used for calibration	No	Molecular weight distribution, concentration
Viscometry	More accurate from Universal Calibration	Yes, hydrodynamic radius (Rh).	Conformation, branching. Works with copolymers
Light Scattering	Absolute determination	Yes, Radius of Gyration (Rg) directly.	Conformation, branching.
Triple	Absolute determination	Yes, Rg and Rh, directly.	The ultimate configuration for comprehensive polymer characterisation

Summary – The Value of GPC

Molecular weight distribution is critical for the polymer chemist, with further information obtained from the same experiment using advanced detectors such as Light Scattering and Viscosity





- **Distribution** of Polymer Chain Lengths -- GPC
- Molecular Weight – **Length** of Chains -- GPC
- **Polymer Structure** – Branching -- GPC

Maximising the technique of GPC is extremely valuable to the polymer chemist and is widely used today in key stages of the polymer industry:

- Quality Control/Production
- Polymer R&D
- Product Troubleshooting

Agilent GPC/SEC Portfolio

Aqueous GPC

RT-GPC

Multi Detector GPC

Conventional GPC

Organic GPC

HT-GPC

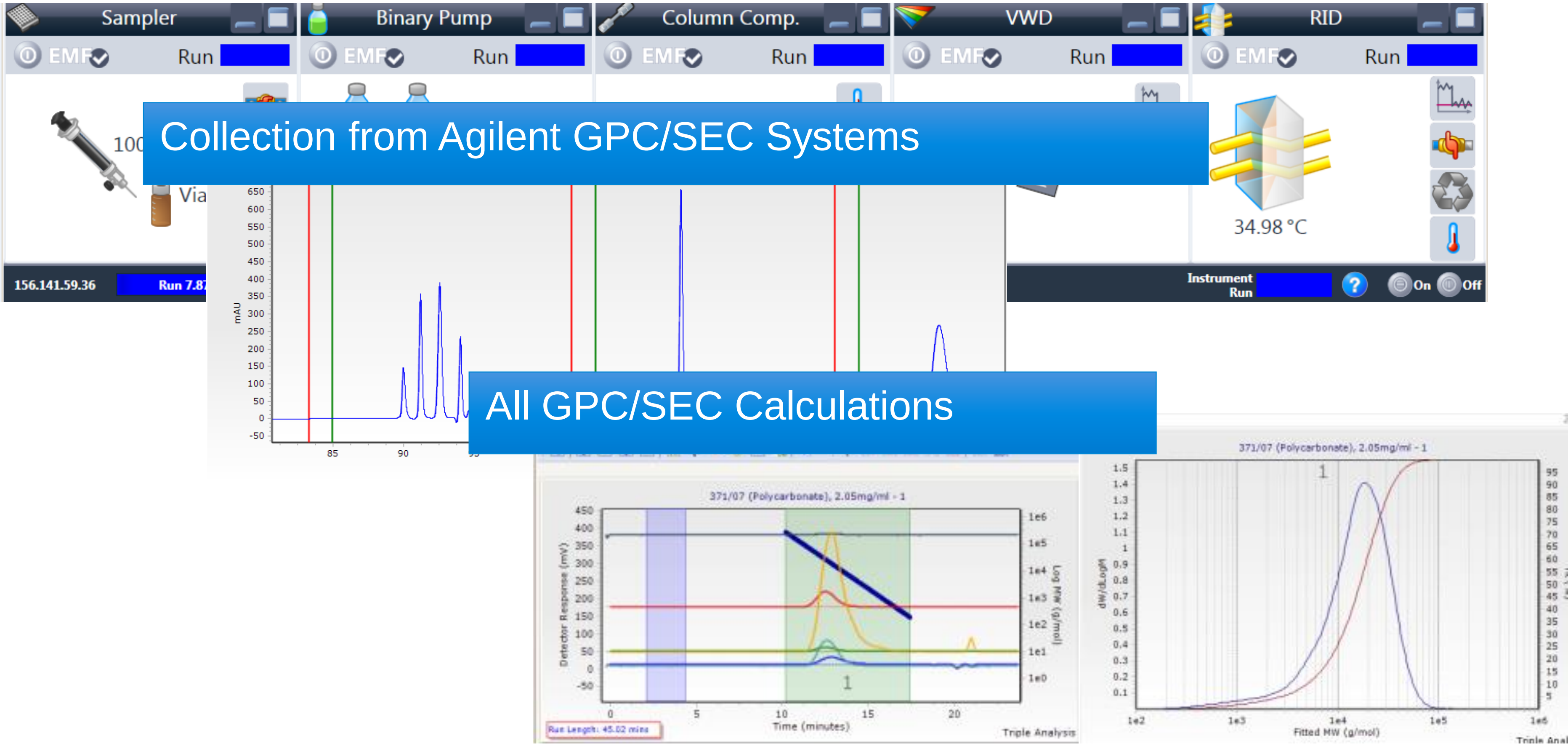
Agilent GPC/SEC Software

Single solution for all GPC/SEC Requirements

Control of Agilent GPC/SEC Systems

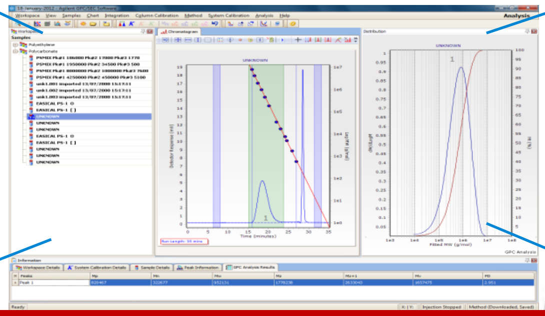
Collection from Agilent GPC/SEC Systems

All GPC/SEC Calculations



Agilent GPC Instrumentation Portfolio

Agilent 1260 Infinity
GPC-SEC system



Agilent 1260 Infinity-MDS
Multi Detector Suite

Agilent GPC/SEC Software

Agilent PL-GPC 50
Ambient to 50 °C

Agilent PL-GPC 220
Ambient to 220 °C

Thanks for Listening

Any Questions