Polymer Materials

Lecture 5: Molecular weight of polymer

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Molecular weight of polymers

Short polymers : Molecular weight: 100 – 1000 g/mol

(1000 g/mol: waxes, soft resins)

Long polymers: 10,000 to several million g/mol – solids

•Long chain →increased bonding between molecules.

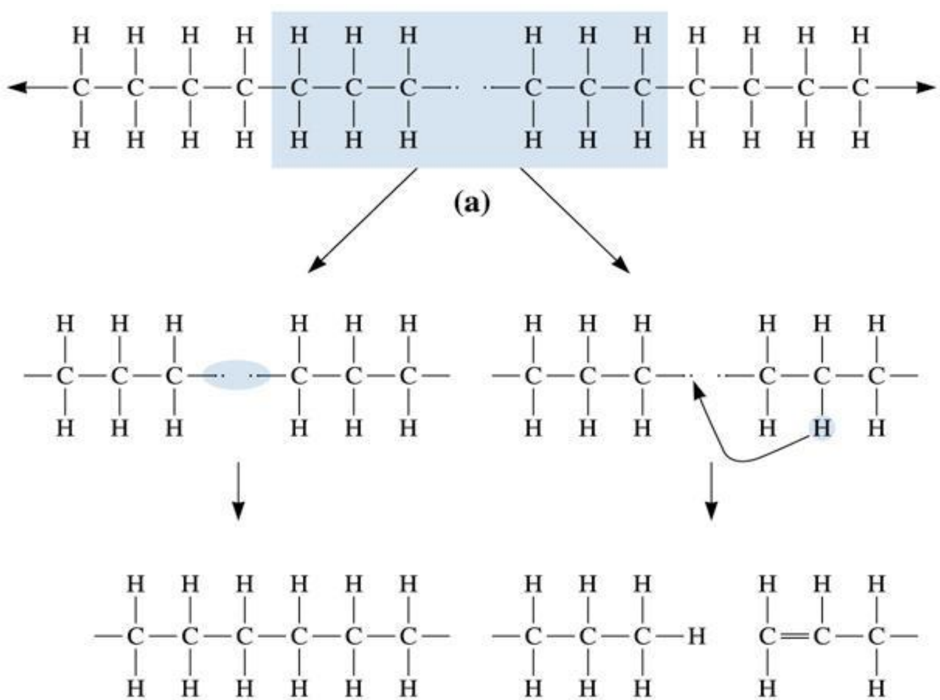
(Van der Waals or hydrogen bond) → higher mechanical properties

- Melting point increases with molecular weight

  i.e. increased intermolecular forces

Why polymer has different molecular weight?

- During termination of polymerization, it can be combination or disproportion polymers
- Different size → different molecular weight



Larger

Combination
(b)

Disproportionation
(c)

Smaller

Number and weight average molecular Weights

Definition:

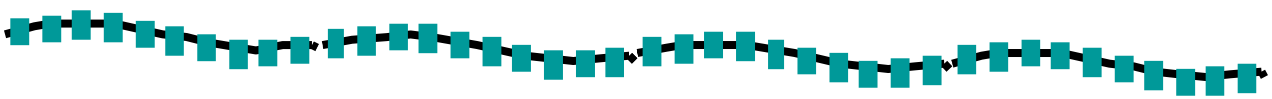
(1) Number average molecular weight (M_n) = based on **number fraction**

(2) Weight average molecular weight (M_w) = based on **weight fraction**

The length of the linear polymers can be varied largely

Different length → different molecular weight M_i.

Lower *M*



higher *M*

M_n: Number-Average Mol. Wgt.

- **The number-average molecular weight (molar mass) of a polymer containing N_i molecules of mass M_i is the arithmetic mean of the molar mass distribution:**

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

- **M_n determines the polymer's colligative properties** (boiling point, melting point changes due to solute concentration)
- **M_n may be determined directly by end-group analysis, osmometry, ebullioscopy (bp elevation), and cryoscopy (fp depression).**

M_w: Weight-Average Mol. Wgt.

- **The weight-average molecular weight (molar mass) is the sum of the products of the molar mass of each fraction multiplied by its weight fraction (w_i).**

  In terms of w_i or numbers of molecules, M_w is

$$M_w = \sum w_i M_i$$

- **M_w accounts for the** distribution **of molar mass in the polymer.**
- **M_w may be determined directly by light scattering.**

Molecular Weight Distribution

- **The molecular weight distribution, or polydispersity index, is the ratio of the weight-average molecular weight to the number-average molecular weight:**

$$\mathrm{PDI} = \frac{M_w}{M_n}$$

- **The polydispersity index of a monodisperse polymer is 1.00.**
- **The polydispersity index increases as the polymer distribution broadens.**

Number and weight average molecular Weights

The number average is always smaller than weight average.

$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

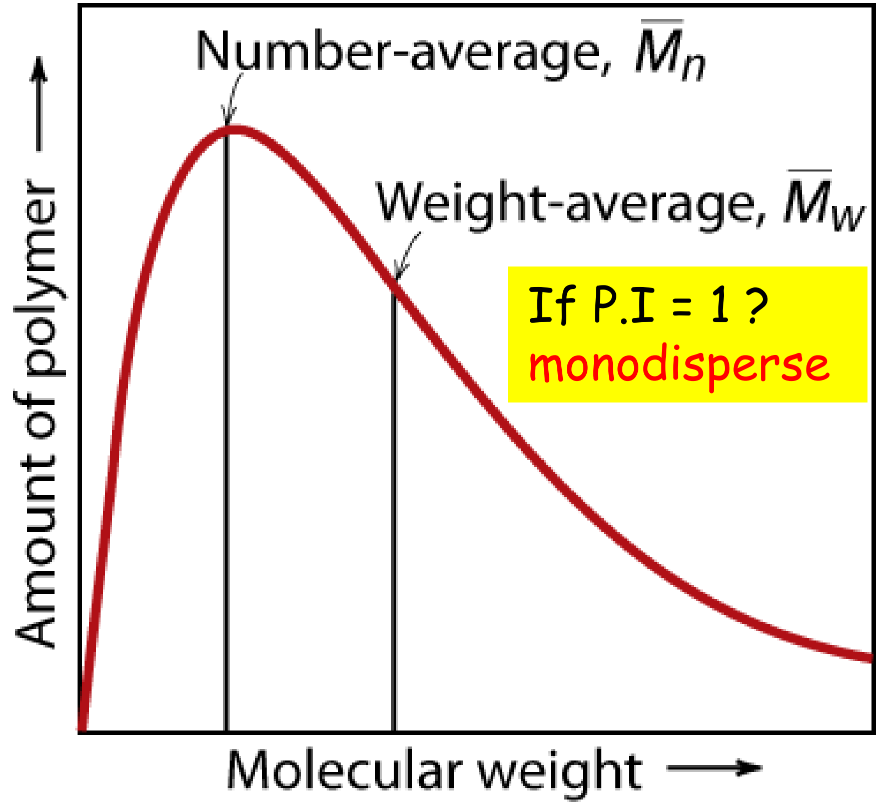
$$\overline{M}_n = \Sigma n_i M_i$$

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

M_i is the mass of chain

n_i is the number fraction

W_i is the weight fraction



Adapted from Fig. 14.4, *Callister 7e.*

Example

You have a polymer sample that contains the following molecules:

M, Da*	*N*
1,000,000	2
700,000	5
400,000	10
100,000	4
50,000	2
Total:	23

*Da = dalton, g/mol

What are M_n, M_w, and the polydispersity index?

Solution

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

$$M_n = \frac{10{,}000{,}000 \text{ Da}}{23}$$

M_n = 435,000 Da

$$M_w = \sum w_i M_i$$

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

M_w = 609,500 Da

$$PDI = \frac{M_w}{M_n}$$

$$PDI = \frac{609{,}500 \text{ Da}}{435{,}000 \text{ Da}}$$

PDI = 1.40

M, Da	*N*	*N·M*, Da	*w*	*w·M*, Da
1,000,000	2	2,000,000	0.20	200,000
700,000	5	3,500,000	0.35	245,000
400,000	10	4,000,000	0.40	160,000
100,000	4	400,000	0.04	4,000
50,000	2	100,000	0.01	500
Totals:	23	10,000,000	1.00	609,500

$$w = \frac{2{,}000{,}000}{10{,}000{,}000} = 0.2$$

Degree of polymerization (n)

How many units of monomer in a polymer?

$$\overline{M}_n = \frac{\text{total wt of polymer}}{\text{total \# of molecules}}$$

n_n=Number average degree of polymerization

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

$\overline{m}$= Monomer's molecular weight

Example 2:

- Polyvinyl chloride (PVC) sample containing main chains with different molecular weight
  - 4000 chains of molecular weights of 0 –5000 g/mol
  - 8000 chains of molecular weights of 5000 – 10,000 g/mol
  - 7000 chains of molecular weights of 10,000 – 15,000 g/mol
  - 2000 chains of molecular weights of 15,000 – 20,000 g/mol

- Determine:

(1) number average molecular weights

(2) weight average molecular weights

(3) degree of polymerization

Answer

- (1) Calculated the number average molecular weight

Number of Chain	Average weight (M_i)	Number fraction (x_i)	x_iM_i
4000	2500	0.191	477.5
8000	7500	0.381	2857.5
7000	12,500	0.333	4126.5
2000	17,500	0.095	1662.5
$\Sigma = 21{,}000$		$\Sigma = 1$	$\Sigma = 9160$

$$M_n = \Sigma x_i M_i = 9160\ g/mol$$

Answer

- (2) Calculated the weight average molecular weight

Number of Chain	Average weight (M_i)	Total weight	w_i	w_iM_i
4000	2500	10×10^6	0.0519	129.75
8000	7500	60×10^6	0.3118	2338.50
7000	12,500	87.50×10^6	0.4545	5681.25
2000	17,500	35×10^6	0.1818	3181.50
$\Sigma = 21{,}000$		$\Sigma = 192.5 \times 10^6$	$\Sigma = 1$	$\Sigma = 11{,}331$

$$M_w = \Sigma w_i M_i = 11{,}331 \text{ g/mol}$$

$$M_w > M_n$$

Answer

- (3) calculate the degree of polymerization

PVC: C_2H_3Cl

	C	H	Cl
Atomic weight (g/mol)	12.01	1.01	35.45

$$\overline{m} = 2(12.01) + 3(1.01) + 35.45$$

$$\overline{m} = 62.50 g/mol$$

$$n_n = \frac{\overline{M}_n}{\overline{m}} = 146.56 \rightarrow 146$$

M_z: Z-Average Mol. Wgt.

- The z-average molecular weight (molar mass) is

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

- M_z is especially sensitive to the presence of high-MW chains.
- M_z may be determined directly by sedimentation equilibrium (ultracentrifugation) and light scattering.

M_v: Viscosity-Average Mol. Wgt.

- **The viscosity-average molecular weight (molar mass) is :**

$$M_v = \left(\frac{\sum N_i M_i^{(1+a)}}{\sum N_i M_i} \right)^{1/a}$$

where the exponent *a* (0.5 ≤ *a* ≤ 2.0) is determined by the polymer, solvent, and temperature.

- **For typical polymers, $M_w > M_v > M_n$.**
- **$M_w = M_v$ when $a = 1$.**
- **M_v may be determined indirectly by dilute solution viscometry.**

Polymer Size and Shape

- **Most polymers are** polydisperse **— they contain more than one chain length.**
- **The average distribution of chain masses can be described in more than one way:**
  - M_n, **the number-average molecular weight**
  - M_w, **the weight-average molecular weight**
  - M_z, **the z-average molecular weight**
  - M_v, **the viscosity-average molecular weight**
- $M_z \geq M_w \geq M_v > M_n$
- **Each value is determined** certain properties **of polymer structure.**

Impact of Molecular weight on physical properties

- M_n: Brittleness
- M_w: Hardness
- M_z: Stiffness
- M_v: Molding properties