Class: MPhil (Pharmaceutics)

Semester: First (Spring 2020)

Course Name: Advanced Pharmaceutics-I

Course Code: PHM-701

Topic No. 1.

POLYMERS AND ITS CLASSIFICATIONSS

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Introduction

Definition

“Polymers are defined as the class of natural or synthetic chemicals that are characterized by having repetitive structural units”

What are polymers?

Polymer is Greek word derived from poly-, "many" + -mer, "parts “. A polymer is a large molecule made up of many small repeating units

Examples

- Polyethylene (ethylene +ethylene +….) n=4000
- Polypropylene
- PVC
- PVP etc.

IUPAC Definition

A polymer is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional repeating units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition of oneor a few of the constitutional repeating units.”

Common Polymers

A polymer is a substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (Constitutional repeating units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition of one or a few of the constitutional repeating units.

Terminologies

1. **MONOMER:**

A monomer is a small molecule that combines with other molecules of same or different types to form polymer.

2. **POLYMERIZATION:**

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain or network

3. **DEGREE OF POLYMERIZATION:**

The number of repeating units (n) in the chain (polymer) so formed is called the ‘’degree of polymerization’’. Denoted by “n”

DP is used to calculate the average molecular weight of polyme.

History of polymer:

1. Science of polymer chemistry began in Early 20th century.
2. The term polymer was first coined by Jons Jacob Berzelius1883
3. Preparation of methyl cellulose Suida 1905
4. Preparation of Sodium Carboxymethyl cellulose 1918
5. Modern concept of polymers was introduced by Hermann Staudinger 1920

Characteristics Of Ideal Polymer

1. Should be inert and compatible with the environment.
2. Should be non-toxic.
3. Should be easily administered.
4. Should be biocompatible and biodegradable.
5. Degradation products should be non-toxic &should not create inflammatory response.
6. Degradation should occur within reasonable time as required by the application.
7. S h o u l d be easy and inexpensive to fabricate.
8. S h o u l d have good mechanical strength.

Properties of polymers

- Optical properties Monomers and repeating units
- Mechanical properties Polymer morphology
- Transport properties Microstructure
- Chemical properties Phase behavior

Monomers and repeating units

- The nature and properties of polymers depends on the type and arrangement of monomers and repeating units
- Polymers may be made up of same or different monomers. Some biological polymers contain different but structurally related monomers

Polymer morphology

Polymer morphology includes two parameters

1. Crystallinity
2. Chain conformation

1. Crystallinity

The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers

2. Chain conformation

This property explains the space occupied by the polymer chain and the geometric changes in structure. The space occupied by the polymer chain is describe as a function of "radius of gyration"

- **Microstructure**

The microstructure of a polymer relates to the physical arrangement of monomer residues along the backbone of the chain. These are the elements of polymer structure that require the breaking of a covalent bond in order to change. This Structure has a strong influence on the other properties of a polymer.

For example:

Two samples of natural rubber may exhibit different durability, even though their molecules comprise the same monomers.

- **Phase behavior**

Phase behavior basically depends on the following properties

1. Melting point of polymer
2. Glass transition temperature
3. Mixing behavior

1. Melting point of polymer

- The term melting point, in case of polymers, suggests not a solid–liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase, abbreviated as Tm.
- But this term is more properly called the crystalline melting temperature. Among synthetic polymers, crystalline melting is only discussed with regards to thermoplastics, as thermosetting polymers will decompose at high temperatures rather than melt.

2. Glass transition temperature

- Glass transition temperature (Tg) is a temperature, at which amorphous polymers undergo a transition from a rubbery, viscous liquid, to a brittle, glassy amorphous solid on cooling.
- The glass transition temperature may be engineered by altering the degree of branching or crosslinking in the polymer. Or by the addition of plasticizer

- **Mixing behavior**

- Polymeric mixtures are far less miscible than mixtures of small molecule materials because of their large size.
- In general polymer swells and occupies more volume in miscible or good solvent while in immiscible solvent polymer chain contracts.

➢ **Tacticity**

Tacticity describes the relative stereochemistry of chiral centers in neighboring structural units within a macromolecule.

On this basis polymers may be

A. A t a c t i c
B. I s o t a c t i c
C. Syndiotactic

A. Atactic

Type of arrangement in which characteristic groups are arranged on the same side of the main chain

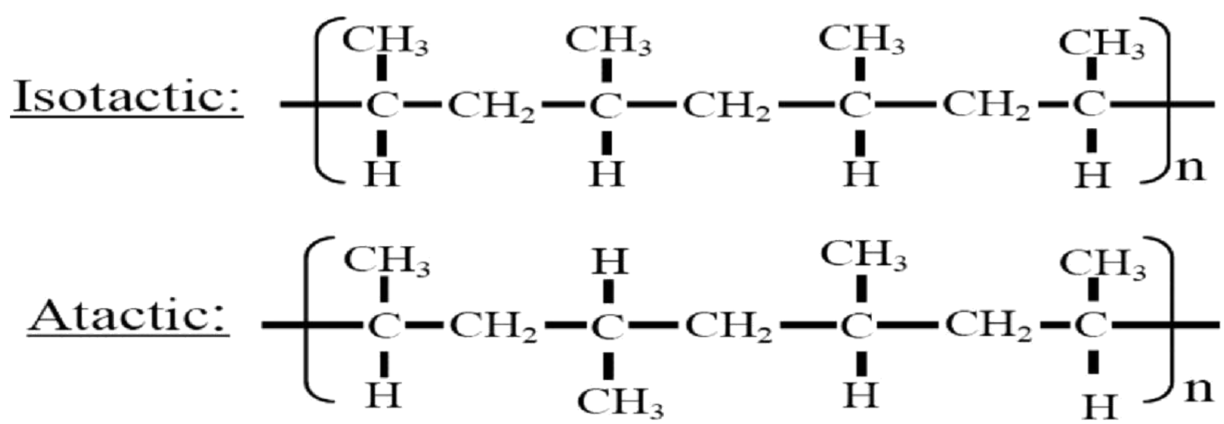
B. Isotactic

The type of arrangement in which side groups are attached in an irregular fashion It has more elasticity.

E.g. poly (1, 2-gycerol carbonate)

C. Syndiotactic

Type of arrangement in which side groups are attached in an alternate fashion



A. Chemical properties

The attractive forces between polymer chains play a large part in determining polymer's properties. Because polymer chains are so long, these interchain forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymer can lend the polymer to ionic bonding or hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength and higher crystalline melting points.

Transport properties

Transport properties such as diffusivity relate to how matrix. These are very important in many applications of rapidly molecules move through the polymer polymers for films and membranes

B. Mechanical properties

The bulk properties of a polymer are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale. These properties include

- Tensile strength
- Young's modulus of elasticity

Classification of polymers

A. Source

1. Natural

- Polymers found in nature mostly obtained from plants and animal sources, are called natural polymers. A few examples are:

a) Polysaccharides e.g. starch and cellulose etc.
b) Proteins e.g. wool, natural silk and leather etc.
c) Nucleic Acids e.g. RNA & DNA etc.
d) Natural Rubber.

2. Semi-synthetic

- These are mostly derived from naturally occurring polymers by carrying out chemical modifications. For example, H2SO4
- Cellulose + (CH3CO) 2O → Cellulose diacetate
- (Acetic anhydride)
- Cellulose diacetate is used in making threads, films, glasses, etc.

Synthetic

- The polymers which are prepared in the laboratory are referred to as synthetic polymers. Some examples of the synthetic polymers are Polyethylene

Polystyrene

- PTFE synthetic rubber
- Nylon, PVC etc.

<u>Composition</u>

a) **Co-polymer**

Co-polymers are the polymers composed of two different types of repeating units or monomers in their molecule.

Dimethyl tetraphthalate+ ethylene glycol → polyester

<u>Types of co-polymer</u>

A. **R a n d o m Copolymers:**

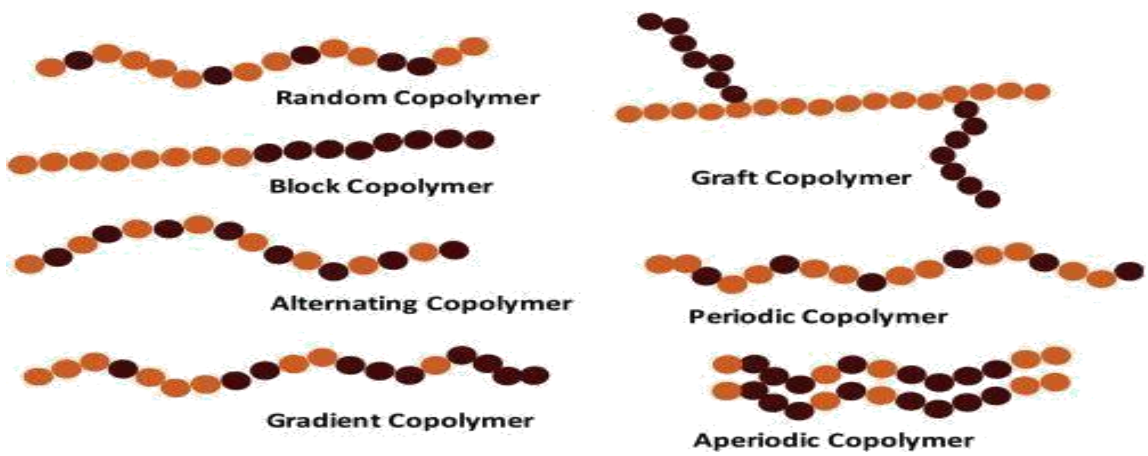
Polymers in which there is a random arrangements of monomers the two monomers may not follow any order.

B. **G r a f t Copolymers:**

Main polymer chain is of one type of monomer while Branches are made up of different monomer.

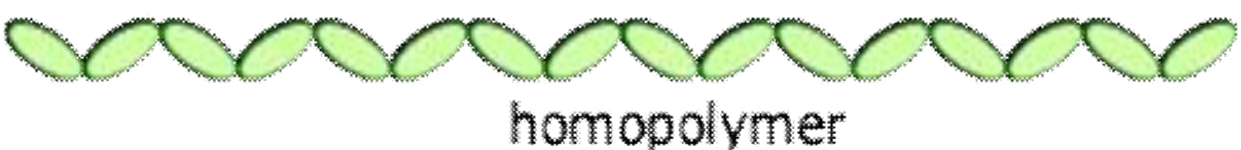
C. **B l o c k Copolymer:**

Same type of monomers grouped together



b) **<u>Homo polymer</u>**

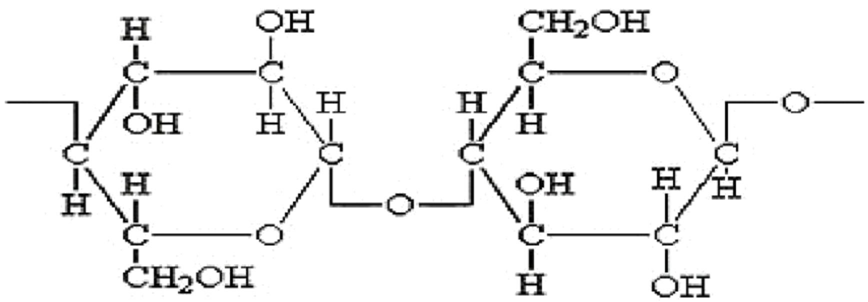
Homo-polymers are the polymers composed of only one type of monomers. E.g. polyethylene, polypropylene and polystyrene etc.



<u>Backbone of chain</u>

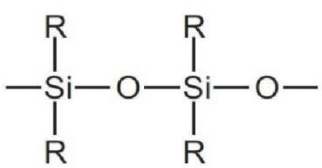
a) **<u>Organic</u>**

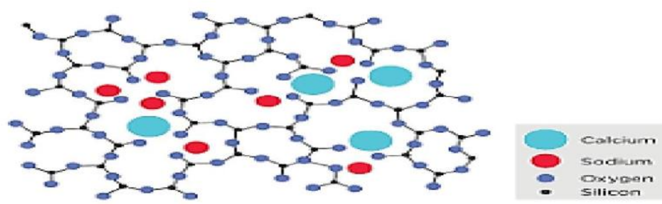
A polymer whose backbone chain is essentially made of carbon atoms ids termed as organic polymer e.g. cellulose, proteins etc



b) Inorganic

A polymer having backbone chain made up of atoms other than carbon is termed as inorganic polymer e.g. silicone, glass etc.





Structure

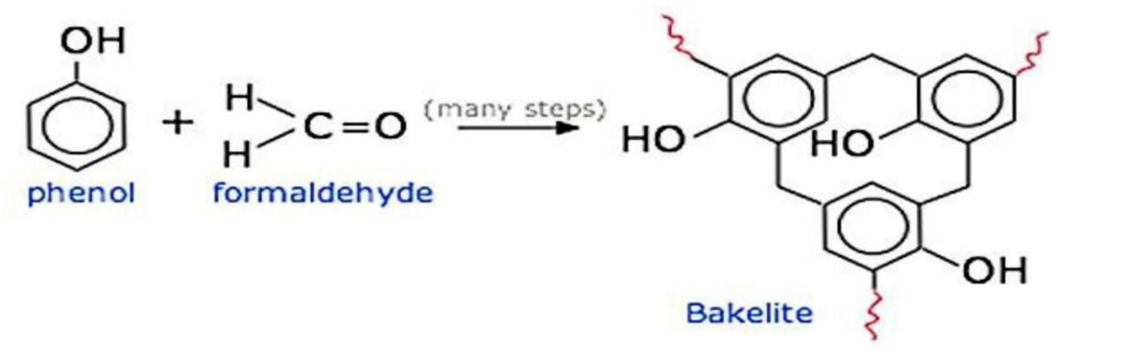
a) Linear

In these polymers, monomers are attached in a straight line and form long chains. They have no side chains. Molecules are closely packed and have high density e.g. Nylon and HDPE etc.

Nylon 6

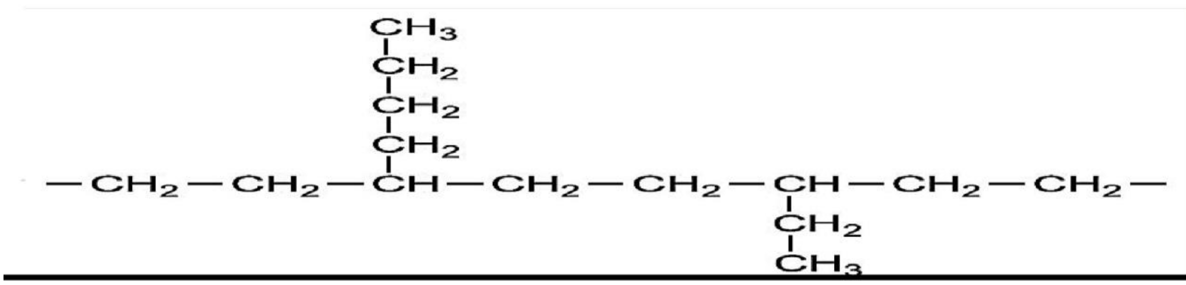
b) Cross-linked

In this type of polymer, monomeric_units are attached in 3-D network. They are hard, rigid and brittle due to their network structure. e.g. Bakelite, melamine and vulcanized rubber etc.



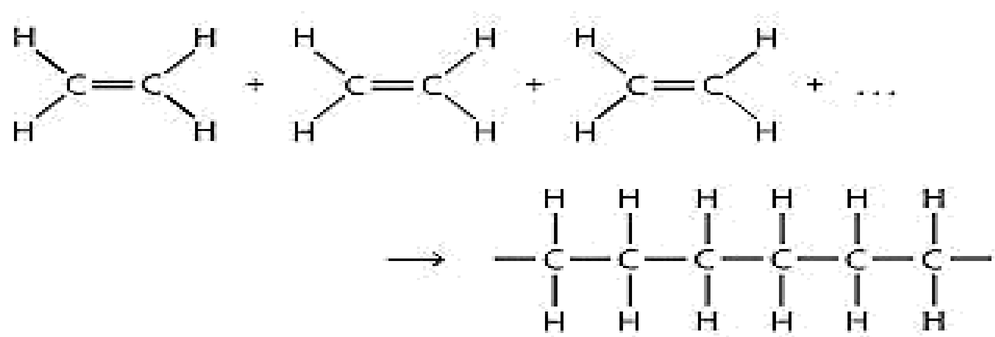
c) **Branched**

They have straight chains along with different side chains. Molecules are irregularly packed hence they have low density e.g. LDPE



Mode of polymerization

Polymerization is a process of reacting monomer molecules together in a chemical reaction to form polymer chains or three-dimensional networks

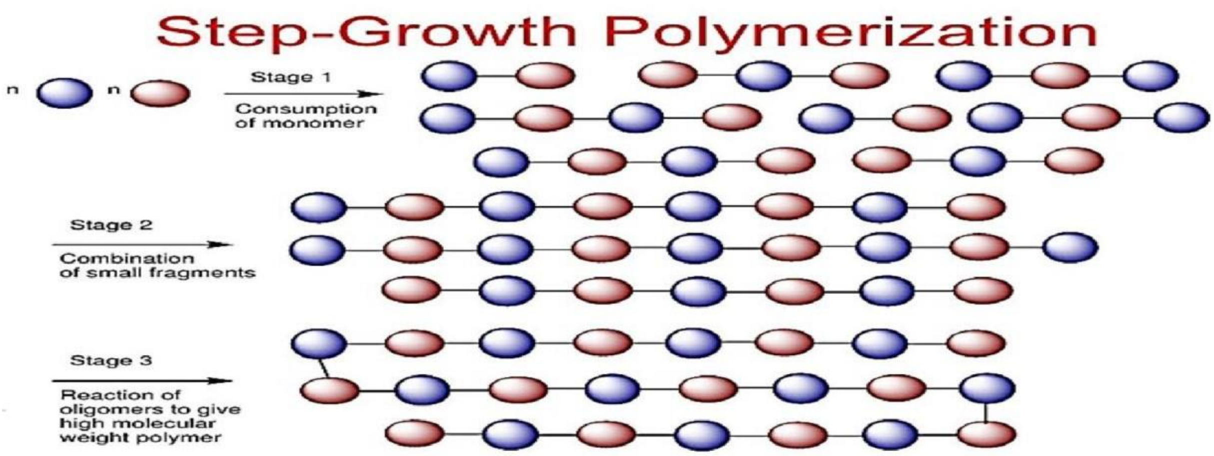


A. **Addition**

- These types of polymers are formed by the repeated addition of monomer molecules.
- In this reaction small particles are not eliminated like water, HCl, NH3 etc.
- In this type of polymers monomers are unsaturated hydrocarbons.
- Ex: Vinyl chloride to Poly vinyl chloride.

B. **Condensation**

- These types of polymers are formed_by repeated Condensation between two different bi-functional or tri-functional monomeric units.
- In this reaction small particles are eliminated like water, HCl, NH3 etc.
- Ex: Nylon – 66 is formed by condensation of Hexa-methylene diamine and adipic acid.



Molecular forces

A. **Fibers**

- These polymers have strong inter-molecules forces between the chains. These forces are either hydrogen bonds or dipole – dipole interaction. Because of these strong forces, the chains are closely packed giving high tensile strength and less elasticity.
- Therefore, these polymers have high melting points.
- Ex: nylon 66, Dacron, silk etc.

B. **Thermo-plastics**

- The polymers in which inter-molecules forces are between the elastomer polymers and fiber polymers.
- T h e s e polymers are softened when it heated and hardened when it cooled.
- T h e s e polymers do not have any cross bond.
- T h e s e polymers can easily convert into any shape by heating.
- Ex: Polyethylene, Polystyrene, PVC etc.

C. **Thermo-setting**

- These polymers are made by low molecular mass semi fluid substance.
- These polymers cannot convert in other shape by heating.

- On heating, they become hard and in-fusible because these polymers have cross bond.
- Ex: Bakelite, Melamine formaldehyde, Resin etc.

Elastomers

- The polymers that have elastic character like rubber are called elastomers. In elastomers, the polymer chains are held together by weak inter-molecular forces. Because of these weak forces, the polymers can be easily stretched by applying small stress and regain their original shape when the stress is removed.
- Ex: Vulcanized rubber
    - In this rubber polymers chains are held by Sulphur cross bond.
    - Cause of these cross bond it can be stretched by small stress.

Bio stability

A. Bio-degradable

- Those polymers which get decompose by microorganism or by enzymatic action under aerobic or anaerobic conditions. They decompose after their intended purpose. As a result of their decomposition, natural byproducts such as gases, water, biomass and inorganic salt are produced.
- Examples
    - Poly hydroxyl butyrate
    - Poly lactic acid
    - Poly glycolic acid etc.

B. Non-biodegradable

- They consist of long chain of carbon and hydrogen atom. The interaction bonding is adamant that makes it difficult for microbes to break the bond and digest them. Decomposition of these polymers requires long period of time.
- Examples
    - Polyethylene
    - Teflon etc.

Applications of Polymers in Pharmaceutical Dosage Form

Polymers have wide ranges of applications in different areas.

1. In pharmaceutical industry
2. In Bio-medical system

1. In pharmaceutical industry:

i. Polymers as rheology modifiers:

They are used as viscosity modifiers, increase flow properties, increase solubility of a drug product in a given medium whether organic or in organic. For example carboxymethyl cellulose, hydroxypropyl methyl cellulose, Solubilize the drug product in aqueous solvents.

ii. **In immediate release dosage forms**

Polymers are used in immediate release dosage forms like tablets, capsule and film coated tablets.

1. **Tablets:**

- Polymers are used as binder
  e.g. HPMC.
- Polymers are also used as disintegrantes e.g. starch and cellulose which swell on contact with water and result in tablet bursting. It is also used as diluents
  e.g. MCC (micro crystalline cellulose)

2. **Capsules:**

- Polymers are used as diluents and fillers in capsules to ensure proper fill of capsules and in making capsule shells. Polymers are used as plasticizers for controlling release rate of capsules
  e.g.
  gelatin
  shellac

3. **Disperse systems:**

- Disperse system is prone to physical instability like segregation and caking leading to inaccurate dosing so polymers are used to enhance their stability. Different natural hydrophilic polymers are used for this purpose e.g. alginates, carrageenan and xanthan gum etc. Various synthetic polymers including PVP, PVA and cellulose ethers are used for this purpose also.
- As suspending agent in suspensions.
- As emulsifying agent in emulsions.
  e.g.
  Gum acacia
  Gum Arabica

iii. **In controlled release dosage forms:**

a) Extended release dosage form:

- Therapeutic effect of the drugs having shorter half-life can be enhanced Prolong the time that systemic drug levels are within the therapeutic range
- Examples
- ➢ Ammonium methacrylate copolymers i-e Eudragit RS & RL.
- ➢ Eudragit RL is more permeable to water as compared to RS
- ➢ Cellulose derivatives i.e. ethyl cellulose, cellulose acetate.
- ➢ Polyvinyl derivatives i.e. polyvinyl acetate

b) **Gastro retentive dosage forms.**

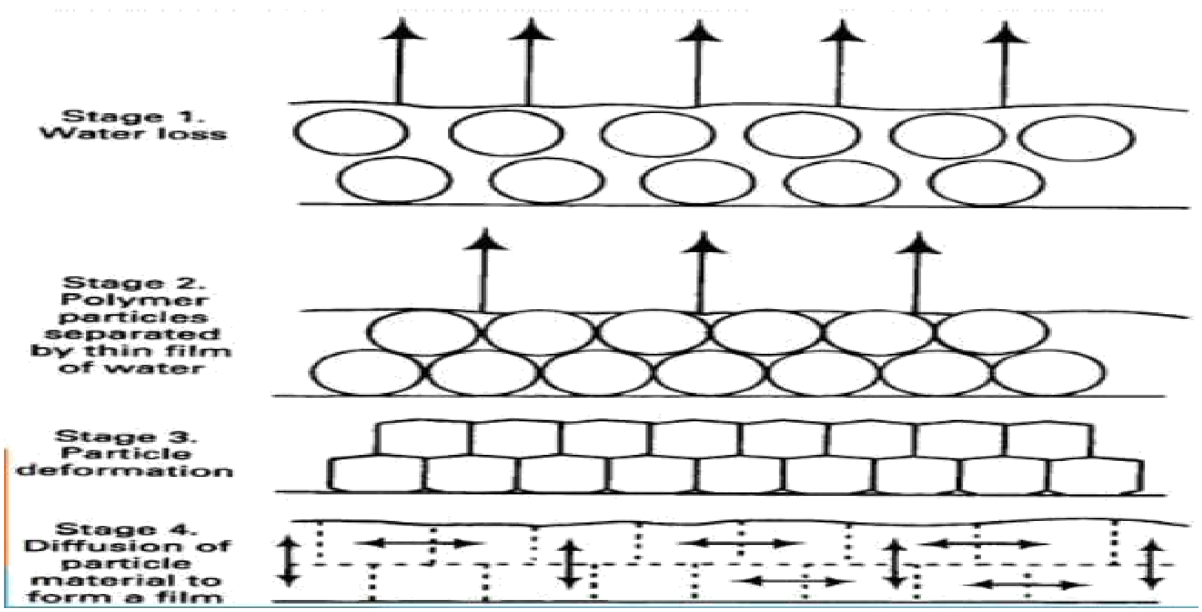
- For gastro retention, mucoadhesives and low density polymers are used which adhere to mucus lining and remaining in stomach for longer periods.
- E.g. HPMC etc.

c) Colon Specific tablets

- Polymers are used in colon specific tablets.
- E.g. pectin

d) In Film coated tablets:

- Coating tablets with a thin polymeric film is commonly performed to modify drug release, mask the taste of therapeutic agents, to enhance the stability of the drug within gastrointestinal fluids.



Three classes of polymers are used as coatings for solid dosage forms, namely:

1. Water soluble polymers, (e.g., MC, HEC and HPMC)
2. Water insoluble polymers such as EC, which are used mainly for controlled drug delivery.
3. Polymers used as enteric coating materials that are soluble above a certain pH, such as HPMC, phthalate, cellulose acetate phthalate, or those that dissolve following enzymatic degradation.

e) Taste Masking:

- Polymers are used in taste masking of bitter taste drugs i.e. Caffeine, Ondansetron.
- For example

    Eudragit,

    Chitosan etc.

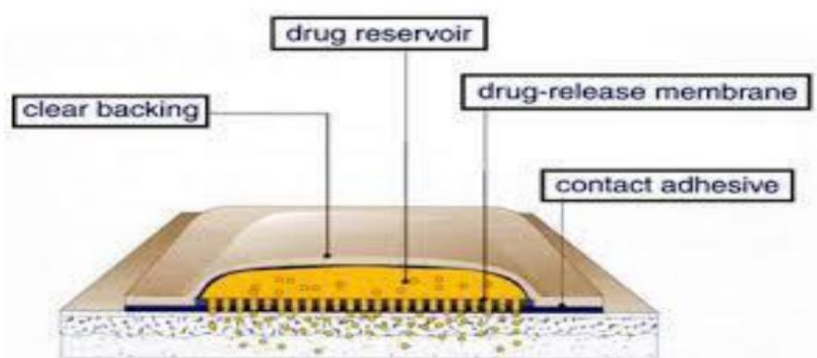
In Gels:

- Cross-linked polymers are used as gelling agents that are biocompatible and hydrophilic in nature so referred as hydrogels. These are used drug delivery system.
- For example:
  - poly(hydroxyethyl methacrylate),
  - poly(meth acrylic acid) and
  - poly(acrylamide).

4. **In tissue engineering:**
   - Gelatin is used for trachea and bone engineering

5. **Polymer-drug conjugates:**
   - It is used for controlled release and improved targeting of drug to a particular site.
   - E.g. HPMA-doxorubicin

6. **Transdermal Drug Delivery Systems:**
   - Polymers are used to make protective layer of transdermal patches or sometimes drug in incorporated in polymer matrix. Some polymers like acrylates and silicones are used as adhesives in transdermal patches. E.g. dimethyl silicon, is used in Nicotine patches



7. **Bio degradable system:**
   Polymers are used in Bio-degradable system.
   e.g. poly lactide co glycolic acid

8. **Hydrogels:**
   Polymers are also used in hydro gels
   e.g. HPMC

2. **Bio-medical Application of Polymers:**

1. **Treatment of Liver Metastasis:**
   Polyalkylcyanoacrylate Nano spheres loaded with doxorubicin.

2. **Intracellular Infections:**
   Polyisohexylcyanoacrylate Nano spheres in capsulation ampicillin have 120 times increased efficacy in treating Salmonella typhimurium infection in mice.

3. **In the Treatment of Arthritis:**
   Micelle formation of copolymer of PEG and poly (L-amino acids) by entrapping indomethacin.

4. **In Treatment of Breast Cancer:**
   PEG and poly (D, L- lactic acid) incorporating paclitaxel have increased solubility as well as reduced toxicity.

5. **In Gene Therapy:**
   Polyethylenimine anticancer gene formulation are able to achieve tumor regression through a combination of gene transfer and anti-proliferative activity, but is not yet clinically approved.

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