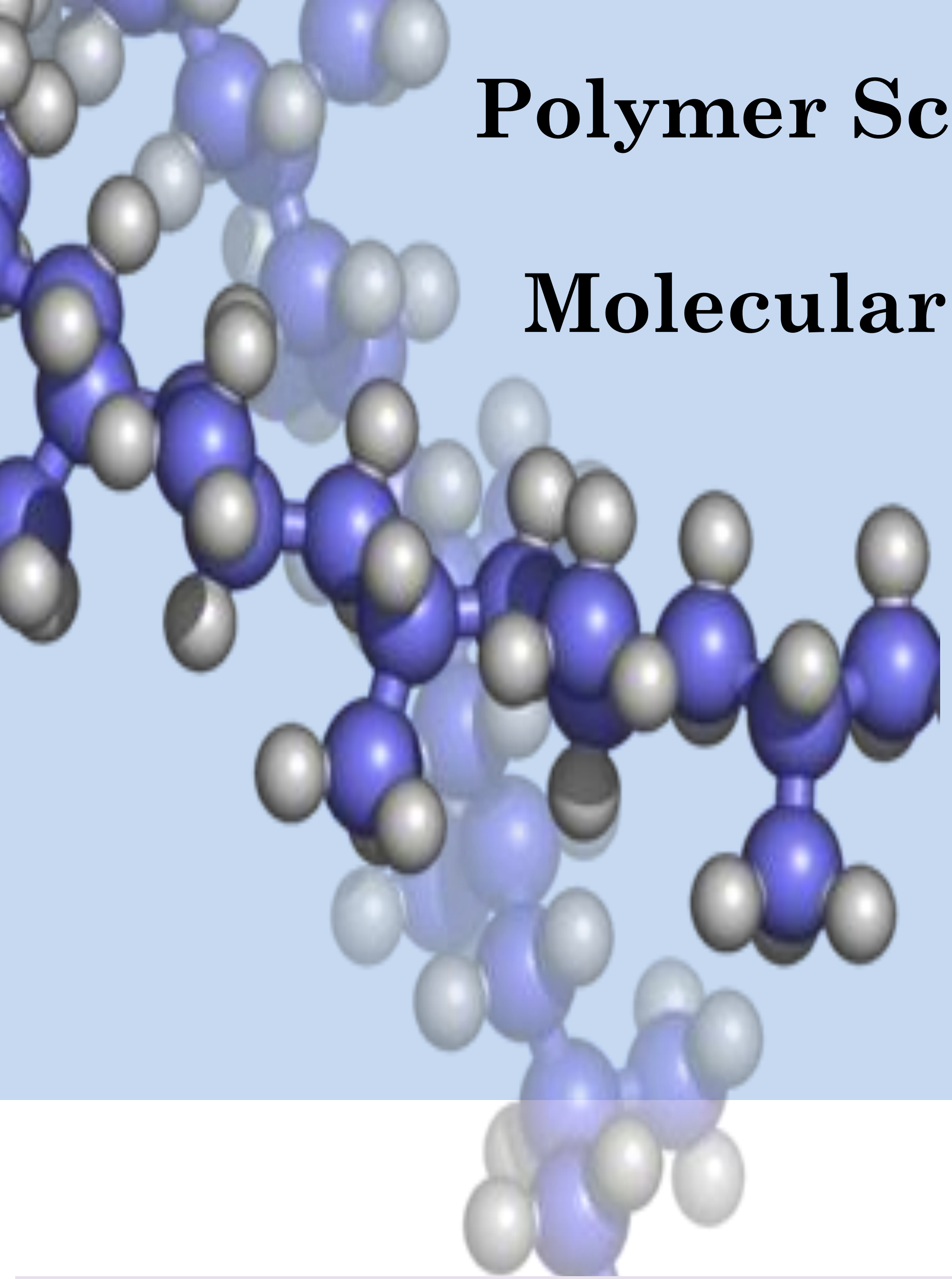
Polymer Science & Engineering

Molecular Weight Distribution



Dr. Motasem Saidan

M. Saidan@gmail.com

From little molecules to big molecules

$$H - (CH_2)_n - H$$

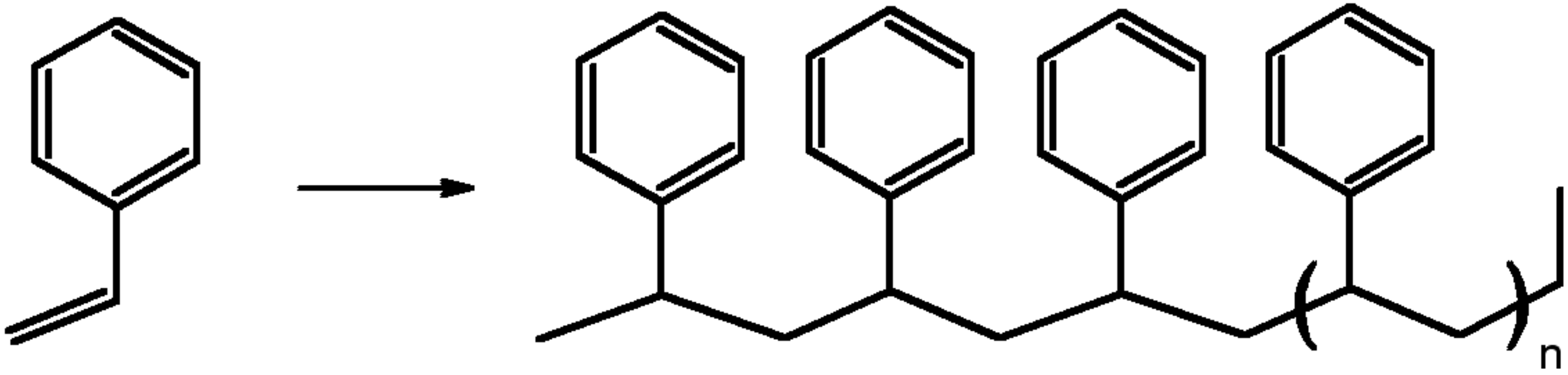
Number of Carbons in Chain	State and Properties of Material	Applications
1–4	Simple gas	Bottled gas for cooking
5–11	Simple liquid	Gasoline
9–16	Medium-viscosity liquid	Kerosene
16–25	High-viscosity liquid	Oil and grease
25–50	Crystalline solid	Paraffin wax candles
50–1000	Semicrystalline solid	Milk carton adhesives and coatings
1000–5000	Tough plastic solid	Polyethylene bottles and containers
$3–6 \times 10^5$	Fibers	Surgical gloves, bullet-proof vests

L. H. Sperling, Introduction to Physical Polymer Science, Wiley, 2006

increase in molecular weight

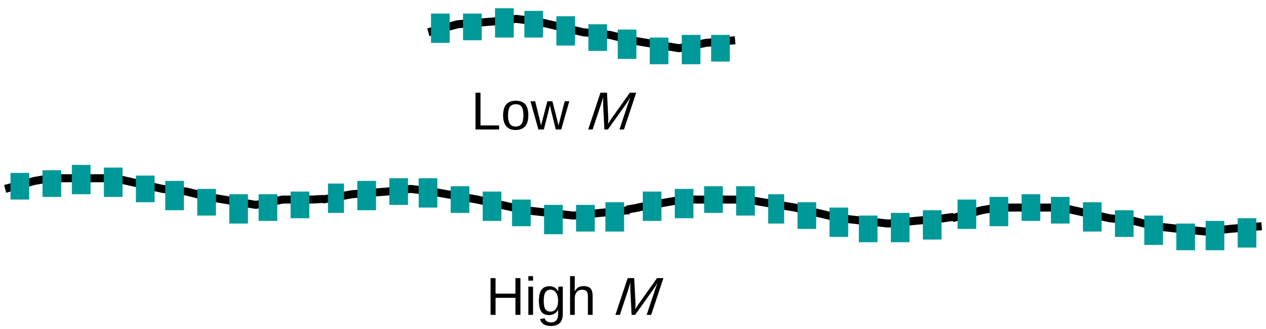
Introduction

- The molecular weight of a polymer is a way of describing how long the polymer chains are
- Each monomer has a molecular weight (often called the formula weight)
- Adding the monomers together to make polymers increases the molecular weight
- The longer the chains, the higher the molecular weight
- In polymer science it is the molecular weight distribution that is important



Introduction

Molecular weight, *M*: Mass of a mole of chains



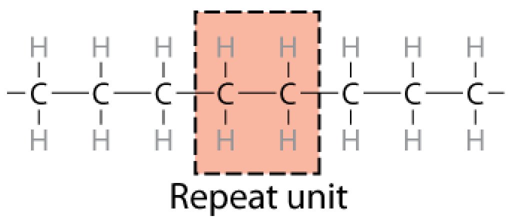
- Polymers can have various lengths depending on the number of repeat units.
- During the polymerization process not all chains in a polymer grow to the same length, so there is a distribution of molecular weights.
- The molecular weight distribution in a polymer describes the relationship between the number of moles of each polymer species and the molar mass of that species.

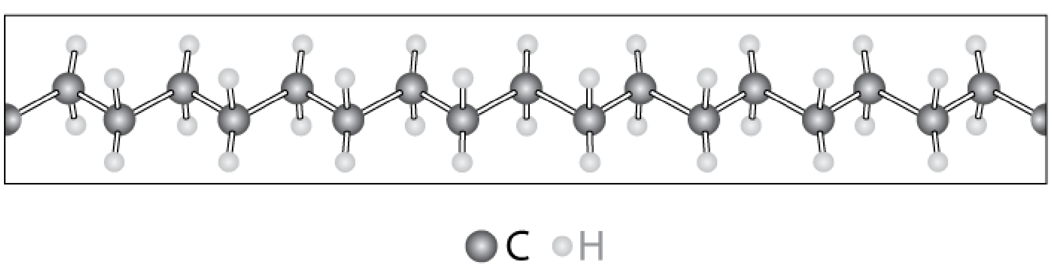
Polymer = Macromolecule

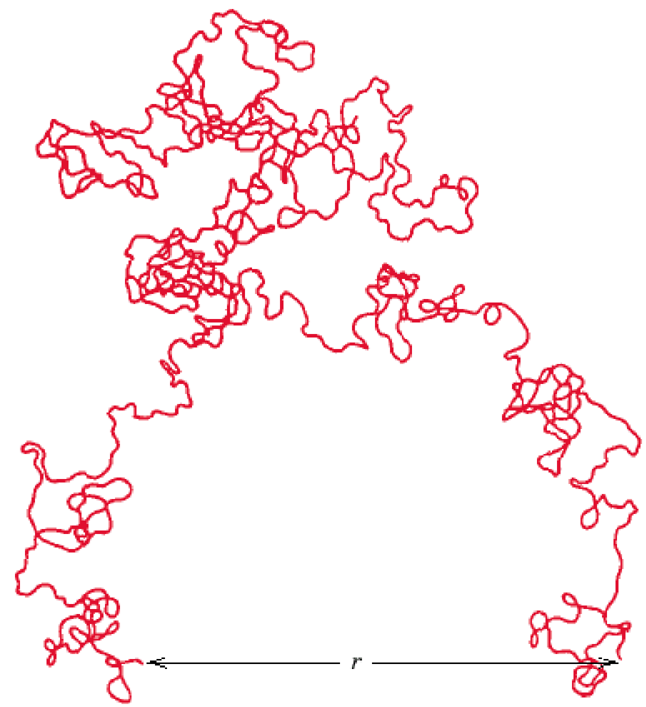
The high molecular weight is the principal characteristic, which

1. distinguishes polymers from other chemical substances, and

2. provides unique and diverse properties to polymeric materials finding infinite applications in various areas of human society



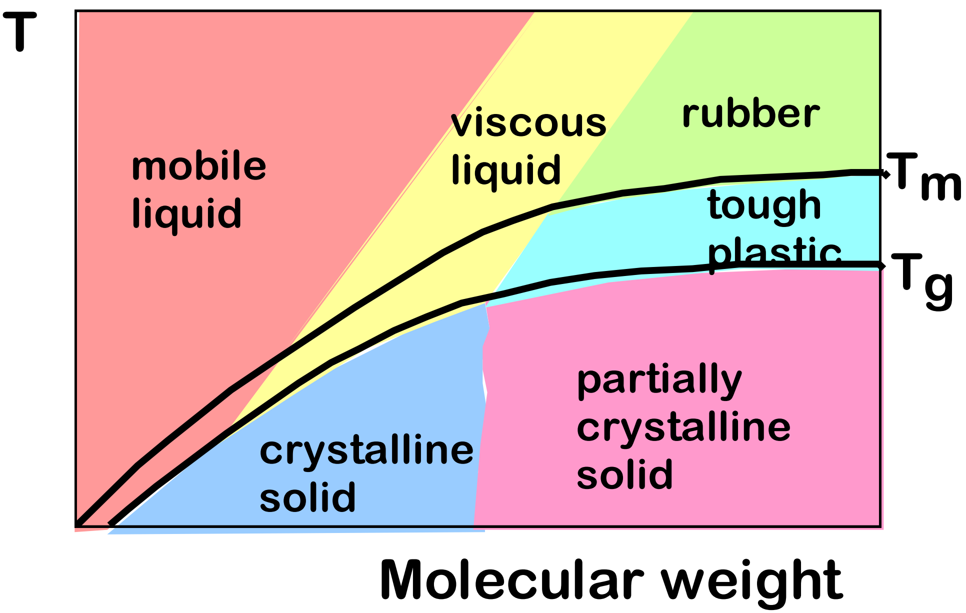


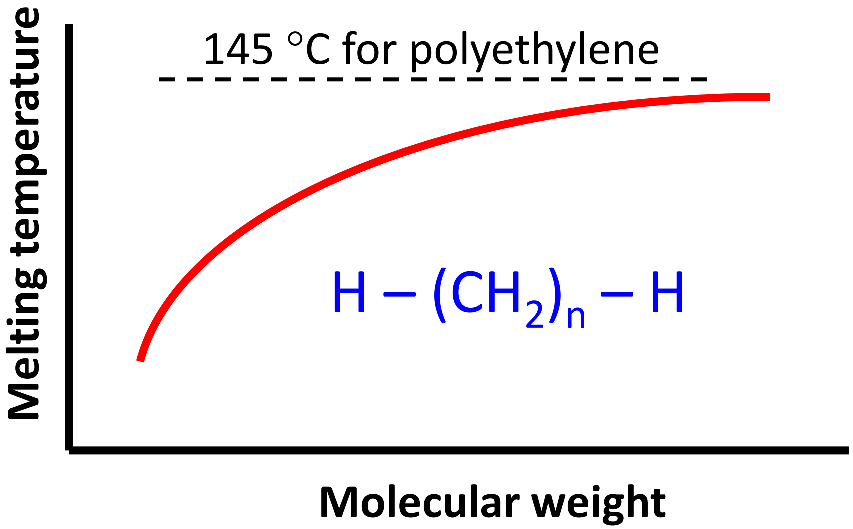


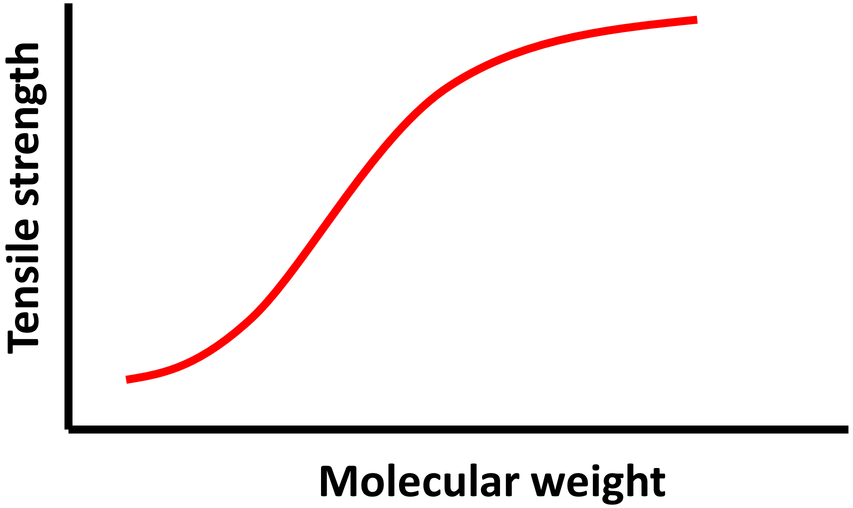
From little molecules to big molecules

Effect on:

- melting point
- the degree of polymer entanglement
- the degree of intermolecular interactions
- physical and mechanical properties
- tensile strength
- melt-processing conditions
- application







For example, let’s look at hydrocarbons

- Very short chain hydrocarbons are the predominant component of petrol – liquid at room temperature

- Longer chain hydrocarbons are present in various waxes such as candle wax – soft, pliable and easy to melt

- Polythene is a very long chain hydrocarbon – tough, strong and very resistant to heat and solvents

Distribution of molecular weights

M_i molecular weight of the *i*th polymer chain
N_i number of polymer chains with molecular weight M_i
w_i weight fraction of polymer chains with molecular weight M_i

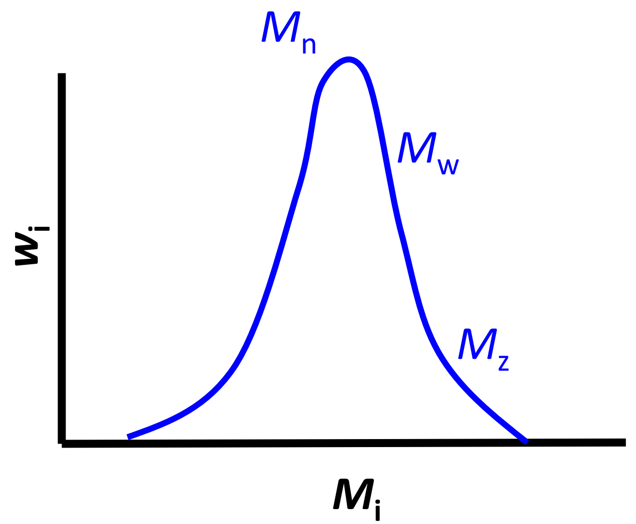
$$w_i = \frac{N_i M_i}{\sum N_i M_i}$$

Number average molecular weight (M_n)

$$\overline{M}_n = \frac{\Sigma N_i \overline{M}_i}{\Sigma N_i}$$

Weight average molecular weight (M_w)

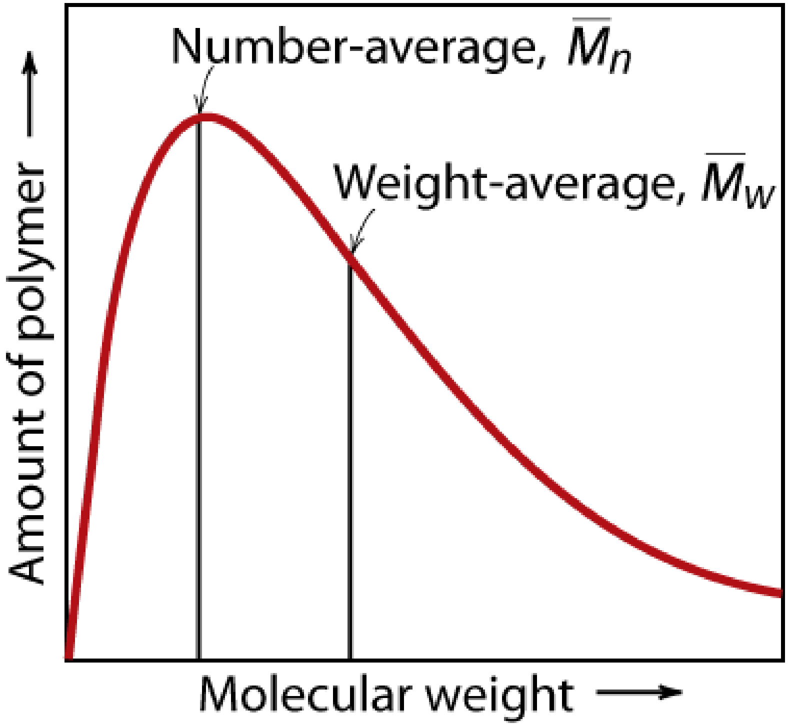
$$\overline{M}_w = \frac{\Sigma W_i \overline{M}_i}{\Sigma W_i}$$



$Đ = M_w / M_n$
dispersity (1 – 10)

$$\overline{M}_n = \Sigma x_i M_i$$

$$\overline{M}_w = \Sigma w_i M_i$$



$\overline{M}_n$ = the number average molecular weight (mass)

M_i = mean (middle) molecular weight of size range i

x_i = number fraction of chains in size range i

w_i = weight fraction of chains in size range i

Molecular Weight Averages

Number average $M_n = \dfrac{\Sigma N_i M_i}{\Sigma N_i}$

Mn can be correlative with polymer colligative properties, e.g. freezing point depression

Weight average $M_w = \dfrac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$

Mw may be correlated with properties such as melt viscosity

Z average $M_z = \dfrac{\Sigma N_i M_i^3}{\Sigma N_i M_i^2}$

Mz may be correlated with properties such as toughness

Polydispersity, $d = \dfrac{M_w}{M_n}$

Polydispersity characterizes the shape of the distribution

Number-average molecular weight (*M*n)

- based on methods of counting the number of molecules in a given weight of polymer

  - the total weight of a polymer sample, *w*, is the sum of the weights of each molecular species present

$$w = \sum_{i=1}^{\infty} w_i = \sum_{i=1}^{\infty} N_i M_i$$

$$\overline{M}_n = \frac{w}{\sum_{i=1}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i}$$

N = number of molecules
M = molecular weight

Example - a polymer sample consists of 9 molecules of mw 30,000 and 5 molecules of mw 50,000

$$\overline{M}_n = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} = \frac{(9 \times 30{,}000) + (5 \times 50{,}000)}{(9+5)} = 37{,}000$$

Weight-average molecular weight (Mw)

- determination of molecular weight based on size rather than the number of molecules
  - the greater the mass, the greater the contribution to the measurement

$$\overline{M}_w = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i} = \frac{\sum_{i=1}^{\infty} N_i M_i^{\,2}}{\sum_{i=1}^{\infty} N_i M_i}$$

w = weight fraction
M = molecular weight
N = number of molecules

Consider the previous example - 9 molecules of molecular weight 30,000 and 5 molecules of molecular weight 50,000

$$\overline{M}_w = \frac{9(30{,}000)^2 + 5(50{,}000)^2}{9(30{,}000) + 5(50{,}000)} = 40{,}000$$

Z-average molecular weight (*Mz*)

some molecular weight determination methods (e.g. sedimentation equilibrium) yield higher molecular weight averages - M_z

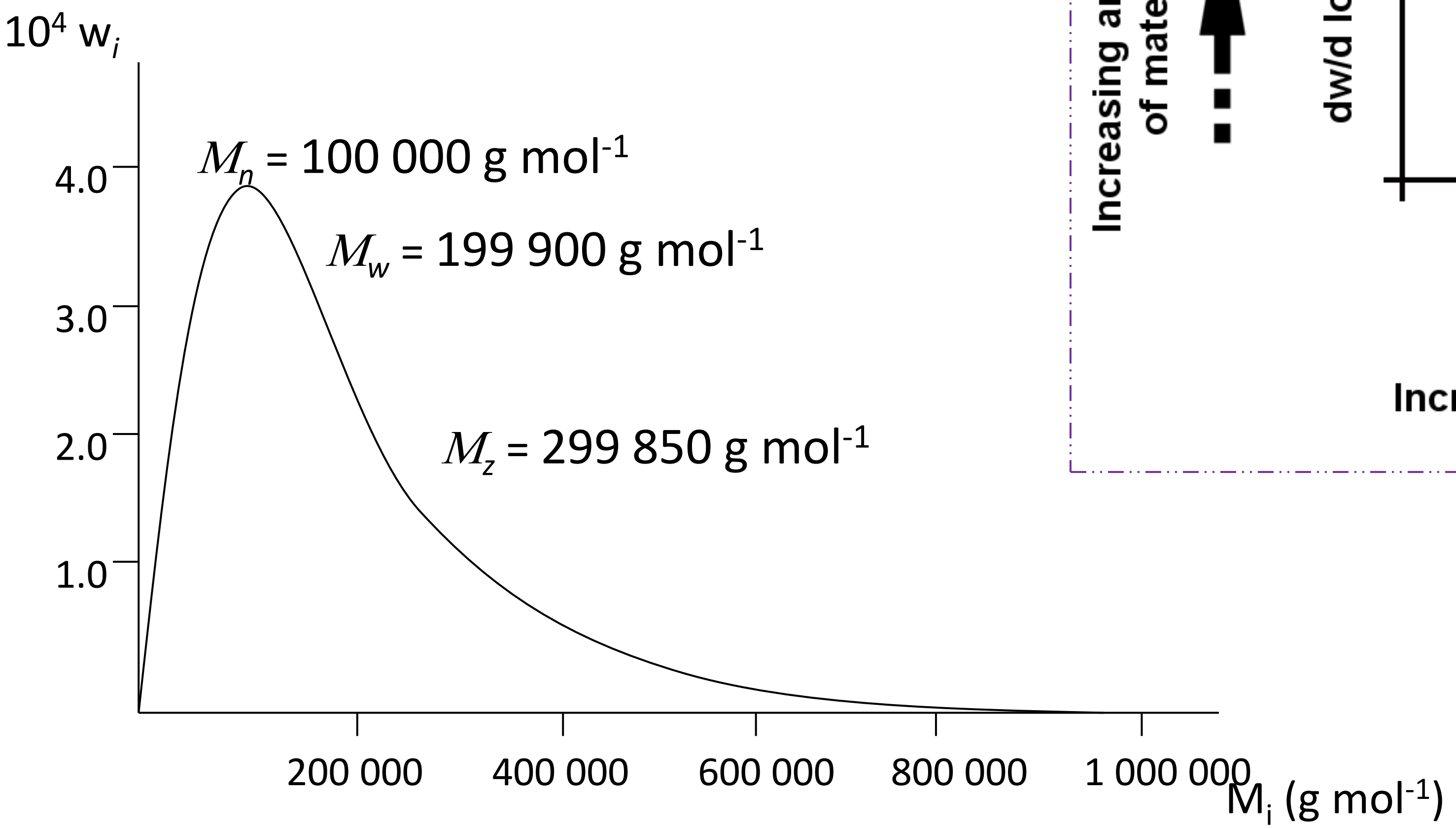
$$\overline{M}_z = \frac{\sum_{i=1}^{\infty} N_i M_i^3}{\sum_{i=1}^{\infty} N_i M_i^2} = \frac{\sum_{i=1}^{\infty} w_i M_i^2}{\sum_{i=1}^{\infty} w_i M_i}$$

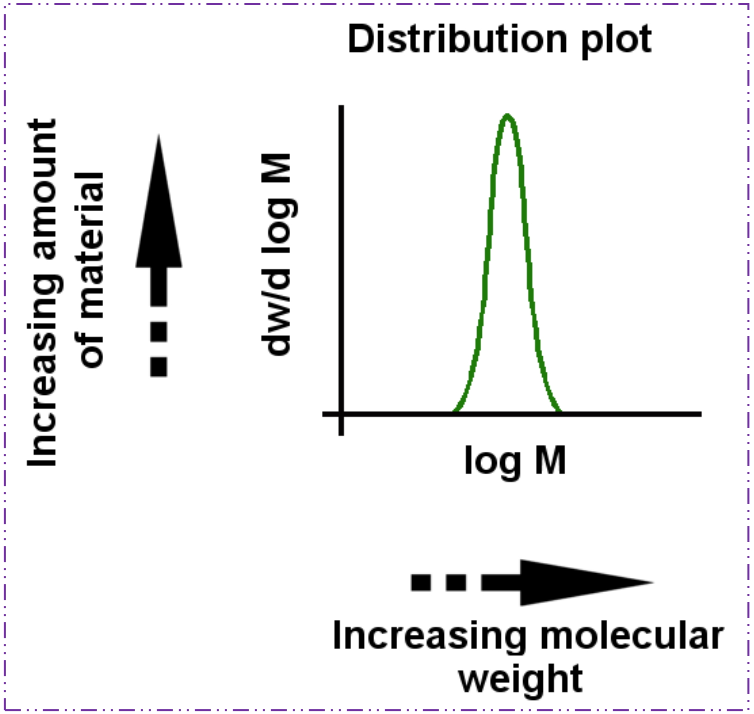
w = weight fraction
M = molecular weight
N = number of molecules

Consider the previous example - 9 molecules of molecular weight 30,000 and 5 molecules of molecular weight 50,000

$$\overline{M}_z = \frac{9(30{,}000)^3 + 5(50{,}000)^3}{9(30{,}000)^2 + 5(50{,}000)^2} = 42{,}136$$

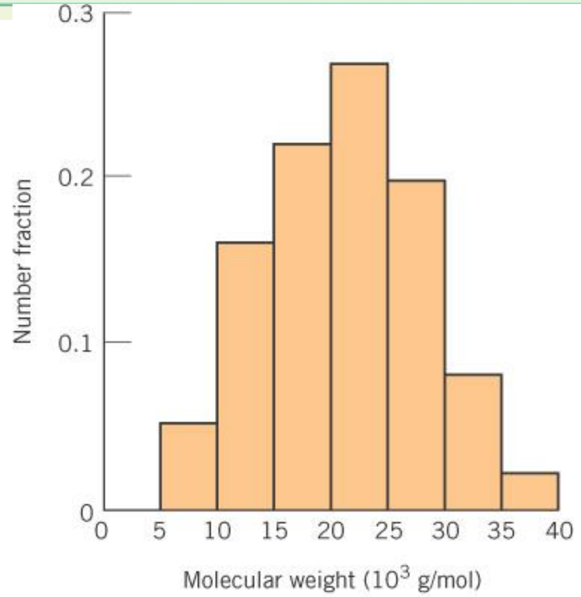
A Typical Molecular Weight Distribution Curve





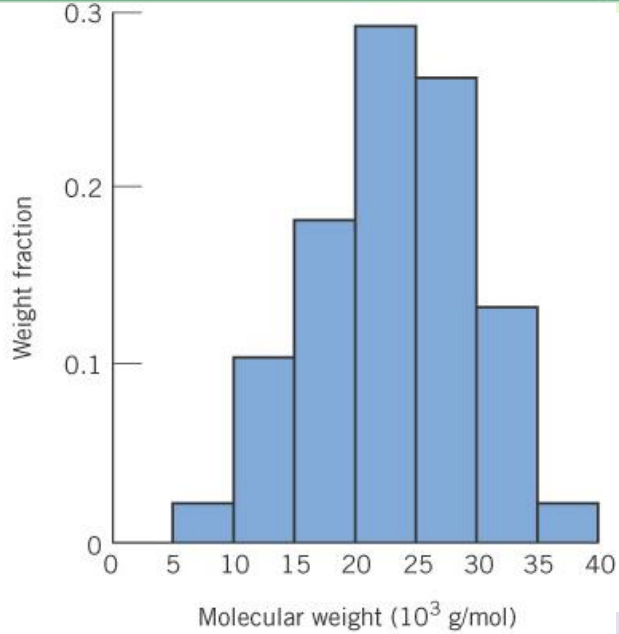
Example 1

Molecular Weight Range (g/mol)	*Mean M_i (g/mol)*	x_i	$x_i M_i$
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750
			$\bar{M}_n$ = 21,150



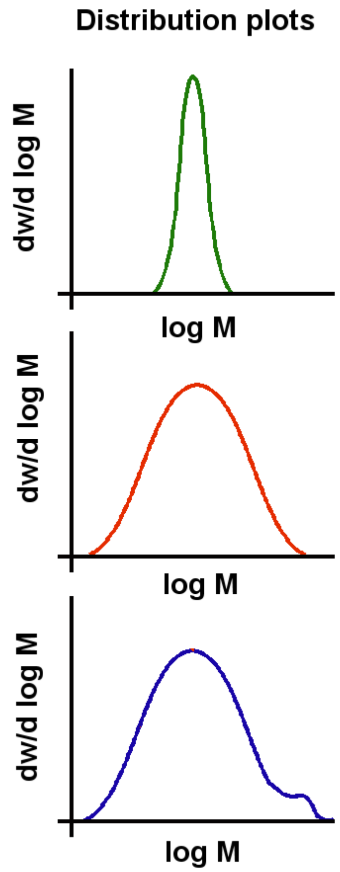
Example 2

Molecular Weight Range (g/mol)	*Mean M_i (g/mol)*	w_i	w_iM_i
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750
			$\bar{M}_w = 23{,}200$



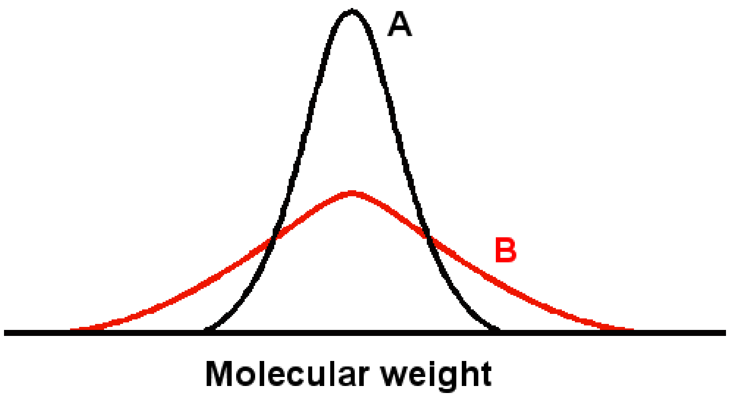
MWT Distribution Shape

- Even for the same type of polymer, each of these distributions will describe a polymer that behaves differently
- The **red** and **green** plots are for low and high polydisperity materials
- The **blue** plot shows a high polydispersity material with a additional high molecular weight component
- The narrower the molecular weight range, the closer are the values of M_w and M_n, and the ratio M_w / M_n may thus be used as an indication of the breadth of the molecular weight range in a polymer sample.
- The ratio is called the **polydispersity index**, and any system having a range of molecular weights is said to be **polydispersed**
- In general, a narrow molecular weight distribution leads to more uniform property values, a narrower softening/ melting temperature range, a lower stress cracking sensitivity, and better chemical resistance.



- A broad molecular weight distribution has advantages for processing because the low molecular weight fractions behave like lubricants. The polymer is less brittle because the low molecular weight fractions can act as plasticizers.

Effect of Polydispersity on a Polymer



- As the broadness of the distribution decreases the strength and toughness of the polymer increases
- However as the broadness of the distribution decreases the polymer becomes more difficult to process
- GPC provides key information to predict the processability and material properties of a polymer

	Strength	Toughness	Brittleness	Melt viscosity	Chemical resistance	Solubility
Increasing Mw	+	+	+	+	+	-
Decreasing distribution	+	+	-	+	+	+

Degree of Polymerization, DP

DP = average number of repeat units per chain

$$DP = \frac{\overline{M}_n}{m}$$

where $m =$ repeat unit molecular weight

Poly(vinyl chloride) (PVC)

,

for PVC: m = 2(carbon) + 3(hydrogen) + 1(Clorine)

= 2(12.011) + 3(1.008) + 1(35.45)

= 62.496 g/mol

DP = 21,150 / 62.496 = 338.42

Viscosity-Molecular Weight Relations

Intrinsic viscosity [*h*] can be related to molecular weight by the **Mark-Houwink-Sakurada Equation**

Applicable for a given polymer-solvent system at a given temperature

$$[\eta] = K\overline{M}_{\upsilon}^{a}$$

Log [*η*] *vs* log *M* (M_w or M_n) for a series of fractionated polymers produces log *K* (intercept) and *a* (slope)

$$\log[\eta] = \log K + a \log \overline{M}_v$$

A wide range of values have been published

- *a* ~ 0.5 (randomly coiled polymers)

  ~ 0.8 (rod-like, extended chain polymers)
- *K* between 10^{-3} and 0.5

Typical Mark-Houwink-Sakurada Equation Constants for Several Polysaccharides

	Solvent	Temp °C	K ($x10^{-3}$) ml g^{-1}	a	MW ($x10^{-3}$)	Method
Cellulose						
	Cadoxen	25	33.8	0.77	20-100	SD
	Cuprammonium	25	8.5	0.81	10-100	OS
Amylose						
	DMSO	25	1.25	0.87	20-300	LS
	Water	20	13.2	0.68	30-220	LS
Dextran						
Linear	Water	25	97.8	0.50	2-10	LS
Branched	Water	34	10.3	0.25	80	LS

	Solvent	Temp °C	[η] dl g^{-1}	*a*	K ($x10^{-3}$) ml g^{-1}	MW
Kraft Lignin	Dioxane	25	0.06	0.12	1638	50,000
Celluose	CED	25	1.81	0.75	54.0	50,000
xylan	CED	25	2.16	1.15	0.85	50,000

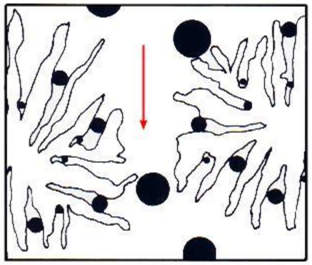
Gel Permeation Chromatography: GPC

- Gel permeation chromatography is used to analyze the molecular weight distribution of organic-soluble polymers

- GPC is a method in which molecules in solution are separated by their size, and in some cases molecular weight

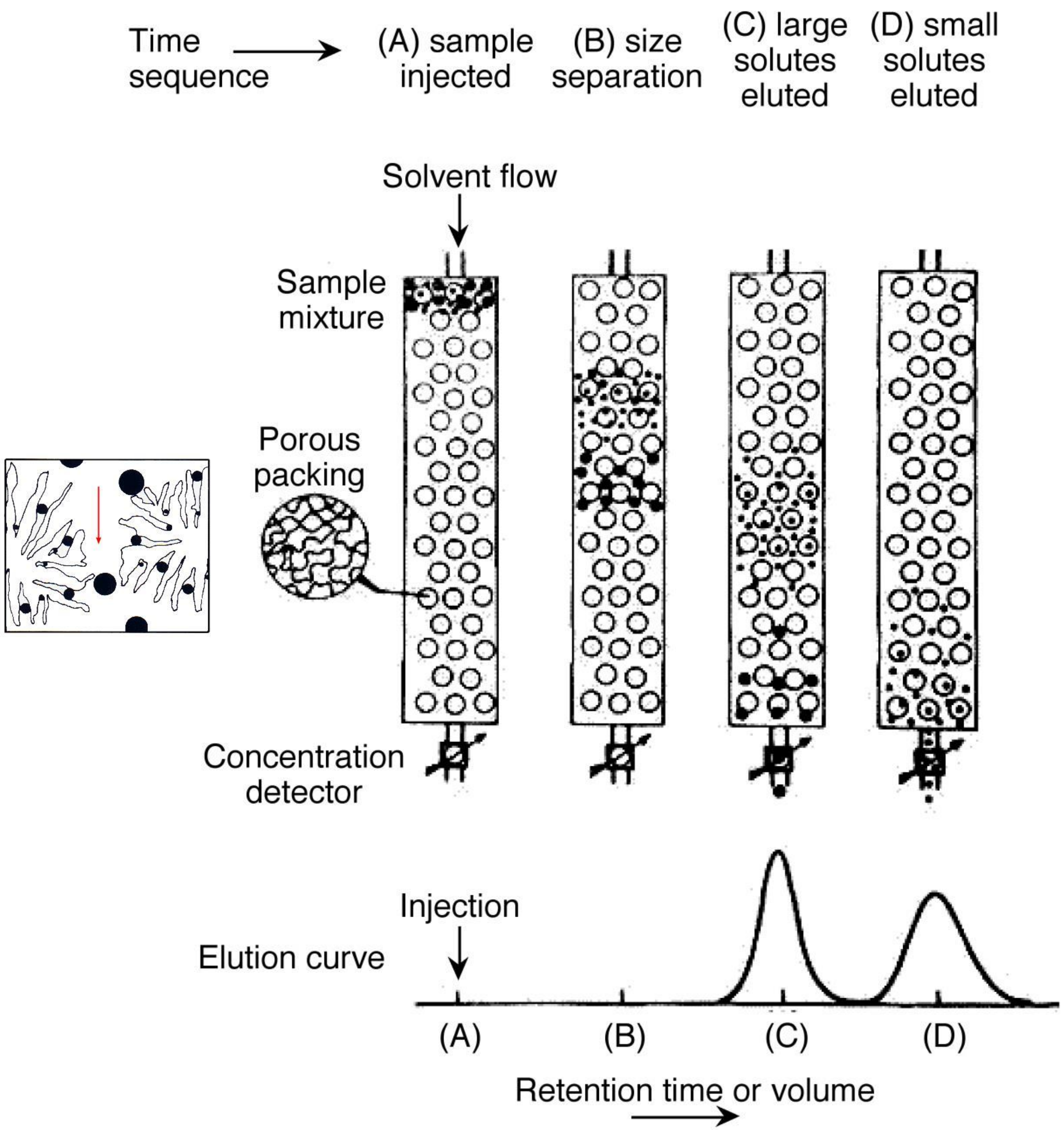
- The advantages of this method include good separation of large molecules from the small molecules with a minimal volume of eluate.

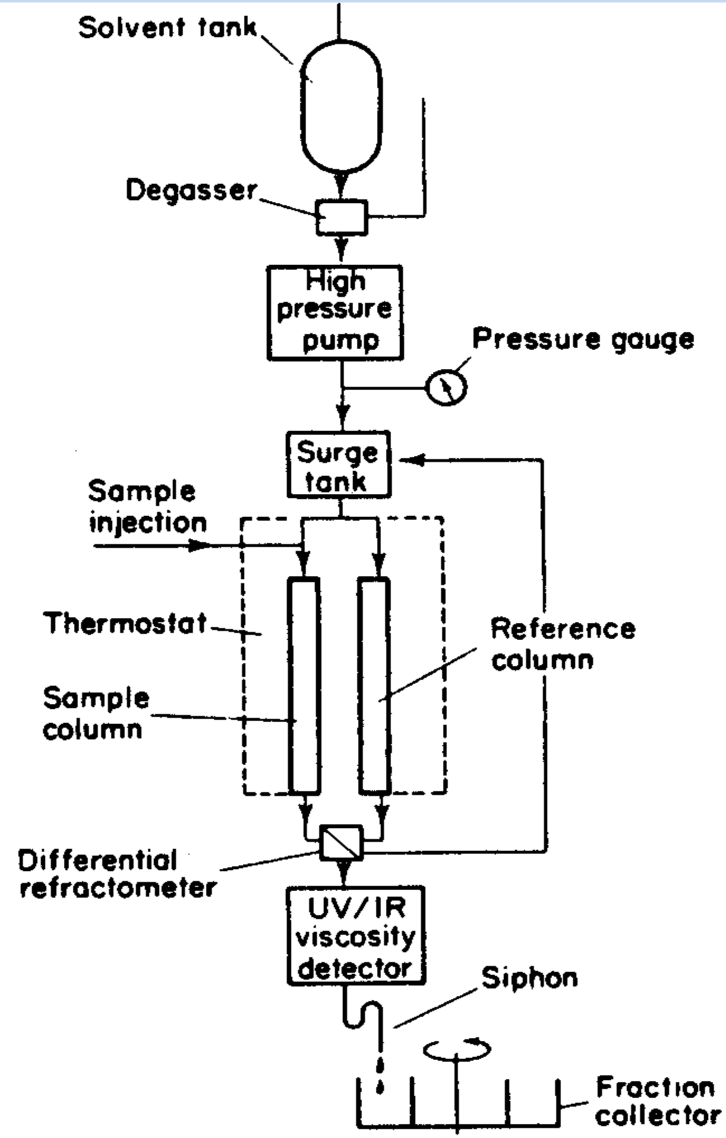
- Gels are used as stationary phase for GPC.



- The eluent (mobile phase) should be a good solvent for the polymer.

Gel Permeation Chromatography: GPC





Analytical techniques for measuring molecular weights of various ranges

Technique	Measures	Range, g/mol
End Group	M_n	up to 2500
Osmometry	M_n	15000 – 750000
Ebulliometry	M_n	up to 100000
Light scattering	M_w	20000 to 10^7
Ultra centrifuge	M_w, M_z, MWD	2000 to 10^7
Solution viscosity	M_v, M_w	15000 – 10^6
Vapour-phase osmometry	M_n	up to 25000
Gel-permiation chromatography	M_n, M_w, M_v, M_z, MWD	up to 10^6