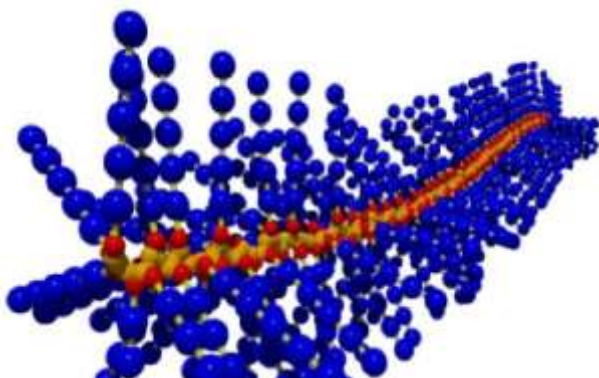
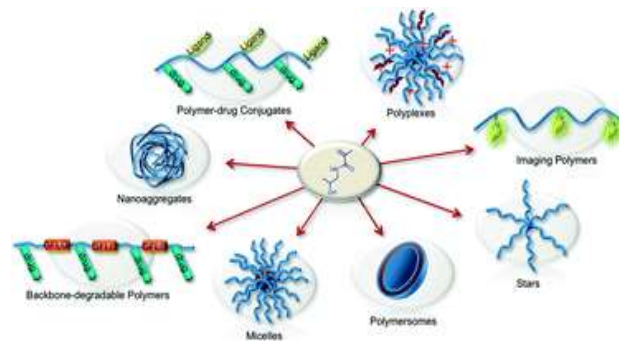
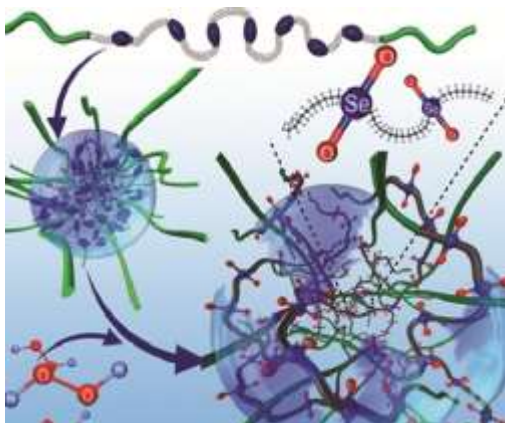


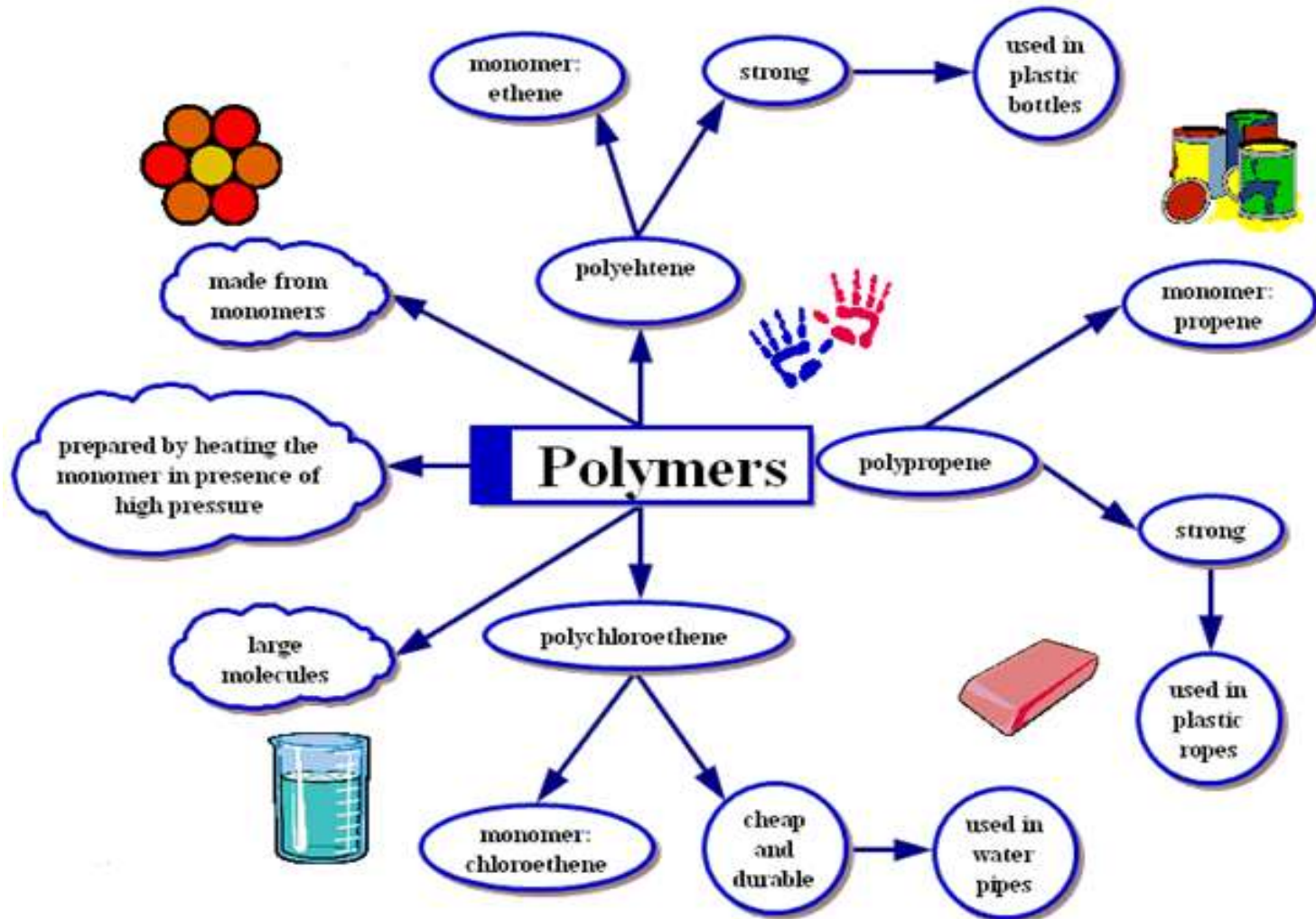
Polymer Chemistry



Lecture No. 1

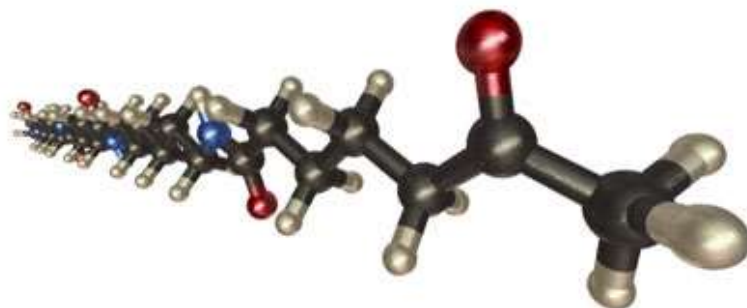
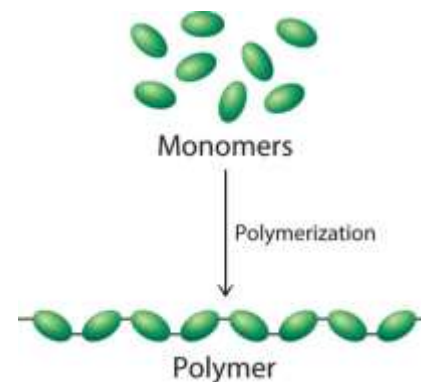
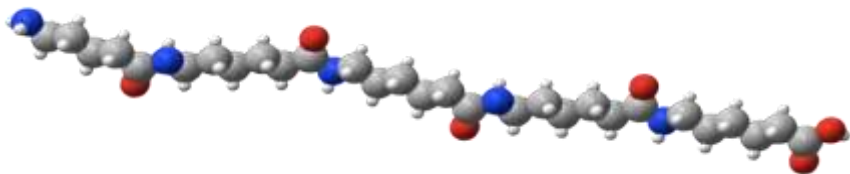
- **Introduction**
- **Polymers in day today life**
- **Functionality of monomer**
- **Polymerization**

Introduction



What are Polymers

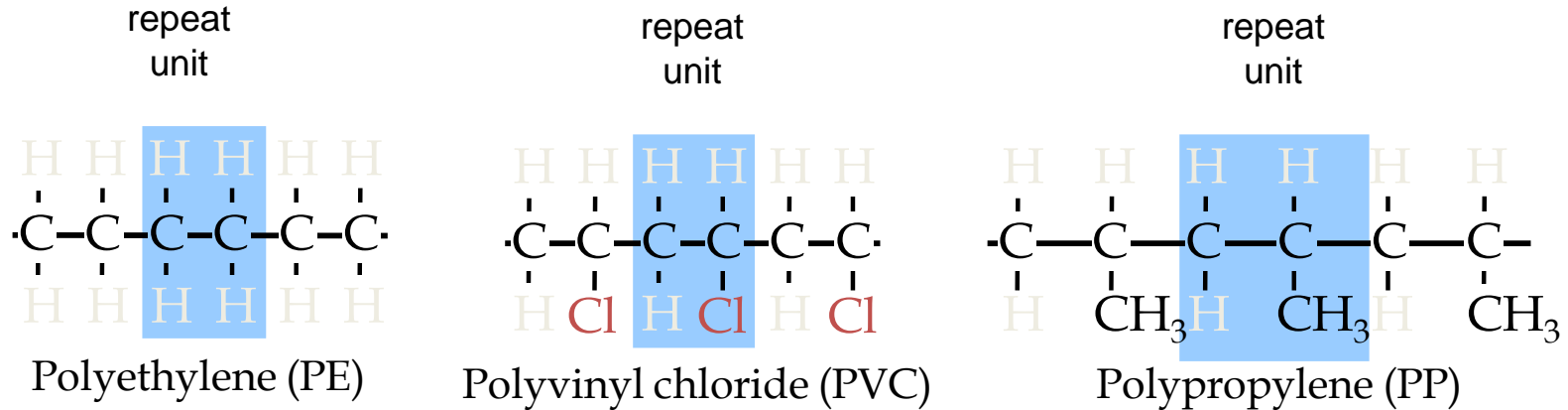
A **Polymer** (Greek, Poly - many and mer – parts or units) is a large molecule, or macromolecule composed of many repeated subunits (Monomer)



Polymers in day-today life



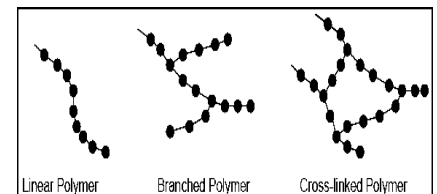
Formation of Polymers



- Natural polymers - wood, rubber, cotton, wool, leather, silk etc
- Synthetic polymers – PE, PS, PP, PVC etc

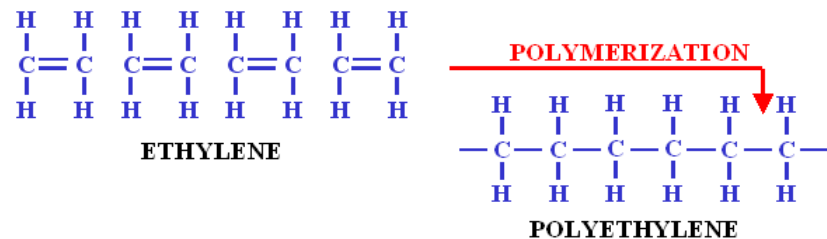
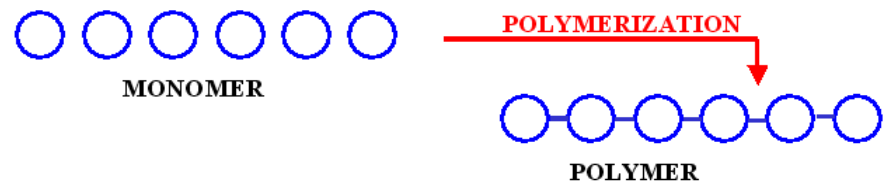
Functionality of monomer

- Functionality – number of reactive sites
- Monomer - Polyfunctional
- Polyfunctionality -unsaturation or functional group
- **Bifunctional** monomer – 2 reactive sites - linear polymer
eg: PE, PP, PVC (unsaturation), PS (functional group)
- **Trifunctional** monomer -3 reactive sites - branched (short or long) eg: Phenol (unsaturation), glycerol (functional group)
- **Higher functionality** monomer – 4,5,or more reactive sites - crosslinked polymer respectively
- eg: Acetylene, urea, butadiene etc



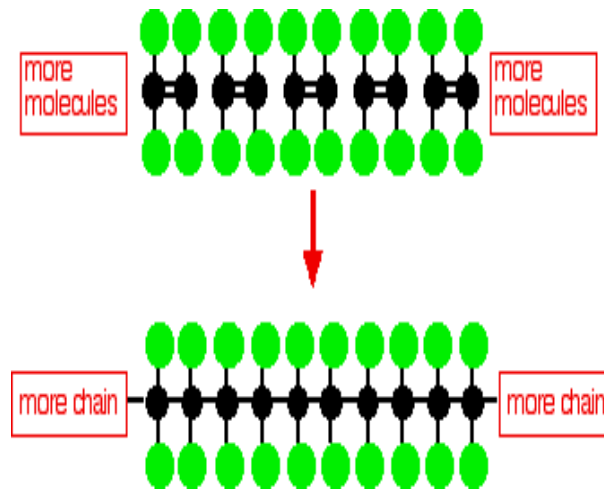
Polymerization

- Chemical process by which monomers get converted to polymers
- Degree of Polymerization (DP) - number of monomeric units in Polymer molecule.
- Denoted by 'n'
- Molecular weight of polymer can be determined using 'n'
- Higher the DP, greater is the molecular weight, greater is the strength with more complex structure of Polymer.



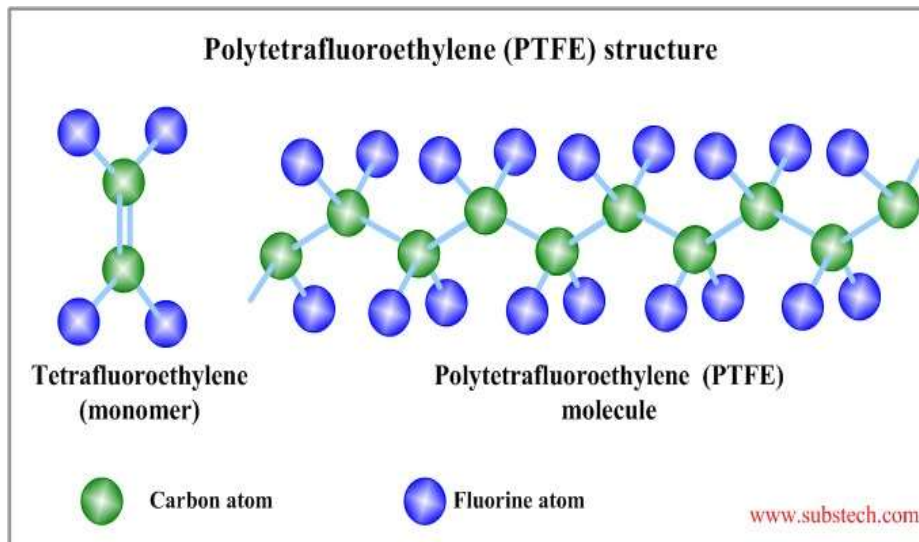
Lecture No. 2

- Addition polymerization
- Condensation polymerization
- Chain growth polymerization
- Free radical mechanism



Reactions of Polymerization

- Carothers in 1929 – classified polymers on the basis of compositional difference
- Addition polymerization
- Condensation polymerization

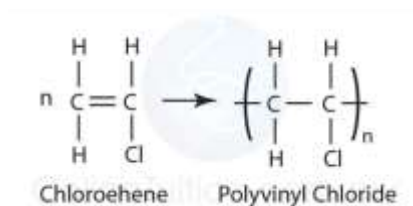
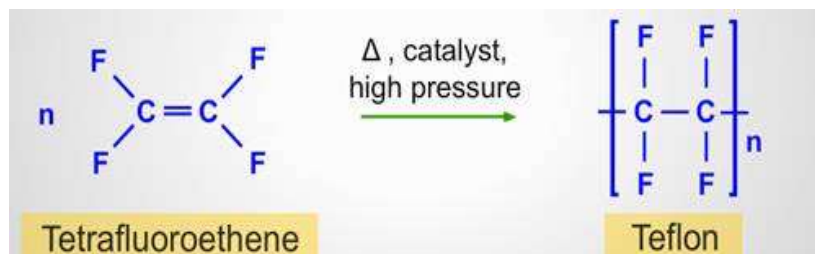
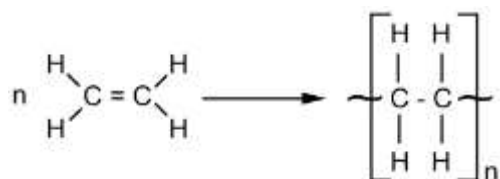


Addition Polymerization

- Monomers polyfuctionality - unsaturation
- Polymerization by addition reaction
- Polymers with low or medium molecular weight formed at once
- Fast
- High yields
- Elemental composition of monomer is retained in polymer

Addition Polymerization

- Name of polymers – derived from name of monomer by preceding a prefix ‘poly’ to its name
- eg – PE, PP, PVC, PS etc

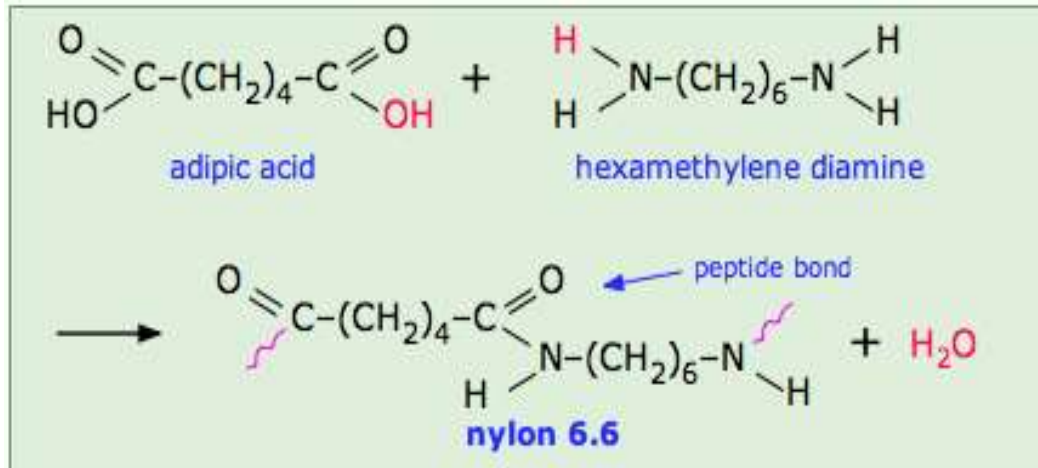


Condensation Polymerization

- Monomers polyfunctionality - functional group
- Polymerization by condensation reaction
- Elimination of small molecule
- New functional group linkage in polymer
- Name of polymer involves name of new functional group linkage
- Elemental composition of monomer not retained in polymer
- Molecular weight increases steadily

Condensation Polymerization

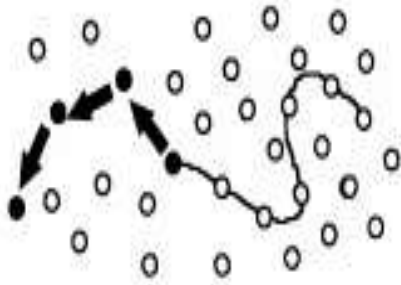
- High molecular weight polymers are found at the end
- Long reaction time needs to synthesize high conversion and high molecular weight
- eg. Nylon 6,6



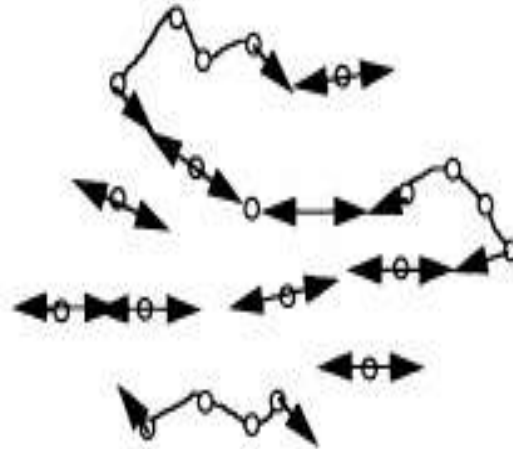
Polymerization Mechanism

- Classification on the basis of polymerization mechanism
 1. Chain polymerization
 2. Step polymerization

Chain Polymerization

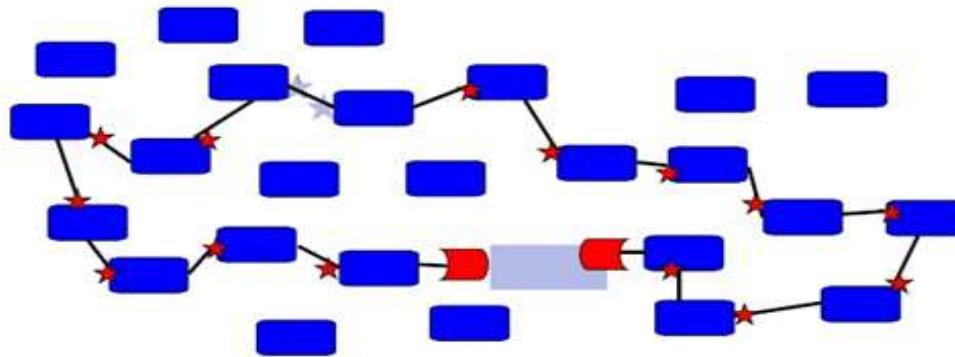


Step Polymerization



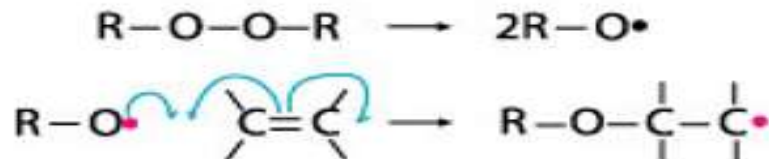
Chain Growth Polymerization

- 3 steps of polymerization –
- Chain initiation – catalyst or initiator generate chain initiating species (free radical, cation or anion)
- Chain Propagation – accounts for growth of polymer
- Chain termination – active polymer chain get terminated

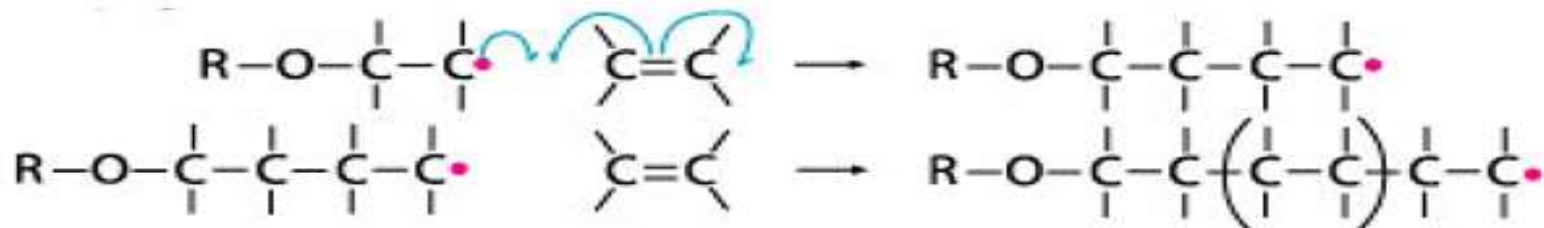


Free radical chain mechanism

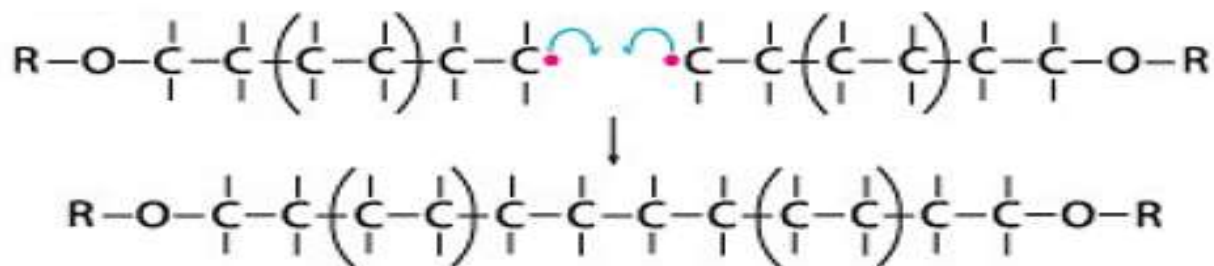
Chain-Initiation step



Chain-propagating step



Chain-terminating step

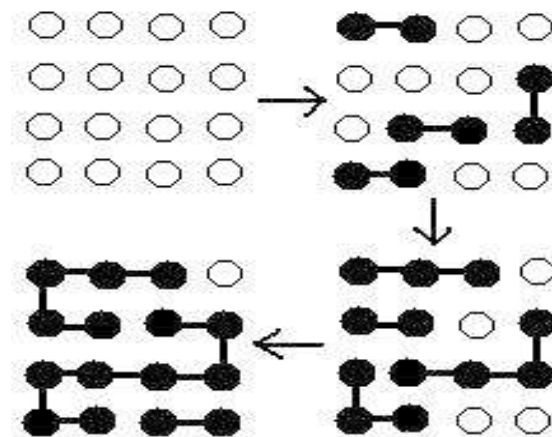


Lecture No. 3

- **Step growth polymerization**
- **T_m and T_g**
- **Thermoplastic and Thermosetting polymers**

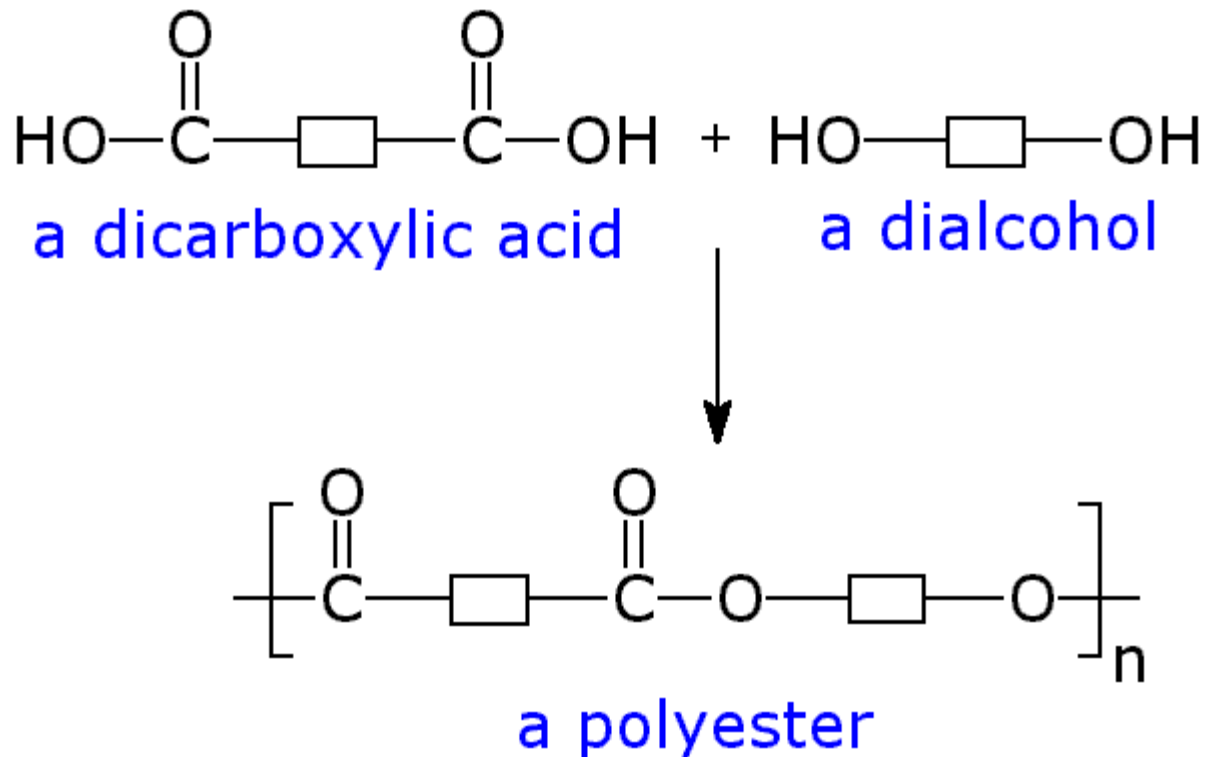
Step Growth Polymerization

- Monomer polyfunctionality – functional group
- Condensation reaction
- Removal of small molecule at each step
- Step mechanism
- Rate of polymerization is greater than chain
- Molecular weight of polymer - either low or medium
- Usually gives linear polymer

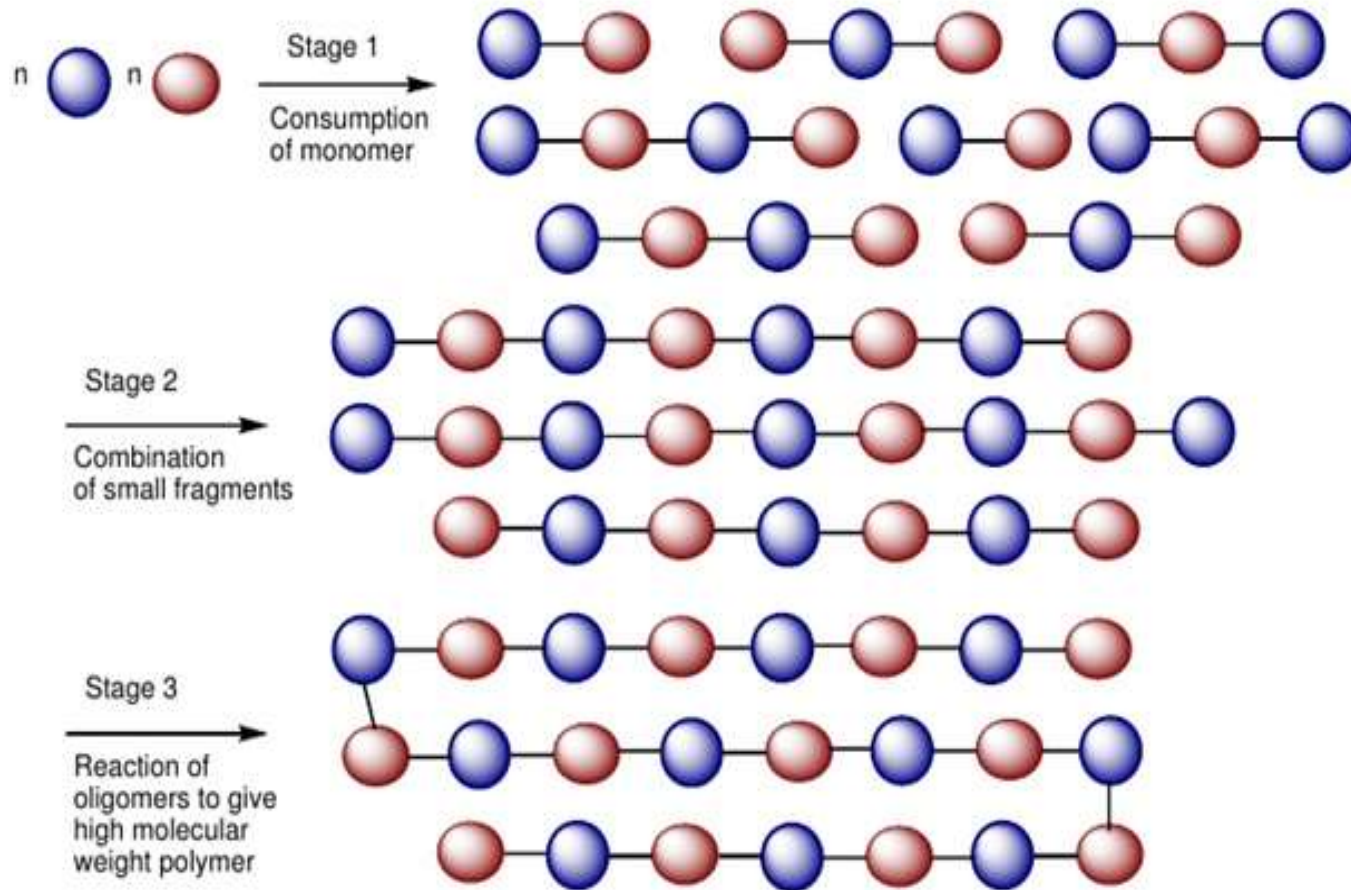


Step Growth Polymerization

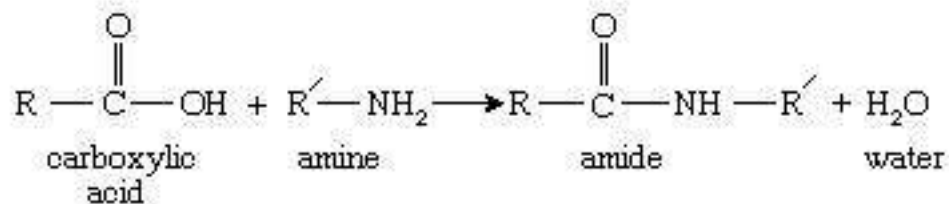
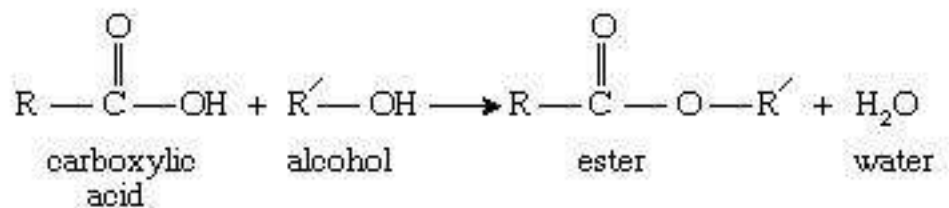
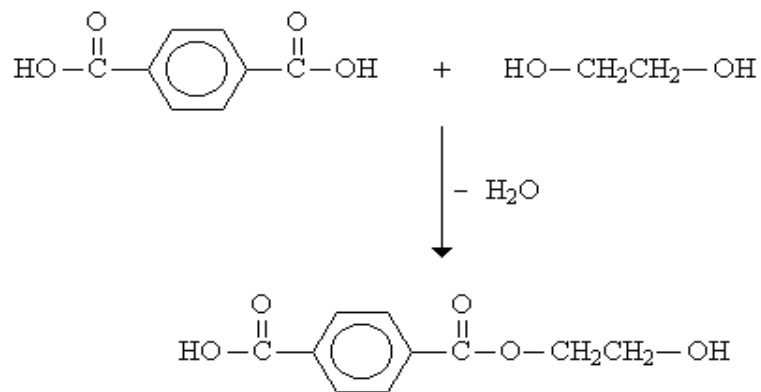
Formation of polymer in stepwise manner



Step Growth Polymerization

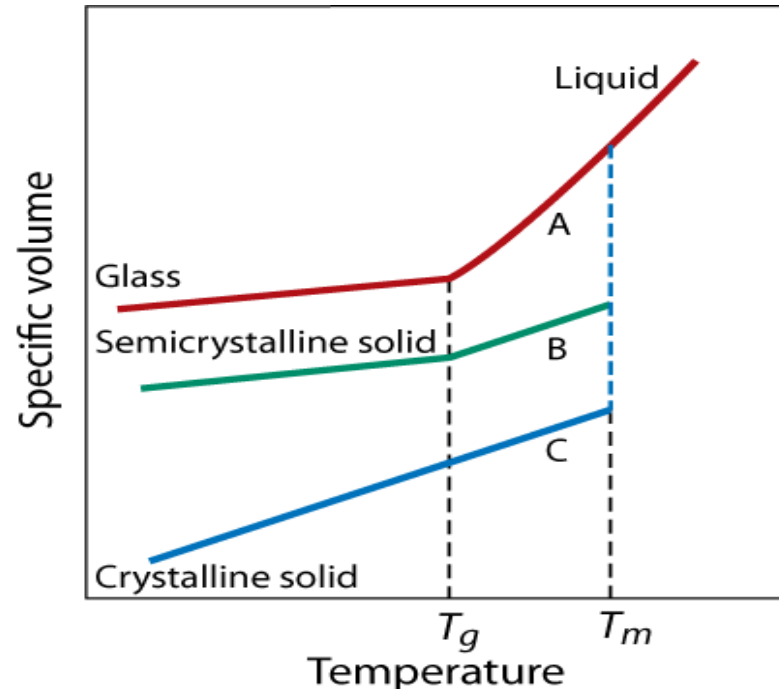


Step Growth Polymerization



Glass transition temperature (T_g)

- Property of crystalline polymers only
- T_g - temperature below which polymers exist as hard and brittle (glassy state) and above which they exist as soft and elastic (rubbery state)
- T_m – temperature above which polymer exist as molten mass



Factors affecting T_g

- **Presence of Bulky Side Group** slower down C-C bond rotation (Steric crowding). Poly styrene has more T_g than PE because of Bulky Side Group
- Nylon-66 has **hydrogen bonding** causing T_g to higher side
- **Addition of plasticizer** reduces intermolecular forces and increase flexibility and hence decreases T_g
- Higher **crystallinity** in polymers leads to tight close packing leading to high T_g
- **Branching** reduces spacing among polymer chain by increasing free volume in polymer chain and decreases t_g
- **Cross linking** will make polymer chain tight and hence T_g increases

Thermoplastic and Thermosetting polymers

Classification on thermal behavior of polymers

Sr. No.	Description	Thermoplastic polymers	Thermosetting polymers
1	Monomer	Unsaturation	Functional group
2	Reaction	Addition	Condensation
3	Mechanism	Chain growth	Step growth
4	Mol.Wt.	Low or medium	High
5	Structure	Linear or branched (small branches)	Highly branched or cross-linked
6	Solubility	Soluble in some organic solvents	Insoluble
7	Action of heat	Reversible	Irreversible
8	Reshaping	Shapes can be changed many times	Once shaped, reshaping is impossible
9	Reclaimed	Reclaimed from waste	Not possible
10	Examples	PE, PP, PVC, PS etc	Urea formaldehyde, melamine formaldehyde etc

Lecture No. 4

Techniques of polymerization

- **Bulk polymerization**
- **Solution polymerization**
- **Suspension polymerization**
- **Emulsion polymerization**

Polymerization Techniques

- Polymerization - Chemical Process by which monomers get converted to polymers

Addition Polymerization

- Bulk Polymerization
- Solution Polymerization
- Suspension Polymerization
- Emulsion Polymerization

Condensation Polymerization

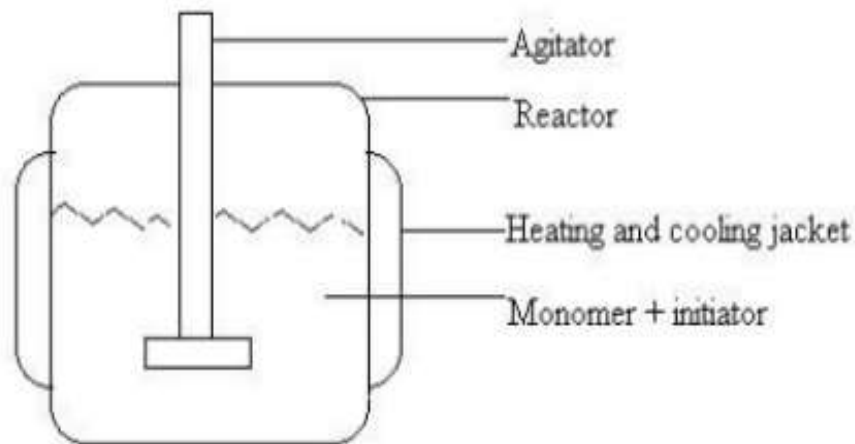
- Melt Polycondensation
- Solution Polycondensation

Bulk Polymerization

- Mass or block polymerization: Polymerization of undiluted monomer.
- Carried out by adding a soluble initiator to pure monomer (in liquid state)
- The mixture is constantly agitated and heated to polymerization temperature
- Once the reaction starts, heating is stopped as reaction is exothermic
- The heat is dissipated by circulation water jacket
- Viscosity increases drastically during conversion
- Used for polymerization of liquid state monomers
- Usually adopted to produce low density PE, PS, PVC, polymethyl methacrylate etc

Bulk Polymerization

- In the reactor :-
- Liquid monomer
- Initiator (soluble in monomer)
- Chain transfer agents (soluble in monomer)



Advantages of Bulk Polymerization

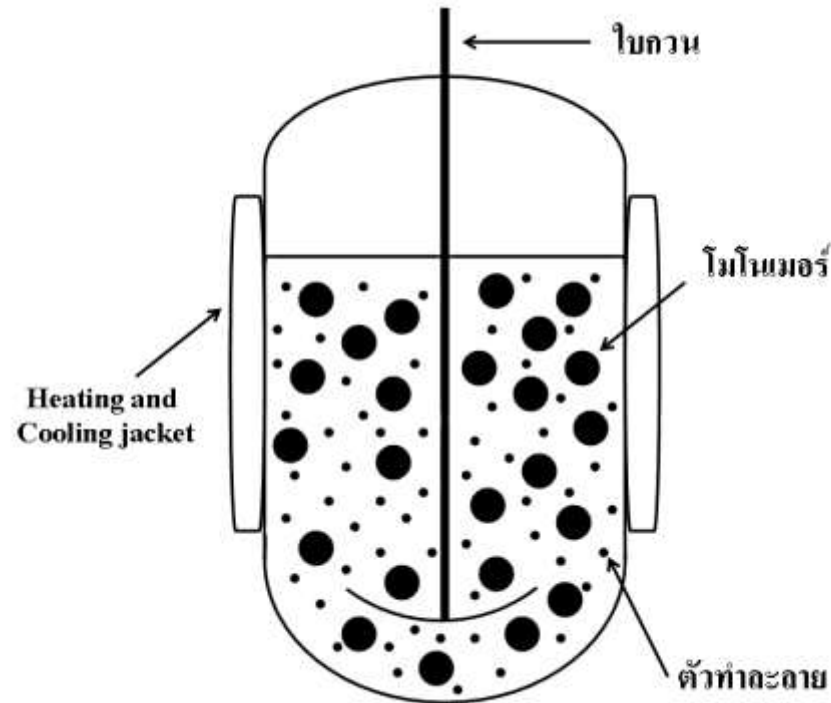
- The system is simple and requires thermal insulation
- Large castings may be prepared directly
- Molecular weight distribution can be easily changed by using chain transfer agent
- Obtain purest possible polymer
- Make objects with a desirable good shape

Disadvantages of Bulk Polymerization

- Heat transfer and mixing becomes difficult as the viscosity of reaction mass increases
- Highly exothermic
- Difficult to control
- Reaction has to be run slowly
- Cannot get high rate and high MW at the same time
- Difficult to remove last traces of unreacted monomer

Solution Polymerization

- Some disadvantages of bulk polymerization are eliminated in solution polymerization
- Monomer along with initiator dissolved in solvent and the formed polymer stays dissolved



Solution Polymerization

- After the reaction is over the polymer formed is used as such in the form of polymer solution or the polymer is isolated by evaporating the solvent
- The polymer so formed can be used for surface coating
- The method is used for the production of PVC, polyvinyl alcohol, poly acrylamide, poly acrylic acid, poly butadiene, PMMA etc

Advantages of solution polymerization

- The solvent acts as diluent and helps in facilitating continuous transfer of heat of polymerization. Therefore temperature control is easy.
- Solvent allows easy stirring as decreases the viscosity of reaction mixture
- Solvent also facilitates ease of removal of polymer from the reactor
- Viscosity build up is negligible
- Reduces the tendency toward autoacceleration

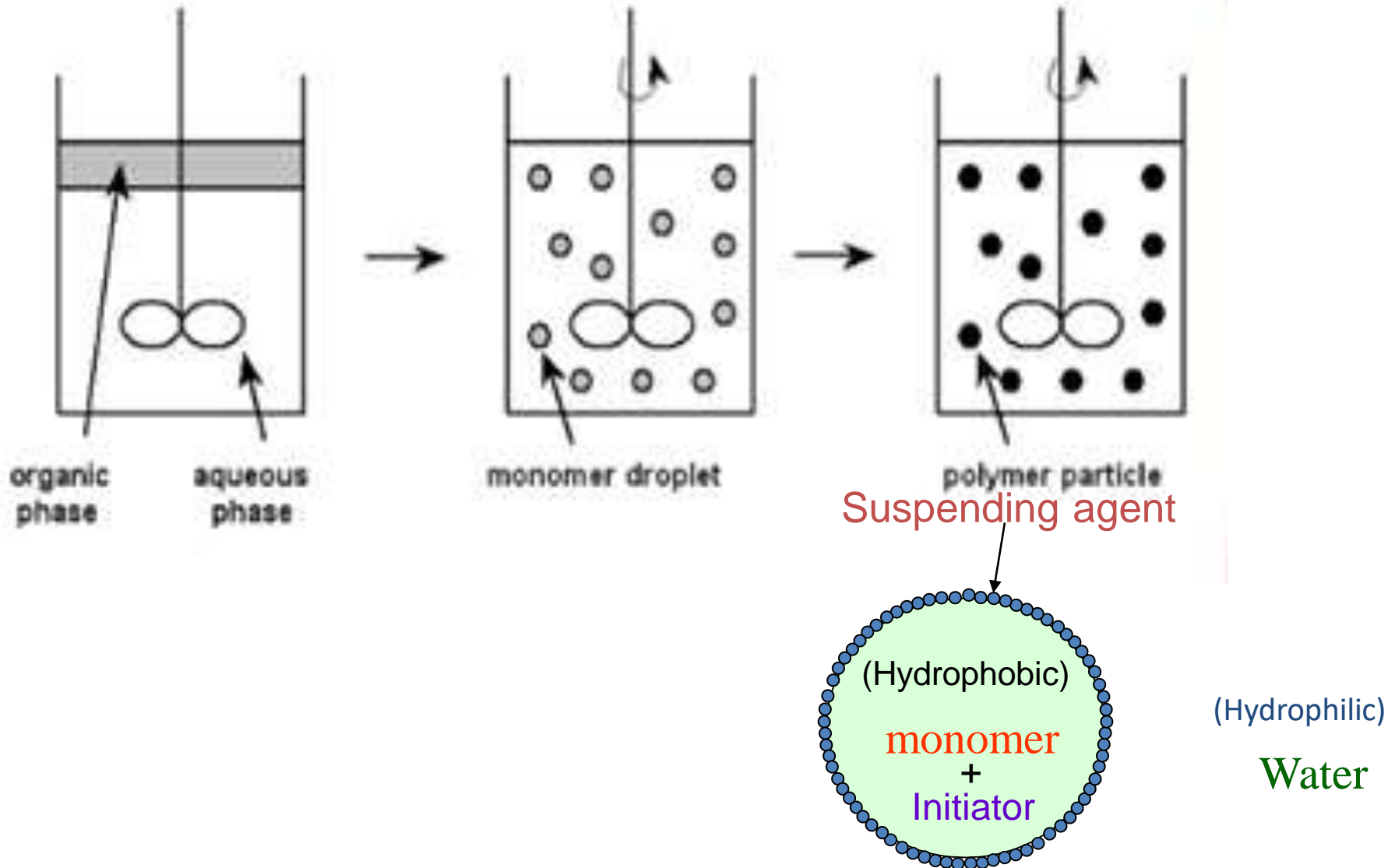
Disadvantages of Solution Polymerization

- The method is costly as it uses costly solvents
- Need solvent separation & recovery
- This technique gives smaller yield of polymer per reactor volume as solvent waste the reactor space
- The purity of polymer is also not as high as that in bulk polymerization
- Removal of last traces of solvent is difficult
- Solvent wastage
- Lower yield
- Solvent may not be really inert

Suspension Polymerization

- Liquid or dissolved monomer suspended in liquid phase like water
- Initiators used are monomer soluble eg. dibenzoyl peroxide
- Thus polymer is produced in heterogeneous medium
- Size of monomer droplet is 50-200 μm in diameter
- The dispersion is maintained by continuous agitation and the droplets are prevented to accumulate by adding small quantity of stabilizer
- Organic stabilizers used are PVA, gelatine, cellulose etc
- Inorganic stabilizers are kaolin, magnesium silicate, aluminium hydroxide, calcium/magnesium phosphate etc

Suspension Polymerization



Suspension Polymerization

- Each droplet is a tiny bulk reactor
- Polymerization takes place inside the droplet and the product formed is insoluble in water
- The product is separated out in the form of bead, pearl or granule
- Hence the technique is also known as Also known as bead, pearl or granular polymerization
- The product can be used directly for some applications as precursors of ion exchange resins
- They can be dissolved in suitable medium for use as adhesives and coatings
- Used to form PVC, PS, polyvinyl acetate etc

Advantages of Suspension Polymerization

- The process is comparatively cheap as it involves only water instead of any other solvent
- Viscosity increase is negligible
- Agitation and temperature control is easy
- Product isolation is easy since the product is insoluble in water
- Easy heat removal and control
- Obtain polymer in a directly useful form

Disadvantages of Suspension Polymerization

- Adopted only for water insoluble monomer
- Difficult to control polymer size
- Polymer purity is low due to suspending and stabilizing additives that are difficult to remove completely
- It is highly agitation sensitive
- Larger volume of reactor is taken up by water
- Low yield / reactor volume
- Traces of suspending agent on particle surfacesCannot run continuously
- Cannot be used for condensation polymers

Emulsion Polymerization

- This technique is used for the production of large number of commercial plastics and elastomers
- Water insoluble monomer, dispersion medium, emulsifying agent of surfactant (soaps and detergents) and water soluble initiator (potassium persulphate, H_2O_2 etc)
- Monomer is dispersed in aqueous phase in the form of uniform emulsion
- Size of monomer droplet is 0.5 to 10 μm in diameter depending upon the rate of agitation and temperature of polymerization

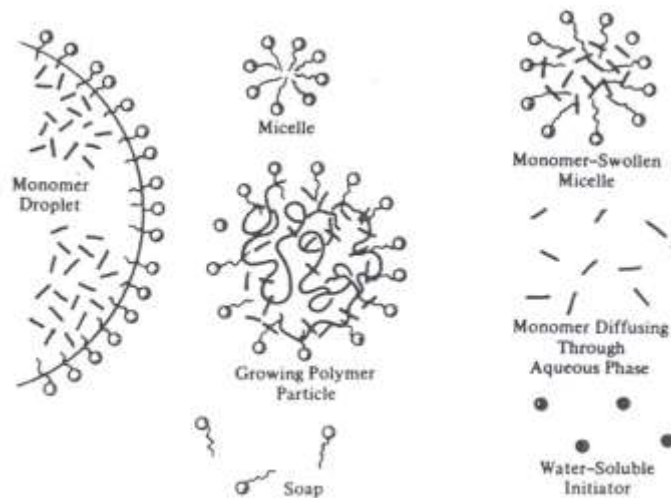
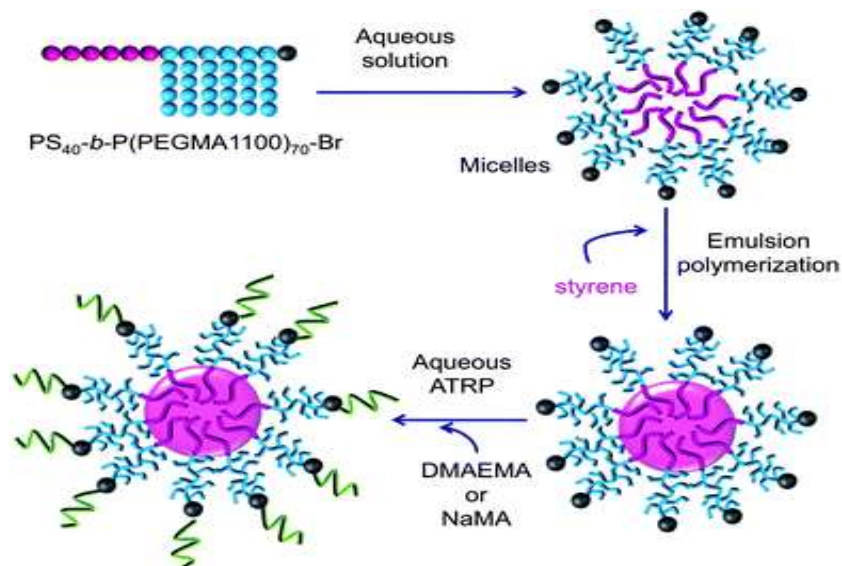
Emulsion Polymerization

- The emulsion of monomer in water is stabilized by surfactant
- A surfactant has hydrophilic and hydrophobic end in its structure
- When it is added to water, the surfactant molecules gather together into aggregates called micelles
- In the micelles, hydrocarbon tails (hydrophobic) orient inward and heads (hydrophilic) orient outwards in water
- Monomer molecules diffuse from monomer droplets to water and from water to micelles

Emulsion Polymerization

- Water, monomer, surfactant
- Examples –
- Synthetic SBR, polybutadiene, polychloroprene
- Plastics – PVC, PS, ABS
- Dispersions – Polyvinyl acetate, polyvinyl acetate copolymers, latexacrylic paints, styrene butadiene

Emulsion Polymerization



Advantages of Emulsion Polymerization

- High molecular weight polymers
- Fast rate of polymerization
- Allows removal of heat from the system
- Viscosity remains close to that of water and is not dependent on molecular weight
- The final product can be used as such, does not need to be altered or processed



Disadvantages of Emulsion Polymerization

- Surfactants and polymerization adjuvants – difficult to remove
- Cannot be used for condensation, ionic, Ziegler Natta polymerization

Lecture No. 5

- **Compounding of plastics**
Specialty polymers –
- **Conducting polymers**
- **Biodegradable polymers**

Compounding of Plastics

- The Process by which ingredients / additives / compounding agents are intimately mixed with the polymer to get a homogeneous mass is known as compounding.
- To add a new property or increase the degree / extent of the existing property
- eg. Stabilizers, flame retarding agents, coloring agents, emulsifying agents, plasticizer etc

Components used in Compounding

- **Stabilizers** : used to prevent degradation of polymer from air and light e.g. Alkyl Phenol and Phenyl Salicylate
- **Accelerators** : to accelerate the overall process e.g. Benzoyl peroxide
- **Plasticizers** : used to convert rigid polymer into flexible by lowering intermolecular forces e.g. Di-isooctyl Phthalate in PVC
- **Fillers** : used either to reduce cost or to increase strength of polymer e.g. Asbestos ,clay , mica , Nylon

Creators of Conducting polymers

Yet Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa have changed this view with their discovery that a polymer, polyacetylene, can be made conductive almost like a metal.



Alan G. MacDiarmid

Professor at the University of Pennsylvania,
Philadelphia, USA.

Hideki Shirakawa

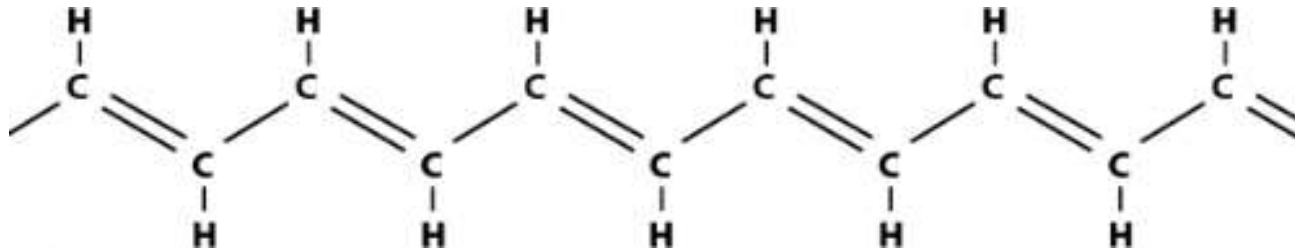
Professor Emeritus,
University of Tsukuba, Japan.

Alan J. Heeger

Professor at the University of California
at Santa Barbara, USA.

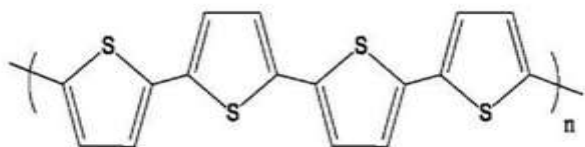
Conducting Polymers

- Free electrons are needed
- Conductivity due to -
- Conjugated compounds

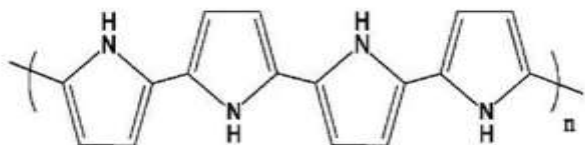


- The second condition is that the plastic has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. The process is known as ***Doping***.
- There are two types of doping
- oxidation with halogen (or *p*-doping)
- Reduction with alkali metal (called *n*-doping).

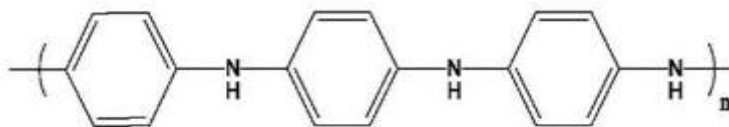
Examples of conducting polymers



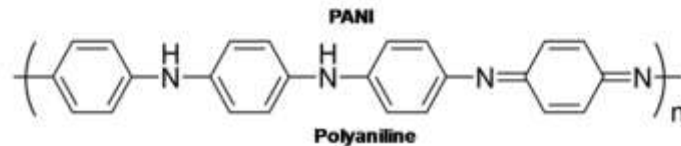
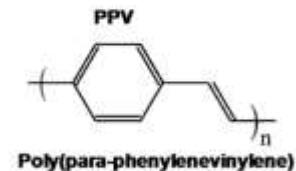
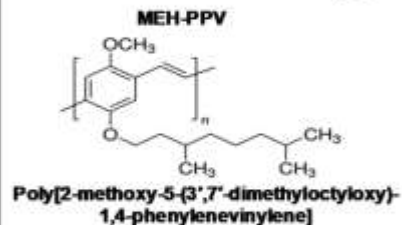
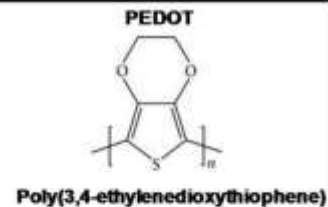
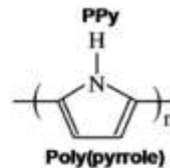
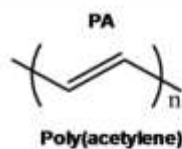
polythiophene



polypyrrole



polyaniline



Applications of conducting polymers

- Anti-static substances for photographic film
- Corrosion Inhibitors
- Compact Capacitors
- Anti Static Coating
- Electromagnetic shielding for computers "Smart Windows"
- Transistors
- Light Emitting Diodes (LEDs)
- Lasers used in flat televisions
- Solar cells
- Displays in mobile telephones and mini-format television screens

Conducting Polymers

Photographic Film



With antistatic coating



Without antistatic coating



PHOTO: FRANZ WÄNDIGER/JOSEL

Solar cell

Light-emitting diodes



PHOTO: JANSCHON/STRELLER
CHALLMERS

By varying the molecular structure, light of different colours can be obtained.



smart" windows

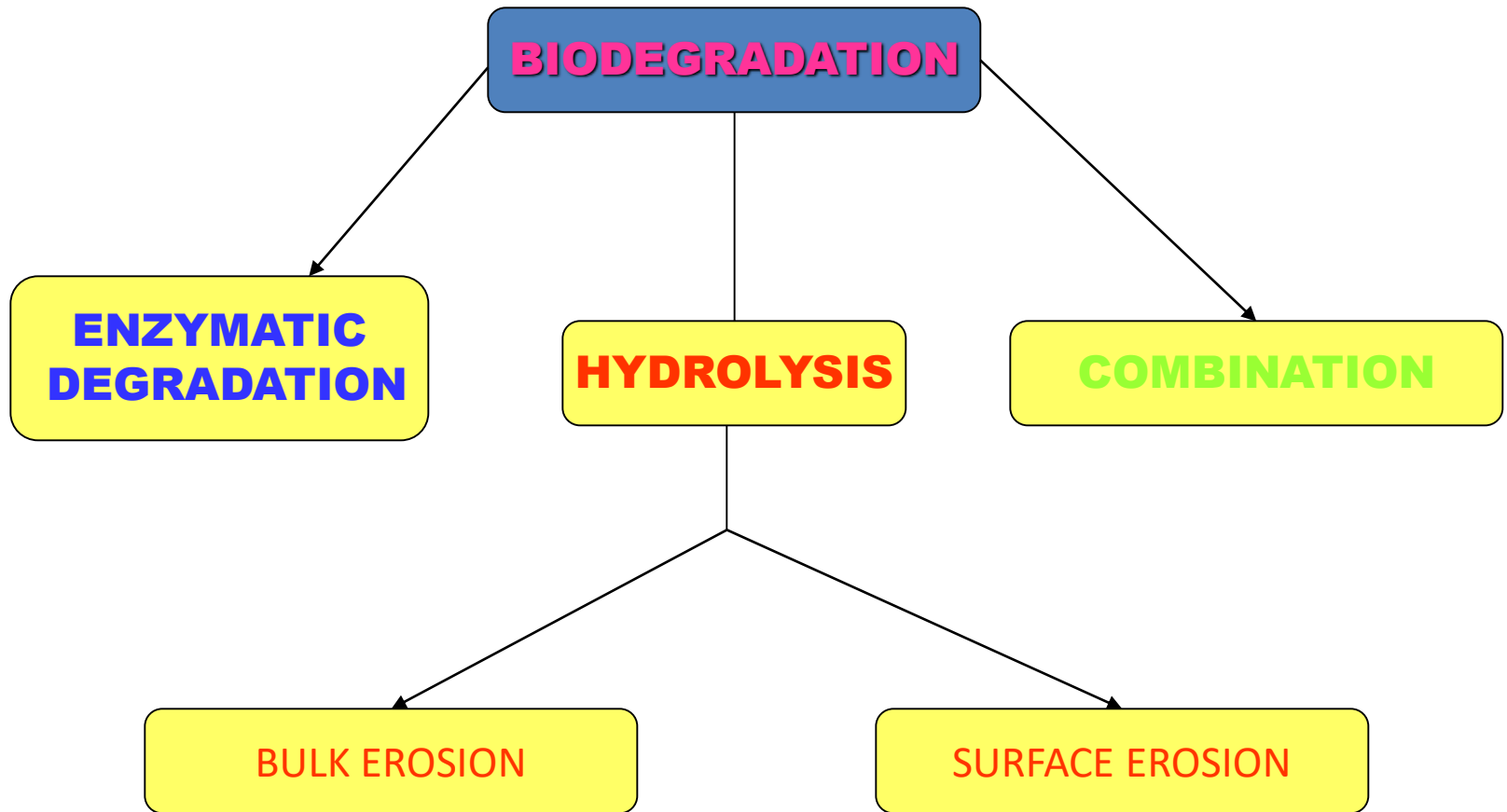


Shield for computer screen
against electromagnetic
"smart" windows
radiation

Biodegradable Polymers

- Polymers comprised of monomers linked to one another through functional groups and have unstable links in the backbone.
- They are broken down into biologically acceptable molecules that are metabolized and removed from the body via normal metabolic pathways.
- Based on biodegradability polymers are classified as:
 - Biodegradable polymers
eg: collagen, poly glycolic acid etc.,
 - Non biodegradable polymers
eg: poly vinyl chloride, polyethylene etc.,

Mechanism of Biodegradable Polymers

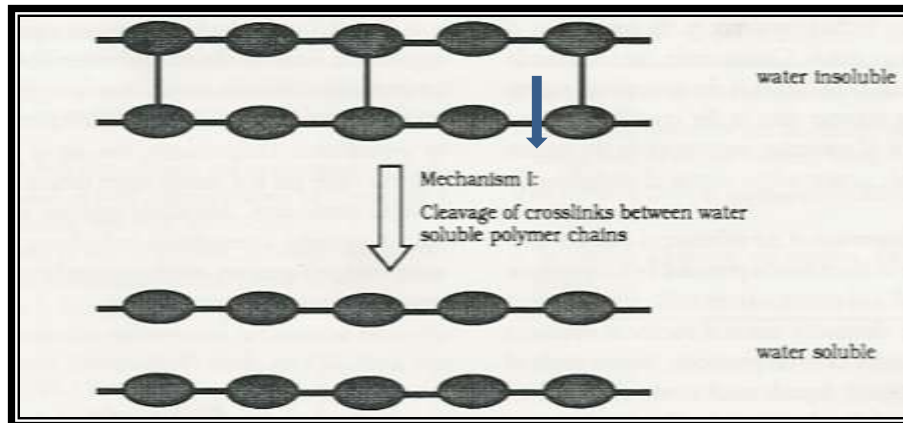


- eg: Aliphatic poly(esters), Polyanhydrides, polyaminoacids, Albumin, Collagen, Dextran, Gelatin, Pectin, starch etc

Enzymatic or chemical degradation

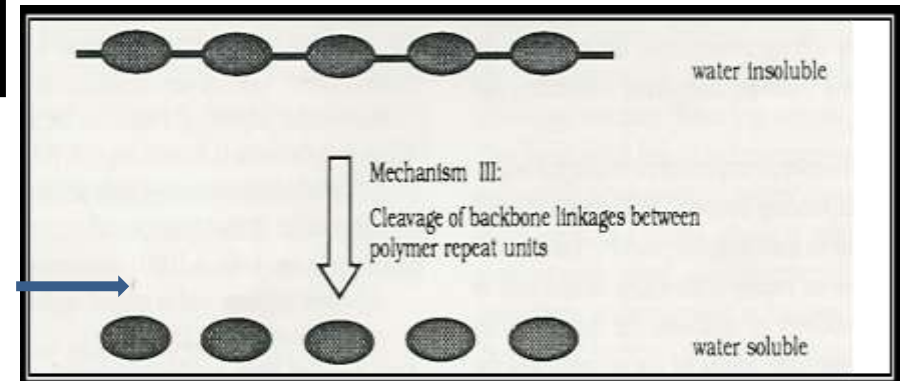
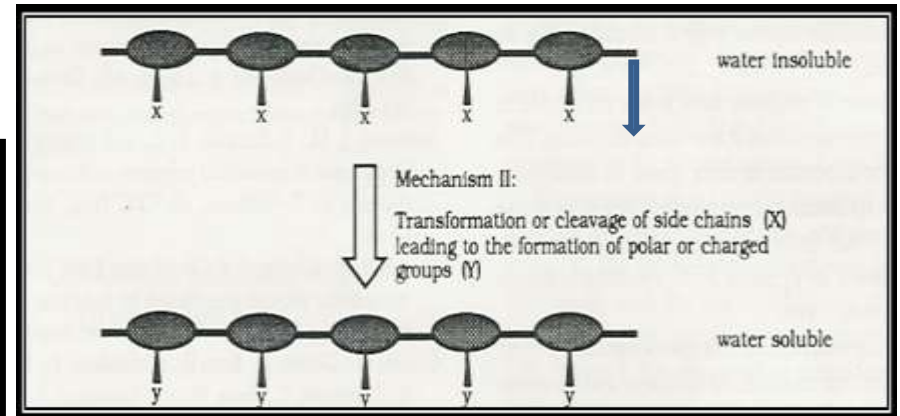
- It is mediated by water, enzymes, microorganisms.

CLEAVAGE OF CROSSLINKS



CLEAVAGE OF BACKBONE

TRANSFORMATION OF SIDE CHAINS

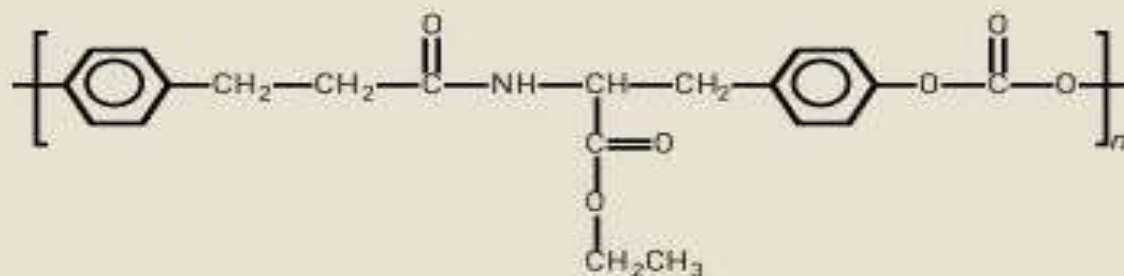


Mechanism of biodegradation

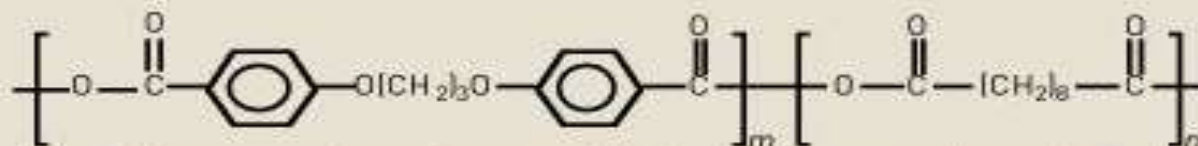
Examples of biodegradable polymers

BIODEGRADABLE POLYMERS

Temporary medical implants require materials that decompose safely



Poly(DTE carbonate)



Bis(*p*-carboxyphenoxy)propane (PCPP)

Sebacic acid (SA)

Poly(PCPP-SA anhydride)



Poly(lactic acid-co-glycolic acid)

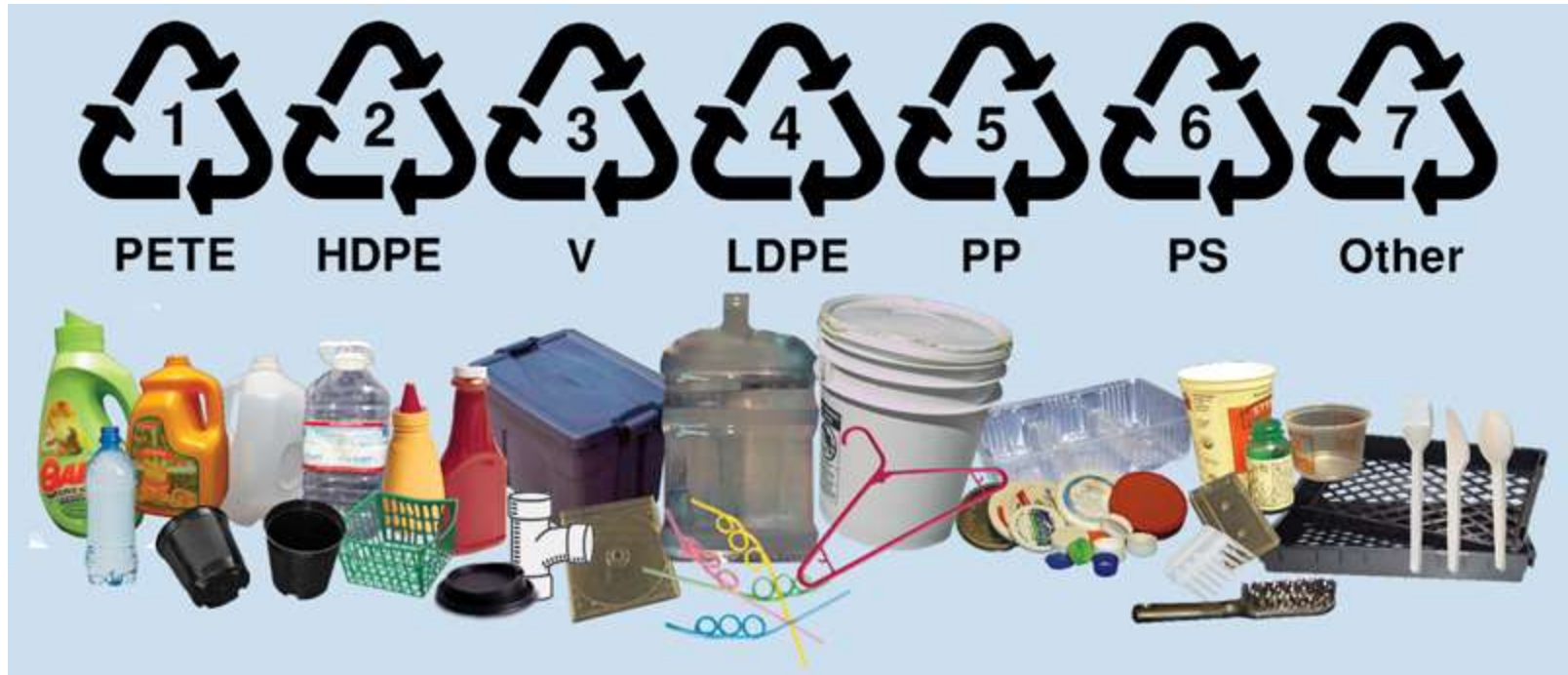
DTE = desaminotyrosyltyrosine
ethyl ester

Applications of biodegradable polymers

- Polymer system for gene therapy.
- Biodegradable polymer for ocular, tissue engineering, vascular, orthopedic, skin adhesive & surgical glues.
- Bio degradable drug system for therapeutic agents such as anti tumor, antipsychotic agent, anti-inflammatory agent.
- Used in and on soil to improve aeration, and promote plant growth and health.
- Many biomaterials, especially heart valve replacements and blood vessels, are made of polymers like Dacron, Teflon and polyurethane.

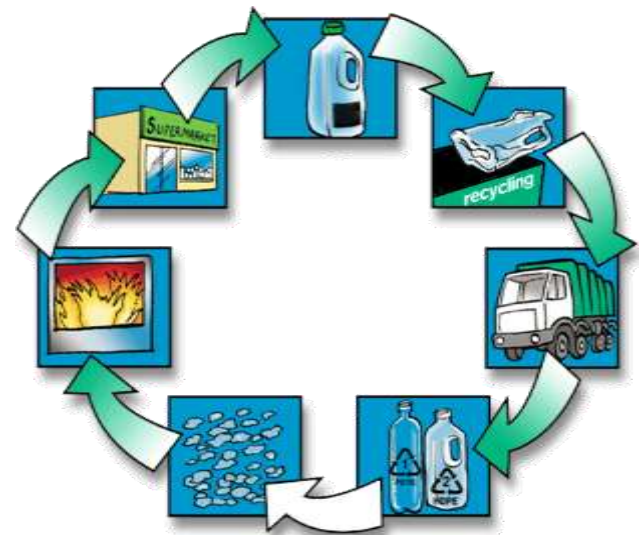
Lecture No. 6

- **Recycling of polymers**
- **Revision**



Why to recycle plastic

- Plastic in the ocean is responsible for the deaths of millions of sea animals.
- Plastic never degrades.
- Incinerating plastic contributes to greenhouse gases.
- Plastics contain harmful chemicals.
- Making new plastics requires significant amount of fossil fuels.

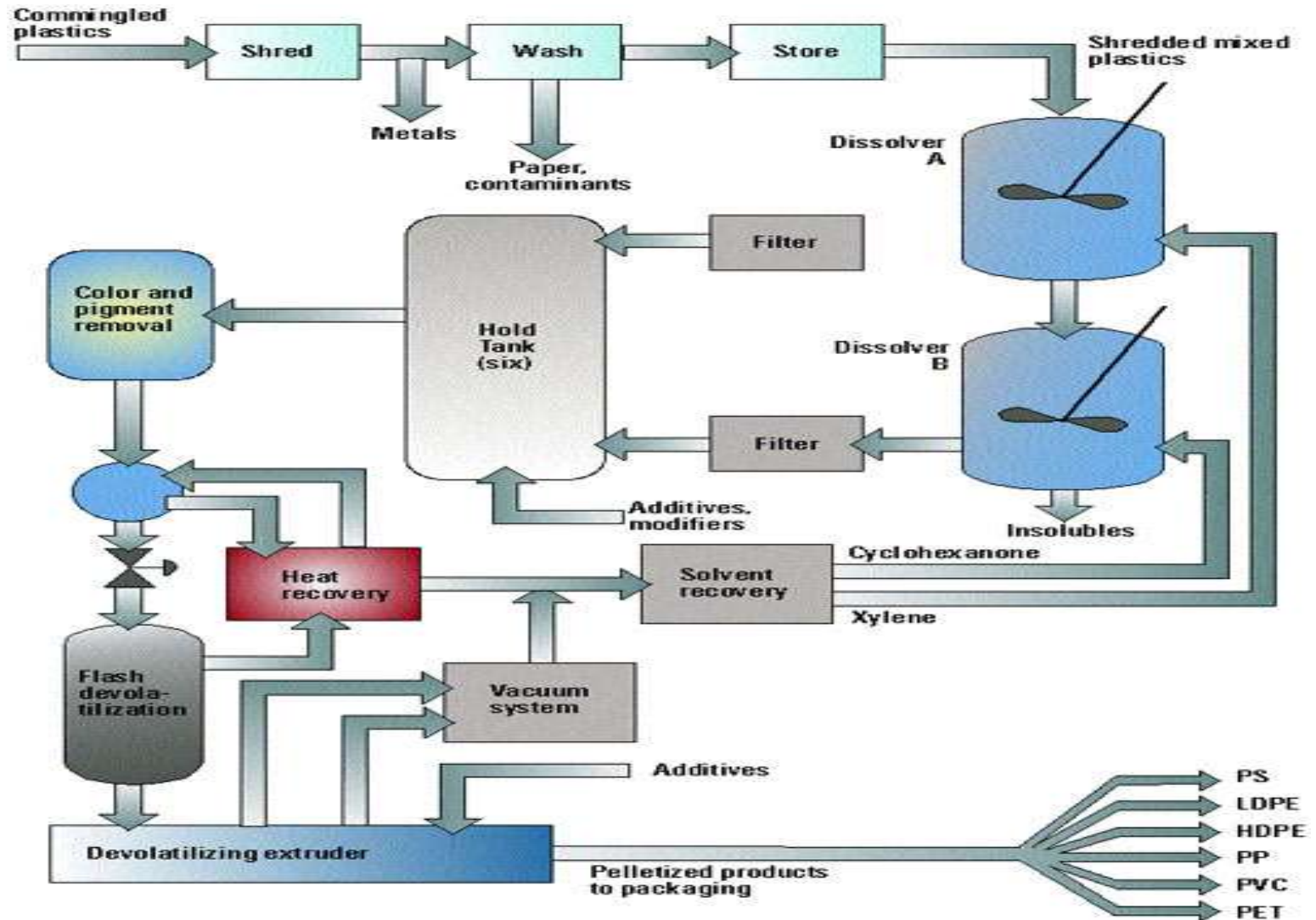


Recycling of Polymers

- **Plastic recycling** is the process of recovering scrap or waste plastic and reprocessing the material into useful products.
- Since the vast majority of plastic is non-biodegradable, recycling is a part of global efforts to reduce plastic in the waste stream
- This helps to reduce the high rates of plastic pollution.



Process of recycling



Benefits of recycling plastic

- Conserving energy
- Lower emissions
- Conservation of resources
- Reusability
- Saves landfills space
- Creates job opportunities

