Characterisation of Polymers Using Gel Permeation Chromatography and Associated Techniques

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Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC) is a technique for obtaining information on the molecular weight distributions of polymers. After polymer type (chemical composition), the molecular weight distribution is the next most fundamental property and this will determine if a particular material is well suited to any given application. In crude terms, the higher the molecular weight, the stronger and more resilient a polymer material is likely to be, but also the harder it will be to process. This can be much more complicated with either extreme of the molecular weight distribution potentially contributing significantly to the properties of the material.

It is rarely possible to measure the molecular weight distribution of a polymer and to declare it as being 'good' or 'bad' – the intended application and processing route are also very important. A polymer producer may 'improve' the specification of a grade of polymer by minor adjustment of the molecular weight distribution, but this can then require changes in the processing conditions and without such changes, the 'improved' material might well fail in use.

GPC has greatly simplified the characterisation of the molecular weight distribution of most polymer types but some aspects of the technique remain difficult to apply and even for the simpler variations of the technique, results can depend on the detail of how individual laboratories apply the technique. Agreement between laboratories and longer term repeatability can be poor, unless very strict adherence to the detail of the procedures and chromatographic conditions are kept to, but if used in a comparative manner the technique can give a lot of information and detail not obtainable in any other way.

The problems of inter-laboratory agreement and longer term repeatability mean that polymer manufacturers rarely use molecular weight data in their specification of polymer grades but GPC is a valuable 'in-house' technique for these manufacturers. The GPC family of techniques are also of substantial value in a range of other laboratories for polymer development, quality control, failure investigation and establishing molecular weight/physical property relationships.

Background

There were various techniques available for the molecular weight characterisation of polymer before the introduction of GPC but these were generally difficult and time consuming. Typically light scattering would be used to measure the weight-average molecular weight and a technique based on colligative properties (e.g. osmometry) would be used to measure the number-average molecular weight – the ratio of these, the polydispersity, giving a measure of the breadth of the distribution. To actually obtain more information on the shape of the molecular weight distribution, it was necessary to fractionate the polymer (e.g. solvent precipitation/dissolution approaches) and to use the above techniques to obtain molecular weight data for individual fractions and then combine all of the data. Obtaining detailed characterisation of a molecular weight distribution would take days or weeks of effort.

GPC has been in wide use since the introduction of more robust chromatographic packing's by J C Moore in 1964 [1]. The first generation of GPC instruments and columns reduced polymer molecular weight characterisation time to hours, rather than days, but also gave information on the whole distribution – it is important to appreciate that it is possible to have two different materials with very similar weight-average and number-average molecular weights but very differently shaped distributions.

GPC is a variation on liquid chromatography and early developments of the GPC technique have contributed substantially to the more general development of higher performance liquid chromatography. While some aspects of GPC have remained similar to when initially introduced, nearly fifty years has seen significant developments in the range of applicable solvents, refinement of column types available and in the use of multiple detector approaches.

Conventional GPC

The term 'conventional GPC' is used for those applications simply using a concentration detector and normally calibration of the columns with a series of narrow distribution polymers.

The concentration detector monitors the elution of the polymer fractioned by the columns and the log (molecular weight) versus elution volume (or elution time) calibration allows computation of the molecular weight averages and molecular weight distribution.

Many early applications of GPC were carried out using tetrahydrofuran (THF), which is a good solvent for a very wide range of polymer types, but it was also found to be practical to apply the technique at high temperature or with difficult solvents to allow characterisation of polymer types that would previously have been almost impossible. The more obvious applications of this type were application to polyolefin's (at over 135°C) and use of phenolic solvents for polyamides and polyesters (such as PET). These more difficult aspects had initial enthusiasm but it has taken time, development of equipment and experience to really get them to be routine.

Conventional GPC is still the most accurate and precise approach if dealing with linear polymers and the calibrants are of the same chemical composition as the sample polymer (e.g. obtaining the molecular weight distribution of polystyrene using polystyrene calibrants or polymethylmethacrylate using PMMA calibrants). Unfortunately the range of polymer types for which a wide range of narrow distribution calibrants is available is very limited.

In practice, polymers are fractionated as a function of solvated size, rather than actual molecular weight. For samples of the same chemical composition and structure (branching), the solvation will be the same and expressing the results as relative molecular weights (e.g. as 'polystyrene equivalent' molecular weights) will give good comparative results. As the degree of solvation will change with chemical composition, polymers of different composition cannot be compared using conventional GPC – users of the technique are sometimes perplexed when addition of a functional group or block of different chemical composition appears to cause a decrease in measured molecular weight whereas it is the solvation that is decreasing. Long-chain branching also restricts solvation and gives underestimate of molecular weight as compared to the linear polymer.

Concentration Detectors for Conventional GPC

Conventional GPC only requires a concentration detector and the most commonly used is differential refractive index (DRI). This detector type is almost universal in application but the response can be weak for some polymer/solvent combinations (e.g. chlorinated solvents) – GPC of poly(dimethylsiloxane) is unusual in that the common solvent, THF, happens to be isorefractive with PDMS and hence there is no DRI detector response. Ultra-violet detectors can be used in some circumstances but many polymer types lack a UV absorbing group and some solvents have too strong a UV spectrum to allow useful application. Evaporative light scattering detectors (ELSD) are also universal in application but are relatively expensive both for initial purchase and in operating costs – these detectors monitor the light scattered by eluate particles after evaporation of the solvent and the response is purely mass sensitive, providing that the eluate of interest is not volatilised with the solvent.

Fixed wavelength infrared detectors have been used as concentration detectors and one instrument manufacturer is currently using this type of detector. Infrared detectors tend to be most useful when looking at polyolefin's.

Universal Calibration and Mark Houwink Parameters

It was identified early in the existence of GPC that if the calibration were expressed as the product of log(molecular weight) and log(intrinsic viscosity) versus elution volume, then a 'universal calibration' is obtained [2]. This can be achieved using a viscosity detector combined with a concentration detector (see later section) or a mathematical correction can be applied from use of Mark Houwink parameters derived from solution viscosity experiments. When used with a mathematical correction, the practical aspects are identical to conventional GPC and it is just a change in the data handling.

There are a host of literature values of Mark Houwink parameters available (often many

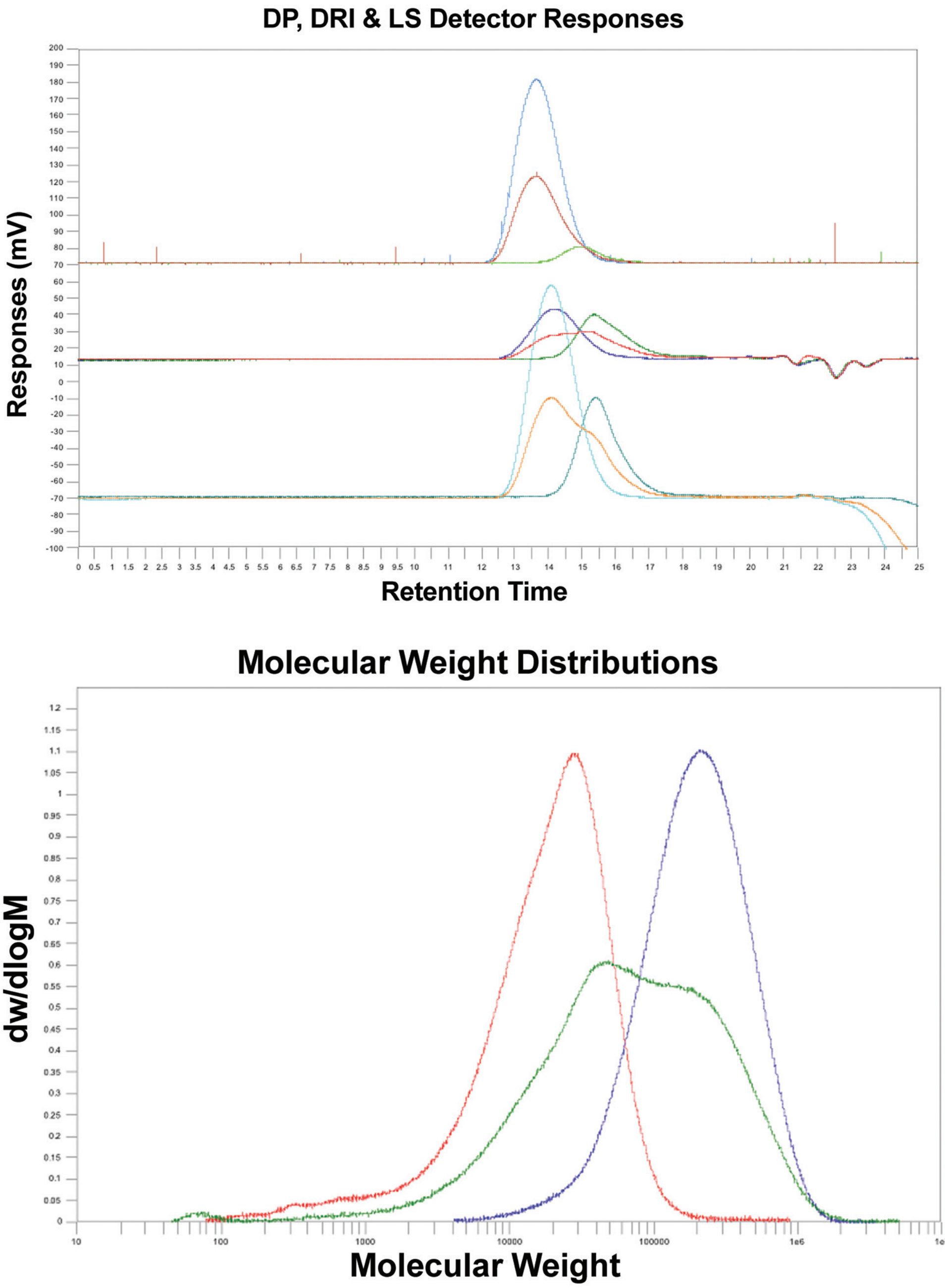

Figure 1 a and b: Comparison of the differential pressure (viscosity), DRI and light scattering chromatograms and corresponding computed molecular weight distributions for two polymers and a blend of them – Triple Detection GPC with THF

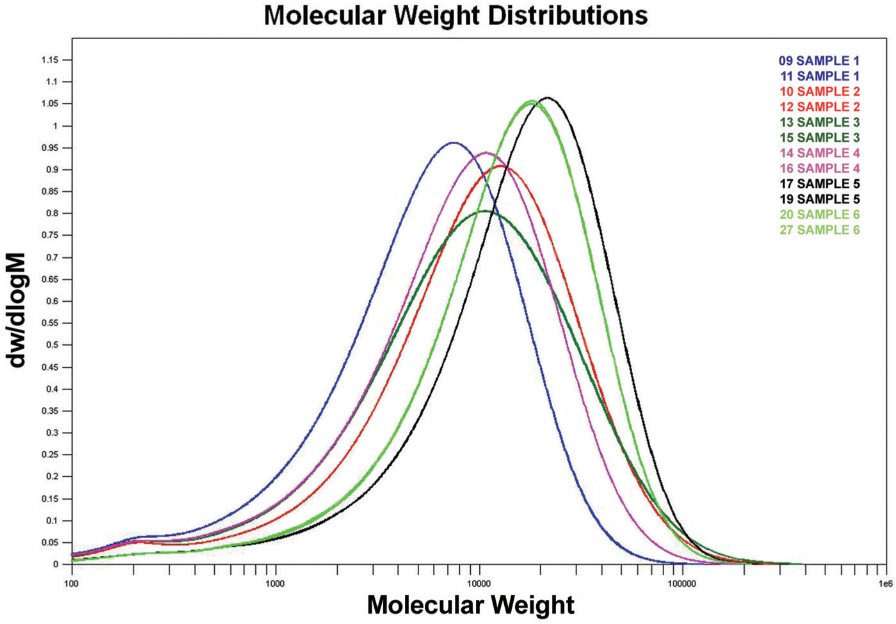

Figure 2: Comparison of the molecular weight distributions for duplicate runs of a series of PET samples – GPC with HFIP/sodium trifluroacetate

different values for the same polymer/solvent combination) and use of the mathematical correction should only be used with care. The author's laboratory restricts this to values available in BS ISO 16014-2, 2003.

Molecular Weight Sensitive Multi-Detector GPC

The development of laser light sources gave a light intensity that made 'on-line' determination of molecular weight practical and different types of classical or static laser light scattering detectors have been available for over 30 years [3]. Also the measurement of differential pressure as solutions pass through a capillary has been used for 'on-line' viscosity measurements for over 20 years [4] and these have been variously combined to give 'triple detection GPC'.

The combination of GPC with viscosity effectively gives direct universal calibration and allows determination of the 'true' molecular weight distributions without a mathematical correction - it still requires a column calibration and a series of narrow distribution calibrants but these no longer need to be the same chemical composition as the sample polymer and data can also be obtained on chain branching.

When classical or static light scattering is combined with GPC this then uses a detector calibration and this is normally based on running a single narrow distribution polymer calibrant, with possible refinement from running of a broad distribution material. Triple detection GPC is primarily a GPC-light scattering approach but with a viscosity detector to give additional information or to provide a correction if required.

These molecular weight sensitive multi-detector approaches do allow measurement of true molecular weight data and light scattering based approaches can give a simpler calibration but these are often not the absolute measurement sometimes claimed. The use of multiple detectors will also normally increase the overall noise and give poorer repeatability for replicate runs. For broad distribution polymers there can be difficulties due to mismatch of detector sensitivities – there can be good light scattering or viscosity detector response at high molecular weight but minimal concentration detector response – similarly at low molecular weight, a strong concentration response might exist at the same elution volume as weak light scattering or viscosity detector responses.

The molecular weight sensitive multi-detector approaches are particularly valuable for looking at long-chain branching in polymers and can (depending on the system) give other useful data such as radius of gyration. These techniques also allow good comparison of samples that might be related but have different chemical composition (and hence differences in solvation).

Multi-detector approaches are now used in a considerable number of laboratories, however, considerably more skill and understanding of polymers is required to obtain good results and the author still feels that conventional GPC can give the best discrimination of similar molecular weight distributions providing that the samples are all of the same chemical type and structure.

The multi-detector approaches can be applied to quite low molecular weights but their sensitivity is poor for lower molecular weights and the quality of results will not be as good.

Quasi-Elastic Light Scattering (QUELS) or Dynamic Light Scattering

The molecular weight sensitive light scattering approaches described above measure the Rayleigh scatter of polymer molecules and this is fundamentally related to the weight-average molecular weight. There is also QUELS or dynamic light scattering which is more related to the motion of polymer molecules and gives a measure of the hydrodynamic radius. This type of detector appears to be getting more use to provide structural information on polymers in solution.

Ambient Temperature GPC

GPC can be carried out at near ambient temperatures with a wide range of solvents. Control of the temperature to slightly above ambient gives better control and repeatability.

The use of THF has long been the mainstay for this type of application and it remains as the standard solvent for a lot of applications. THF has a refractive index that gives reasonably good DRI detector response and this is also important for the light scattering detector response. Other 'simple' solvents such as chloroform and dichloromethane widen applicability but have generally weak DRI and LS detector responses and are being discouraged due to environmental concerns. Toluene has been a traditional choice of solvent for many soluble rubber materials and can be used at elevated temperatures to advantage but most such applications are also possible using THF.

The use of fluorinated alcohols (e.g. 1,1,1,4,4,4-hexafluoro-2-propanol or HFIP) with appropriate columns is now a much easier approach to characterising polyamides, polyesters and a wide range of other polymers – the exceptionally low refractive index for these solvents gives exceptionally strong DRI signals. The historically high cost of HFIP has prevented wide use as a GPC solvent but with solvent saving approaches this is being used for an increasingly wide range of polymer types.

High Temperature GPC

The bulk use polymers polyethylene and polypropylene are not soluble in any solvents at room temperature and were particularly difficult to characterise prior to the introduction of GPC but instruments capable of high temperature use and able to handle these polymers were soon introduced. These polymers are now normally analysed using chlorinated aromatic solvents (such as 1,2,4-trichlorobenzene) at temperatures above 140ºC. The absence of cool-spots was critical to this application but modern (often fully integrated) instruments make this measurement relatively routine. These instruments now normally include molecular weight sensitive multi-detector capability.

High or raised temperatures are also often required to get difficult polymers into solution and/or to reduce the viscosity of the eluent. The use of phenolic solvents (e.g. 1,3-cresol or 1,2-chlorophenol) at temperatures of around 120ºC have been used for polyamides and aromatic polyesters but these are now better handled using fluorinated alcohols at much lower temperatures. The use of phenol/trichlorobenzene at around 120ºC remains the standard practice for polyetheretherketone (PEEK) and other polyketones.

GPC at temperatures of around 80ºC is normal practice when using the viscous polar solvents (e.g. N,N'-dimethylformamide or N,N'-dimethylacetamide) for characterising polar polymer types. Salts are also normally added for polar solvent work.

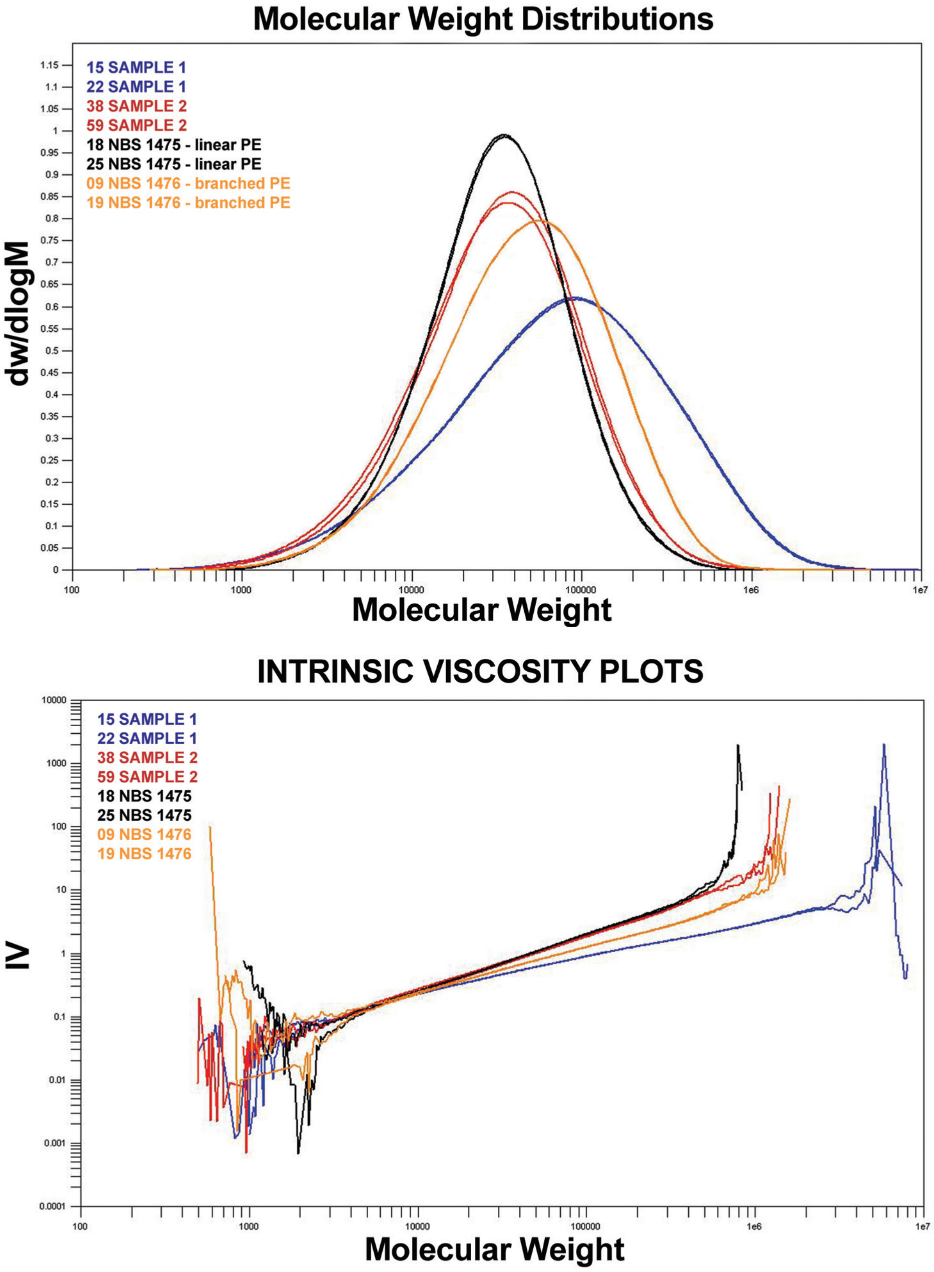

Figure 3: Comparison of the molecular weight distributions and intrinsic viscosity plots for duplicate runs of a series of polyethylene samples – GPC with 1,2,4-trichlorobenzene @ 160ºC

Column Packing's for GPC

Most column packing's for GPC with organic solvents are based on polymers of styrene and divinylbenzene (or totally DVB). These are available with different porosities, or molecular weight ranges, and it used to be normal practice to use a series of columns with different molecular weights ranges in series, however, most column manufactures now provide columns with a mixture of porosities in a single column to give a 'tailored' molecular weight range. These 'mixed-bed' columns are more likely to give a linear calibration (on a log(molecular weight) versus elution volume basis) and are often described as 'linear' columns. Poor combinations of columns can give discontinuities in the calibration and potentially misleading results.

Over the years the typical column packing particle size has decreased to give higher chromatographic efficiency and shorter analysis times, however, these smaller particle sizes are not generally appropriate for use with very high molecular weight polymer and it is possible for poor choice of column packing to give rise to shear degradation of the polymer being analysed. The smallest column packing particles available are best used with pore sizes best suited to low molecular weight polymers and it is possible to get much improved discrimination between similar molecular weights but larger column packing particles (and possibly reduced flow-rates) are best for the larger pore size/higher molecular weight range packing's.

Many column manufacturers have now brought out chemically modified columns that make them particularly suited to specific solvents or applications. The main examples of modified columns being improved compatibility for polar polymers or polar solvents.

Aqueous Based GPC

The comments above for GPC with organic solvents also apply to GPC with aqueous based eluents but there are added complexities that can make aqueous based GPC considerably more complex. Aqueous based GPC is only rarely practical with pure water and selection of salt type and concentration and pH is normally important – for polymers with some hydrophobic content, it is also often necessary to also add an organic modifier to minimise unwanted interactions with the column packing.

The range of column packing types for aqueous based GPC is much wider than for organic solvent work and the success of a

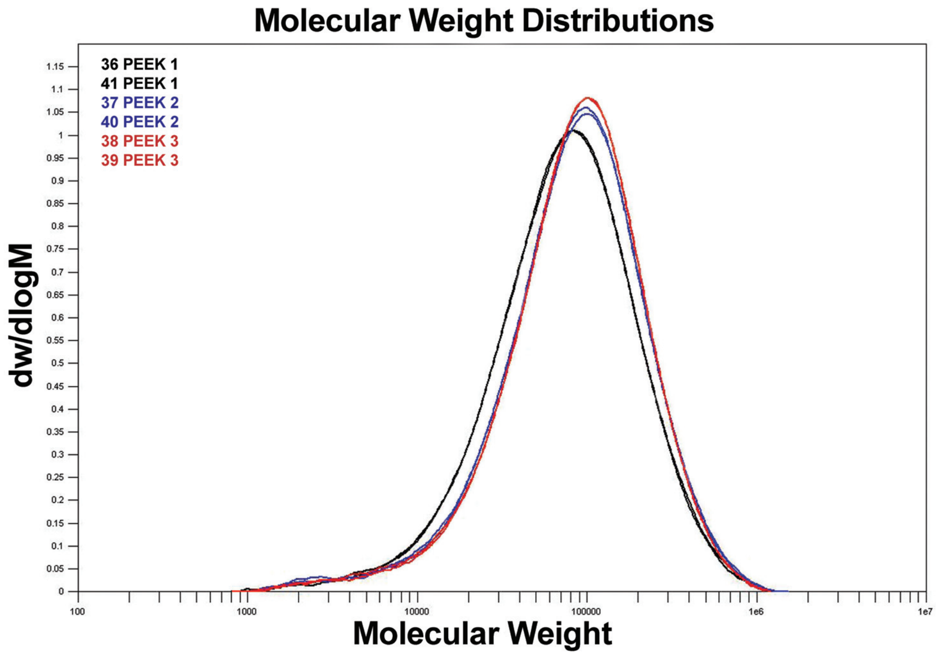

Figure 4: Comparison of the molecular weight distributions for duplicate runs of a series of PEEK samples – GPC with phenol/TCB @ 115°C

GPC approach can depend on the chemical nature of the packing.

The range of variables for aqueous based GPC is much greater and selection of correct conditions probably more important – once appropriate chromatographic conditions are identified, aqueous based GPC can be straightforward but for novel polymer types there can be considerable development work required to get to this point.

There are many water-soluble polymers that are encountered with extremely high molecular weights and broad distributions and these can be particularly difficult materials to handle. For some such polymers, operation at extremely low concentrations is required and this can have inherent difficulties with concentration detector response – confidence in full solubility often being needed if multi-detector applications are being used.

GPC of Low Molecular Weight Polymer

There are column packing's available that give excellent resolution of oligomers and low molecular weight polymer and in many respects characterisation of these materials is straightforward, however, there is an on-going difficulty with the detector response for low molecular weight materials.

The fundamental difficulty is that concentration detector response is likely to be different for the polymer end-groups as compared to the polymer chain and while this is insignificant at high molecular weight, the influence for oligomers and low molecular weight polymer can be significant. There are polymer/eluent combinations where the lowest molecular weight oligomers have opposite differential refractive index detector polarity to higher oligomers. While this problem is often appreciated for use of differential refractive index detectors, variation in response will also be normal for all spectroscopic detectors and with the ELSD, the lowest molecular weights might be (partially) lost with the evaporation of the solvent.

Light scattering and viscosity detectors can give response down to quite low molecular weight but the response will be poor and assigning the correct concentrations may be ambiguous due to the problem of concentration detector variable response. It should also be appreciated that change in differential refractive index increment (dn/dc) will have an impact on the light scattering detector response.

The Future for GPC

It is anticipated that column and instrument manufacturers will continue to refine existing capability but that GPC will largely remain as it is. The technique already has very wide applicability but some of the currently more difficult aspects are likely to become more routine.

Many have suggested that mass spectroscopy will have increasing influence (or even replace) GPC but for broad distribution polymers, mass spectroscopy detectors also have variation in response with molecular weight that is difficult to allow for.

The number-average molecular weight is a value that has room for improvement in terms of current methods of measurement. Perhaps an Instrument manufacturer may consider developing an on-line detector which responds to this parameter as currently there is unfulfilled interest in the area.

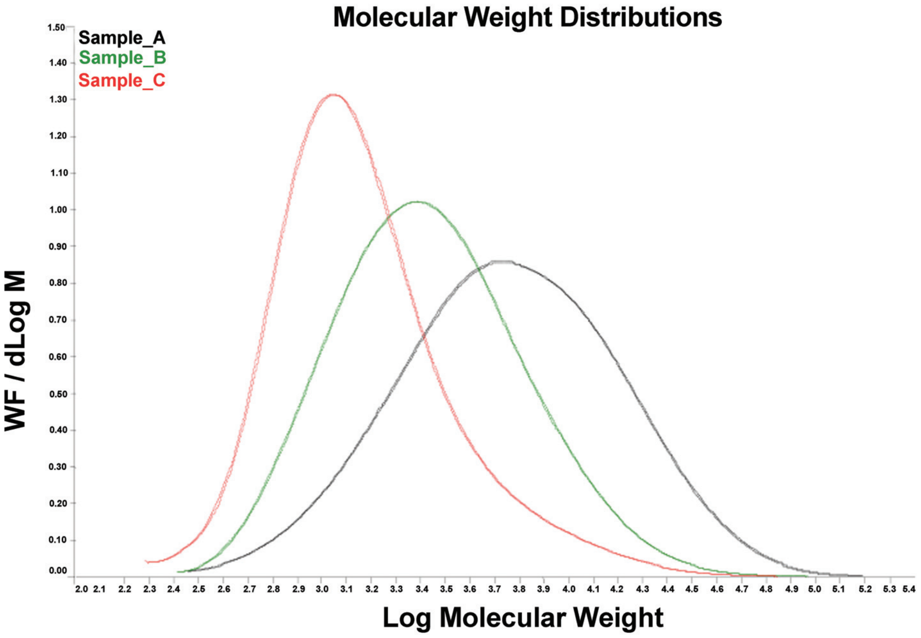

Figure 5: Comparison of the molecular weight distributions for duplicate runs of sodium polyacrylate samples – GPC with sodium nitrate/phosphate buffer @ pH 7.0

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