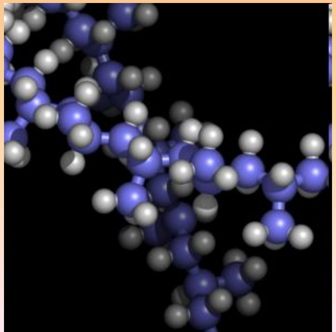
ECO-FRIENDLY POLYMERS

Introduction

- **A polymer is a molecular compound with high molecular mass, ranging into thousands and millions of gram.** It is composed of a large number of repeating units of identical structure called ***monomers***.
- The number of repeating units in a chain formed in a polymer, is known as the **"degree of polymerization".** Polymers with high degree of polymerization are termed as "**high polymers**" and those with low degree of polymerization are called **oligopolymers**.

Common Polymers

- Polymers are common in nature. **Wood, rubber, cotton, silk, proteins, enzymes, and cellulose are all examples of polymers**
- A wide variety of **synthetic polymers** have been produced, largely from **petroleum based raw materials**. These include **polyurethane, teflon, polyethylene, polystyrene, and nylon.**



For Information-Polymer Recycling Codes

	Code	Name	Uses
1	PETE	poly(ethylene terephthalate)	soda bottles; clothing
2	HDPE	high-density polyethylene	toys; milk and water jugs
3	V	poly(vinyl chloride) (PVC)	pipes; flooring; bottles for cleaning materials
4	LDPE	low density polyethylene	plastic bags; squeeze bottles
5	PP	polypropylene	deli containers; microwaveable containers
6	PS	polystyrene	disposable cups; fast-food containers; insulating foam; cassette-tape boxes
7	Other	mixed polymers, poly(methyl methacrylate), phenolic resins, etc.	insulators; dentures, etc.

Plastics in categories #2, #4 and #5 are generally considered safe. Plastic #1 is safe but should not to be re-used due to the risk of growing bacteria

CLASSIFICATION OF POLYMERS

- On the basis of chemical structure
- On the basis of polymeric structure
- On the basis of arrangement of monomers
- On the basis of tacticity
- On the basis of thermal behaviour
- On the basis of ultimate form

CLASSIFICATION BASED ON CHEMICAL STRUCTURE

Homopolymer

If a polymer consists of identical monomer, the polymer is termed as **homopolymer**.

∼ A — A — A — A — A ∼

Homopolymer

Copolymer

If the polymer is a mixture of more than one type of monomer it is termed as **copolymer**

∼ A — B — A — B — A — B ∼

Copolymer

CLASSIFICATION BASED ON POLYMERIC STRUCTURE

Linear polymers(long chains)

Eg : High density polythene,

Poly vinyl chloride.

Branched chain(chain with branches)

Eg : Low density polythene

Cross linked or Network polymer

(strong covalent bond between chains)

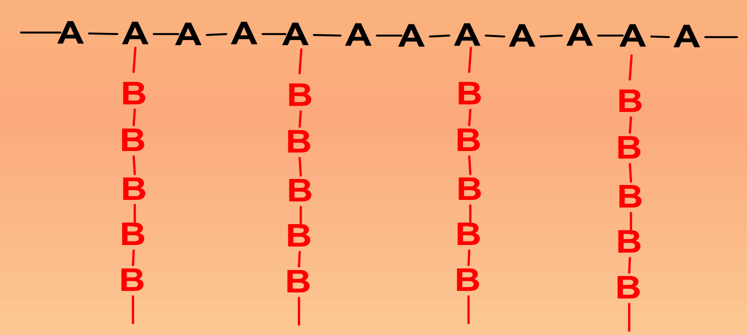
Eg : Bakelite , Melamine

CLASSIFICATION BASED ON ARRANGEMENT OF MONOMERS

Block Copolymers

Linear polymers in which the identical monomeric units occur in relatively long sequences are called block copolymers

Graft Copolymers

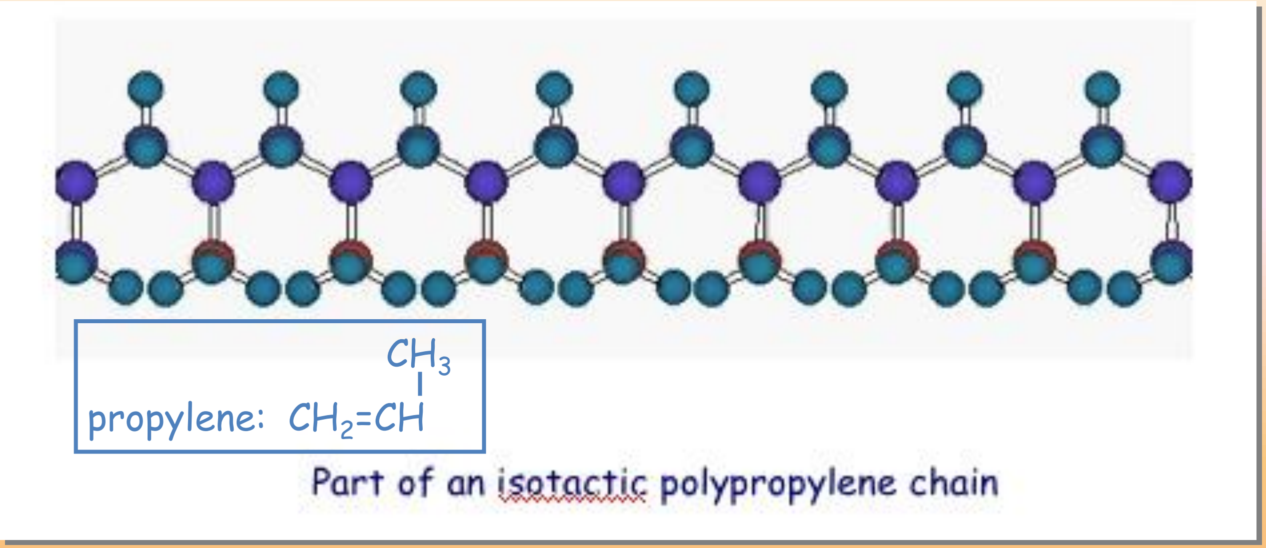


Graft copolymers are branched copolymers in which the backbone is formed from one type of monomer and branches are formed of the other

CLASSIFICATION BASED ON TACTICITY

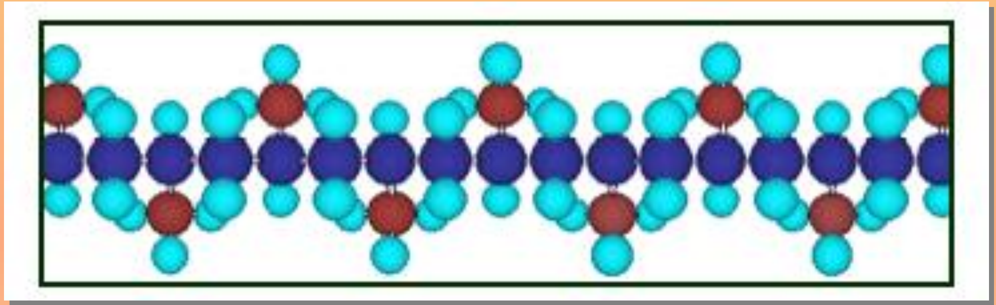
(Orientation of monomer units in polymer)

Isotactic polymer	Syndiotactic polymer	Atactic polymer
(side groups of monomers lie on the same side of the chain)	*(side groups of monomers are arranged in alternate fashion)*	*(side groups of monomers are arranged in irregular fashion)*

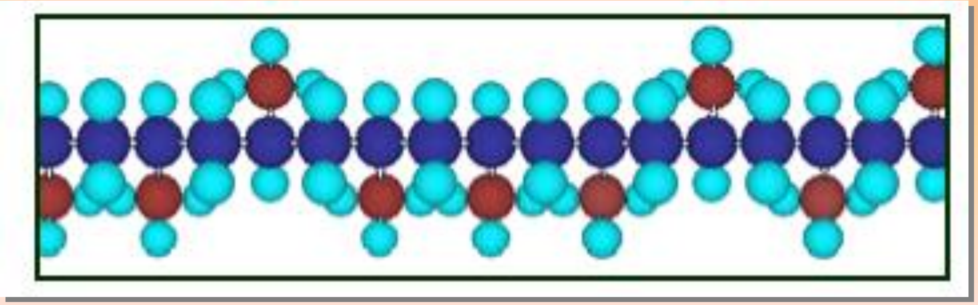


isotactic

syndiotactic



atactic



CLASSIFICATION BASED ON ULTIMATE FORM

Elastomers

weakest intermolecular forces, capable of being stretched

Eg : Rubber, buna-S etc

Fibres

Strongest inter molecular forces.

Eg : Nylon, Polyesters, terylene etc

Thermoplastics can be remoulded by

heating and cooling

Eg : Polythene , PVC etc

Thermosetting Plastics cannot be reused

Eg : Bakelite, urea formaldehyde

Functionality of monomer

- **The functionality of a molecule is the number of reactive sites it has.** For a substance to act as a monomer, it must have two reactive sites.
- ***A molecule should have a functionality of at least two to act as monomer.***
- A compound assumes functionality because of the presence of reactive functional groups like –OH, –COOH, $–NH_2$, –SH etc.
- The number of functional group present in a compound defines its functionality.

Compound	Chemical Formula	Functionality
Acetic Acid	$CH_3\ COOH$	1
Malonic acid	$HOOC\ CH_2\ COOH$	2
Ethyl alcohol	$C_2\ H_5\ OH$	1
Ethylene glycol	$HOCH_2\ CH_2\ OH$	2
Lactic acid	$CH_3\ CH\ (OH)\ COOH$	2
Tartaric acid	$HOOC\ (CHOH)_2\ COOH$	4

- Some compounds, however, **do not contain any reactive functional groups but the presence of double or triple bonds in the molecules makes them bifunctional or polyfunctional**. Hence these act as monomers.

- For example, **in olefins the double bond can be considered as a site for two free valencies.** When a double bond is broken, two single bonds become available for combination.

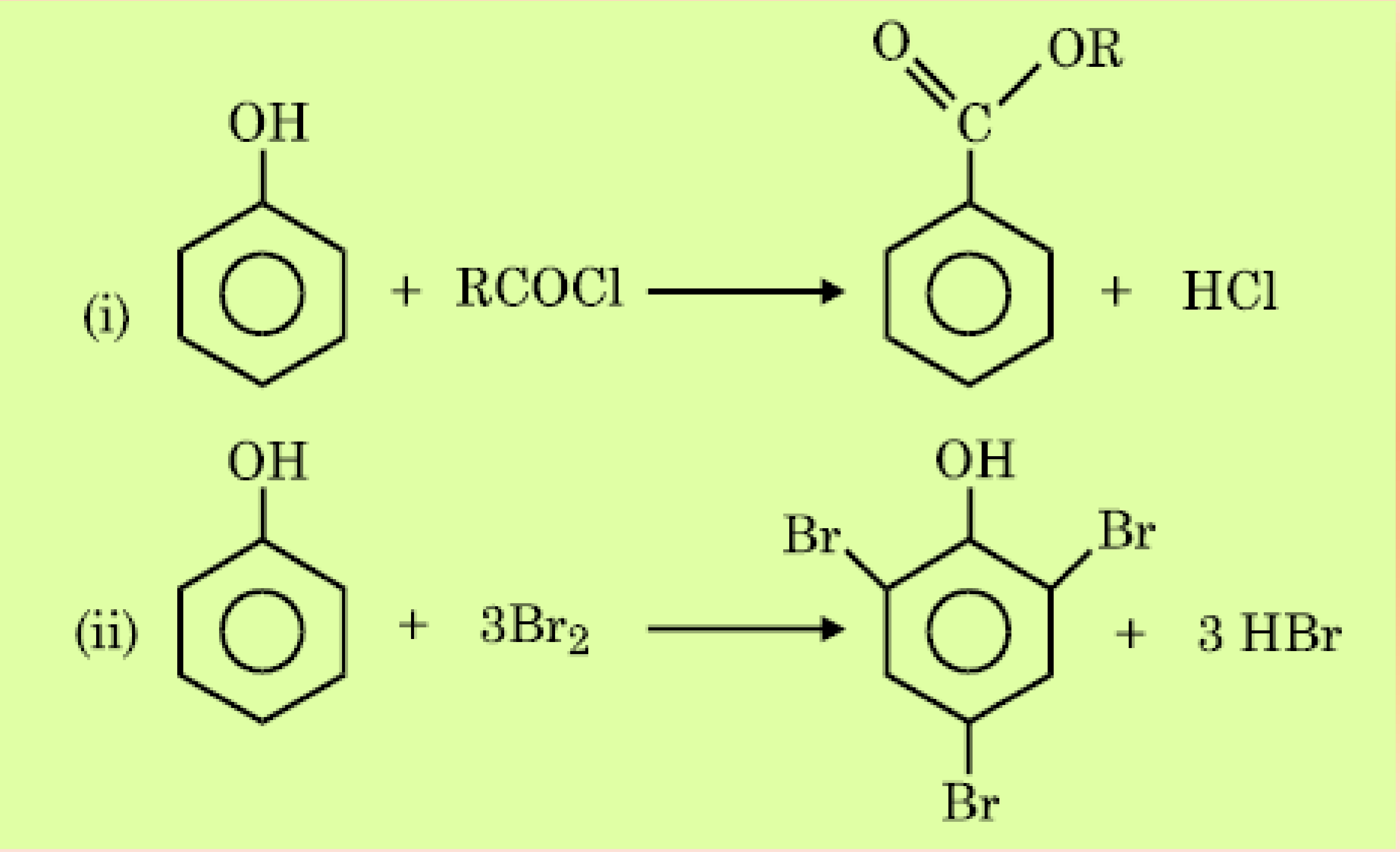
$$CH_2=CH_2 \rightarrow —CH_2-CH_2—$$

- **Acetylene, on the other hand, has a functionality of four**.

$$CH \equiv CH \longrightarrow \text{---}CH=CH\text{-----} \longrightarrow \text{---}\overset{\vdots}{C}H—\overset{\vdots}{C}H\text{---}$$

- There are some other compounds in which the **presence of easily replaceable hydrogen atoms impart functionality**. For example, **phenol.**
- It has got –OH groups as a functional group but can also undergo substitution reaction at three sites replacing its three hydrogen atoms.

- For example, in reaction (i), phenol exhibits monofunctionality and in reaction (ii), it exhibits a functionality of three.



POLYMER SYNTHESIS

- Polymers can be synthesized from monomers by two processes:
  1. Addition Polymerization
  2. Condensation polymerization

Mode of polymerization

Addition polymers

Condensation polymers

ADDITION POLYMERS

(a) Polythene (two types)

- Low density polythene

$$n\ CH_2{=}CH_2 \xrightarrow[350-570\ K]{1000\text{-}2000\ atm} \text{-}\!\!(CH_2-CH_2)\!\!\text{-}_n$$

peroxide initiator

- Chemically inert, flexible and poor Conductor of electricity

- high density polythene

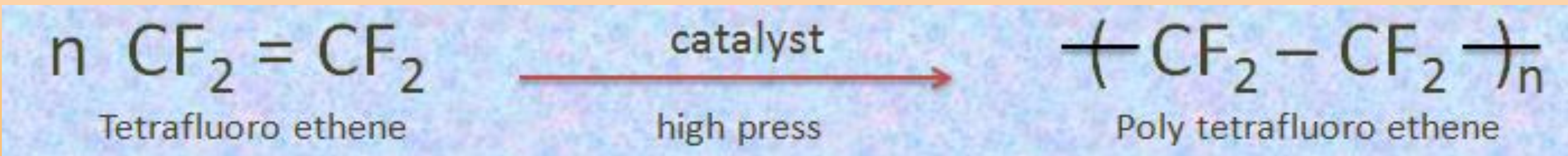
$$n\ CH_2{=}CH_2 \xrightarrow[333-343\ K]{\text{Zeigler Nata Catalyst}} HDP$$

6 – 7 atm

- Tougher and Harder

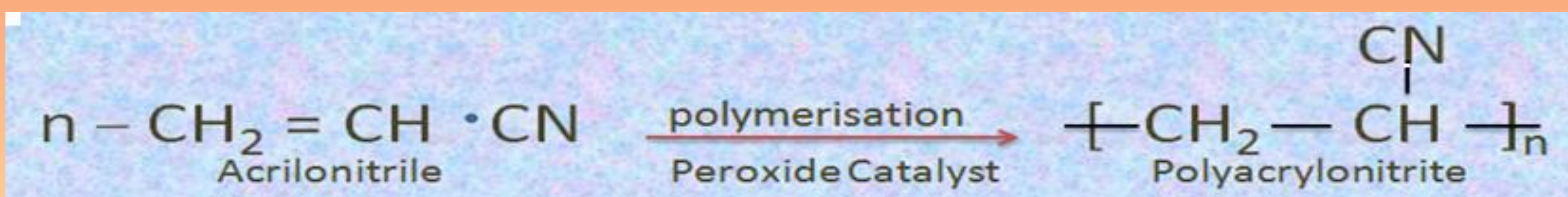
(b)Teflon(Polytetrafluoroethene)

Nonstick coating chemically inert and resistance to attack by reagents.



(c) Polyacrylonitrile

(Good resistance to stain, chemicals, insects and fungi)



Substitute for wool in making commercial fibers as orlon or acrilon.

(d) Rubber (cis-1,4 poly-isoprene)

n- $CH_2 = C - CH_2$ (with CH_3 on C) $\longrightarrow$ $(-CH_2-C = CH-CH_2-)_n$ (with CH_3 on C)

```
n- CH2 = C —CH2                         (—CH2—C = CH—CH2—)n
         |                                     |
        CH3                                   CH3
```

2-Methyl 1,3 butadiene → poly isoprene

(e)Neoprene (poly-chloroprene) (Synthetic rubber)

```
         Cl                                       Cl
         |            polymerization              |
n   CH2 = C — CH = CH2  ——————————>   (—CH2 — C = CH—CH2—)n
    Chloroprene                              Neoprene
(2-chloro 1,3-butadiene)
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Vulcanisation of rubber

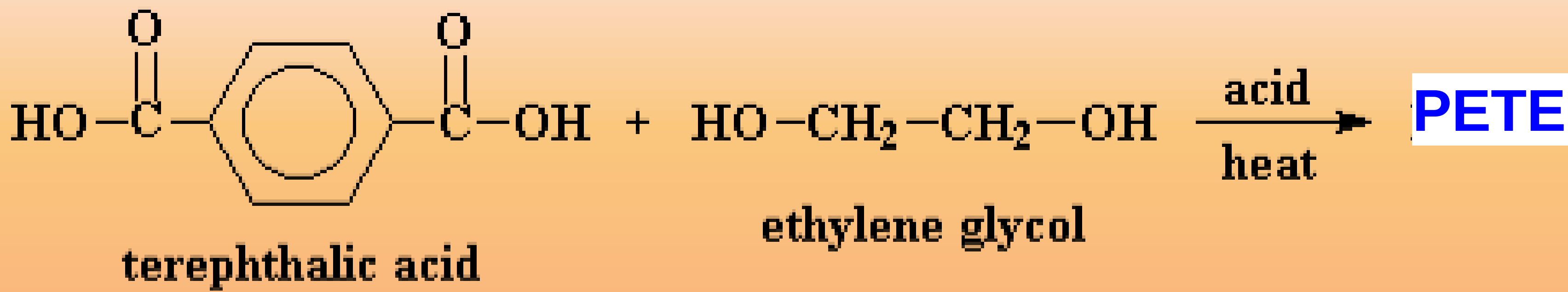
To improve upon the physical properties of natural rubber, it is heated with sulphur and an appropriate additive at 373 – 415 K, so that sulphur forms cross links at double bonds and thus rubber gets stiffened.

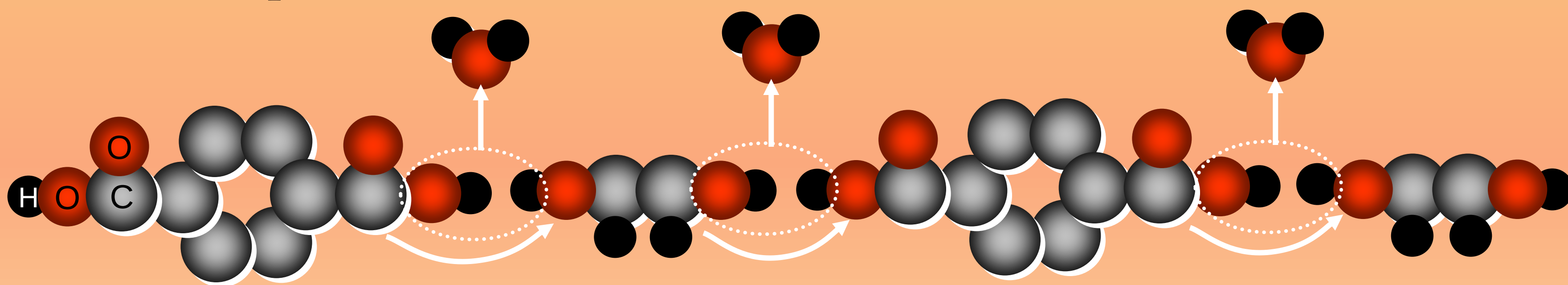
CONDENSATION POLYMERS

- This involves repetitive condensation between two bifunctional monomers, with loss of some simple molecules such as water, alcohol etc.

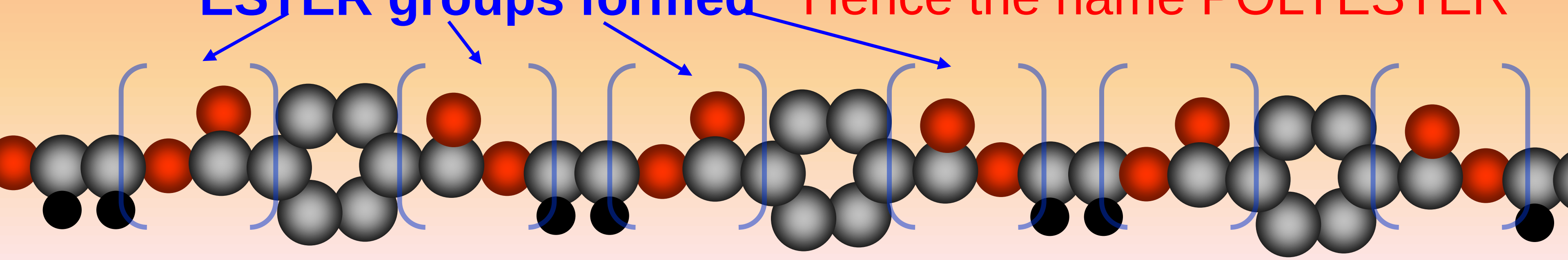
- Eg: Polyester, urea formaldehyde polymer, phenol formaldehyde polymer, melamine formaldehyde polymer etc.

Polyester is made from the two monomers, terephthalic acid and ethylene glycol. This makes a popular plastic called Polyethylene Terephthalate **(PETE).** The synthesis is also a ***dehydration* reaction** because water is given off.

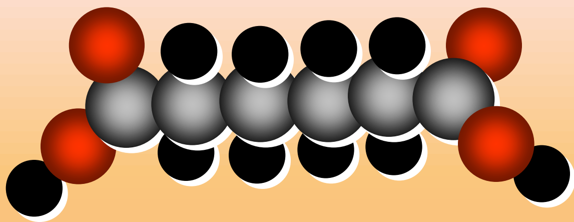




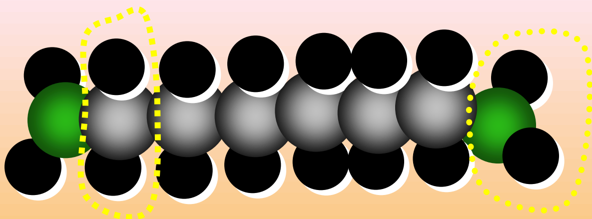
ESTER groups formed Hence the name POLYESTER



Tetramethylene dicarboxylic acid (adipic acid)



Hexamethylene diamine



methylene x 6 (hexa)

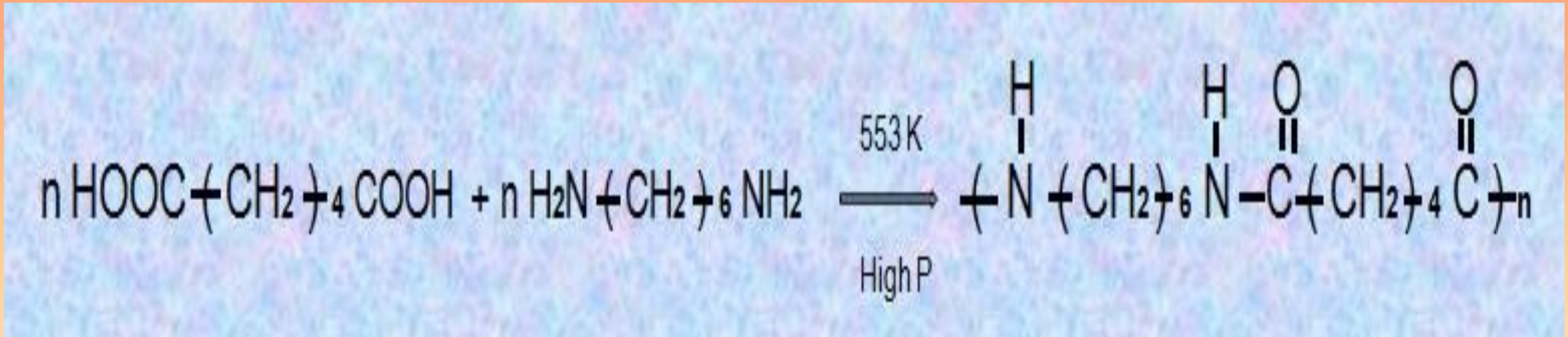
amine x 2 (di)

Nylon **is actually a "copolymer" because it is made from two monomers. When these two monomers are in the same beaker, they combine and give off a molecule of water.**

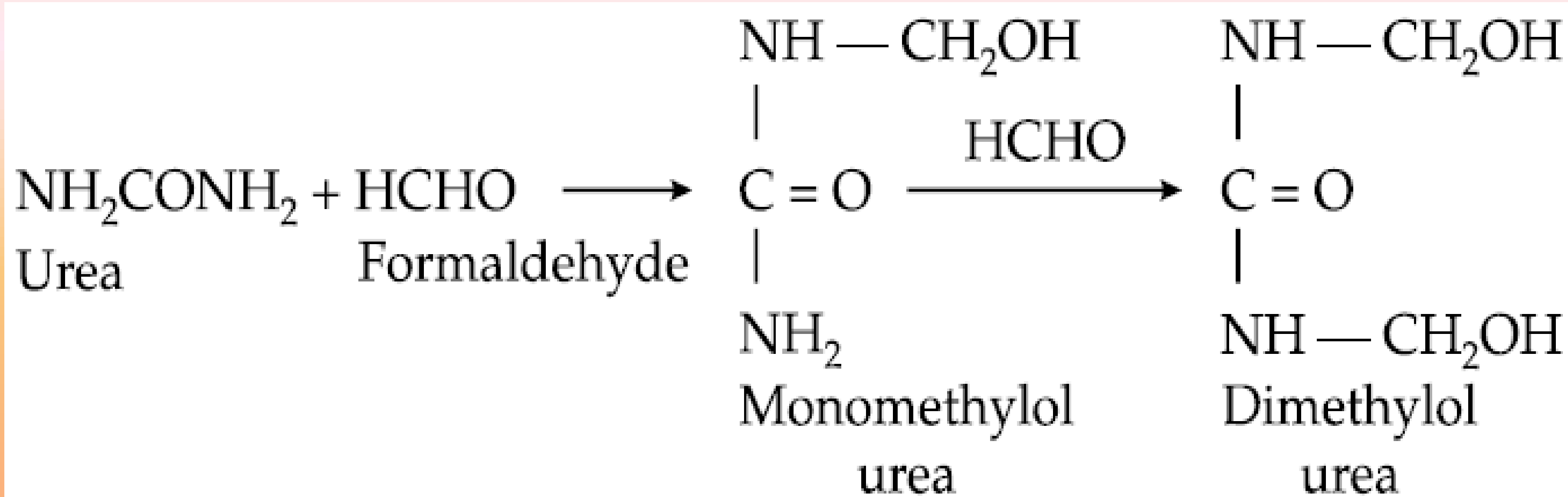
Polyamides: Nylon 6,6 and nylon 6

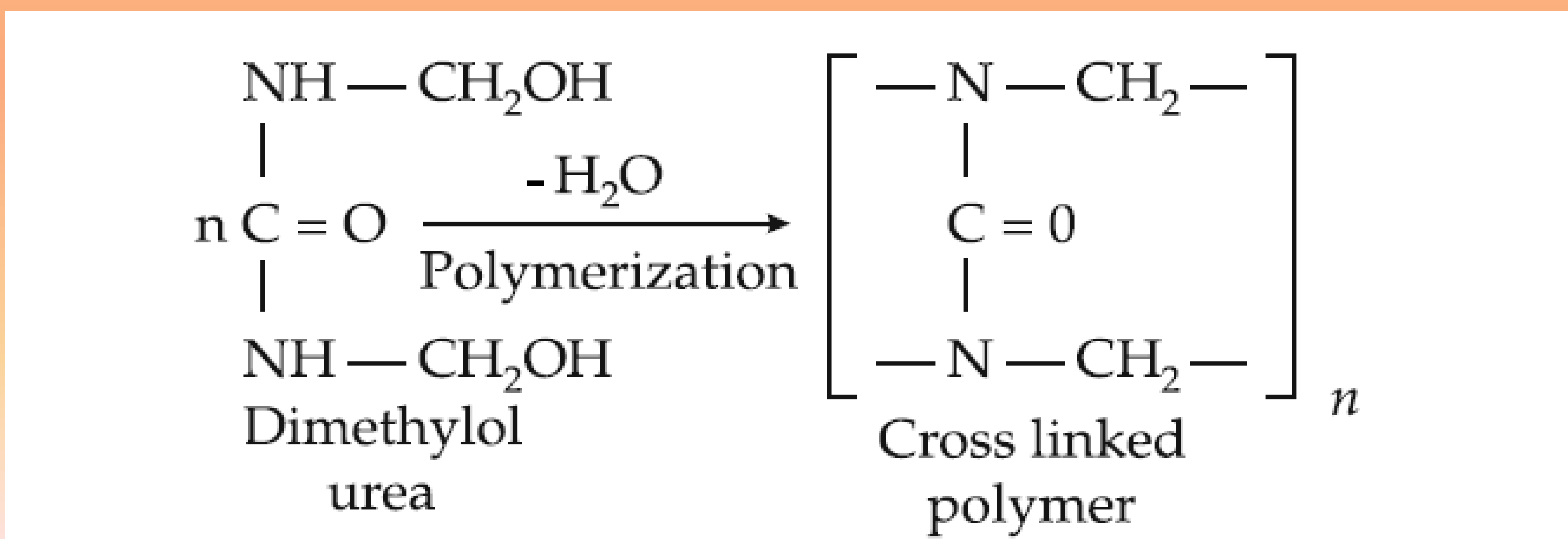
A) Nylon 6,6

Monomers- Hexamethylene diamine and adipic acid



UREA FORMALDEHYDE POLYMER

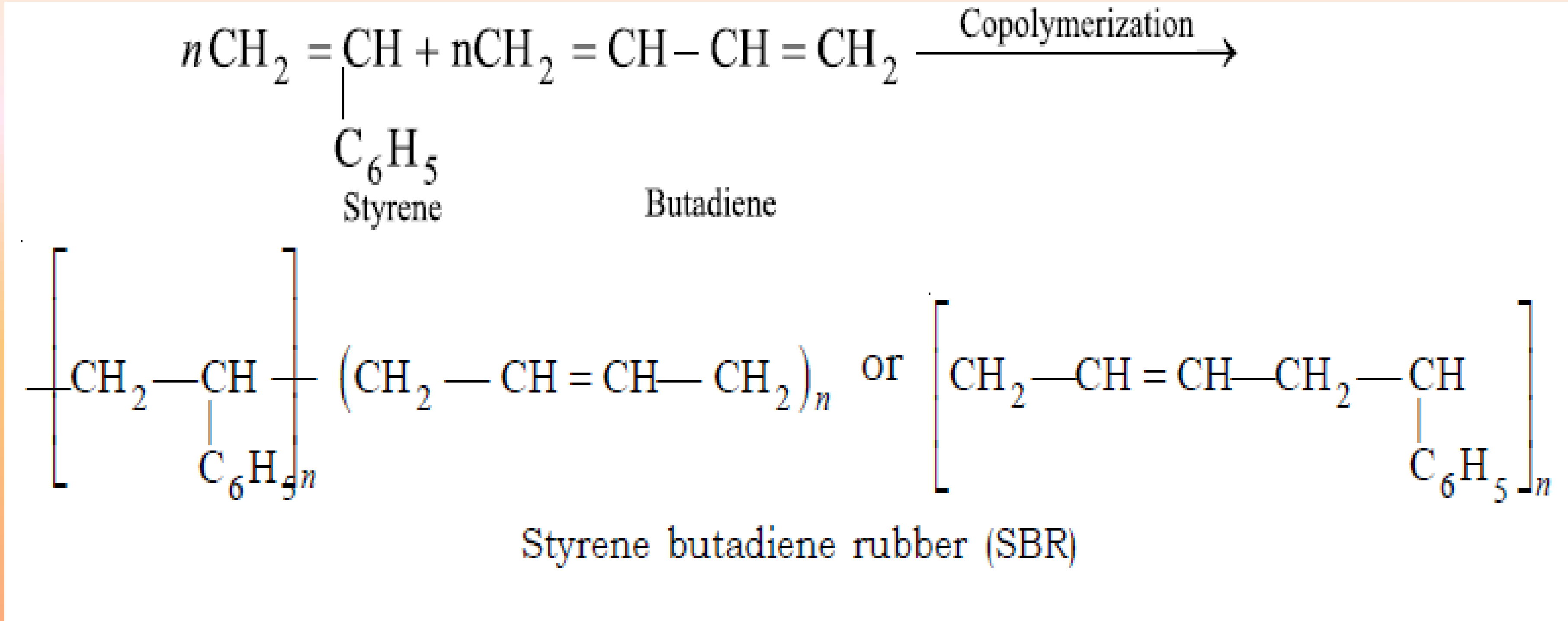




COPOLYMERISATION

- Most general and powerful method of affecting modification in polymers to obtain products for performing desired functions.
- It provides a technique to combine the properties of two or more different polymers in a single polymer.

It is defined as any process whereby two or more monomers are copolymerised to form a single polymer.



The Styrene butadiene rubber so formed after copolymerisation of butadiene and styrene has better overall properties than polystyrene or polybutadiene alone

ENVIRONMENTAL DEGRADATION OF POLYMERS

- Since the development of (plastics) polymers, these have become a popular material which has almost replaced materials such as metal, glass, wood, paper, fiber etc.
- The use of plastic has become an integral part of our modern day living.
- **The same properties that made the synthetic polymers to be so useful have contributed to a huge environmental pollution problem.**

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- Most of today's plastics and synthetic polymers are produced from petrochemicals. These **polymers persist in the environment and do not degrade or decompose easily.**
- Therefore, the **disposal of these products poses a serious environmental problem and their unhygienic recycling also causes great concern** and pose a serious health and environmental menace.
- **It becomes essential to produce eco-friendly polymers so that their by-products or wastes can be easily degraded.**

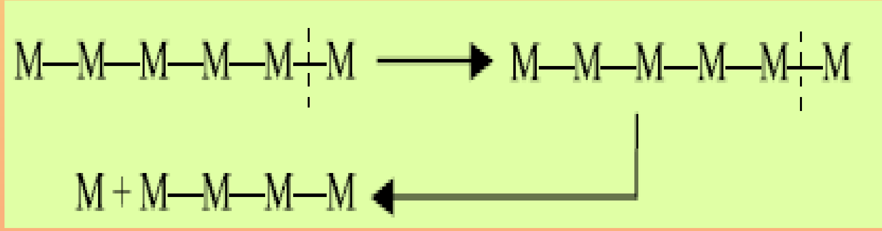
Degradation of Polymers

- **Any change in a polymer during its service, whether good or bad, can be technically termed as degradation**. For example, if a plastic bucket is left for long in the sun and rain, it loses its lustre and strength.
- In other words it has undergone degradation. **In the process of degradation, the molecular weight of the polymer is reduced.**

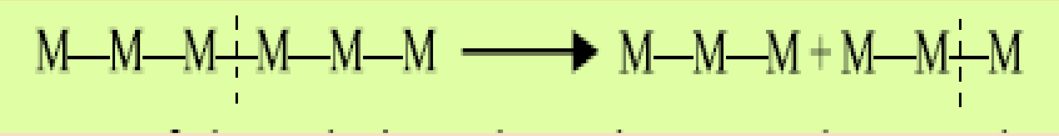
Types of polymer degradation

Polymer degradation can be of two types:

- ***Chain end degradation****: In chain end degradation, the degradation* starts from the chain ends resulting in the release of monomer units.



- ***Random degradation****: It takes place at any random point along the* polymer chain In this type of degradation, the polymer undergoes degradation into low molecular weight fragments but unlike first case, no monomer units are released.



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Factors responsible for degradation:

Degradation of polymers can be brought up by-

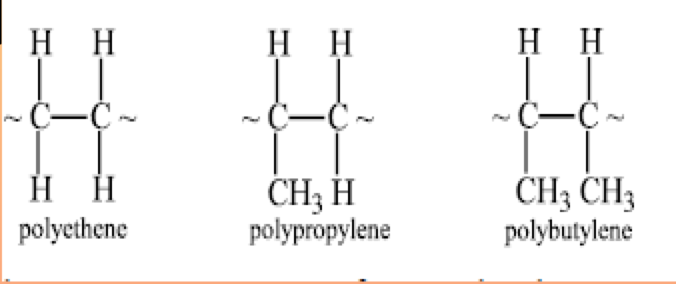
- physical factors such as heat, light etc.
- chemical agents such as oxygen, ozone, acid or alkalies.

We will be discussing these under the following heads:

- **Thermal Degradation**
- **Photo-degradation**
- **Oxidative degradation**
- **Hydrolytic degradation**
- **Mechanical degradation**
- **Biodegradation**

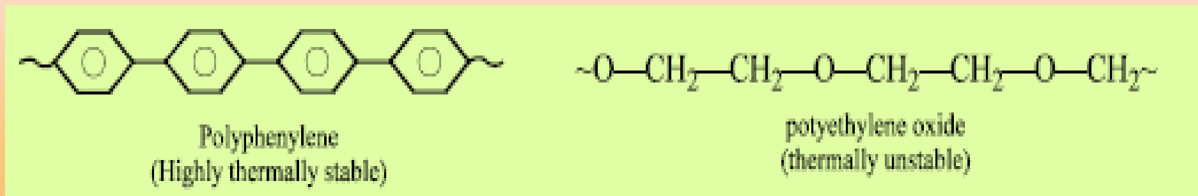
THERMAL DEGRADATION

- Degradation under the **influence of heat** is known as thermal degradation. The thermal stability of the polymer is dependent upon the stability of C—C bond of the backbone. Generally, bulkier substituents decrease the stability of C—C bond

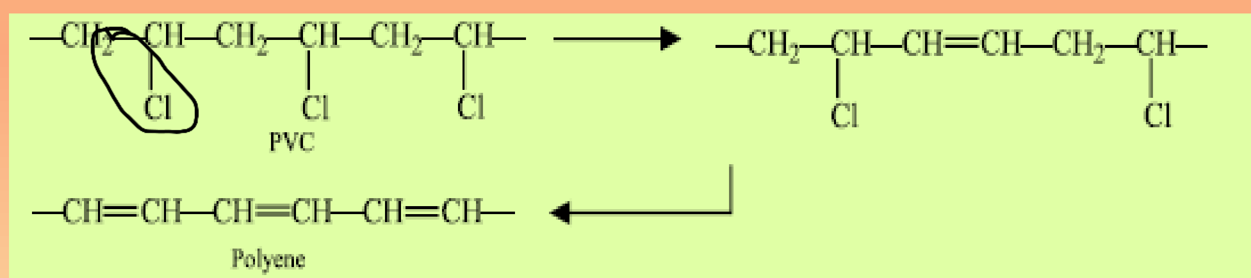


- For example, in the above polymers, as one moves from polyethene to polybutylene, bulkier substituent (—CH_3) replaces H and hence the stability of C—C bond also decreases. Thus **polybutylene is least stable whereas polyethene is most stable**

- Also, **aromatic groups in polymer backbone increase the thermal stability** whereas **presence of oxygen atom in the polymer chain decreases the thermal stability**.



- Polymer **degradation is also possible because of the breaking of the substituent groups**, but not the main chain. Example polyvinyl chloride (PVC) degrades at about 200^{0}C releasing HCl.



- As a result of degradation PVC changes colour from white to black (white $\longrightarrow$ pale yellow $\longrightarrow$ orange $\longrightarrow$ brown $\longrightarrow$ black) depending upon the number of concentration of conjugated double bonds.

PHOTO-DEGRADATION

- Photodegradation is brought about by the ultra-violet (UV) light. Some of the **transparent plastics become yellowish and brittle on storage.This is due to photodegradation.**
- The UV light has wavelength less than 400 nm corresponding to energy of 390 kJ/mole, sufficient to break chemical bonds and form free radicals.
- Example: energy required to break a C—H and C—C bond is 99 and 83 kcal/mole respectively.

PHOTODEGRADABLE POLYMERS

- Homolytic bond fission occurs readily to give free-radicals. **These free radicals can then react with any oxygen present, leading to the oxidation of polymer chain**.
- This is the phenomenon of “**ageing or weathering**” which is seen quite often.
- Photo-biodegradable polymers are broken down in two stages – initial photodegradation stage followed by biodegradation.
- For photodegradation to take place, the **polymer must absorb the photons when exposed to UV radiation or sunlight**. The photodegradable polymers need to contain light absorbing groups (**chromophores**).

- If functional groups such as ***carbonyl groups, peroxides or hydroperoxides*** are present in the polymer, it can undergo photodegradation.
- These groups are commonly formed during oxidation of polyolefins and are introduced in trace amounts during processing of the polyolefins and make them photodegradable.
- Photodegradation begins with the **production of macro radical (P*)** in the amorphous regions of polymer substrate.

$$\underset{\text{Polymer}}{PH} \xrightarrow{h\nu} P^{\bullet} + H^{\bullet}$$

- This **radical rapidly reacts with oxygen to given a macroperoxy radical.**

$$P^{\bullet} + O_2 \longrightarrow POO^{\bullet}$$

- The **macroperoxy radical abstracts a hydrogen atom from polymer backbone** to produce a hydroperoxide group

$$POO^{\bullet} + PH \longrightarrow POOH + P^{\bullet}$$

- The **hydroperoxide group is photolytically cleaved** to produce the highly reactive radicals which continue the cycle of chain degradation in the polymer.

$$POOH \xrightarrow{h\nu} PO^{\bullet} + \dot{O}H$$

- Photodegradable polymers are thus produced intentionally by adding certain chemicals or ***photosensitive substances, called promoters*** to the otherwise non-photodegradable polymers.

Promoters or photosensitizers aid in absorption of UV rays by the polymers. Two common promoters are:

- **Carbonyl Group: (Ketone Carbonyl Copolymers or carbon monoxide copolymers):** The photodegradable polymer is produced by **adding a carbonyl group, or carbon monoxide to the polymer such as polyethylene and polystyrene**. The resulting **copolymer degrades when the carbonyl group absorbs sunlight**.
- **Metal complexes:** The metal salts can be added to the polymer to initiate breakdown process. **The metal complexes initiate peroxide formation from molecular oxygen.** However, the main concern with these materials is the heavy toxic metal residues remaining after degradation takes place.
- In contrast to photosensitizers, sometimes **photostabilizers** are added to protect polymer from photodegradation**. 2, 4 dihydroxy benzo-phenone and 2 hydroxy, 4 methoxy benzophenone** are used as **photostabilizers** in plastic industry

OXIDATIVE DEGRADATION

- Oxidative degradation of a polymer results in hardening, discolouration and surface changes of the polymer.
- Oxidative degradation of a polymer is dependent upon the structure of the polymer. **The double bonds in polymers such as polyisoprene or polybutadiene are easily attacked by oxygen.**
- In the **first stage of oxidative degradation free radicals are formed on the backbone chain of polymer** by the attack of molecular oxygen or ozone.
- Sometimes **free radicals are also formed by thermal decomposition** of initiator molecule which may be present as impurity.

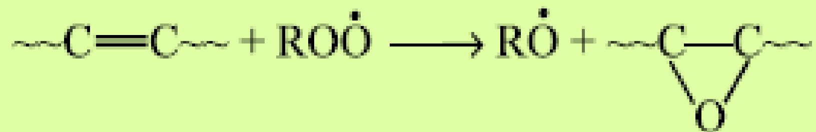
$$R{-}R \longrightarrow 2R^{\bullet}$$

- Oxygen adds on the radical site forming peroxide radical

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

- Peroxide radical attacks the polymer chain and generates a new radical site.

$$\underset{\text{Monomer peroxide}}{RH + ROO^{\bullet}} \longrightarrow \underset{\text{Hydroperoxide}}{ROOH + R^{\bullet}}$$



- The hydroperoxide can form several free radical sites.

$$ROOH \longrightarrow RO^{\bullet} + OH^{\bullet}$$

$$\underset{\text{Monomer Radical}}{R^{\bullet} + ROOH} \longrightarrow ROH + RO^{\bullet}$$

$$RO^{\bullet} + ROOH \longrightarrow ROH + ROO^{\bullet}$$

- Recombination reactions of free radicals result in termination of the chain reactions.

$$2ROO^{\bullet} \longrightarrow ROOR + O_2$$

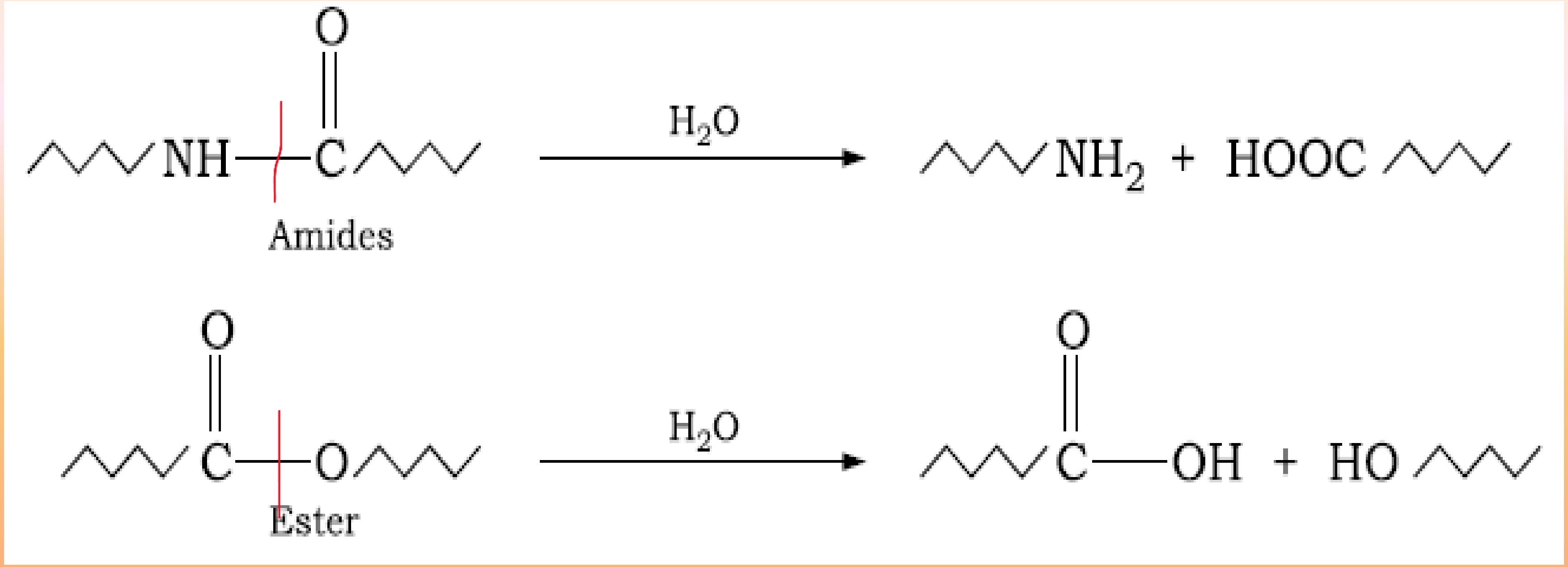
$$2RO^{\bullet} \longrightarrow ROOR$$

$$M^{\bullet} + \dot{O}H \longrightarrow MOH$$

$$2M^{\bullet} \longrightarrow M{-}M \text{ etc.}$$

HYDROLYTIC DEGRADATION

- Polymer chains containing **ester** functional group in their backbone undergo degradation by hydrolysis. Though, polymers containing **amides, alcohol, acetal groups** etc. can also undergo hydro-degradation.
- Polymer hydrolysis involves the susceptible molecular groups by reaction with H_2O.

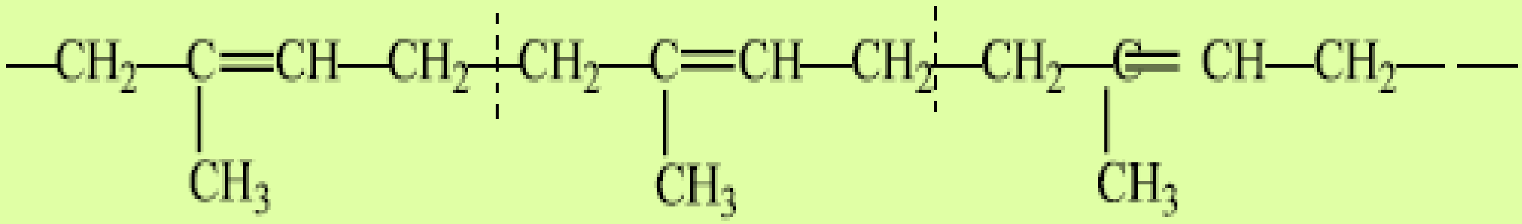


The amine or alcohol group formed during hydrolysis serve as ***auto catalyst*** to further cleave the amide or ester linkages.

MECHANICAL DEGRADATION

- When a polymer material is subjected to a mechanical stress, the **most vulnerable part of the structure gets ruptured**, thus bringing about degradation in the polymer. This type of degradation is called **mechanical degradation**.
- For example when **polystyrene dissolved in a suitable solvent is subjected to vigorous stirring**, it undergoes considerable **molecular degradation or fragmentation**.

- In rubber industry, **rubber is converted into soft, flexible mass from hard and tough material through mechanical degradation**. The process is called ***mastication*** in which the rubber is passed through rotating rollers to decrease its molecular weight. The rubber so obtained is more processable
- The $CH_2—CH_2$ links undergo fission during mastication because they are the weakest links



Polyisoprene

BIODEGRADATION

- Biodegradation is the breakdown of polymer by microbial organisms (such as bacteria, fungi etc.) into smaller compounds. **The microbial organisms degrade the polymer through metabolic or enzymatic processes.**
- The biodegradability of a given polymeric material is defined by the chemical structure of the polymer.
- Photodegradation is often subsequently followed by microbial or biodegradation. **Natural products which are susceptible to biological attack are: starch, cellulose etc.**

ENVIRONMENTALLY DEGRADABLE POLYMERS

- A variety of natural, synthetic and biosynthetic polymers are bio- and environmentally degradable.
- A polymer based on the C-C backbone tends to be non-biodegradable, whereas **heteroatom-containing polymer backbone confers biodegradability.**
- **Biodegradability can therefore be engineered into polymer** by the judicious addition of chemical linkages such as **anhydride, ester or amide bonds** among others.
- Many polymers that are claimed to be **'biodegradable' are in fact 'hydro-biodegradable' or 'photo-biodegradable'.** These different polymer classes all come under the broader category of ***'environmentally degradable polymers.***

Thus the classes of biodegradable plastics considered, in terms of the degradation mechanism are:

1. Biodegradable
2. Compostable
3. Hydro-biodegradable
4. Photo-biodegradable
5. Bio-erodable

Biodegradable

- American society of Testing and Materials (ASTM) defines 'biodegradable' as: "*capable of undergoing decomposition into* ***carbon dioxide, methane, water, inorganic compounds, or biomass*** *in which the predominant mechanism is the* ***enzymatic action of microorganisms****, that can be measured by standardized tests, in a specified period of time, reflecting available disposal condition.*"
- **Biodegradable plastics should break down cleanly, in a defined time period, to simple molecules found in the environment such as carbon dioxide and water**.

Compostable

- **Compostable plastics are a subset of biodegradable plastics.**
- Compostable biodegradable **plastics must biodegrade and disintegrate in a compost system** during the composting process (typically around 12 weeks at temperatures over 50°C).
- The **compost must meet quality criteria** such as **heavy metal content, ecotoxicity and no obvious distinguishable residues** caused by the breakdown of the polymers.

Hydro-biodegradable and Photo-biodegradable

- Two closely linked mechanisms of degradation that are frequently confused with biodegradation are Hydro-degradation (degradation via hydrolysis) and Photo-degradation (degradation via photolysis).
- Since both mechanisms are often subsequently followed by microbial degradation, confusion of definition frequently occurs.
- Hydro-biodegradable and photo-biodegradable polymers are broken down in a **two-step process - an initial hydrolysis or photo-degradation stage**, followed by further **biodegradation**.

Bio-erodable

- **Many polymers that are claimed to be 'biodegradable' are in fact 'bioerodable'** and **degrade without the action of micro-organisms** – at least initially in the first step.
- This is also known as **abiotic disintegration**, and may include processes such as **dissolution in water, oxidative embrittlement, thermal embrittlement (heat ageing) or photolytic embrittlement (UV ageing).**

BIOPOLYMERS AND BIOPLASTICS

- **Biopolymers are polymers which are present in, or created by, living organisms.** These include polymers from renewable resources that can be used to create bioplastics. **Carbohydrates and proteins, for example, are biopolymers**.
- **Bioplastics or biopolymer plastic are a subset of biopolymers, which means that all bioplastics are biopolymers, but not all biopolymers are bioplastics. Bioplastics or Green Plastics is frequently used for sustainable plastics, For instance, Polylactic acid (PLA) is a bioplastic and a biopolymer, while silk can be classed as a biopolymer but not a bioplastic.**

BIOPOLYMERS

Bioplastics or Green Plastics are manufactured using biopolymers, and are biodegradable. Green plastics are the focus for making living convenient along with protection of environment.

There are two main types of biopolymers:

- Those that come from living organisms; and
- Those which need to be polymerized but come from renewable resources.

Both types are used in the production of ***bio-plastics***

Biopolymers From Living Organisms

- These biopolymers are **present in, or created by, living organisms**. These include **carbohydrates, and proteins**. These can be used in the production of plastic for commercial purposes.
- Examples are listed in the table (next slide)

Biopolymer	Source	Remarks
Cellulose	In plants cellulose is synthesized from glucose. It is the main component of plant cell walls Examples include wood, cotton, corn, wheat, and others	• Cellulose is the most plentiful carbohydrate in the world; 40 percent of all organic matter is cellulose • It has β glucose as the repeat unit. • Cellulose is insoluble in most of the solvents and hence it is converted to its derivatives to make it process able.
Soy protein	Soy protein and zein (from corn) are abundant plant proteins.	• They are used for making adhesives and coatings for paper and cardboard.
Starch	Starch is found in corn (maize), potatoes, wheat, tapioca (cassava), and some other plants.	• Starch is also made up of glucose units and is stored in plant tissues. It is not found in animal tissues. • It has β glucose as the repeat unit • Annual world production of starch is well over 70 billion pounds, with much of it being used for non-food purposes, like making paper, cardboard, textile sizing, and adhesives.

Polymerizable Molecules

- These **molecules come from renewable natural resources**, and can be polymerized to be used in the manufacture of biodegradable plastics.

Biopolymer	Natural Source	Remarks
Lactic Acid	Beets, corn, potatoes, and others	• Produced through fermentation of sugar feedstocks, such as beets, and by converting starch in corn, potatoes, or other starch sources. • It is polymerized to produce polylactic acid — a polymer that is used to produce plastic.
Triglycerides	Vegetable oils mainly from soybean, flax, and rapeseed.	• Triglycerides are another promising raw material for producing plastics.

Bioplastics

- Bioplastics must be **strong, resiliant, flexible, elastic, and above all, durable**.
- Current research on bio-plastics is focusing on how to **use natural polymers to make plastics that are degradable** and how to make products that allow us to control when and how it degrades, while ensuring that the product remains strong while it is still in use.

There are at least three factors that decide how environment-friendly a material is:

- **Renewability**: how quickly are the ingredients that go into making the plastic **created in the environment**?
- **Degradability:** how quickly can the plastic be **re-integrated into the environment** after it is no longer being used?
- **Production of waste:** how much **pollution or waste is created during the process** of actually making the plastic?

Traditional plastics fail on all these three points.

Manufacture of bioplastics

There are two methods used to produce plastics:

- Fermentation
- Growing Plastics in Plants

Fermentation to Produce Plastics

- Fermentation is the use of microorganisms to break down organic substances in the absence of oxygen.
- Fermentation can be carried out with genetically engineered microorganisms, specially designed for the conditions under which fermentation takes place, and for the specific substance that is being broken down by the microorganism.
- Fermentation can be used to create biopolymers and bioplastics, some of the examples are:

➢ ***Bacterial Polyester Fermentation***

➢ ***Lactic Acid Fermentation***

➢ ***Trigyceride Fermentation***

Bacterial Polyester Fermentation

- Fermentation is the process by which bacteria can be used to create polyesters.
- Eg., Bacteria called ***Ralstonia Eutropha*** uses the sugar of harvested plants, such as corn, to fuel their cellular processes.
- **The by-product of these cellular processes is the polymer,** which is then separated from the bacterial cells.

Lactic Acid Fermentation

- Lactic acid is fermented from sugar.
- **The final product of fermentation is lactic acid,** which **is converted to polylactic acid (PLA) using traditional polymerization processes**.

Triglyceride Fermentation

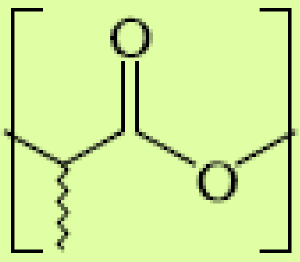
- **Triglyceride is fermented from vegetable oils**
- Poly-triglyceride polymer is then prepared.

Growing Plastics in Plants

- Plants are becoming factories for the production of plastics. Researchers created plants (**eg., *Arabidopsis thaliana***) through genetic engineering in lab.
- The **plant contains the enzymes used by bacteria to create plastics**. Bacteria create the plastic through the conversion of sunlight into energy.
- The researchers have **transferred the gene that codes for this enzyme into the plant**, as a result the plant produces plastic through its cellular processes.
- The **plant is harvested and the plastic is extracted** from it using a solvent.
- **liquid is distilled to separate the solvent from the Polymer.**

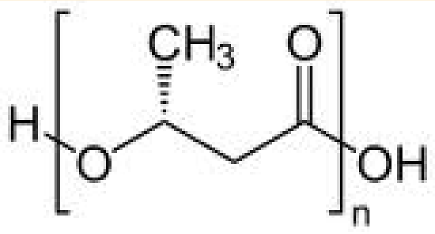
EXAMPLES OF BIOPLASTICS

POLYLACTIC ACID (PLA)


Polylactic acid

- Highly versatile thermoplastic material
- Made from 100% renewable resources
- Lactic acid is derived from various sources
  - Corn
  - Sugarcane
  - Wheat
- **Bacterial fermentation is used to produce lactic acid** from corn starch or sugarcane feedstocks. PLA has a melting temperature of 173-178°C

- **PLA is a biodegradable, thermoplastic ,** currently used in a number of ***biomedical applications***, **such as sutures, stents, dialysis media and drug delivery devices**
- It is also evaluated as a **material for tissue engineering.**
- Useful for producing **loose-fill packaging, compost bags, food packaging and disposable tableware**.
- In form of fibers and non-woven textiles PLA is used as **upholstery, disposable garments, feminine hygiene products and nappies**.



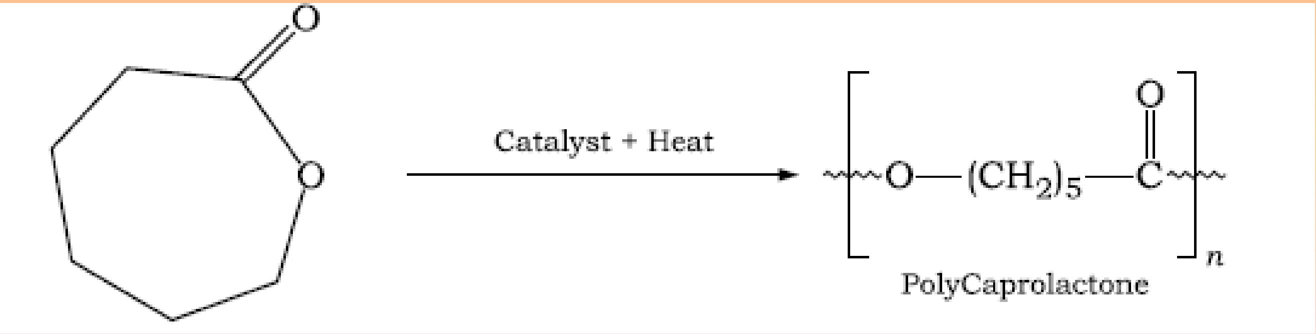
Polyhydroxybutyrate

- **Polyhydroxybutyrate (PHB)** produced from ***fermentation of carbohydrate*** ***is a biodegradable***, thermoplastic polymer derived from renewable resources.
- PHB appears **stiff and brittle**, it also exhibits a high degree of crystallinity, a **high melting point of about 180 °C**.
- The **poly-3-hydroxybutyrate (P3HB) form of PHB is probably the most common type of polyhydroxyalkanoate**,

- PHB is **water insoluble and relatively resistant to hydrolytic degradation**.
- PHB is used as **bio-material for implantation** (as medical device) inside human body (eg., **bone implants**). **PHB is bio-compatible**, does not produce any immune response and the body does not reject the implantation.

Polycaprolactone

- Polycaprolactone (PCL) is a biodegradable polymer derived by the **chemical synthesis from crude oil.**
- Used in **biomedical applications and as an additive to bioplastics made from other polymers**.
- It can be **added to starch to lower its cost and increase biodegradability** or it can be **added as a polymeric plasticizer to PVC to increase its impact resistance**.
- **PCL is prepared by ring opening polymerization of – caprolactone** using a catalyst such as **stannous octanoate**



- PCL has **good water, oil, solvent and chlorine resistance**. PCL has a melting temperature of around 60°C

Applications:

- **PCL is degraded by hydrolysis of its ester linkages** in physiological conditions (such as in the human body) and is therefore used as an ***implantable biomaterial.***
- **PCL is a Food and Drug Administration (FDA) approved material that is used in the human body as a *drug delivery device, suture, adhesion barrier**** and is being investigated as a ***scaffold for tissue repair via tissue engineering.***
- In Dentistry it is used in ***root canal filling***.

* Adhesion barrier is a medical implant that can be used to reduce abnormal internal scarring (adhesions) following surgery by separating the internal tissues and organs while they heal

Monetary Costs

3x higher than petroleum-based plastics

- – **High start-up costs**
- – **Labor intensive processing**
- – **High energy demands**

Is there a future for Biopolymers?

Presently biodegradable polymers have greater financial costs.

Research is required to produce economically viable biopolymers.

Recycling of synthetic polymers is essential.

PLASTIC RECYCLING

- **Plastic recycling is the process of recovering scrap or waste plastics and reprocessing the material into useful products, sometimes completely different from their original state.**
- Recycling involves collecting plastic products, sorting by resin type, and then depolymerizing the plastics back into their basic building blocks or monomers.
- The recovered monomers are then used to produce new resins of the same type so they may be fabricated into new, useful, and marketable products.

- Recycling is beneficial in two ways: **Plastics can be recovered from waste via mechanical recycling and it also reduces the amount of waste produced for disposal.**

There are four stages of recycling*;*

- ***Primary****: Reprocessing waste plastics to produce new plastic having* similar properties as those of the original plastic is defined as primary recycling
- ***Secondary****: Melt recycling is considered secondary recycling, and* the products obtained have inferior properties to the original plastic.

- ***Tertiary****: The waste plastic is recycled by altering its chemical* structure to produce monomers through depolymerisation.
- ***Quaternary****: No new products are produced. Burning plastic waste* for energy recovery is considered quaternary recycling.

Tertiary recycling is based on the decomposition of polymers by means of **heat, chemical, or catalytic agent**, to yield a variety of products ranging from the **chemical monomers to a mixtures of compounds** with possible application as a source of chemicals or fuels.

Molecular Weight of Polymers

- The **molecular weight of polymers is related to the chain length and the extent of cross-linking** between different chains.
- The extent of cross-linking depends on the concentration of the monomer during polymerization.
- *The **length of the polymer chain depends on the random encounter between the monomer and the reactive site of the chain.***
- Due to the **randomness**, **some polymeric chains grow longer** than the others. Thus, **a polymer sample is a mixture of different molecules having different chain lengths**.
- Hence **molecular weight of a polymer is always expressed as some sort of <u>average of molecular weight</u>**.

(i) Number Average Molecular Weight M_n:

$$\bar{M}_n = \frac{\text{Total Mass of the polymer sample}}{\text{Number of molecules present in the sample}}.$$

or

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2 + n_3\,M_3 + \ldots}{n_1 + n_2 + n_3 + \ldots}$$

$$= \frac{\Sigma n_i\,M_i}{\Sigma n_i}$$

where n_1, n_2, n_3 etc. are the number of molecular species having molecular mass M_1, M_2, M_3 etc ... respectively. Measurement of an appropriate colligative property affords the Number Average Molecular Weight.

(ii) Weight Average Molecular weight Mw:

$$\bar{M}_W = \frac{W_1M_1 + W_2M_2 + W_3\,M_3 + \dots}{W_1 + W_2 + W_3 + \dots}$$

$$= \frac{W_1\,M_1 + W_2M_2 + W_3M_3 + \dots}{W}$$

where W_1 = Total mass of the species having molecular weight M_1.

$W_1 = n_1M_1$

W = Total weight of the polymer sample

$$\therefore \quad \bar{M}_W = \frac{\sum n_i\,M_i^2}{W}$$

Example 1. Calculate the number average molecular weight, if two polymers, having mass equal to 100 & 10,000 are mixed.

Solution: $\bar{M}_n = \dfrac{100 + 10{,}000}{2} = 5050.$

Example 2. Calculate the number and weight average molecular weights of a polymer sample containing 20% of polymer *A* and 80% of polymer *B*. The molecular mass of *A* and *B* are 3000 and 30,000 respectively.

Solution: $\bar{M}_w = \dfrac{0.2 \times 3000 + 0.8 \times 30{,}000}{0.2 + 0.8} = 24600.$

For finding out $\bar{M}_n$ we have to calculate the number of molecules of *A* and *B*.

$\boxed{W_A = n_A \times M_A \text{ and } W_B = n_B \times M_B}$

$\boxed{\dfrac{n_B}{n_A} = \dfrac{W_B}{M_B} \times \dfrac{M_A}{W_A}}$

$$\frac{\text{Number of molecules of } B \text{ having molecular mass } 30{,}000}{\text{Number of molecules of } A \text{ having molecular mass } 3000} = \frac{80 \times 3000}{20 \times 30{,}000} = \frac{2}{5}$$

Thus for every 5 macromolecules of mass 3000, there are 2 molecules of mass 30,000. Hence,

$$\bar{M}_n = \frac{5 \times 3000 + 2 \times 30{,}000}{(5 + 2)} = 10714.$$

Example 3. Equal weights of polymer molecules with molecular weights 20,000 g/mol and 200,000 g/mol are mixed. Calculate $\bar{M}_n$ and $\bar{M}_w$.

Solution: Let the weight of one of the polymer = W_1

Weight of the other polymer = W_2

$$W_1 = W_2$$

Let it $\quad W_1 = W_2 = 400{,}000\text{ g}$

Number of molecules of first monomer

$$n_1 = \frac{400{,}000}{20{,}000} = 20$$

Number of molecules of second polymer

$$n_2 = \frac{400{,}000}{200{,}000} = 2$$

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2}{n_1 + n_2} = \frac{20 \times 20{,}000 + 2 \times 200{,}000}{20 + 2}$$

$$\bar{M}_n = 36{,}363.6\ g/mol$$

$$\bar{M}_w = \frac{n_1M_1^2 + n_2M_2^2}{n_1M_1 + n_2M_2} = \frac{20 \times (20{,}000)^2 + 2 \times (200{,}000)^2}{20 \times 20{,}000 + 2 \times 200{,}000}$$

$$= \frac{20 \times 4 \times 10^8 + 2 \times 4 \times 10^{10}}{8 \times 10^5}$$

$$= \frac{8 \times 10^9 + 8 \times 10^{10}}{8 \times 10^5} = \frac{8 \times 10^9 (1 + 10)}{8 \times 10^5}$$

$$= 110{,}000\text{ g/mol.}$$

Example 4. If 1000 g of a polymer of molecular weight 1000 g/mole is mixed with 1000 g of another polymer of molecular weight 10^6 g/mole, what is the ratio of $\bar{M}_w / \bar{M}_n$.

Solution:

Polymer	Weight	Mol.wt.	No. of moles
1	1000 g	1000 g/mol	1 (n_1)
2	1000 g	10^6 g/mol	10^{-3}(n_2)

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2}{n_1 + n_2} = \frac{(1 \times 1000) + (10^{-3} \times 10^6)}{1 + 10^{-3}}$$

$$= \frac{2000}{1.001} \approx 2000$$

$$\bar{M}_w = \frac{n_1M_1^2 + n_2M_2^2}{n_1M_1 + n_2M_2} = \frac{1 \times (1000)^2 + 10^{-3} \times (10^6)^2}{(1000 + (10^6 \times 10^{-3}))}$$

$$= \frac{10^6 + 10^9}{1000 + 1000} = \frac{10^6(1 + 10^3)}{2000} = \frac{10^6(1001)}{2000}$$

$$= 500.5 \times 10^3$$

$$\frac{\bar{M}_w}{\bar{M}_n} = \frac{500.5 \times 10^3}{2000} = 250.25$$


Recycle or we will have a polymer planet.