

Module-2 Quantum Materials and Polymers

Quantum Dots: Introduction, size dependent properties-quantum confinement effect, surface-to-volume ratio & band gap. Synthesis of Cd-Se Quantum dots by wet chemical method and its applications. Construction, working principle and applications of quantum dot sensitized solar cells (QDSSCs).

Polymer: Introduction, number average and weight average molecular weight of the polymers and numerical problems. Structure-properties relationship of polymers (Crystallinity, Strength, Elasticity and chemical resistivity]. Synthesis and properties of nylon 6,6 and its advantages in 3D printing applications. Synthesis and properties of chlorinated polyvinyl chloride (CPVC), and polymethyl methacrylate (PMMA) and their uses in device applications.

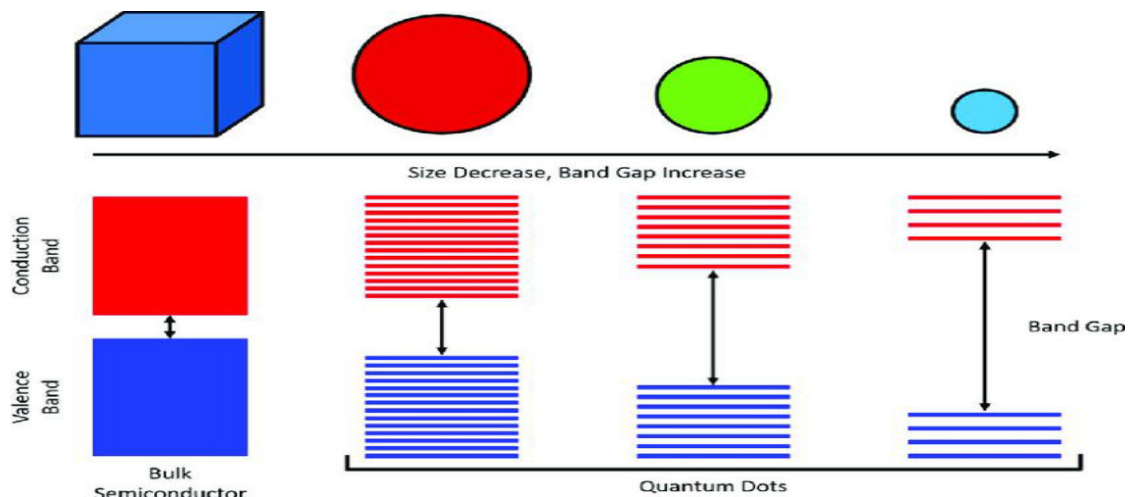
Conducting polymers- Introduction, synthesis of polyaniline, conduction mechanism and its engineering applications.

Quantum dots (QDs):

- Quantum dots (QDs) are nanoscale semiconductor particles typically ranging from 2 to 10 nanometres in size.
- Due to their quantum confinement effects, QDs exhibit unique optical and electronic properties, such as size-dependent light emission.
- They are often called "artificial atoms" because their electron energy levels are quantized, similar to those in a real atom.
- These properties make them highly valuable in various applications including display technology, solar cells, biomedical imaging, and quantum computing.
- Their ability to emit specific wavelengths of light by simply changing their size makes them a versatile tool in nanotechnology and materials science.
- Examples: Cadmium Selenide (CdSe), Lead Sulfide (PbS), Indium Phosphide (InP), etc.,



Quantum Confinement Effect:



- When QD's are very small—around the size of a few nanometers, their electrons and holes become spatially confined.
- This confinement restricts their movement, forcing their energy levels to become discrete and quantized, similar to the discrete energy levels of an atom. For this reason, quantum dots are often referred to as “artificial atoms”.
- At this tiny scale, the movement of electrons and holes inside the QD is limited in all directions.
- This causes the energy levels to become separate, like steps, instead of being continuous.
- As the size of the QD gets smaller, the gap between energy levels (called the band gap) becomes larger.
- Because of this, small QDs give off blue light, while bigger ones give off red light. So, the color of light from a QD depends on its size.

Surface-to-Volume Ratio:

As the size of a material decreases, its **surface-to-volume ratio** dramatically increases. For a quantum dot, this means that a significant fraction of its atoms is located on the surface rather than in the bulk interior. This high ratio has several consequences:

- **Increased Reactivity:** Atoms on the surface have incomplete or unsaturated bonds, making them highly reactive. This can lead to unwanted chemical reactions and degradation of the QD.
- **Surface Defects:** The large number of surface atoms means there's a higher chance of defects or "trapping sites" on the surface. These defects can act as non-radiative recombination pathways, where the electron and hole recombine without emitting a photon. This reduces the QD's **photoluminescence quantum yield** (the efficiency of light emission).
- **Surface Passivation:** To combat this, QDs are often coated with a shell of another semiconductor material, creating a core-shell structure. This process, known as **surface passivation**, helps to stabilize the QD, reduce surface defects, and significantly improve its quantum yield and stability.

Band Gap Variation:

- The band gap of quantum dots (QDs) is the energy difference between the highest occupied energy level (valence band) and the lowest unoccupied energy level (conduction band). Unlike bulk semiconductor materials, the band gap of a quantum dot is **not fixed**; it is **tunable** and depends on the dot's physical size due to a phenomenon called the **quantum confinement effect**.
- The **smallest** quantum dot has the most confinement, leading to a **larger** band gap. This requires more energy to excite the electron, and as it relaxes, it emits a higher-energy photon, resulting in **blue light**.
- The **largest** quantum dot has the least confinement, resulting in a **smaller** band gap. This requires less energy for excitation and releases a lower-energy photon, producing **red light**. The ability to tune the color simply by changing the size is a key feature of quantum dots.

SYNTHESIS OF CdSe QUANTUM DOTS BY WET CHEMICAL METHOD:

In this method, cadmium selenide (CdSe) quantum dots synthesized through a water-based chemical reaction relatively at low temperature. The process involves forming a cadmium complex, preparing a selenium source, combining them to form quantum dots, and then purifying the final product. The following steps are involved in the process:

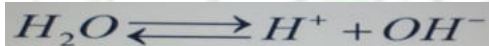
Step 1: Ligand Complexation:

- Dissolve cadmium chloride (CdCl_2) in distilled water to create a clear solution.
- Next, add thioglycolic acid (TGA) to this solution in a specific ratio, we need 2 to 4 molecules of TGA for every 1 cadmium atom.
- The TGA acts protective coating that will surround the quantum dots and prevent them from clumping together.
- After mixing these chemicals, adjust the pH of the solution to approximately 11 using sodium hydroxide (NaOH) solution.
- This high pH causes the cadmium and thioglycolic acid to form a cadmium-thiolate stable complex, resulting in a clear solution that's ready for the next step.



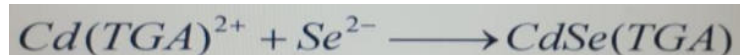
Step 2: Prepare Selenium Source:

- Prepare the selenium source by making sodium hydrogen selenide (NaHSe) through a chemical reduction reaction.
- Mix selenium powder with sodium borohydride (NaBH_4) in water while keeping the entire setup under an inert gas atmosphere (like nitrogen or argon) to prevent unwanted reactions with oxygen.
- The sodium borohydride acts as a reducing agent that converts the selenium powder into a soluble form that can react with cadmium.
- This reaction must be done carefully under inert conditions because selenium compounds can be sensitive to air and moisture.



Step 3: Quantum Dot Formation:

- Add the freshly prepared NaHSe solution drop by drop to the cadmium-thiolate solution while continuously stirring at room temperature.
- The changes as the quantum dots begin to form the solution typically changes from clear to yellow, orange, or red depending on the size of the quantum dots being formed.
- After the injection is complete, heat the mixture to temperature between $60\text{--}90^\circ\text{C}$ for a controlled amount of time to allow the quantum dots to grow to the desired size.
- Lower temperatures and shorter times produce smaller, blue-emitting dots, while higher temperatures and longer times create larger, red-emitting dots.



Step 4: Purification and Collection:

- Once the quantum dots have reached the desired size, purify them by adding ethanol to the reaction mixture, which causes the quantum dots to precipitate out of solution.
- Collect the precipitated quantum dots through centrifugation or filtration, then wash them several times with ethanol to remove any unreacted starting materials and byproducts.

- Finally, dry the purified CdSe quantum dots under vacuum or in an oven at low temperature to obtain the final product as a solid powder that can be stored or redispersed in various solvents for different applications.

Advantages of this method: This aqueous synthesis method offers several advantages over traditional high temperature organic methods. It operates at much lower temperatures (60-90°C instead of 300°C), uses water instead of toxic organic solvents, and provides good control over quantum dot size through temperature and time adjustments. The thioglycolic acid ligands make the quantum dots water-soluble, which is useful for biological applications, and the entire process can be completed in a regular chemistry laboratory without specialized high-temperature equipment.

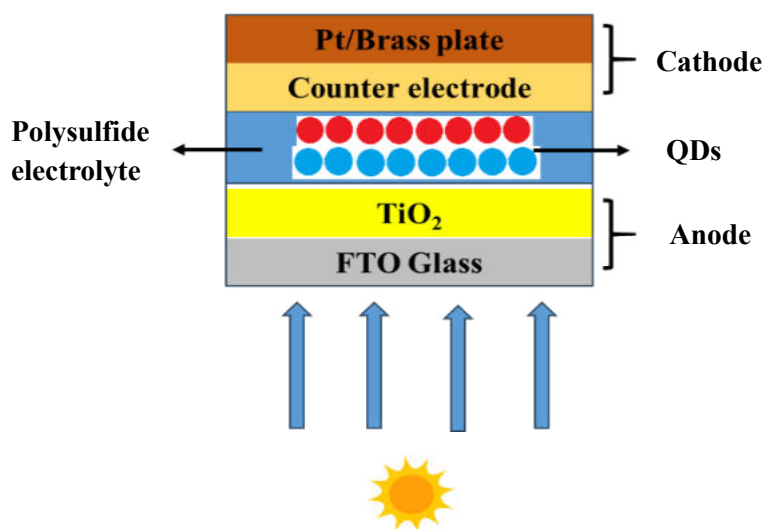
Applications:

- Optoelectronics:** Used in light-emitting diodes (QLED displays), lasers, and photovoltaic cells.
- Bio-imaging and Medical Diagnostics:** Serve as fluorescent probes due to tunable emission and high photostability.
- Solar Cells:** Improve efficiency of quantum dot-sensitized solar cells (QDSSCs).
- Sensors:** Employed in chemical and biosensors for detecting heavy metals, biomolecules, and pH changes.
- Photocatalysis:** Useful in degradation of pollutants and water splitting for hydrogen production.
- Medical Applications:** Potential use in targeted drug delivery and cancer therapy (though toxicity issues exist due to Cd).

Quantum Dot Sensitized Solar Cells (QDSSC's):

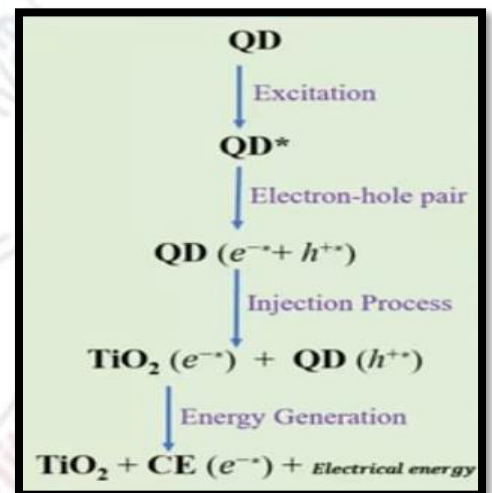
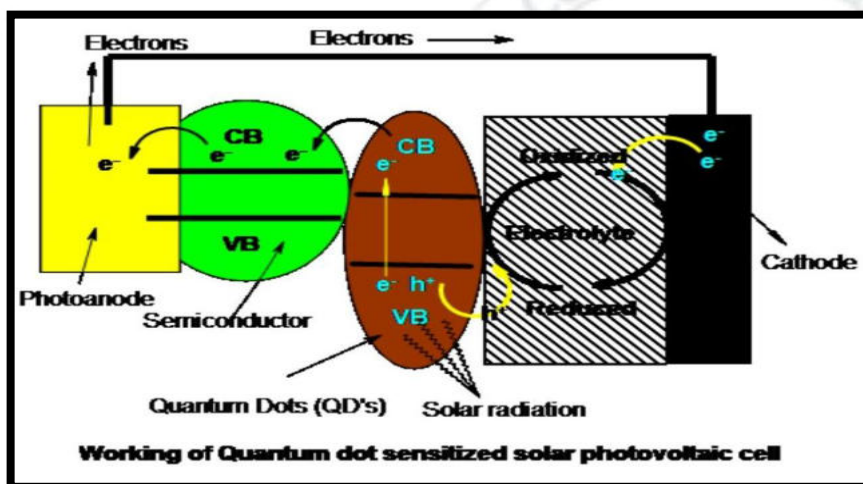
- QDSSC is a solar cell design that uses quantum dots as the light absorbing photovoltaic material.
- Quantum dots are special class of semiconductors and are nano crystals.
- The energy band gap increases with decrease in size of quantum dots.
- The adjustable band gap of quantum dots allows the construction of nano structured solar cell, that is able to harvest maximum amount of solar spectrum.
- They are a promising, low-cost alternative to traditional silicon solar cells and are an evolution of dye-sensitized solar cells (DSSCs).

Construction:



- **Photoanode:** A conducting glass substrate is coated with Fluorine-doped Tin Oxide (FTO). It acts as the front contact and allows sunlight to pass through to the active layers. It is coated with a semiconductor layer (commonly TiO_2). This layer provides a large surface area for the quantum dots to attach to and serves as the electron transport medium.
- **Quantum Dot Sensitizer:** These are semiconductor nanocrystals, such as Cadmium Sulfide (CdS), Cadmium Selenide (CdSe), or Lead Sulfide (PbS), which are deposited onto the photoanode. The QD's for absorbing sunlight and generating electron-hole pairs. Their bandgap can be tuned by changing their size, allowing them to absorb a wider range of the solar spectrum.
- **Electrolyte:** A liquid or solid material containing a redox couple (e.g., $\text{S}^{2-}/\text{S}_x^{2-}$), usually polysulfide, that regenerates the oxidized QDs by accepting holes and transports the charge to the counter electrode.
- **Counter Electrode (CE):** This is a conductive material, often Platinum (Pt) or Carbon, that is coated onto the QD layer, acts as Cathode. It collects the electrons from the external circuit and transfers them to the electrolyte.

Working Principle:



• Step 1: Excitation

QD's present on photo anode is exposed to sunlight. Upon absorption of a photon, a quantum dot is excited from the ground state (QD) to a higher energy state (QD*). QD and QD* are the quantum dot in its ground state and excited state respectively.



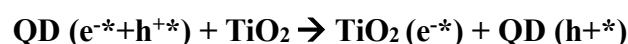
• Step 2: Formation of Electron - Hole Pair

QD's absorb solar energy and eject electrons, generating electron - hole pair. The absorption process results in the creation of electron-hole pair in the form of exciton. Dissociation of the exciton occurs if the thermal energy exceeds its binding energy. Electrons then move from valence band to conduction band leaving holes in the valence band.



• Step 3: Injection Process

The excited electrons from conduction band of QDs are then injected to conduction band of wide band gap semiconductor TiO_2 . This process will cause the oxidation of the photo sensitizer QD (h^+). This prevents recombination of electrons with holes on the surface of QD's and causes electrons to drive through external circuit to produce electric current.



- **Step 4: Energy Generation**

The injected electrons from conduction band of semiconductor TiO_2 are transferred to anode and driven through external circuit to reach cathode. This produces electric current.



- At the surface of cathode, polysulphide anion of electrolyte dissociates producing Sulphur atom which takes up electrons and gets converted to sulphide anion. $\text{S}^{2-} + 2h^{+} \rightarrow \text{S}; \text{S} + 2e^{-} \rightarrow \text{S}^{2-}$

Properties:

- **Tunable Bandgap:** The properties of QDs can be tuned by changing their size.
- **Multiple Exciton Generation (MEG):** Quantum dots can generate multiple electron-hole pairs (excitons) from a single absorbed photon.
- **Solution Processability:** Quantum dots can be synthesized and processed using solution-based methods, which makes them cost-effective and suitable for large-scale production.
- **Versatility:** Quantum dots can be applied to various substrates, including flexible and transparent materials, making them useful for integration into different types of solar cell designs.

Advantages:

- High power-to-weight ratio with excellent efficiency.
- Low power consumption during operation.
- Cost-effective with improved electrical performance.
- Flexible in use, enabling applications not limited to rooftops but also windows and other transparent surfaces.

Disadvantages:

- Cadmium selenide (CdSe)-based QDs are highly toxic and require a stable polymer shell for safe use.
- Cadmium and selenium ions are cytotoxic, raising environmental and health concerns.

Applications:

- Biological labelling and imaging.
- Detection systems and fluorescence resonance energy transfer donors.
- Used in LEDs, photodetectors, photoconductors, and photovoltaic devices.
- Biomedical and environmental applications.
- Catalysis and chemical reactions.

POLYMERS

Introduction

Polymers are the high molecular weight compounds obtained by repeated union of simple molecules. (Monomers).

Ex: Starch, Polyvinyl chloride, Polyethylene, Nylon 6, 6 and etc.

Classification of polymers.

Polymers are classified into two types as follows:

i) Natural polymers: These are the polymers obtained naturally by plants and animals.

Ex: Silk, wool, natural rubber, protein, starch, cellulose, etc.

ii) Synthetic Polymers: These are artificially prepared polymers also known as manmade polymers. Ex: PVC, Nylon 6.6, Polythene, Phenol, Formaldehyde, Resin etc.,

Terms used:

Monomers: These are simple molecules, which combine with each other to form polymers. These are the building blocks of Polymer.

Polymerization: The process of linking monomers to form polymers with or without the elimination of by-products is called polymerization.

Degree of Polymerization (n): The total number of monomers present in a single chain of polymer is called the degree of polymerization.

Functionality: The total number of bonding sites or functional groups present in a monomer is called the functionality of the monomer

Based on the method of preparation, polymers are classified as:

1.Addition polymerization: The process in which the polymers formed by the addition of several monomers without elimination of byproducts are called as addition polymers.

Example: Polythene, PVC, Teflon etc.

2.Condensation Polymerization: The process in which the monomers undergo intermolecular condensation reactions to form a polymer with the elimination of simple molecules like water, HCl, ammonia, phenol etc.

Example: Nylon, polyurethane, Bakelite



3.Free-radical polymerization: It is a method of polymerization that is a chain reaction started with the introduction of an initiator leading to the formation of free radicals and successive addition of these free-radical to form polymers. Free radical polymerization consists of 3 fundamental steps.

- **Initiation** involves the formation of radicals followed by the radical's reaction with a monomer,
- **Propagation** is the rapid and progressive addition of monomers to the growing polymer chain without a change of the active center.
- **Termination** is the destruction of the growth active centre, usually by *combination* or *coupling* of the radicals of two growing polymer chains or by *disproportionation*.

Based on the composition, polymers are classified as:

1. Homopolymers: Polymers which are made by the combination of only one kind of monomer are called as homopolymers.

Example: Polythene, PVC, polystyrene, Teflon etc.

2. Copolymers: Polymers which are made by the combination of more than one kind of monomers are called as copolymers or mixed polymers.

Example: Bakelite, nylon, buna-S rubber, polyurethanes etc.

Based on their behaviour to heat treatment, polymers are classified as:

1. Thermoplastic polymers: The polymers which soften on heating, which can be converted into any shape and harden on cooling are called thermoplastic polymers. The process of heating, reshaping and cooling can be repeated number of times without affecting their properties.

Example: Polyethylene, polymethylmethacrylate, etc.

2. Thermosetting polymers: These are the polymers which undergo chemical changes on heating and become permanently hard, rigid, infusible on cooling.

Example: Phenol - formaldehyde, urea - formaldehyde, etc.

Based on their structure, polymers are classified as:

1. Linear polymers: These are the polymers in which monomeric units are linked together to form long straight chains. The polymeric chains stacked over one another to give well packed structure. As a result of close packing, such polymers have high densities, high tensile strength and high melting points.

Example: High density polythene, nylons and polyesters.

All thermoplastics are essentially linear molecules.

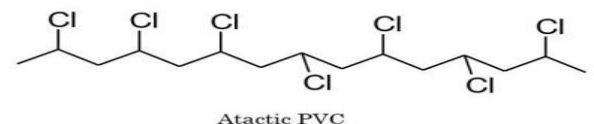
2. Branched chain polymers: These polymers contain molecules having a linear backbone with branches arising randomly from it. Branched chain polymers are irregularly packed and thus, they have lower densities, tensile strength and melting points.

Example: LDPE, polystyrene, PMMA etc.

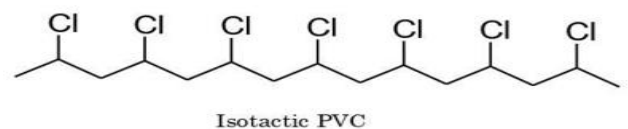
3. Cross-linked polymers: These polymers contain molecules having number of straight chains of varying lengths interlinked (cross-linked) together. Cross-linked polymers are hard, rigid and brittle because of their network structure. Example: Bakelite, urea-formaldehyde resin etc.

Based on the stereo-regularity, polymers are classified as:

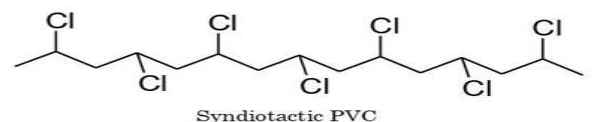
1. Atactic polymers: The polymers in which arrangement of side groups is random around the main chain are termed as atactic polymers.



2. Isotactic polymers: The polymers in which all the side groups are arranged on the same side of the main chain are called as isotactic polymers.



3. Syndiotactic polymers: The polymers in which arrangement of the side groups is in alternating fashion around the main chain are known as syndiotactic polymers.



MOLECULAR WEIGHT OF POLYMERS:

- Molecular weight of any polymer is one of the important parameters as it links directly to the physical properties of polymers. In general, higher the molecular weight, tougher is the polymer.
- During the formation of polymers, different polymers have different degrees of polymerization i.e, they have different chain lengths.
- Thus, molecular masses of individual macromolecules in a particular sample of polymer are different. Hence, an average value of the molecular mass is taken.
- There are two ways through which average molecular masses can be calculated.
 1. Number - average molecular weight (M_n)
 2. Weight - average molecular weight (M_w)

Number Average Molecular weight [M_n]: The number average molecular weight is the total weight of the sample divided by the number of molecules in the sample.

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

Where,

- n_1, n_2, n_3 are the number of molecules having masses M_1, M_2, M_3 , respectively.



$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

Where

- n_i = masses of simple monomer molecules.
- M_i = number of monomer molecules.

Weight Average Molecular weight [M_w]: It gives representation to various molecular species in proportion to their average weight in the given material.

$$\overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}$$



$$\overline{M}_w = \frac{n_1 M_1^2 + n_2 M_2^2 + n_3 M_3^2 + \dots}{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots}$$

Where,

- n_1, n_2, n_3 are the number of molecules having masses M_1, M_2, M_3 , respectively.

Where

- n_i = number of monomer molecules.
- M_i = masses of monomer molecules.

STRUCTURE - PROPERTY RELATIONSHIP OF POLYMERS:

- Various physical and mechanical properties possessed by polymers decide the usefulness of a polymer in human life.
- The properties of a polymer such as density, tensile strength, elasticity, chemical resistivity, etc., depend upon the structural aspects of polymer such as molecular mass, arrangement of chains, presence of polar groups etc.
- Some of the polymeric properties and their relationship with the structure are briefly discussed below:
 1. **Crystallinity**
 2. **Tensile strength**
 3. **Elasticity**
 4. **Chemical Resistivity**

1. Crystallinity:

Linear polymers have straight chains without side branches or large groups sticking out. This lets the chains pack closely and neatly, making them crystalline.

- Linear polymers with more symmetry are highly crystalline, while crystallinity decreases in branched polymers.
- A homopolymer is more crystalline than a copolymer.
- Presence of polar groups in the molecule increases the crystallinity whereas, bulky side groups decrease the crystallinity.
- Higher crystallinity leads to sharp melting point, lower solubility, lower permeability to gases and liquids, higher chemical resistance, higher density and rigidity etc.
- **For example:** Polyethylene (linear) is more crystalline than polystyrene (bulky side groups) or polymethylmethacrylate (more branched).
- Similarly, Nylons are more crystalline due to hydrogen bonding.

Factors increasing crystallinity:

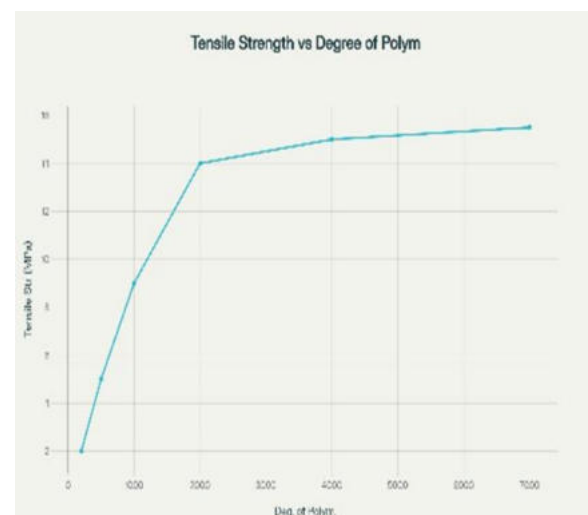
- Linear and regular chains, especially with polar groups, boost crystallinity.
- Isotactic polymers, where all side groups are on the same side, are more crystalline than atactic polymers (random side groups).

How Crystallinity Affects Properties

- High crystallinity makes polymers stronger, stiffer, opaquer, and less soluble in solvents.
- As crystalline increases, solubility decreases.

2. Tensile strength:

- Tensile strength is the maximum stress that the material can withstand. Tensile strength of a polymer depends on the molecular weight. Tensile strength increases with molecular weight up to 2,000 and thereafter increase is negligible.
- Low molecular weight polymers are soft and gummy, but high molecular mass polymers are tough and heat resistant. Cross-linked polymers are stronger than linear polymers and less than branched polymer.



3. Elasticity:

Elasticity is the ability of a polymer to stretch when a force is applied and to return to its original shape when the force is removed. This behaviour occurs because the molecular chains uncoil during stretching and recoil when the force is released. Polymers exhibit elasticity as long as the chains do not separate from each other, preventing breakage during extended stretching.

Elasticity can be enhanced by:

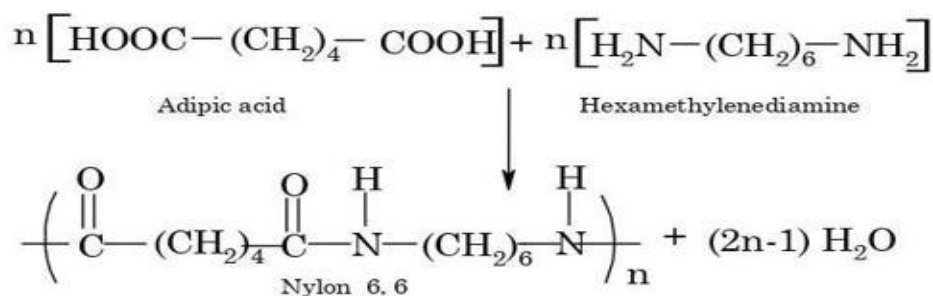
- Introducing cross-links at appropriate molecular positions to connect the chains,
- Avoiding bulky groups such as aromatic and cyclic structures in the repeating units, which hinder chain movement,
- Incorporating more non-polar groups in the chain to increase cohesion between chains, thereby reducing chain separation during stretching.

4. Chemical Resistivity:

- Chemical resistivity of a polymer refers to its ability to resist swelling, softening, dissolving, and loss of strength when exposed to solvents or chemicals.
- Polymers containing polar groups such as $-\text{OH}$ or $-\text{COOH}$ are typically dissolved by polar solvents like water or alcohols.
- Polymers with non-polar groups such as $-\text{CH}_3$ and C_6H_5 are not easily dissolved by polar solvents but dissolve readily in non-polar solvents like petrol, benzene, and carbon tetrachloride.
- Polymers with a higher degree of crystallinity exhibit greater chemical resistance than their amorphous counterparts.
- Chemical resistivity increases as the degree of cross-linking in the polymer structure increases.

Nylon-6,6:

Preparation: Nylon 6,6 is obtained by condensation polymerization of hexamethylenediamine and adipic acid under high pressure and temperature (553 K).



Properties:

1. It is a synthetic fiber with high mechanical strength and high rigidity.
2. It exhibits high thermal stability with high melting point.
3. It has high chemical resistance; resists oils, greases, and many chemicals.
4. It has high resistance for abrasion.
5. It absorbs less moisture than other plastics.

Advantages in 3D Printing:

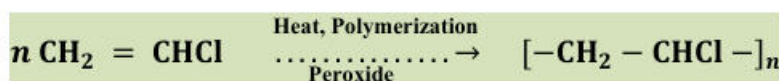
- Makes strong, flexible, and tough printed parts.
- Works well for mechanical components.
- High melting point prevents bending in hot conditions.
- Durable, even with regular use.
- Resists damage from chemicals and oils—great for industrial parts.

Chlorinated Polyvinyl Chloride (CPVC):

Synthesis of CPVC is carried out in two main steps as follows:

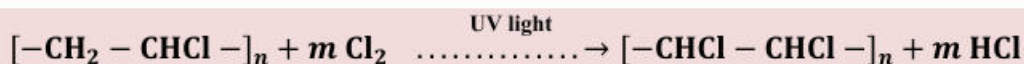
Step I: Preparation of PVC

Vinyl chloride monomers (VCM) undergo free-radical addition polymerization in the presence of a peroxide initiator under controlled heat and pressure to form polyvinyl chloride (PVC).



Step II: Chlorination of PVC

The obtained PVC is exposed to chlorine gas under UV irradiation, during hydrogen atoms in the PVC chain are replaced by chlorine atoms, leading to the formation of chlorinated polyvinyl chloride (CPVC).



Properties of CPVC:

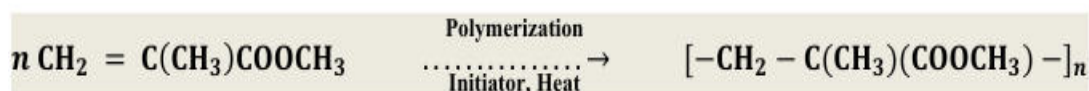
- CPVC is stronger and tougher than normal PVC.
- It has higher chlorine content, which makes it more rigid.
- CPVC can withstand higher temperatures (up to about 90–110 °C).
- It has good resistance to corrosion and many chemicals.
- It is resistant to hot and cold water, so it is used in plumbing.
- CPVC has long service life and good mechanical strength.

Applications:

1. Due to its ability to bend, shape, and weld, CPVC is used for self-supporting constructions.
2. It is used in water-piping systems for hot and cold-water delivery.
3. It is used for storing industrial chemicals and solvents.
4. It is used in fire-resistance materials.
5. It is used as an electrical insulator.

Polymethyl methacrylate (PMMA) or Plexiglass:

PMMA is synthesized by the free-radical bulk polymerization under an inert atmosphere using methyl methacrylate (MMA) monomers using initiators such as benzoyl peroxide or potassium persulfate and heat by addition polymerization.



Properties:

1. It is an amorphous and transparent plastic.
2. It has high optical clarity (Refractive Index = 1.4), but poor scratch resistance.
3. It is resistant to water, alkalies and inorganic salts but dissolves in organic solvents.
4. It has good resistance to acids and environmental deterioration.

PMMA in Device Applications:

- **Optical devices:** Used in lenses, optical fibers, and light guides due to high transparency.
- **Display panels:** Utilized in LCD and LED screens for light transmission.
- **Medical devices:** Applied in intraocular lenses, bone cement, and dentures.
- **Solar cells:** As a transparent protective layer and encapsulant.
- **Microfluidic devices:** Due to easy machining and chemical resistance.
- **Automobile parts:** Headlight covers and indicator lamps because of clarity and weather resistance.
- **Protective shields:** Used as a glass substitute in safety windows and aquariums.

Conducting polymers:

- These are the organic polymers having a conductivity band similar to that of conductors with a highly delocalized π electron system.
Examples: Polyaniline, Polypyrrole, Polythiophene, Polyacetylene, etc.
- Conducting polymers are obtained by doping an oxidizing or a reducing agent into organic polymers with conjugated backbone consisting of alternating double and single carbon – carbon bonds.

Conducting polymers are classified as extrinsic and intrinsic conducting polymers.

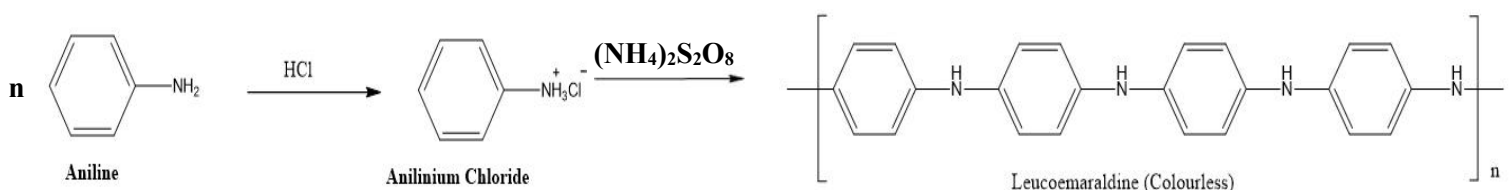
1. **Extrinsic conducting polymers** are prepared by mixing polymers with conducting fillers like metal fibres, metal oxides, carbon black etc. In these polymers, conductivity is not due to matrix polymer but due to added conducting fillers.
2. **Intrinsic conducting polymers** are prepared by mixing polymers with conducting fillers like metal fibres, metal oxides, carbon black etc. In these polymers, conductivity is due to organic polymers themselves which start conducting upon doping with suitable agents.

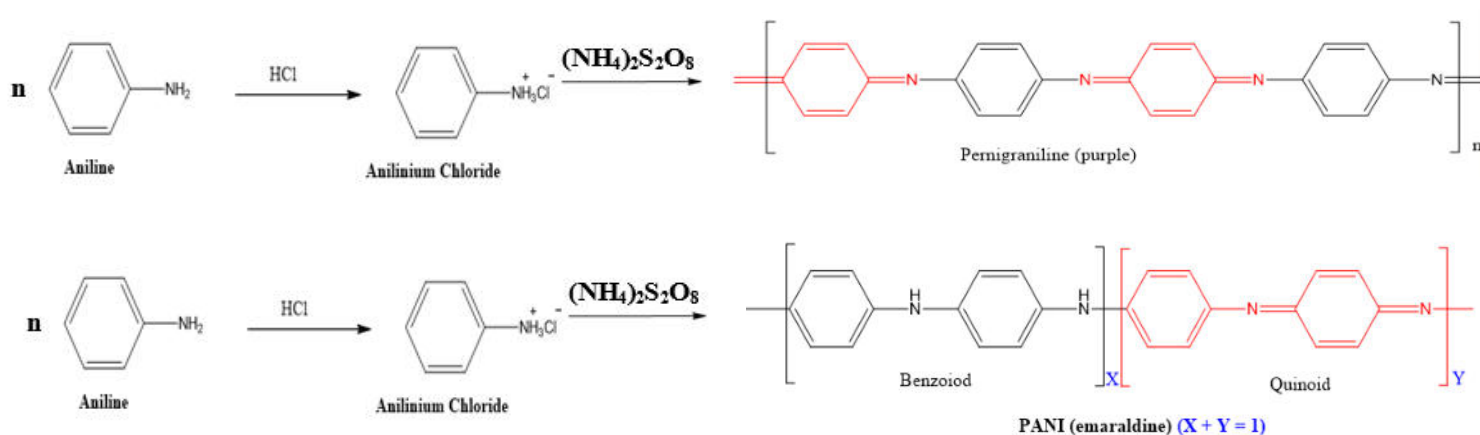
The important doping methods are;

- a) **Oxidative doping (p-type doping):** The polymer is treated with an oxidizing agent like iodine, aluminium chloride, perchloric acid etc. Oxidizing agent takes away electrons from π - back bone of the chain creating a hole. Thus, polymer becomes p-type conductor as it conducts by the movement of holes.
- b) **Reductive doping (n-type doping):** The polymer is treated with a reducing agent like sodium or lithium naphthalids. Reducing agents supplies electrons to π - back bone of the chain. The polymer becomes n-type conductor as it conducts by free mobile electrons.

Synthesis of Polyaniline:

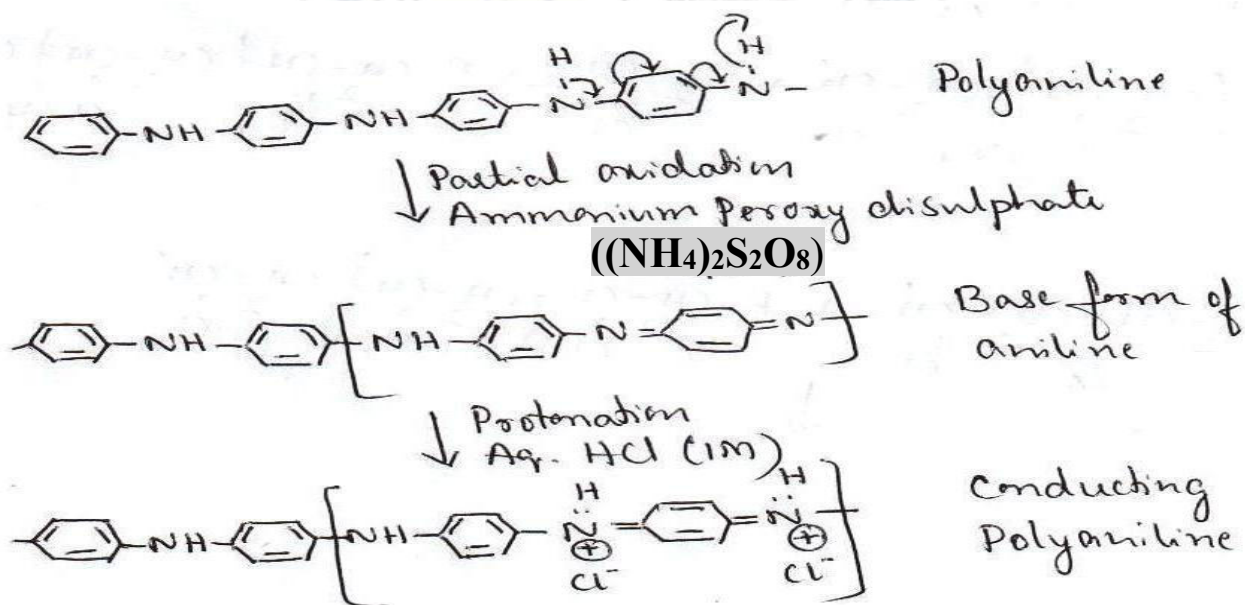
When n number of aniline molecules undergo oxidative polymerization in presence of dil HCl and ammonium persulfate to form polyaniline.





Mechanism of conduction in Polyaniline (PANI)

The synthesis of conducting polyaniline is an example of doping technique. In this technique current carrying species (-ve /+ve) are created by the protonation of imine nitrogen.



Polyaniline exists in several different oxidation states of which only emeraldine salt (Reduced form aniline) conducting.

Polyaniline is partially oxidized using a suitable oxidizing agent, into a base form of aniline which contains alternating reduced and oxidized forms of aniline polymer back bone.

Base form of aniline treated with aqueous HCl (1M), undergoes protonation of imine nitrogen atom, creating current carrying species (+ve) in the polymer backbone. These charges are compensated by the anions (Cl^-) of the doping agent giving the corresponding salt.

Applications:

- **Conductive coatings** for electronics and textiles (antistatic applications).
- **Corrosion protection** on metals through protective coatings.
- **Chemical and biosensors** for detecting gases, humidity, and biomolecules.
- **Electrode material** in batteries, supercapacitors, and rechargeable devices.
- **Flexible electronics** such as OLEDs, wearable sensors, and smart textiles.
- **Electromagnetic interference (EMI) shielding** in electronic devices.
- **Environmental and biomedical applications**, including water purification and drug delivery.

Assignment numerical:

1. A polymer has following composition 100 molecules of molecular mass 1000 g/mol, 2000 molecules of molecular mass 2000g/mol and 500 molecules of molecular mass 5000 g/mol. Calculate the number average and weight average molecular weight of the polymer and PDI.
2. In a polymer sample, 20% molecules have molecular mass 15000 g/mol, 45% molecules have molecular mass 25000 g/mol remaining molecules have molecular mass 27000 g/mol. Calculate the number average and weight average molecular weight of the polymer.
3. In a polymer sample, 20% of molecules have molecular mass 15000g/mol, 35% molecules have molecular mass 25000 g/mol and remaining molecules have molecular mass 20000 g/mol. Calculate the number and weight average molecular weights of the polymer.
4. A polymer sample contains 100,200,300 and 400 molecules having molecular mass 1000, 2000, 3000 and 4000 respectively. Calculate the number and weight average molecular weights of the polymer.
5. A polymer sample containing 50, 100 and 150 molecules having molar mass 1000, 2000 and 3000 respectively. Calculate the number and weight average molecular weights of polymer.
6. In a polymer sample, 20% of molecules have molecular mass 15000g/mol, 45% molecules have molecular mass 25000 g/mol and remaining molecules have molecular mass 50000 g/mol. Calculate the number and weight average molecular weights of the polymer and also calculate PDI.
7. A polymer sample contains 200 molecules of molecular mass 2000, and 200 molecules of molecular mass 40,000 g/mol. Calculate the number and weight average molecular weights of polymer.
8. A polymer sample contains 100 molecules of molecular mass 20,000 g/mol, 300 molecules of molecular mass 3000 and 500 molecules of molecular mass 5000. Calculate the number and weight average molecular weights of polymer.
9. A polymer sample contains 1, 2, 3 and 4 molecules having molecular weight 1×10^5 , 2×10^5 , 3×10^5 and 4×10^5 respectively calculate the number average and weight average molecular weight of the polymer.
10. The polymer has a following molar mass distribution

Number of molecules	-	Molar mass (g/mol)
50	-	5000
75	-	6000

Calculate the number and weight average molecular weights of the polymer and also calculate PDI.