Advanced GPC

The use of Advanced Detectors in GPC

GPC On Tour, Barcelona, 28th February 2012
What does Conventional GPC give?

- Molecular weight averages – Relative to the standards used

  - Mw: Weight Average Molecular Weight
  - Mn: Number Average Molecular Weight
  - Mp: Peak molecular Weight
  - Mz: Z Average Molecular Weight
  - Mz+1: Z+1 Average Molecular Weight
  - Mw/Mn: Polydispersity

This is good if you only want to do comparative GPC since it is very unlikely that standards exist for the specific polymer.....

How can we improve this???
Improving the experimental information?

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**

- **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**
Let’s Focus on Viscometry

• All polymers increase the viscosity of solutions by increasing the resistance to flow

• Different types of polymers have differing viscosities depending on the interactions with the solvent

• Viscometers are used to determine intrinsic viscosity, IV or $[\eta]$

• At any given MW, a high IV means the sample is a large diffuse molecule, a small IV means a compact, dense molecule

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
Why do Viscometry? – The Universal Calibration

- If a calibration of size instead of MW vs retention time could be generated then one true calibration would hold for all sample types

Hydrodynamic volume(size) = [\eta] M

- A Universal Calibration plot of log[\eta]M versus RT holds true for all polymer types

- Can using a viscometer we measure intrinsic viscosity and retention time and get accurate molecular weights

Accurate Molecular Weights

• As a result of using the viscometer, a universal calibration can be set up that gives the same calibration line regardless of the type of standards employed.

• The chemistry of the sample is also unimportant – the column is separating on size and that is the parameter we have calibrated.

• The GPC/viscometer experiment will give accurate molecular weights for any samples regardless of the sample's or the standard's chemistry.

• We are still doing chromatography – the column must be calibrated.
A Example of Conventional and Universal Calibrations

- Conventional calibrations are offset due to differences in the molecular size of polystyrene and polyethylene.
- Universal calibrations account for the offset to the calibrations overlay.
Viscometer Operation – 4 capillary bridge viscometer

IP = Inlet pressure
DP = Differential pressure

Specific viscosity = \frac{4DP}{IP-2DP}

IV = \frac{Specific viscosity}{Concentration}

In the limit as conc. tends to zero
GPC/Viscometry Experimentation

- Calibration with a series of narrow standards of known $M_p$ and concentration
- Calculate detector constant ($K_{\text{visc}}$) using one standard for which IV is known
- For the remainder of the standards, calculate $[\eta]$ from the viscometer response
- Plot $\log M[\eta]$ versus retention time to generate the Universal Calibration
- For unknown sample, for each slice across the distribution determine $[\eta]$ from the viscometer, and then convert to molecular weight via the Universal Calibration curve
Typical Chromatograms

- Viscometer response is greater as molecular weight increases

- What additional information can we obtain from GPC/Viscometry?
How Does Branching Effect Molecular Properties

The effect of branching is to **decrease the size** and **increase the density** of a polymer molecule at any given molecular weight in solution.

If we can measure the density or size of a branched molecule and compare it to a linear molecule of similar chemistry, we might be able to get information on the nature of the branching.
If we consider a linear polymer versus branched polymer

- Comparing both polymers on Mark-Houwink and Conformation plots,
- Branched polymer is more dense and smaller at any given molecular weight so IV and Rg will be lower

This is illustrated in the following application
Example Branched Polyesters – Effect of Branching on IV

Polyester AB/AB₂ polymers produced by the condensation of A and B end groups

Branching introduced by the addition of AB₂ monomers into the reaction

A Hyperbranched polymer structure is formed

Different chain length AB₂ monomers can be used to vary the ‘compactness’ of the polymer molecule in solution

S. Kunamaneni, W. Feast, IRC in Polymer Science and Technology, Department of Chemistry, University of Durham, UK
Molecular Weight Distributions of Hyperbranched Polyesters

There is no trend in molecular weight distributions.
Mark-Houwink Plots of Hyperbranched Polyesters

Clear trend in Mark-Houwink plots
Increased branching/decreased molecular size leads to a decrease in IV
Polyethylene – Calculating Branching Numbers

Polyolefins are important high-tonnage engineering polymers

Crystalline materials, only soluble at >120 C

Polymers can contain branching structures depending on the method of synthesis

Long chain branching (over 6 carbons in length) can serious effect viscosity, density and processability

Multi detector GPC is an ideal means of probing the structure of polyolefins
Polyethylene Triple Detection Data
Mark-Houwink Plot

Downward curvature of the plot at high molecular weight indicative of branching
Summary

• Conventional GPC has limitations in that the results obtained are purely comparative to the standards employed

• The situation can be remedied by adding a viscometer to the system

• The viscometer allows calibrations of retention time as a function of molecular size to be generate

• This give accurate molecular weight information regardless of the type of standards used in the analysis

• The Mark-Houwink plot allows the change in density of the polymers as a function of molecular weight to be analysed

• Through the Mark-Houwink plot factors such as conformation and branching can be determined
Advanced GPC

GPC and Light Scattering

The use of Light Scattering Detection in GPC
Introduction

• Light scattering detectors have some of the same advantages as viscometers, they give molecular weights that are not dependent on calibrants

• With light scattering detectors, you don’t rely on a column calibration

• They also give other information relating to the polymer molecules in solution

• They do however, require more stringent lab practice and data interpretation is more complex
In static light scattering, coherent incident radiation (usually a laser) interacts with components of the polymer backbone in a small scattering volume.

Excitation of the polymer chain results in re-emission of the radiation at the same wavelength and frequency but at variable intensity.

Measurement of the intensity of the scattered radiation allows the calculation of molecular weight and the chain dimensions.
Determination of Molecular Weight by Classic Light scattering

\[ \frac{K^*c}{R_\theta} = \left( \frac{1}{M_w} \right) \left[ 1 + \left( \frac{16\pi^2}{3\lambda^2} \right) <s^2>_z \sin^2 \left( \frac{\theta}{2} \right) \right] + 2A_2c + 3A_3c^2 + ... \]

Where \( K^* = 4\pi^2 n_0^2 \left( \frac{dn}{dc} \right)^2 \lambda_0^4 N^{-1} = K \left( \frac{dn}{dc} \right)^2 \)

- We measure \( R_\theta \), the excess scattering of light from the solute in the solvent
- For any given solute/solvent system, we assume \( K \) is a constant
- The scattering function \( P_\theta \) relates to the size and shape of the molecule
- The virial expansion describes intermolecular interactions

Background information – do not need to learn for GPC!
The Classic Zimm Method

• The classic way of analysing light scattering data that shows scattering is the Zimm plot

• We plot $K^*c/R_\theta$ versus $\sin^2(\theta/2) + c$ and perform a double extrapolation of the plot to zero angle and concentration

• Calculation of molecular weight from the intercept and virial coefficients from the slope of the plot

• The data shown is for a sample of polytetrahydrofuran Mw 2,000,000 g/mol in iso-propanol at 46 °C
Light Scattering with GPC – simplified equation

• The Zimm method is a batch method where we analyse a sample at a range of concentrations and molecular weights

• This is not appropriate for a GPC method where the sample is flowing through the light scattering cell

• So we make some simplifications…

• If the molecule under investigation is small, then $P_\theta$ is equal to one and can be ignored

• The virial coefficient describes intermolecular interactions, so we can assume that under very dilute conditions these terms are equal to zero

\[
\frac{K^*c}{R_\theta} = \left( \frac{1}{M_w} \right)
\]

Therefore

\[
R_\theta = M_w K \left( \frac{dn}{dc} \right)^2 c
\]

So

\[
R_\theta = M_w K^* c
\]
Scattering for Larger Molecules

• If we are looking at smaller molecules, we can measure the light at any angle **typically 90deg** and determine molecular weight from the simplified equation.

• However, when the molecules are large, the simplification does not work because $P_{\theta}$ is not equal to one.

• This causes a problem as we now need to know $P_{\theta}$.

• But it is also useful, as $P_{\theta}$ is related to $s$, the radius of gyration, a measure of the size of the molecule.

• If we can measure $P_{\theta}$, not only will we be able to determine the molecular weight of the polymer using the light scattering equation, but we should be able to determine the molecular size.
Why Does $P_\theta$ Change with Big Molecules?

• When the scattering molecule is small, $P_\theta$ is equal to 1
• As the molecule grows in size compared to the wavelength of the light, $P_\theta$ falls below 1
• This is because the molecule stops acting like a single point scattering light, and starts acting like a collection of points
• This causes interference in the light scattered from the different points which affects the total amount of scattered light we can measure
• The degree of interference is extremely angular dependent
• Trying to measure this interference affect is why light scattering measurements are often performed at different angles or at more than one angle
Results and Angular Dependence

• Angular dependence can affect the accuracy of the calculated results too, especially at high molecular weight (large molecular sizes)

• Options Available:
  
  • Zero angle not possible we see unscattered laser beam
  • Low angle 5-7deg more accurate but very noisy data - lower precision
  • High angle less accurate, but better data quality

We have a dilemma!
High Angle Light Scattering Analysis of PS Standard, $M_w = 2 \times 10^6$ g/mol

- At high angle, the large polymer molecule gives asymmetric scattering and an underestimation of the molecular weight is made.

90 degree LS
1.2M (40% too low)
Multi Angle Light Scattering Analysis of PS Standard, Mw = 2x10^6 g/mol

### Debye

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### Zimm

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Multi Angle Extrapolations

Many now use a multi angle system

• Multi data points are used to extrapolate to the zero angle
• Errors tend to be much lower than single angle calculations
• Different designs of instrument employ different numbers of data points to make the extrapolation, and manufacturers also use different techniques
• Two or more angles are used and the ratio of scattered light for each of the angles is measured
• From this, it is possible to determine the particle scattering function, $P_\theta$
• From this value we can correct the scattering value at 90° to give accurate molecular weight and allow us to calculate radius of gyration
No column calibration necessary – but often still done because viscometer present

Calculate detector constant \((K_{LS})\) using one standard for which molecular weight and concentration is known

A concentration detector that tells us how much material is eluting from the column

For unknown sample, for each slice across the distribution determine molecular weight directly from the LS
Eluent  - Use high quality solvent, filter before use to remove particulates (e.g. 0.02 µm). Choose solvent to give good dn/dc for optimum LS detector response

Injector  - Dirty rotor seal can contribute to excess noise immediately after switching valve from load to inject position

Columns  - Column shedding can contribute to baseline noise, bleed decreases with time, special low shedding columns available (e.g. PLgel MIXED LS)

Sample preparation  - Polymer solutions must be prepared at accurate concentration, take care with samples containing solvents or fillers. Use higher concentrations for lower molecular weight polymers
• Combining light scattering and viscometry detection gives the most information from a Multi detector GPC experiment

• IV from the viscometer, molecular weight from the light scattering detector, branching from either IV or Rg

• Molecular weights generated by different methods can be compared to better understand the materials analysed.
Multi Detector Gel Permeation Chromatography
Getting the most from your GPC Experiment

PL-LS 15/90 Light Scattering Detector
- Absolute molecular weights without the need for a column calibration
- Accurate assessment of molecular size, radius of gyration (Rg) and hydrodynamic radius (Rh)
- Accurate branching measurements

Four Capillary Bridge Viscometer
- Accurate molecular weights regardless of the standards used to generate the column calibration
- Accurate assessment of intrinsic viscosity
- Structural analysis and Mark-Houwink parameters

The Complete System - Triple Detection
- Absolute molecular weights without the need for a column calibration
- Accurate assessment of molecular size and dimensions
- Accurate assessment of molecular viscosity
- Complete information regarding polymer structure and branching

Over-laid multi-detector chromatogram for an example of polybromostyrene.

Retention time / min

15° Light scattering
90° Light scattering
Viscometer
Differential refractive index
Summary

• Light scattering is a powerful tool for the analysis of polymers allowing the calculation of molecular weight without the need for a column calibration
• The theory of light scattering is complex and the treatment of the data is very mathematical
• Different light scattering systems treat the data in different ways
• Multi angles have a strong advantage over single angle systems
• Combinations of light scattering with viscometry expands the GPC experiment considerably
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GPC and FTIR

Opportunities to Couple GPC with online FTIR
GPC FTIR

- Fourier-transform infra-red (FTIR) spectroscopy is a well-established laboratory analytical technique
- Very sensitive to functional groups and for ‘fingerprinting’ of compounds
- Typically used to obtain a ‘batch’ type static measurement using the spectrometer and a sample holding system, e.g. pressed pellets, windows or ATR crystals
- Flow FTIR interfacing the spectrometer with a liquid flow system via a flow cell historically far less common due to difficulties with sensitivity and with data handling
- Some interfaces available to interface FTIR spectrometers with chromatographic systems
- With increasing sensitivity of detectors and development of new data handling routines FTIR detection coupled to chromatographic systems is now possible
Flow cell for Online GPC FTIR

FTIR Flow Cell

Heated Transfer Line (when used for High Temperature GPC)
Applications of GPC coupled to FTIR Detection

- FTIR can be used to investigate a wide variety of monomers and polymers
- Limited only by the spectral windows of the solvent
- Dichloromethane and chloroform are most applicable
GPC in Dichloromethane

- Suitable solvent for a variety of polymer types
- Good solvent windows in the regions of interest
- Chromatographic conditions:

  Column: PLgel 5µm MIXED-C (300x7.5mm)
  Eluent: Dichloromethane
  Flow rate: 1.0ml/min
  Temperature: Ambient
  Injection volume: 200µl
Spectrum of Lexan Polycarbonate
3D image of the data collected for the polycarbonate

- Each of the characteristic absorption bands for the polymer could be used to obtain a concentration versus time plot which could be used as a chromatogram
Absorbance of Lexan Polycarbonate

- The absorbance measured on the FTIR is directly proportional to concentration up to 2 absorbance units.
- The response of the detector can be calibrated for quantitative measurements.
- For the polycarbonate the intensity of the peak at 1772 cm\(^{-1}\) was monitored.
- The plot can be used as a GPC chromatogram.
Spectrum of Polydimethyl siloxane
Analysis of a Polydimethyl siloxane / Polycarbonate Blend
3D Image Analysis of a PDMSO/ PC Blend

- 3D image of the data collected for the polydimethyl siloxane / polycarbonate blend
- Characteristic bands for the two components are easily identified from the spectra of the homopolymers
Can produce RMS intensity versus retention time plots for the individual components by monitoring different absorption bands.

Composition can then be calculated from the calibrations of the homopolymers.

In this case the blend is 48% polycarbonate, 52% polydimethyl siloxane.
GPC Calibrations with FTIR Detection

- Analysis of a series of polymethylmethacrylate narrow standards
- Can choose any absorption band to generate a GPC chromatogram
- Generate the calibration and analyse the individual chromatograms
- Molecular weight distribution analysis of co-eluting polymers is feasible
Conclusions

- GPC coupled with FTIR detection is a potentially powerful tool for polymer analysis.
- A wide range of polymers can be investigated but are restricted by solubility in ‘good’ FTIR solvents.
- Compositional information about polymer blends and copolymers can be readily generated as long as the components exhibit different absorption bands.