



Department of Chemistry
National Institute of Technology Srinagar

Study Material for B. Tech. 1st. Semester
Engineering Chemistry
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(Common to all Branches)

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Unit-I: HIGH POLYMERS

POLYMERS

Polymers are high molecular weight organic compounds in which a large number of simple units repeat themselves in a regular fashion. The simple units are called as monomers. For any compound to be recognized as a true monomer, it should possess at least two functionalities (Not two functional groups necessarily---- as in some compounds, one functional group gives rise to only one functionality while in some compounds, one functional group gives rise to two functionalities), e.g.,

CH_3OH has **one functional group** and **one functionality** (Not a true monomer)

$\text{CH}_2=\text{CH}_2$ has **one functional group** and **two functionalities** (A true monomer)

$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ has **two functional groups** and **two functionalities** (A true monomer)

Therefore, it is clear that what is actually required for polymerization, is presence of at least two functionalities and not two functional groups, in the monomer.

Classification of Polymers

Polymers have been classified on different basis as follows:

(A). Classification on the basis of Origin/Source

On this basis, polymers have been broadly classified into **two types**:

1. Natural Polymers

They occur naturally and are found in plants and animals.

Examples: Proteins, Nucleic acids, Starch, Cellulose and Natural rubber.

2. Synthetic Polymers

These are man-made polymers. Plastic is the most common and widely used synthetic polymer.

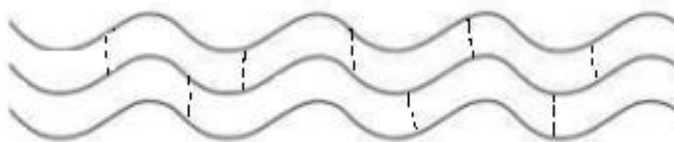
e.g., Nylons, Polythene, PVC, Synthetic rubbers, etc.

(B). Classification on the basis of Structure

On this basis, polymers have been broadly classified into **three types**:

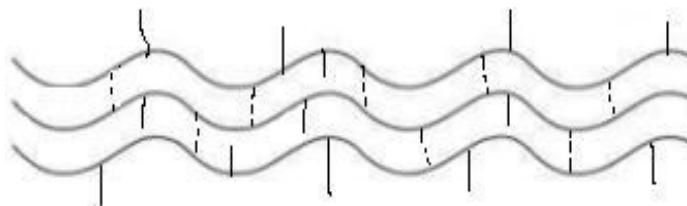
1. Linear Polymers

Polymers comprising of long and straight chains are called as linear or straight chain polymers. e.g., High density polyethene (HDPE)



2. Branched-chain Polymers

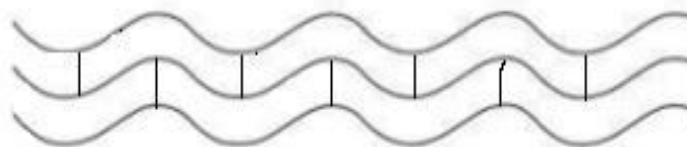
Polymers comprising of linear chains with branches are called as branched chain polymers. e.g., Low-density polyethene (LDPE).



3. Cross-linked Polymers

Polymers in which various individual chains are connected together by covalent bonds (cross links) are called as cross linked polymers. These polymers are formed from bi-functional and tri-functional monomers and the additional functionality produces the cross links.

e.g., Bakelite and Melamine.



(C). Classification on the basis of nature of Monomers

On this basis, polymers have been broadly classified into **two types**:

1. Homo-polymers

Polymers which are comprising of only one type of monomers are called as homo-polymers. e.g., Polyethene, PVC, Nylon-6, etc. This can be represented as:



2. Co-polymers

Polymers which are comprising of more than one (generally two) types of monomers are called as homo-polymers. e.g., Nylon-6'6, Terylene, SBR, etc.

Co-polymers have further been classified into four types on the basis of relative arrangement of the monomer units with respect to each other. These are:

- i). **Alternate Co-polymers:** Polymers comprising of alternating A and B units. The order is regularly followed throughout the chain. This can be represented as:

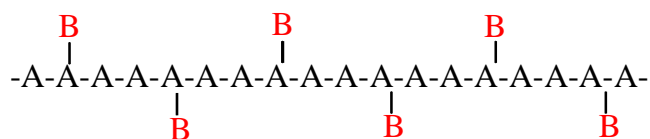


- ii). **Block Co-polymers:** Polymers comprising of regular alternating blocks of A and B units. The order is regularly followed throughout the chain. This can be represented as:



- iii). **Graft Co-polymers:** Polymers in which the main chain is comprising of one type of monomers and the other monomer forms the branches. Therefore, for being a graft co-polymer, the polymer must be branched.

This can be represented as:



- iv). **Random Co-polymers:** Polymers in which no regular order of arrangement is followed by the monomer units. This can be represented as:



The most common type of co-polymers are alternate co-polymers.

(D). Classification on the basis of Inter-molecular Forces

On this basis, polymers have been broadly classified into **four types**:

1. Elastomers

Polymers in which intermolecular (inter-chain) forces are very weak (van der Waals forces) are called as elastomers. These are rubber-like solids weak interaction forces are present. e.g., Rubber.

2. Fibres

Polymers in which intermolecular (inter-chain) forces are very strong (Hydrogen bond or dipole-dipole interaction) are called as Fibres. These are strong, tough, with high tensile strength. e.g., Nylons, Terrylene, etc.

3. Thermo-plastics

Polymers in which intermolecular (inter-chain) forces are intermediate are called as thermo-plastics. These polymers on heating become soft and on cooling again become hard and retain their original shape. In this case, the intermolecular forces, on heating, get weaken and the polymer becomes soft and vice-versa. It is purely a physical change and physical changes are generally reversible. Therefore, these polymers are recyclable, i.e., they can be moulded and re-moulded again and again. e.g., Polyethene, Polyvinyl chloride, Polystyrene, etc.

4. Thermo-settings

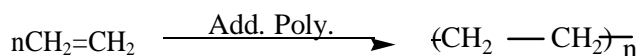
Polymers in which there is extensive cross linking, are called as thermo-settings. These polymers on heating become soft and on cooling again become hard but do not retain their original shape. In this case, the cross links get broken and rearranged on heating. It is purely a chemical change and chemical changes are generally irreversible. Therefore, these polymers are not recyclable, i.e., once moulded, they cannot be moulded again. These polymers greatly improve the material's mechanical properties. e.g., Bakelite, Epoxy resins, etc.

(E). Classification Based on Synthesis

On this basis, polymers have been broadly classified into **two types**:

1. Addition Polymers

Polymers which are formed by addition reaction are called as addition polymers. e.g., Poly ethane, Teflon, Polyvinyl chloride, etc. For addition polymerization to take place, the monomer must be unsaturated. Taking the example of polyethene, the addition polymerization reaction can be shown as:

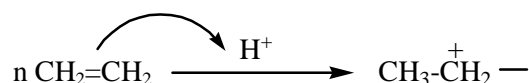


Addition polymerization is a chain reaction, which once initiated, propagates itself till the chain is not terminated. It involves three steps: Chain initiation, Chain propagation and Chain termination. Addition polymerization can take place via three different types of mechanisms:

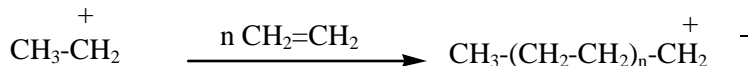
I). Cationic Mechanism II). Anionic Mechanism III). Free Radical Mechanism

I). Cationic Mechanism: In this mechanism, the reaction is initiated by an electrophile resulting in the formation of a carbocation as intermediate, thus known as cationic mechanism. The reaction can be terminated by a nucleophile. We can summarize that in this reaction, Initiator is Electrophile, Intermediate is Carbocation, Inhibitor (Terminator) is Nucleophile. The mechanism can be shown as:

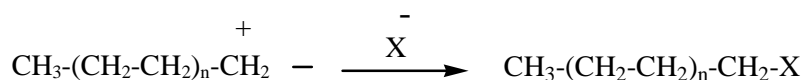
a) Chain Initiation step



b) Chain Propagation step

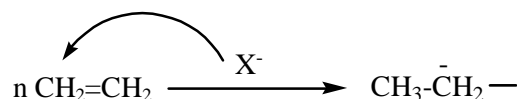


c) Chain Termination step

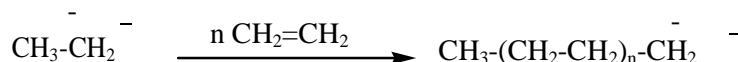


II). Anionic Mechanism: In this mechanism, the reaction is initiated by a nucleophile resulting in the formation of a carbanion as intermediate, thus known as anionic mechanism. The reaction can be terminated by an electrophile. We can summarize that in this reaction, Initiator is Nucleophile, Intermediate is Carbanion, Inhibitor (Terminator) is Electrophile. The mechanism can be shown as:

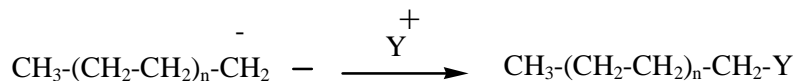
a) Chain Initiation step



b) Chain Propagation step

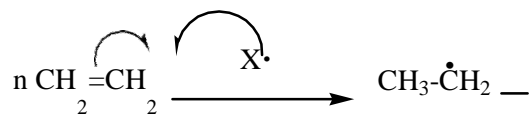


c) Chain Termination step

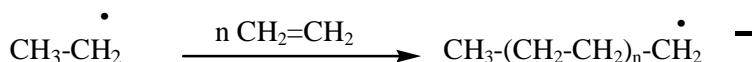


III. Free Radical Mechanism: In this mechanism, the reaction is initiated by a free radical resulting in the formation of a free radical as intermediate, thus known as free radical mechanism. The reaction can be terminated by a free radical. We can summarize that in this reaction, Initiator is Free radical, Intermediate is Free radical, Inhibitor (Terminator) is Free radical. The mechanism can be shown as:

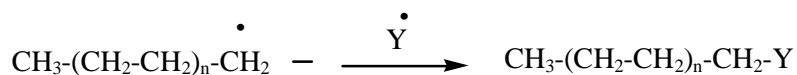
a) Chain Initiation step



b) Chain Propagation step

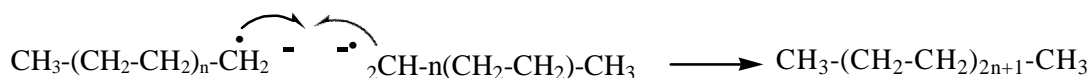


c) Chain Termination step

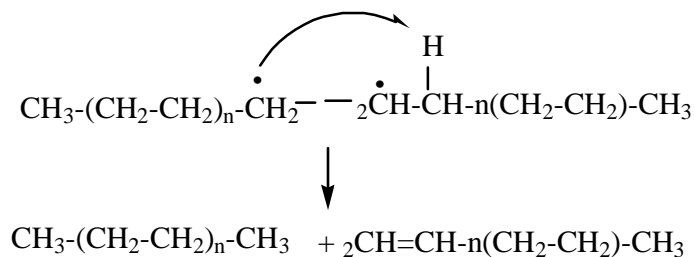


In case of free radical mechanism, in addition to the normal chain termination by introducing a free radical, there are also other ways wherein the chains can terminate themselves. These are:

i). By Coupling: There is possibility that two propagating chains can collide with each other and couple. In this way, both the chains are terminated and the polymer chain obtained has molecular weight more than expected.



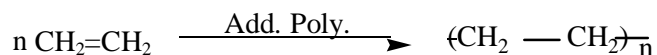
ii). By Dis-proportionation: There is possibility that a hydrogen radical from one propagating chain can be abstracted by another, thereby terminating both the chains, however, unsaturation is created in the chain from which H-radical is being abstracted.



Some Commercially Important Addition Polymers

Polyethene

Polyethene is a homo-polymer and its monomer unit is ethene (ethylene). It is the most common and with simplest structure among all plastics. The reaction for preparation of polyethene can be shown as:



Polyethene is broadly of two types:

- i). Low Density Polyethene (LDPE) ii). High Density Polyethene (HDPE)

i). Low Density Polyethene (LDPE): As the name itself indicates, it is a polymer of very low density. It is prepared via free radical mechanism at a temperature of 80 to 350 °C under high pressure (1000 to 3000 atm) in presence of a oxygen or a peroxide (Benzoyl peroxide) as initiator, wherein extensive branch formation takes place and the density of the resultant polymer is very low in the range of 0.910 to 0.940 g/cm³.

Properties:

- It is a waxy translucent material, exhibits high impact strength, low brittleness temperature, film transparency and outstanding electrical insulating properties.
- It is chemically inert and has good resistance to acids and alkalis. However, it swells in and is permeable to oils.
- It melts in temperature range of 107-120°C. Its T_g (Glass Transition) value is -120°C.
- It is flexible over a wide temperature range.

Applications: It is used in making packaging materials for food, garments, etc. It is used in production of squeeze bottles, coatings, wrappings, etc. It is also used in cable and wire insulations.

i). High Density Polyethene (HDPE): It is a linear polymer with little or no branching. It is prepared via ionic mechanisms at a low temperature of 60 to 70 °C and very low pressure (6 to 7 atm), wherein little or no branch formation takes place and the density of the resultant polymer is high in the range of 0.945 to 0.965 g/cm³. However, HDPE is also prepared by coordination polymerization using Ziegler-Natta catalyst (Triethyl aluminium and Titanium tetrachloride).

Properties:

- It is opaque and has less impact strength, but, better barrier properties than LDPE.
- It has better chemical resistance than LDPE.
- It melts in temperature range of 130-138°C. Its T_g (Glass Transition) value is -20°C.
- It exhibits better stiffness, toughness, good tensile strength and heat resistance.

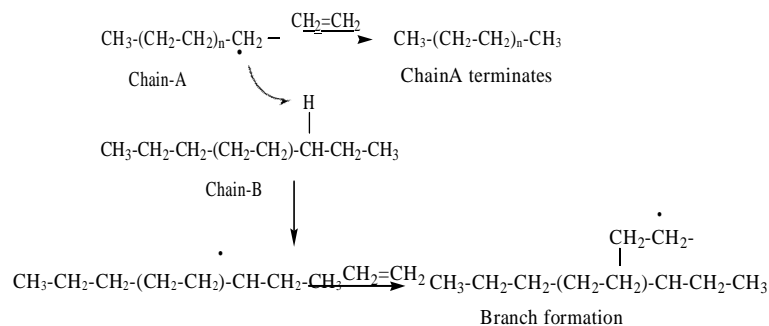
Applications: It is used in manufacture of dust bins, cans, buckets, fuel tanks, etc. It is used for making corrugated pipes. It is also used in cable and wire insulations.

Information

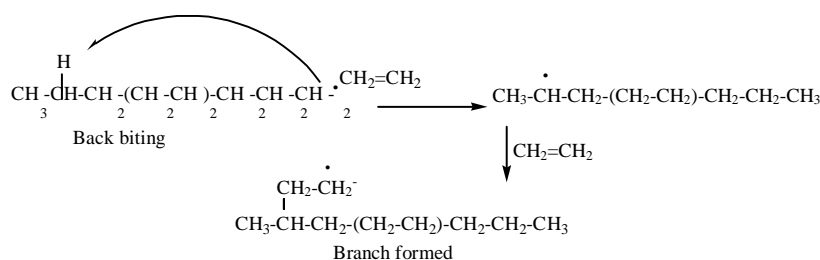
Why Free Radical Mechanism results in Extensive Branching ?

In free radical mechanism, during propagation step, there is high possibility of some side reactions, resulting in the formation of highly branched polymer chains as:

- **By H-Radical Abstraction from Another Chain:** The propagating chain (A), instead of reacting with one more monomer unit, attacks some already terminated chain (B) and abstracts H-radical from it at any carbon except the terminal carbon (in order to generate a 2° free radical). Due to this, chain (A) gets itself terminated, however, generating a free radical in chain (B) at the carbon where from H-radical has been abstracted. With the result, the monomer which was supposed to add to chain (A), attacks the chain (B) and forms a branch. This process may take place repeatedly.



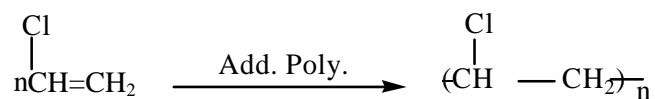
- **By Self Back-Biting:** The propagating chain (A), sometimes attacks itself and abstracts H-radical from its own back end carbon (but not from the terminal carbon in order to generate a 2° free radical), generating a free radical there. With the result, the monomer adds to this newly generated free radical and forms a branch.



Such types of interactions generally do not take place in case of ionic mechanism (Cationic & Anionic), because, it is very difficult (but not impossible) for a carbocation (in case of cationic mechanism) to abstract a hydride ion and for a carbanion (in case of anionic mechanism) to abstract a proton from a neighbouring chain or itself. However, a little branching cannot be ruled out. Therefore, a hundred percent branch free polymer cannot be obtained by either of the three mechanisms, but, can be obtained by *coordination polymerization. * Discussed ahead

Polvinylchloride (PVC)

Polyvinylchloride is a homo-polymer and its monomer unit is vinyl chloride (Chloroethene). It is a thermoplastic polymer. The reaction for preparation of Polyvinylchloride can be shown as:



Polyvinylchloride is of two types:

- i). Un-plasticized PVC ii). Plasticized PVC

Un-plasticized PVC is also known as Rigid PVC (PVC-R or PVC-U). It is strong, rigid, inherently flame retardant and with relatively good chemical resistance.

Plasticized PVC (PVC-P) is that PVC in which some chemical agents, called as plasticizers, have been incorporated to make the polymer more flexible.

Information

Plasticizers are the materials added to polymers to decrease rigidity and increase flexibility. Generally, the plasticizers used for polymers are esters. Most commonly used plasticizers are; Dioctylphthalate, Tricresylphosphate, Vegetable oils, etc. The possible mechanism of action of plasticizers is that these plasticizer particles embed themselves between the polymer chains spacing them apart (increasing the free volume) and significantly lowering the glass transition temperature of the polymers and making them much softer.

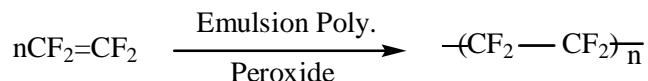
Properties:

- It is a colourless, odourless, non-flammable material.
- It is a chemically inert and is highly resistant to acids and alkalis. However, plasticized PVC is relatively less resistant to chemicals.
- It is resistant to atmospheric oxygen, i.e., resistant to oxidation.
- It possesses greater stiffness and rigidity compared to polyethene.
- Due to its versatile properties, such as lightweight, durability and easy processability, PVC is now replacing traditional building materials like wood, metal, concrete, etc.

Applications: PVC is used for making building and construction materials, pipes, flooring, vinyl siding. Plasticized PVC is used mainly in wire and cable insulations and in packaging materials. Flexible films and sheets are used as pool liners and roof coatings, carpet backing, rain coats, etc.

Polytetrafluoroethylene (PTFE)

Polytetrafluoroethylene is commercially known as Teflon. It is a homo-polymer and its monomer unit is tetrafluoroethylene. It is a thermoplastic polymer. It is usually prepared emulsion polymerization of tetrafluoroethylene using peroxide or ammonium persulphate as initiators. The reaction for preparation of Teflon can be shown:



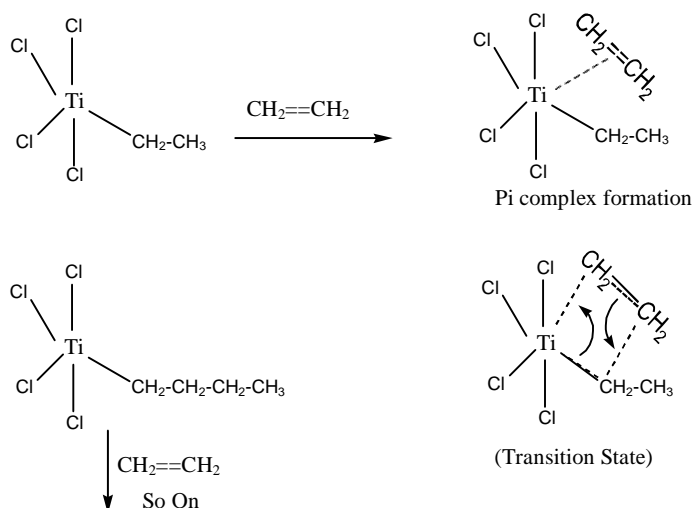
Properties:

- It is a highly crystalline polymer (93-98% crystallinity).
- It has high chemical resistance.
- It is practically insoluble in all solvents and is not wetted by either water or oil.
- It has low coefficient of friction and remains slippery over a wide range of temperature (-40-300°C).
- It is resistant to temperature with high temperature stability.
- It has excellent electrical insulating properties.

Applications: Teflon is used as a non-sticky coating on frying pans, iron. It is used on weapons as an anticorrosive coat. It is used as a coating on pipes and tanks for carrying and storing corrosive chemicals, respectively. It is also used as dry lubricant on burette stoppers.

***Coordination Polymerization**

Coordination polymerization is carried out in presence of Ziegler-Natta catalysts. The most commonly used Ziegler-Natta catalyst is a combination of triethyl aluminium and titanium tetrachloride. The mechanism can be explained by taking the example of polyethene. The ethene monomer first approaches towards the catalyst surface (Ti) and forms a π -complex. Then, it partially uses its π -es and also interacts with the alkyl group, yielding a transition state. Ultimately Ti-alkyl bond breaks resulting in the formation of Ti-monomer and alkyl-monomer bonds, i.e., the monomer induces itself in between Ti and the alkyl group. The mechanism can be shown as:



Significance of Coordination Polymerization:

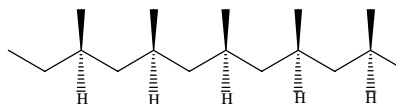
1. It is used for preparation of branch free polymer. Since, the chain stands already terminated, as the monomer units are added in between the catalyst surface and the alkyl group already present, there is no possibility of branch formation and the polymer formed will be 100% branch free.
2. It is used for preparation of highly **stereo-regular polymer*****.

Information

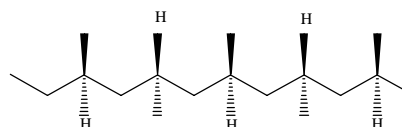
***Tacticity/Orientation/Stereochemistry of Polymers

On the basis of stereochemistry, polymers are classified into three types:

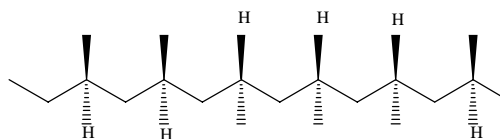
Isotactic Polymers: In which the pendant groups are present on the same side of the polymer chain.



Syndiotactic Polymers: In which the pendant groups are present alternately on opposite sides of the polymer chain.



Atactic Polymers: In which there is no regularity in orientation of pendant groups.



Among the three, first two are called as stereo-regular polymers, however, Isotactic polymers are regarded as Highly Stereo-regular Polymers.

1. Condensation Polymers

Polymers which are formed by condensation reaction are called as condensation polymers. e.g., Nylon-6'6, Nylon-6, Terylene, Bakelite, etc. This type of polymerization is called as condensation polymerization. Condensation polymers are mainly of three types:

I. Polyamides

II. Polyesters

III. Resins

I. Polyamides

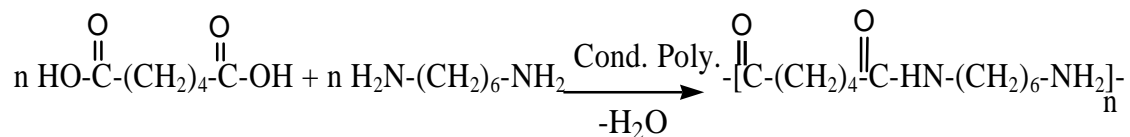
Polymers in which monomer units are linked together by amide bonds. For polyamide formation, the monomers should be polcarboxylic acids and polyamines. Generally, dicarboxylic acids and diamines are used. Polyamides belong to the fibres as per the classification on the basis of intermolecular forces.

Some Commercially Important Polyamides

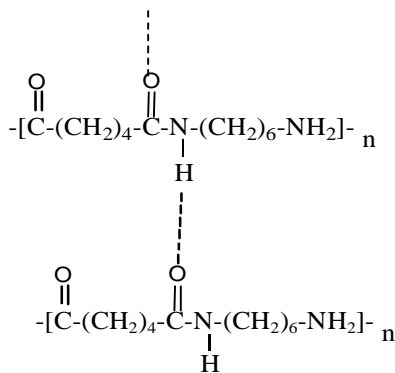
There are many synthetic polyamides known as nylons like, Nylon-6,6, Nylon-6, Nylon-6,10, Nylon-11, etc. However, so far as our syllabus at B. Tech. 1st. year level is concerned, we have to discuss only two among them, i.e., Nylon-6'6 and Nylon-6.

Nylon-6'6

Nylon-6'6 is a co-polymer and its monomer units are adipic acid (Hexan-1,6-dioic acid) and heamethylene diamine (Hexan-1,6-diamine). Both these monomers can in turn be obtained from Buta-1,3-diene. The reaction for preparation of Nylon-6'6 can be shown as:



Innylon-6'6, various polymer chains are connected together by strong intermolecular forces, i.e., hydrogen bonding as;



provide insulation and resistance to abrasion. Nylon-6 is mainly used for making cords for tyres. Nylon-6'6 fibres are used for making fabric for clothing, socks, sportswear, carpets, etc.

II. Polyesters

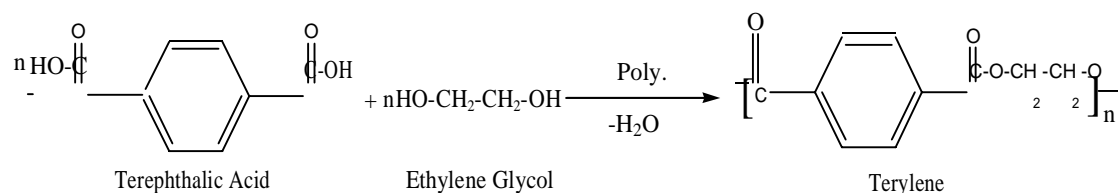
Polymers in which monomer units are linked together by ester bonds. For polyester formation, the monomers should be polycarboxylic acids and polyols. Generally, dicarboxylic acids and diols are used. Polyesters belong to the fibres as per the classification on the basis of intermolecular forces.

Some Commercially Important Polyesters

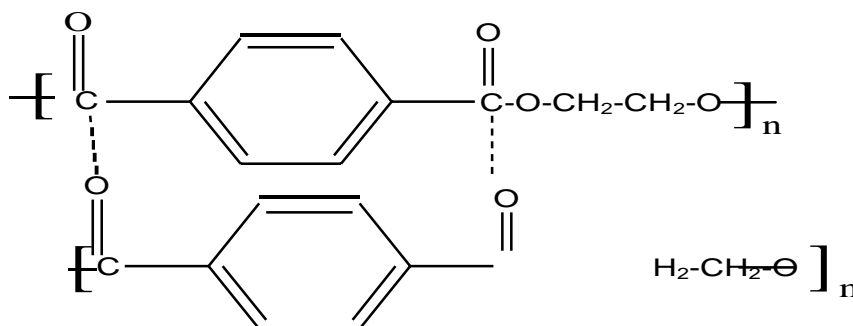
There are many synthetic polyesters like, Polyethylene Terephthalate (Terylene), Polyethylene Phthalate (Glyptal), Polybutylene Terephthalate, Polytrimethylene Terephthalate, etc. However, so far as our syllabus at B. Tech. 1st. year level is concerned, we have to discuss only one among them, i.e., Polyethylene Terphthalate (Terylene).

Polyethylene Terephthalate (PET)

Polyethyleneterphthalate is a copolymer and its monomer units are terephthalic acid (Benzene-1,4-dicarboxylic acid) and ethylene glycol (Ethane-1,2-diol). It is commercially known as Terylene. The reaction for preparation of Terylene can be shown as:



In Terylene various polymer chains are connected together by strong intermolecular forces, i.e., dipole-dipole interactions, next stronger to hydrogen bonding, as;



Properties of Terylene:

- Terylene has high mechanical strength and dimension stability.
- It is a very strong fibre and will suffer very little loss in strength when wet.
- It is elastic in nature and possesses the property of high crease resistance.
- It is stable in the temperature range of -40 - 100°C.
- It shows creep and abrasion resistance and good insulating properties.
- It shows low water absorption and at room temperature, it is resistant to water, dilute acids, salts, aliphatic and aromatic hydrocarbons and alcohols.

Applications of Terylene: It is used for making video and audio tapes. It is used in textile industry for making hard wear clothes and other dress material. It is used for making clear bottles for food and beverages. The fibre may be blended with cotton and wool to form another fabrics like terycot and terywool, respectively.

III. Resins

Resins are basic binding materials which are present as essential ingredients in polymers. However, resins can be moulded as such into polymers themselves. They belong to the class of thermo-setting as per the classification on the basis of intermolecular forces.

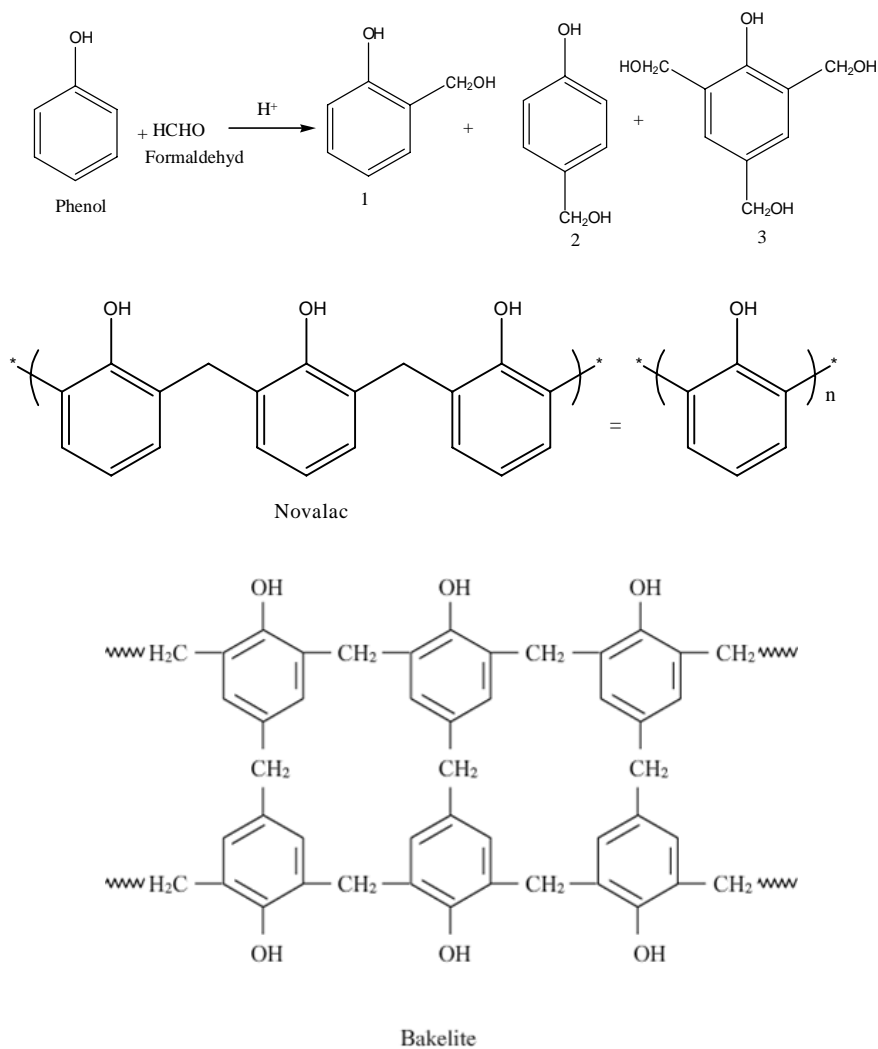
Some Commercially Important Resins

There are many resins known as Phenol-formaldehyde resin (Bakelite), Melamine-formaldehyde resin (Melmac), Urea-formaldehyde resin, etc. However, so far as our syllabus at B. Tech. 1st. year level is concerned, we have to discuss only one among them, i.e., Phenol-formaldehyde resin (Bakelite)

Phenol-formaldehyde resin

Phenol-formaldehyde resin, commercially known as bakelite, is a co-polymer and its monomer units are Phenol and Formaldehyde (Methanal). However, the first step involved during the polymerization process is electrophilic aromatic substitution reaction between phenol and formaldehyde in presence of a mineral acid like HCl to yield 2-Hydroxymethylphenol (1) and 4-Hydroxymethylphenol (2) in addition to 2,4,6-Trihydroxymethylphenol (3), which are the real monomers. Now, if only one type of monomers, for example (1) react together in a head to tail manner, a linear (straight chain) polymer is obtained which is called as Novalac. But, if cross polymerization takes place with

some concentration of the polysubstituted phenol, a highly cross-linked polymer, called as bakelite, is formed. The reaction for preparation of bakelite can be shown as:



Properties of Terylene:

- Bakelite is a rigid, hard and scratch resistance material.
- It displays good electrical insulation property.
- It has thermal stability up to of 200°C.
- It is resistant to water and shows low flammability.

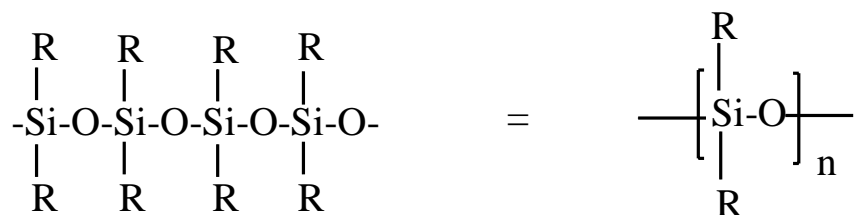
Applications of Terylene:

It is used for making electrical equipment parts such as switches, plugs, switch boards, cooker handles, electric iron parts, telephone parts, combs, etc. Due to its hardness, it is used

for making golf balls and heads for type writers. It is also used as hot setting adhesive for plywood, etc.

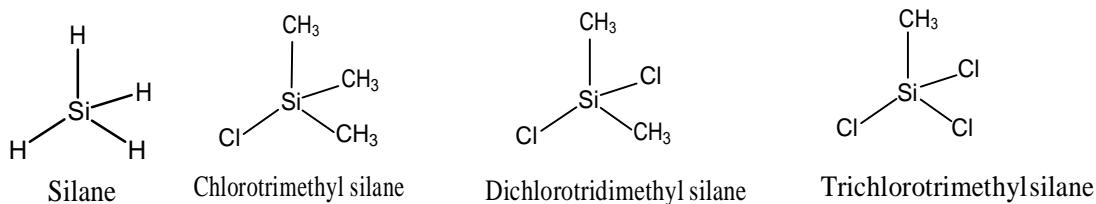
SILICONES (Organo-Silicon Polymers)

Silicones are comprising of alternate silicon oxygen structure, in which alkyl or aryl groups (mostly alkyl groups) are directly attached to silicon atoms. They are also called as polydialkylsiloxanes. They can be represented as:

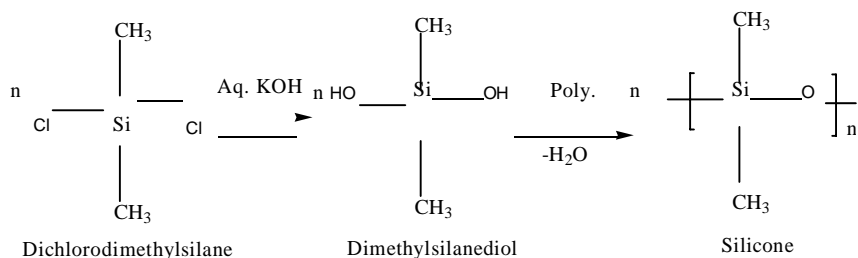


Synthesis:

Silicones can be prepared from chloroalkylsilanes, which are derivatives of silanes (SiH_4), just like the chloro-derivatives of methane. There are three types of chloroalkylsilanes, viz; chlorotrimethylsilanes, dichlorodimethylsilanes and trichloromethylsilanes. Among these, the real monomers are dichlorodimethylsilanes and trichloromethylsilanes, as these possess two and three functionalities, respectively. Trichloromethylsilanes are generally added during the polymerization of dichlorodimethylsilanes in order to create cross linkages. Chlorotrimethylsilanes being monofunctional, are used for chain termination.



During the synthesis of silicones, dichlorodimethylsilanes are first subjected to alkaline hydrolysis, yielding dimethylsilanediols, which being geminal diols undergo dehydration and form the polymer chain (polydimethylsiloxane). The reaction can be shown as:



Information

Chloroalkylsilanes can be prepared from Grignard Reagents and silicon tetrachloride as:


Classification:

Silicones have been classified, on the basis of physical state, into four types:

1. Liquid Silicones (Silicone Oils)
2. Semi-solid Silicones (Silicone Greases)
3. Silicone Rubbers
4. Solid Silicones

1. Liquid Silicones (Silicone Oils)

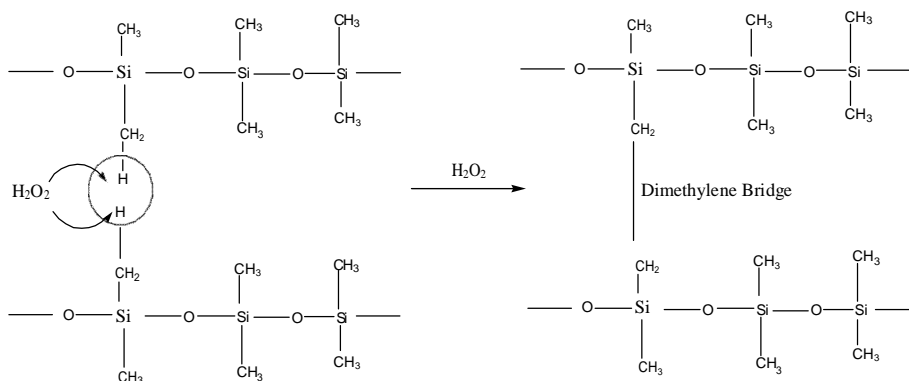
These are low molecular weight silicones obtained by polymerization of dichlorodimethylsilanes (Low molecular weight polydialkylsiloxanes).

2. Semi-solid Silicones (Silicone Greases)

These are low molecular weight silicones obtained by polymerization of dichlorodimethylsilanes (Low molecular weight polydialkylsiloxanes) with addition of some fillers which impart strength and increase the viscosity. The fillers used can be mica, carbon black, etc.

3. Silicone Rubbers

These are high molecular weight silicones obtained by polymerization of dichlorodimethylsilanes with addition of some fillers like mica, carbon black, etc. and hydrogen peroxide. The peroxide causes the formation of dimethylene bridges by eliminating hydrogen atoms from adjacent methyl groups in two polymer chains at various places which improve the strength and impart elastic character to the polymer.



4. Solid Silicones

These are high molecular weight silicones obtained by co-polymerization of dichlorodimethylsilanes with trichloromethyl silanes. The co-polymerization results in the formation of cross-linked polymers called as solid silicones. The extent of cross linkages and the strength of the solid silicones depends upon the concentration of trichloromethyl silanes added. Since solid silicones are cross-linked, they are thermosetting polymers.

Properties:

- Silicones are possess high thermal.
- They are highly resistant to oxidation, weathering and many chemicals .
- They are very flexible at temperature, except solid silicones.
- They are good electrical insulators.

Applications:

Silicone oils and silicone greases are used as high temperature lubricants and in polishes as these have high water repellent tendency. Silicon rubbers inert to chemicals and are biocompatible and hence, are used for making artificial heart valves, for plastic surgery, etc. Silicones are also used to manufacture laminates which can stand fairly high temperatures without undergoing degradation. Light weight foams are made from silicone resins by using foaming agents. Vulcanized silicon rubbers are used for making tyres and these rubbers remain flexible in the temperature range of -90 to + 150°C.

CONDUCTING POLYMERS

Conducting polymers are organic polymers that conduct electricity. Until 1970, all organic polymers were used in electrical, electronic and other applications as insulators, taking advantage of their excellent insulation properties.

Information

The idea that a polymer can conduct electricity as good as metals, was discovered accidentally by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid at the plastic research laboratory of BASF, Germany in 1974. The first polymer they synthesized, with significant conductivity, was polyacetylene, prepared as a silvery film from acetylene, using a Ziegler-Natta catalyst. Despite its metallic appearance, the first attempt did not yield a very conductive polymer. However, three years later in 1977, they discovered that oxidation with halogen vapor produces a much more conductive polyacetylene film. Its conductivity was significantly higher than any other previously known conductive polymer. This discovery started the development of many other conductive organic polymers.

Thus, organic polymers having electrical conductance of the order of conductors are now called as conducting polymers. Conducting polymers have been classified into two types:

1. Extrinsicly Conducting Polymers
2. Intrinsically Conducting Polymers

However, our main discussion will be focussed on Intrinsically Conducting Polymers.

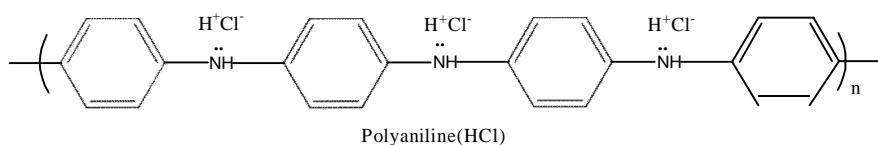
1. Extrinsicly Conducting Polymers

They are prepared by mixing conducting fillers like metal fibres, metal oxides or carbon black with insulating polymers. These are also called as conductive element filled polymers. Here, insulating polymer forms the continuous phase and added fillers form the conducting network. A minimum concentration of conducting filler has to be added so that the polymer starts conducting. The conductivity in this type of polymer is not due to the matrix polymer but due to conducting fillers which are added.

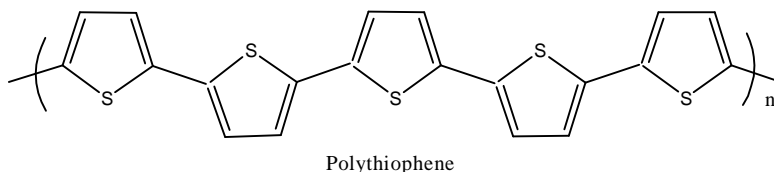
2. Intrinsically Conducting Polymers

In these type of polymers, conductivity is due to the organic polymers themselves. They conduct electricity when doped with oxidizing or reducing agents or protonic acids. The factor responsible for conductance in these polymers are conjugated electrons. Organic polymers with highly de-localized π -electrons having electrical conductance of the order of conductors are called as inherently or intrinsically conducting polymers or synthetic metals. Some important intrinsically conducting polymers are:

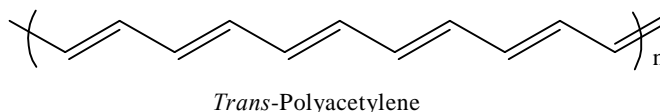
1. Polyaniline



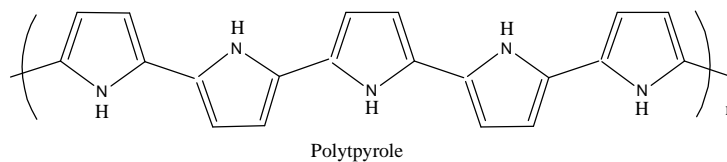
2. Polythiophene:



3. *Trans*-Polyacetylene



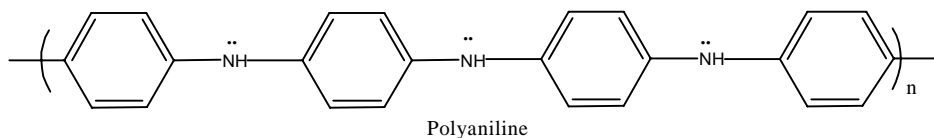
4. Polypyrrole:



Mechanism of Conduction

These conjugated organic polymers in their pure state are insulators or semi-conductors. The π -electrons are normally localized and do not take part in conductivity. But, these electrons delocalize on doping and conduct electricity. The dopant may be oxidizing or reducing agent or protonic acid. Accordingly they are called as *p*-doping, *n*-doping or H-doping polymers. In practice, most organic conductors are doped oxidatively to give *p*-type materials. The redox doping of organic conductors is similar to the doping of silicon semi-conductors with electron rich phosphorous or electron poor boron atoms to create *n*-type and *p*-type semi-conductors, respectively.

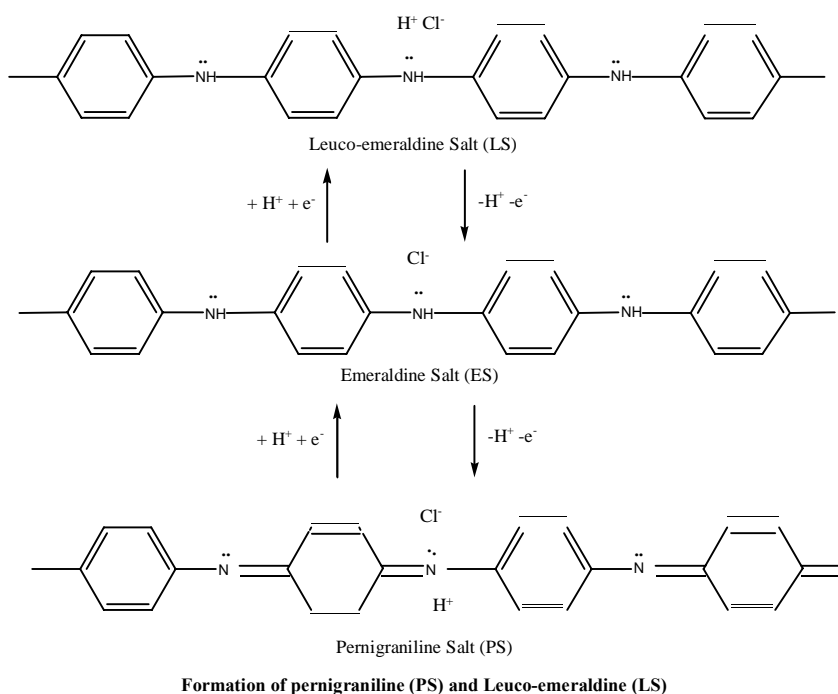
Polyaniline is a typical phenylene based polymer having a flexible -NH- group flanked on either side by a phenylene ring. The various physico-chemical properties of polyaniline are due to the presence of -NH- group. It is represented as:



Polyaniline exists in a variety of forms (Oxidation states) that differ in their conductivity. The most common form, i.e., green protonated emeraldine has conductivity of the order of semiconductor level (1 S/cm). This is higher than that of ordinary polymer ($<10^9$ S/cm) but lower than that of metals ($>10^4$ S/cm).

The emeraldine form of polyaniline can also be electrochemically oxidized or reduced in aqueous acid resulting in pernigraniline (PS) and leuco-emeraldine (LS) salts, respectively. This process is known as protonic acid doping. The redox reaction occurs with the motion of protons and the electrons in protonic acid ($\text{pH} < 3$). The addition of protons and electrons to nitrogen is observed during the reduction. This leads to change of ring from phenyl to quinoid structure upon oxidation and vice versa during reduction. The generation of these charged carriers is responsible for conductivity of the polymer. Protonated polyaniline converts into a non-conducting blue emeraldine base when treated with a base.

Different oxidation states of polyaniline can also be generated by doping with oxidants such as iodine. The conductivity of the resulting form of polyaniline is, however, lower than that obtained by protonic acid doping.



Applications of Conducting Polymers

Conducting polymers are used:

- In antistatic materials and as electrode materials in rechargeable batteries.
- In light emitting diodes and display devices.
- As conductive track on printed circuit boards (Polyaniline).
- As resistors for lithography (emeraldine base).
- In information storage devices.
- As humidity sensors, gas sensors, radiation sensors.
- In electro-chromic display windows.
- In fuel cells as electro-catalytic materials.
- As membrane for gas separation.