Polymer Molecular Weight and its Measurement Methods

At the end of this lecture, you should be able to:

- Understand the distribution of polymer M.wt.
- Learn the ways to present the average M.wt
- Understand the measurement methods of polymer average M.wt.
- Calculate polymer average M.wt using different formula.

Mustansiriyah University/ Materials Eng. Dept.
Dr Ahmed AYASH

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Molecular Weight:

Molecular weight of a chemical compound can be defined, simply, as the sum of the atomic weights of each of the atoms in the molecule.

Examples:

Water (H_2O) is 2 H (1g) and one O (16g) = 2*(1) + 1*(16)= 18 g/mol
Methane CH_4 is 1 C (12g) and 4 H (1g)= 1*(12) + 4 *(1) = 16 g/mole
Polyethylene $-(C_2H_4)-_{1000}$ = 2 C (12g) + 4H (1g) = 28g/mole * 1000 = 28,000 g/mole

Average Molecular Weight

Polymers are made up of many molecular weights or a distribution of chain lengths. In other other words, if one takes polyethylene as an example, this polymer may have chains of ethylene (C_2H_4) with different lengths; some longer than others.

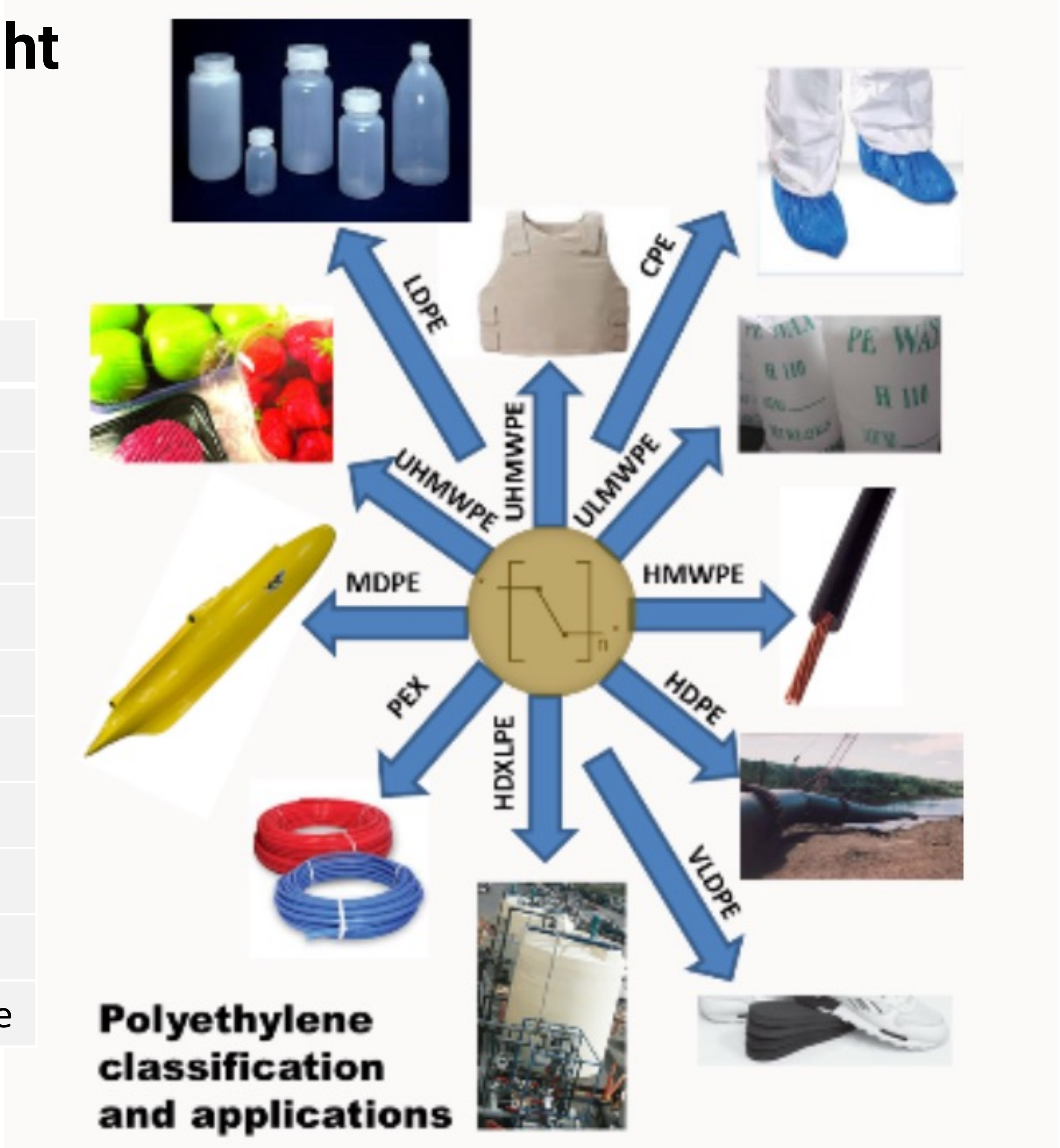
Example:

Polyethylene has some chains with **801** repeating ethylene units, some with **810** ethylene units, some with **799** repeating units, and some with **790** repeating units. The average number of repeating units or chain length is 800 repeating ethylene units [i.e. $-(C_2H_4)-_{800}$] for a molecular weight of 28*800 or 22,400 g/mole .

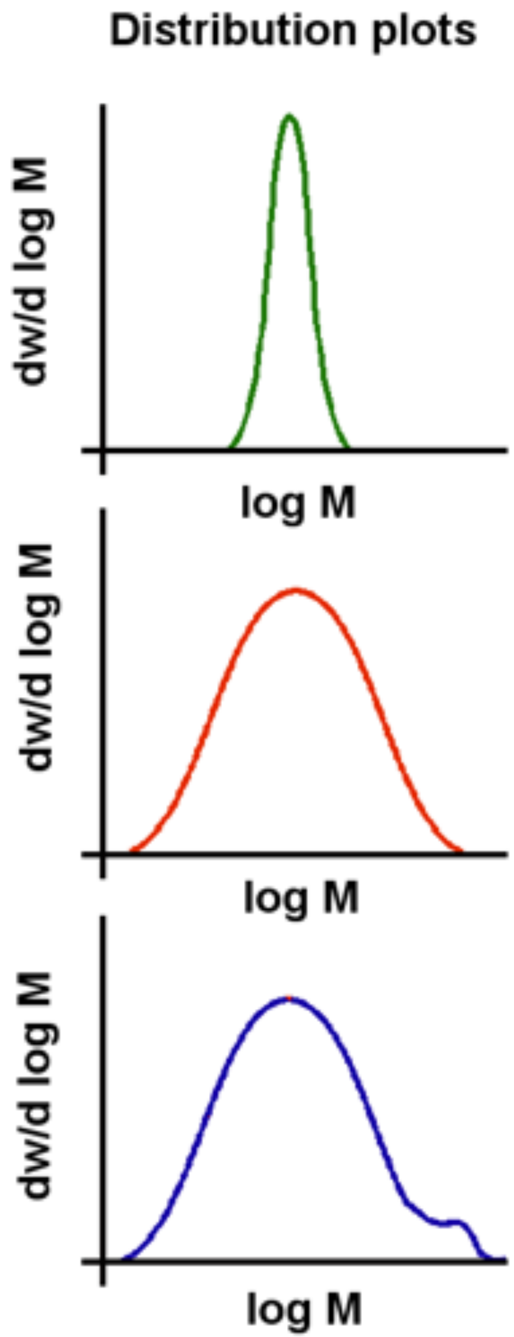
As a conclusion, a polymer does not have a certain molecular weight and it must be represented by the value of average molecular weight.

Why the change in molecular weight makes Polymers Unique ?

Abbreviation	Meaning
CPE	Chlorinated polyethylene
LDPE	Low Density Polyethylene
HDPE	Low Density Polyethylene
MDPE	Medium-density polyethylene
PEX	cross-linked polyethylene
UHMWPE	Ultra High Molecular Weight Polyethylene
HMWPE	High Molecular Weight Polyethylene
VLDPE	Very-low-density
HDXLPE	High-density cross-linked polyethylene
ULMWPE	Ultra low molecular weight polyethylene



- 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
- Describing these distributions is not easily, especially if they are complex

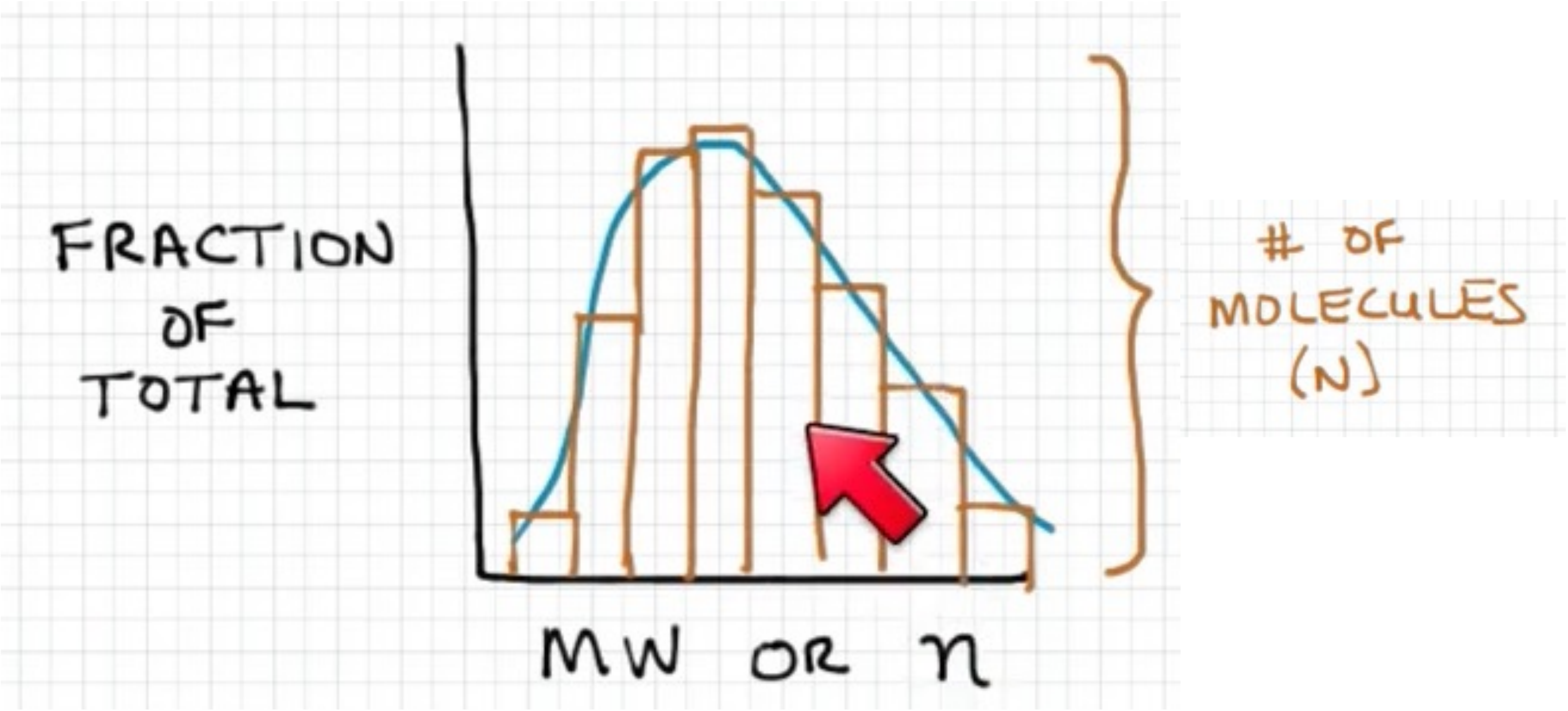


QUESTIONS FOR DISCUSSION

1) QUESTION (1): Does every polymer have a specific molecular weight? if No, explain why?

2) QUESTION (2): Does every polymer have a distribution of molecular weight? why ?

Calculation of polymer average molecular weight:



There are four ways to represent the average molecular weight:

(1) ***Number-average molecular weight (Mn)*** for a discrete distribution of molecular weights is given as:

$$\bar{M}_n = \frac{\sum_{i=1}^{N} N_i M_i}{\sum_{i=1}^{N} N_i} = \frac{\sum_{i=1}^{N} W_i}{\sum_{i=1}^{N} (W_i / M_i)}$$

where *Ni* indicates the number of moles of molecules having a molecular weight of *Mi and Wi*, is the weight of molecules with molecular weight *Mi. Thus, Wi* = *Ni Mi*.

The expression for the number-average molecular weight of a continuous distribution function is:

$$\bar{M}_n = \frac{\int_0^{\infty} NM\,dM}{\int_0^{\infty} N\,dM}.$$

(2) ***Weight-average molecular weight (Mw)*** for a discrete distribution of molecular weights is given as:

$$\bar{M}_w = \frac{\sum_{i=1}^{N} W_i M_i}{\sum_{i=1}^{N} W_i} = \frac{\sum_{i=1}^{N} N_i M_i^2}{\sum_{i=1}^{N} N_i M_i}$$

The expression for the weight-average molecular weight of a continuous distribution function is:

$$\bar{M}_w = \frac{\int_0^\infty N M^2 dM}{\int_0^\infty N M dM}.$$

(3) ***Z-average molecular weight (Mz)*** for a discrete distribution of molecular weights is given as:

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

GENERAL FORMULA

$$M = \frac{\sum N M^{\lambda+1}}{\sum N M^{\lambda}}$$

where $\lambda = 0$ gives M_n
$\lambda = 1$ gives M_w
$\lambda = 2$ gives M_z

(4) *Viscosity-average* molecular weight (*M*v) can be obtained, experimentally, from dilute-solution viscometer using Mark-Howink equation. The viscosity-average molecular weight falls between *M*n and *M*w depending upon whether the solvent is a good or poor solvent for the polymer. In the case of a good solvent, *M*v = *M*w .

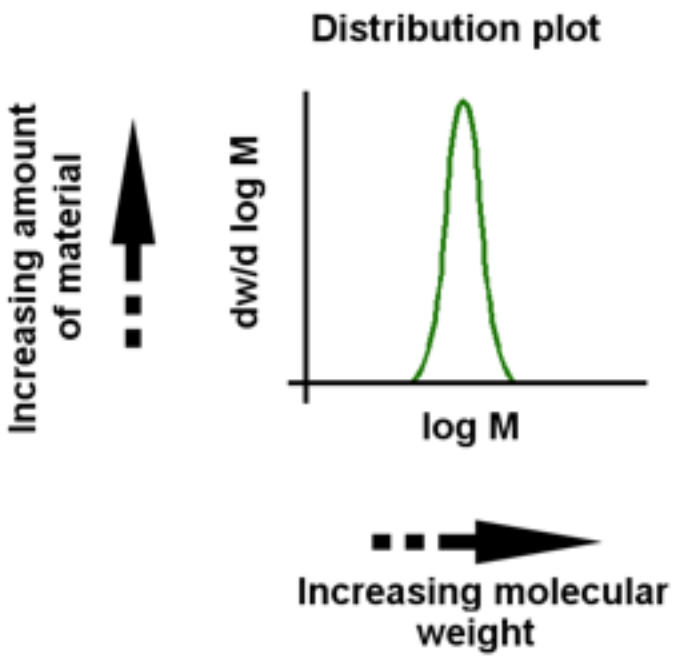
Mark-Howink-Sakurada equation:

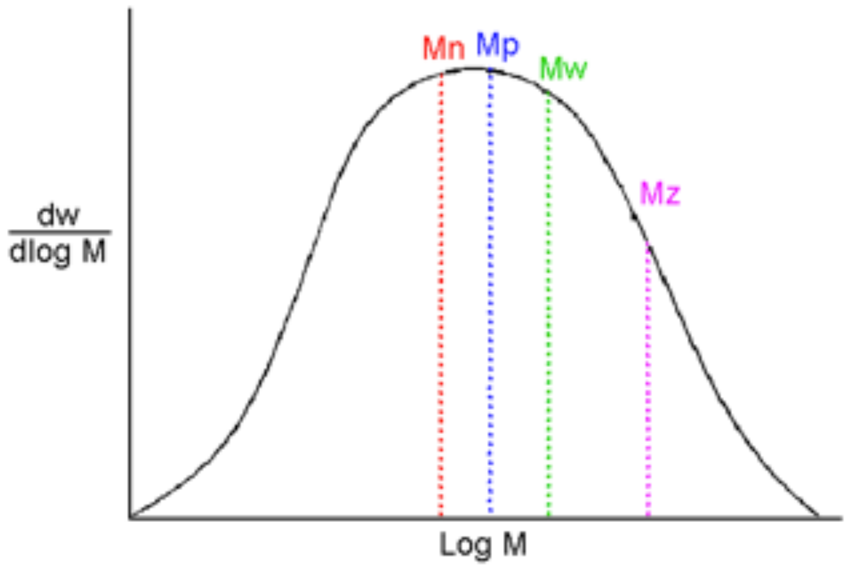
$$[\eta] = K\overline{M}^{a}$$

$[\eta]$: intrinsic viscosity
K , a : constant for specific polymer and solvent
$\overline{M}$: average molecular weight

Mark-Howink Parameters

Polymer	Solvent	Temperature, °C	Molecular Weight Range × 10^{-4}	$K^b \times 10^3$	a^b
Polystyrene (atactic)[c]	Cyclohexane	35 [d]	8-42[e]	80	0.50
	Cyclihexane	50	4-137[e]	26.9	0.599
	Benzene	25	3-61[f]	9.52	0.74
Polyethylene (low pressure)	Decalin	135	3-100[e]	67.7	0.67
Poly(vinyl chloride)	Benzyl alcohol	155.4[d]	4-35[e]	156	0.50
	Cyclohexanone	20	7-13[f]	13.7	1.0
Polybutadiene					
98% cis-1,4, 2% 1,2	Toluene	30	5-50[f]	30.5	0.725
97% trans-1,4, 3% 1,2	Toluene	30	5-16[f]	29.4	0.753
Polyacrylonitrile	DMF[g]	25	5-27[e]	16.6	0.81
	DMF	25	3-100[f]	39.2	0.75
Poly(methyl methacrylate-co-styrene)					
30-70 mol%	1-Chlorobutane	30	5-55[e]	17.6	0.67
71-29 mol%	1-Chlorobutane	30	4.18-81[e]	24.9	0.63
Poly(ethylene terephthalate)	M-Cresol	25	0.04-1.2[f]	0.77	0.95
Nylon 66	M-Cresol	25	1.4-5[f]	240	0.61





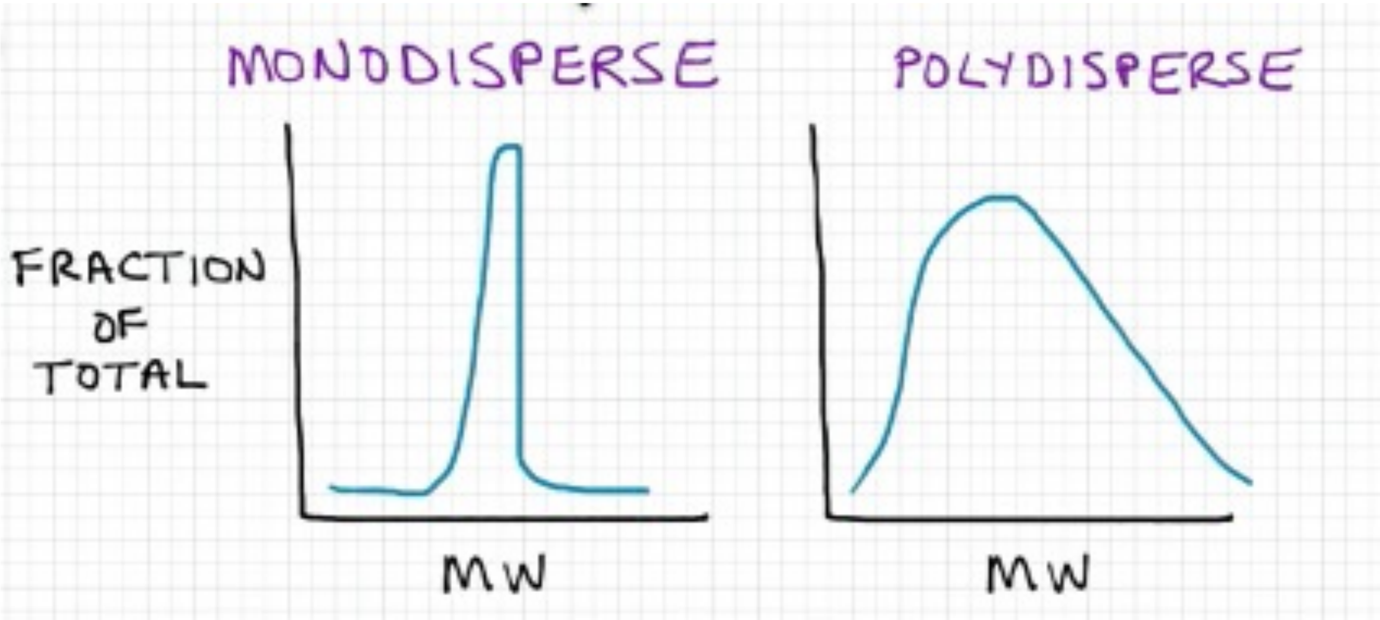
- A molecular weight distribution can be defined by a series of average values
- Except Mp, these are various moments of the average of the molecular weights of the distribution
- Mp is the molecular weight of the peak maxima
- For any polydisperse peak:

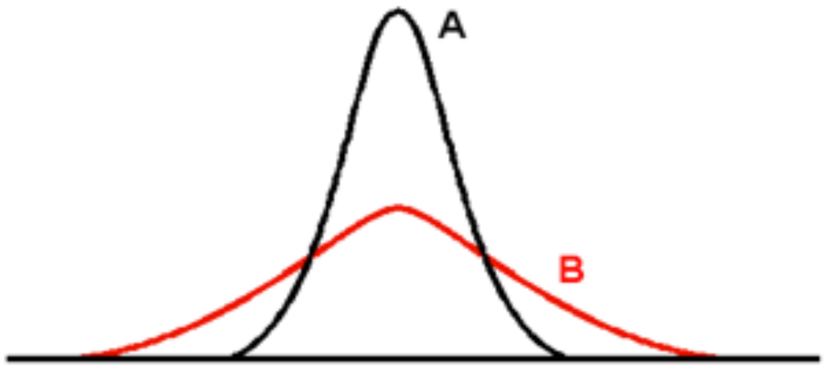
$$M_n < M_w < M_z$$

Polydispersity Index (PDI)

It is a measure of the breadth of the molecular-weight distribution and is given by the ratios of molecular-weight averages. Thus, the *polydispersity index* can be represented as follows:

$$PDI = \frac{Mw}{Mn} > 1$$; polymers having PDI = 1 are called mono-diseperse polymers





- As the broadness of the the distribution decreases the strength and toughness of the polymer increases
- However as the broadness of the the distribution decreases the polymer becomes more difficult to process

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

Degree of Polymerization (*DP*)

Degree of Polymerization (*DP*): is the number of monomeric units in a macromolecule or **polymer** or oligomer (consists of a few repeating units Or *DP* is the number of repeat units.

Based on Weight Average Mwt: $DP_w = \frac{Mw}{Mo}$,

Based on Number Average Mwt: $DP_n = \frac{Mn}{Mo}$; where M_0 is the monomer molecular weight.

Example 2.1: polystyrene has a number average molecular weight of 312 000 g/mole. What is the degree of polymerization of this polymer ? Take the molecular weight of styrene 104 g/mole.

Solution:

$$DP_n = \frac{Mn}{Mo} = \frac{312\,000}{104} = 3000 \text{ units.}$$

There are several reasons why we might want to measure polymer average molecular weight and its distribution:

1. The molecular weight and its distribution determine the viscous and elastic properties of the molten polymer. This affects the processing of the melt and also the behavior of the resulting solid material. For example, a resin suitable for extrusion must have a high viscosity at low shear rates so that the extrudate maintains its integrity. To be suitable for injection molding, however, the same resin must have a low viscosity at high shear rates so that the injection pressure not be excessive.

2. The molecular weight of a polymer can determine its applications. For example, the resin used for making polycarbonate water bottles, for example, differs significantly in molecular weight from the polycarbonate that goes into compact disks.

3. Differences in molecular weight distribution also influence the polymer properties. As a consequence, two chemically similar polymers, processed identically, that have the same molecular weight but different molecular-weight distributions may result in products that show significantly different shrinkages, tensile properties, and failure properties. For this very important reason, it is advantageous to know the molecular weight and molecular-weight distribution of the polymers used.

4. Other situations where the molecular weight and its distribution directly influence results include phase equilibrium and crystallization kinetics.

Example 2.1:

A polydisperse sample of polystyrene is prepared by mixing three *monodisperse* samples in the following proportions:

1 g 10,000 molecular weight
2 g 50,000 molecular weight
2 g 100,000 molecular weight

Using this information, calculate the number-average molecular weight, weight- average molecular weight, and PDI of the mixture.

Solution:

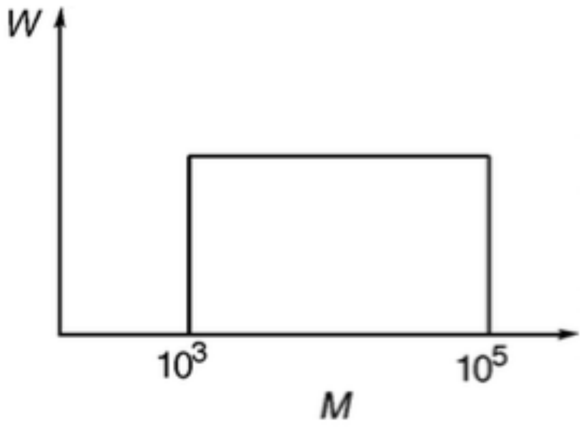
$$\bar{M}_n = \frac{\sum_{i=1}^{3} N_i M_i}{\sum_{i=1}^{3} N_i} = \frac{\sum_{i=1}^{3} W_i}{\sum_{i=1}^{3} \left(W_i / M_i\right)} = \frac{1+2+2}{\frac{1}{10,000}+\frac{2}{50,000}+\frac{2}{100,000}} = 31,250$$

$$\bar{M}_w = \frac{\sum_{i=1}^{3} N_i M_i^2}{\sum_{i=1}^{3} N_i M_i} = \frac{\sum_{i=1}^{3} W_i M_i}{\sum_{i=1}^{3} W_i} = \frac{10,000+2(50,000)+2(100,000)}{5} = 62,000$$

$$\text{PDI} = \frac{\bar{M}_w}{\bar{M}_n} = \frac{62,000}{31,250} = 1.98$$

Example 2.2:

A polymer is fractionated and is found to have the continuous molecular-weight distribution shown below as a plot of the weight, *W*, of molecules having molecular weight, *M*, versus *W*. Given this molecular-weight distribution, calculate *M*n and *M*w.



Solution:

$$\bar{M}_{\mathrm{n}} = \frac{\int_{10^3}^{10^5} dM}{\int_{10^3}^{10^5} (1/M)\, dM} = \frac{10^5 - 10^3}{\ln\left(10^5/10^3\right)} = 21{,}498$$

$$\bar{M}_{\mathrm{w}} = \frac{\int_{10^3}^{10^5} M dM}{\int_{10^3}^{10^5} dM} = \frac{\left(M^2/2\right)_{10^3}^{10^5}}{9.9\times 10^4} = 50{,}500$$