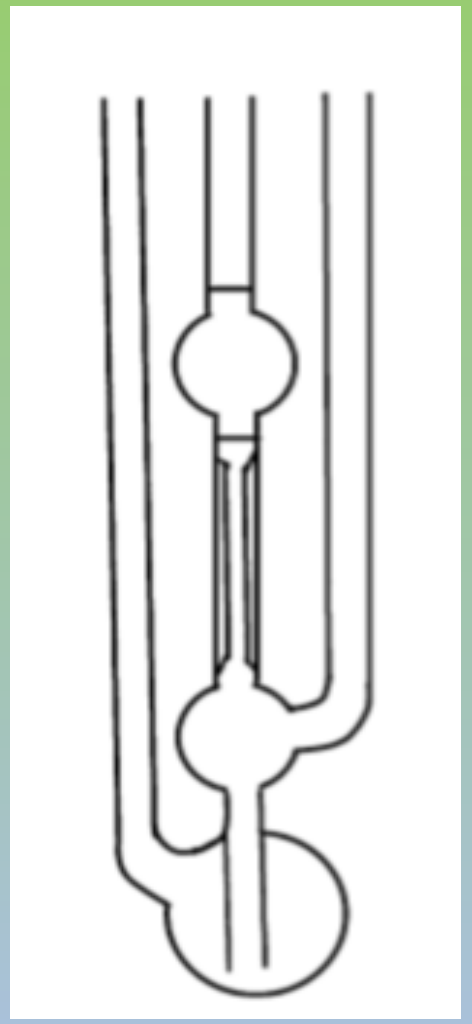
## Experimental and theorical polymerization rate

If Mw is quoted for a molecular weight distribution, there is an equal weight of molecules on either side of Mw in the distribution. The average molecular weight is obtained from light-scattering

**Solution viscosity** is also useful for molecular-weight measurements. Viscosity, like light scattering, is greater for the larger-sized polymer molecules than for smaller ones.

For a polydisperse polymer

$$\overline{M}_w > \overline{M}_v > \overline{M}_n$$



A modified Ubbelohde viscometer with improved dilution characteristics

- GPC is based on the behaviour of polymer molecules in solution
- In the solid state polymers can be considered like spaghetti – a confusing mass of intertwined chains
- In solution, polymer molecules are discrete entities
- Due to entropic effects all but the most rigid of polymer chains curls up in solution to form a ball like shape

Dissolution

However, solution viscosity does not measure Mw since the exact dependence of solution viscosity on molecular weight is not exactly the same as light scattering. Solution viscosity measures the viscosity-average molecular weight Mv defined by

$$\overline{M}_v = \left[\sum w_x M_x^a\right]^{1/a} = \left[\frac{\sum N_x M_x^{a+1}}{\sum N_x M_x}\right]^{1/a}$$

where $a$ is a constant. The viscosity- and weight-average molecular weights are equal when $a$ is unity. $\overline{M}_v$ is less than $\overline{M}_w$ for most polymers, since $a$ is usually in the range 0.5–0.9. However, $\overline{M}_v$ is much closer to $\overline{M}_w$ than $\overline{M}_n$, usually within 20% of $\overline{M}_w$. The value of $a$ is dependent on the hydrodynamic volume of the polymer, the effective volume of the solvated polymer molecule in solution, and varies with polymer, solvent, and temperature.

The polydispersity index is used as a measure of the broadness of a molecular weight distribution of a polymer, and is defined by:

$$\text{Polydispersity index} = \frac{Mw}{Mn}$$

The larger the polydispersity index, the broader the molecular weight. A monodisperse polymer where all the chain lengths are equal (such as a protein) has an Mw/Mn = 1. The best controlled synthetic polymers (narrow polymers used for calibrations) have Mw/Mn of 1.02 to 1.10. Step polymerization reactions typically yield values of Mw/Mn of around 2.0, whereas chain reactions yield Mw/Mn values between 1.5 and 20.

REF: Wendy Gavin Biomolecular Characterization Laboratory Version 1 May 2016, GPC - Gel Permeation Chromatography

with the differences between the various average molecular weights increasing as the molecular-weight distribution broadens. A typical polymer sample will have the molecularweight distribution shown in Figure.

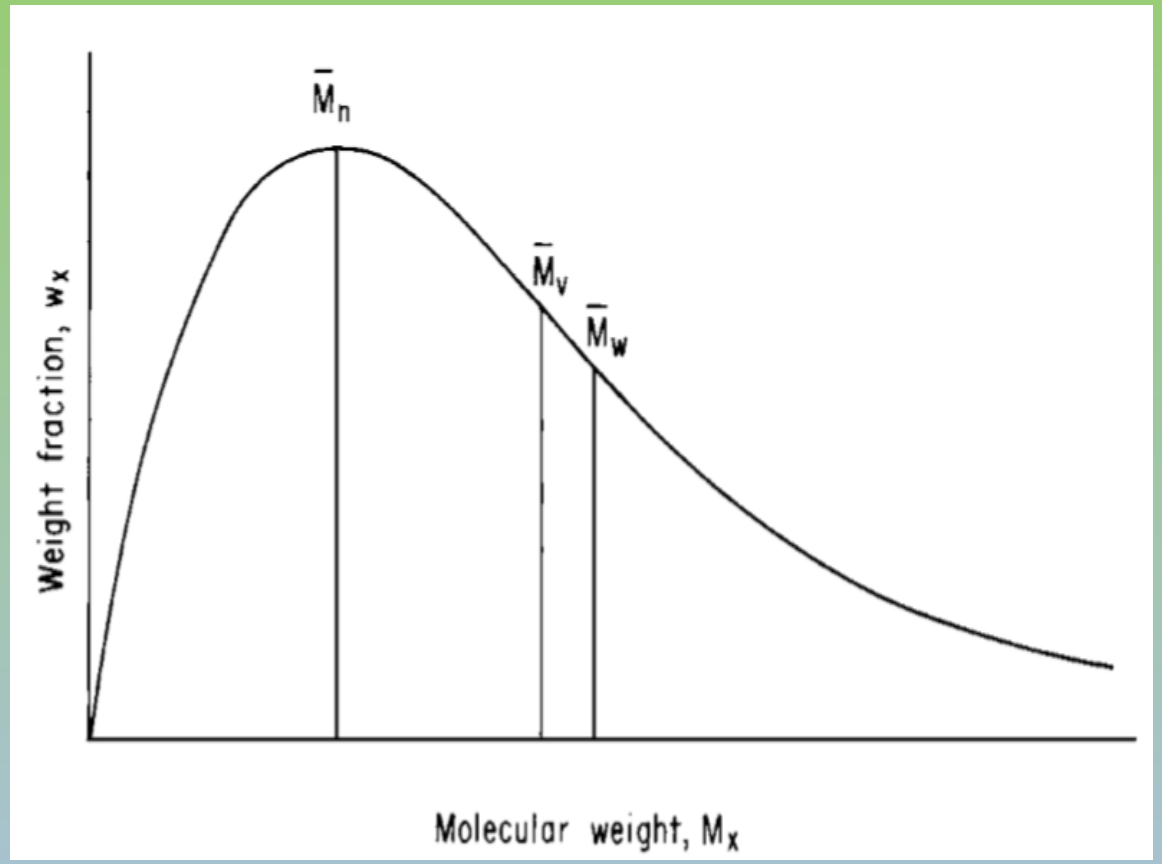
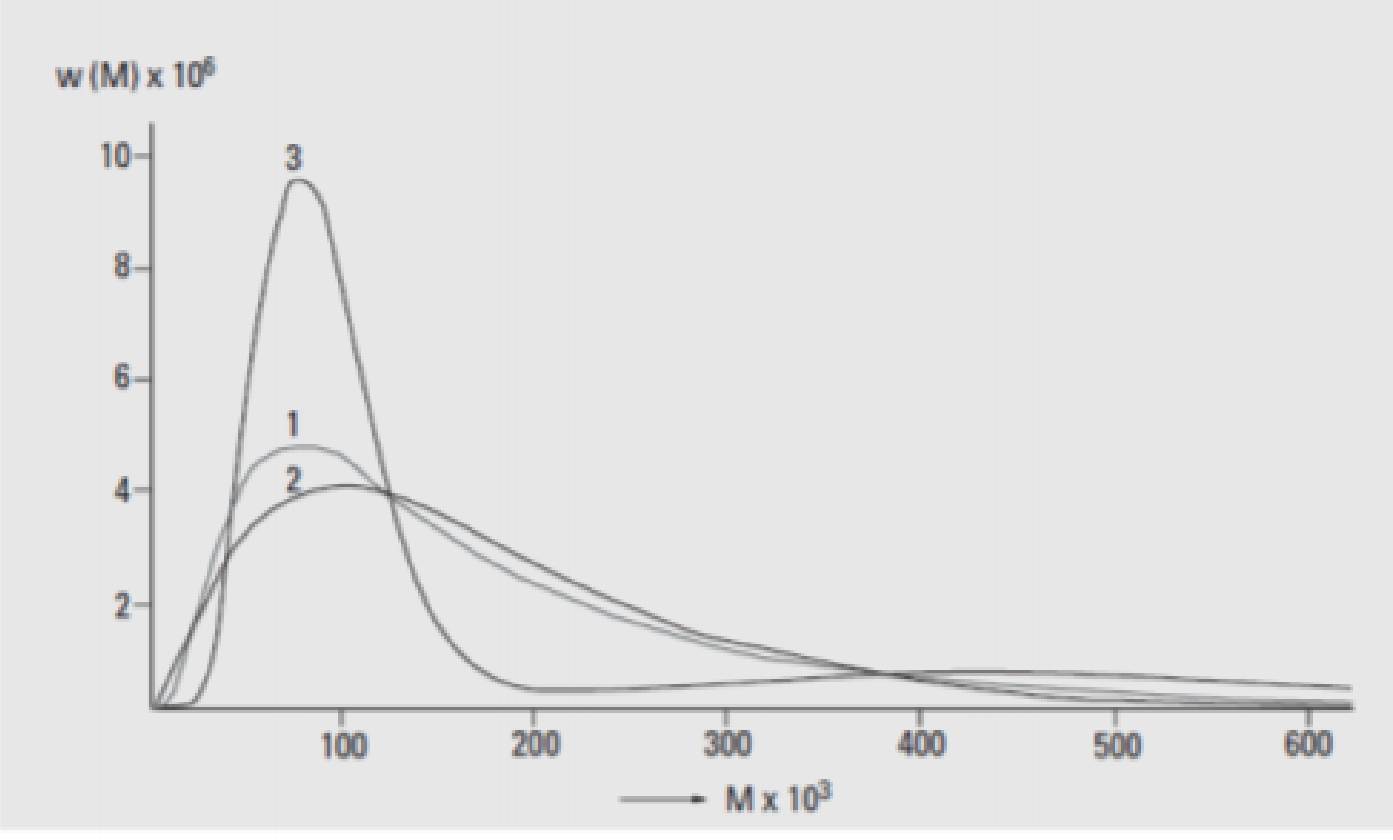


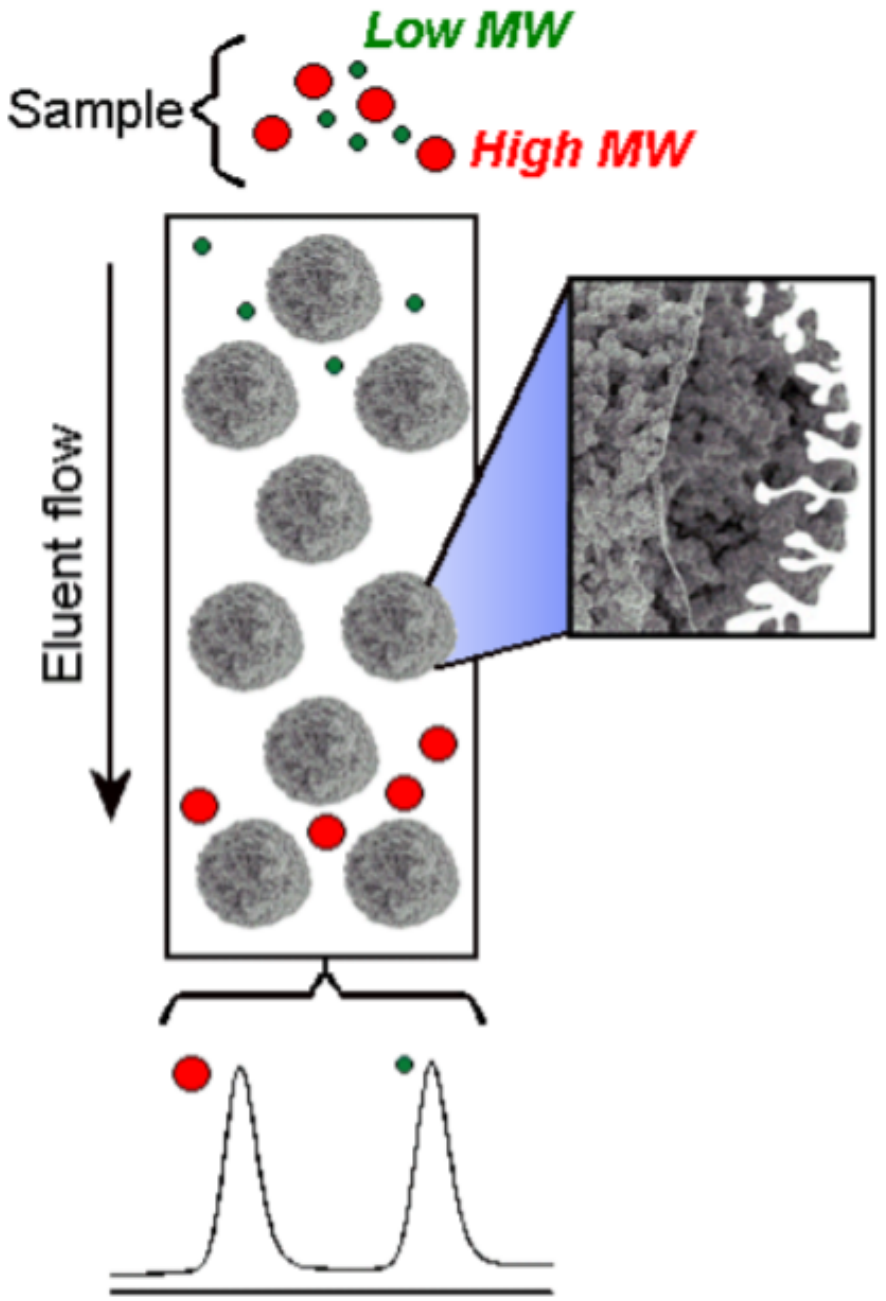

Figure indicates distribution of molecular weights in a typical polymer sample.

The width of the individual peaks reflects the distribution of the size of molecules for a given resin and its components. The distribution curve is also known as the molecular weight distribution (MWD) curve. Taken together the peaks reflect the MWD of a sample. The broader the MWD, the broader the peaks become.

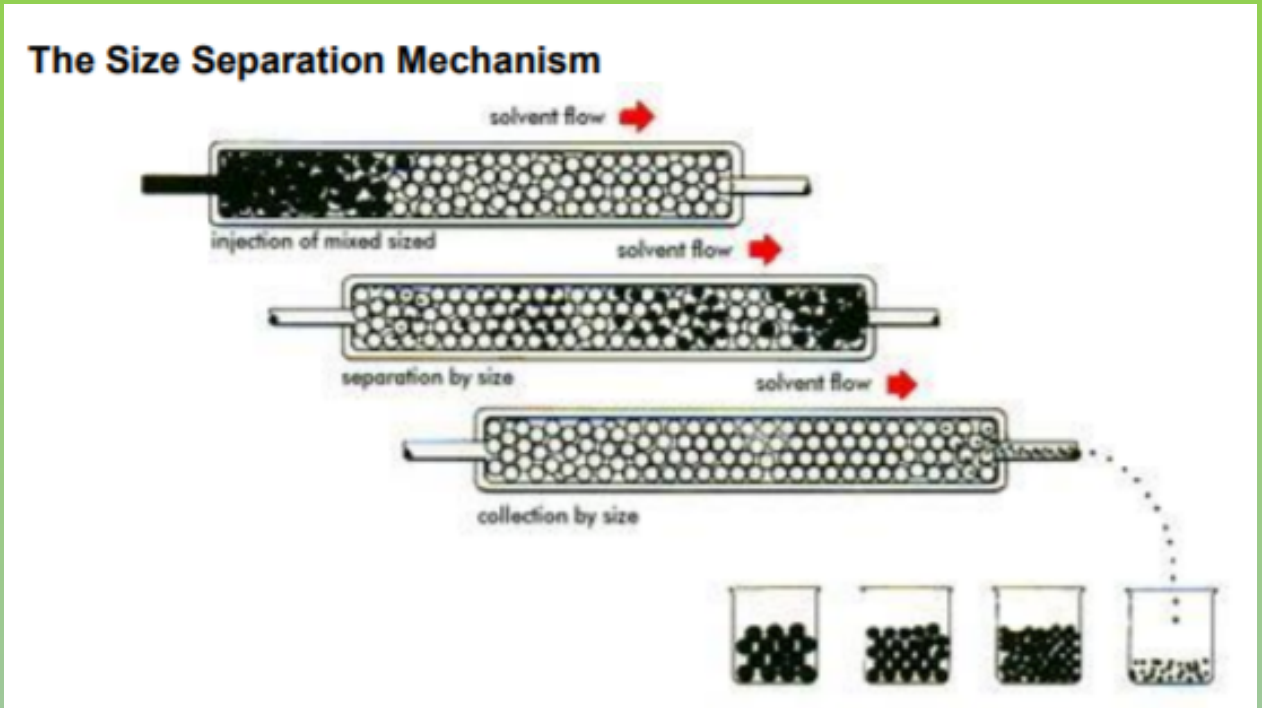
The higher the average molecular weight, the further along the molecular weight axis the curve shifts.




Molecules of various sizes elute from the column at different rates. The column retains low molecular weight material (small black dots) longer than the high molecular weight material (large black dots). The time it takes for a specific fraction to elute is called its "retention time".




- Polymer is prepared as a dilute solution in the eluent and injected into the system
- The GPC column is packed with porous beads of controlled porosity and particle size
- Large molecules are not able to permeate all of the pores and have a shorter residence time in the column
- Small molecules permeate deep into the porous matrix and have a long residence time in the column
- Polymer molecules are separated according to molecular size, eluting largest first, smallest last
- As a result of the GPC separation mechanism, polymer molecules elute from the column in order of size in solution
- Largest elute first, smallest elute last




Number average, Mn, may be obtained by membrane osmometry, or end group analysis, (titration, NMR, etc.)

Weight Average, Mw, may be obtained by light scattering

There are other techniques to obtain these molecular weight averages:

Z Average, Mz, and Z + 1 Average, Mz + 1, may be obtained by ultracentrifugation

Once we have calibrated our GPC system, we can obtain all of these averages with a single injection