Polymers

Dr. Subrata Dutta
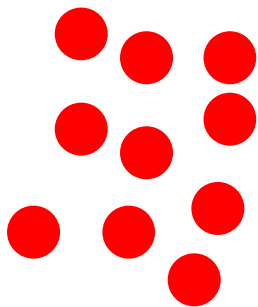
What is a polymer?

- **Very Large molecules structures chain-like in nature**

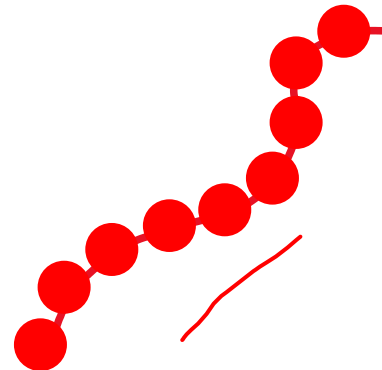**Poly**　**mer**
many　**repeat unit**

- Made up by linking together of large number of small molecule (repeating units called **monomers**) held together by covalent bonds (two or more binding sites)

Click to add text
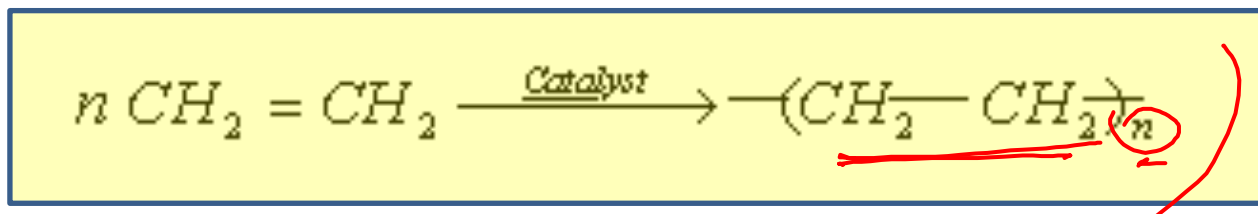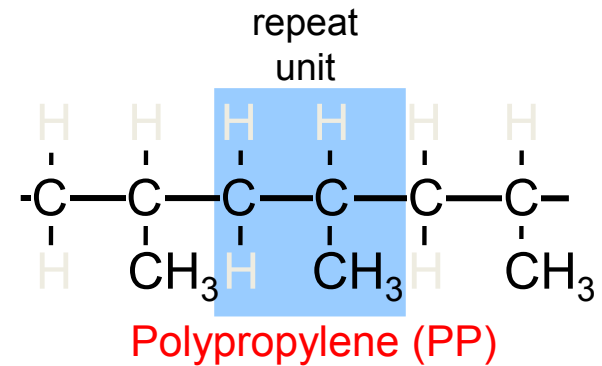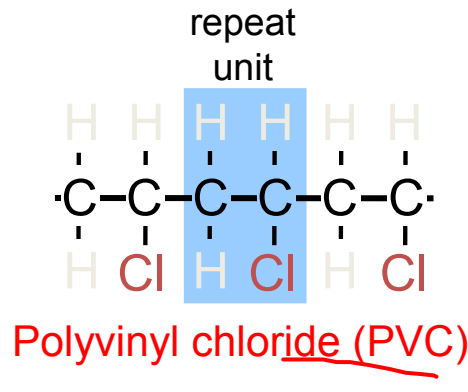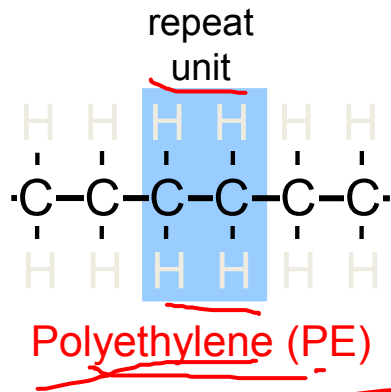

Many small molecules
(**monomer**)

One large molecule
(polymer)

Polymers

What is a polymer?

- **Very Large molecules structures chain-like in nature**

Poly   **mer**
many   **repeat unit**

repeat unit

$$H \quad H \quad H \quad H \quad H \quad H$$
$$\cdot C - C - C - C - C - C \cdot$$
$$H \quad H \quad H \quad H \quad H \quad H$$

Polyethylene (PE)

repeat unit

$$H \quad H \quad H \quad H \quad H \quad H$$
$$\cdot C - C - C - C - C - C \cdot$$
$$H \quad Cl \quad H \quad Cl \quad H \quad Cl$$

Polyvinyl chloride (PVC)

repeat unit

$$H \quad H \quad H \quad H \quad H \quad H$$
$$\cdot C - C - C - C - C - C \cdot$$
$$H \quad CH_3 \quad H \quad CH_3 \quad H \quad CH_3$$

Polypropylene (PP)

$$n\, CH_2 = CH_2 \xrightarrow{\text{Catalyst}} -(CH_2 - CH_2)_n-$$

Degree of Polymerization

❖ Number of repeating units in the polymer chain formed is called the **degree of polymerization** (**n**)

❖ **Polyethene** : $(C_2H_4)_n$, where **n** stand for **degree of polymerization (DP)**

❖ Molecular weight of PE, **M = n x Mo**
   Where **Mo** is molecular weight of monomer

❖ **Strength** of the polymer can be increased by increasing its degree of polymerization (DP)

➢ High DP ⟶ hard and heat resistant
➢ Low DP ⟶ soft, gummy

Degree of Polymerization

❖Data : if MW of PE, M = **28000**,

MW of repeating unit, Mo = **28**

$$M = n \; x \; Mo$$

Thus , n = M / Mo

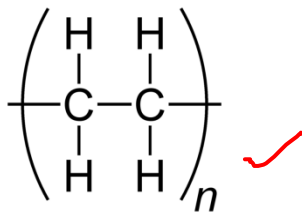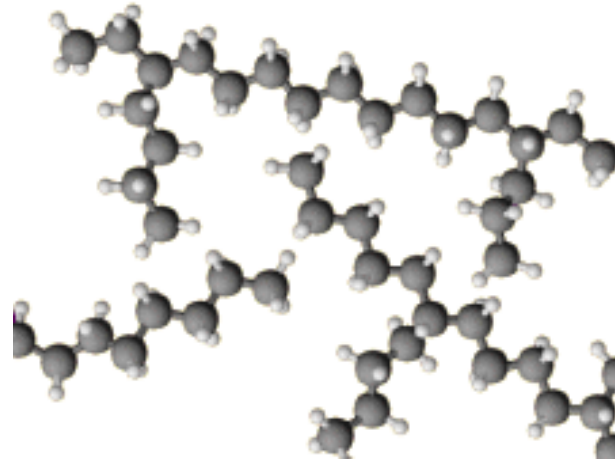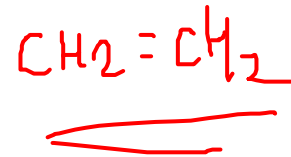= 28000 / 28
= 1000

❖ **Degree of polymerization (n)** = 1000

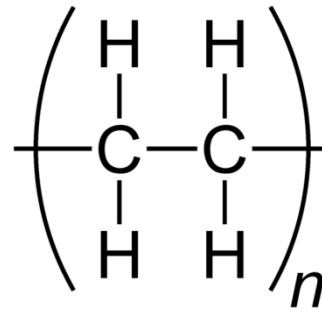# Low-Density Polyethylene (LDPE)

SVNIT SURAT

Chain Length: 1000 - 2000

$CH_2 = CH_2$
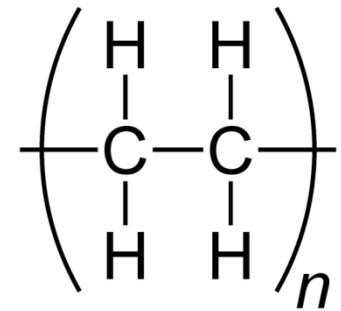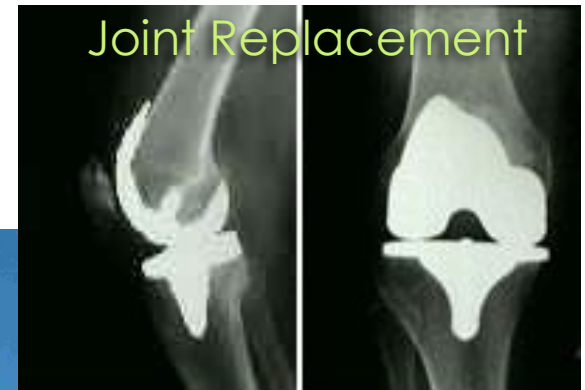

04
PE-LD

High-Density Polyethylene (HDPE)

Chain Length: 10,000 – 100,000

02
PE-HD
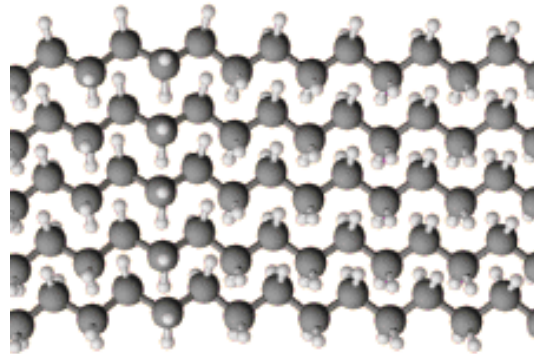
Ultra-high-molecular-weight polyethylene (UHMWPE)

Chain Length: 2-6 million

Helmet

Gears

Joint Replacement

Chain Length: 4,000 – 5,000

PVC – (polyvinyl chloride)

$CH_2 = CH$
Cl
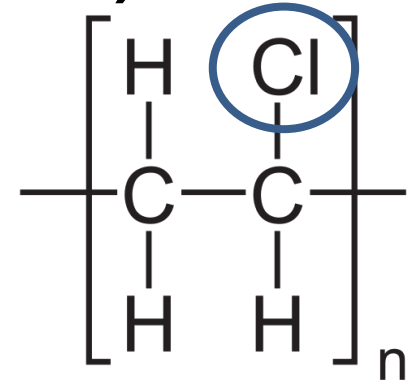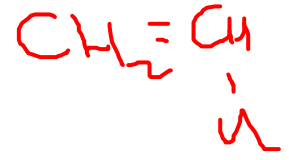
More Polar → Stronger Bonding

03
PVC

Classification of polymer

Classification of polymer

Based on origin Of source
- 1.Natural polymers
- 2.semi synthetics
- 3. synthetics polymer

Based on structure
- 1.Linear polymers
- 2.Branched chain polymers
- 3.Crossed linked polymers

Based on molecular forces
- 1.Elastomrs
- 2.Fibers
- 3.Thermoplatics
- 4.Thermosetting polymers

Based on mode of polymerization
- 1.Addition polymers
- 2.Condensation polymers

Nomenclature

➢ **Homopolymers** : Homopolymers can be linear, branched or cross linked.
➢ Same repeating unit (**monomers**)
  - A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A
➢ **Copolymers** : different repeating units

A) Random copolymers : Two or more random repeating units

  -A – **B-B**-A-A-A-**B**-A-**B**-A-A-**B**-A-B-B-B-A-A-B-A-B-A-A-A-B-B-A-B-

B) Alternating copolymers : Alternating sequences of different monomers

- A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-

(C) Block copolymers : Long sequences of a monomer are followed by long sequences of another monomer.
-**A-A-A-A-A-A-A-A**-B-B-B-B-B-B-B-B-B-**A-A-A-A-A-A-A-A**-**A**-**B-B-B-B-B**-

(D) Graft polymer : Chain made from one type of monomer with branches with another type.
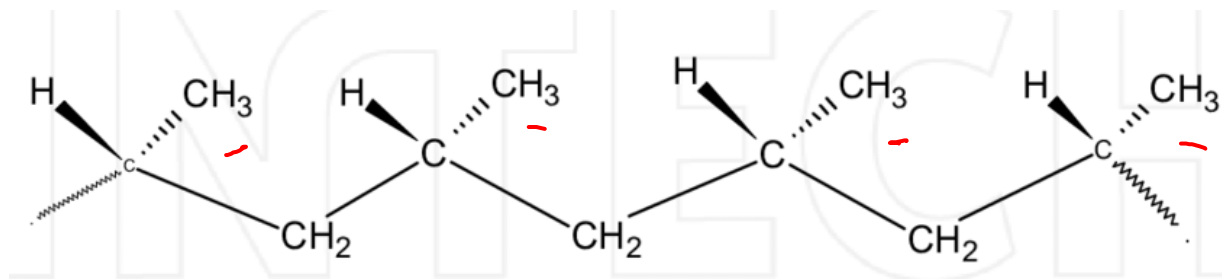
Tacticity : Orientation of monomeric units in polymer takes place in orderly or disorderly fashion w.r.t main chain.

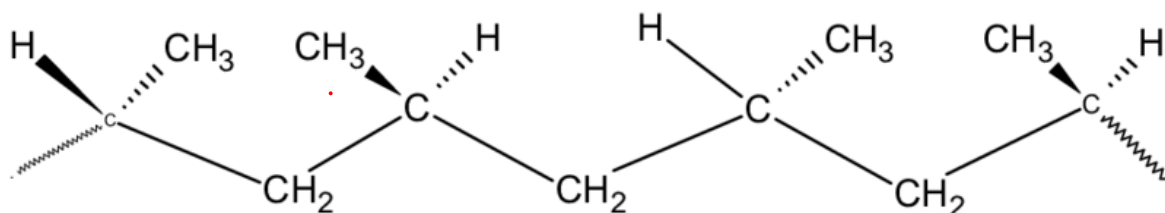The difference in configuration affects their physical properties.

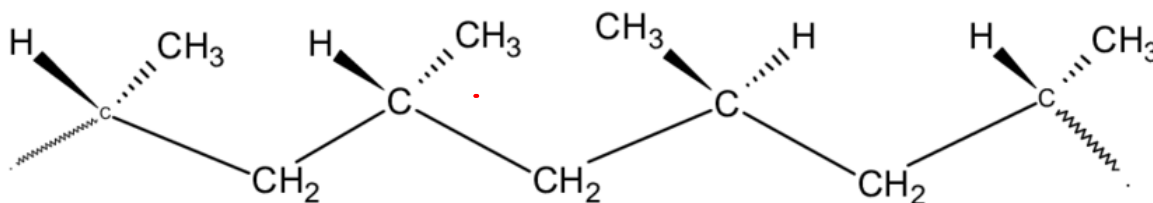A. **Isotactic** : Head – to – tail configuration
Functional groups are all on the **same side** of the mail chain.

Tacticity

B. Syndiotactic : Functional groups occupy alternating position

C. Atactic : Functional groups arranged in random manner

Atactic polypropylene is a gummy solid, while isotactic is highly crystalline and solid.

Classification of polymer

SVNIT
SURAT

Classification of polymer

Based on origin Of source

- 1.Natural polymers
- 2.semi synthetics
- 3. synthetics polymer

Based on structure

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- 3.Crossed linked polymers

Based on molecular forces

- 1.Elastomrs
- 2.Fibers
- 3.Thermoplatics
- 4.Thermosetting polymers

Based on mode of polymerization

- 1.Addition polymers
- 2.Condensation polymers

Classification of polymer

Classification based on origin:

➤ **Natural polymer** : Polymers from plants or animals.
                          Polysaccharides: cellulose, starch, cotton
                          Natural rubber : cis 1,4- polyisoprene
                          Biopolymers : proteins, polynucleotides, wool, silk

➤ **Semi -synthetic polymers**: chemically modified natural polymers to get useful polymers.

                       e.g. cellulose acetate (Rayon), cellulose nitrate.

In 1870, American inventor John Wesley Hyatt reacted cellulose nitrate with camphor at high temperature and pressure to get celluloid – **world's first plastic**.

➤ **Synthetic polymers**: Polymers that are synthesized in lab.
   e.g Polyethylene (plastic), Nylon 6,6.

Classification of polymer

Based on structure

<u>Linear polymer</u> : A linear polymer is one in which each repeating unit is linked only to two others

<u>Branched polymer</u>: Branched polymers are defined as having secondary polymer chains linked to a primary backbone, resulting in a variety of polymer architectures such as star, H-shaped

<u>Cross- linked polymer</u> : The formation of covalent bonds which hold portions of several polymer chains together is called cross-linking.
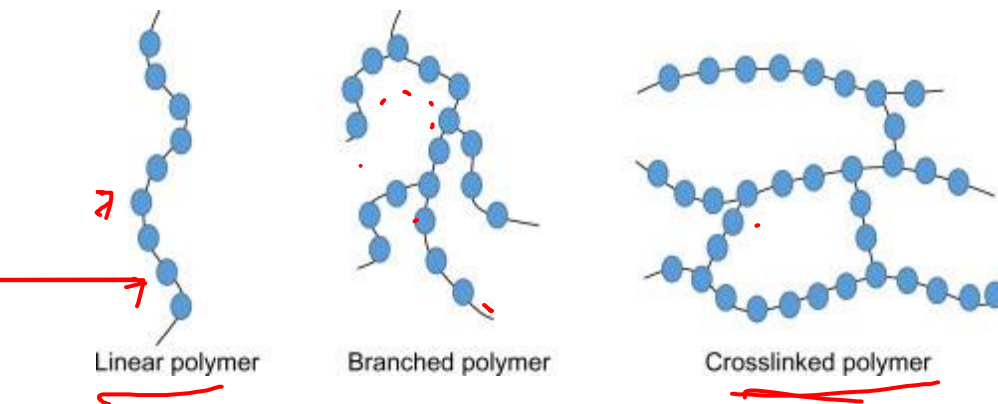
Linear polymer   Branched polymer   Crosslinked polymer
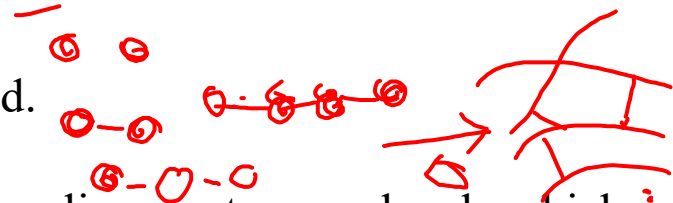
Based on Thermal Behavior

Thermoplastic:

- As the name suggests that 'thermo' means 'heat' and 'plastics' means 'formable'.

- Soften with heat, hard at room temp.

- Can be re-melt and re-processed.

- On heating, the material becomes soft, and once it becomes soft, it can be given a shape as per requirement.

- Thermoplastics are formed from large linear or branched unconnected molecules.

- During the melting process or cooling process, these polymer molecules do not undergo any chemical reaction. all the commercial polymers are mainly thermoplastics material.

Example: PVC, PE

Classification of polymer

Thermosets:
- As name suggests, 'thermo' is heat and 'set' means hardened.

- Before heating at room temperature, it is a small molecule or oligomer type molecule which has low viscosity. On heating, they react with each other, and form interlinked polymer molecules which gives cross-linking between the polymer chains in presence of a catalyst or without catalyst and forms an infinite molecular network.

- In network polymers, if there is a high degree of cross linking, then the chain motions are greatly restricted, and we have a rigid material.

- if there is less cross linking, then there could be a possibility of some amount of motion between the polymer chains within the network. So, it can be a little bit softened, elastic type material.

- As they are chemically cross-linked, so once they are formed, they are permanent and if we heat it further, it will degrade rather than become fluid again.

- Thermosets are not recyclable material. It is not like thermoplastic.

Example: Bakelite, polyester, resins.

Based on Thermal Behavior

Elastomers:

Crosslinked rubbery networks that can be stretched easily to extension (e.g., 3x or 10 x of their original dimensions) which rapidly come back to their original dimensions when the applied stress is released.

Fibers:

Polymer fibers are **a subset of man-made fibers**, which are based on synthetic chemicals by a purely physical process. These fibers are made from: polyamide nylon. PET or PBT polyester. phenol-formaldehyde (PF)

Polymerization Processes

Modern classification of polymerization according to polymerization mechanism

❖ **Step growth polymerization** : Polymers build up stepwise.

❖ **Chain growth polymerization** : Addition polymerization molecular weights increase successively, one by one monomer

Based on mode of polymerization

➤ Addition polymer:

Addition reaction : addition reactions are the reactions where two or more molecules combine to form one molecule without elimination of any small molecule as byproduct.

| | Ethylene | Bromine (brownish-red) | 1,2-Dibromoethane (colorless) |
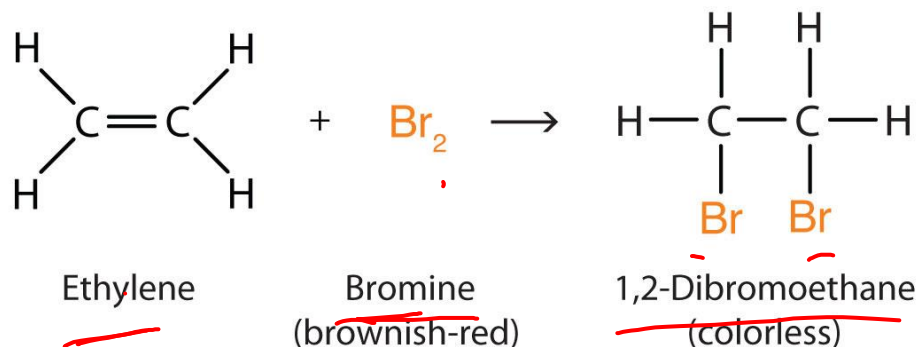
For example, if we consider this reaction between ethylene and bromine, this is a simple example of an addition reaction where two molecules are reacting and forming a product without any small molecular byproduct.
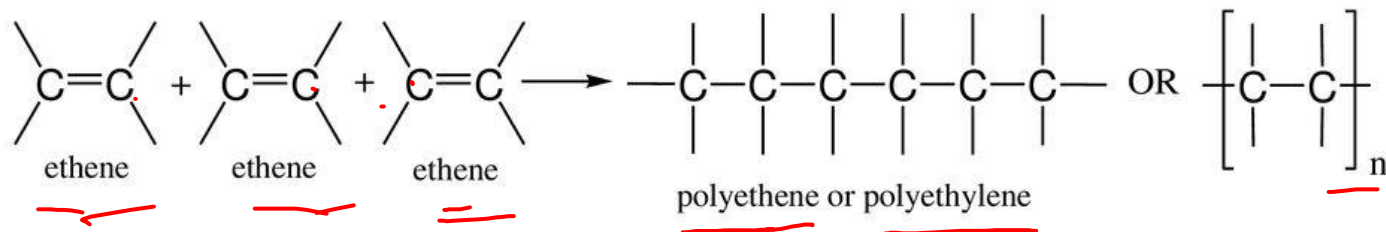
Classification of polymer

Based on mode of polymerization

Addition Polymers

• Addition polymers result from addition reactions of monomers containing carbon-carbon double bonds.

• Some examples of addition polymers include polyethene, polypropene, polyvinyl chloride, polystyrene and Teflon
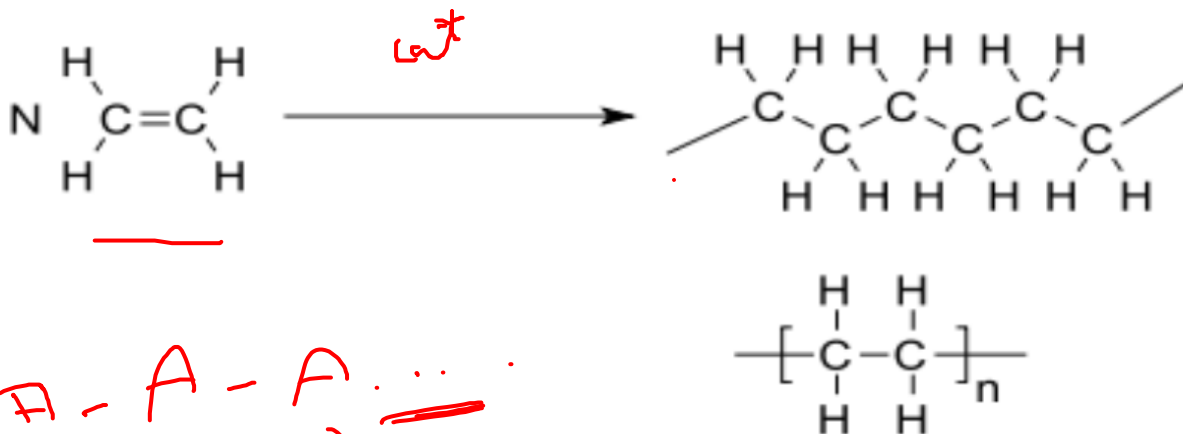
Example

ethene   ethene   ethene   polyethene or polyethylene

What is Chain Growth Polymerization

Chain growth polymerization is the process in which polymers are formed from unsaturated monomers. Chain growth polymerization is also called **addition polymerization** because monomers are added to the ends of polymer chains. The monomers are attached to the chain in the active site of the growing polymer chain, one monomer at a time. The growth of polymer chains occurs only at the ends. The steps of chain polymerization include,
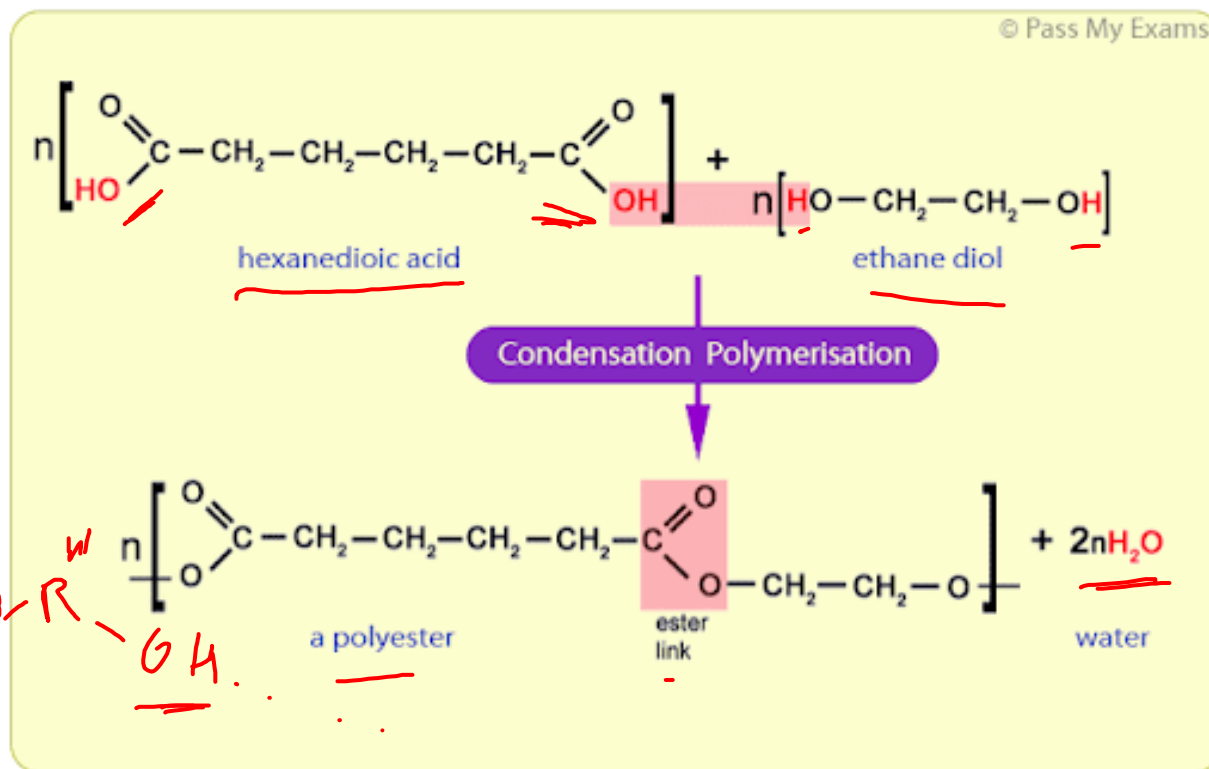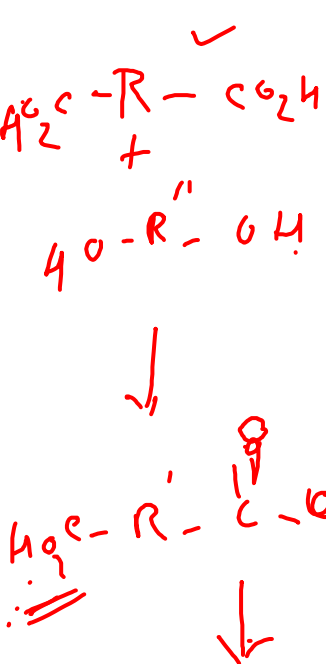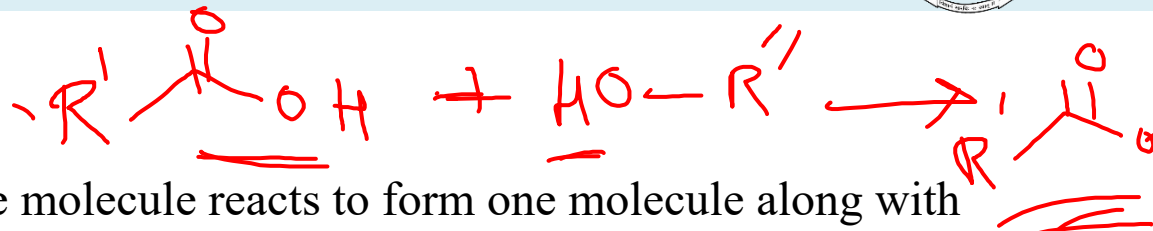
1. Initiation
2. Propagation
3. Termination

A—A—A—A⁻

Classification of polymer

Condensation polymer:

Condensation reaction: Two or more molecule reacts to form one molecule along with production of small molecule by-products like water, methanol etc.
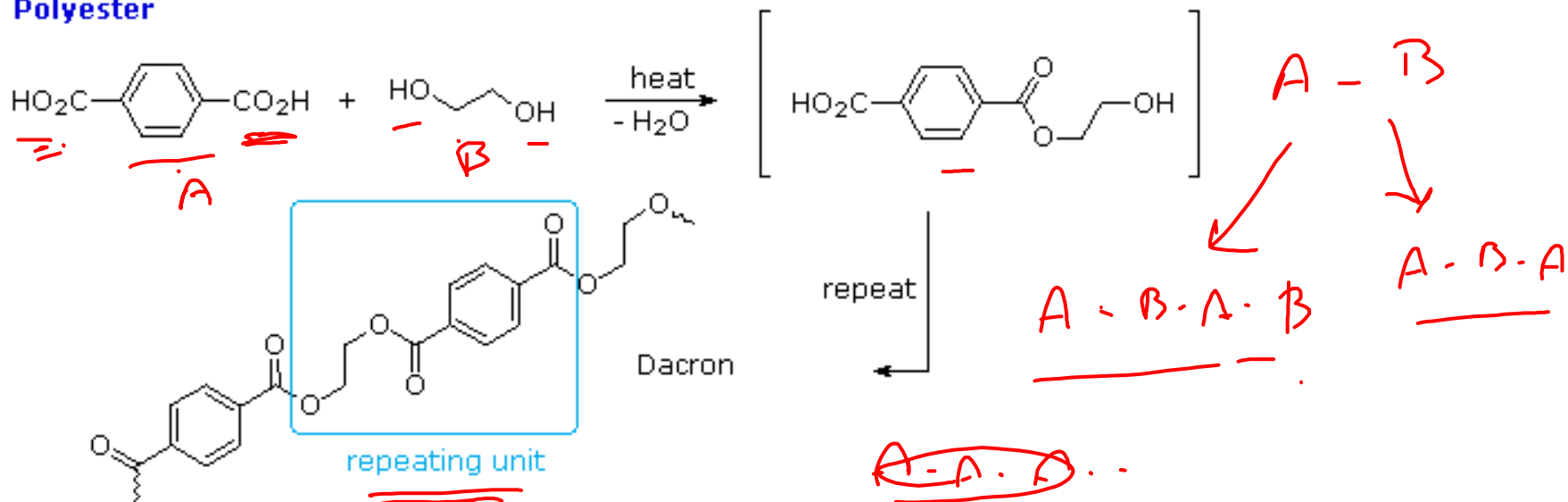

a polyester

hexanedioic acid   ethane diol

Condensation Polymerisation

ester link   water

© Pass My Exams

Condensation polymer

Examples of Condensation Polymers

Polyester
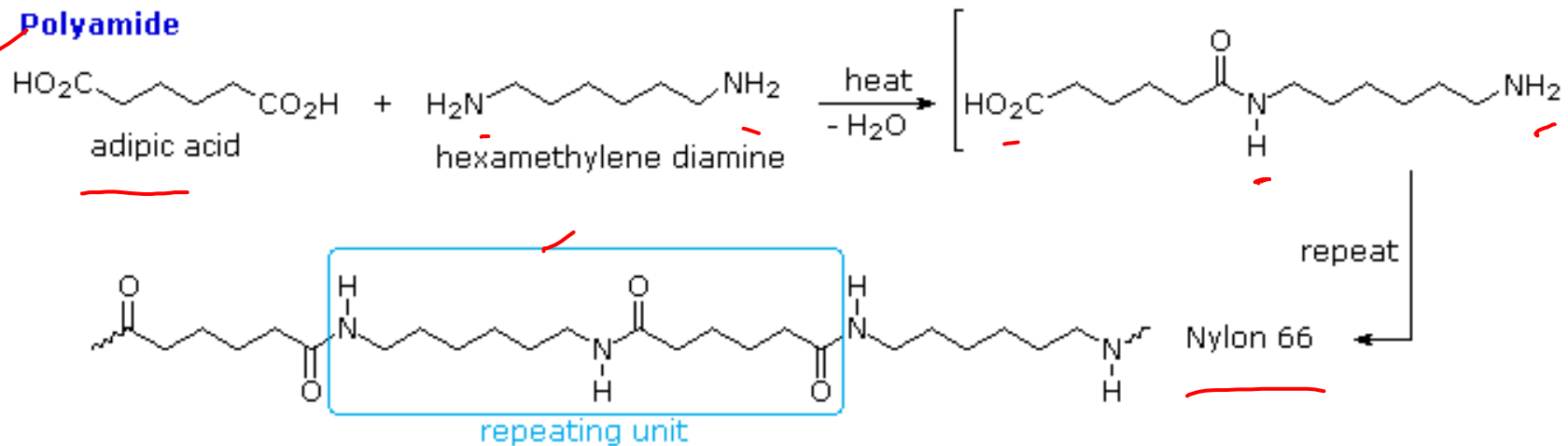
HO_2C —⟨benzene ring⟩— CO_2H + HO ⌒ OH $\xrightarrow[- H_2O]{heat}$ $[\; HO_2C$ —⟨benzene ring⟩— $C(=O)-O$ ⌒ $OH \;]$

A   *B*   A – B

repeat

Dacron

A · B · A · B   A – B – A

A – A · B ..

Polyamide

HO_2C ⌒⌒⌒ CO_2H + H_2N ⌒⌒⌒ NH_2 $\xrightarrow[- H_2O]{heat}$ $[\; HO_2C$ ⌒⌒⌒ $C(=O)-N(H)$ ⌒⌒⌒ $NH_2 \;]$

adipic acid   hexamethylene diamine

repeat

Nylon 66

repeating unit

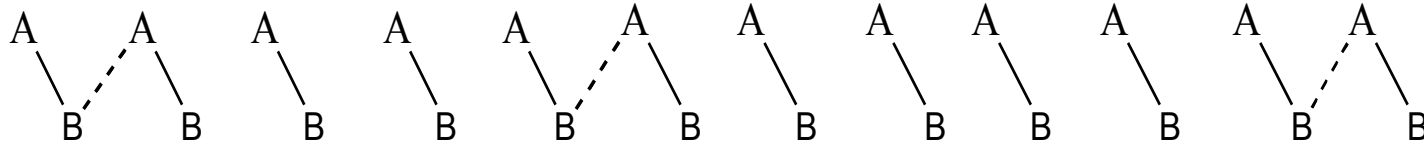- Step growth polymerization is the formation of a polymer from bi-functional or multi-functional monomers. Step growth polymerization is also known as **condensation polymerization**. Unlike in chain growth polymerization, the polymer chains here are not formed at the beginning. First, dimers, trimmers, and tetramers are formed. Then these oligomers combine with each other forming long polymer chains.

- Therefore, the monomers are not attached to the ends of polymer chains as in chain growth polymerization.
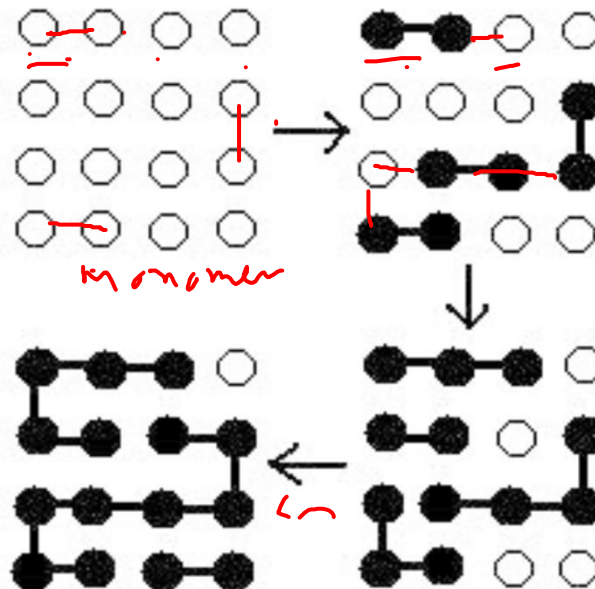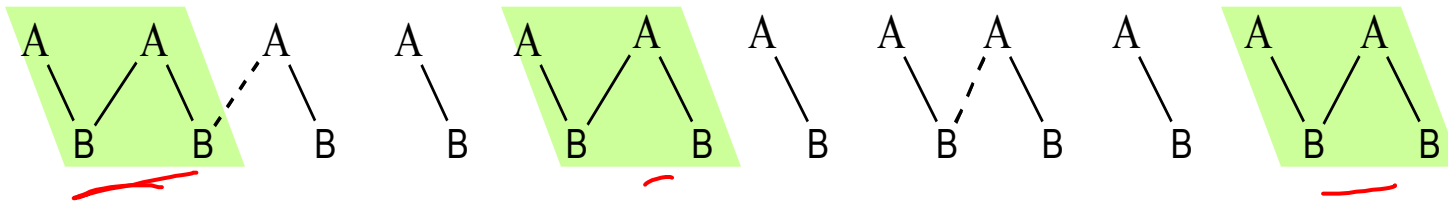
Step growth polymerization

(A) Unreacted monomer

(B) 50% reacted,

(C) 75% reacted
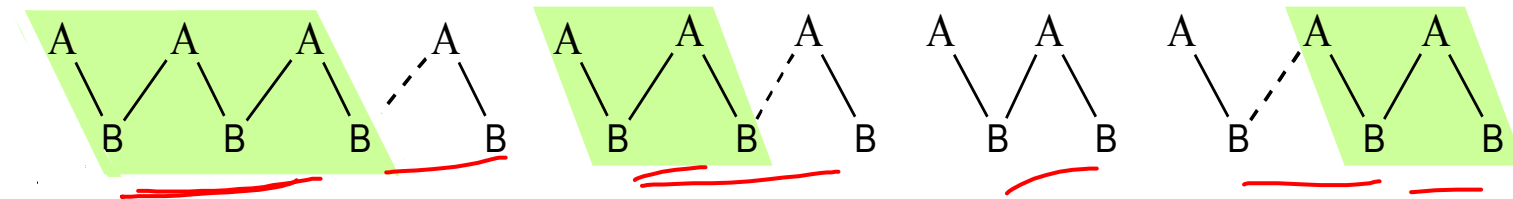
(D) 100% reacted
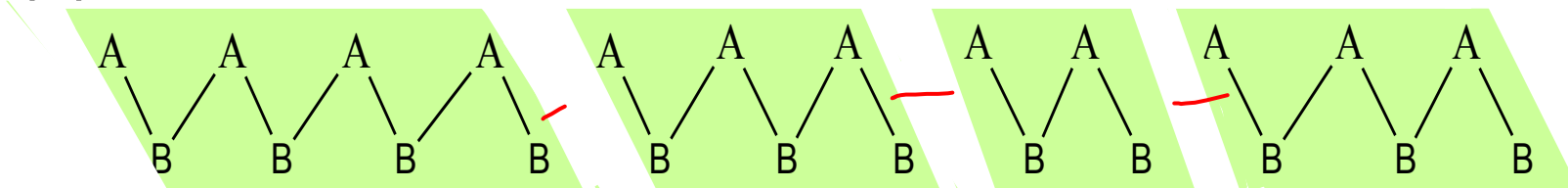
Step growth polymerization

A. Monomer to have difunctional group

1. One having both reactive functional groups in one molecule

A—R—B $\longrightarrow$ $-[R-X]-$

$$HO-R-CO_2H \longrightarrow -[O-R-\overset{\overset{O}{\|}}{C}]_n + H_2O$$

$$H_2N-R-CO_2H \longrightarrow -[NH-R-\overset{\overset{O}{\|}}{C}]_n + H_2O$$

HO—R—CO₂H
+
HO—R—CO₂H

HO—R—$\overset{O}{\overset{\|}{C}}$—O—R
co₂H
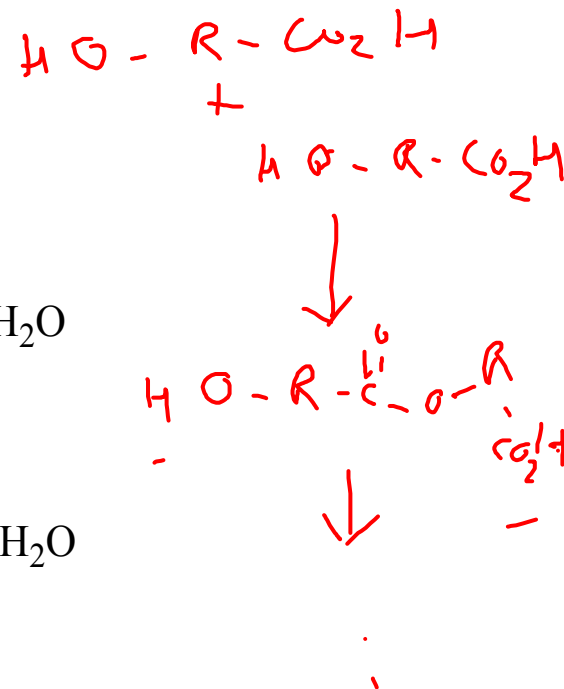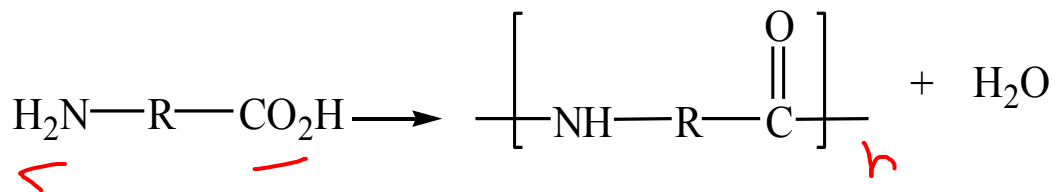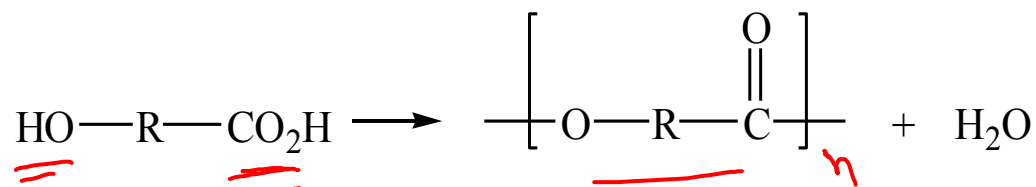
Step growth polymerization

B. Having two difunctional monomers

$$A-R-A \;+\; B-R'-B \;\longrightarrow\; -[R-X-R'-X]-$$

$$OCN-R-NCO \;+\; HO-R'-OH \;\longrightarrow$$

$$-\!\left[\underset{\overset{\|}{O}}{C}NH-R-NH\underset{\overset{\|}{O}}{C}O-R'-O\right]\!-$$

$$H_2N-R-NH_2 \;+\; \underset{\overset{\|}{O}}{Cl C}O-R'-O\underset{\overset{\|}{O}}{C}Cl \;\longrightarrow$$

$$-\!\left[\underset{\overset{\|}{O}}{C}NH-R-NH\underset{\overset{\|}{O}}{C}O-R'-O\right]\!- \;+\; 2HCl$$
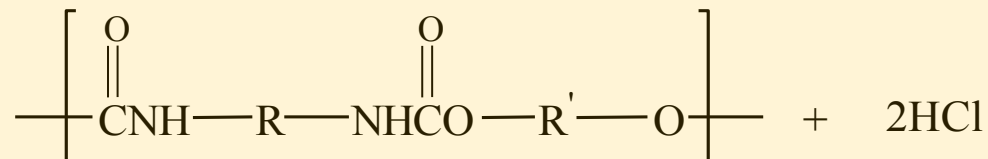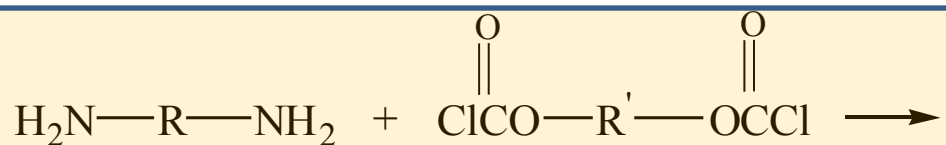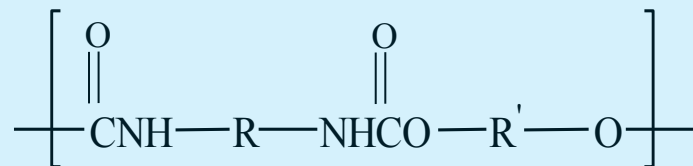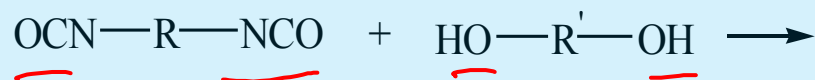
Step growth polymerization

Examples:

$$n\ HO\!-\!\!\bigcirc\!\!-\!CO_2H \longrightarrow \left[O\!-\!\!\bigcirc\!\!-\!\overset{\overset{O}{\parallel}}{C}\right]_n + nH_2O$$

$$nHO_2C\!-\!\!\bigcirc\!\!-\!CO_2H\ +\ nHOCH_2CH_2OH \longrightarrow$$

$$\left[\overset{\overset{O}{\parallel}}{C}\!-\!\!\bigcirc\!\!-\!\overset{\overset{O}{\parallel}}{C}OCH_2CH_2O\right]_n + 2nH_2O$$
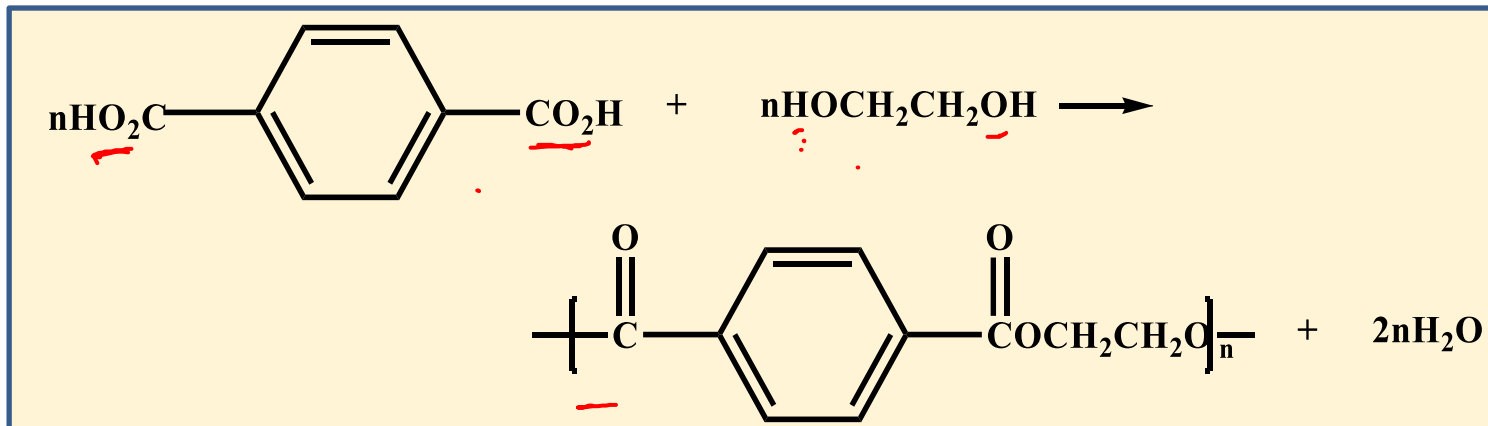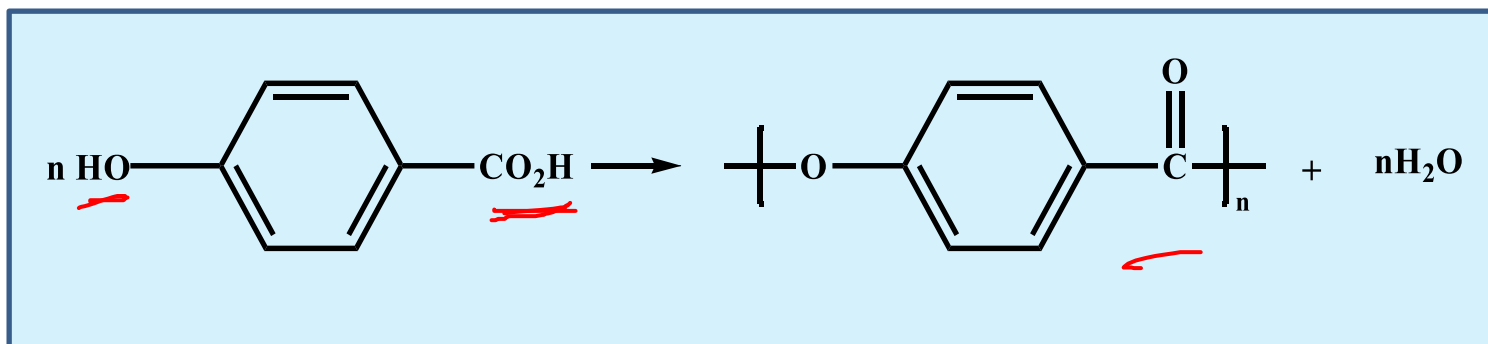
Chain Length: 4,000 – 8,000

Polyethylene Terephthalate (PETE)
"Polyester"

Ester

terephthalic acid

$$CH_2 = CH_2 \longrightarrow$$

$$-\overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}} - \overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}} - \overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}} -$$
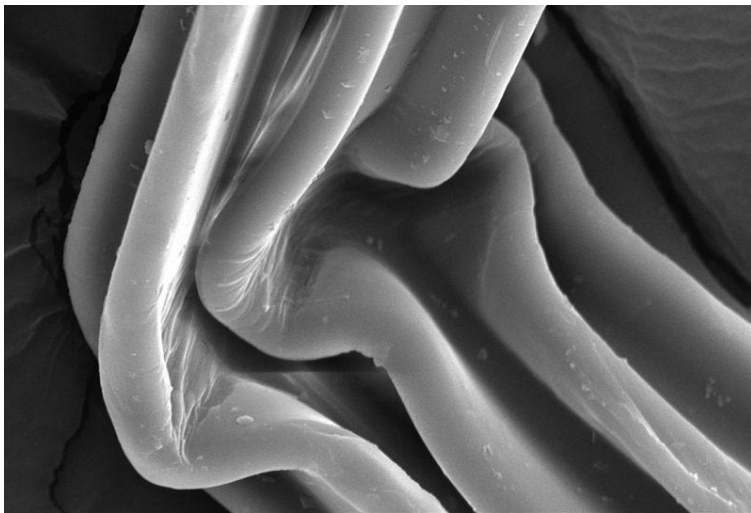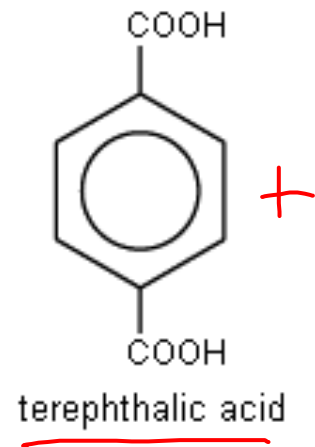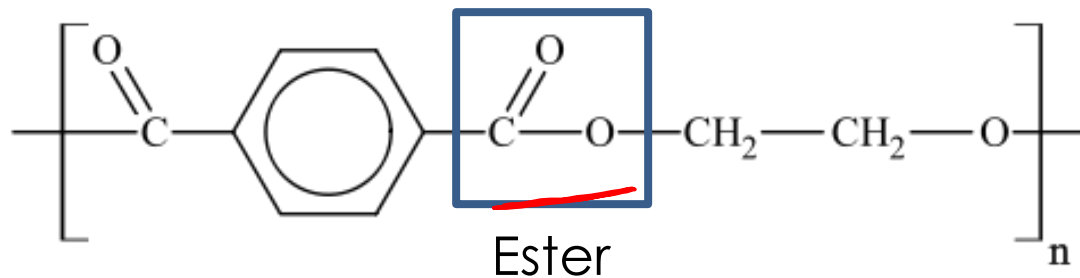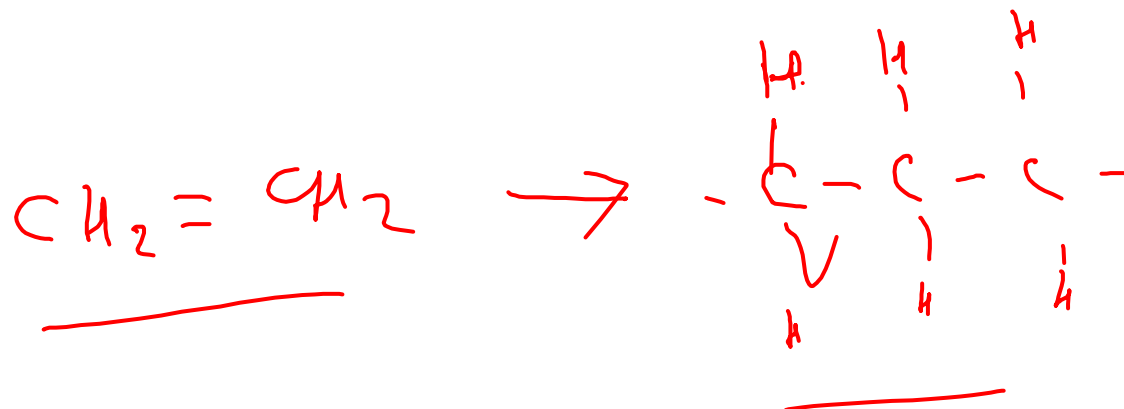
Mechanism of addition polymerization

$$CH_2 = CH_2 \xrightarrow{\text{Cat}}$$

$$-\overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}} - \overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}} - \overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}} - \overset{\overset{\displaystyle H}{\mid}}{\underset{\underset{\displaystyle H}{\mid}}{C}} -$$

- Free Radical
- Cationic
- Anionic

"Free" radical

—C•
with H above and X below
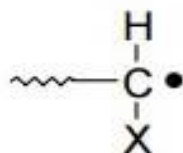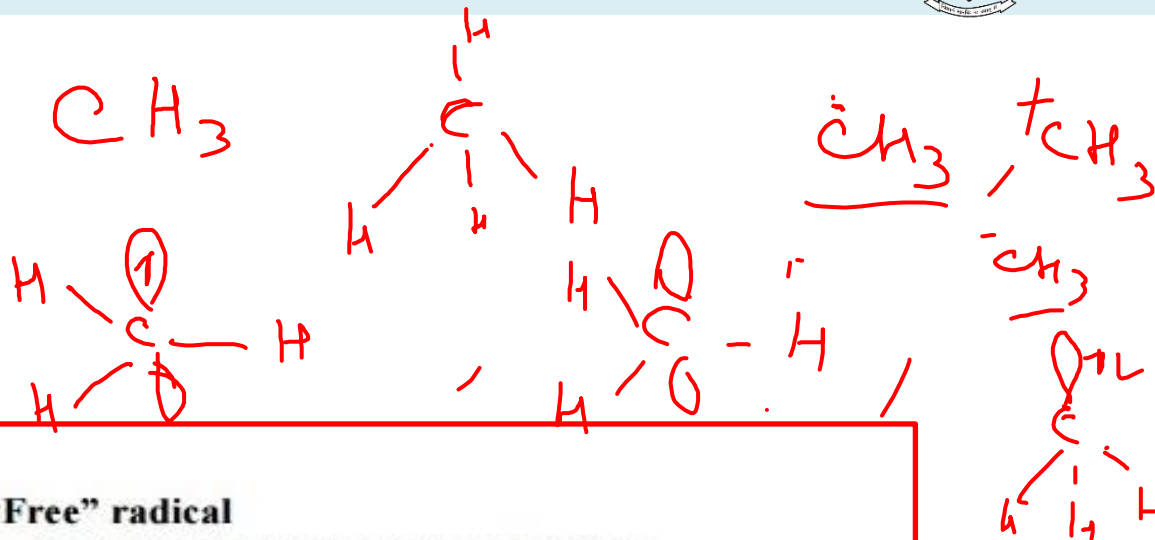
7 valence electrons, electron deficient
Charge = 0 (usually, radical ions are possible)
sp^2, planar, odd electron in "p" orbital
Stabilized by X = electron donating

Carbocation

—C ⊕
with H above and X below
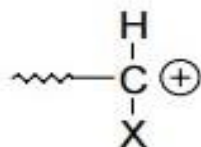
6 valence electrons, electron deficient, Lewis **acid**
Charge = +1
sp^2, planar, vacant "p" orbital
Stabilized by X = electron donating

Carbanion

—C :⊖
with H above and X below
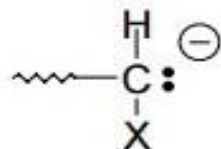
8 valence electrons, lone pair, Lewis **base**
Charge = −1
sp^3, tetrahedral, lone pair in "sp^3" orbital
Stabilized by X = electron withdrawing

❖ Usually, many low molecular weight alkenes undergo rapid polymerization reactions when treated with small amounts of a radical initiator.

❖ For example, the polymerization of ethylene .
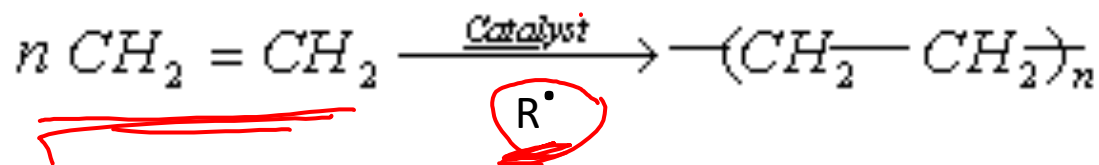
$$n\,CH_2 = CH_2 \xrightarrow[\ R^{\bullet}\ ]{Catalyst} -(CH_2 - CH_2)_n$$

Free radical polymerization

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step 1: Initiation

$$R\text{-}R \longrightarrow 2R\bullet$$

$$R^I \quad CH_2=CH_2 \longrightarrow R-CH_2CH_2\bullet$$

step 2: Propagation

$$R-CH_2CH_2\bullet \quad CH_2=CH_2 \longrightarrow R-CH_2CH_2CH_2CH_2\bullet$$

$$R-CH_2CH_2CH_2CH_2\bullet \quad CH_2=CH_2 \longrightarrow R-CH_2CH_2CH_2CH_2CH_2CH_2\bullet$$

R^I

step 3: Termination

$$2\,R{-}(CH_2CH_2)_nCH_2CH_2{\bullet} \longrightarrow R{-}(CH_2CH_2)_nCH_2CH_2{-}CH_2CH_2(CH_2CH_2)_nR$$

$$2\,R{-}(CH_2CH_2)_nCH_2CH_2{\bullet} \longrightarrow R{-}(CH_2CH_2)_nCH{=}CH_2\;+\;R{-}(CH_2CH_2)_nCH_2CH_3$$

(handwritten annotations:)

$R - CH_2 - CH_2$

$R - CH - CH_2$ with H

O^-

$- R - CH_2\ CH_3$
$+$
$- R - CH = CH_2$
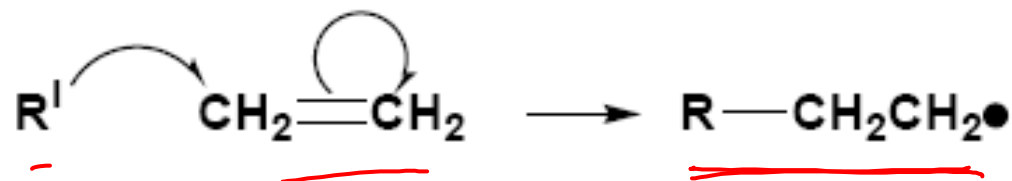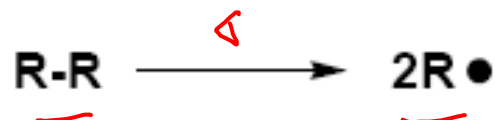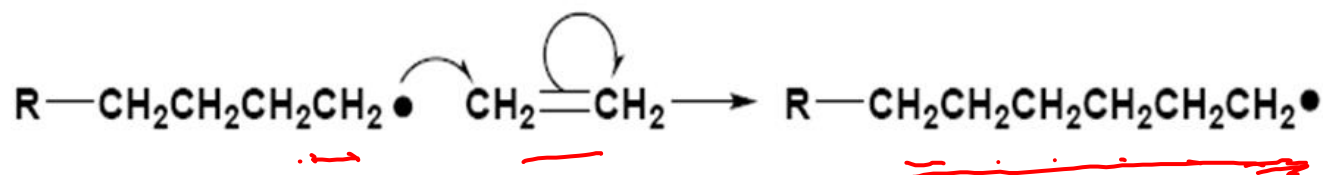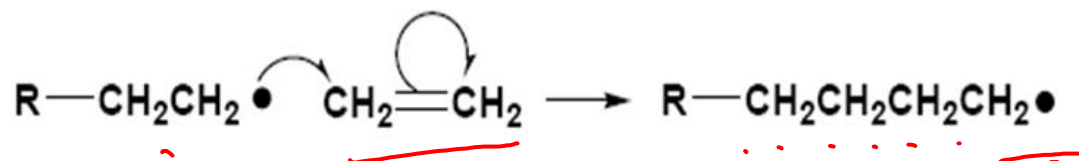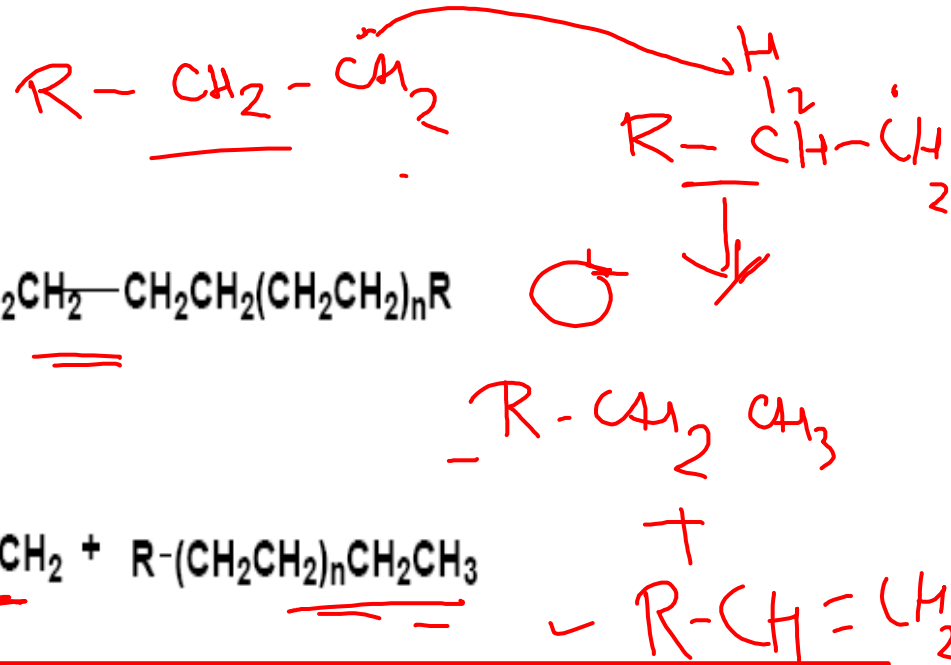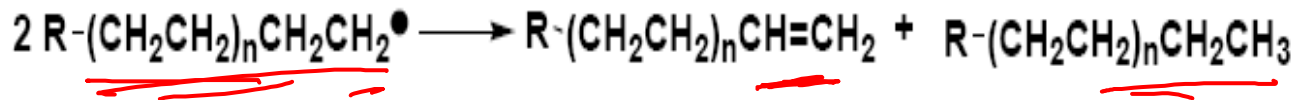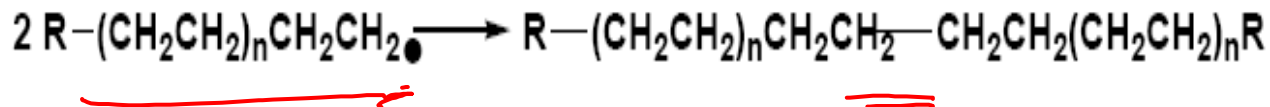
Branching of the Polymer Chain

$$R{-}CH_2CH_2CH_2\dot{C}H_2 \;+\; R{-}CH_2CH_2\dot{C}HCH_2CH_2CH_2{-}$$
(with H above)

$$\downarrow$$

$$-CH_2CH_2CH_2\overset{H}{C}H_2 \;+\; -CH_2CH_2\overset{\cdot\cdot}{C}HCH_2CH_2CH_2{-} \xrightarrow{\;CH_2=CH_2\;} -CH_2CH_2\overset{}{C}HCH_2CH_2CH_2{-}$$

$\dot{C}H_2$
|
CH_2

Application
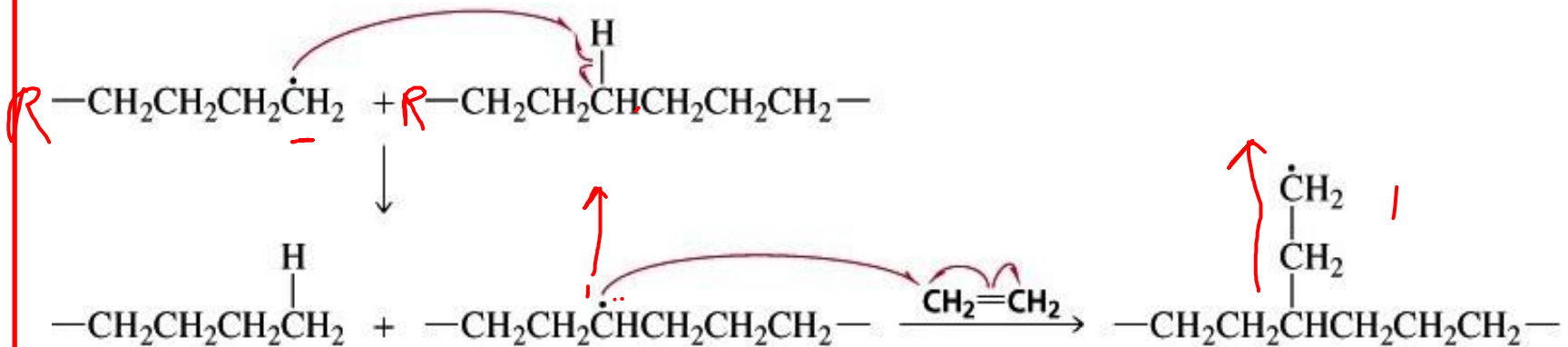
Table 28.2   Examples of Alkenes That Undergo Radical Polymerization
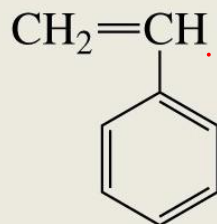
$CH_2=CH$

(benzene ring)

styrene

$CH_2=CH$
$OCCH_3$
O

vinyl acetate

$CH_2=CCH_3$
$COCH_3$
O

methyl methacrylate

$CH_2=CH$
Cl

vinyl chloride

$CH_2=CH$
$C\equiv N$

acrylonitrile

$CH_2=CH$
$CH=CH_2$
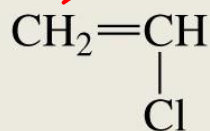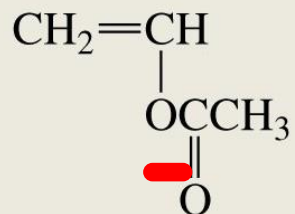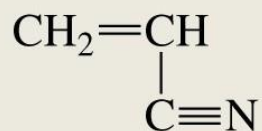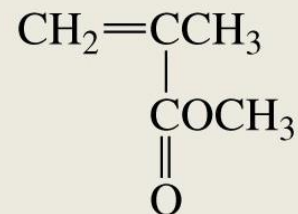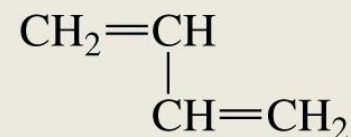
1,3-butadiene

Cationic polymerization

chain-initiating step
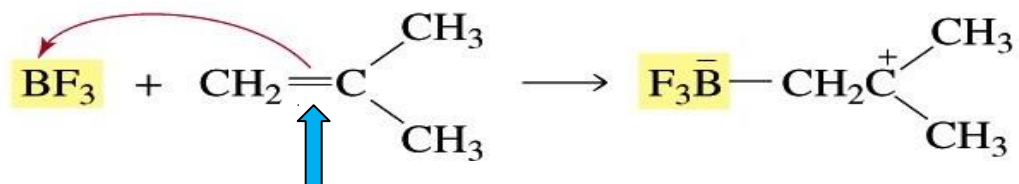
the alkene monomer
reacts with an electrophile

chain-propagating steps

propagating sites
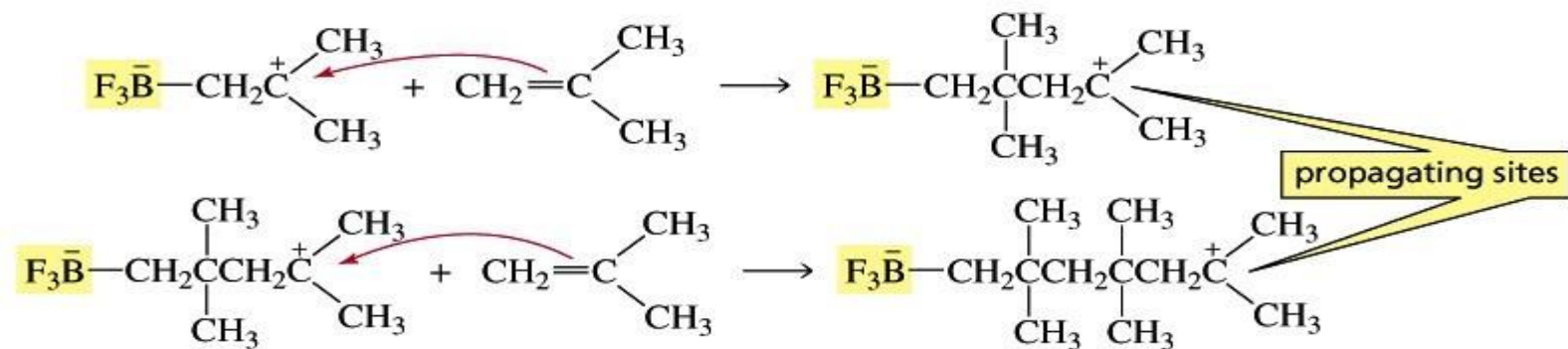
Cationic polymerization

chain-terminating steps
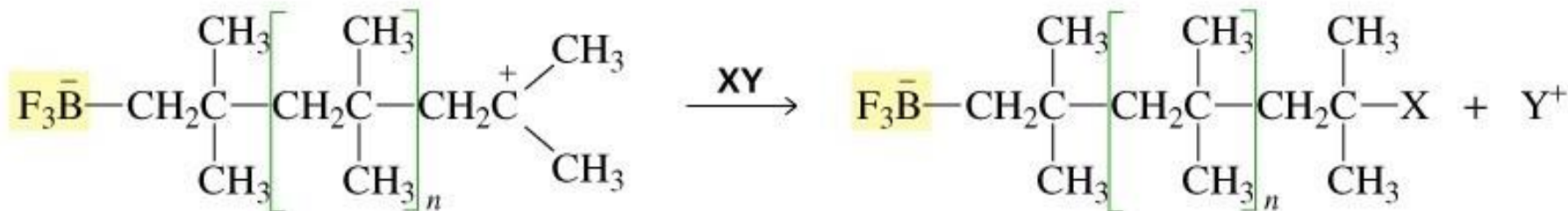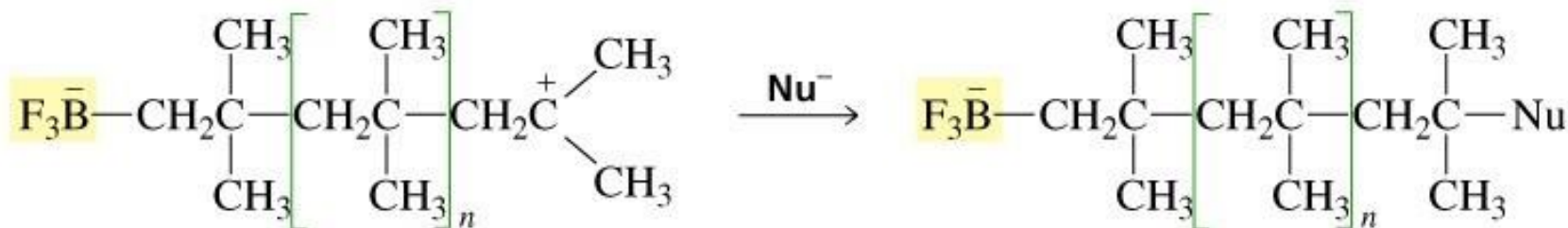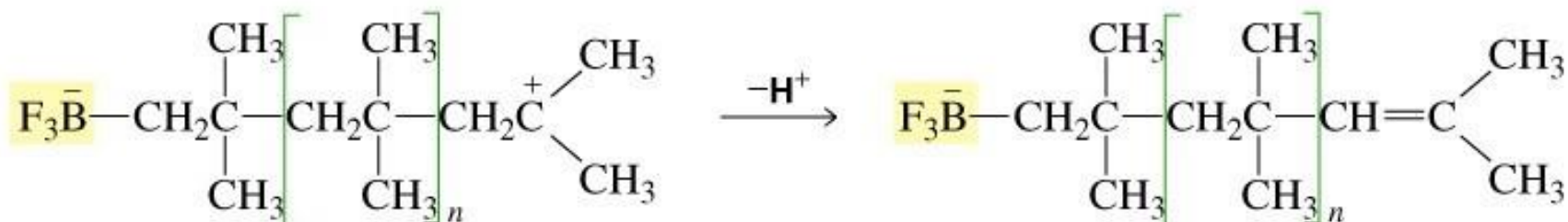
Cationic polymerization

Table 28.4   Examples of Alkenes That Undergo Cationic Polymerization
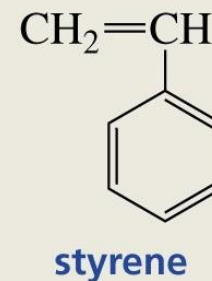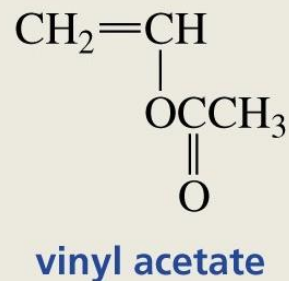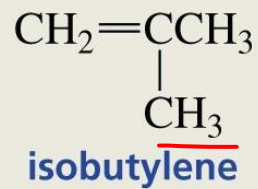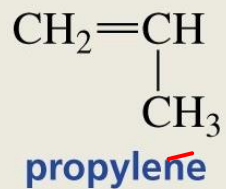
$$CH_2\!\!=\!\!CH$$
$$|$$
$$CH_3$$
propylene

$$CH_2\!\!=\!\!CCH_3$$
$$|$$
$$CH_3$$
isobutylene

$$CH_2\!\!=\!\!CH$$
$$|$$
$$OCCH_3$$
$$\|$$
$$O$$
vinyl acetate

$$CH_2\!\!=\!\!CH$$
styrene

CHAIN GROWTH POLYMERIZATION
V E R S U S
STEP GROWTH POLYMERIZATION

CHAIN GROWTH POLYMERIZATION	STEP GROWTH POLYMERIZATION
Chain growth polymerization is the formation of polymers from unsaturated monomers	Step growth polymerization is the formation of a polymer from bi-functional or multifunctional monomers
A polymer chain is formed at the beginning by the attachment of one monomer at a time	Oligomers are formed at the beginning and are later combined together, forming the polymer chain
Monomers are unsaturated	Monomers are bi-functional or multifunctional
There is no rapid loss of monomers at the beginning	A rapid loss of monomers can be observed at beginning

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CHAIN GROWTH POLYMERIZATION
VERSUS
STEP GROWTH POLYMERIZATION

Chain Growth Polymerization	Step Growth Polymerization
An active site can be observed at the end of the polymer chain	All the monomers are active themselves
Requires initiators to break the double bond in monomer molecule	Does not require initiators
Shows no growth of polymer chain after termination	Shows no termination
Any type of molecules can be observed	Only monomers and polymers are observed

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Polymerization Processes

Polymerization Techniques

❖ Bulk Polymerization

❖ Solution Polymerization

❖ Suspension Polymerization

❖ Emulsion Polymerization

Bulk Polymerization

Monomer + Initiator + Chain transfer agent
(liquid state)

↓
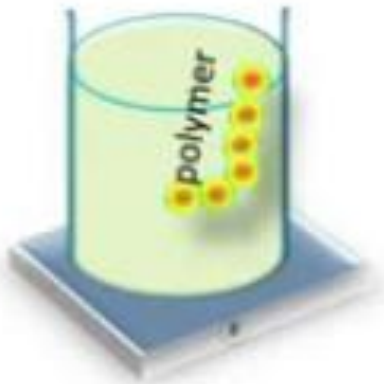
Polymer

Mass or block polymerization:

❖ Polymerization of the **undiluted** monomer.

❖ Carried out by adding a soluble <u>initiator</u> to pure <u>monomer</u> (**in liquid state**).

❖ The mixture is constantly agitated & heated to polymerization temperature.

❖ Once the reaction starts, heating is stopped as the reaction is exothermic.

❖ The heat generated is dissipated by circulating water jacket.

❖ Viscosity increases dramatically during conversion.

• It is usually adopted to produce polystyrene, polyvinyl chloride, polymethyl methacrylate and low density polyethylene.

Bulk Polymerization

Monomer + Initiator + Chain transfer agent
(liquid state)

↓
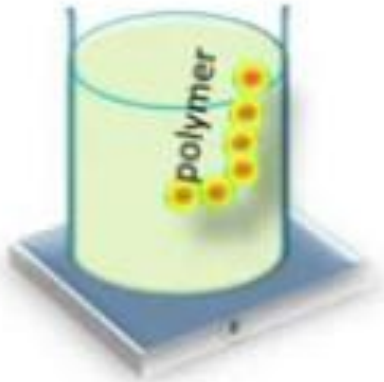
Polymer

Advantages:

❖ High yield per reactor volume

❖ Easy polymer recovery

❖ The option of casting the polymerisation mixture into final product form.

Bulk Polymerization

Advantages

- The system is simple and requires thermal insulation.
- The <u>polymer</u> is obtained pure.
- Large castings may be prepared directly.
- Molecular weight <u>distribution</u> can be easily changed with the use of a chain transfer agent.

Disadvantages

- Heat transfer and mixing become difficult as the viscosity of reaction mass increases.
- Highly exothermic.
- The polymerization is obtained with a broad molecular weight distribution due to the high viscosity and lack of good heat transfer.
- Very low molecular weights are obtained

Chain Transfer Reactions

Solution Polymerization
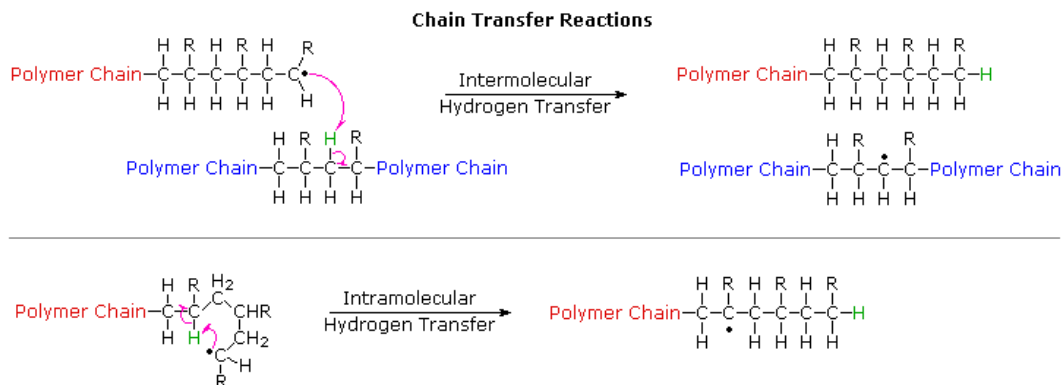
Solution Polymerization

Definition: A polymerization process in which the monomers and the polymerization initiators are dissolved in a nonmonomeric liquid solvent at the beginning of the polymerization reaction. The liquid is usually also a solvent for the resulting polymer or copolymer.

❏ Some disadvantages of bulk polymerization are eliminated in solution polymerization.

❏ Monomer along with initiator dissolved in solvent.

❏ The mixture is kept at polymerization temperature & constantly agitated.

❏ Depending on concentration of monomer the viscosity of solution does not increase.

Solution Polymerization

❑ After the reaction is over, the polymer is used as such in the form of polymer solution or the polymer is isolated by evaporating the solvent.

❑ Polymer so formed can be used for surface coating.

❑ It is used for the production of Polyacrylonitrile, PVC, Polyacrylic acid, Polyacrylamide, Polyvinyl alcohol, PMMA, Polybutadiene, etc

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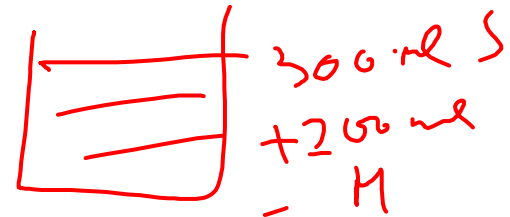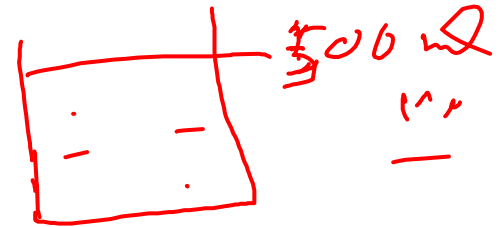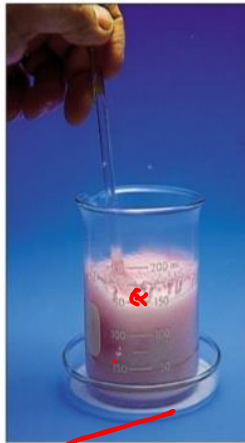
Advantages

- The solvent acts as a diluent & helps in facilitating continuous transfer of heat of polymerization. Therefore temperature control is easy.

- The solvent allows easy stirring as it decreases the viscosity of reaction mixture.

- Solvent also facilitates the ease of removal of polymer from the reactor.

- Viscosity build up is negligible.

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Disadvantages

- To get pure polymer, evaporation of solvent is required additional technology, so it is essential to separate & recover the solvent.

- The method is costly since it uses costly solvents. Polymers of high molecular weight polymers cannot be formed as the solvent molecules may act as chain terminators.

- The technique gives a smaller yield of polymer per reactor volume, as the solvent waste the reactor space.

- The purity of product is also not as high as that of bulk polymerization. Removal of last traces of solvent is difficult.

Suspension Polymerization

➤ Liquid or dissolved *monomer suspended in liquid* phase like water.

➤ *Initiators used are monomer soluble* e.g. dibenzoyl peroxide.

➤ Thus, polymer is produced in heterogeneous medium.

➤ The size of monomer droplets is **50-200 µm** in diameter.

➤ The dispersion is maintained by continuous agitation and *the droplets are prevented to coalesce* (unite or merge) by *adding small quantity of stabilizers*.

Suspension Polymerization

Suspension Polymerization

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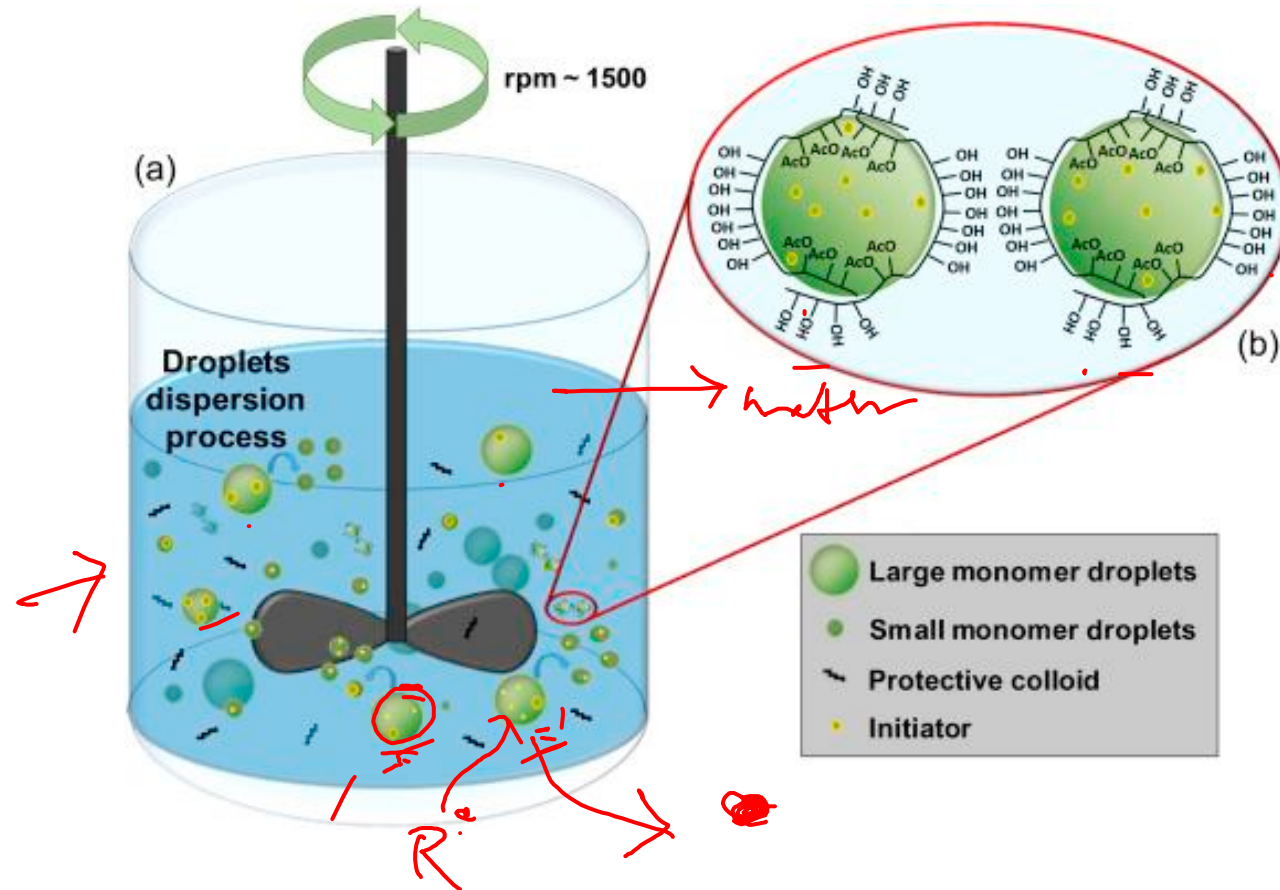
➢ The stabilizers used are ***PVA, gelatin, cellulose*** are used along with inorganic stabilizers such as ***kaolin, magnesium silicate, aluminum hydroxide, calcium/magnesium phosphate***, etc if necessary.

➢ As it concerns with droplets, ***each droplet is tiny bulk reactor***. The polymerization takes place ***inside the droplet*** & product formed being ***insoluble in water***.

➢ The product separated out in the form of ***spherical pearls or beads*** of polymer.

➢ Hence the technique is also known as **Pearl polymerization / Granular polymerization / Bead polymerization.**

Suspension polymerization

Styrene + BPO + rGO

H₂O + Gelatine

Digital photos of pure PS and PS/rGO beads

SEM images of PS/rGO beads

Suspension Polymerization

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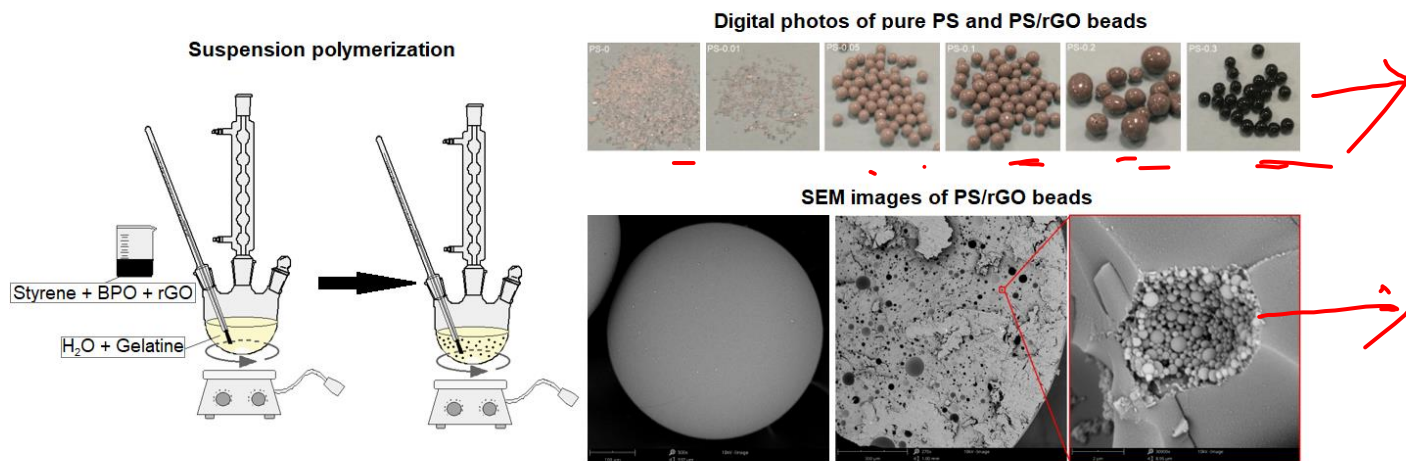
Advantages

- The process is comparatively cheap as it involves only water instead of solvents.
- Viscosity increase is negligible.
- Agitation & temperature control is easy.
- Product isolation is easy since the product is insoluble in water.

Disadantages

- The method can be adopted only for water insoluble monomers.
- It is difficult to control polymer size.
- Polymer purity is low due to the presence of suspending & stabilizing additives that are difficult to remove completely.
- Suspension polymerization reaction is highly agitation sensitive.
- Larger volume of reactor is taken up by water.
- The method cannot be used for tacky polymers such as elastomers because of the tendency for agglomeration of polymer particles.

Emulsion Polymerization

Emulsion polymerization is a type of radical polymerization that usually starts with an emulsion incorporating water, monomer and surfactant.

Emulsion polymerization process

Monomer droplet

Monomer droplet (µm) (reservoir)

Polymerization

Polymer particles (nm)

Entry initiator

Emulsion polymerization occurs within the swollen micelles by reposition the monomer
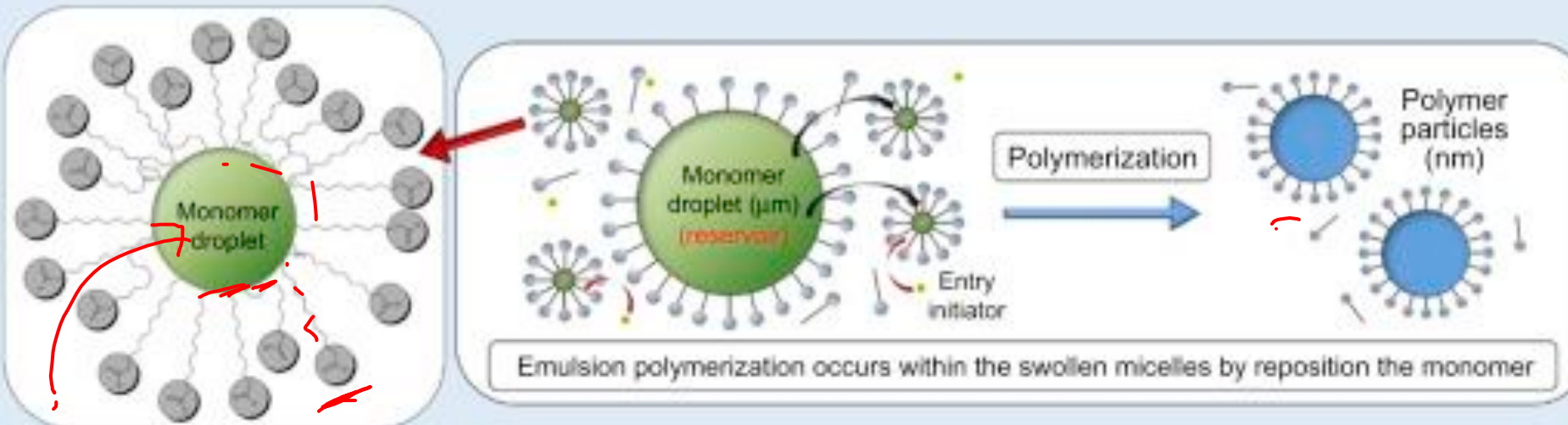
Emulsion Polymerization

- The technique is used for the production of large number of commercial plastics & elastomers.

- The system consists of water insoluble monomer, dispersion medium & emulsifying agents or surfactants (soaps and detergents) and a water soluble initiator (potassium persulphate / H_2O_2, etc).

- The monomer is dispersed in the aqueous phase, not as a discrete droplets, but as a uniform emulsion.

- The size of monomer droplet is around 0.5 to 10 μm in diameter depending upon the polymerization temperature & rate of agitation.

Emulsion Polymerization

- The emulsion of monomer in water is stabilized by a surfactant.

- A surfactant has a hydrophilic and hydrophobic end in its structure.

- When it is put into a water, the surfactant molecules gather together into aggregates called micelles.

- The hydrocarbon tails (hydrophobic) orient inwards & heads (hydrophilic) orient outwards into water.

- The monomer molecules diffuse from monomer droplets to water & from water to the hydrocarbon centre of micelles.

Emulsion Polymerization

Advantages

- High molecular weight polymers
- fast polymerization rates.
- 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

- Surfactants and polymerization adjuvants -difficult to remove
- For dry (isolated) polymers, water removal is an energy-intensive process
- Designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.
- Can not be used for condensation, ionic polymerization.

This process involves fabrication of plastic material into desired shape under the influence of heat and pressure in a closed chamber.

Types of Moulding:
1. **Compression Moulding**
2. **Injection Moulding**
3. **Transfer Moulding**
4. **Extrusion Moulding**
5. **Blow Moulding**

Moulding Processes
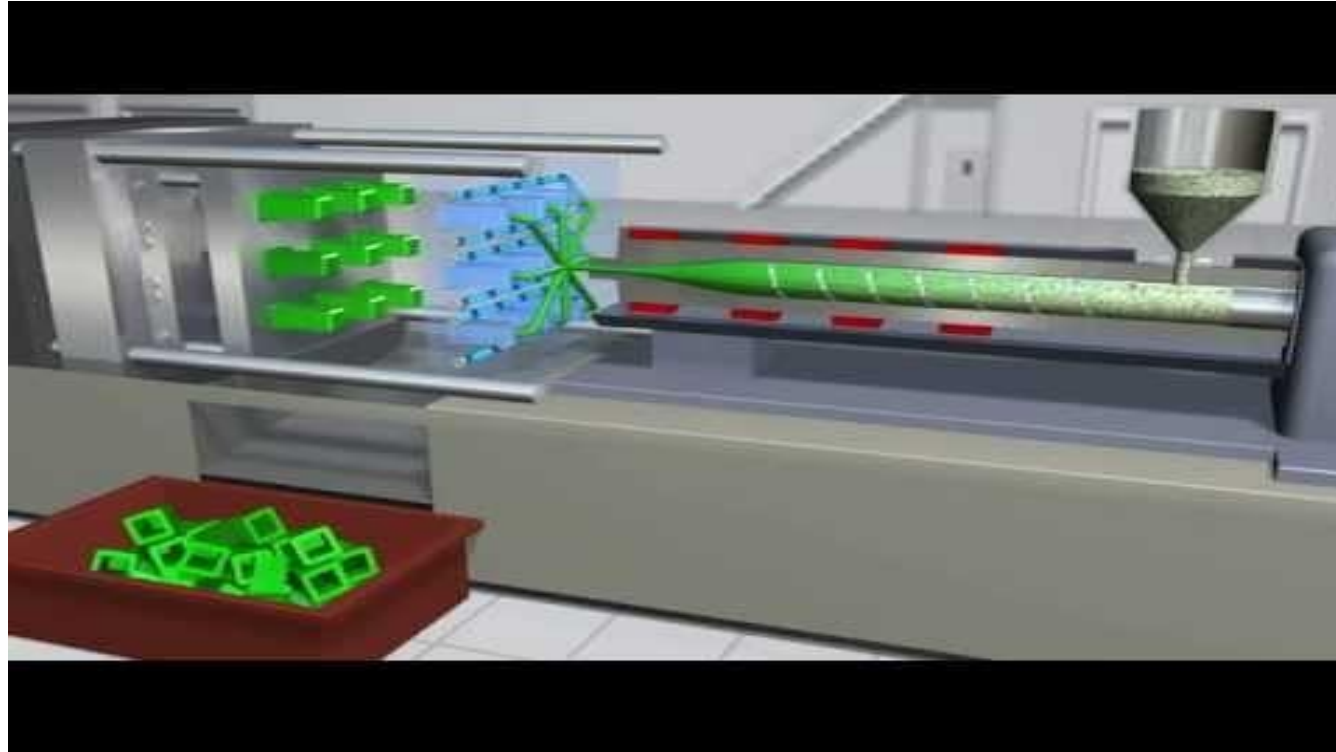
Extrusion Moulding

- Extrusion is a process of manufacturing long products of constant cross-section (rods, sheets, pipes, films, wire insulation coating) forcing soften polymer through a die with an opening.

- Polymer material in form of pellets is fed into an extruder through a hopper. The material is then conveyed forward by a feeding screw and forced through a die, converting to continuous polymer product.

- Heating elements, placed over the barrel, soften and melt the polymer. The temperature of the material is controlled by thermocouples.

- The product going out of the die is cooled by blown air or in water bath.

Extrusion of polymers

Extrusion Moulding
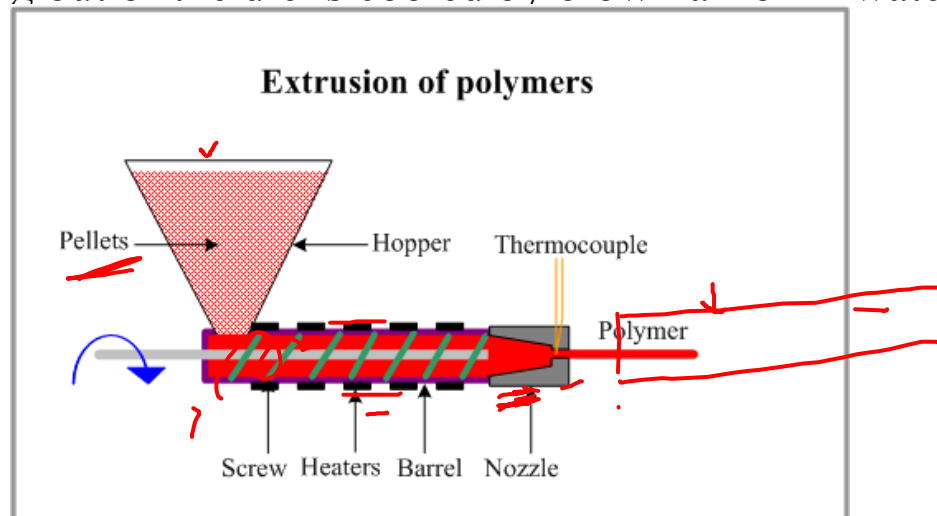
- Extrusion of polymers (in contrast to extrusion of metals) is continuous process lasting as long as raw pellets are supplied.

- Extrusion is used mainly for Thermoplastics, but Elastomers and Thermosets may also be extruded. In this case cross-linking forms during heating and melting of the material in the extruder.

- The thermoplastic extruded products may be further formed by the Thermoforming method.

Injection Moulding

- Injection Molding is a process in which molten polymer is forced under high pressure into a mold cavity through an opening (sprue).

- Polymer material in form of pellets is fed into an Injection Molding machine through a hopper. The material is then conveyed forward by a feeding screw and forced into a split mold, filling its cavity through a feeding system with sprue gate and runners.
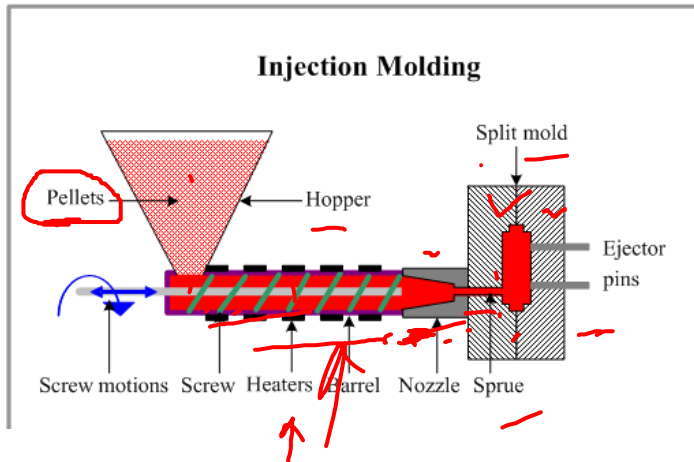
Injection Molding

Injection Moulding of polymers

- Injection Molding machine is similar to Extruder. The main difference between the two machines is in screw operation. In extruder screw rotates continuously providing output of continuous long product (pipe, rod, sheet). Screw of injection molding machine is called reciprocating screw since it not only rotates but also moves forward and backward according to the steps of the molding cycle.

- It acts as a ram in the filling step when the molten polymer is injected into the mold and then it retracts backward in the molding step.

- Heating elements, placed over the barrel, soften and melt the polymer.

- The mold is equipped with a cooling system providing controlled cooling and solidification of the material.

- The polymer is held in the mold until solidification and then the mold opens and the part is removed from the mold by ejector pins.

- Injection Molding is used mainly for Thermoplastics, but Elastomers and Thermosets are also may be extruded. In this case cross-linking occurs during heating and melting of the material in the heated barrel.

Injection Moulding of polymers

- Injection Molding is highly productive method providing high accuracy and control of shape of the manufactured parts. The method is profitable in mass production of large number of identical parts.

- Thermoplastics commonly used in Injection Molding are as follows:

- Polypropylene (PP)
- Polycarbonate (PC)
- Acrylonitrile-Butadiene-Styrene (ABS)
- Nylon 6 (N6)

- Injection Molding is used for manufacturing DVDs, pipe fittings, battery casings, toothbrush bases, bottle lids, disposable razors, automobile bumpers and dash boards, power-tool housing, television cabinets, electrical switches, telephone handsets, automotive power brake, automotive fascias, transmission, and electrical parts, mirror housings, steam irons, washer pumps, spoilers, butter tubs, moisture vaporizers, yogurt containers, toilet seats, cell-phone housings, cradles or bases for personal digital assistants, case of a notebook-computer, computer mouse, electrical connector housings, lawn chairs, automotive ashtrays, and cookware appliance handles and knobs, aerosol caps, household items, bottle caps, toys

Compression molding of polymers

- Compression Molding is a process in which a molding polymer is squeezed into a preheated mold taking a shape of the mold cavity and performing curing due to heat and pressure applied to the material.

- The method is used mostly for molding thermosetting resins (thermosets), but some thermoplastic parts may also be produced by Compression Molding.

- The method uses a split mold mounted in a hydraulic press

Compression Molding

Upper movable mold half
Charge
Lower fixed mold half
Ejector pin

Compression Molding process involves the following steps

- A pre-weighed amount of a polymer mixed with additives and fillers (charge) is placed into the lower half of the mold. The charge may be in form of powders, pellets, putty-like masses or pre-formed blanks.

- The charge is usually preheated prior to placement into the mold. Preheated polymer becomes softer resulting in shortening the molding cycle time.

- The upper half of the mold moves downwards, pressing on the polymer charge and forcing it to fill the mold cavity.
- The mold, equipped with a heating system, provides curing (cross-linking) of the polymer (if thermoset is processed).

- The mold is opened and the part is removed from it by means of the ejector pin.
- If thermosetting resin is molded, the mold may be open in hot state – cured thermosets maintain their shape and dimensions even in hot state.

- If thermoplastic is molded, the mold and the molded part are cooled down before opening.

Compression molding of polymers

- Materials commonly processed by Compression Molding are:

- Epoxies (EP)
- Urea Formaldehyde (UF)
- Melamine Formaldehyde (MF)
- Phenolics (PF)

- Compression Molding is used for manufacturing electrical wall receptacles, brush and mirror handles, meter cases, trays, circuit breakers, cookware knobs, clothes dryer blower fan blade, electronic and cooking utensils, milling machine adjustment wheel, automotive parts, water testing equipment buttons, television cabinets, dinnerware, appliance housings, radio cases, aircraft main power terminal housing, hoods, pot handles, spoilers, electric plugs and sockets, fenders, dinnerware plates, scoops.

Molecular weight of polymers

❖ Polymer molecular weights are very large, typically ranging from a few thousands to a million.

❖ Unlike conventional chemicals, the molecular weight within any polymer sample is not uniform.

❖ Polymers are not typical molecules. They contain a mixture of chain lengths.

❖ The number of repeat units that a polymer chain has is referred to as the degree of polymerization. Moreover, it is common to refer to a polymer chain as an "i-mer" where "i" represents the number of repeat units on that particular chain.

8-mer

16-mer

21-mer
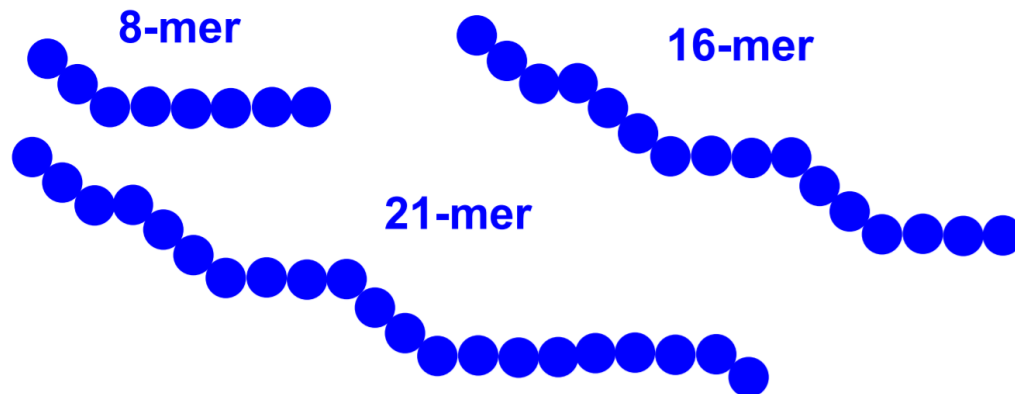
❖ Owing to this non-uniformity, molecular weights of a polymer sample is expressed in average quantity.

- The **number-average molecular weight** provides a measure of the likelihood of selecting a _**polymer chain**_ from the mixture with a given molecular weight.

6-mer   **10-mer**   **16-mer** $M_0 = 100$ g mol^{-1}
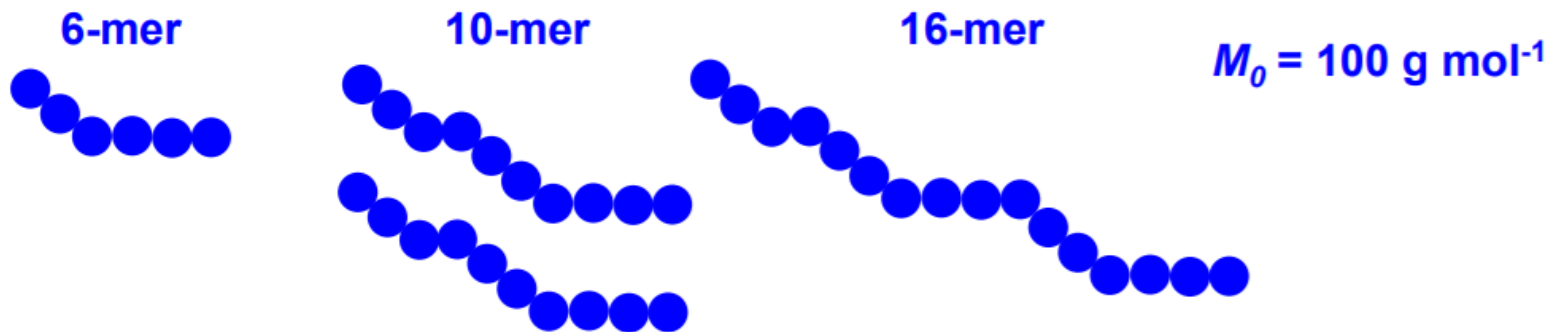
Probability of selection an i-mer from Mixture = Mole Fraction of an i-mer: $x_i = \dfrac{n_i}{\sum\limits_i n_i}$

Molar Mass of a Repeat Unit: M_0

Molecular Weight of an i-mer with i number of repeat units: $M_i = i \times M_0$

Number-average Molecular Weight:

$$M_n = \sum_i x_i M_i = \frac{\sum\limits_i M_i n_i}{\sum\limits_i n_i} = M_0 \frac{\sum\limits_i i n_i}{\sum\limits_i n_i} = 1{,}050 \; g \; mol^{-1}$$

Determination of the Number-average Molecular Weight (Mn)

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The following the molecular weight distribution obtained from Size Exclusion Chromatography

Number of Molecules	Mass of each Molecule
1	800,000
3	750,000
5	700,000
8	650,000
10	600,000
13	550,000
20	500,000
13	450,000
10	400,000
8	350,000
5	300,000
3	250,000
1	200,000

❖ The number average molecular weight is the total weight of the sample divided by the number of molecules in the sample.

❖ What's the total weight of the sample?

Determination of the Number-average Molecular Weight (Mn)

First find the total weight of each type (or weight) of polymer. This means that you multiply the weight of the molecule by the number of molecules of that weight. For example, there are 13 molecules with a weight of 550,000 so the total weight of molecules with a weight of 550,000 is 13 x 550,00 or 7,150,000.

Number of Molecules, N_i	Mass of Each Molecule, M_i	Total Mass of Each Type of Molecule, $N_i M_i$
1	800,000	800,000
3	750,000	2,250,000
5	700,000	3,500,000
8	650,000	5,200,000
10	600,000	6,000,000
13	550,000	7,150,000
20	500,000	10,000,000
13	450,000	5,850,000
10	400,000	4,000,000
8	350,000	2,800,000
5	300,000	1,500,000
3	250,000	750,000
1	200,000	200,000

Total Mass = $\Sigma N_i M_i$ = 50,000,000

To get the number average molecular weight you divide the total weight of the sample by the total number of the molecule.

In this case, ΣN_i = 100, The number average molecular weight for this sample is then = 50,000,000 / 100 = 500, 000.

The calculation of the weight average molecular weight requires that you know the *Weight Fraction*, W_i, of each type of molecule. it's the amount of the thing of interest divided by the total amount. For weight fraction of one type of molecule, it is the weight of that type of molecule divided by the total weight of the sample

Number of Molecules	Mass of Each Molecule	Total Mass of Each Type of Molecule	Weight Fraction Type of Molecule	
(N_i)	(M_i)	(N_iM_i)	$(N_iM_i/\sum N_iM_i)$	(W_iM_i)
1	800,000	800,000	0.016	12,800
3	750,000	2,250,000	0.045	33,750
5	700,000	3,500,000	0.070	49,000
8	650,000	5,200,000	0.104	67,600
10	600,000	6,000,000	0.120	72,000
13	550,000	7,150,000	0.143	78,650
20	500,000	10,000,000	0.200	100,000
13	450,000	5,850,000	0.117	52,650
10	400,000	4,000,000	0.080	32,000
8	350,000	2,800,000	0.056	19,600
5	300,000	1,500,000	0.030	9,000
3	250,000	750,000	0.015	3,750
1	200,000	200,000	0.004	800

Weight Average Molecular Weight = $\sum W_iM_i$ = 531,600

$$M_w = \frac{M_1 n_1 \times M_1 + M_2 n_2 \times M_2}{\sum n_i M_i} = \frac{\sum m_i n_i^2}{\sum n_i M_i / \sum n_i M_i}$$

Determination of the weight-average Molecular Weight (Mw)

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Number of Molecules	Mass of Each Molecule	Total Mass of Each Type of Molecule	Weight Fraction Type of Molecule	
(N_i)	(M_i)	(N_iM_i)	$(N_iM_i/\sum N_iM_i)$	(W_iM_i)
1	800,000	800,000	0.016	12,800
3	750,000	2,250,000	0.045	33,750
5	700,000	3,500,000	0.070	49,000
8	650,000	5,200,000	0.104	67,600
10	600,000	6,000,000	0.120	72,000
13	550,000	7,150,000	0.143	78,650
20	500,000	10,000,000	0.200	100,000
13	450,000	5,850,000	0.117	52,650
10	400,000	4,000,000	0.080	32,000
8	350,000	2,800,000	0.056	19,600
5	300,000	1,500,000	0.030	9,000
3	250,000	750,000	0.015	3,750
1	200,000	200,000	0.004	800

Weight Average Molecular Weight = $\sum W_iM_i$ = 531,600

(ii) **Weight average molecular weight** If m_1, m_2, m_3,... are the weights of species with molecular masses M_1, M_2, M_3, ..., respectively, then the weight average molecular weight is

$$\overline{M}_w = \frac{m_1M_1 + m_2M_2 + m_3M_3 + \ldots}{m_1 + m_2 + m_3}$$

$$\overline{M}_w = \frac{\sum m_iM_i}{\sum m_i}$$

But $m_i = n_i M_i$

hence $\overline{M}_w = \frac{\sum n_iM_i^2}{\sum n_iM_i}$

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

Polydispersity index The ratio of mass average molecular mass to the number average molecular mass is called polydispersity index PDI.

$$PDI = \frac{\overline{M}_w}{\overline{M}_n}$$

Example:

1. In a polymer sample, 30% molecules have a molecular mass 20,000, 40% have molecular mass 30,000 and the rest have 60,000. Calculate mass average and number average molecular masses.

Solution

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{(30 \times 20,000) + (40 \times 30,000) + (30 \times 60,000)}{30 + 40 + 30}$$

$$= 36000$$

$$\overline{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{30(20,000)^2 + 40(30,000)^2 + 30(60,000)^2}{30 \times 20,000 + 40 \times 30,000 + 30 \times 60,000}$$

$$= 43333.$$

$$PDI = \frac{43333}{36000}$$