GPC / SEC Theory and Understanding

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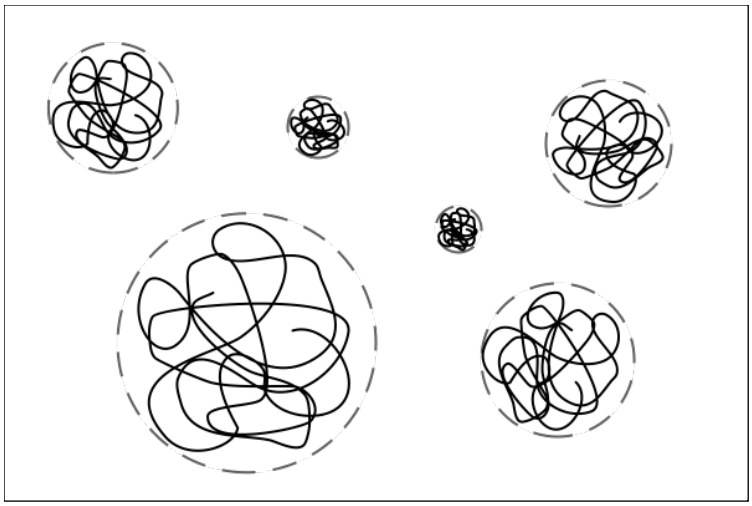
Gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC) is a branch of liquid chromatography specifically concerned with characterisation of polymer molecular weight.

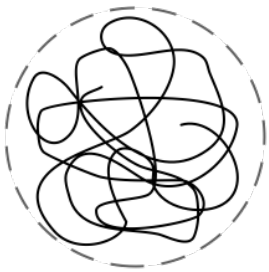
The solvent / eluent used for GPC must be compatible with the polymer type to be characterised in order that a *true solution* is formed. Each polymer chain forming a *random coil* and the solution sufficiently dilute to avoid any interaction between individual polymer molecules. Of course GPC will only characterise soluble polymer, any insoluble gel will be removed from solution in order to protect fine capillary tubes and the fractionation columns.



A True Solution

Polymer molecules forming random coils in dilute solution with no interaction between individual chains

Different solvents / eluents will solvate and swell the polymer molecule to different degrees. A moderate to high degree of solvation is preferred. A polymer molecule of a certain polymer type, and certain chain length in a particular solvent will occupy a particular volume.



Polymer in solution with good degree of solvation

Polymer in solution with poor degree of solvation

Degree of Solvation

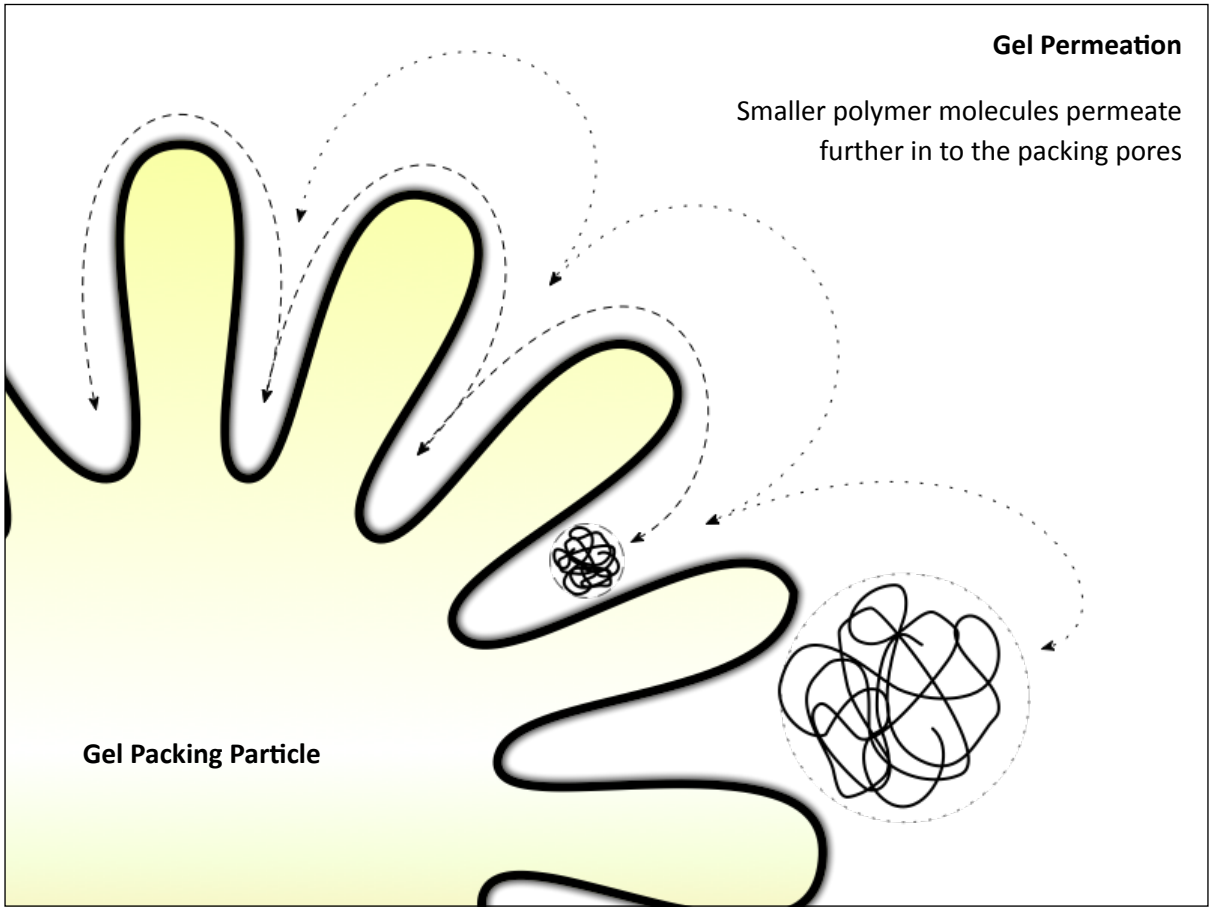
GPC fractionates polymer according to its solvated molecular size. A moderate to high degree of solvation is preferred

The dilute polymer solution is injected on to a chromatography column containing a *packing*. The packings used for GPC are porous and the size of the pores will determine the molecular weight range that they are appropriate for. Different packings are available dependant on the polymer type, application, and expected molecular weight range. Most packings used with organic solvents / eluents are formed from cross-linked (insoluble) polymer gels.

A flow of eluent through the column carries the solvated polymer. Polymer molecules of large solvated size (volume) will be unable to permeate into a proportion of the packing pores and have a short residence time in its journey and will therefore exit the column first. Polymer molecules of small solvated size (volume) will have a longer residence time in each packing pore encountered and will therefore exit the column later. Fractionation of the polymer is therefore by the principal of *size exclusion*.

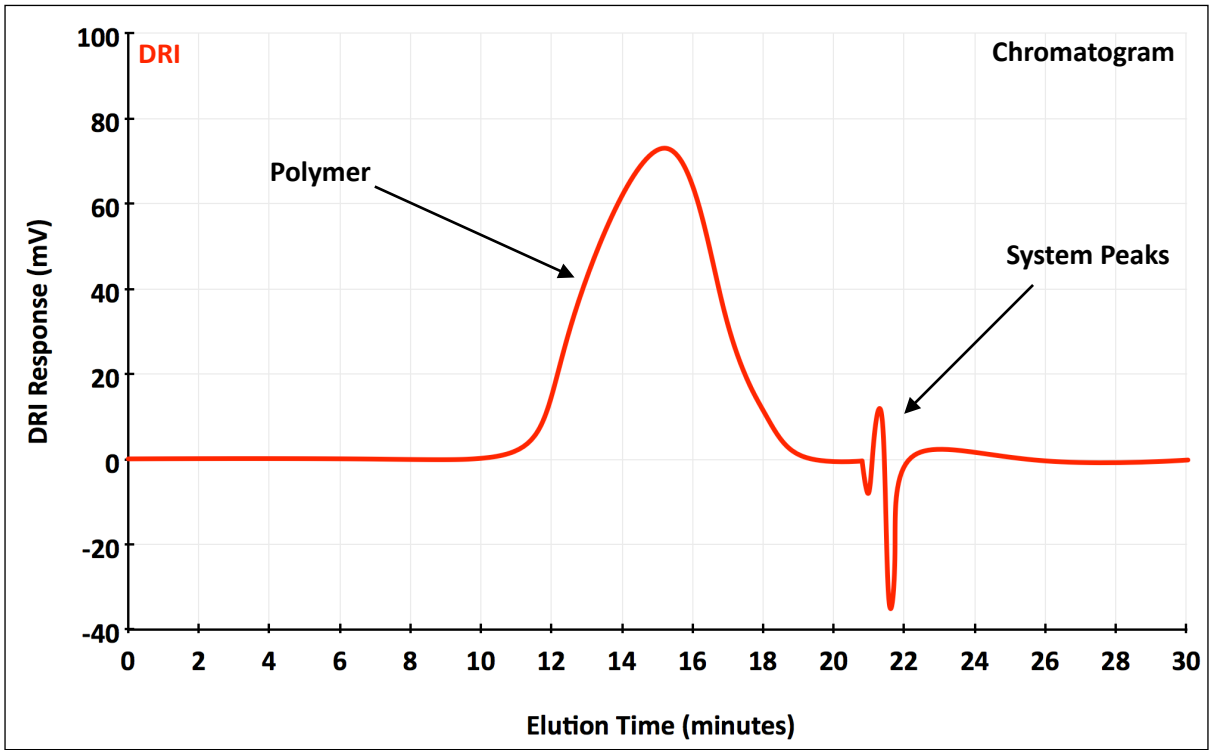
If the polymer molecule is too large to permeate into any of the packing pores it will travel through the interstitial space between packing particles and it is said to be *excluded* – the molecule is above the *exclusion limit* of the column. The

appropriate column is chosen so that all solvated polymer has some residence time in some pores.



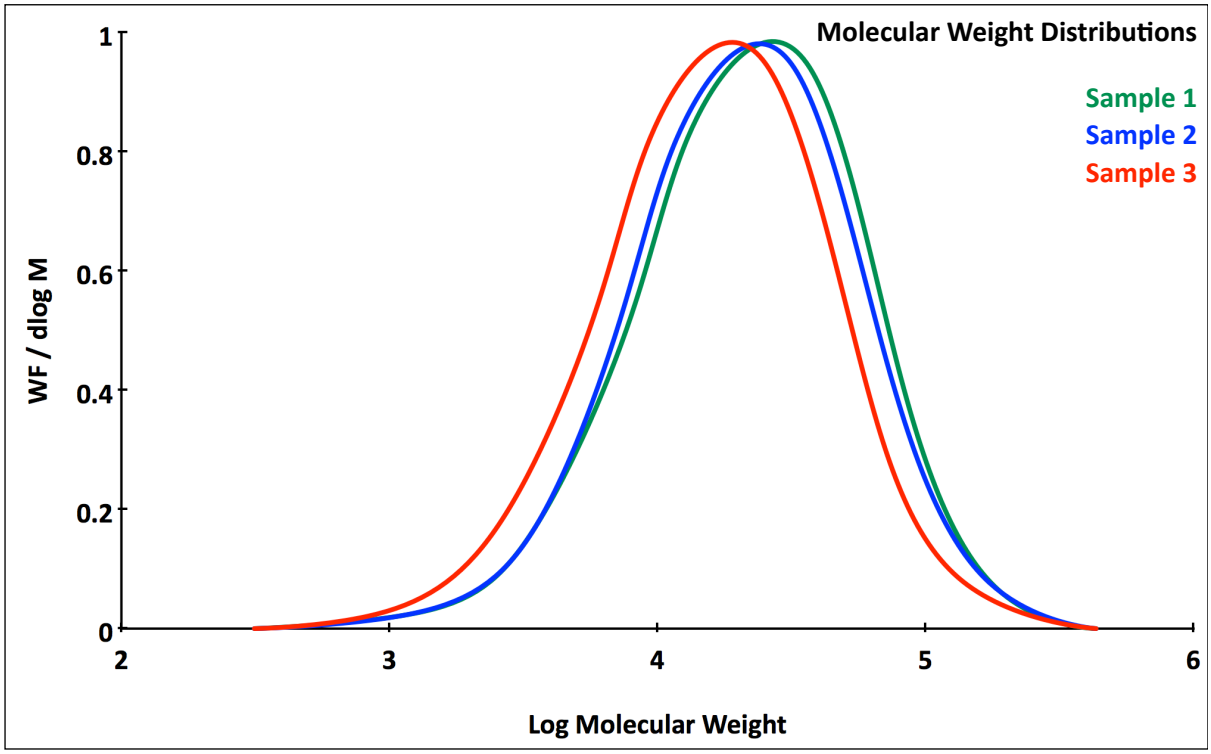
For true size exclusion to occur there must be no chemical interaction of the polymer molecule with the packing particles.

A concentration detector, usually differential refractive index (DRI) but may be infrared (IR), ultraviolet (UV) or evaporative light scattering (ELS), is used to record the amount of polymer, fractionated by molecular size, eluting from the column over time, resulting in a chromatogram.



By appropriate calibration of the columns and / or detectors, the molecular size distribution of the polymer is then translated to a molecular weight distribution. Computation is applied to the data to provide average molecular weights – typically number average (Mn), weight average (Mw) and polydispersity (Mw/Mn) are provided though additional *averages* can be described. Whilst a useful summary, care should be exercised on concentrating too much on these mathematical averages – it is the comparison of the whole distribution plot between several sample polymers that will provide the *context* and *story* behind the issue investigated.

Conventional GPC (only using a concentration detector) usually gives the best *comparison* of molecular weight distributions providing that samples are of the same chemical composition and structure.



Combined GPC-viscosity, *GPC-light scattering*, or *Triple detection GPC* (concentration, viscosity and light scattering) will allow for differences in chemical composition and / or structure and should give *true molecular weight* data and comparison of structural branching information.