Chapter - 5

POLYMER CHEMISTRY

Introduction to polymers: Nomenclature – Functionality. Types of polymerization. Mechanism of polymerization: Free radical mechanism – Cationic mechanism – Anionic mechanism. Plastics: Types – Thermoplastics and Thermosetting plastics. Properties: Strength – Crystalline and amorphous state – Average molecular weight – Polydispersity. Compounding of plastics. Moulding of plastics: Compression moulding - Injection moulding - Extrusion moulding. Introduction to Conducting polymers.

5.1 INTRODUCTION

A polymer is a large molecule composed of many repeated subunits, known as monomers. The term was coined in 1833 by Jöns Jacob Berzelius. The distinct piece of each monomer that is incorporated into the polymer is known as a repeat unit or monomer residue. The monomer units composing polymers are of low molecular weight compounds.

Polymers, both natural and synthetic, are formed by polymerization of monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semicrystalline structures rather than crystals. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function.

Polymers are studied in the fields of biophysics and macromolecular science, and polymer science (which includes polymer chemistry and polymer physics). Recognition that polymeric macromolecules make up many important natural materials was followed by the creation of synthetic analogs having a variety of properties. Indeed, applications of these materials as fibers, flexible films, adhesives, resistant paints and tough but light solids have transformed modern society. Because of their broad range of properties, both synthetic and natural polymers play an essential and ubiquitous role in everyday life.

EXAMPLES OF POLYMERS

Natural polymeric materials: All biological macromolecules i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides are purely polymeric. Shellac, amber, wool, silk and natural rubber (Polyisoprene)

Synthetic polymeric materials: synthetic rubber, phenol formaldehyde resin (or Bakelite), neoprene, nylon, polyvinylchloride (PVC or vinyl), polystyrene, polyethylene, polypropylene, polyacrylonitrile, PVB, silicone etc.

The backbone of a polymer is usually made of carbon atoms. A simple example is polyethylene ('polythene' in British English), whose repeating unit or the monomer is the ethylene monomer. The backbone of a polymer can also have other atoms as in the case of silicones, examples being Silly Putty and waterproof plumbing sealant. Oxygen is also commonly present in polymer backbones, such as those of polyethylene glycol, polysaccharides (in glycosidic bonds), and DNA (in phosphodiester bonds)

5.2 MONOMER AND POLYMER

1) Under the proper conditions of temperature, pressure and catalyst, the micro (Smaller) molecules are combining together to form a macro (big) molecule. This process is called Polymerization. Micro molecules are called ‘Monomer’. Macro molecule is ‘Polymer’.

2). Requirements of a monomer: a) multiple bonds or b) reactive functional groups.

3). The number of monomers present in a polymer is ‘ Degree of polymerization’ (n).

$$\text{Degree of Polymerization} = \frac{\text{Mol. Wt of polymer}}{\text{Mol. Wt of monomer}}$$

If n = low , Mol.Wt = 500 – 5000 Dalton units, it is Oligo polymer.

If n = High, Mol.Wt = 10,000 – 2,00,000 Dalton units, it is High polymer.

5.2.1 NOMENCLATURE OF POLYMERS

Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer.

A. Homopolymers: Polymers that contain only a single type of repeat unit are known as homopolymers.

Examples : Polystyrene is composed only of styrene monomer residues, and is therefore classified as a homopolymer. Other examples are: polyethylene, polypropylene.

M-M-M-M-M-M-M

where, M is a monomer unit

Structural Example: Monomer: Ethylene; Polymer: Polyethylene

B. Heteropolymers or Copolymers: Polymers containing a mixture of repeating units are known as copolymers or heteropolymers.

Example: Ethylene-vinyl acetate polymer contains more than one type of repeating unit and is thus a copolymer. The two monomers are ethylene and vinyl acetate

$$M_1\text{-}M_2\text{-}M_1\text{-}M_2\text{-}M_1\text{-}M_2\text{-}M_1$$

where, M_1 and M_2 are the different monomer units

Structural Example: Monomers: Ethylene and Acrylic acid; Polymer: Ethylene acrylic acid copolymer

Based on the arrangement of the monomers along the backbone of a copolymer, the following types of copolymers are obtained:

- **Alternating copolymers** : They possess regularly alternating monomer units.

  $$M_1\text{-}M_2\text{-}M_1\text{-}M_2\text{-}M_1\text{-}M_2\text{-}M_1$$

  M_1 = vinyl chloride and M_2 = vinyl acetate

- **Statistical copolymers**: They are polymers having the monomer units arranged according to a known statistical rule. A statistical copolymer in which the probability of finding a particular type of monomer residue at a particular point in the chain is independent of the types of surrounding monomer residue may be referred to as a truly random copolymer.

  $$M_1\text{-}M_2\text{-}M_1\text{-}M_2\text{-}M_2\text{-}M_1\text{-}M_2$$

  M_1 = Styrene and M_2 = Butadiene

- **Block copolymers** : These polymers have two or more homopolymer subunits linked by covalent bonds. Polymers with two or three blocks of two distinct chemical species (e.g., M_1 and M_2) are called diblock copolymers and triblock copolymers, respectively. Polymers with three blocks, each of a different chemical species (e.g., M_1, M_2, and M_3) are termed triblock terpolymers.

  $$M_1\text{-}M_2\text{-}M_2\text{-}M_2\text{-}M_2\text{-}M_1\text{-}M_1\text{-}M_1\text{-}M_1\text{-}M_2\text{-}M_2$$

  M_1 = acrylic acid and M_2 = methylmethacrylate

Graft or grafted copolymers: These polymers contain side chains that have a different composition or configuration compared to the main chain.

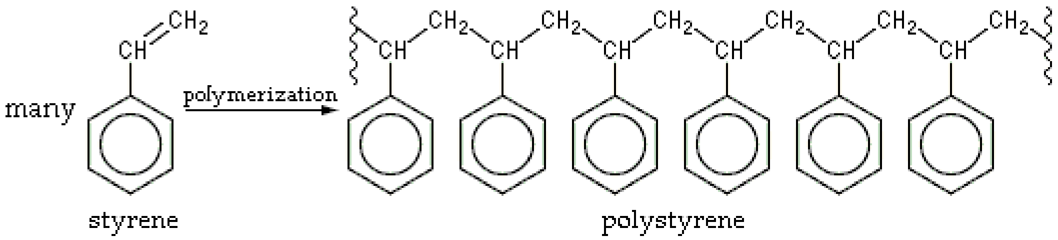
$M_1-M_1-M_1-M_1-M_1-M_1-M_1-M_1-M_1-M_1-M_1$
|
$M_2-M_2-M_2-M_2-M_2$

M_1 = vinyl chloride and M_2 = styrene

C. Homochain polymer: It is a polymer in which the main chain is made up of same atomic species.

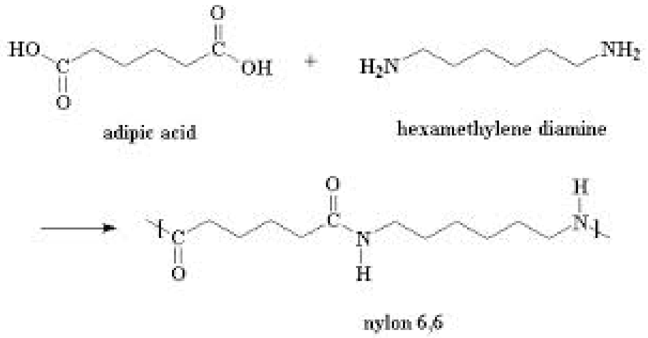
Example: Polyethylene, Polystyrene

Structural Example: Monomer: Styrene; Polymer: Polystyrene



D. Heterochain polymer : A polymer in which the main chain has more than one atomic species is called
a heterochain polymer. Example : Nylon 6,6

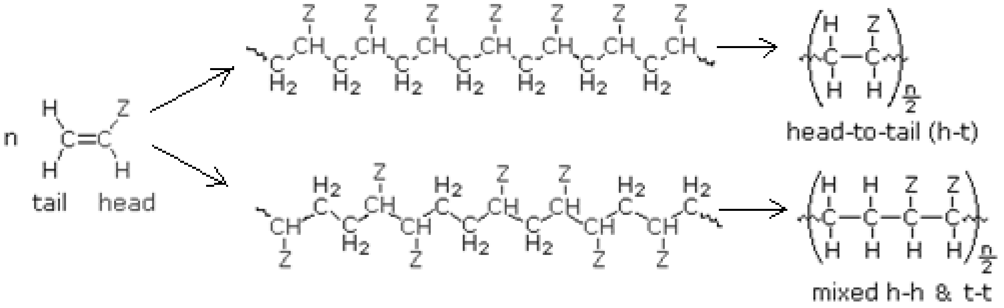
Structural Example: Monomer: adipic acid and hexamethylene diamine; Polymer: Nylon 6,6



E. Stereospecific polymer or Tacticity

Tacticity describes the relative stereochemistry of chiral centers in the neighbouring structural units within a polymer. The classification is based on the orientation of the monomeric units or functional groups with respect to the main chain of the polymer. The orientation of the substituents can be in an orderly fashion or disorderly fashion. Based on this there are three types of polymers:

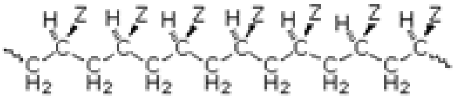
Symmetrical monomers such as ethylene and tetrafluoroethylene can join together in only one way. Monosubstituted monomers, on the other hand, may join together in two organized ways, described in the following diagram, or in a third random manner. Most monomers of this kind, including propylene, vinyl chloride, styrene, acrylonitrile and acrylic esters, prefer to join in a head-to-tail fashion, with some randomness occurring from time to time.



Regioisomeric Polymers from Substituted Monomers

If the polymer chain is drawn in a zig-zag fashion, as shown above, each of the substituent groups (Z) will necessarily be located above or below the plane defined by the carbon chain. Consequently we can identify three configurational isomers of such polymers. If all the substituents lie on one side of the chain the configuration is called isotactic. If the substituents are alternatively present with respect to the main chain in a regular manner the configuration is termed syndiotactic. Finally, a random arrangement of substituent groups is referred to as atactic. Examples of these configurations are shown here.

Isotactic polymer: It is a polymer with all substituents on the same side with respect to the main chain of the polymer. Example: Polypropylene, cis-polyisoprene

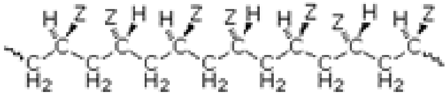


isotactic

Atactic polymer: It is a polymer with the random orientation of the substituents with respect to the main chain of the polymer. Example: Polypropylene, trans-polyisoprene

atactic

Syndiotactic polymer: It is a polymer having substituents that are alternatively placed with respect to the main chain of the polymer. Example: Polypropylene



syndiotactic

Many common and useful polymers, such as polystyrene, polyacrylonitrile and poly(vinyl chloride) are atactic as normally prepared.

Catalysts that effect stereoregular polymerization of polypropylene and some other monomers have been developed, and the improved properties associated with the increased crystallinity of these products have made this an important field of investigation. The following T_g (glass transition temperature) values of some polymers have been reported.

Polymer	Tg atactic	Tg isotactic	Tg syndiotactic
PP	–20 ºC	0 ºC	–8 ºC
PMMA	100 ºC	130 ºC	120 ºC

The properties of a given polymer will vary considerably with its tacticity. Thus, atactic polypropylene is useless as a solid construction material, and is employed mainly as a component of adhesives or as a soft matrix for composite materials. In contrast, isotactic polypropylene is a high-melting solid (ca. 170 ºC) which can be molded or machined into structural components.

5.2.2 FUNCTIONALITY

It is the number of covalent bonds that a monomer molecule or monomeric unit in a macromolecule or oligomer molecule can form with other reactants. In other words, functionality (F) denotes the number of bonding sites or active centers or reacting functional groups in a monomer. It can also be defined as number of reactive sites present in a monomer is called ‘ Functionality.

Examples:-

$CH_2 = CH_2$, The double bond is acting as two reactive site, So, Ethylene functionality is 2.

1. There are no monofunctional monomers.
2. If F = 2, a linear chain macromolecule or a macrocycle can be formed.
3. If F > 2, a branch point can be formed leading to a branched macromolecule, a network or a micronetwork.
4. Ethene and ethylene glycol are examples of bifunctional monomers, glycerol is an example of a trifunctional monomer, and divinylbenzene and pentaerythritol are examples of tetrafunctional monomers.

5.2.2.1 Significance of Bifunctional Monomers: A bifunctional monomer forms a linear or straight chain polymer in which the monomer units are linked by strong covalent bonds and the chains are held by weak Van der waal's force of attraction. Hence the movement of polymer chains is restricted, whereby; soft and flexible polymers with less strength, low heat resistance are formed. Bifunctional monomers can also form branched chain polymers in which there is high resistance to movement of the polymer chains.

5.2.2.2 Significance of Trifunctional Monomers: A trifunctional monomer forms a cross-linked, three dimensional polymer network in which the monomers are held by strong covalent bonds which completely prevents the movement of the polymer chains. Such polymers have high strength, hardness, toughness, high heat resistance and are commonly insoluble in all organic solvents.

$CH_2 – OH$ In glycerol three –OH groups present. So, functionality = 3
|
$CH – OH$
|
$CH_2 – OH$

5.2.3 SIGNIFICANCE OF FUNCTIONALITY:

1. Substances having only one bonding or reactive site are called "monofunctional monomers". Eg. $CH_3 – COOH$

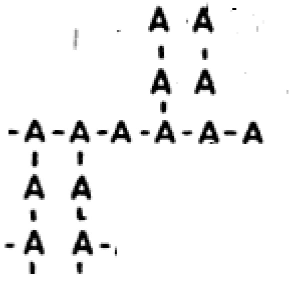
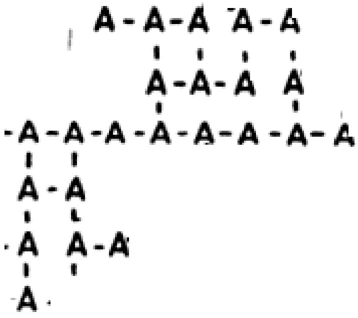
They cannot undergo polymerization.

2. If F = 2, they form linear chain structure. (eg) Ethylene

Because of the weak Vander Waal's attraction, there is no restriction for the movement of one polymer chain over another chain. They have less strength, low heat resistance, softness and flexibility.

3. If F=3, they form branched structure. (Eg) Glycerol

Because of the strong covelent bond, the movement polymer chain is restricted. They have high strength, high heat resistance, hardness .

4. If F≥ 4, then they form complexed 3D structure.

5.3 TYPES OF POLYMERIZATION

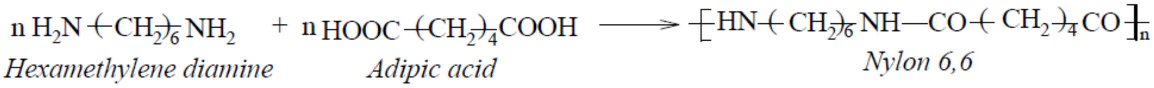
The reaction in which monomers combine to give polymers is known as polymerization. It can be broadly classified into three categories as addition, condensation and copolymerization

5.3.1 ADDITION POLYMERIZATION

Monomers having multiple bonds (double or triple bond) undergo addition polymerization. Monomers combine to give polymer through addition reaction without elimination of any smaller molecules.

5.3.2 CONDENSATION POLYMERIZATION

Monomers having same or different types of functional groups undergo condensation polymerization. The polymerization proceeds by step wise reaction between reactive functional groups and small molecules are eliminated.



$$n\, H_2N\text{-}(CH_2)_6\text{-}NH_2 + n\, HOOC\text{-}(CH_2)_4\text{-}COOH \longrightarrow \left[HN\text{-}(CH_2)_6\text{-}NH\text{—}CO\text{-}(CH_2)_4\text{-}CO \right]_n$$

5.3.3 COPOLYMERIZATION

1. It is a special kind of polymerization, otherwise known as “Joint polymerization”.

The product is known as ‘Co-polymers’. This is superior to other polymerization because it is used to alter the hardness, strength, rigidity and crystallinity of the monomers.

The differences between two major polymerization methods are tabulated as follows:

S. No	Addition Polymerization	Condensation Polymerization
1	Eg. PVC	Eg. Nylon 6,6
2	Otherwise known as “Chain growth Polymerization”.	Otherwise known as “Step wise Polymerization”.
3	Monomers are adding together to form polymers.	Monomers are condensed to form polymer.
4	No elimination of other molecules.	Elimination of smaller molecules occur.
5	At least one multiple bond presence is essential condition.	Monomers must have two or more functional groups.
6	Homo polymers are formed.	Hetero polymers are formed.
7	Thermoplastics are formed.	Thermo set plastics are formed.
8	Molecular weight of the polymer is the integral multiple of monomers.	Need not be so.
9	Monomers disappear slow and steadily.	Monomers disappear at the initial stage of the reaction.
10	Longer processing time is needed to increase yield.	Longer time is essential for increasing molecular weight.

5.4 MECHANISM OF POLYMERIZATION

The general mechanism consists of three following steps, irrespective of the method.

A) Initiation
B) Propagation
C) Termination

5.4.1 MECHANISM OF FREE RADICAL ADDITION POLYMERIZATION

The free radical mechanism also involves 3 steps as mentioned earlier

1. Initiation, 2. Propagation and 3. Termination

Step I - Initiation:

1a) Initiator → Radical

I → $R^{\cdot}$

1b) Radical + Monomer → Chain Initiating Species (CIS)

$R^{\cdot}$ + M → $R - M^{\cdot}$

Step II - Propagation:

CIS + n (monomer) → Living polymer

R- M . + n M → R –$(M)_n$ - M .

The growing chain the polymer is known as Living Polymer.

Step III - Termination;

3a) By Coupling : Radical + Radical → Macromolecule (Dead polymer)

R- M . + . M – R → R – M – M - R

3b) By disproportionation by Hydrogen transformation:

Radical + Radical → Unsaturated polymer + Saturated polymer

The product of addition polymerization is known as Dead polymers.

EXPLANATION OF FREE RADICAL MECHANISM (eg) PVC polymerization

1. Initiation

a) Initiator → Radical

1.The substance which undergoes homolytic cleavage to form radical is called 'Initiator'. (e.g) acetyl peroxide initiator

2.The substance with single electron is called ' radical'. It is represented as R.

(e.g) acetyl peroxide radical

e.g Acetyl peroxide → Radicals (at 80^0C)

CH_3COO - CH_3COO → 2 CH_3COO .

Example of Initiators

1. Benzoyl peroxide Initiator (used around 80-95^oC)

2. Azobis Isobutyro Nitrile (AIBN) Initiator(used around 50-70^{o}C)

b) Radical + Monomer → Chain Initiating Species (CIS)

2. Propagation:

CIS + n (monomer) → Living polymer

3. Termination:

a) Coupling

CIS /Radical + CIS / Radical → Macromolecule (Dead polymer)

b) Disproportionation (by Hydrogen transformation)

C is / Radical + CIS / Radical → Unsaturated polymer + Saturated polymer

The products are known as dead polymers.

5.4.2 MECHANISM OF ANIONIC ADDITION POLYMERIZATION

When the chain reaction is initiated and carried by negatively charged (carbanion) intermediates, the reaction is known as anionic polymerization.

- Monomers with electronegative groups like Cl^- , CN^- follow this mechanism.
- Lewis bases like KNH_2 , $NaNH_2$ are used as initiators.
- Eg. Vinyl chloride, Acrylonitrile polymerization

There are 3 steps involved in Anionic mechanism:

1. Initiation
2. Propagation
3. Termination

Step I - Initiation :

Anion from lewis base + monomer → Chain Initiating Carbanion (CIC)

A- + M → A - M^-

Step II - Propagation;

CIC + n (monomer) → Living polymer

$A\text{-} M^{-} \quad + n M \quad \rightarrow \quad A -(M)_n - M^{-}$

The growing chain the polymer is known as Living Polymer.

Step III - Termination;

Living Polymer + Proton Medium → Dead Polymer + Anion

EXPLANATION OF ANIONIC POLYMERIZATION (eg) Acrylonitrile

1.Initiation:

Here, Chain Initiating carbanion formation is taking place.

$$KNH_2 \rightarrow K^{+} + NH_2^{-}$$

2. Propagation:

Here, the growth of the carbanion takes place. It involves the transfer of negative charge along the chain.

3. Termination:

The chain reaction is terminated when the carbanion reacts with the medium such as Ammonia, water
etc,m

5.4.3 MECHANISM OF CATIONIC ADDITION POLYMERIZATION

When the chain reaction is initiated and carried by positively charged (carbocation) intermediates, the reaction is known as anionic polymerization.

Monomers with electropositive groups like CH_3, C_6H_5 follow this mechanism.

The lewis acids like $AlCl_3$, BF_3, $TiCl_4$ are generally acting as initiators.

Examples: Isoprene, Styrene

The 3 steps involved in Cationic mechanism are:

1. Initiation
2. Propagation
3. Termination

Step I - Initiation:

Cation from lewis acid + monomer → Chain Initiating Carbocation (or)
Carbonium ion (CIC)

$H^+ + M \rightarrow H - M^+$

Step II - Propagation:

CIC + n (monomer) → Living polymer

$H\text{-} M^+ + n\,M \rightarrow H - (M)_n - M^+$

The growing chain the polymer is known as Living Polymer.

Step III - Termination;

Living Polymer → Dead Polymer + Lewis acid

EXPLANATION OF CATIONIC POLYMERIZATION. (eg) Polystyrene

1. Initiation:

Here, Chain Initiating carbonium ion formation is taking place.

$$AlCl_3 + H_2O \rightarrow H^+AlCl_3OH^-$$

2. Propagation:

Here, the growth of the carbonium ion takes place. It involves the transfer of positive charge along the chain. It produces living polymer.

(Chain Initiating Carbanion) (monomers) Living Polymer

3. Termination:

When the catalyst is splitting from Living polymer, it results in Dead polymer product.

Living Polymer Product + Lewis acid catalyst

5.5 PLASTICS

Definition: Plastics are high polymers which can be moulded into any desired shape under proper conditions of temperature, pressure and catalyst. (e.g) PVC , PET

They are made up of resins, fillers, plasticizers, lubricants etc.,

Differences between Thermoplastics and thermosetting plastics

S.No	THERMOPLASTICS	THERMOSETTING PLASTIC
1	Eg. PVC , Polyethylene	Polyester, Bakelite
2	Plastics which are melted at high temperature, solidified at low temperature They can be remelted and remoulded into any desired shapes for any number of times.	They cannot be remoulded after their first usage.
3	Scrap can be used again.	Scrap cannot be used again.
4	Formed by addition polymerization	Formed by condensation polymerization
5	The bond strength is low	The bond strength is high
6	Molecular weight is low	Molecular weight is high
7	Soluble in organic solvents.	Insoluble in organic solvents.
8	Prepared by Injection moulding	Prepared by compression moulding.
9	They have linear structure	They have complex 3D structure.

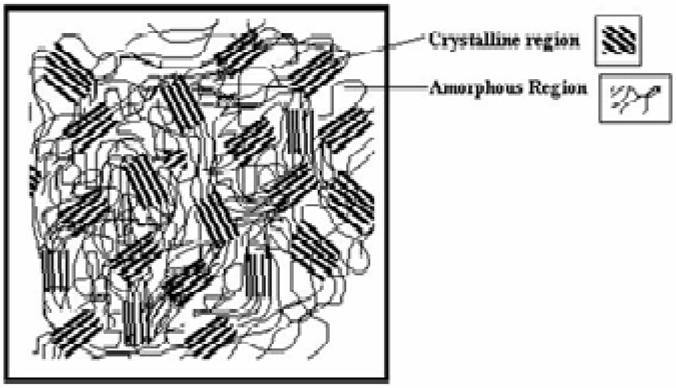
Advantages and disadvantages of plastics are listed below:

Advantages of plastics	Disadvantages of low quality plastics
1. Insulator 2. Corrosion resistant 3. Easy mouldability 4. Used as shock absorbers 5. Has adhesive property 6. Less weight 7. Chemical inertness 8. Available in various colours	1. Very soft 2. Embrittlement 3. Ageing (Low durability) 4. Cannot withstand high temperatures 5. Creep (shape deformation due to load)

5.6 POLYMER MORPHOLOGY

Polymer morphology describes the arrangement and microscale ordering of polymer chains in space. Properties of polymers varies with morphology and are determined by their chemical structure, degree of polymerization, orientation of the chain molecules, crystallinity, package density and cross linking between the molecules. Polymer crystallinity is one of the important properties of all polymers. Polymer exists in two forms such as crystalline and amorphous forms.

A synthetic polymer is called crystalline, if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from the intramolecular folding and/or stacking of adjacent chains. Synthetic polymers can have both crystalline and amorphous regions as shown in the following figure. The regions where the molecules are in regular order of arrangement are called crystalline regions. In between these orderly arranged regions, molecules are arranged in random disorganized states which are called amorphous regions.



Crystallinity is an indication of the amount of crystalline region in the polymer with respect to the amorphous content. Crystallization takes place in between glass transition and melting state and is always exothermic. Crystallinity influences many polymer properties like hardness, modulus, tensile strength, stiffness and melting point.

One of the methods to measure polymer crystallinity is by differential scanning calorimerty (DSC). The DSC instrument is designed to measure the amount of heat absorbed or evolved from the sample under isothermal conditions. Another method to measure polymer crystallinity is by X-Ray diffraction method. It is used to determine the nature of polymer and the extent of crystallinity in it. The degree of crystallinity is expressed in terms of weight fraction or volume fraction of crystalline material. There are few synthetic polymers which are entirely crystalline in nature.

The crystallinity of polymers, characterized by degree of crystallinity, ranges from zero for a completely non-crystalline polymer to one for a completely crystalline polymer. Polymers with microcrystalline regions are generally tougher (can be bent more without breaking) and more impact-resistant than totally amorphous polymers.

Polymers with degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. Thus for many polymers, reduced crystallinity may also be associated with increased transparency.

The term amorphous means to have no defined shape, or an easily altered shape, like a liquid or a rubber.

A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g). It is the temperature at which amorphous polymers undergo a transition from a rubbery, viscous liquid, to a brittle, glassy amorphous solid on cooling. The glass transition temperature may be engineered by altering the degree of branching or crosslinking in the polymer or by the addition of a plasticizer. Inclusion of plasticizers tends to lower T_g and increase polymer flexibility. The portion of the segment that is in the amorphous state is no different from that part of the polymer which got trapped in the crystallized state.

The only difference between amorphous polymer and crystalline polymer is that the amorphous form physically could not enter the crystalline lattice at the time when the polymer was crystallized. The amorphous state, therefore, consists of loose chain ends, loops of polymer segments that exit and reenter the same crystalline domain. Polymer segments which crystallize in two adjacent lattices are called tie molecules. Tie molecules are amorphous polymer segments which hold the crystalline segments together and they act as the mortar between the bricks which enhances the properties of semi-crystalline polymers. Without these intercrystalline links, there would be nothing holding the polymer together except for the weak secondary attractive forces between them.

5.7 MOLECULAR WEIGHT OF POLYMERS

The molecular weight of polymers is not unique like small molecules. Since polymeric molecular weights are in the range, it is always given as average molecular weight.

5.7.1 NUMBER AVERAGE MOLECULAR WEIGHT ($\bar{M}_n$)

It is the ratio of sum of molecular weights of individual molecules to the total number of molecules in the mixture.

It is obtained by measuring the colligative properties.

It is a good index of physical properties such as impact and tensile strength.

Consider, a polymer mixture contains:

n_1 molecules are with molecular weight M_1

n_2 molecules with molecular weight M_2 and so on.,

If n_i molecules are with molecular weight M_i then,

$$\overline{M}_n = \frac{n_1M_1 + n_2M_2 + \ldots..+ n_iM_i}{n_1 + n_2 + \ldots.. + n_i}$$

$$\overline{\mathbf{M}}_{\mathbf{n}} = \mathbf{\Sigma n_iM_i \;/\; \Sigma\, n_i}$$

5.7.2 WEIGHT AVERAGE MOLECULAR WEIGHT ($\overline{M}_w$)

It is the ratio of sum of molecular weights of individual molecules to the total weight of molecules in the mixture. It is obtained by light scattering and ultra centrifugation techniques.

Consider, a polymer mixture contains

w_1 is the weight of polymer with molecular weight M_1

w_2 is the weight of polymer with molecular weight M_2

and so on .,

Let w_i molecules are with molecular weight $M_{i,}$ Then,

$$\overline{M}_w = \frac{w_1 M_1 + w_2M_2 + \ldots..+ w_{i\,i}M_i}{w_1 + w_2 + \ldots.. + w_i.}$$

$$\overline{\mathbf{M}}_{\mathbf{w}} = \mathbf{\Sigma w_iM_i \;/\; \Sigma\, w_i}$$

But, number of moles n = w / M

So, w = nM

We can replace w_1 by n_1M_1, w_2 by n_2M_2 and w_i by n_iM_i

$$\overline{M}_w = \frac{n_1M_{1.}\, M_1 + n_2M_2\, M_2 + \ldots..+ n_iM_iM_i}{n_1\, M_1 + n_2\, M_2 + \ldots.. + n_iM_i}$$

$$\bar{M}_w = \Sigma n_i M_i^{\,2} / \Sigma n_i M_i$$

5.8 POLYDISPERSITY INDEX (PDI)

The ratio of weigth average molecular weight $\bar{M}_w$ to number average molecular weight $\bar{M}_n$ is known as polydispersity index or distribution ratio.

$$\textbf{Polydispersity index} = \bar{M}_w / \bar{M}_n$$

For polydispersed system, $\bar{M}_w > \bar{M}_n$

For monodispersed system, $\bar{M}_w = \bar{M}_n$

- If a polymer contains molecules of same molecular weight, such system is known as monodispersed system. But it is unreal condition. Such possibility is available only in simple chemical compounds like water, alcohol etc.,
- If a polymer contains molecules of different molecular weight, it is polydispersed system. The deviation of ratio from the unity is taken as a measure of polydispersity of the polymer sample. For all synthetic polymers, PDI is higher than 1.
- Higher values of the ratio indicate greater polydispersity. It means all the molecules of the polymers will not have identical molecular weight.

5.9 COMPOUNDING OF PLASTICS (OR) MOULDING CONSTITUENTS

Compounding is the process of incorporating additives, modifiers into polymers for achieving uniformity on a scale appropriate to the quality of the articles subsequently made from the compound. It is the first step in most plastic fabrication. Each compounding ingredient will contribute towards final properties of the product. Plastics are compounded to enhance features like:

- Mechanical/Physical and Thermal Properties
- Opticals (color/visuals)
- Functional properties
- Reduced cost

5.9.1 INGREDIENTS PLAYING KEY ROLE IN PLASTIC COMPOUNDING ARE:

1. Fibers: increase strength and stiffness
2. Plasticizers: for flexibility

3. Lubricants: to increase moulding property
4. Antioxidants: for high temperature stability
5. UV stabilizers: for resistance to sunlight
6. Fillers: for economy
7. Flame retardants and smoke suppressants
8. Conductive fibers: for electrical properties
9. Color concentrates: for colored plastics
10. Polymer alloys & blends: for performance plastics

Moulding constituents and their functions

S. No	Compounding ingredients	Examples	Functions
1.	Resin	It forms the major part	It is the binder material which holds the constituents together
2.	Stabilizers	For transparent polymers: stearates of lead, cadmium or barium. For opaque polymers: Red lead or lead monoxide	They are thermal stabilizers added to improve the stability of the polymer
3.	Accelerators or Catalysts	Hydrogen peroxide, benzoyl peroxide and metals like lead, copper and oxides like zinc oxide	Added to accelerate the process of polymerization reaction during moulding process
4.	Lubricants	Waxes, oils and soap	It gives a shiny appearance to the polymer material and to take out the material easily from the mould
5.	Fillers or extenders	Fillers used to increase hardness are: mica, carborundum, quartz. Asbestos powder is a filler used to improve thermal and corrosion resistance	They are inert materials added to plastics to increase bulkiness and thereby reduce the cost of production
6.	Plasticizers	Vegetable oils, camphor, organic phosphates	They are added to increase softness and flexibility of the product. It neutralizes the intermolecular forces present in the material, thereby the movement of the molecular layer will become possible.
7.	Pigments	Titanium dioxide – white color Carbon black – black color Prussian blue – Blue	They will provide the desired color to the product.

		Chromium oxide – green Ferrous oxide – red Lead chromate -- yellow	
8.	Antioxidants	Phenylparanaphthylamine	They protect the polymer against oxidative degradation

5.10 MOULDING OF PLASTICS INTO ARTICLES

Moulding is the process of manufacture or fabrication of raw plastic material, whether it is thermoplastic or thermosetting resin, into a definite shape by using a rigid frame or model.

Polymer Processing

There are five basic processes to form polymer products or parts. These include; injection moulding, compression moulding, transfer moulding, blow moulding, and extrusion moulding.

The type of moulding method is selected based on the type of resin used. For thermoplastic resins, compression moulding or transfer moulding methods are used. For thermosetting resins, injection moulding or extrusion moulding methods are used.

5.10.1 COMPRESSION MOULDING

It is a method of moulding in which a specific quantity of raw, un-polymerised plastic is placed into a preheated mould which is closed under pressure compressing the molten plastic into the cavity to produce the desired shape of the plastic material. Pressure is applied to force the material into contact with all mould areas with continuous application of heat and pressure until the moulding material is cured. The process employs thermosetting resins in a partially cured stage, either in the form of granules, putty-like masses, or preforms. It is a high-volume, high-pressure method.

This type of moulding is the first method to be used to form plastics. The steps involved in this moulding method are:

1. Pre-formed blanks, powders or pellets are placed in the bottom section of a heated mold or die.
2. The other half of the mould is lowered and the pressure is applied.
3. The material softens under heat and pressure, flowing to fill the mould. Excess is squeezed from the mould. For a thermosetting plastic, cross-linking occurs in the mould.
4. The mould is opened and the polymer product is removed.

For thermoplastics, the mould is cooled before removal so the part will not lose its shape. Thermosetting plastic may be ejected while they are hot and after curing is complete.

Compression moulding was first developed to manufacture composite parts for metal replacement applications. This method is typically used to make larger flat or moderately curved parts. This method of moulding is greatly used in manufacturing automotive parts such as hoods, fenders, scoops, spoilers, as well as smaller more intricate parts.

Compression-molding is suitable for ultra-large basic shape production in sizes beyond the capacity of extrusion techniques. Materials that are typically manufactured through compression molding include: Polyester fiberglass resin systems (SMC/BMC), Torlon, Vespel, Poly(p-phenylene sulfide) (PPS), and many grades of PEEK

Advantages of compression molding :

- It is a method suitable for moulding complex, high-strength fiberglass reinforcements.
- Advanced composite thermoplastics can also be moulded with unidirectional tapes, woven fabrics, randomly oriented fiber mat or chopped strand.
- Compression moulding has the ability to mould large, fairly intricate parts
- It is one of the lowest cost moulding methods compared to other methods such as transfer molding and injection molding
- It wastes relatively little material, giving it an advantage when working with expensive compounds
- There is a small investment for presses and moulds
- Low cost production for samples and pilot production

Limitations :

- It is difficult to mould complex articles with undercuts or small holes
- It has fair tolerances
- Flash can be a problem

Disadvantages:

- It provides poor product consistency and difficulty in controlling flashing.
- It is not suitable for some types of parts
- Fewer knit lines are produced and a smaller amount of fiber-length degradation is noticeable when compared to injection molding.

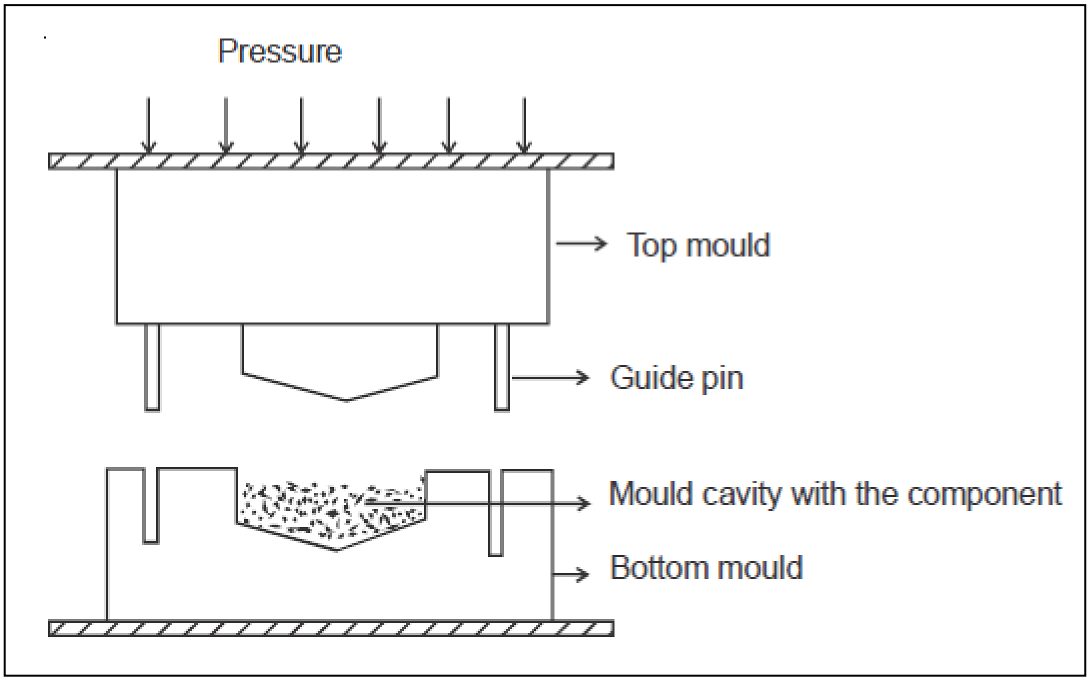


Figure 5.1 Compression moulding

Applications

Components produced by compression moulding are generally electrical components and fittings as thermosets are good electrical insulators e.g. electrical switches and sockets.

The process is also used for panels, housings, container caps, dishes and automotive parts.

5.10.2 INJECTION MOULDING

Injection molding consists of high pressure injection of the raw material into a mould which shapes the polymer into the desired shape. Injection molding can be performed with a host of materials, including metals, glasses, elastomers, confections, and most commonly thermoplastic and thermosetting polymers.

Material such as polymer granules is fed into a feed hopper, mixed and heated to a molten state and then injected at high pressure into a prefabricated mould cavity where it cools and hardens to the configuration of the cavity. The moulds are made from metals like steel or aluminum. Injection molding is widely used for manufacturing a variety of parts, from the smallest components to a big one.

The injection moulding process requires strict control of the mould temperature, speed and pressure of injection, condition of the molten plastic and dwelling/cooling times to ensure high quality products. It is necessary to have a sufficient clamping force proportional to the projected area of the mould to prevent creation of excess flash.

The process uses thermoplastics, such as polycarbonate (PC), polyethylene (PE), polystyrene (PS), polypropylene (PP) and acrylonitrile-butadiene-styrene (ABS).

Injection blow moulding is used for the fabrication of small hollow components which more intricacies. Injection moulding allows the final component design to be highly complex. Holes, inserts, threads, bosses, minor undercuts and use of colour are all possible.

Different types of injection molding processes

Although most injection moulding processes are covered by the conventional process described above, there are other several important molding methods. They are:

- Die casting
- Metal injection moulding
- Thin-wall injection moulding
- Injection moulding of liquid silicone rubber.

Advantages

- Injection moulding is capable of high production rates of 1–50 components/min and the process becomes highly economical at medium to high production volumes.
- Costs are reduced through good material utilisation: sprues, risers and scraps are all recyclable. The finishing process is minimal and has low economic impact.
- It has the shortest cure time
- It does not require preforms
- Precise volumes of the raw material can be injected into the mould
- There is high homogeneity of cross linking throughout the product
- There is minimal wastage of the raw material
- Automatisation of the production is possible

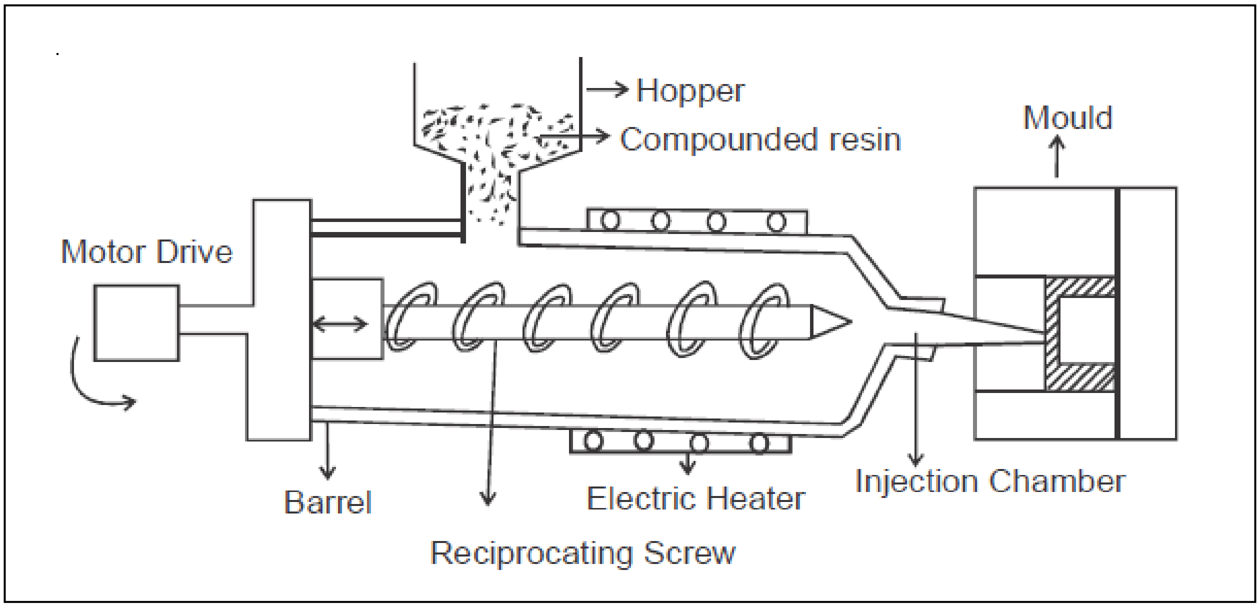


Figure 5.2 Injection moulding

Disadvantages

- A significant capital investment is necessary for injection moulding due to high equipment and tooling costs.
- Fabrication of complex die cavities usually made from hardened tool steel, will result in longer lead times.
- The flexibility of the process is limited by its dedicated dies, high cost of tool change over and machine set up times. However the process lends itself to full automation and the use of robotics is common for loading and unloading of machines.

Applications

Injection moulding is the most common manufacturing technique for plastic components. It is capable of producing high precision, complex components with an excellent surface finish which makes it ideal for production of automotive and aerospace components as well as electrical parts and housings e.g. computer enclosures and mobile phone cases. Other applications are fittings, tool handles, crates and containers.

5.10.3 EXTRUSION MOULDING

Extrusion moulding is similar to injection moulding except that a long continuous shape is produced. In extrusion moulding, a preheated polymer, placed in a feed hopper, is injected through an orifice with a particular cross section (the die), and a continuous shape is formed with a uniform cross section similar to that of the orifice.

This process makes parts of constant cross section like pipes and rods. Molten polymer goes through a die to produce a final shape which involves four steps:

1. Pellets of the polymer are mixed with coloring and additives
2. The material is heated to its proper plasticity
3. The material is forced through a die
4. The material is cooled

Shapes that can result from extrusion include T-sections, U-sections, square sections, I-sections, L-sections and circular sections.

One of the most famous products of extrusion moulding is the optical fiber cable.

Although thermosets can be extruded and cross-linked by heating the extrudate, thermoplastics are commonly extruded and solidified by cooling. The products that are produced by extrusion moulding method are film, sheet, tubing, pipes, insulation, and home siding. In each case the profile is determined by the die geometry, and solidification is by cooling.

Most plastic grocery bags and similar items are made by the continuous extrusion of tubing.

The process uses thermoplastics, such as: polyvinyl chloride (PVC), polyethylene (PE) and polypropylene (PP).

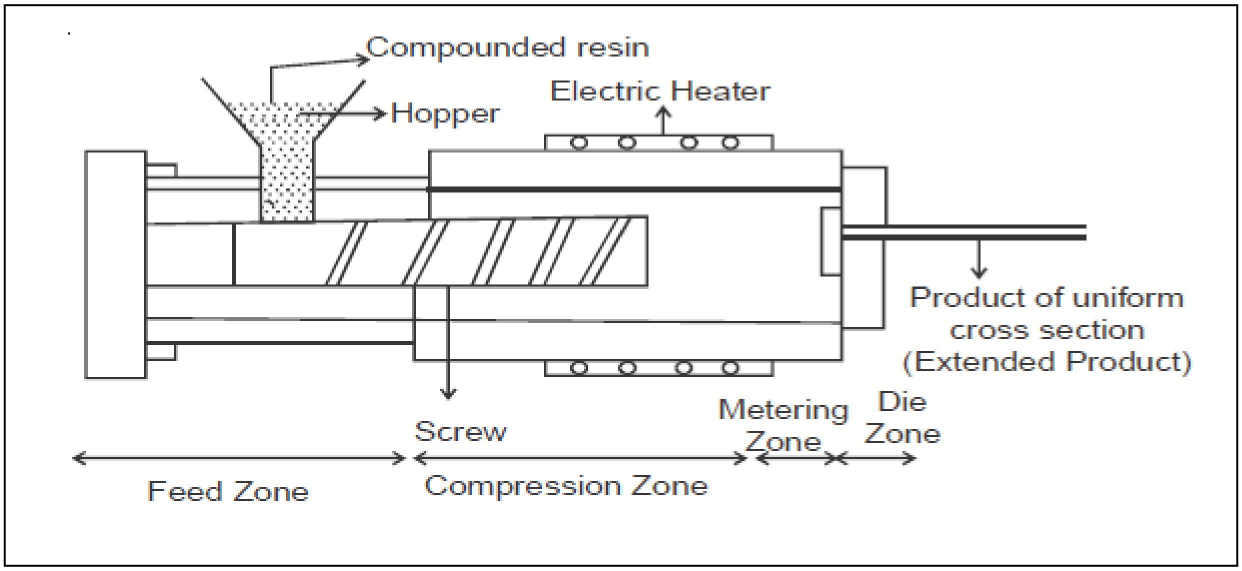


Figure 5.3 Extrusion moulding

Advantages

- The process has extremely high production volumes as continuous lengths are produced at 60m/min and 5m/min for tube profiles and sheet/rod profiles respectively.
- Multiple holes in the die increase the production rate but to allow smooth running the extrusion is operated below its maximum speed capability.
- It is economical to run production for 1000kg of profile extrusion and 5000kg for sheet extrusions and costs are dramatically increased with a high output range.
- Cutting a continuous section to length is the only time there is waste material produced and the only major finishing cost which is relatively inexpensive.

- The final component design always has a uniform cross section which can be highly complex.
- Open or closed profiles are possible and solid forms can include re-entrant angles.
- Holes, inserts and grooves are possible but require secondary operations when they are not parallel to the axis of extrusion. Part consolidation features should be integrated into the design for increased ease of assembly.

Limitations

- Components made by the process are prone to shrinkage and distortion so that the accurate control of uniformity and cooling rate is important to reach accurate dimensions.
- The extruded product may increase in size as it leaves the die and may be compensated by decreasing extrusion rate or the melt temperature.
- One problem that affects the output and quality of extrusion is the possibility of trapped gases in the extrusion screw which is particularly common when using powdered raw materials.

Disadvantages

- The process has high equipment costs as materials that give off toxic or volatile gases during extrusion demand air extraction or a washing plant.
- Lead times are usually within weeks depending on die complexity.
- The process flexibility is limited to the dedicated tooling but with short set-up and changeover times.

Applications

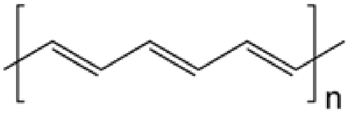
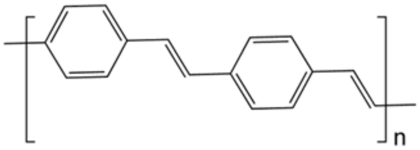
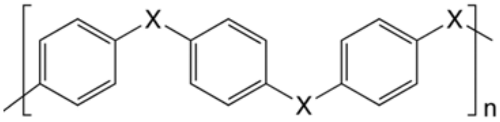
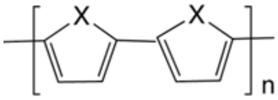
Continuous extrusion produces components have complex profiles such as rods, bar, tubing and sheets, pipes, guttering, window sills, insulation on wires, cling-film and tyre reinforcement.

5.11 CONDUCTING POLYMERS

Conductive polymers are polyconjugated organic polymers that conduct electricity because of their conjugated π-bonds. Such compounds can have either metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Some examples of conducting polymers are given in the table

S.No	Conducting	Structure	Conductivity

	Polymer		**(S/cm)**
1.	Polyacetylene		10^3 - 1.7x10^5
2.	Polyphenylene vinylene		3 – 5x10^3
3.	Polyaniline (X = NH/N) Polyphenelene sulfide (X = S)	 (X = NH/N, S)	30 - 200
4.	Polypyrrole (X = NH) , Polythiophene (X = S)	 (X = NH, S)	10^2 – 7.5x10^3

In pure form (undoped or pristine state), conducting polymers have low electrical conductivity and behaves like an insulator or as a semiconductor. These polymers can be converted to polymer salts having electrical conductivities comparable to that of metals by treating with suitable oxidizing or reducing agents. These types of doped polymers having high electrical conductivities are called as synthetic metals.

The electrical conductivities of undoped conjugated polymers have the range in the order of 10^{-10} S/cm from those of the typical insulators and in the range of 10^{-5} S/cm from those of the semiconductors.

5.11.1 MOLECULAR BASIS OF ELECTRICAL CONDUCTIVITY

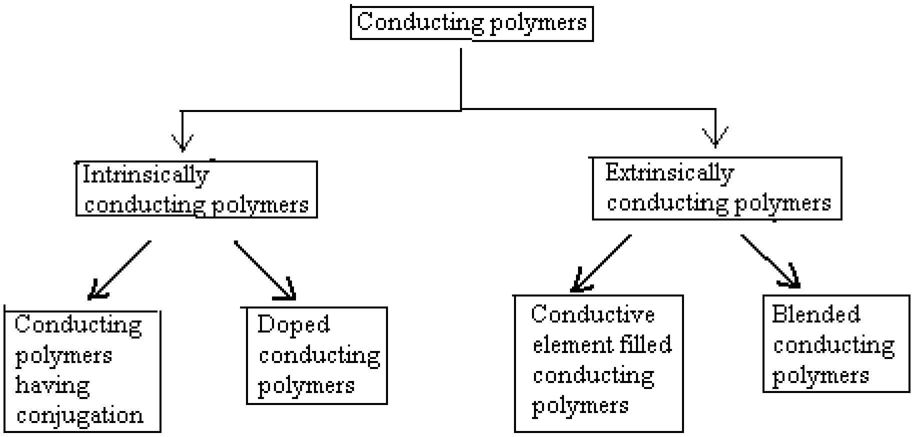
In traditional polymers such as polyethylenes, the covalent bonds are formed as a result of sp^3 hybridization. Such sigma bonds have low mobility and do not contribute to the electrical conductivity of the material. But, in conjugated polymers, the covalent bonds are formed as a result of sp^2 hybridization. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. All the p_z orbitals combine with each other to a set of delocalized orbitals. Hence the electrons are delocalized over the entire molecule rather than residing at one particular carbon atom. The electrons in these delocalized orbitals have high mobility when the polymer is doped by oxidizing or reducing agents, which donate or removes some of the delocalized electrons respectively.

In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction silicon atoms are replaced by electron-rich, *e.g.*, phosphorus, or electron-poor, *e.g.*, boron, atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

Undoped conjugated polymers state are semiconductors or insulators. In such compounds, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyactetylene are delocalized along the chain, pristine polyacetylene is not a metal.

5.11.2 TYPES OF CONDUCTING POLYMERS



5.11.2.1 INTRINSICALLY CONDUCTING POLYMERS

5.11.2.1.1 CONJUGATED CONDUCTING POLYMERS

They are conducting polymers having alternate single and double bonds. Single bonds are the sigma (σ- bonds). Double bonds are made of one σ bond and one π-bond. Conjugated polymers have a sigma bond backbone formed by the overlap of sp^2 hybrid orbitals. The remaining orbital of the carbon atoms overlap sidewise with the neighbouring p_z-orbital to form π –bonds.

The electrons involved in π –bond formation are delocalized over the entire polymer chain which results in the formation of valence band and conduction band. When the energy gap between the two band is low, the electrons undergo excitation from the low energy valence band to the high energy conduction band and show increased conductivity.

5.11.2.1.2 DOPED CONDUCTING POLYMERS

Conjugation alone is not sufficient to make a polymer conducting. The conductivities of pristine polymers (pure conjugated polymers) can be increased from insulating type (10-10 – 105S/cm) to conducting type (0.1 – 105 S/cm) by a process called ‘Doping’.

Doping of conjugated polymers involves partial oxidation (removal of electrons from the π-bonds of the polymer backbone) and partial reduction (addition of electrons to the π-bonds of the polymer backbone).

Dopants are the chemical species or agents used to increase the conductivity of the polymers by the doping process. Dopants are introduced into the polymer by exposing the polymer film or powders to the vapour or solutions of the dopants or by electrochemical oxidation and reduction.

There are two types of dopants : p-type dopants and n-type dopants.

p-type dopants are oxidizing agents capable of removing electrons from the valence band to create a positive charge on the polymer backbone.

$[\text{Polymer}] + OA \rightarrow [\text{Polymer}]^{n+} + OA^{-}$

Where, OA = I_2, Cl_2, AsF_5, BF_6, $LiClO_4$, $FeCl_3$ etc.

n-type dopants are reducing agents which donates electrons to the conduction band and make the polymer negatively charged.

$[\text{Polymer}] + RA \rightarrow [\text{Polymer}]^{n-} + RA^{+}$

Where, RA = Na, K, Li etc.

Addition of small amount of dopants to the conjugated polymer produces a drastic change in the electrical, electronic, magnetic, optical and structural properties of the polymers. By adjusting the concentration of the dopants, conductivity of the polymer can be changed anywhere between the insulating type (undoped form) and that of the highly conducting type (fully doped form).

5.11.2.2 EXTRINSICALLY CONDUCTING POLYMERS

5.11.2.2.1 CONDUCTIVE ELEMENT FILLED POLYMERS

These polymers are obtained by blending an insulating type of polymer with suitable conducting elements such as carbon black, metallic fibers, metallic oxides etc to make the polymer conducting. The minimum amount of the conducting element required for an insulating polymer to make it conducting is called percolation threshold.

5.11.2.2.2 BLENDED CONDUCTING POLYMERS

It is obtained by blending a conventional polymer with a suitable conducting polymer. Polymers obtained by this method possess better physical, chemical, electrical and mechanical properties which can also be easily processed.

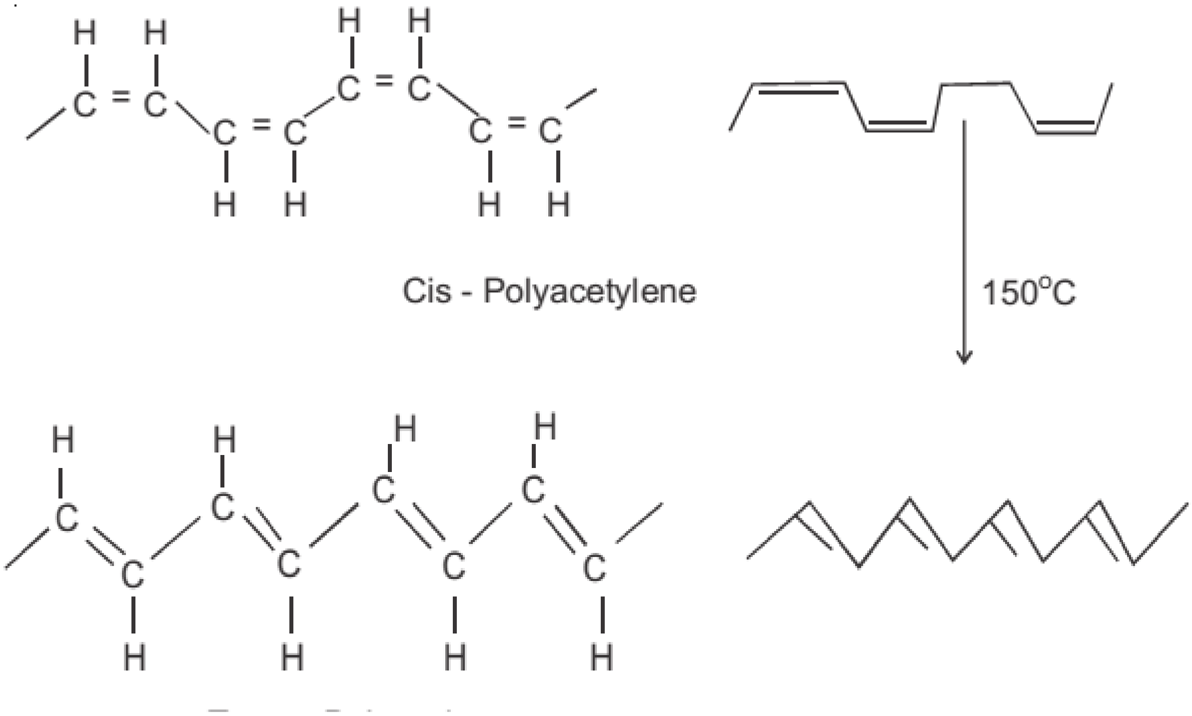
5.11.3 POLYACETYLENE

It is the first conducting polymer to be synthesized. Poly(acetylene) is the simplest conjugated polymer. In its linear form it precipitates as a black, air sensitive, infusible and intractable powder out of solution and cannot be processed.

In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. For this research, they were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conducting polymers. Polyacetylene itself did not find practical applications, but drew the attention of scientists and encouraged the rapid growth of the field.

Polyacetylenes exists in isomeric forms: cis-polyacetylene and trans-polyacetylene.

In cis-configuration, the hydrogen atoms are bound on the same side of the carbon-carbon doube bonds.



Trans-polyacetylene

In trans-configuration. the hydrogen atoms are bound on the alternative sides of the carbon-carbon double bonds.

Synthesis

The scientist, Shirakawa, prepared poly(acetylene) by passing acetylene gas over the Zeigler-Natta catalyst. Zeigler-Natta catalyst is the coordination complex of tetra butoxy titanium, [Ti(OBu)$_4$], an organo metallic compound and triethyl aluminium, [Et$_3$Al].

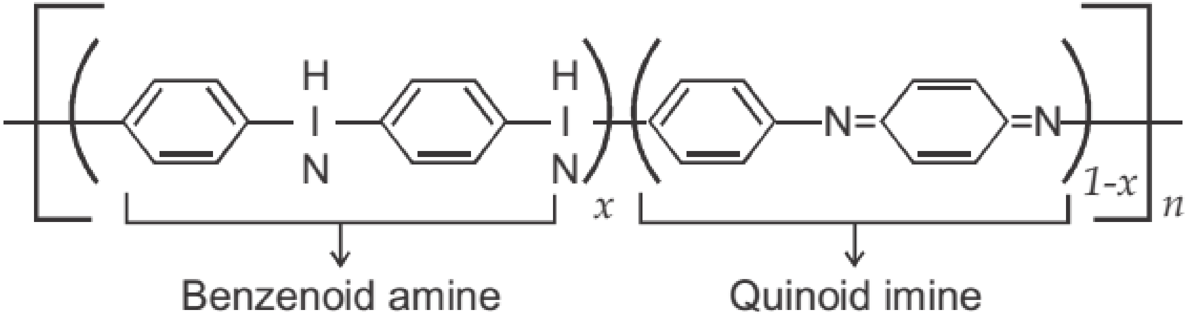
$$nHC{=}CH \xrightarrow{Ti(OC_4H_9)_4/Al(C_2H_5)_3} -[-CH{=}CH-]_n-$$

The reaction forms copper coloured cis-poly(acetylene), having conductivity in the range 10^{-8}-10^{-7} S/cm, at low temperature (-78^{0}C). At higher temperatures (150^{0}C), more stable silver coloured trans-poly(acetylene), having conductivity in the range 10^{-3}-10^{-2} S/cm is formed. Cis-poly(acetylene) can be converted to trans-poly(acetylene) by heating it at 150^{0}C for few minutes.

5.11.4 POLYANILINE

Polyaniline was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that reduced form was colourless but the oxidized forms were deep blue.

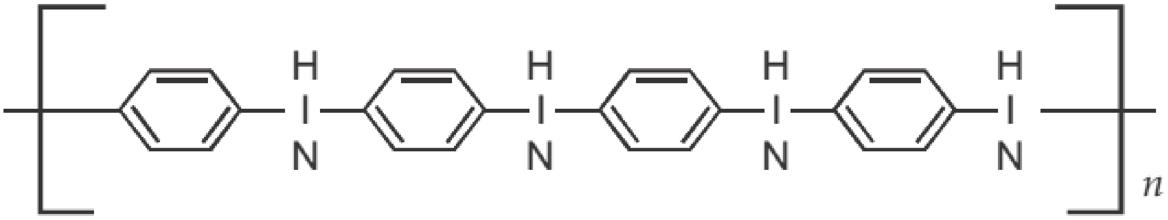
Polyaniline consists of alternate benzenoid amine (reduced form) and quinoid imine (oxidized form) structure.



5.11.4.1 OXIDATION STATES OF POLYANILINE

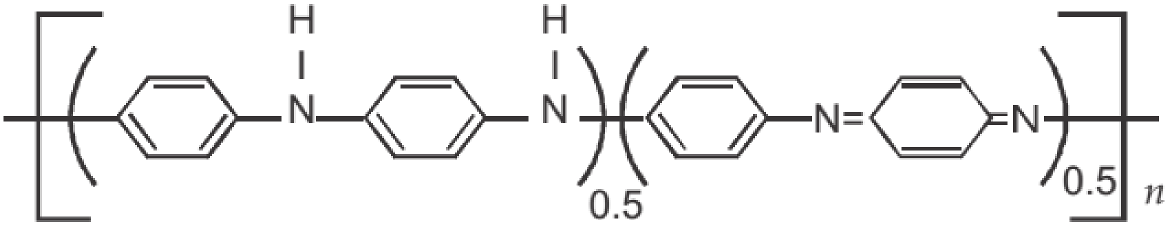
From the generalized formula of polyaniline, it is possible to have three different oxidation states.

1. When x=1, completely reduced form the polymer consisting of only benzenoid amine structure is obtained. This type of polyaniline is called "Leucoemeraldine". This form undergoes easy oxidation when exposed to air. Therefore it is less stable.



Leucoemeraldine

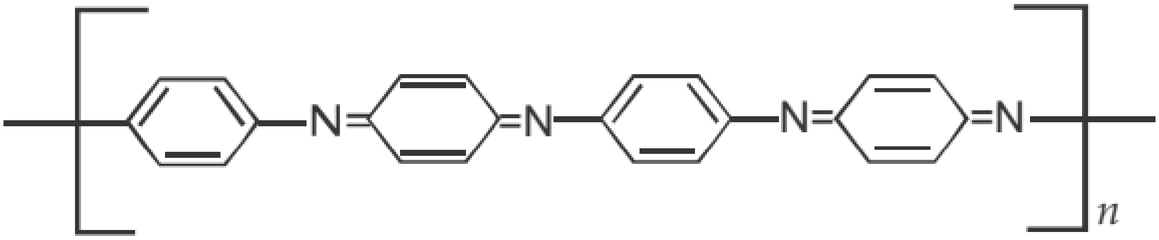
2. When x= 0.5, the polymer consisting of partially oxidized quinoid imine structure and partially reduced benzenoid amine structure called "emeraldine" is obtained.



Emeraldine

The emeraldine base form is the most stable form.

3. When x=0, completely oxidized state of polymer consisting of quinoid imine structure called “pernigraniline” is obtained. This form undergoes degradation easily.



Pernigraniline

5.11.4.2 PROTONIC ACID DOPING

It involves the treatment of emeraldine base form of polyaniline with protonic acid (1M HCl) to give a fully protonated emeraldine hydrochloride salt having conductivity in the order of magnitude 9-10.

5.11.5 FACTORS INFLUENCING THE CONDUCTIVITY OF POLYMERS

The conductivity of organic polymers is influenced by the following factors:

1) Conjugation length: The conductivity of a polymer increases with the increase in the length of the polymer chain and increase in the number of conjugation

2) Doping level: The conductivity of a polymer increases with the increase in doping level till the saturation point is reached

3) Temperature: Conductivity of a polymer increases with increase in temperature. Sometimes, it the conductivity becomes constant at a particular temperature

4) Frequency of current: Conductivity of a polymer depends on the frequency of current as dopping is the transport mechanism in these materials

5.11.6 APPLICATIONS OF CONDUCTING POLYMERS

Due to their poor processability, conductive polymers have few large-scale applications.

- They have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process.
- Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide.
- It is used for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes their electroactivity. The extended π-systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state. The two groups of applications are shown below:

Group 1

Electrostatic materials
Conducting adhesives
Electromagnetic shielding
Printed circuit boards
Artificial nerves
Antistatic clothing
Piezoceramics
Active electronics (diodes, transistors)
Aircraft structures

Group 2

Molecular electronics
Electrical displays
Chemical, biochemical and thermal sensors
Rechargeable batteries and solid electrolytes
Drug release systems
Optical computers
Ion exchange membranes
Electromechanical actuators
'Smart' structures
Switches

Group I applications uses the polymer's conductivity. The polymers are used because of either their light weight, biological compatibility for ease of manufacturing or cost.

Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability.

With the availability of stable and reproducible dispersions, PEDOT (poly(3,4-ethylenedioxythiophene)) and polyaniline have gained some large scale applications. While PEDOT is mainly used in antistatic applications and as a transparent conductive layer in the form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

5.11.7 BARRIERS TO APPLICATIONS

Most conductive polymers require oxidative doping in which the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Also, the charged organic backbone is often unstable towards atmospheric moisture. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis.

Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion.

Questions

Part A

1) Define polymer and monomer.
2) What is a heterochain polymer? Give an example.
3) Define degree of polymerization.
4) What is functionality of a monomer?
5) What is tacticity? Give one example of stereo regular polymer.
6) Differentiate addition and condensation polymerization.
7) What is copolymerization? How are copolymers superior to other types of polymers?
8) What is a dead polymer?
9) Define Tacticity.
10) Write short note on atactic polymers.
11) Define syndiotactic polymer.
12) What is meant by isotactic polymer?
13) Mention any two significance of functionality.
14) Write any two thermal initiators used in free radical polymerization.
15) Mention the monomers which are polymerized in anionic polymerisation.
16) What are homochain and heterochain polymer?
17) Give the formula for M_n Number average molecular weight.
18) Give the formula for M_W Number average molecular weight.
19) Write notes on poly dispersity index (PDI).
20) Why the polymers have only average molecular weights?

21) What is the value of PDI for small molecules?

22) What is a plastic? How it is different from resins?
23) Compare and contrast thermoplastics and thermosetting plastics.
24) What is compounding of plastics?
25) What plastic properties are enhanced by using moulding constituents?
26) What are plasticizers? Give examples.
27) Give the role of stabilizers and antioxidants in compounding of plastics.
28) What are a filler? Give its significance in plastic moulding.
29) Give two examples of lubricants used in compounding of plastics.
30) What is moulding of plastics? What are the types?
31) What type of plastics is moulded by compression moulding method?
32) List out the advantages of compression moulding method.
33) What are the limitations of compression moulding methods?
34) Give the disadvantages of compression moulding method.
35) Write the principle of injection moulding method.
36) Give the advantages of injection moulding method over other moulding methods.
37) Give two advantages and disadvantages of extrusion moulding method.
38) What is the principle behind extrusion moulding method
39) Give two applications of extrusion moulding method.
40) Compare compression and injection moulding methods.
41) Define conducting polymers. Give examples.
42) Give the types of conducting polymers.
43) What are blended conducting polymers?
44) What is Zeiglar-Natta catalyst?
45) What are the three different oxidation states of polyaniline?
46) Give the applications of conducting polymers.
47) What are synthetic metals?
48) What is doping of conducting polymers?
49) Write the structures of cis and trans-polyacetylene.
50) What are engineering plastics?
51) Why thermosetting plastics cannot be remolded?
52) What is glass transition temperature.
53) Mention any 2 factors affecting the conductivity of polymers.
54) Write notes on application of conducting polymers.

Part B

1. Write in brief on classification of polymers
2. Write notes on types of polymers.
3. Give an brief account on tacticity of polymers.
4. Explain addition and condensation polymerization reactions with one example each.
5. List out the differences between addition and condensation polymerization.
6. Explain the mechanism of addition polymerization
7. Discus cationic polymerisation mechanism
8. Discuss free radical polymerization mechanism
9. Compare anionic and cationic polymerization mechanism.
10. Distinguish between thermoplastics and thermosetting plastics.
11. Comment on molecular weight of polymers.
12. What is compounding of plastics. What are the ingredients used and give their significance?

13. Explain compression and injection moulding methods.
14. Explain with a neat diagram the compression moulding method and compare it with the injection moulding method.
15. Explain extrusion moulding method with a neat diagram.
16. Write in detail on morphology of polymers
17. Write notes on types of conducting polymers.
18. What are conducting polymers? Give the types and explain.
19. Explain polyacetylene as a conducting polymer.
20. Describe in detail the different oxidation states of polyaniline.
21. Explain in detail the molecular basis of electrical conductivity in conducting polymers.

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