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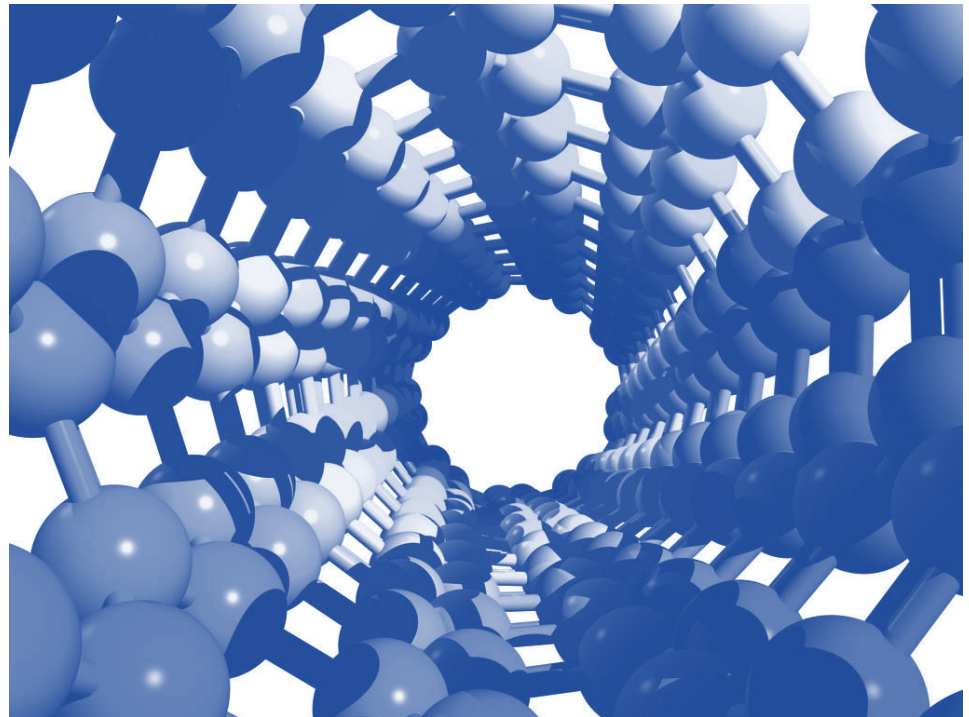
Physical Pharmacy

Lecture 8

Pharmaceutical Polymers

Hamid Alghurabi

Assistant Lecturer
in Pharmaceutics



Overview

Structure

- Definition

- Branching

- Copolymers

Molecular weight

- Polydispersity

- Number Average Molecular Weight

- Weight Average Molecular Weight

- Polydispersity Index

Pharmaceutical Applications

- Water-soluble (Hydrophilic) Polymers

- Water-insoluble (Hydrophobic) Polymers

Learning Objectives

1. Know the basic concepts of polymers, definitions, and descriptive terms.
2. Distinguish the basic principles of homogeneous and dispersion polymerizations.
3. Understand how polymer molecular weight affects its properties.
4. Know what types of polymers are generally used in the pharmaceutical area.
5. Explain why polymers are used in drug delivery applications.



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Structure

Definition

Branching

Copolymers

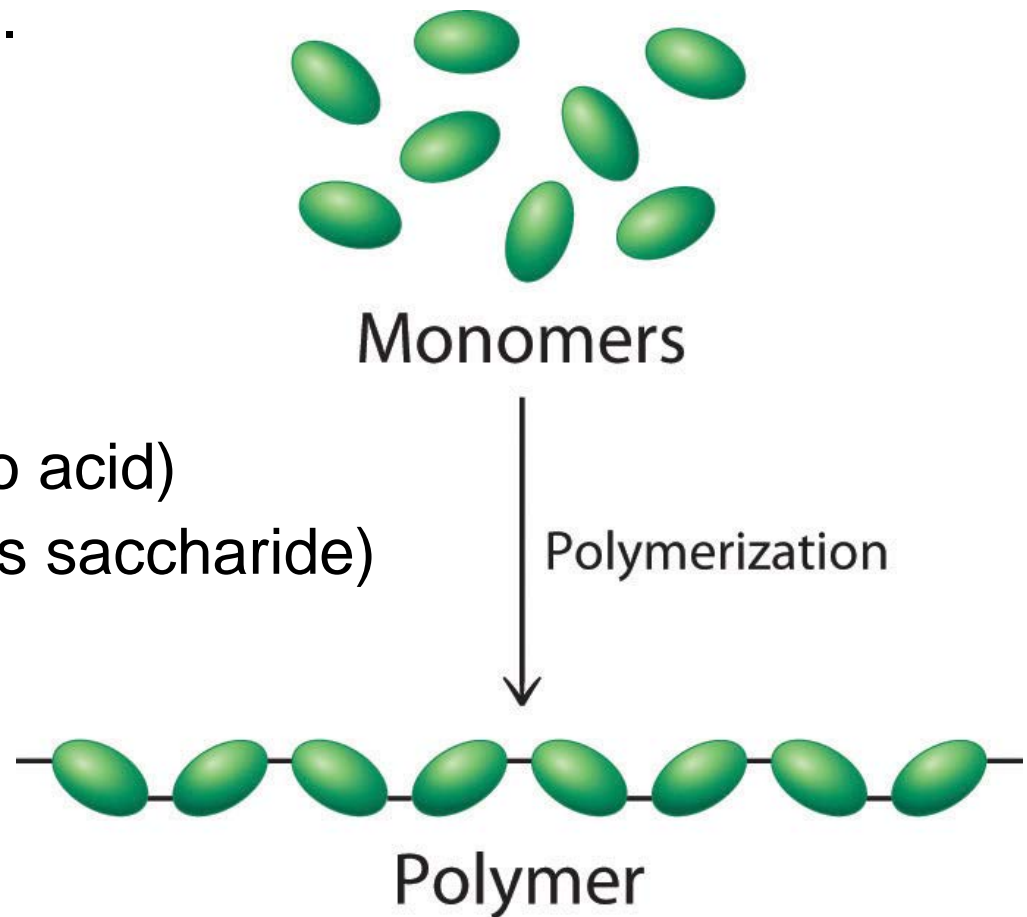
Definition

Polymers are substances of high molecular weight made up of repeating *monomer* units.

Examples:

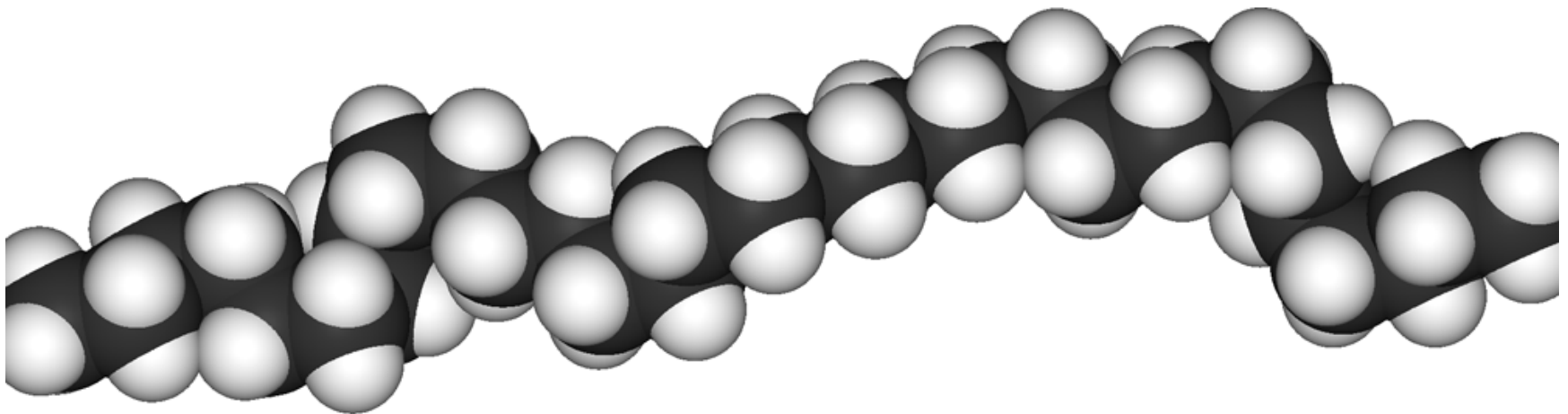
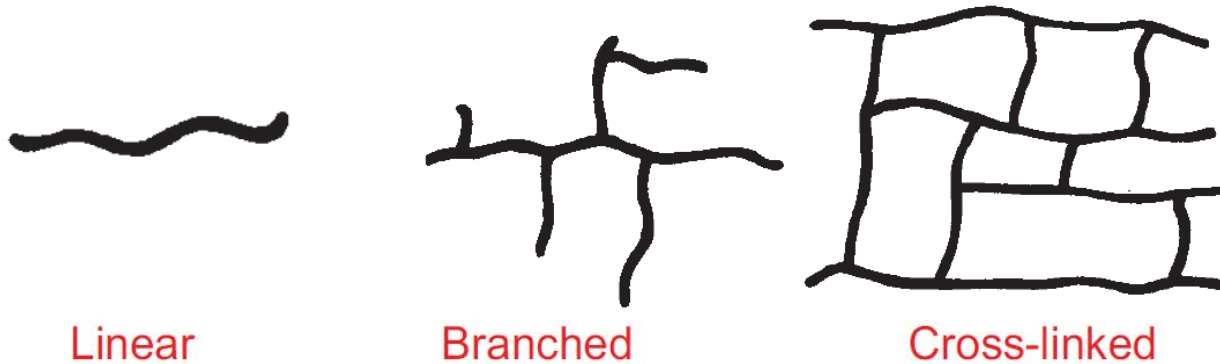
Proteins (monomer is amino acid)

Polysaccharide (monomer is saccharide)



Branching

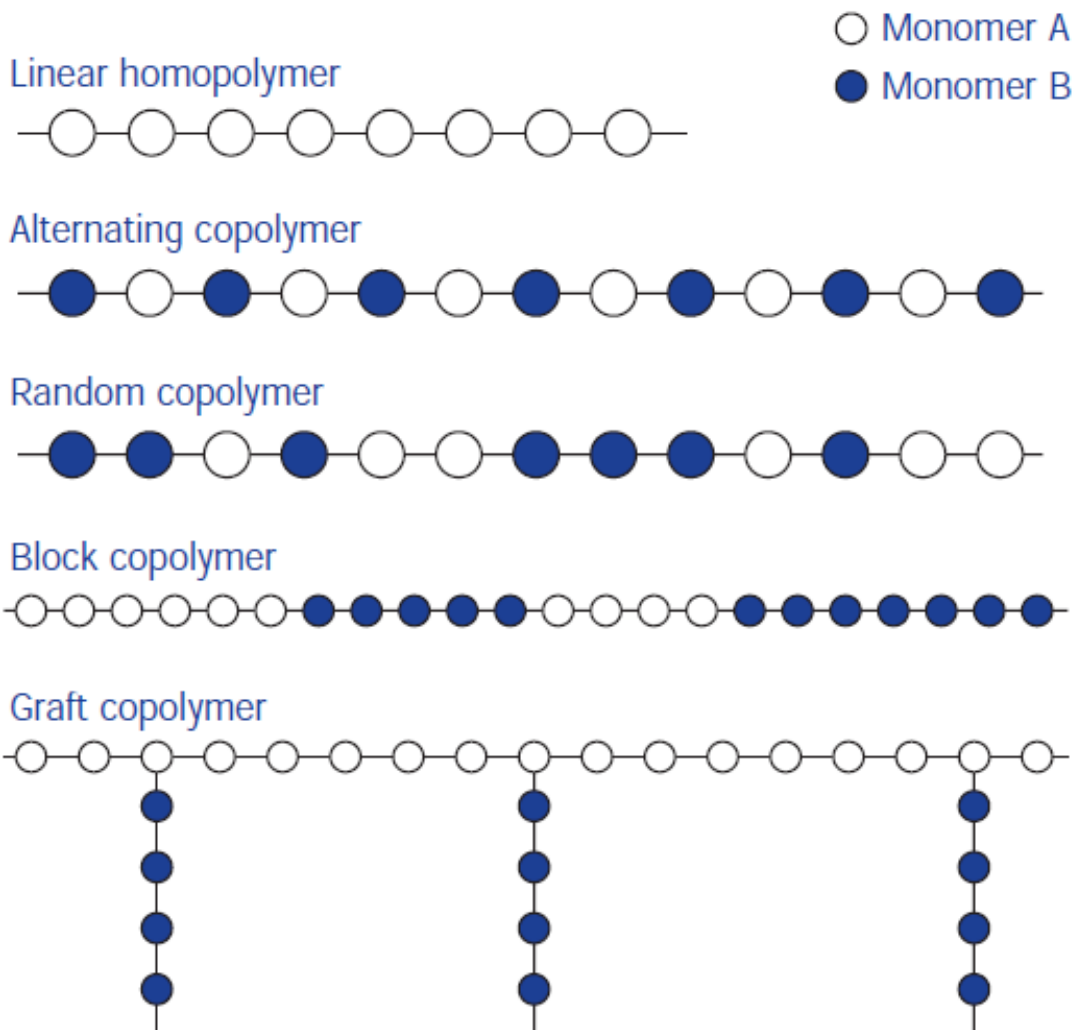
Polymer molecules may be linear or branched, or branched chains may be joined by crosslinks.



Copolymers

Polymers in which all the monomeric units are identical are referred to as *homopolymers*;

Polymers formed from more than one monomer type are called *copolymers*.



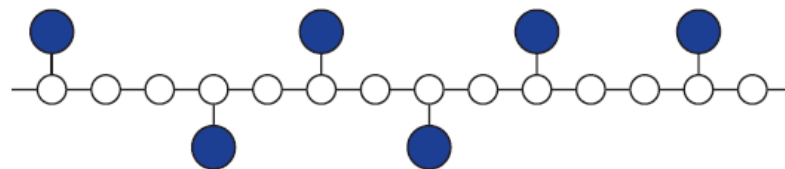
Copolymers

Graft Copolymers

Side chains or substituents (R) may be attached to the backbone of the polymer. These may be:

Atactic: a random arrangement of R groups above and below the backbone.

Random atactic copolymer



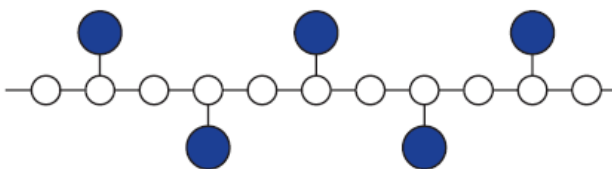
Isotactic: all R groups on the same side of the polymer backbone

Isotactic copolymer



Syndiotactic: a regular alternation of R groups above and below the backbone

Syndiotactic





Molecular Weight

Polydispersity

Number Average Molecular Weight

Weight Average Molecular Weight

Polydispersity Index

Polydispersity

Small molecules of a given pure compound all have the same molecular weight (Monodispersed)



During synthesis, polymer chains grow at different rates. The resulting polymer has a range of molecular weights (polydispersed) described by an average molecular weight and a molecular weight distribution

Depending on the experimental method of measurement, An average molecular weight is expressed by two terms:

1. **Number average molecular weight** (M_n)
2. **Weight average molecular weight** (M_w)

Number Average Molecular Weight

1. **Number average molecular weight** (M_n)

It is determined by chemical analysis or osmotic pressure measurement.

In a mixture containing $n_1, n_2, n_3 \dots$ moles of polymer with molecular weights $M_1, M_2, M_3 \dots$, respectively, the number average molecular weight is calculated by:

$$M_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots} = \frac{\sum n_i M_i}{\sum n_i}$$



Weight Average Molecular Weight

2. **Weight average molecular weight** (M_w):

It is determined by light scattering methods

In a mixture containing $m_1, m_2, m_3 \dots$ masses of polymer with molecular weights $M_1, M_2, M_3 \dots$, respectively, The weight average molecular weight is calculated by:

$$M_w = \frac{m_1 M_1 + m_2 M_2 + m_3 M_3 + \dots}{m_1 + m_2 + m_3 + \dots} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

$m_i = n_i M_i$. Thus, the molecular weight appears as the square in the numerator of the equation for M_w



Polydispersity Index

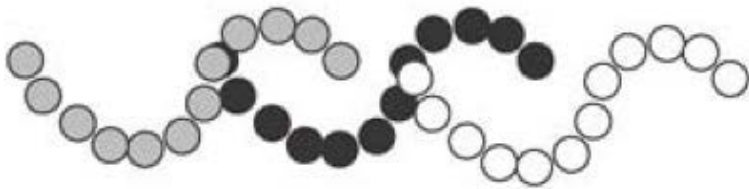
For polydispersed polymers, the weight average molecular weight (M_w) is always larger than the number average molecular weight (M_n) because M is squared, thus:

If $M_w > M_n$ (polydispersed),

If $M_w = M_n$ (monodispersed).

The ratio M_w/M_n is called Polydispersity Index, expresses the degree of polydispersity.

Monodispersed
Polydispersity = 1
 $M_w = M_n$



Polydispersed
Polydispersity $\gg 1$
 $M_w \gg M_n$



Polydispersity Index

Example

Calculate each of number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index for a polymer composed of two components:

| Component | n | M |
|-----------|---------|------|
| | (moles) | (Da) |
| 1 | 0.04 | 1000 |
| 2 | 0.06 | 2000 |



Polydispersity Index

Example

**Number average
molecular weight (M_n):**

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

Polymer comprises:

Component A (0.04 moles; M_r 1000Da)

Component B (0.06 moles; M_r 2000Da)

$$M_n = \frac{(0.04 \times 1000) + (0.06 \times 2000)}{(0.04 + 0.06)}$$

$$M_n = 1600 \text{ Da}$$

**Weight average
molecular weight (M_w):**

$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

Polymer comprises:

Component A (0.04 moles; M_r 1000Da)

Component B (0.06 moles; M_r 2000Da)

$$M_w = \frac{(0.04 \times 1000^2) + (0.06 \times 2000^2)}{(0.04 \times 1000) + (0.06 \times 2000)}$$

$$M_w = 1750 \text{ Da}$$

$$\text{Polydispersity index} = 1750/1600 = 1.09$$





Pharmaceutical Applications

Water-soluble (Hydrophilic) Polymers

Water-insoluble (Hydrophobic) Polymers

Water-soluble (Hydrophilic) Polymers

Water-soluble polymers are widely used in pharmacy as:

1. Suspending and emulsifying agents.
2. Binding agents in tablets,
3. Thickeners of liquid dosage forms
4. Film coating agents in tablets.

Examples

1. Carboxypolymethylene (e.g. Carbopol)
2. Some Cellulose derivatives (e.g. methylcellulose)
3. Natural gums (e.g. tragacanth gum)



Water-insoluble (Hydrophobic) Polymers

Water-insoluble polymers are mainly used in:

1. Packaging material and tubing,
2. Fabrication of membranes, matrices and films (to control release rate of drugs from their formulation).

Examples

1. Some Cellulose derivatives (e.g. ethyl cellulose)
2. Polymers of lactic and glycolic acid (e.g. PLGA)



References

- Attwood, D. & Florence, A. T. 2008. *Physical pharmacy*, London. Chicago, Pharmaceutical Press.
- Sinko, P. J. M. A. N. 2006. *Martin's physical pharmacy and pharmaceutical sciences: physical chemical and biopharmaceutical principles in the pharmaceutical sciences*, Philadelphia, Lippincott Williams & Wilkins.

