APPLIED CHEMISTRY

Polymers

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Outline : Lecture 1

- Polymers- Introduction/Definition

- Polymerisation

- Classification of polymers

Polymers

Introduction

❖The word ' Polymer' is coined from two Greek words: poly means many and mer means unit or part. The word mer indicates smallest repetitive unit.

❖ Polymers are extremely large molecules and contribute towards an indispensable portion for our existence.

❖ They are a main constituent of our food (starch, protein, etc.), our clothes (polyester, nylons, etc.), our houses (wood cellulose, alkyd paints/oil based paints, etc.), and our bodies (polynucleic acids, proteins, etc.).

Polymers

Definition:

Polymers are compounds of very ***high molecular weights*** formed by the combination of a large number of ***small repeating units. The repeating*** structural units are derived from some simple and reactive molecules known as ***monomers and are linked to*** each other by **covalent bonds**.

These are also referred to as **macromolecules** *because* *of their* ***big size*** and **being formed from smaller subunits on a large scale.**

Polymers and ***Macromolecules*** though are often used synonymously but on strict basis, a polymer contains same subunits / repeating units (monomers), whereas a macromolecule is a giant molecule that may or may not contain same subunits or monomer units.

DNA is a polymer formed from all nucleotides as monomers and in proteins the monomers are all amino acids whereas triglycerides (fat) are made of glycerol backbone and several fatty acid chains.

So, all polymers are macromolecules but not all macromolecules are polymers
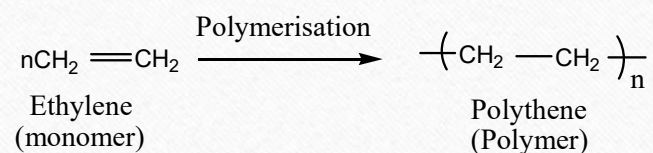
Polymers

Polymerization: **The process by which the simple molecules (monomers) are converted into polymers is called polymerization**

OR

The chemical reaction in which high molecular mass molecules are formed from monomers is called polymerization

For example, many ethylene molecules combine to form a giant molecule of polythene.

$$nCH_2 = CH_2 \xrightarrow{\text{Polymerisation}} \left(CH_2 - CH_2 \right)_n$$

Ethylene   Polythene
(monomer)   (Polymer)

where *n = number of monomers in the polymeric chain.*

Polyethene is both a polymer as well as a macromolecule as it contains a large number of repeating units.

Polymers

Degree of polymerization

The number of repeating units in a polymeric chain is called 'degree of polymerization'. In other words, degree of polymerization is a number that indicates the number of repetitive units (monomers) present in the polymer. DP is represented as 'n'.

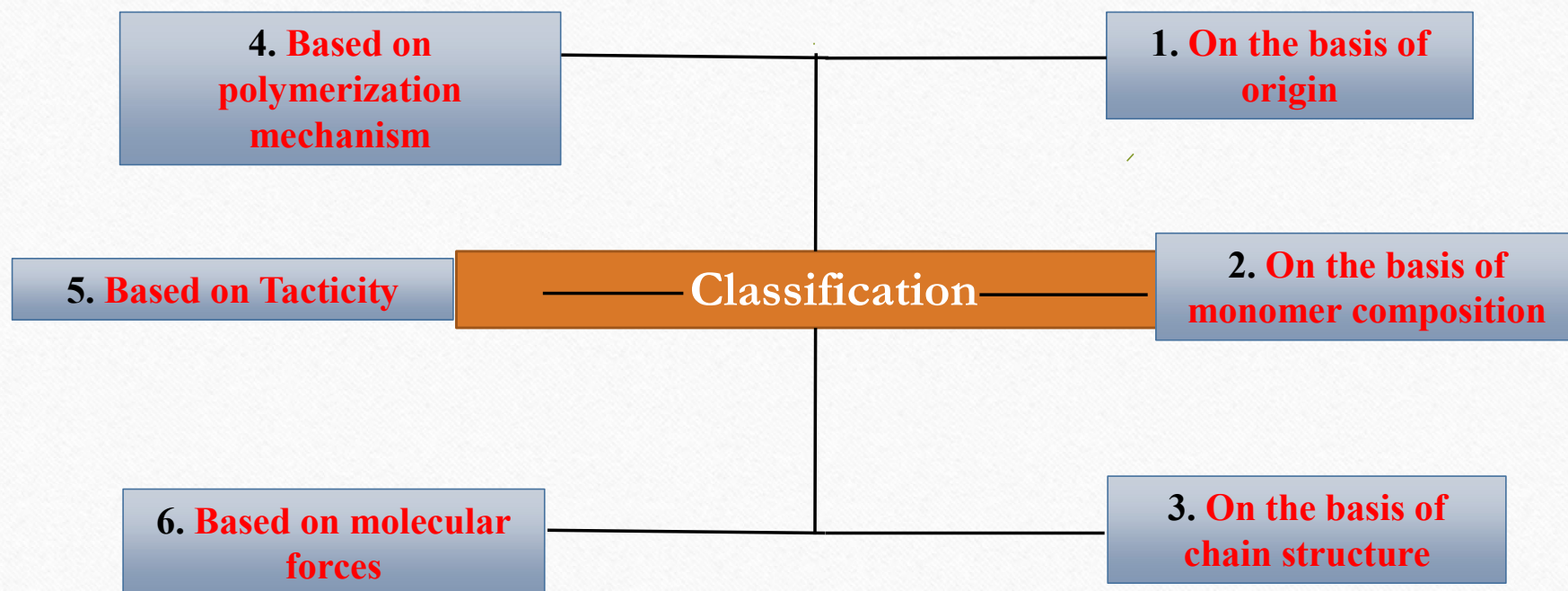The molecular weight of the polymer can be calculated by knowing the value of DP.

[Molecular wt of the polymer] = DP × Molecular wt of each monomer.

Example: Calculate the molecular weight of the polythene polymer whose DP value is 100.

Solution: Molecular weight of the polythene = DP × Molecular weight of Ethylene

$$= 100 \times 28 = 2800.$$

Polymers

1. On the basis of origin

i. **Natural Polymers-** These are naturally occurring polymers existing in plants and animals. Example : Starch (polymer of α-D-glucose*)*, Cellulose *(polymer of β*-D-glucose*)*, proteins (polymer of α-amino acids) etc.
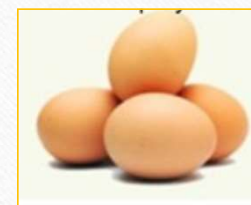

Cotton

Natural latex from rubber tree

Rubber tyres

Rubber bands

Proteins from eggs and other foods

[https://www.slideshare.net/Albairaq/polymers]
[https://www.barnwell.co.uk/content/uploads/2017/10/Natural-Polymers.jpg]

ii. **Synthetic Polymers-** These are prepared in the lab artificially. Example : polyethylene, polyvinylchloride, nylon, Bakelite etc.

Polymers

Examples: Synthetic Polymers

Polyethylene

Polyvinylchloride

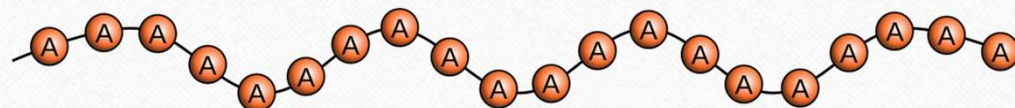
Polytetrafluoroethylene

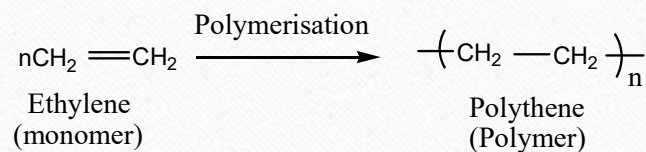Polystyrene

Polyester, Nylon, Lycra etc

[https://slideplayer.com/slide/3503952/]

2. On the basis of monomer composition

(a) **Homopolymer**: These are formed by combination of identical monomers.

$$nA \longrightarrow (A)_n$$

Examples:

$nCH_2 = CH_2 \xrightarrow{\text{Polymerisation}} -(CH_2 - CH_2)_n$

Ethylene (monomer) → Polythene (Polymer)

and

$nCH_2 = CHCl \xrightarrow{\text{Polymerisation}} -(CH_2 - CHCl)_n$

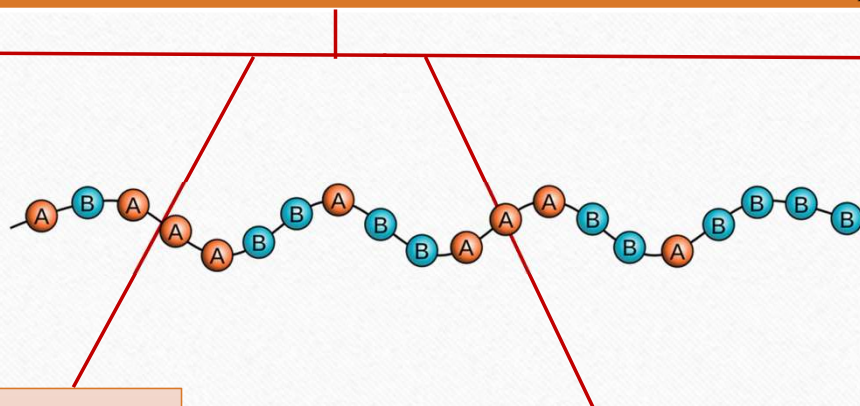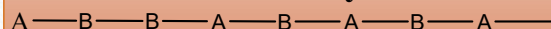Vinyl Chloride (monomer) → Polyvinylchloride (Polymer)
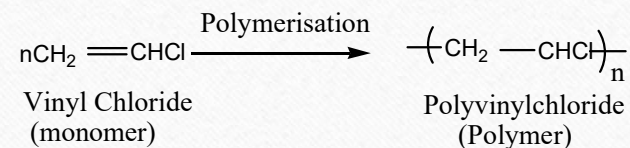
Polymers

Copolymer : These are formed by the combination of more than one type of monomers. The general equation for their formation can be represented as: $nA + mB \longrightarrow$ A——A——B——B——A——B

Depending upon the arrangement of the monomeric units, further classification of copolymers is as follow:

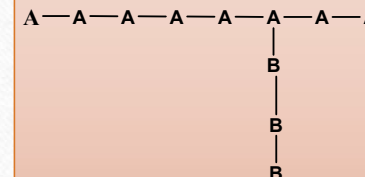**Random copolymers:**
Monomeric units arranged randomly

A——B——B——A——B——A——B——A——

Graft copolymers:

A——A——A——A——A——A——A——A
|
B
|
B
|
B

Branched copolymers The backbone is formed of one type of monomers while the branches formed of the other types of monomers.

Alternating copolymers:
Monomeric units arranged alternatively

A——B——A——B——A——B

Block copolymers: Monomeric units arranged in blocks

A——A——A——A——B——B——B——B

Copolymers have properties different from the polymers made from either of the constituent homo-polymers, so is advantageous

Polymers

3. On the basis of chain structure

Linear polymers:

Long and straight chains with no other branching.

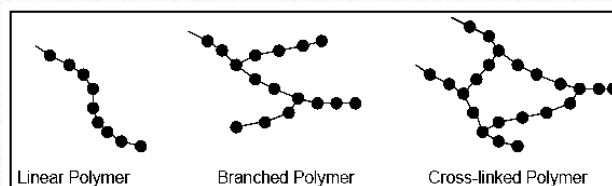**Linear polymers are well packed**

Have higher densities

Examples: High density polythene, PVC (polyvinylchloride)

Branched polymers: **Monomers are joined to form long chains with side chains of varying lengths.**

These are irregularly packed

Have low densities

Examples: Low density polythene, glycogen

Cross-linked polymers:

Formed from bi-functional and tri- functional monomers

Various linear chains held together by strong covalent bonds to form three dimensional network

Hard and rigid so do not melt rather get softened

Examples: Vulcanised rubber, Bakelite etc

Linear Polymer   Branched Polymer   Cross-linked Polymer

Polymers

In the next session:

Classification based on polymerization mechanism

Outline : Lecture 2

❑ **Classification based on types of polymerization/polymerization mechanism**

- **Chain polymerization / Addition polymerization**

- **Step growth polymerization / Condensation polymerization**

Polymers

Classification of Polymers

Based on polymerization mechanism / Polymer synthesis

Chain reaction polymerization / Addition polymerization

▪ The method involves the repeated addition of monomers to produce long chains without elimination of any by-products / successive addition of monomer molecule onto reactive ends of the growing polymer.

▪ Monomers must have a double or triple bond (unsaturation)

▪ The molecular weight of such a polymer is an exact multiple of the molecular weight of the monomer.

$$n \ (monomer) \longrightarrow polymer$$

Molecular weight of polymer = $n \times$ molecular weight of monomer.

▪ Lewis acids or bases, radical initiators are catalysts in addition polymerization

Polymers

Chain reaction polymerization / Addition polymerization

The mechanism of polymerization takes place in three distinct steps :

1. Chain Initiation step

• The Initiator molecule is thermally decomposed or allowed to undergo a chemical reaction to generate the active species.

• The **active species** that can be **free radical**, **cation or anion**, initiates the polymerization by adding to the monomer's carbon-carbon double bond.

• The reaction occurs in a manner that new **free radical**, **cation or anion** is generated .

$$I\text{———}I \longrightarrow 2\,I^* \qquad \textbf{Chain Initiated}$$
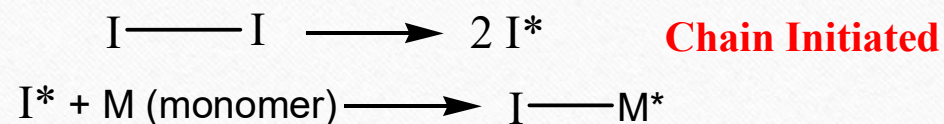
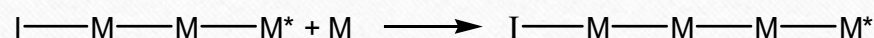$$I^* + M \text{ (monomer)} \longrightarrow I\text{———}M^*$$

• The **initial monomer** becomes the first repeat unit in the incipient polymer chain.

Polymers

Chain reaction polymerization / Addition polymerization

2. Chain propagation step

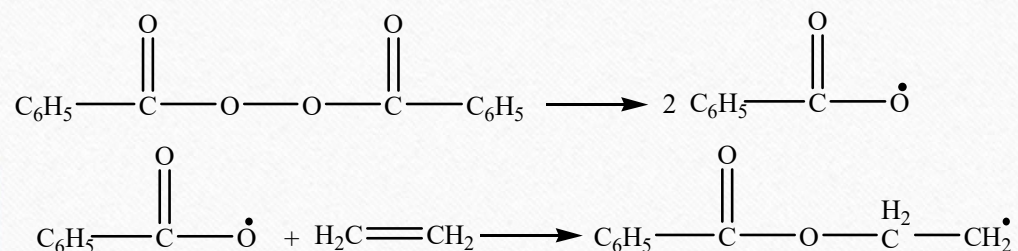Newly generated species adds to another monomer in the same way as in the initiation step.

$$I\text{---}M^* + M \longrightarrow I\text{---}M\text{---}M^*$$

$$I\text{---}M\text{---}M^* + M \longrightarrow I\text{---}M\text{---}M\text{---}M^*$$

$$I\text{---}M\text{---}M\text{---}M^* + M \longrightarrow I\text{---}M\text{---}M\text{---}M\text{---}M^*$$

3. Chain termination step

The active centres are removed or they combine with each other and the chain propagation comes to an end.

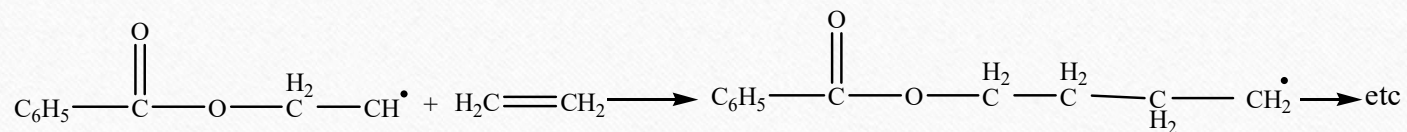$$I\text{---}M\text{---}M\text{---}M^* + M^*\text{---}M\text{---}I \longrightarrow I\text{---}M\text{---}M\text{---}M\text{---}M\text{---}M\text{---}I$$

Polymers

Free radical polymerization of ethylene

1. Chain Initiation step

$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \longrightarrow 2\ C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\bullet}{O}$$

$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\bullet}{O} + H_2C=CH_2 \longrightarrow C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{H_2}{C}-\overset{\bullet}{CH_2}$$

2. Chain propagation step

$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{H_2}{C}-\overset{\bullet}{CH} + H_2C=CH_2 \longrightarrow C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{H_2}{C}-\overset{H_2}{C}-\underset{H_2}{C}-\overset{\bullet}{CH_2} \longrightarrow etc$$

3. Chain termination step

$$2\ R\sim\sim CH_2-\overset{\bullet}{CH_2} \longrightarrow R\sim\sim CH_2CH_2-CH_2CH_2\sim\sim R$$

Polymers

General characteristics of addition / chain polymerization

1. Once initiation occurs, the polymer chain forms very quickly, i.e., 10^{-1} to 10^{-6} sec.

2. Since the carbon-carbon double bonds in the monomers are, in effect, converted to two single carbon-carbon bonds in the polymer, energy is released making the polymerization exothermic.

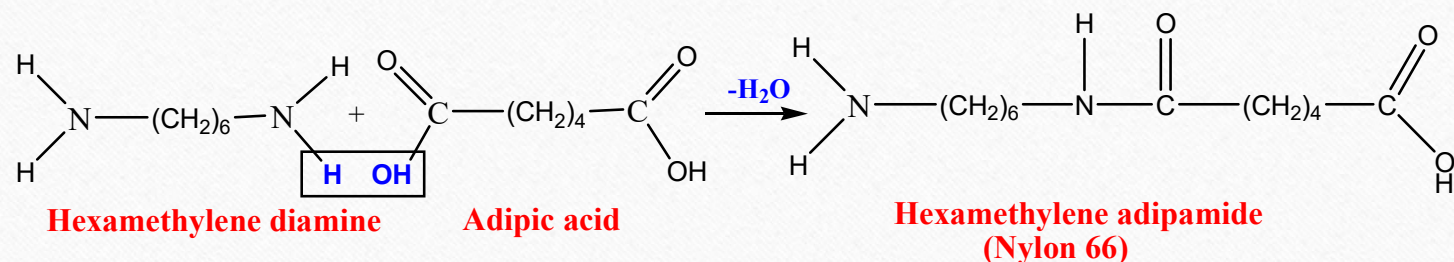3. Chain reactions normally afford polymers with high molecular weights i.e. $10^4 - 10^7$

Polymers

Condensation polymerization

• The polymerization reaction method involves series of condensation reactions (**step by step**), generally involving functional groups of two monomers, with the elimination of small molecules like H_2O, NH_3 or HCl

• Essential condition for polymerization is the presence of **2** or **more reactive groups** or **double bond** in the monomers

Condensation polymerization of Nylon 66

Nylon 66, **a common polymeric clothing material, involving one each of two monomers, hexamethylene diamine and adipic acid, react to form a dimer of Nylon 66.**

Hexamethylene diamine   **Adipic acid**   **Hexamethylene adipamide (Nylon 66)**

Polymers

Condensation polymerization

Hexamethylene diamine   +   Adipic acid $\xrightarrow{-H_2O}$ Hexamethylene adipamide (Nylon 66)
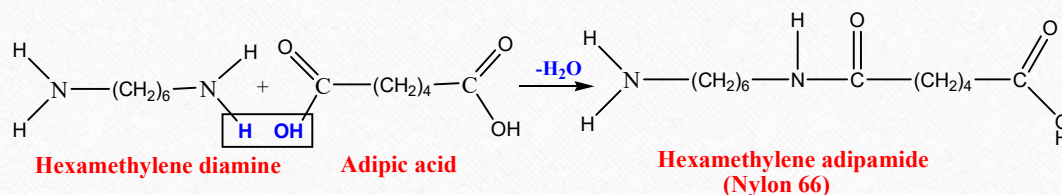
At this point, the polymer could grow in either direction by bonding to another molecule of hexamethylene diamine or adipic acid, or to another dimer

Characteristics- Step Polymerization

• This process is repeated throughout the polymerization mixture until all of the monomers are converted to low molecular weight species, such as dimers, trimers, tetramers, etc.

• These molecules, which are called **oligomers**, can then further react with each other through their free functional groups.

• Polymer chains that have **moderate** molecular weights (< 100,000) can be built in this manner. **The high molecular weights common to chain-reaction polymerizations are usually not reached. This is due to the fact that as the molecular weight increases the concentration of the free functional groups decreases dramatically.**

Polymers

Condensation polymerization

Characteristics- Step Polymerization

• The polymer chain forms slowly, sometimes requiring several hours to several days.

• Since most of the chemical reactions employed have relatively high energies of activation, the polymerization mixture is usually heated to high temperatures

• Branching or cross linking does not occur unless a monomer with three or more functional groups is used.

Polymers

Addition polymerisation	Condensation polymerisation
1. The method involves the **repeated addition of monomers** to produce long chains **without elimination of any by-products**	1. The method involves series of **condensation reactions**, generally involving two monomers with the **elimination small molecules like H_2O, NH_3 or HCl**
2. Monomers must have a **double or triple bond**	2. Monomers must have **two similar** or **different functional groups**
3. The molecular weight of the resultant polymers is a **multiple of monomer's molecular weight**	3. The molecular weight of the resultant polymer is **not a multiple of monomer's molecular weight**
4. **Lewis acids or bases**, **radical initiators** are catalysts in addition polymerization	4. No such catalysts are required
5. **High molecular mass** polymers are formed at once	5. Polymer molecular mass **rises steadily** throughout the reaction
6. Example-polyethylene, Teflon, Polyvinyl chloride (PVC)	6. Example-Nylon -6, 6, perylene, polyesters.

Polymers

In the next session:

Classification based on Tacticity
Classification based on molecular forces

Outline : Lecture 3

❑Classification based on Tacticity

❑ Classification based on molecular forces

Polymers

Classification of polymers : Based on Tacticity

Tacticity is defined as the way pendant groups (side groups/functional groups) are arranged along the backbone chain of polymer. This refers to different atomic configurations for the same composition.
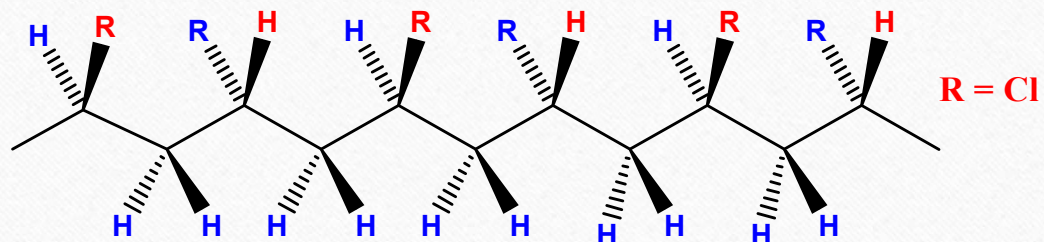
Based on the orientation of the side groups polymers can be classified as isotactic, syndiotactic or atactic polymers: **Structures of PVC as an example are described**

Isotactic: Polymers in which all the side groups are arranged on the same side of main chain are called isotactic polymers

R = Cl

Polyvinyl chloride

Polymers

Syndiotactic polymers: Polymers in which all the side groups are arranged in alternating fashion around the main chain.

R = Cl

Atactic polymers: Polymers in which all the side groups are arranged randomly on main chain.

R = Cl

The **isotactic** and **syndiotactic** forms **are stereoregular structures**, which exhibit strong tendencies to crystallize while **atactic** forms are amorphous indicating absence of crystalline order. **Atactic polypropylene** is gummy solid while **isotactic** version is highly crystalline and tough.

Polymers

Fischer projections

R = Cl
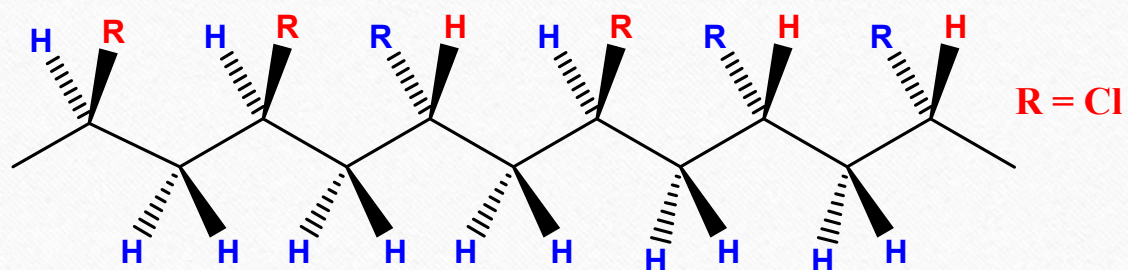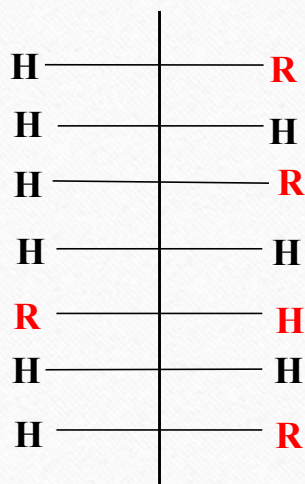
Atactic

The **isotactic** and **syndiotactic** forms **are stereoregular structures**, which exhibit strong tendencies to crystallize while **atactic** forms are amorphous indicating absence of crystalline order. **Atactic polypropylene** is gummy solid while **isotactic** version is highly crystalline and tough.

Fischer projection is not included in video lecture but is part of syllabus
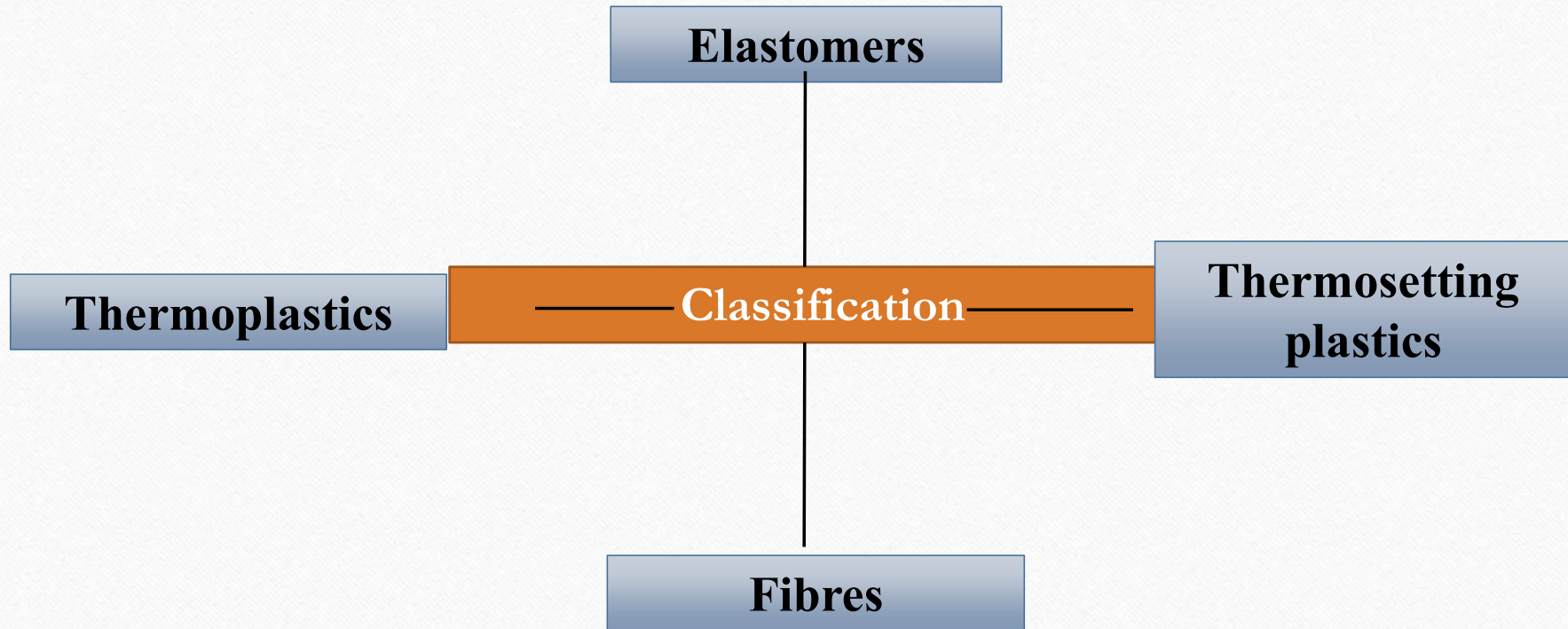
Polymers

Classification based on molecular forces

Elastomers

- Held by weakest intermolecular forces
- Have elastic behavior..
- Can be stretched three times to their original length but return to their original shape and dimension as soon as the stretching force is removed.

Example-natural rubber

Fibres

- Polymeric chains are held together by strong intermolecular forces like hydrogen bonds or dipole–dipole interactions.
- Crystalline in nature and have high tensile strength.

Example-nylon 66, polyster, silk, etc.

Polymers

Classification based on molecular forces

Thermoplastics

• Linear, long-chain polymers generally formed by addition polymerisation reaction.

• Get soften on heating, allowing for molding and harden again when cooled.

• There is no cross-linking between the polymeric chains as the polymeric chains are held together by weak vander Waals forces.

• Can be remolded and recycled without any change in their chemical and mechanical properties. Example-polyethylene, Teflon, Polyvinyl chloride (PVC), PMMA [Poly(methyl methacrylate) / Acrylic glass]

Thermosetting plastics

• Strong and hard polymers formed by condensation polymerisation reaction

• They do not soften on heating, hence once molded cannot be reshaped i.e set permanently.

• There are cross linkages and covalent bonds amongst adjacent polymeric chains

• They cannot be recycled, reused or reclaimed from waste.

• Example-Bakelite, melamine formaldehyde, polyurethane

Polymers

In the next session:

Molecular weight of polymers
Degree of polymerization (DOP)
Variation of mechanical properties of polymers with DOP

Outline : Lecture 4

❑ **Molecular weight of polymers (Number average and weight average)**

❑ **Degree of polymerization (DOP) / Polydispersity Index (PDI)**

❑ **Variation of mechanical properties of polymers with DOP**

Polymers

Molecular weight of polymers

▪ **All the polymeric chains in a polymer are of different lengths as the chain termination step is a random process. Chain length is generally expressed in terms of the molecular weight of the polymer chain, related to the relative molecular mass of the monomers and the number of monomers connected in the chain.**

**In other words, polymer is a complex mixture of molecules of different molecular weights.**

Based on this, polymers may be:

- **Polydisperse** and heterogeneous in composition
- **Monodisperse** and homogeneous in composition

Polymers

Monodisperse Polymers

Monodisperse polymers are uniform in which all molecules have the same degree of polymerization or relative molecular mass. Many biopolymers, especially proteins, are monodisperse.

$$C = 15 \quad N \quad 344$$
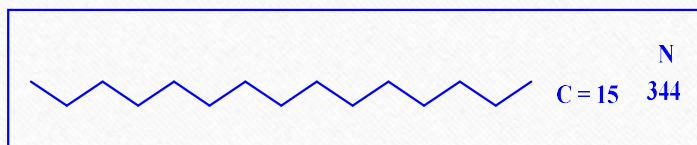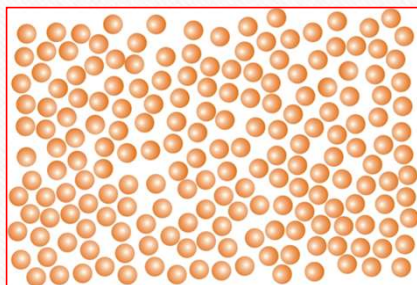
Polydisperse Polymers

Polydisperse polymer is non-uniform and contains polymer chains of unequal length, and so the molecular weight is not a single value - the polymer exists as a distribution of chain lengths and molecular weights.

	N
C = 15	109
C = 13	98
C = 11	82
C = 10	74
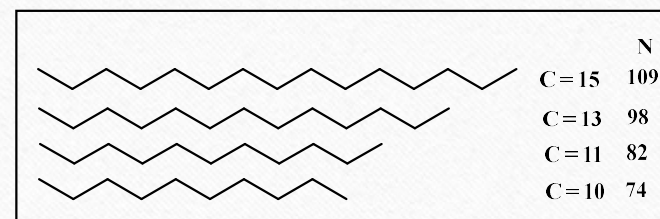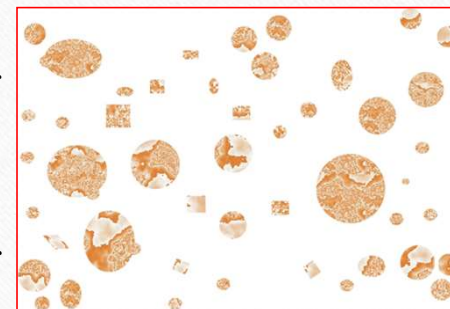
Hence, the molecular weight is expressed in terms of average of the molecular weights contributed by all the individual molecules present in the sample/ Polymer molecular weight is defined as a distribution rather than a specific number.

Polymers

Molecular weight of polymers

The **molar** mass **distribution** (or **molecular weight distribution [MWD]**) describes the relationship between the number of moles of each **polymer** species (N_i) and the **molar** mass (M_i) of that species.

MWD is basically the amounts of component polymers that make up a polymer. Component polymers, refers to convenient term that establishes the fact that all polymeric materials comprise a mixture of different polymers of differing molecular weights. The ratio of the **weight average molecular weight** to the **number average molecular weight** gives an indication of the **MWD**.

Polymers

Molecular weight of polymers

The molecular weight of a polymer is expressed in two ways:

i. Number average molecular weight $\overline{M}_n$

ii. Weight average molecular weight $\overline{M}_w$

<u>**Number average molecular weight of polymers ($\overline{M}_n$):**</u>

If N_1, N_2, N_3, … are the numbers of molecules with molecular masses M_1, M_2, M_3, …, respectively, then the number average molecular weight is:

$$\overline{Mn} = \frac{[N_1M_1 + N_2M_2 + N_3M_3 + \text{-----}]}{N_1 + N_2 + N_3 + \text{----}} = \Sigma N_iM_i / \Sigma N_i = \frac{\text{Total mass of the polymer}}{\text{Total number of molecules present in the sample}}$$
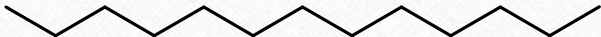
Where N_1, N_2, N_3 -number of molecules, M_1, M_2, M_3 – Mol. wts

Total mass of the polymer sample / Total number of molecules present in the sample

Polymers

Molecular weight of polymers

Example:

Mw	N
212.25	109
184.22	98
156.19	82
142.29	74

$$\overline{M_n} = \frac{(109 \times 212.25) + (98 \times 184.22) + (82 \times 156.19) + (74 \times 142.74)}{(109 + 98 + 82 + 74)}$$

Number average molecular weight can be measured on the basis of colligative properties like lowering of vapour pressure, depression in freezing point etc.

Polymers

Weight average molecular weight of polymers $(\overline{M}_w)$:

• 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:

$$\overline{Mw} = \frac{m_1M_1 + m_2M_2 + m_3M_3+\text{---------}}{m_1+ m_2 + m_3 + \text{-----------}}$$

Hence, $\overline{Mw} = \dfrac{\sum m_i M_i}{\sum m_i}$ But $m_i = N_iM_i$ where N_i = number of molecules of mass M_i

$$\overline{Mw} = \frac{[N_1M_1{}^2 + N_2M_2{}^2 + N_3M_3{}^2 + \text{-----}]}{N_1M_1 + N_2M_2 + N_3M_3 +\text{--}} = \Sigma\, N_iM_i{}^2/ \Sigma\, N_iM_i$$

Weight average molecular weight can be measured by light scattering measurements, viscosity measurements etc.

Polymers

Weight average molecular weight is higher than number average molecular weight in polymers.

Compared to $\overline{M}_n$, $\overline{M}_w$ takes into account the molecular weight of a chain in determining contributions to the molecular weight average. The more massive the chain, the more the chain contributes to $\overline{M}_w$. "$\overline{M}_n$" the number average molecular weight, is evaluated from the mole fraction distribution of different sized molecules in a sample while $\overline{M}_w$, the weight average molecular weight, is calculated from the weight fraction distribution of different sized molecules. Since larger molecules in a sample weigh more than smaller molecules, the weight average ($\overline{M}_w$) has higher values, and is always greater than $\overline{M}_n$.

https://www.doitpoms.ac.uk/tlplib/polymerbasics/mw.php
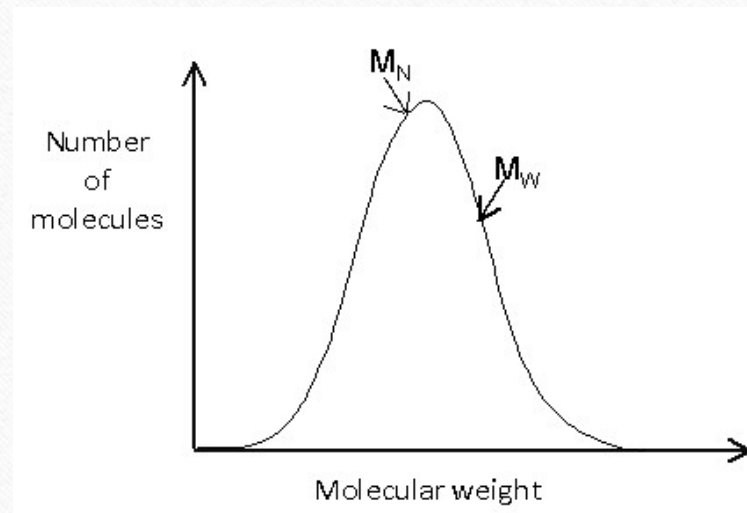
Polymers

Polydispersity Index (PDI) $\dfrac{\overline{M_w}}{\overline{M_n}}$

The PDI calculated is the weight average molecular weight divided by the number average molecular weight.

•**The polydispersity index or heterogeneity index is a measure of the distribution of molecular mass in a given polymer sample**.

•Indicates the distribution of individual molecular masses in a batch of polymers.

• The PDI has a value equal to or greater than **1**, but as the polymer chains approach uniform chain length or as the weight dispersion of molecules in a sample narrows, M_w approaches M_n, and in the unlikely case that all the polymer molecules have identical weights (a pure mono-disperse sample), the ratio(**i.e PDI**) becomes unity.

$\overline{M}_n = \overline{M}_w$, **in case all the polymer molecules are of identical molecular weight**

Polymers

Mechanical properties of polymers

For the practical applications of polymer, it is of great relevance to be familiar with some its basic mechanical properties such as:

- how much it can be stretched?

- how much it can be bent?

- how hard or soft it is?

- how it behaves on the application of repeated load

- threshold molecular weight and so on.

The properties of a polymer like tensile strength, impact resistance, resistance to cracking and melt flow viscosity are related to molecular weight and molecular weight distribution of a polymer.

In other words, DOP has direct impact on these properties whereas properties like density, refractive index, solubility are independent of molecular weight.

Polymers

Mechanical properties of polymers

Threshold molecular weight is the minimum molecular weight that a polymer must attain to develop the properties needed for a particular application. Therefore, polymerization process should be controlled after certain stage depending upon the application.

- Low molecular weight polymers – Brittle and possess less mechanical strength
- High molecular weight polymers – Tough and non-flexible, cannot be easily handled

Degree of polymerization

The number of repeating units in a polymeric chain is called 'degree of polymerization'. In other words, degree of polymerization is a number that indicates the number of repetitive units (monomers) present in the polymer. DP is represented as 'n'.

Polymers

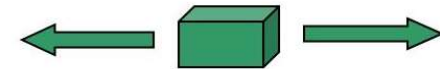## Mechanical properties of polymers

Tensile strength of a polymer

Strength of a polymer refers to **stress** (force applied divided by the cross-sectional area of the material) necessary to break the sample. The various types of strength in context of polymers are : **tensile** (stretching of the polymer), **compressional** (compressing the polymer), **flexural** (bending of the polymer), **torsional** (twisting of the polymer), **impact** (hammering) and so on.

Tensile strength is a **measure** of the **stress** needed to break a material by stretching. **Tensile strength** is important for a material that is going to be stretched or under tension.

The tensile strength is the highest load applied before it snaps in two

OR

Tensile strength is material's ability to resist tearing. An example of **tensile strength** is how much force can be put on a material before it tears apart.

Polymers

Impact Resistance

Impact resistance is generally mistaken as **impact strength**, when in fact it is not about strength at all. Strength refers to a **force** while impact resistance is an **energy**; **it is the energy required to break the sample in two or more pieces.**

In other words

It is a measure of the ability of a material or manufactured article to withstand the suddenly applied load without "**failure**". It may also be defined as the **threshold of force per unit area** before the material undergoes **fracture**. **Impact resistance is therefore a complex function of geometry, environment (thermal and chemical), material properties such as molecular structure, molecular weight (distribution), chain length, packing, tacticity, alignment and bonding forces.**

The near-instantaneous implementation of load causes the material to absorb the energy. When the amount of energy exceeds that which it can accommodate, the material will experience fracture, tear, or damage.

Polymers

•**Tensile strength** and **impact resistance** increase with increase in degree of polymerization upto a point after which slow increase is there.
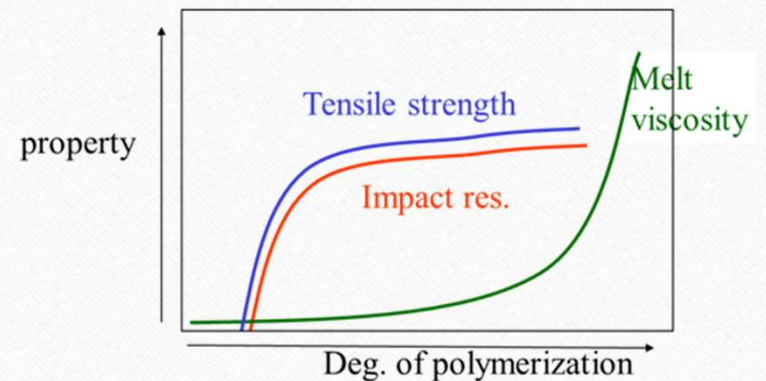

The strength of the polymer rises with increase in molecular weight and reaches the saturation level at some value of the molecular weight

• *At lower molecular weight* - *the polymer chains are loosely bonded by weak van der Waals forces and the chains can move easily, responsible for low strength,.*

• *At higher molecular weight* - *the polymer chains become large and hence are cross linked. Due to cross linking motion of the chains is restricted imparting strength to the polymer. The higher degree of entanglement allows the material to be pulled further before the chains break*

Polymers

## Variation of Tensile strength, Impact resistance and Melt flow viscosity with DOP
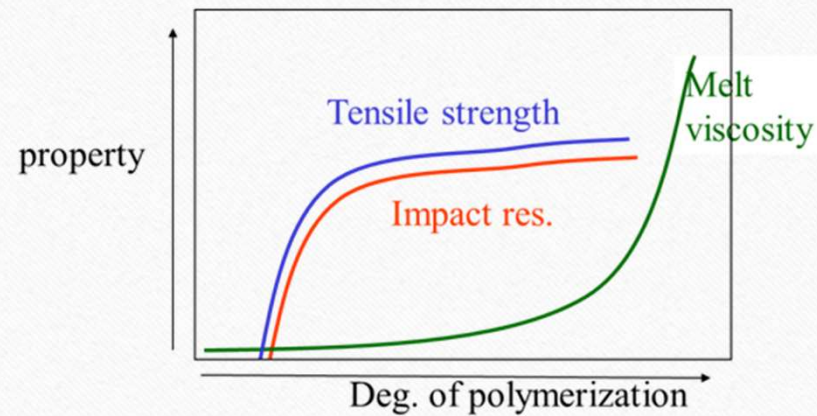
*A **high molecular weight** and **narrow molecular weight distribution** enhances the **impact resistance** of the material. A greater degree of entanglement means that in order to rupture, more polymer bonds need to be broken, this means that the polymer can absorb more energy before failing.*

Polymers

The **melt viscosity of a polymer** at a given temperature is a measure of the rate at which chains can move relative to each other. This will be controlled by the ease of rotation about the backbone bonds, i.e. the chain flexibility, and on the degree of entanglement.
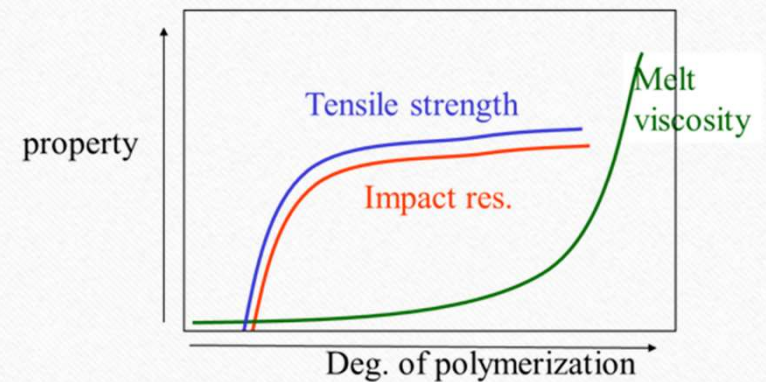
- **Melt flow viscosity** initially increases slowly, then rapidly after the polymer has attained a certain degree of polymerization,
- A high molecular weight increases the viscosity of the material making it harder to process the material using conventional methods. The longer the chains, the harder it is to get them to flow because they are more tangled.
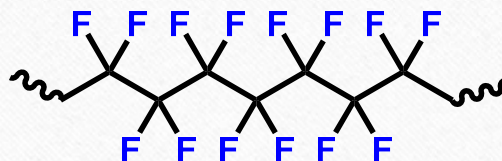
POLYMERS -III

- **Conducting Polymers**

- **Inorganic Polymers**

- **Biodegradable Polymers**

CONDUCTING POLYMERS

Development of polymers from electrical insulators to electrical conductors

R = Cl : Polyvinyl Chloride (PVC)
R = H : Polyethylene

Teflon

Polyacetylene

Due to the presence of ONLY sigma bonds, electrones have low mobility and therefore poor conductivity

Presence of delocalized π-bonds mobility of electrones increases

Generally, polymers like polyethylene, PVC, Teflon etc., are poor conductors as these are held by <u>single covalent bonds</u>. The <u>sigma-bonds</u> in such polymers have <u>low mobility of electrones</u> and does not contribute to the electrical conductivity of the material. Thus, these are <u>good insulators</u>.

Some polymers, under certain conditions, have electrical conductivities comparable to that of metallic conductors due to delocalized π **electrons.** Such polymers are called **CONDUCTING POLYMERS.**
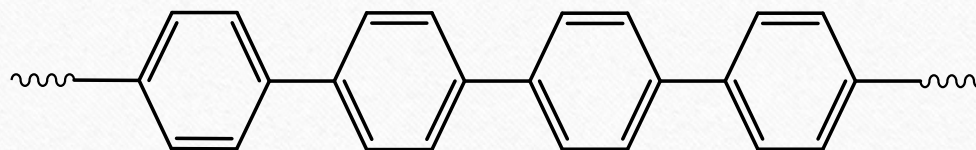
CONDUCTING POLYMERS

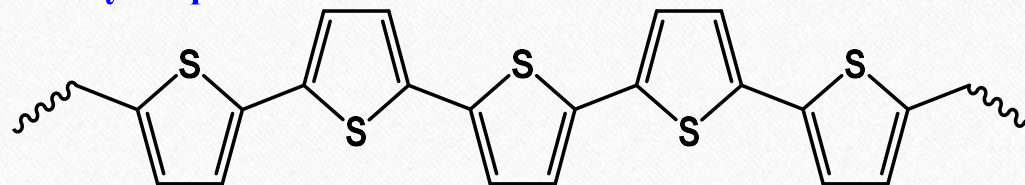However, conjugated bonds do not render polymeric materials to be highly conductive.

To enhance their conductivity a dopant needs to be added that either generates a free electron or a hole, as in case of semiconductors.

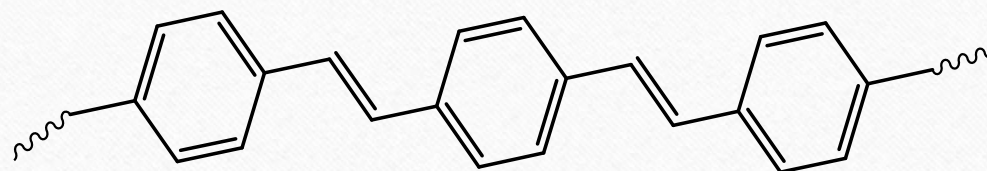Thus, depending upon which dopant has been added, Conducting Polymers can be p-Type or n-Type
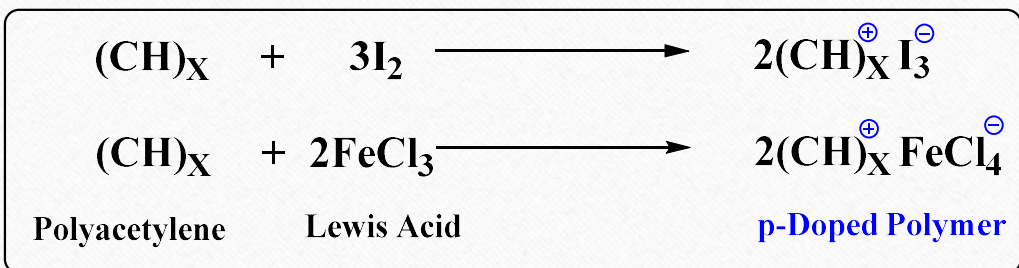
Polyphenylene
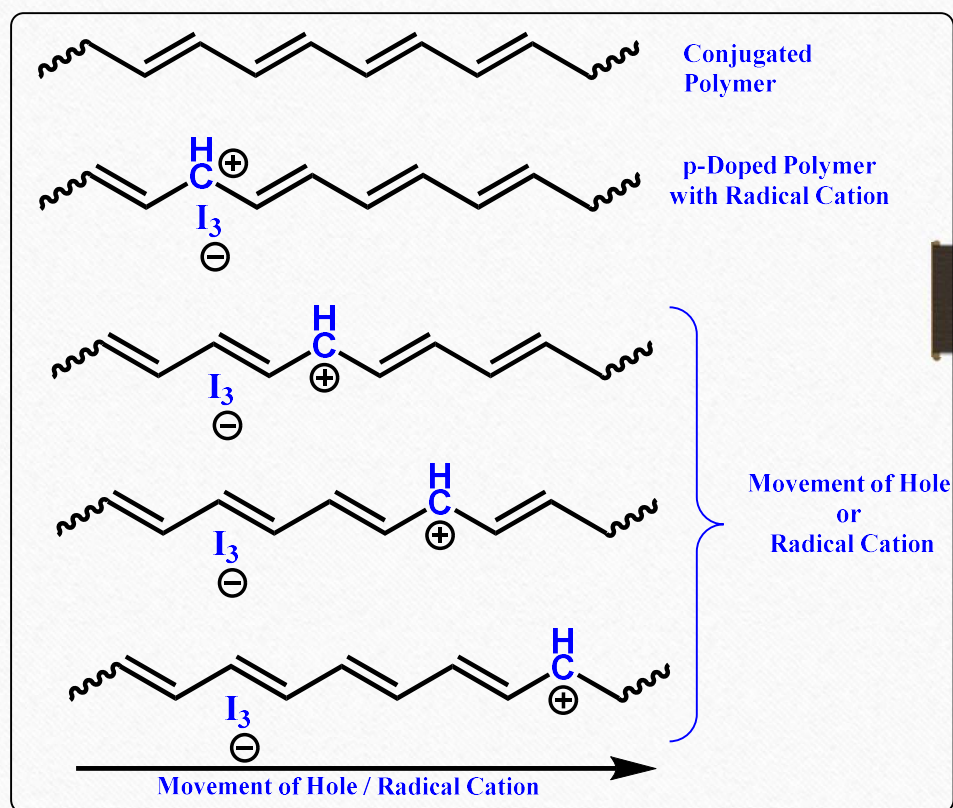
Polythiophene

Polyphenylvinylene

CONDUCTING POLYMERS

p-Doping: An electron-deficient species (Lewis acids) like $FeCl_3$, I_2 vapours or I_2/CCl_4 is added in the conjugated system to induce oxidation and thus generate a positive charge. Thus, a radical cation or a hole is generated that when moves through the doped conjugated system causes electrical conduction.

$$(CH)_X \ + \ 3I_2 \longrightarrow 2(CH)_X^{\oplus} I_3^{\ominus}$$

$$(CH)_X \ + \ 2FeCl_3 \longrightarrow 2(CH)_X^{\oplus} FeCl_4^{\ominus}$$

Polyacetylene   **Lewis Acid**   **p-Doped Polymer**

Mechanism of Conduction in p-Doped Polymers

Conjugated Polymer

p-Doped Polymer with Radical Cation

Movement of Hole or Radical Cation

Movement of Hole / Radical Cation

CONDUCTING POLYMERS

Mechanism of Conduction in n-Doped Polymers

Conjugated Polymer

n-Doped Polymer with Radical Anion

Movement of Electron or Radical Anion

Movement of Electron / Radical Anion

n-Doping: An electron-rich species (Lewis bases) like napthyl radical anion is added in the conjugated system to induce reduction and thus generate a <u>radical anion</u>. Thus, a radical anion or an electron is generated that when moves through the doped conjugated system causes electrical conduction.

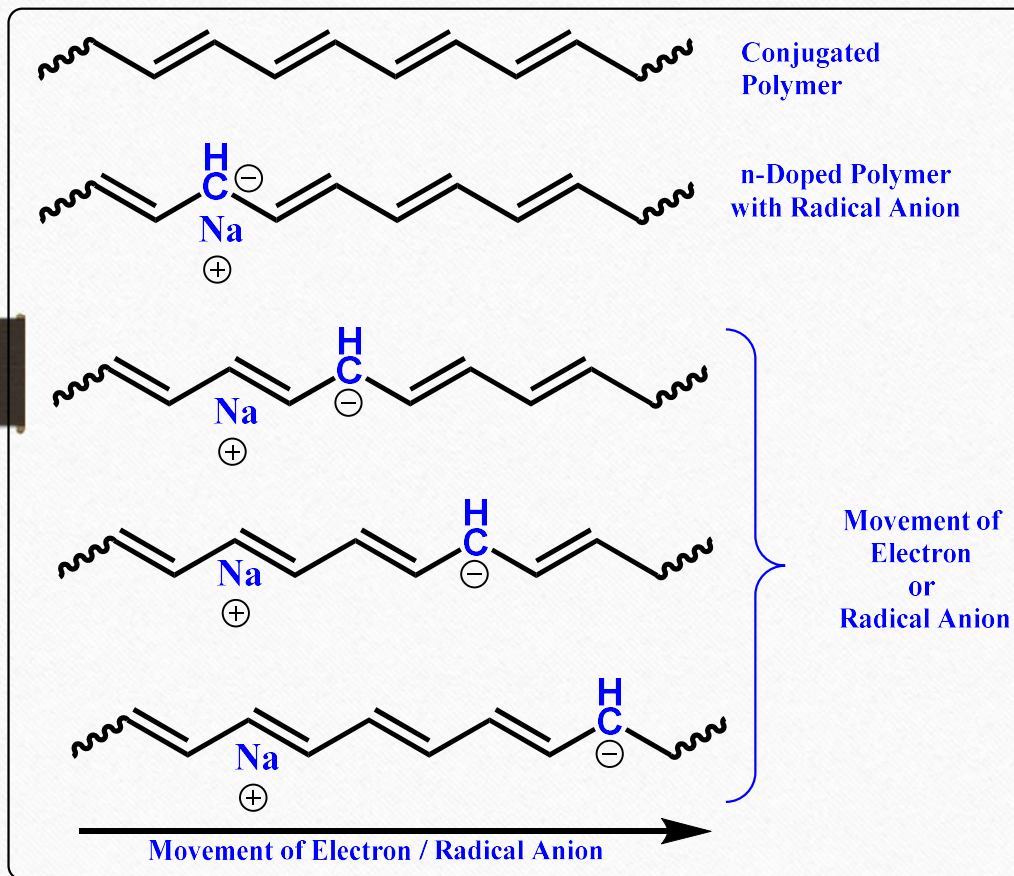$(CH)_X$ + [Sodium Napthillide] $Na^{\oplus}$ $\longrightarrow$ $2(CH)_X^{\ominus} Na^{\oplus}$ + [Napthalene]

Polyacetylene   (Sodium Napthillide)   p-Doped Polymer   Napthalene

Lewis Base
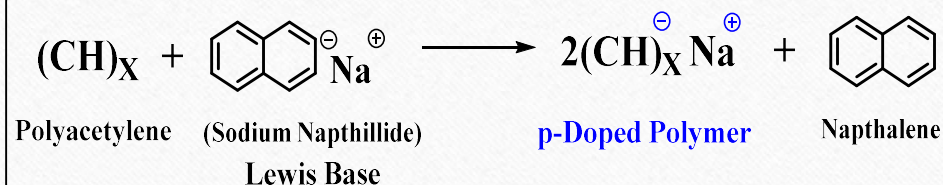
CONDUCTING POLYMERS
Applications

- **Replacement of Metal Conductor :** Conducting Polymers have replaced conventional metalic conductors due to their light weight and comparable conductivities in electronic devices.

- **Chemical Sensors :** Conducting polymers, such as polypyrrole, polyaniline, polythiophene and their derivatives, have application as gas sensors.

- **Printed Circuit Boards (PCBs) :** Conducting Polymer coated polymer sheets for PCBs are inexpensive and have better adhesive properties compared to metallic conductors coated with epoxy resins.

- **Rechargeable Batteries :** The capability of repeated oxidation and reduction of CPs make them eligible for rechargeable batteries as compated to conventional Ni-Cd Cells.

- Numerous other applications such as **Light Emitting Diodes (LEDs)**, in **Display Device**

CONDUCTING POLYMERS

Development of polymers from electrical insulators to electrical conductors

Nobel Prize in Chemistry (2000)
For the discovery and development of conducting polymers
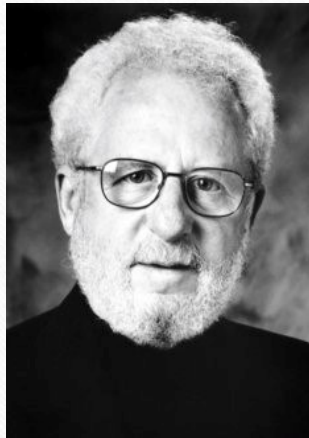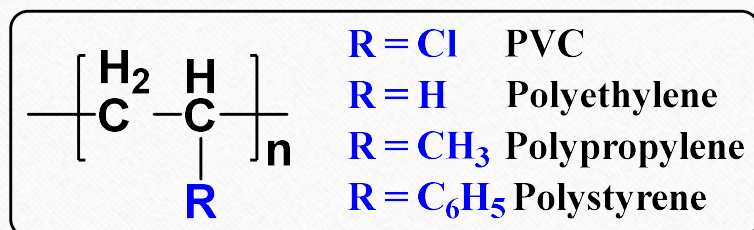
Alan J. Heeger

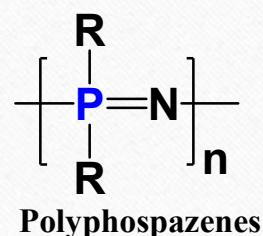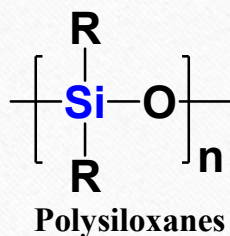**Alan G. Macdiarmid**

Hideki Shirakawa

INORGANIC POLYMERS

- Most of the polymers have a backbone of carbon.

$$\left[\begin{array}{cc} H_2 & H \\ C & C \\ & | \\ & R \end{array}\right]_n$$

R = Cl   PVC
R = H   Polyethylene
R = CH$_3$ Polypropylene
R = C$_6$H$_5$ Polystyrene

Organic Polymers have carbon in backbone

- The polymers in which backbone of the carbon is replaced by silicon, phosphorous or any other inorganic atom are called **Inorganic Polymers**.

$$\left[\begin{array}{c} R \\ | \\ Si \\ | \\ R \end{array}\right]_n$$

Polysilanes

$$\left[\begin{array}{cc} R \\ | \\ Si - O \\ | \\ R \end{array}\right]_n$$

Polysiloxanes

$$\left[\begin{array}{cc} R \\ | \\ P = N \\ | \\ R \end{array}\right]_n$$

Polyphospazenes

- Inorganic Polymers offer **properties different from Organic Polymers**

Nonflammability   **Low Temperature Flexibility**   **Electrical Conductivity**

BIODEGRADABLE POLYMERS

All natural polymers are biodegradable

Polymers produced by nature are called Natural Polymers

- **Proteins** - have monomer unit as <u>Amino Acids</u>
- **Starch & Cellulose** - have <u>Glucose</u> as monomer unit.
- **DNAs** – have <u>Nucleic acids</u> as monomer unit.

Why natural polymers are biodegradable ?

All natural polymers are biodegradable because nature has all the enzymes to degrade them. The enzymes, also called biocatalysts, are present in soil, water and all the living organisms.

How about synthetic polymers also being degraded by biocatalysts (enzymes)?

BIODEGRADABLE POLYMERS

*How about synthetic polymers also being degraded by biocatalysts (enzymes)?*

Yes, this may be possible only if a synthetic polymers also same chemical linkage as that of natural polymers like ester, amide bond or a glycosidic bond.
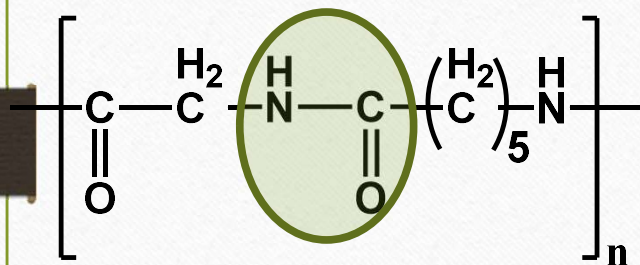
Nylon-2-nylon-6

This synthetic polymer has a peptide linkage that can be hydrolyzed by same enzymes that degrade a protein in the nature.

Polylactic acid (PLA)
is DEGRADABLE
but
NOT
BIODEGRADABLE
polymer
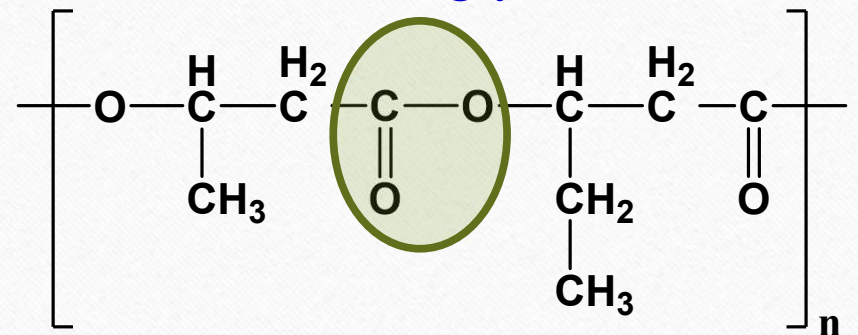
PHBV
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
The synthetic polymer has an ester linkage that can be hydrolyzed by living organisms & the products of hydrolysis further metabolized by soil microbes.

BIODEGRADABLE POLYMERS

Naturally Biodegradable
Starch, Cellulose, Proteins, DNA
Polyhydroxyalkanoates (PHA)

Synthetic Biodegradable
Nylon-2-nylon-6, PHBV
Polylactic acid

Applications

- **POTENTIAL :** These polymers have the potential to replace all available polymers
- **FOOD PACKAGING INDUSTRY:** Single use disposable materials
- **MEDICAL APPLICATION:** Slow release of medicine & in the hygiene products