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

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:

- 6%
- 12%
- 70%
- 10%
- 2%
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
- 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**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>- number average molecular weight</td>
</tr>
<tr>
<td>Mw</td>
<td>- weight average molecular weight</td>
</tr>
<tr>
<td>Mz</td>
<td>- z average molecular weight</td>
</tr>
<tr>
<td>Mz+1</td>
<td>- z+1 average molecular weight</td>
</tr>
<tr>
<td>Mp</td>
<td>- peak molecular weight</td>
</tr>
<tr>
<td>Mw/Mn</td>
<td>- polydispersity by GPC</td>
</tr>
</tbody>
</table>
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
Testing of material batches
Analysis of synthetic rubber

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

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

The greater the concentration, the greater the viscosity

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

![Graph showing molecular weights](image-url)

- PS
- PS "Comb"
- PS "Star"
- Hetero Graft Copol
- Poly (methyl methacrylate)
- Poly (vinyl chloride)
- Graft Copol. PS/PMMA
- Poly (phenyl silicone)
- Polybutadiene
Molecular Weights
Using a Light Scattering Detector

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

\[ R(\theta) = CM (dn/dc)^2 P(\theta) K(\theta) \]

*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
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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conventional Calibration</th>
<th>Light Scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic rubber</td>
<td>Mn 251000 Mw 604800</td>
<td>Mn 154700 Mw 382900</td>
</tr>
</tbody>
</table>

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

These advanced detectors can be added to any HPLC/GPC and achieve ‘information rich’ GPC...
Characterization of Polymers

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  (shape and size of polymer)
- **Different Monomer Units** -- FTIR
- **Chemical Structure of Monomer Unit** -- FTIR
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

There is no trend in 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
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.

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

Agilent Technologies
Thanks for Listening

Any Questions