Gel Permeation Chromatography: an Evolving Technique for a Changing Polymer Industry

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Stimulated by the sustainability agenda, the polymer industry is actively engaged in developing new materials that combine excellent performance with low carbon footprint. Molecular weight is a defining characteristic of all polymers and often is one of the parameters manipulated to achieve desired performance. Gel permeation chromatography (GPC) is the method of choice for molecular weight characterisation. This paper provides an introduction to GPC and examines how it is evolving to meet the changing needs of this dynamic industry.

The sheer volume of polymers used for consumer and automotive applications makes the polymer industry a major consumer of oil and gas resources, these feeds currently providing the building blocks for some of our most useful materials.

As the sustainability agenda has gained ground, society's use, and indeed disposal, of polymers has come under increasing scrutiny. The industry has responded with new and exciting product innovations that reduce the impact of use without compromising performance or consumer appeal. Cradle-to-grave analysis has prompted the evolution of a number of different strategies, including:

- Replacing fossil fuel feeds with renewables – increasing the use of biopolymers such as polylactic acid [1]
- Developing materials with a higher performance/volume gearing that deliver, for example, lighter automotive components or more efficient packaging solutions
- Enhancing recyclability or reducing the impact of disposal, by using mixed waste streams to produce new materials, for example, or switching to biodegradable materials

Against this backdrop, and considering the potential of polymers to support greater sustainability in so many sectors, it is clear that polymer scientists will continue to face both change and challenge.

The importance of molecular weight

Polymers generally consist of a distribution of molecular chains of varying lengths because of the way polymerisation processes proceed. Some chains are very long, some very short, but the majority cluster around a central size range forming a bell curve molecular weight distribution.

The molecular weight distribution influences many material properties including:

- Tensile strength
- Durability
- Flexibility
- Barrier properties – resistance to penetration by water or air
- Density
- Thermal and chemical resistance
- Processability

Manipulating these properties is the very essence of a polymer scientist's role. In fact, developers tailor not just chain length but also chain branching, and the degree of cross-linking, to reach their goals. Access to molecular weight and structural data enable rational decisions to changes in process conditions.

Introducing GPC

Gel permeation chromatography is the primary tool used for the molecular weight characterisation of polymers that can be completely dissolved in an appropriate solvent, either aqueous or organic, within the temperature range of the instrument (typically up to a maximum of around 160°C). Applicable to the vast majority of commercial polymers GPC is routinely used for materials of all types from biopolymers such as polypeptides to polyolefins such as polyethylene and polystyrene, polycarbonates and a whole host of others, with molecular weights ranging from 2,000 Daltons up to several million. Like all separation techniques, GPC is a two-stage process – separation followed by detection.

Analysis begins with dissolution of the sample in a suitable solvent. This is introduced into a mobile phase, pumped through a column packed with a stationary phase, which is typically a cross-linked polymeric gel, selected for the application on the basis of pore size and inertness to the mobile phase. Solute molecules passing through the column, because of their different hydrodynamic radii, have a different dwell or retention time in the pores of the packing. The column therefore effects a separation on the basis of molecular size. Generally speaking larger polymer molecules are unable to fit into the pores so well and pass through the column more quickly (shorter elution time) than smaller molecules, which fit into the pores more easily and are retained for longer (longer elution time).

So, the separation column produces an eluting stream of dissolved solute molecules, separated on the basis of size. The detector(s) selected for subsequent analysis determines the information that is gathered

about the resulting size fractions. Traditionally, in the polymer industry GPC systems are configured with a single refractive index (RI) detector that measures concentration. This may well be adequate for QC applications and for certain well-characterised polymers but is somewhat limiting for wider ranging exploratory studies and detailed research. There are now a host of detectors commercially available which can be combined to produce a rich information flow closely tailored to the needs of today's polymer scientists.

Choosing GPC detectors for polymer characterisation

To choose between detectors and select the best array for a given application it is necessary to understand the principles of operation of the different detector types and the information they provide. Recognising how certain detectors can work symbiotically is also important in maximising efficiency.

The following four detector types are the ones most commonly employed by polymer scientists:

- Refractive Index
- Ultraviolet (UV)
- Static light scattering
- Viscometer

Let's explore why.

Refractive index (RI)

The refractive index of a solution (n) is an optical property, a measure of optical density related to the speed of light in the medium. The degree of refraction, and therefore the magnitude of the signal generated by an RI detector, is a function of solution concentration, and of the polymer being analysed. The refractive index increment, dn/dc, where c is concentration, is therefore required for detector calibration. Since the plot of refractive index against concentration is linear, dn/dc can be derived by measuring refractive index at a known concentration, c, and comparing this value with that of the pure solvent.

On this basis an RI detector determines the concentration of solute in the eluting polymer. Importantly though, the column separates by hydrodynamic diameter, not molecular weight which means that RI data in isolation, without calibration, will produce a size, rather than molecular weight distribution for the sample. Calibration, with a known standard, correlates size and molecular weight allowing the determination of a relative (to the standard) molecular weight distribution.

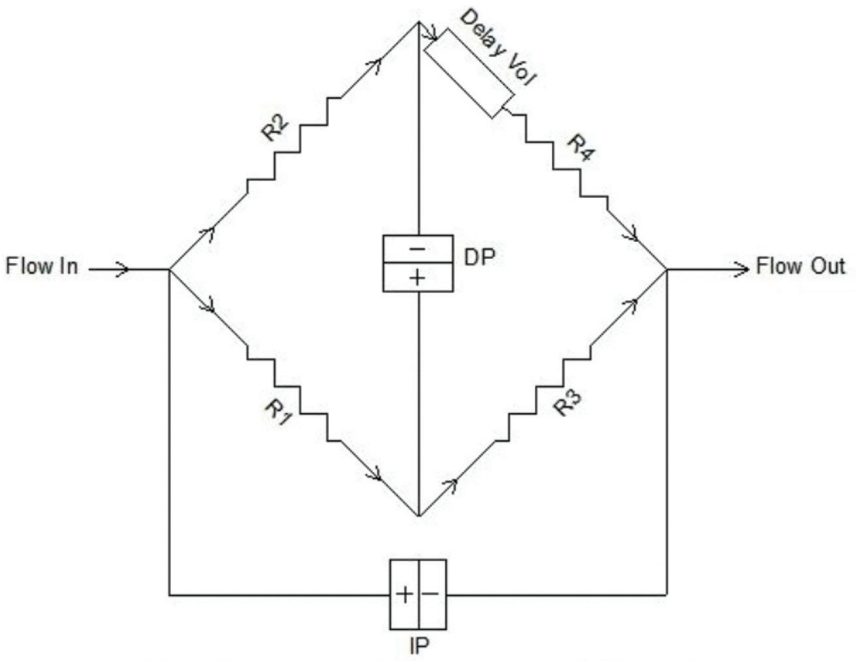

Figure 1: Schematic diagram of the most common form of differential viscometer used for GPC applications.

Ideally the calibration standard used should be closely similar in nature to the polymer being analysed, however this is not always feasible. Polystyrene standards are commercially available and so for this industrially important polymer, and materials like it, the molecular weight distribution reported by RI detection alone may be relatively precise. RI detection alone may also be adequate for QC when the goal is, in reality, to detect difference rather than to make an absolute measurement.

Relying solely on calibration using just RI detection is more difficult when the polymer being analysed has a different structure to any available standard, or perhaps is so new that its structure is not yet fully characterised. For these materials, this method of calibration may report molecular weight results far from the absolute value. This error in reported result can be removed by the addition of a viscometer detector.

Viscometry

For long chain molecules or polymers, solution viscosity parameters are a function of the molecular weight and concentration of the material present. A differential viscometer detector (see Figure 1) measures solution viscosity enabling the calculation of a number of viscosity descriptors including intrinsic viscosity (IV).

This viscometer works on the principle of balancing resistances. Differential pressure transducers measure the pressure drop across the centre of the bridge, DP, and from inlet to outlet, IP; all four capillaries present essentially equal resistance to flow.

Prior to measurement, the viscometer is filled with pure solvent. As the eluting sample flows it rapidly displaces solvent from R1, R2 and R3, but not from R4, because of the delay volume. At this point the readings of IP and DP enable calculation of the pressure drop resulting from flow of the solution relative to flow of the pure solvent. This can be converted into viscosity data via Poiseuille's Law, which correlates the pressure drop across a tube with its physical dimensions, the flow rate of fluid through it, and viscosity. Intrinsic viscosity is the most important viscosity descriptor determined from the resulting data because of its well-defined correlations with molecular weight and structure. Indeed, many polymers, polyethylene terephthalate being a prime example, are sold on an IV specification because it is so closely related to molecular weight.

In combination with an RI detector a viscometer enables Universal Calibration, a procedure that reduces reliance on having appropriate standards. Intrinsic viscosity (IV) and molecular weight (MW) are related to hydrodynamic volume (V_h), the parameter by which the sample is separated, via the following equation (Equation 1):

$$MW \bullet IV = 5/2 \bullet N_A \bullet V_h$$

Equation 1

Where N_A is Avogadro's number.

The Universal Calibration curve is a plot of Log (MW.IV) against retention volume. Being independent of structure, it is applicable to all sample types. Calibration with a number of samples of known molecular weight provides the necessary data for its construction for a given GPC system. The resulting curve then holds for all polymer types. Once intrinsic viscosity and retention volume data have been gathered for an eluting sample, molecular weight can be read directly from the curve. In combination with concentration data (RI detector), Universal Calibration therefore enables the construction of a true molecular weight distribution.

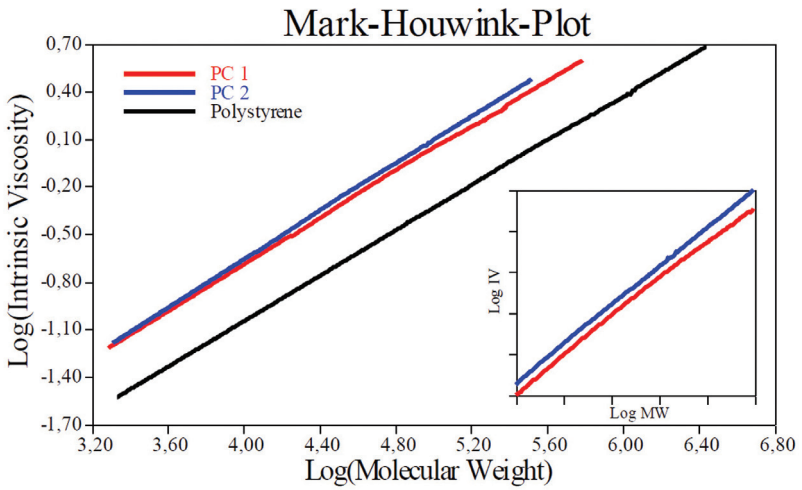

Figure 3: Mark-Houwink plot of two common polymers, polystyrene and polycarbonate.

Although this configuration clearly represents an improvement relative to RI detection alone, to use viscometry data for molecular weight measurement alone is to fail to exploit its full potential to uncover structural information about a polymer, such as the extent of branching. Using an alternative method to measure absolute molecular weight enables the better use of viscometry data maximising the information generated rather than simply minimising the calibration burden.

Static light scattering

Light illuminating a molecule is scattered by that molecule across a range of angles at varying intensity. Scattered light intensity and the weight average molecular weight of the molecule are linked by the Rayleigh equation (Equation 2):

$$\frac{Kc}{R_{\theta=0}} = \frac{1}{M_w} + 2A_2c$$

Equation 2

With a static light scattering detector the total intensity of scattered light is measured to directly determine molecular weight, utilising equation (2). An important feature of this equation is that it relates molecular weight to the scattered light intensity at an angle of 0° to the incident beam. Practically this is difficult, but accurately determining scattering intensity as close as possible to the incident beam is essential for analytical accuracy, especially for polymers. This is because polymers being relatively large macromolecules tend to scatter light asymmetrically (anisotropically) (see Figure 2). The angular dependence of the signal is not constant and consequently difficult to calculate or predict.

Different static light scattering detectors have been developed to tackle this problem. One method employs a number of detectors. The intensity is measured at each detector angle and then an extrapolation is made to determine the scattering intensity at zero degrees. While this seems eminently sensible, the accuracy of the method is determined by the form of the extrapolation selected. A simpler and more accurate solution is the use of a very low angle light scattering detector or LALS. With these systems a clever optical design enables a single measurement close enough to 0o for errors to be negligible.

The major attraction of light scattering detectors is their ability to measure absolute molecular weight directly. Calibration remains necessary but is far simpler. There is no need for the specific calibration standards required with RI detection alone because the molecular weight measured is independent of polymer type or structure.

For polymer applications a triple detector array – RI, viscometer and LALS – has much to recommend it. The RI detector measures concentration and the LALS detector produces absolute molecular weight data. These in combination with the IV results from the viscometer can be used to construct a Mark-Houwink plot (log molecular weight versus log intrinsic viscosity) – a classic analytical tool for probing polymer branching and molecular structure. The magnitude of the slope of the Mark-Houwink plot and the intercept on the y axis reflect structural changes in the polymer such as branching and chain rigidity. For example, in Figure 3, the black line, representing polystyrene, is well separated from the two polycarbonate lines (red & blue) as they have two quite different structures. There is a smaller but still significant difference between the branched (red) and unbranched (blue) polycarbonate samples, which represents the difference due to the level of branching.

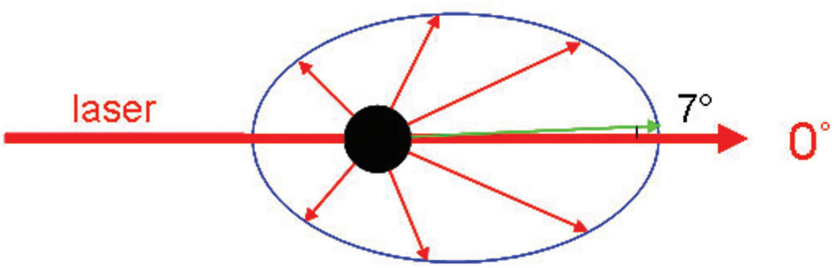

Figure 2: Larger macromolecules scatter light anisotropically.

UV detection

Chromaphores present in certain polymers absorb light in the UV spectrum, producing a detectable signal that correlates with the concentration of chromaphore present. Prime examples include polystyrenes, poly(styreneacrylonitrile), poly(methyl methacrylate), polybutadienes, polycarbonates, polyamides and polyacrylic acids. For polymers such as these a UV detector operating at just a single wavelength can monitor concentration in the eluting flow providing a more sensitive alternative to RI detection, especially for

dilute solutions. On the other hand, for copolymers (polymer made from two different monomers) UV and RI detection together, enable the discrimination of the proportion of one group within the sample. This can be a really valuable capability in co- and indeed ter-polymer development when it may be challenging to ensure optimal incorporation of a specific monomer in material of the required molecular weight.

In certain circumstances a single wavelength detector may be sufficient but in others a photodiode array (PDA) may be employed to simultaneously measure the absorbance of the sample across the entire UV spectrum. This provides more detailed insight into the compositional variation of the macromolecule under investigation and is especially useful if the UV 'fingerprint' of the eluting sample is unknown.

Analysis across the polymer lifecycle

The selection of the right detector array can transform the productivity and relevance of GPC experimentation extending the value of this core analytical technique across the product lifecycle. Whether developing new polymers or optimising the production of existing materials, GPC provides valuable information because of the defining influence of molecular weight and structure.

Consider the development and application of new polymers from sustainable sources such as Ingeo, (Natureworks, USA) [1] which is produced from plant sugars, with field-corn the primary feedstock. The success of materials such as these relies on manipulating their properties to ensure that the final product meets existing specifications – whether that product is a film for food packaging, a textile or a bottle for example. Equally important for replacement applications is to ensure that processing can be carried out on existing equipment with minimal modification.

In developing products such as these there is a need for extensive understanding of the impact of molecular weight structure on key properties, since it is this knowledge that supports the intelligent modification of a polymer towards a successful commercialisation. Maximising the data flow from GPC is one important strategy for developing the necessary understanding quickly and efficiently.

The development of new products also carries with it the task of optimising new production processes centred on well-controlled polymerisation reactions. Crucial to success is controlling the relative rates of initiation, of a new chain or active site, propagation (chain growth), and chain termination. With the molecular weight specification fixed by performance targets, those charged with optimising manufacture must learn how best to manipulate the operating parameters at their disposal to give economic production. Once again the right GPC data can inform these choices, underpinning the development of an optimal design and operating strategy.

Once production is established, GPC analysis becomes a routine task used simply for QC. Here automation and speed may be the key criteria governing system choice and the detector array may be streamlined down to just a single detector – either RI or UV. However the need for greater insight doesn't stop at this part of the product lifecycle.

Recycling is a major theme in polymer development, but a potential problem is 'downcycling', which is the degradation of polymer properties brought about by the recycling process. Understanding the impact of disposal processing on the molecular weight of a polymer is an important step in completing the life cycle analysis of the product, determining whether it can be recycled or alternatively how fast it may degrade.

While traditional GPC systems with single detectors may have been the answer when the demands on the polymer industry were simpler, today's activities call for much greater knowledge and the capability to quickly and easily generate the information. Detector technology has moved on considerably in the last decade or so with the commercial introduction of low noise LALS detectors a particular highlight. Modern GPC systems configured with multi-detectors arrays, meet the industrial need to more fully understand molecular weight and how to control it to ensure commercial success, underpinning progress in this vital sector.

To find out more about detector technology, GPC operation and calibration please refer to the Malvern website www.malvern.com

References

[1] www.natureworksllc.com