

## MODULE 1

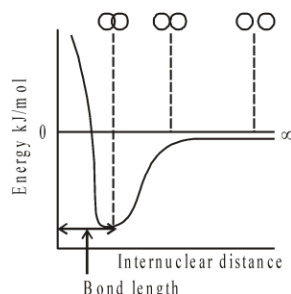
### 1. CHEMICAL BOND

Chemical bonding, any of the interactions that account for the association of atoms into molecules, ions, crystals, and other stable species that make up the familiar substances of the everyday world. When atoms approach one another, their nuclei and electrons interact and tend to distribute them in space in such a way that the total energy is lower than it would be in any alternative arrangement. If the total energy of a group of atoms is lower than the sum of the energies of the component atoms, they then bond together and the energy lowering is the bonding energy.

A chemical bond is a sort of attraction which keeps the two atoms together. These chemical bonds are what keep the atoms together in the resulting from the loss, gain, or sharing of electrons between two atoms/molecules. Thus depending upon the variety of force, there may be variety of chemical bonds.

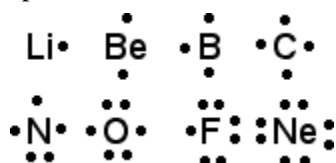
#### 1.1 REASONS FOR THE FORMATION OF A CHEMICAL BOND

**1.1.1 Energy concept:** When two atoms approach each other, the attractive and repulsive forces operate between them. The distance at which the attractive forces outweigh the repulsive forces is known as the bond distance, the potential energy of the system is minimum and the bond is said to be formed.



**1.1.2 Lewis and Langmuir (Octet Rule) :** Concept of stable electronic configuration. Atoms enter into chemical bonding to acquire the stable inert gas electronic configuration. They can do so by losing, gaining or sharing of electrons.

**1.1.3 Lewis symbols :** The electrons present in the outermost energy level of an atom and known as valence electrons. Only valence electrons are involved in the combination of two atoms. The representation of valence electrons on an atom called Lewis Symbol eg-



## 1.2 TYPES OF CHEMICAL BOND:

**Primary bond**- Primary bonds are formed when the bonding process involves a transfer or sharing of electrons. Primary bonds are those which are strong in nature. They have electronic attractions and repulsions just like secondary bonds but in equilibrium they are stronger than the later. They are broadly classified into four types:

- Ionic bonds
- Covalent bonds
- Metallic bonds.
- Coordinate bond

### 1.2.1 IONIC BOND

Ionic bond is formed by the complete transference of one or more valence electrons of one atom to the valence shell of the other atom. Both atoms are converted into ions and have the electronic configuration of nearest noble gases. The electrostatic attraction between these oppositely charged ions, which always tends to decrease the potential energy of the system is known as the ionic bond. Consider the formation of KCl. The electronic configuration of K, Cl and their ions ( $K^+$  and  $Cl^-$ ) are given below

K (19)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

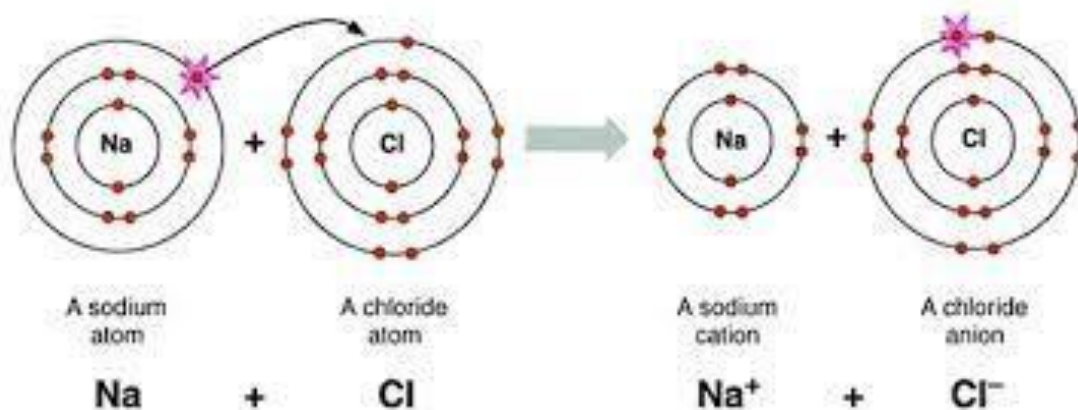
$K^+$ (18)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$  Inert gas (Ar) configuration

Cl (17)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

$Cl^-$  (18)  $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$  Inert gas (Ar) configuration

$K^+ + Cl^- \rightarrow KCl$

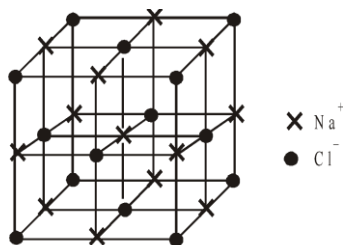
The number of electrons lost or gained by an atom represents the electrovalence of the atom.



## PROPERTIES OF IONIC COMPOUNDS

The important properties are as follows

1. **Crystal structure** : The crystalline ionic compounds have well defined crystal structure or crystal lattice eg in NaCl each  $\text{Na}^+$  is surrounded by six  $\text{Cl}^-$  ions and vice versa



Cubical structure of sodium chloride crystal

2. **Melting and boiling points**: Ionic compounds have high m.pt and b.pt due to powerful electrostatic force between ions.

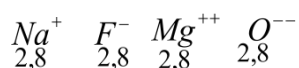
3. **Solubility**: They are generally soluble in polar solvents (having high value of dielectric constant). The solubility of ionic compounds decreases with increase in covalent character of ionic compounds. It is also governed by-

a. **Lattice energy**: More the lattice energy, lesser is the solubility, Eg. sulphates and phosphates of Ba and Sr are insoluble in water due to high lattice energy.

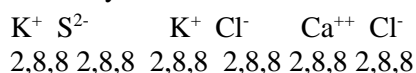
b. **Heat of hydration**: More the heat of hydration, more is the solubility. Eg.  $\text{AlCl}_3$  though covalent in nature is soluble in water due to high value of heat of hydration.

4. **Electrical conductivity**: In solid state they do not conduct electricity since there is no free movement of electrons but in molten state and in solution they conduct electricity.

5. **Isomorphism**:  $\text{NaF}$  and  $\text{MgO}$  are isomorphous due to similar electronic structure



Similarly  $\text{K}_2\text{S}$  and  $\text{CaCl}_2$  are isomorphous

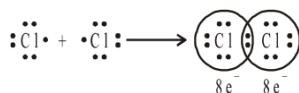


### 1.2.2 COVALENT BOND :

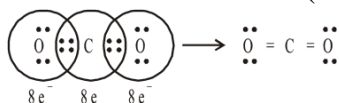
According to G. N. Lewis atoms may also combine by sharing of electrons present in their outermost shells and attain noble gas electronic configuration. One shared pair of electrons constitute a single bond, two electron pairs constitute a double bond and so on. The bonds thus formed are known as covalent bonds.

### EXAMPLES OF COVALENT COMPOUNDS

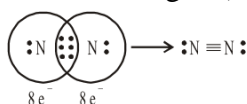
1. Chlorine ( $\text{Cl}_2$ )



2. Carbon dioxide ( $\text{CO}_2$ )



3. Nitrogen ( $\text{N}_2$ )



## PROPERTIES OF COVALENT COMPOUNDS

1. **Physical state** - They may be gases, liquids or solids.
2. **Crystal structure** - They may exist as simple molecules held together by weak forces, giant molecules united by covalent link Eg. diamond, silicon carbide, alumina, aluminum nitride etc. and can have layer structure. Eg. graphite.
3. **Solubility** - Generally soluble in non-polar solvents.
4. **Melting/ boiling points** - Low as compared to ionic compounds.
5. **Electrical conductivity** - Being non-electrolytes they do not conduct electricity, graphite does due to presence of free electrons.
6. **Stereo-isomerism** - They exhibit structural and stereo-isomerism both.

## HYBRIDISATION

Hybridisation is the redistribution of energy levels at the time of formation of molecules. It may also be defined as intermixing of atomic orbitals of nearly the same energy and resulting in the formation of new atomic orbitals same in number and identical in all respects (shape, energy and size). The new atomic orbitals are known as hybrid atomic orbitals.

The completely filled or half-filled atomic orbitals can take part in hybridization and hybrid atomic orbitals form stronger bonds.

## METHOD FOR FINDING THE TYPE OF HYBRIDISATION

Apply the following formula to find the hybridization of central atom.

$$\frac{1}{2} \left( \begin{array}{l} \text{Number of valence electrons of central atom} \\ + \text{number of monovalent atoms attached to it} \\ + \text{negative charge if any} - \text{positive charge if any} \end{array} \right) = z$$

**Value of z** 2 3 4 5 6 7

**Hybridization**  $sp$   $sp^2$   $sp^3$   $sp^3d$   $sp^3d^2$   $sp^3d^3$

*Examples:*

1. hybridization of  $NH_3$  =  $[5 + 3 + 0 - 0] = 4$ ;  $sp^3$
2. hybridization of  $H_2O$  =  $[6 + 2 + 0 - 0] = 4$ ;  $sp^3$
3. hybridization of  $SO_3$  =  $[6 + 0 + 0 - 0] = 3$ ;  $sp^2$
4. hybridization of  $SO_4^{2-}$  =  $[6 + 0 + 2 - 0] = 4$ ;  $sp^3$
5. hybridization of  $CO_3^{2-}$  =  $[4 + 0 + 2 - 0] = 3$ ;  $sp^2$
6. hybridizations of  $PCl_5$  =  $[5 + 5 + 0 - 0] = 5$ ;  $sp^3d$
7. hybridization of  $SF_6$  =  $[6 + 6 + 0 - 0] = 6$ ;  $sp^3d^2$

**Note:** Species having same hybridization are isostructural in nature.

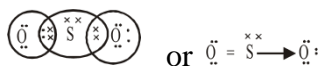
### 1.2.3 COORDINATE COVALENT BOND OR DATIVE BOND

When both the electrons for sharing between two atoms are contributed by one atom only the bond formed is known as coordinate bond or dative bond.

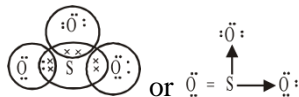
The atom donating the pair of electrons is called donor and the atom which accepts the pair of electrons is called acceptor. The compounds containing coordinate bonds are known as coordination compounds. The bond is represented by an arrow ( $\rightarrow$ ) pointing head towards the acceptor.

Some examples are:

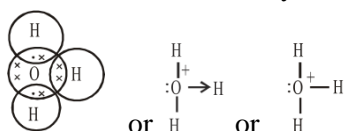
1. Formation of  $\text{SO}_2$



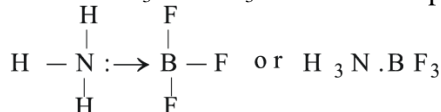
2. Formation of  $\text{SO}_3$



3. Formation of Hydroxonium ion



4.  $\text{NH}_3$  and  $\text{BF}_3$  form addition product by Coordinate covalent bond



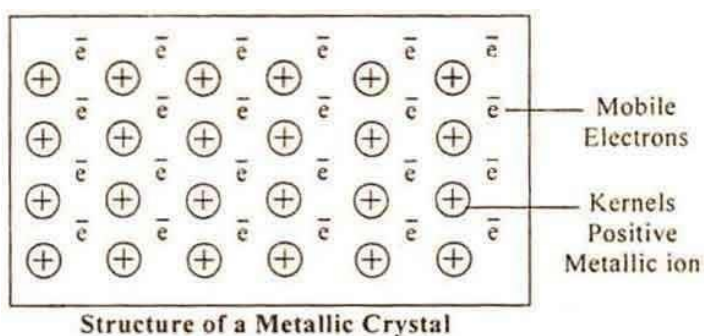
## PROPERTIES OF COORDINATE COMPOUNDS

Coordinate compounds have volatile character in between ionic and covalent compounds. Other properties like solubility, electrical conductivity and stereo-isomerism are similar to covalent compounds.

### 1.2.4 METALLIC BOND

'Metallic bond' is a term used to describe the collective sharing of a sea of valence electrons between several positively charged metal ions. Metallic bonding is a type of chemical bonding and is responsible for several characteristic properties of metals such as their shiny lustre, their malleability, and their conductivities for heat and electricity.

Both metallic and covalent bonding can be observed in some metal samples. For example, covalently bonded gallium atoms tend to form crystal structures that are held together via metallic bonds. The mercurous ion also exhibits metallic and covalent bonding.



The factors that affect the strength of a metallic bond include:

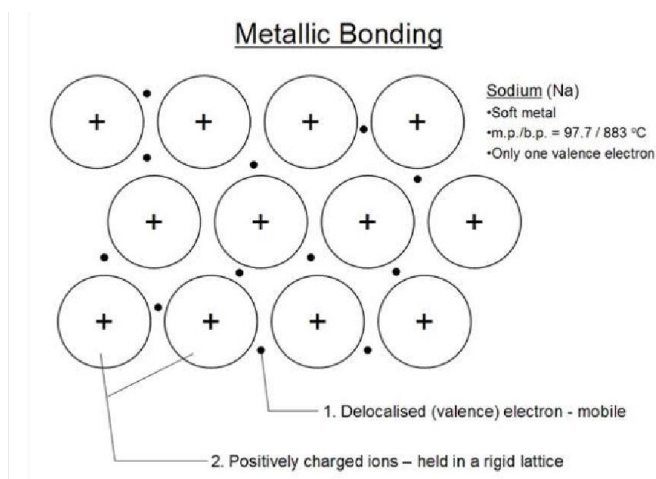
- Total number of delocalized electrons.
- Magnitude of positive charge held by the metal cation.
- Ionic radius of the cation
- Metallic bonds are not broken when the metal is heated into the melt state. Instead, these bonds are weakened, causing the ordered array of metal ions to lose their definite, rigid structure and become liquid. However, these bonds are completely broken when the metal is heated to its boiling point.

### Example – Metallic Bonding in Sodium

The electron configuration of sodium is  $1s^2 2s^2 2p^6 3s^1$ ; it contains one electron in its valence

shell. In the solid-state, metallic sodium features an array of  $\text{Na}^+$  ions that are surrounded by a sea of 3s electrons. However, it would be incorrect to think of metallic sodium as an ion since the sea of electrons is shared by all the sodium cations, quenching the positive charge.

An illustration describing the metallic bonding in sodium is provided below.



The softness and low melting point of sodium can be explained by the relatively low number of electrons in the electron sea and the relatively small charge on the sodium cation. For example, metallic magnesium consists of an array of  $\text{Mg}^{2+}$  ions. The electron sea here contains twice the number of electrons than the one in sodium (since two 3s electrons are delocalized into the sea). Due to the greater magnitude of charge and the greater electron density in the sea, the melting point of magnesium (~650°C) is significantly higher than that of sodium.

## CONSEQUENCES OF METALLIC BOND

1. **Electrical conductivity** - It is due to presence of mobile valence electrons.
2. **Thermal conductivity** - On heating one part of metal, the K.E. of electrons is increased and they conduct heat to the other parts of the metal.
3. **Metallic lustre** - The mobile electrons are promoted to excited states by absorption of light and on coming back from the excited state light of all wavelengths in the visible region are emitted. The surface therefore emits metallic lustre.
4. **Malleability** - Metals can be made thin sheets
5. **Ductility** - Metals can be drawn into wires since metal kernels can easily be shifted.
6. **Electrical conductivity decreases with temperature** - It is due to random motion of mobile electrons which increases with increase of temperature.

**SECONDARY BOND-** Secondary bonds are formed from the subtle attraction forces between positive and negative charges. Secondary bonds are bonds of a different kind to the primary ones. They are weaker in nature and are broadly classified as:

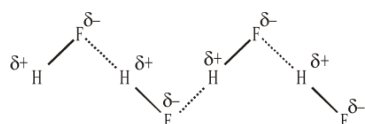
- Van der Waal's forces
- Hydrogen bonds.

## 1.2.5 HYDROGEN BOND

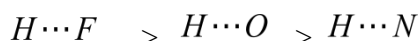
It may be defined as the force of attraction existing between hydrogen atom covalently bonded to highly electronegative atom (N, O or F) and the electronegative atom belonging to another molecule of the same or different substance. It is represented by dotted lines



The chains possess a **Zig-Zag** structure



Hydrogen bond is purely electrostatic in nature. It is a weak bond, the strength of the strongest being about 5 - 10 kcal per mole. The more the electronegativity of atom involved in H - bonding, the more is the bond strength eg.

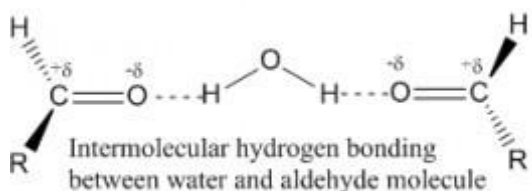


$$10 \text{ kcal/mole} > 7 \text{ kcal/mole} > 2.0 \text{ kcal/mole}$$

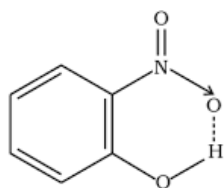
### TYPES OF HYDROGEN BONDS

Hydrogen bond is of two types

1. Intermolecular H-bonding (Association) -. When hydrogen bonding occurs between to atoms of different molecule then it is called intermolecular hydrogen bonding. For such bonding one molecule should have a partially positive hydrogen as acceptor atom and another should have a partially negative or donor atom. As for example, hydrogen bonding between aldehyde and water molecule has given below: H-bonding involving two or more molecules.



2. Intramolecular H-bonding (Chelation)-. When hydrogen bonding occurs between two partially charged atoms of same molecule that is called intramolecular hydrogen bonding. This occurs when two functional groups are present in same molecule and they are in such way that can attract each other to form hydrogen bond. For example salicylic acid has two functional groups alcohol and carboxylic acid. Here intramolecular hydrogen bonding occurs between the hydrogen atom of alcohol group and the oxygen atom of carboxylic acid group. H-bonding taking place within



single molecule. Intramolecular hydrogen bonding in o-nitrophenol molecule

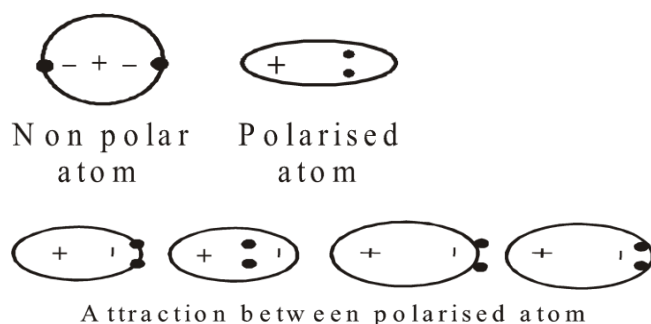
## 1.2.6 VAN DER WAAL'S FORCES

Attractive forces between uncharged molecules are known as van der Waals forces. These forces may be divided into three groups

1. Dispersion or London forces. These are due to transient polarization.
2. Dipole-dipole attraction. These are due to permanent polarization.
3. Dipole-induced dipole forces

### LONDON FORCES

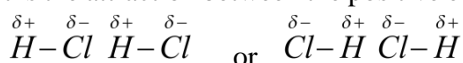
The negative electrons in a neutral molecule are balanced by the positive charges on the nucleus. Since the electrons are in motion the center of density of the electrons does not coincide continuously with the center of density of positively charged nuclei, the molecules acquire an electric dipole. Polarized molecules exert an attraction for other molecules having a dipole. Consider the case of helium.



- The greater the polarizability of a molecule, the stronger are the London forces.
- The polarizability increases with number of electrons and their distance from the nucleus.
- These forces are operative over a very short range.
- The inert gases have weak van der Waals forces of attraction
- The straight chain hydrocarbons boil at higher temperature than isomeric branched chain hydrocarbons due to greater magnitude of van der Waal's forces of attraction.

### DIPOLE-DIPOLE ATTRACTION

It is the attraction between the positive end of the one molecule and negative end of another molecule.



This type of interaction is called dipole - dipole interaction. The force of dipole - dipole attraction is

inversely proportional to fourth power of their separation of distance  $r$ .  $F = \frac{1}{r^4}$ . The dipole dipole attractions in gaseous molecules are particularly small since the gas molecules are in continuous motion. This attraction increases the m.pt. and b.pt. of substances and makes their liquefaction easy.

### DIPOLE-INDUCED DIPOLE ATTRACTION

The attractive forces operate between polar molecules having permanent dipole and non-polar molecules. The polarity in the non-polar molecules is induced by the polar molecule





## Advanced Materials

Advanced materials are materials with mechanical and physical properties that are superior to those of commonly used materials like steel, aluminum, and magnesium. They have many applications, including in aerospace, automobiles, trains, oil and gas exploration, and medical devices.

Here are some properties of advanced materials:

- **Strength and ductility:** Advanced materials can absorb and redistribute high stress concentrations without failing suddenly.
- **Stiffness and modulus:** Advanced materials can maintain their shape and dimensions under external action.
- **Temperature:** Advanced materials can perform well at higher temperatures.
- **Forgiveness:** Advanced materials have good fracture toughness and fatigue-crack growth rate.
- **Reduced density:** Advanced materials can be less dense than other materials.

Some examples of advanced materials include:

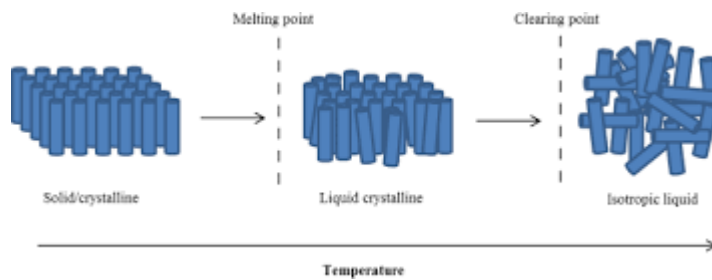
- **Chromo active materials (Liquid crystals)**
- **Nanomaterials**
- **Polymeric Materials- Conducting polymers**
- **Composite concepts: Materials made up of two or more components with different properties**
- **Monolithic metals: Materials like titanium**
- **Nickel-based alloys: Materials with high-temperature strength, low-temperature ductility, and oxidation resistance**

Advanced materials can be used to improve the performance of lightweight structures in a variety of engineering problems. They can also help to mitigate the shortcomings of traditional materials, such as brittleness and high cost.

### CHROMO ACTIVE MATERIALS (LIQUID CRYSTALS)

Liquid crystals form a state of matter intermediate between the solid and the liquid. For this reason, they are referred to as intermediate phases or mesophases.

When molecular crystals are heated to their melting point, they usually change directly into the liquid state. The periodic structure of the lattice as well as the orientational ordering of the molecules is destroyed simultaneously. However, if the constituent molecules have a pronounced anisotropy of shape, such as rod or disc, the melting of the lattice may precede the disappearance of the orientational ordering leading to an intermediate phase composed of molecules which are more or less parallel to each other but at the same time exhibiting a certain degree of fluidity. The molecules can slide over one another while still preserving their parallelism. The fluid is therefore anisotropic; it is turbid and, like a crystal, shows optical birefringence and dielectric anisotropy. At a higher temperature, there is orientational melting and the anisotropic fluid transforms into the ordinary isotropic clear liquid. Such intermediate (or meso) phases are referred to as liquid crystals (LCs). They combine both, order and mobility.



## Classification of liquid crystals

Liquid crystals can be roughly divided into two areas:

1. Thermotropic, whose mesophase formation is temperature dependent,
2. Lyotropic, whose mesophase formation is solvent and concentration dependent.

The Lyotropic liquid crystal can be classified as:

- (a) Nematic liquid crystal
- (b) Smectic liquid crystal
- (c) Cholesteric liquid crystal

### (a) Nematic liquid crystal:

The nematic phase of calamitic liquid crystals is the simplest liquid crystal phase. The name "nematic" comes from the Greek word, nema means thread-like which can be observed under polarizing microscope. This name was given due to the thread-like discontinuities produced by variations in the molecular organization. The nematic phase is essentially a one dimensionally ordered elastic fluid in which the molecules have a high degree of long range orientational order, but there is no long-range translational order (positional order). It is the least viscous and least ordered mesophase with a high degree of fluidity. The phase is usually very easy to identify by optical polarizing microscope. In the nematic phase, the constituent molecules are completely disordered with respect to each other but the long molecular axes statistically point in a preferred direction known as the director ( $q$ ). The most common texture adopted by the nematic phase is schlieren.

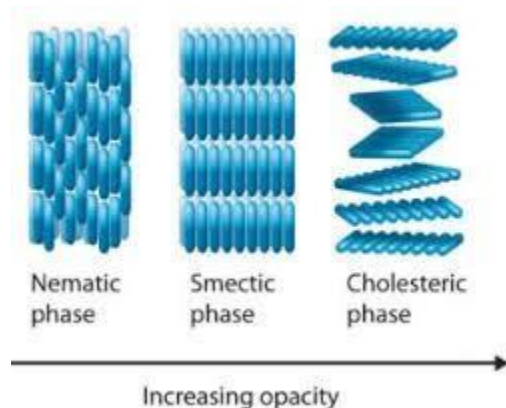
### (b) Smectic liquid crystal:

Smectic liquid crystals differ from nematics as smectics have two degrees of order namely orientational and positional. In smectic mesophase, the molecules form layers and translation of molecules from one layer to another is limited. Within these layered systems, a variety of molecular arrangements is possible leading to different sub phases. The term smectic comes from the word smectos-soap like, as the basic layered structure in the smectic phase gives them a soapy feel. The smectic phase is characterized by a long range orientational order and positional order which gives layered structure. The inter layer attractions are weak when compared with the lateral forces between the molecules and the layers are able to slide freely over one another. As a result, the smectic phase has fluidity and is more viscous than nematic phase. The smectic phase is more ordered than the nematic phase. The smectic phase exhibits polymorphism and the lamellar nature of smectic phase allows various combinations of molecular correlations both within the 'layers' and between the 'layers' each of which consists of different type of smectic phase. The smectic phases are found at lower temperatures than nematics which can be identified under optical polarizing microscope.

### (c) Cholesteric liquid crystal

The cholesteric phase is also called chiral nematic phase or twisted nematic phase. Cholesteric phase was first discovered in cholesterol. The chiral nematic phase exhibits chirality and is associated with the presence of an asymmetric carbon atom, so that left- and right-hand versions of molecules cannot be commuted by simple reorientation. The molecules forming this phase are always optically active, i. e. they have distinct right- and left-handed forms. Only chiral molecules (i.e., those that lack of inversion symmetry) can give rise to such a phase. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director.

### APPLICATIONS



- The most important use of liquid crystals is in displays because the molecules of a liquid crystal can control the amount, color, and direction of vibration of the light that passes through them.
- They are used in the LCDs and in digital watches.
- Also used in handheld calculators; flat-screen monitors; and car, ship, and aircraft instrumentation.
- They are used in all kinds of display devices including computer monitors and laptop screens, TVs, clocks, visors, and navigation systems.

## NANOMATERIALS

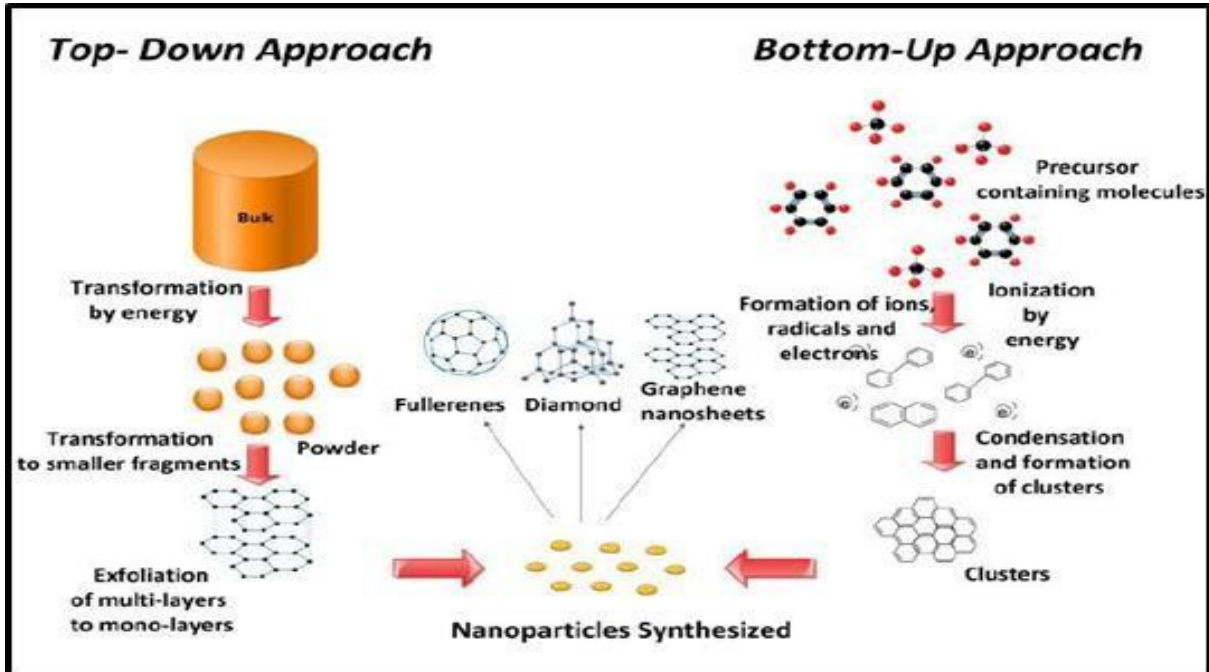
Nanomaterials are 'material with any external dimension in the nanoscale (size range from approximately 1 – 100 nm) or having internal structure or surface structure in the nanoscale'.

Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery.

The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials.

### 1.7.1 PREPARATION OF NANOMATERIALS:

When it comes to the synthesis of metallic Nanoparticles, two distinct approaches are utilized. The first is the top-down strategy and the second approach is referred to as the bottom-up strategy. While the former deals with the reduction in size of current technological devices, the latter performs an



opposite role, which is building of even more complex molecular devices on an atomic arrangement.

#### TOP-DOWN APPROACH

The top-down approach usually involves the following processes:

1. Cutting
2. Grinding
3. Itching
4. Ionic/electronic irradiation

#### BOTTOM-UP APPROACH

The bottom-up approach utilizes physical and chemical processes that function at the nanoscale to integrate main components into bigger structures. A reduction in unit size, the approach yields a relevant consummation to the top-down approach. Biological systems provide a motivation for this approach in which natural forces of life harness their chemical counterparts to produce the structures.

Gold-palladium alloy nanoparticles which were based on carbon treated with acid and breaking down hydrogen peroxide are formed from the combination of white hydrogen and red oxygen when disallowing unwanted decay.

This approach has been used in the production of nanoparticles from condensation to coalescence of atomic vapors and liquids, respectively.

1. Sol-gel techniques

This allows the production of nanomaterials from alkoxides or colloidal based solution. They take the

form of monoliths, crystallized nano pigments, and thin layers. They are centered on reactions in polymerization. Lithography in which growth of thin film is done.

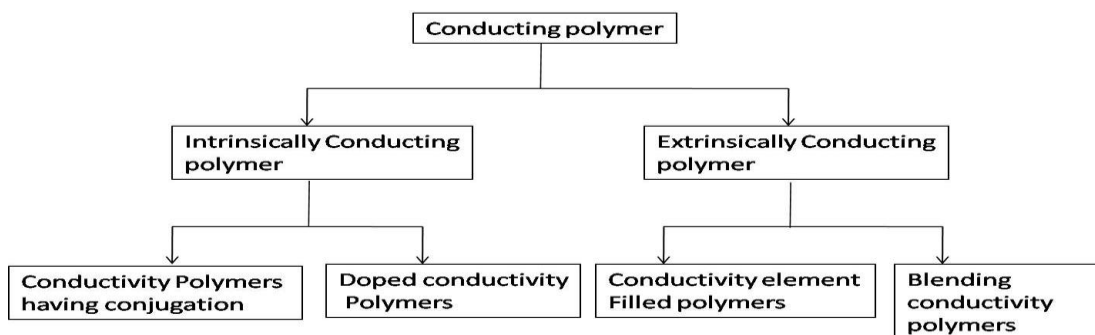
## APPLICATIONS

- Nanoscale additives to or surface treatments of fabrics can provide lightweight ballistic energy deflection in personal body armor, or can help them resist wrinkling, staining, and bacterial growth.
- Clear nanoscale films on eyeglasses, computer and camera displays, windows, and other surfaces can make them water- and residue-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antifog, antimicrobial, scratch-resistant, or electrically conductive.
- Nanoscale materials are beginning to enable washable, durable “smart fabrics” equipped with flexible nanoscale sensors and electronics with capabilities for health monitoring, solar energy capture, and energy harvesting through movement.
- Nanoparticles are used increasingly in catalysis to boost chemical reactions. This reduces the quantity of catalytic materials necessary to produce desired results, saving money and reducing pollutants. Two big applications are in petroleum refining and in automotive catalytic converters.
- Nano-engineered materials make superior household products such as degreasers and stain removers; environmental sensors, air purifiers, and filters; antibacterial cleansers; and specialized paints and sealing products, such as self-cleaning house paints that resist dirt and marks.
- Nanoscale materials are also being incorporated into a variety of personal care products to improve performance. Nanoscale titanium dioxide and zinc oxide have been used for years in sunscreen to provide protection from the sun while appearing invisible on the skin.

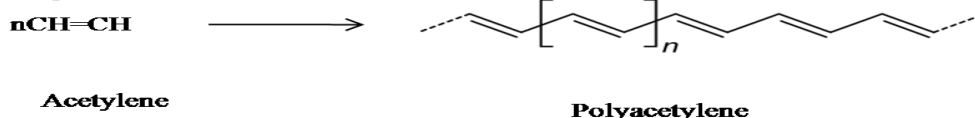
## POLYMERIC MATERIALS- CONDUCTING POLYMERS\

A polymer which can conduct electricity is termed as conductivity polymer.

### Classification of conducting polymer



A) **Intrinsically Conductivity polymer.** These polymers have extensive conjugation in the backbone which is responsible for conducta

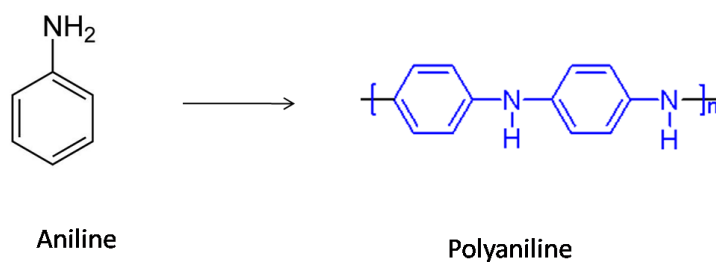


(a) **Conducting polymers having conjugated  $\pi$ -electrons in the backbone.** Such polymers contain conjugated  $\pi$ - electrons in the backbone which increases their conductivity to a large extent. This is because, overlapping of conjugated  $\pi$ -electrons over the entire backbone results in the formation of valence bands as well as conduction band, which extends over the entire polymer molecule. The valence band and conduction bands are separated by a significant band gap. Thus, electrical conduction could occur only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band. Examples:

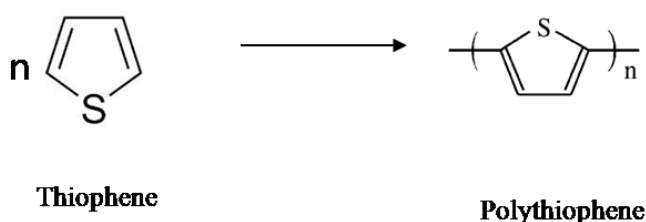
(i) **Polyacetylene**

(ii) **Polypyrrole**

(iii) **Polyaniline**

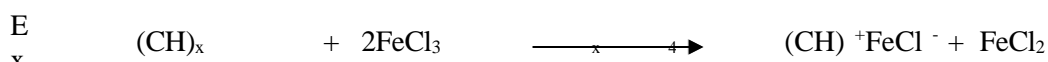


(iv) **Polythiophene**

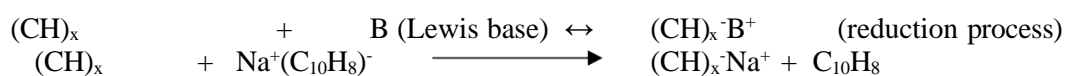


(b) **Doped conducting polymer.** The conducting polymers of type (a) can be easily oxidized or reduced as they have low ionization potentials and high electron affinities. Their conductivity can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction.

**p-doping** It is done by oxidation process. Conductivity polymer of type (a) is treated with Lewis acid or with iodine vapour or iodine in  $\text{CCl}_4$ .



**n-doping** It is done by reduction process. For this, conducting polymer of type (a) is treated with lewis bases like sodium naphthalide.



Conducting polymer	Polyaniline	Polypyrrole	Polythiophene
Dopants	HCl	BF <sub>4</sub> <sup>-</sup>	Tosylate
Conductivity (Scm <sup>-1</sup> )	1000	500-7500	1000

**B) Extrinsically conducting polymer.** In this, the polymer owe their conductivity due to the presence of externally added ingredients in them. These are of following two types

(a) **Conductivity element filled polymer.** In this, the polymer acts as the binder to hold the conducting element (such as carbon black, metallic fibre, metallic oxides) together in the solid entity. Minimum concentration of conductive filler which should be added so that polymer starts conducting is known as percolation threshold. Because at this concentration of filler a conducting path is formed in polymeric material. Generally Carbon black is used as filler which has very high surface area, more porosity.

(b) **Blended conducting polymer.** These polymers are obtained by blending a conventional polymer with a conducting polymer. Such polymer possess better physical, chemical, electrical and mechanical properties. For example, up to 40% of polypyrrole will have little effect on tensile strength and also give a much impact strength than obtained with a carbon black filled compound at only 10% loading.

### **Applications of Conducting Polymer**

- In Rechargeable lithium ion batteries
- In analytical sensors: For making sensors for pH, O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> and glucose
- For making ion exchangers
- In electrochromic displays ad optical filters: conducting polymers can be used as electrochromic material (i.e. the materials which change color reversibly during the electrochemical charge and discharge)
- In electronics: In LED's and Data storage
- In photovoltaic devices: ex Al/conducting polymer/Au photovoltaic cell
- Polypyrrole is used in smart windows: smart windows can change their color in response to change in temperature or amount of sunlight.

## PANI AND PEDOT IN SENSORS

**Polyaniline (PANI)** is a conductive polymer that is used in a variety of sensors, including electrochemical sensors, chemi-resistive sensors, and transistor-based sensors:

- **Electrochemical sensors:** PANI is often used with nanomaterials to improve the sensitivity of electrochemical nanosensors. PANI and its nanocomposites have excellent electrocatalytic properties, which can lead to enhanced detection sensitivity, high conductivity, and reduced fouling.
- **Chemi-resistive sensors:** Polyaniline nanowires can be used as an active layer in chemi-resistive sensors. The conductivity change of the nanowires can be used to detect chemical or biological species.
- **Transistor-based sensors:** PANI-based materials can be used in transistor-based sensors.

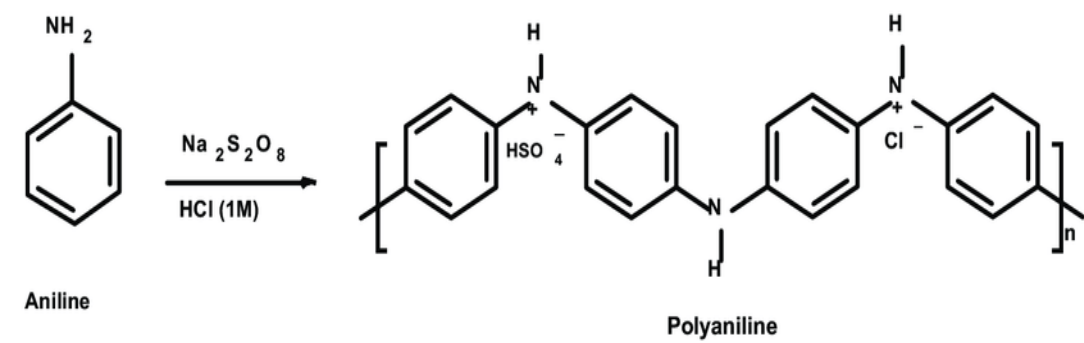
PANI is a popular choice for sensors because of its unique properties, including:

- **Easy synthesis:** PANI is easy to synthesize and dope with different acids and dopants.
- **Environmental stability:** PANI is highly environmentally stable.
- **Biocompatibility:** PANI is highly biocompatible.
- **Tunable electrical conductivity:** PANI's electrical conductivity can be tuned.

Polyaniline (PANI) is a conductive polymer that can be prepared in a variety of ways:

### PREPARATION

PANI can be prepared by chemical or physical methods, such as anodic oxidation of aniline monomers using an inert electrode. PANI can also be prepared by dissolving aniline in HCl, adding ammonium persulfate (APS), and stirring for at least an hour. The resulting solution is then filtered to obtain a green, conducting polymer deposit.



### Oxidative polymerization of aniline monomer by sodium persulfate in HCl solution.

Polyaniline (PANI) is used in sensors in a variety of ways, including:

1. **Chemical vapor sensors:** PANI is used as a selective layer in chemical vapor sensors, such as resistance type detectors, because of its electrical properties.
2. **Electrochemical sensors:** PANI is used in electrochemical sensors, along with nanomaterials, to increase sensitivity.
3. **Biological sensors:** PANI is used as a matrix to immobilize enzymes, which then transduce chemical signals into electrical signals.
4. **Colorimetric sensors:** PANI nanoparticles are used in colorimetric sensors to detect bacterial growth in food and water. PANI is sensitive to protons in its microenvironment, and

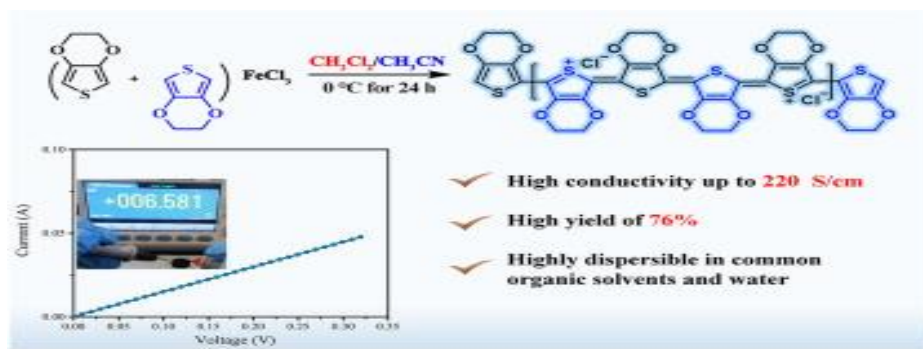


a change in color indicates the presence of protons.

**5. Ammonia sensors:** PANI is known for its affinity with ammonia, and its deprotonation rate upon exposure to ammonia is related to the ammonia concentration.

### PEDOT polymer and its synthesis

PEDOT (Poly(3,4-ethylenedioxythiophene)) is a conjugated polymer which is formed of 3,4-ethylenedioxythiophene (EDOT) monomers. These monomers are joined at 2,5-positions of each five-membered thiophene ring to create linear polymer chains. Poly(3,4-ethylenedioxythiophene) (PEDOT) is the conductive component of PEDOT.



PEDOT (Poly(3,4-ethylenedioxythiophene)) is widely used in sensor applications due to its excellent electrical conductivity, stability, and ease of processing. Here are some key ways PEDOT is utilized in sensors:

#### **1. Chemical Sensors**

- **Conductometric Sensors:** PEDOT can be used as the sensing element in conductometric sensors, where the conductivity changes in response to the presence of specific chemicals (e.g., gases or volatile organic compounds). The change in conductivity is measured and correlated to the concentration of the analyte.
- **Electrochemical Sensors:** PEDOT serves as a working electrode material in electrochemical sensors, allowing for the detection of biomolecules, toxins, or pollutants through redox reactions.

#### **2. Biosensors**

- **Biomolecule Detection:** PEDOT can be functionalized with specific biomolecules (like enzymes or antibodies) to create biosensors that detect biological analytes, such as glucose, proteins, or pathogens. The interaction between the target analyte and the functionalized PEDOT leads to changes in conductivity or electrochemical response.

#### **3. Pressure and Strain Sensors**

- **Flexible Sensors:** Due to its flexibility, PEDOT can be used in pressure and strain sensors that conform to various surfaces. When mechanical stress is applied, the conductivity of the PEDOT changes, which can be monitored to measure strain or pressure.
- **Wearable Sensors:** PEDOT's flexibility and biocompatibility make it ideal for wearable sensors that monitor physiological parameters, such as heart rate or muscle activity.

#### **4. Temperature Sensors**

- PEDOT can be employed in temperature sensors, where changes in temperature affect its conductivity. This property can be utilized for temperature monitoring in various applications, from healthcare to environmental monitoring.

#### **5. Optical Sensors**

- **Electrochromic Sensors:** PEDOT exhibits electrochromic properties, allowing it to change color based on the applied voltage. This can be used in optical sensors to detect changes in chemical environments or to indicate the presence of specific analytes.

#### **Advantages of Using PEDOT in Sensors**

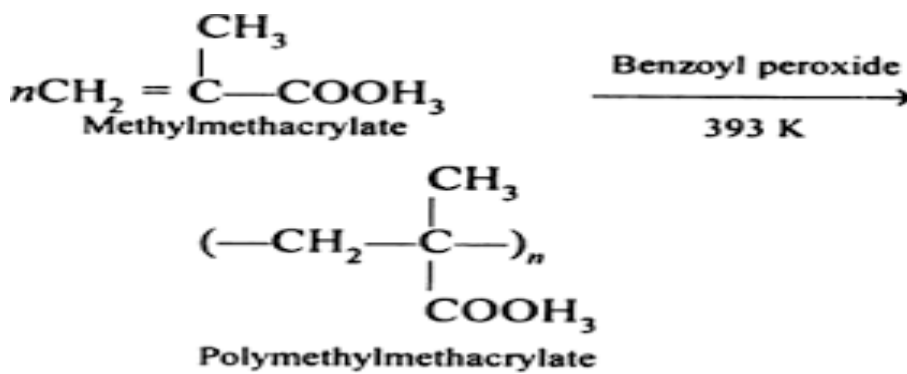
- **High Conductivity:** Provides rapid response times and enhances sensitivity.

- **Stability:** Maintains performance over time, even under varying environmental conditions.
- **Flexibility:** Suitable for a wide range of applications, especially in flexible and wearable technologies.
- **Ease of Functionalization:** Allows for the incorporation of various recognition elements, enhancing selectivity for specific analytes.

## PMMA IN SMART DEVICES,

Polymethyl methacrylate (PMMA), also known as acrylic or plexiglass, is a versatile polymer widely used in smart devices due to its unique properties.

**PREPARATION:** It is prepared by the polymerization of methyl methacrylate in presence of benzoyl peroxide as catalyst.



PMMA contributes to the functionality and design of various smart devices:

### 1. Display Technology

- **Transparent Substrates:** PMMA is often used as a lightweight and shatter-resistant alternative to glass in screens and displays. Its optical clarity makes it ideal for smartphones, tablets, and smart TVs.
- **Optical Coatings:** PMMA can be coated with various materials to enhance its optical properties, such as anti-reflective coatings or anti-scratch treatments.

### 2. Light Guide Applications

- **LED Lighting:** PMMA is used in light guides for LED applications. Its excellent light transmission properties allow for efficient illumination in smart lighting solutions, including smart bulbs and decorative lighting fixtures.

### 3. Sensors and Touch Panels

- **Touchscreens:** PMMA can serve as a protective layer for touch-sensitive displays. Its durability and ability to be easily shaped make it suitable for creating curved or custom-shaped interfaces.
- **Sensor Housing:** PMMA is often used to encapsulate sensors, protecting them while allowing light or signals to pass through.

### 4. Protective Casings

- **Device Enclosures:** PMMA is commonly used in the casings of smart devices, providing both protection and aesthetic appeal. It's resistant to UV light, making it suitable for outdoor devices and wearables.

### **5. 3D Printing and Prototyping**

- **Rapid Prototyping:** PMMA is popular in 3D printing for creating prototypes of smart devices. Its ease of processing allows designers to quickly iterate on designs.

### **6. Smart Home Applications**

- **Smart Appliances:** PMMA can be used in the housings and interfaces of smart appliances, contributing to their modern aesthetic and user-friendly designs.

### **Advantages of PMMA in Smart Devices**

- **Lightweight:** Easier to handle and transport compared to glass.
- **Shatter Resistance:** Safer for consumer products, especially in portable devices.
- **Chemical Resistance:** Durable against various environmental factors, enhancing longevity.
- **Optical Clarity:** Provides excellent visibility and brightness for displays.

## UNIT 1

### (Advanced Materials for Smart Devices)

#### Sustainable polymers ( PLA, PGA, PHBV)

Sustainable polymers are materials designed to minimize environmental impact throughout their lifecycle, from production to disposal. These polymers are materials derived from renewable, recycled and waste carbon resources and their combinations, which at the end of life can be recycled, biodegraded or composted.

##### Types of Sustainable Polymers:

1. **Biodegradable Polymers:**Polymers like Polylactic acid (PLA), polyhydroxyalkanoates (PHA).
2. **Bio-based Polymers:** Bio-polyethylene (bio-PE), bio-polyethylene terephthalate (bio-PET).
3. **Recycled Polymers:** Recycled high-density polyethylene (HDPE).

#### Synthesis and Application of Polylactic Acid (PLA)

PLA is a biodegradable and bio-based polymer primarily derived from renewable resources like corn starch, sugarcane, and other plant materials. It is widely used as an environmentally friendly alternative to petroleum-based plastics, particularly in packaging, 3D printing, and medical applications.

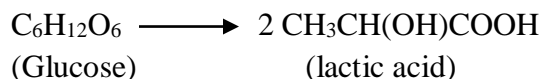
##### Synthesis of PLA

The synthesis of PLA generally occurs in two main steps: the production of lactic acid (or lactide) and its polymerization into PLA.

The synthesis of **Polylactic Acid (PLA)** involves the polymerization of lactic acid or its dimer, lactide, through different processes. The most common method is the **ring-opening polymerization (ROP)** of lactide. Here's a breakdown of the chemical reactions involved in the synthesis of PLA.

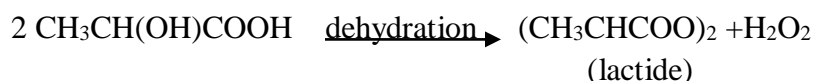
## 1. Fermentation: Production of Lactic Acid

The first step in the PLA synthesis process is the production of lactic acid. This is typically done through the microbial fermentation of carbohydrates (like glucose from corn starch) using bacteria such as *Lactobacillus*. The fermentation reaction is:



## 2. Formation of Lactide (Cyclic Dimer of Lactic Acid)

The lactic acid monomer undergoes a **condensation reaction** to remove water and form a dimer called **lactide**. The reaction typically occurs under heat:



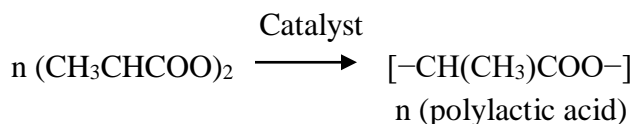
In this step, lactic acid molecules are heated to drive off water and convert the monomer into lactide, a cyclic dimer that is easier to polymerize.

There are three possible forms of lactide:

- **L-lactide** (two L-lactic acid units)
- **D-lactide** (two D-lactic acid units)
- **meso-lactide** (one L- and one D-lactic acid unit)

## 3. Ring-Opening Polymerization (ROP)

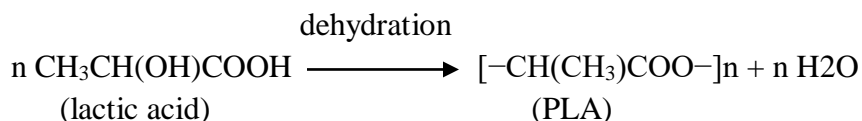
The polymerization of PLA from lactide occurs via **ring-opening polymerization**, which is the most common industrial method. This reaction uses a catalyst, such as **tin(II) octoate** and an initiator like an alcohol, to open the lactide ring and form long PLA chains. The general reaction is:



Here, the cyclic lactide molecule opens up and links with others to form a long polymer chain (PLA). This reaction can be controlled to produce either **low molecular weight** or **high molecular weight** PLA, depending on the conditions and catalysts used.

#### 4. Direct Polycondensation (Alternative Method)

In an alternative process, **direct polycondensation** of lactic acid is used, though this method is less common for industrial PLA due to lower molecular weight products. This process involves the dehydration of lactic acid monomers:



In this case, lactic acid molecules join to form PLA, with water being a byproduct of the reaction. However, this method can result in incomplete polymerization and lower-quality PLA, requiring further processing.

#### Properties of PLA

##### 1. Biodegradability:

- PLA is fully biodegradable under industrial composting conditions (high temperature and humidity), breaking down into water, carbon dioxide, and biomass.
- In home compost or natural environments, PLA may take longer to degrade compared to commercial settings.

##### 2. Renewability:

- PLA is derived from renewable plant resources, making it a more sustainable alternative to conventional plastics derived from petroleum.

##### 3. Mechanical Properties:

- **Tensile strength:** PLA has a relatively high tensile strength and stiffness, making it suitable for packaging, fibers, and 3D printing.
- **Brittleness:** While PLA has good strength, it can be brittle and prone to cracking under stress. To improve flexibility, additives or copolymers like polycaprolactone (PCL) are sometimes mixed with PLA.

##### 4. Thermal Properties:

- **Glass transition temperature (T<sub>g</sub>):** Around 55–60°C, meaning PLA starts to soften at this temperature, limiting its use in high-temperature applications.
- **Melting point:** Around 150–180°C, allowing it to be processed in various applications like injection molding and 3D printing.

##### 5. Transparency:

- PLA can be produced as a clear, glass-like material, making it suitable for use in transparent packaging and films.

#### 6. **Barrier Properties:**

- PLA has decent oxygen barrier properties, which is useful in food packaging, although it is not as good as petroleum-based plastics like PET.

#### 7. **Biocompatibility:**

- PLA is non-toxic and biocompatible, making it ideal for medical applications such as sutures, drug delivery systems, and biodegradable implants.

### **Applications of PLA**

- **Packaging:** PLA is commonly used in food containers, bottles, and packaging films.
- **3D Printing:** PLA is one of the most popular filaments for 3D printing due to its ease of use and low toxicity.
- **Medical Devices:** PLA is used in biodegradable sutures, stents, and scaffolds for tissue engineering.
- **Textiles:** PLA can be used to make fibers for clothing and biodegradable bags.

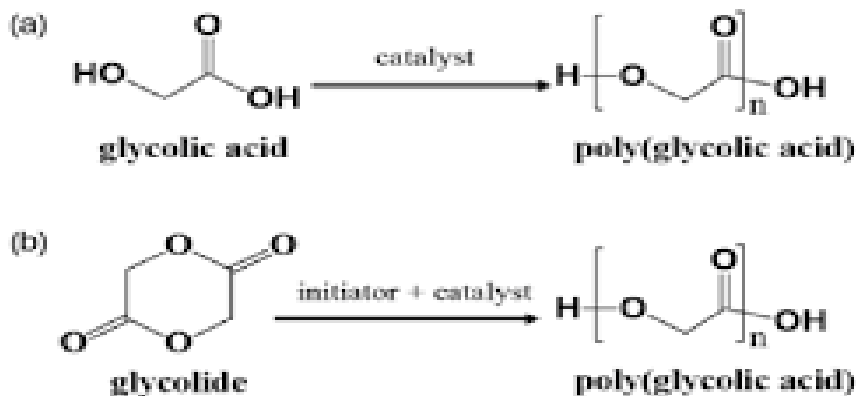
### **Synthesis and Application of Polyglycolic Acid (PGA)**

Polyglycolic acid (PGA) is a biodegradable polymer that is part of the polyesters family. It is synthesized from glycolic acid and has significant applications in medical and environmental fields.

#### **Synthesis:**

Polyglycolic acid is a versatile biodegradable polymer synthesized primarily through the polymerization of glycolic acid. Its unique properties and applications in the medical and environmental sectors make it a key material in the pursuit of sustainable solutions. As research continues, its uses are likely to expand, further enhancing its role in biocompatible and eco-friendly technologies.

The polymerization of polyglycolic acid (PGA) typically involves the ring-opening polymerization (ROP) of glycolic acid, particularly in its cyclic dimer form. Here's a detailed overview of the polymerization reaction:



### Properties:

- **Biodegradability:** PGA degrades in the body through hydrolysis, making it suitable for medical applications.
- **Mechanical Properties:** High tensile strength and modulus, suitable for sutures and implants.
- **Thermal Properties:** Melting temperature around 225°C, making it stable for various applications.

### Applications:

#### 1. Medical Applications:

- **Sutures:** PGA is widely used in absorbable sutures due to its biocompatibility and biodegradability.
- **Drug Delivery Systems:** PGA can be formulated into microspheres for controlled drug release.
- **Tissue Engineering:** Used as scaffolding materials for cell growth and tissue regeneration.

#### 2. Environmental Applications:

- **Biodegradable Packaging:** PGA can be used in packaging materials that decompose naturally, reducing plastic waste.
- **Agricultural Films:** Used for mulch films that can biodegrade, minimizing environmental impact.

#### 3. Biomedical Devices:

- **Implants:** Used in various biodegradable implants for tissue repair and regeneration.



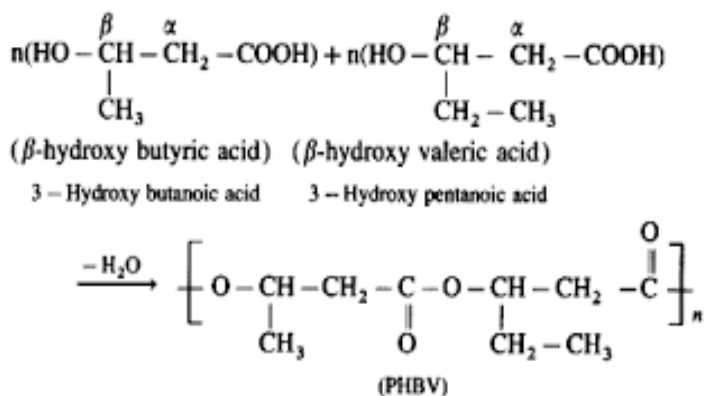
- **Wound Dressings:** PGA can be incorporated into dressings that promote healing while degrading over time.

### Synthesis and Application of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)

PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) is a biopolymer belonging to the family of polyhydroxyalkanoates (PHAs). It's synthesized by various microorganisms, particularly bacteria, through the fermentation of carbon sources. It is a thermoplastic linear aliphatic polyester.

#### Synthesis of PHBV

It is obtained by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



#### Properties of PHBV

1. **Biodegradability:** PHBV is biodegradable, breaking down into harmless byproducts through microbial action, which makes it an environmentally friendly alternative to conventional plastics.
2. **Mechanical Properties:**
  - It exhibits good tensile strength and elasticity, although these properties can vary based on the ratio of 3-hydroxybutyrate (3HB) to 3-hydroxyvalerate (3HV) in the copolymer.
  - PHBV can have a glass transition temperature (T<sub>g</sub>) around 5°C and a melting temperature (T<sub>m</sub>) around 170°C.
3. **Thermal Properties:** PHBV shows thermal stability, which is advantageous for processing. However, it can be more sensitive to heat compared to conventional plastics.
4. **Barrier Properties:** It has good gas barrier properties, making it suitable for packaging applications.

## Applications of PHBV

1. **Packaging:** Due to its biodegradability and good mechanical properties, PHBV is used in biodegradable packaging materials, such as films, containers, and bags.
2. **Medical Applications:**
  - **Sutures and Scaffolds:** PHBV is biocompatible, making it suitable for use in medical sutures and tissue engineering scaffolds.
  - **Drug Delivery Systems:** Its ability to degrade in the body allows for controlled drug release applications.
3. **Agriculture:** PHBV can be used to create biodegradable mulch films, which help reduce plastic waste in farming.
4. **3D Printing:** Its thermoplastic nature makes it suitable for 3D printing applications, allowing for the creation of biodegradable products and components.
5. **Textiles:** PHBV fibers can be used in the textile industry for creating eco-friendly fabrics.

## Leaching of Micro-plastics

**Leaching of microplastics** refers to the process by which chemicals contained within microplastics are released into the environment, particularly water bodies, as the plastics break down or degrade. Microplastics are tiny plastic particles less than 5 mm in size, and they can originate from a variety of sources, such as larger plastic debris breaking down, synthetic fibers from clothing, or microbeads in personal care products.

When microplastics enter ecosystems, especially water, they can leach harmful chemicals. This happens in two primary ways:

1. **Additives in plastics:** Many plastics contain chemical additives like plasticizers (e.g., phthalates), stabilizers, and flame retardants. These chemicals can leach out of the plastic particles over time and potentially contaminate soil and water, posing risks to wildlife and humans.
2. **Adsorption of pollutants:** Microplastics can also absorb and carry external pollutants (such as heavy metals or persistent organic pollutants like PCBs) from the surrounding environment. Once ingested by marine organisms or other animals, these toxic substances can enter food chains.

Leaching of microplastics is a growing environmental concern, as it can affect water quality, ecosystems, and human health, particularly through bioaccumulation in food webs.

reventing the **leaching of microplastics** requires efforts to reduce both the production of microplastics and their release into the environment. Here are some strategies to minimize leaching:

### 1. Reduce Plastic Use

- **Minimize single-use plastics:** Avoid products with excessive plastic packaging and choose alternatives like reusable bags, glass, or metal containers.
- **Choose natural fibers:** Opt for clothing made from natural materials like cotton, wool, or hemp, as synthetic fibers (like polyester) shed microplastics during washing.

### 2. Proper Waste Management

- **Recycling:** Ensure plastic waste is properly sorted and recycled to prevent it from entering ecosystems where it can break down into microplastics.
- **Improved waste disposal:** Encourage proper disposal of plastics and promote systems that prevent littering or leakage of plastic into the environment.

### 3. Use of Advanced Filtration Systems

- **Washing machine filters:** Install filters in washing machines to capture microfibers from synthetic clothes during washing, preventing them from entering water systems.
- **Water treatment upgrades:** Municipal wastewater treatment plants can be upgraded to better capture microplastics before they are discharged into rivers and oceans.

### 4. Designing Eco-friendly Products

- **Biodegradable plastics:** Promote the development of biodegradable plastics that break down into non-toxic components.
- **Safer plastic additives:** Manufacturers can design plastics with fewer harmful additives, reducing the risk of leaching toxic chemicals.

### 5. Legislation and Policy

- **Banning microbeads:** Support or implement bans on microbeads (tiny plastic particles) in personal care products, which directly contribute to microplastic pollution.
- **Plastic regulations:** Advocate for regulations that restrict the production and use of certain harmful plastic additives that can leach into the environment.

## 6. Public Awareness

- **Education and outreach:** Increase public awareness about the dangers of microplastic pollution and how everyday actions contribute to it. This can help drive behavior change and support for policy measures.

By taking these steps, society can reduce the release of microplastics and prevent the harmful chemicals in plastics from leaching into ecosystems.

Microplastic pollution in the environment is a major concern for governments and companies worldwide attempting to understand and reduce the damage they cause. As well as the direct damage these plastic pellets can also act as chemical reservoirs that leach chemical contaminants into the environment and further damage ecosystems. The Column spoke to Manuel Miró from the University of the Balearic Islands, Spain, about his research into the pollution caused by chemical leaching from microplastics.

### Factors that affect leaching

The leaching of chemicals from microplastics is affected by a variety of factors, including:

**Sunlight:** Sunlight can cause photochemical degradation, which can lead to the release of chemicals.

**Water flow:** Microplastics in flowing water may release plasticisers at a faster rate.

**pH levels:** Acidic and basic pH levels are more aggressive to plastic materials than neutral pH levels.

**Plasticizer content:** The concentration of plasticizers in microplastics can affect the rate of leaching

**Effects on organisms**

When aquatic organisms consume microplastics, they can be harmed by the physical ingestion of the microplastics, as well as by the toxic chemicals that leach out during digestion.

**Effects on the environment**

Microplastics can contribute to a buildup of plasticisers in the environment. They can also release dissolved organic carbon (DOC), which can stimulate the growth of marine microbial communities.

**Microplastic sources**

Microplastics can come from a variety of sources, including washing machines and synthetic clothing.