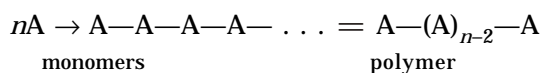


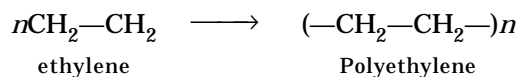
# POLYMER CHEMISTRY

## 1.1 INTRODUCTION

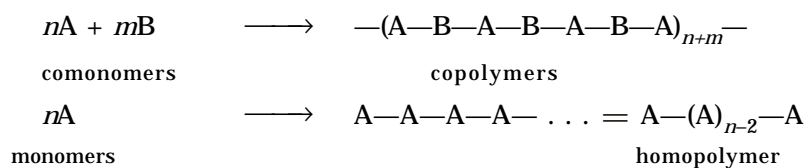
The term 'polymer' derived from the Greek words, *polys*—many and *meros*—parts or units. Thus, polymer is a large molecule, formed by repeated linking of small molecules called '**monomers**'. Therefore, a substance made up of long molecules which are characterized by many repeating molecular units in linear sequence is called a polymer. Polymers are made by sequential addition of many monomer molecules to each other.



For example, polyethylene; a polymer is formed by repeated linkage of simple ethylene molecules (monomers):



In many polymers, the fundamental units are not all the same but are two or more similar molecules. Such substances are called '**copolymers**' to distinguish them from homopolymers, which contain only one kind of fundamental unit.



The products of linking only small number of monomer units are designated by the use of Greek prefixes:

Monomer	A
Dimer	A—A
Trimer	A—A—A

Tetramer                    A—A—A—A  
 Pentamer                    A—A—A—A—A  
 etc.

The above are short chain polymers, also known as oligomers. The monomeric units may combine with each other into a macromolecule to form polymers of linear, branched or cross linked (three dimensional) structures.

Polymers which possess only long sequential strands are called linear polymers, *e.g.*,

A—A—A—A— . . . Homopolymers

or

A—B—A—B—A— . . . Copolymers

Linear copolymers in which the units of each type form fairly long continuous sequences (blocks) are called '**block copolymers**' *e.g.*,

A—A—A—A— . . . — . . . —A—A—B—B—B— . . .

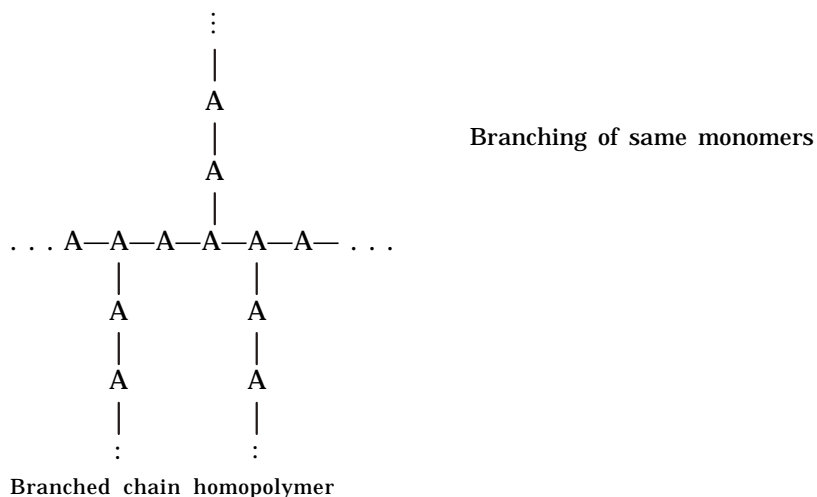
In copolymer molecules, the monomers may be arranged in the chain at random or regularly. Copolymers of the former group are called '**statistical**' or '**irregular**', whereas those of the latter group are called 'regular'.

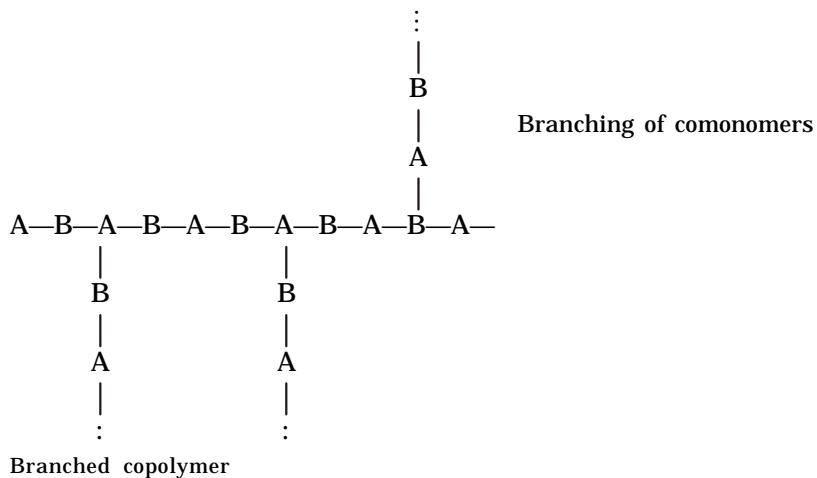
If the main chain is made up of same species of atoms, the polymer is called homochain polymer, and if the main chain is made up of different atoms is called heterochain polymer *e.g.*,

. . . A—A—A—A—A— . . . Homochain Polymer

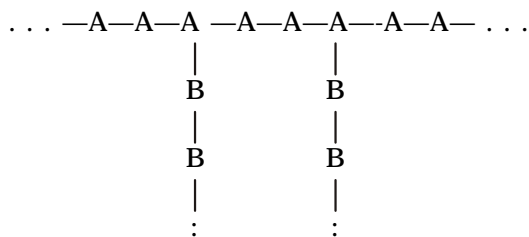
. . . A—A—A—B—A—A—A—B—A—A— . . . Heterochain Polymer

Branched polymers are of following structures:

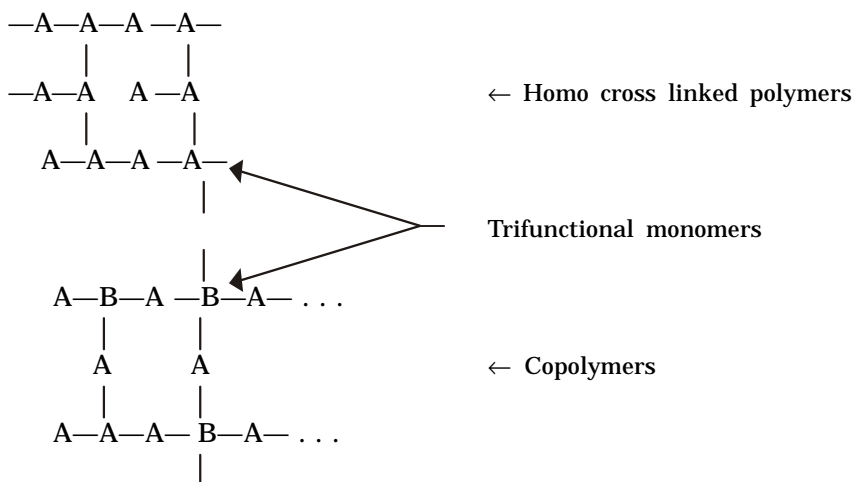




Branched copolymers with one kind of monomers in their main chain and another kind of monomers in their side chains are called '**graft copolymers**'. *e.g.*,



It is also possible, with three functional groups (or two different monomers at least one of which is trifunctional), to have long linkage sequences in two (or three) dimensions and such polymers are distinguished as cross linked polymers, *e.g.*,



Linear polymers are commonly relatively soft, often rubbery substances, and often likely to soften (or melt) on heating and to dissolve in certain solvent, whereas cross linked polymers are hard and do not melt, soften or dissolve in most cases.

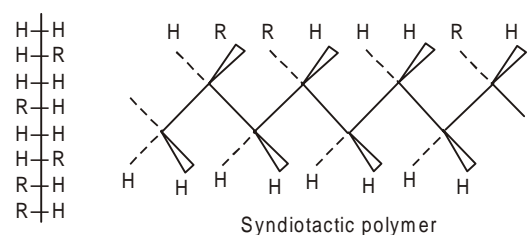
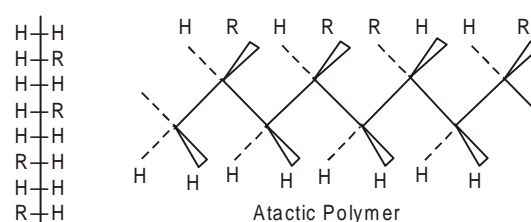
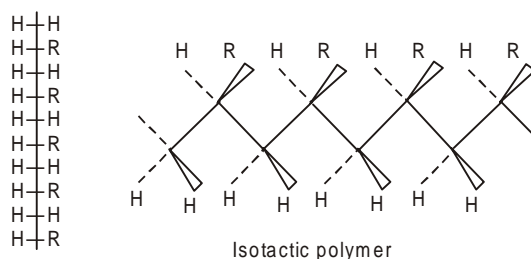
The number of repeating units in the chain so formed is called the 'degree of polymerization' (DP). Polymers with a high degree of polymerization are called 'high polymers' and those with low degree of polymerization are called '**oligopolymers**'. High polymers have very high molecular weights ( $10^4$  to  $10^6$ ) and hence are called as '**macromolecules**'.

The orientation of monomeric units in a macromolecule can take an orderly or disorderly fashion with respect to the chain. If the monomers have entered the chain in a random fashion, it is called an '**atactic**' polymer. If all the side groups lie on the same side of the chain (cis arrangement), it is called an '**isotactic**' polymer. If the arrangement of side groups is in alternating fashion (trans arrangement), it is called a '**syndiotactic**' polymer, *e.g.*,

Atactic polymer: Polypropylene

Isotactic polymer: Natural rubber

Syndiotactic polymer: Guttapercha



The importance of polymers in our life is almost breathtaking. Proteins and carbohydrates, which constitute two of the three principal classes of human foodstuffs, are natural polymers of high molecular weight. Nucleic acids are responsible for transmission of genetic characteristics in living organisms. Natural rubber, synthetic elastomers (synthetic rubbers), plastics, synthetic fibers, and resins are all polymers having uses that reach into every part of our lives. The tonnage of polymers marketed by the American chemical industries exceeds by a wide margin the volume of all other synthetic organic chemicals. Most of the structural tissues of living things are composed of polymers. In plants these are chiefly cellulose

(a polysaccharide) and lignins. In animals the main structural polymers are proteins, which take different forms as skin, hair, muscle, etc.

## 1.2 CHARACTERISTICS OF POLYMER STRUCTURE AND PROPERTIES OF POLYMERS

Following are the main characteristics of the structure and properties of polymers:

- (i) The major structural features of polymeric compounds is the presence of chain molecules in which a large number of atoms are combined successively. They have two types of bonds, chemical and inter-molecular, which greatly differ in energy and length. The atoms in the chain are joined to each other by strong chemical bonds, about 1–1.5 Å in length. Much weaker intermolecular forces interact between the chains at distances of about 3–4 Å. Crossed linked or three dimensional polymers have chemical bonds (cross-links) between their chains.
- (ii) The presence of large molecular and two types of bonds predetermines all properties which are typical of polymers.
- (iii) Polymeric substances exhibit wide varieties of physical and chemical properties. This is naturally expected because of the many possible kinds of macro-molecular composition and arrangement. The broad range of fibrous, adhesive, plastic, foamy, filmy and rubbery polymeric materials so readily available attested to this macromolecular versatility.
- (iv) The chemical nature of the monomeric unit is the primary factor which determines the properties of the polymer. Differences in the thermal stability and mechanical strength of different polymers are related to difference in bonding and structure of the monomer as well. The chemical reactivity of a polymer is mostly due to the reactivity of its molecular components, *e.g.*, natural rubber undergoes deterioration when ozone attacks the double bonds of the polymer chain whereas a saturated hydrocarbon chain like polyethylene resists such attack.
- (v) Cellulosic polymers offer their free hydroxyl groups to a variety of reagents and thus make it possible to incorporate useful modifications of properties, *e.g.*, reaction with nitric acid produces nitro-cellulose, from which propellant (gun cotton) and plastic (celluloid) are formed. On the other hand, reaction with acetic acid produces cellulose acetate, which can be fabricated into films, sheets and other useful forms. Both the above reactions alter the free hydroxyl group of cellulose. There are extensive possibilities for chemical modification and fabrication into products.
- (vi) More drastic chemical differences are capable of yielding wider differences in chemical properties, *e.g.*, silicone polymers, in which the macromolecular chains contain Si—O— linkages. The great thermal stability of the O—Si bonds, mainly due to the *p-d*π bonding (this refers to the π bonding between *p* and *d* orbitals) of O to Si, renders the silicone products to be used at high temperature. The hydrocarbon side chains contribute oily or lubricating properties.
- (vii) The properties of a polymer also depend upon the form and arrangement of its macromolecules. The critical factors are the molecular weight (which depends on

the degree of polymerization), the extent of branching, cross-linking or network structure, the stereotopic disposition of the monomeric units, the degree and the kinds of crystallinity of the macromolecules. Several variations can be brought about even without alteration of chemical functional groups.

- (viii) Stereo-regularity facilitates crystallinity which enhance all the properties related to crystallinity, *e.g.*, stereo-regularity strengthens polyethylene.
- (ix) Mechanical deformation also changes the properties of a polymer. Stretching of rubber offers an example. In the unstretched form, rubber molecules undergo random motion. When rubber is stretched, this motion is restricted, the molecules assume a linear crystalline arrangement and the entropy is reduced. The consequent release of energy in the form of heat is a familiar observation.

### 1.3 CLASSIFICATION OF POLYMERS

On the basis of different chemical structures, physical properties, mechanical behaviour, thermal characteristics, stereochemistry, polymers can be classified into following ways:

#### 1.3.1 Natural and Synthetic Polymers

Depending on their origin, polymers can be grouped as natural or synthetic. Those isolated from natural materials are called natural polymers, *e.g.*, cotton, silk, wool and rubber. Cellophane, cellulose rayon, leather and so on are, in fact, chemical modification of natural polymers.

Polymers synthesized from low molecular weight compounds are called synthetic polymers, *e.g.*, polyethylene, PVC, nylon and terylene.

#### 1.3.2 Organic and Inorganic Polymers

A polymer whose backbone chain is essentially made of carbon atoms is termed as organic polymer. The atoms attached to the side valencies of the backbone carbon atoms are, however, usually those of hydrogen, oxygen, nitrogen, etc. The majority of synthetic polymers is organic. In fact, the number and variety of polymers are so large that we refer to 'polymers' on the other hand, generally contains no carbon atom in their chain backbone. Glass and silicone rubber are examples of inorganic polymers.

#### 1.3.3 Thermoplastic and Thermosetting Polymers

Some polymers soften on heating and can be converted into any shape that they can retain on cooling. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Such polymers, that soften on heating and stiffen on cooling, are termed 'thermoplastics'. Polyethylene, PVC, nylon and sealing wax are examples of thermoplastic polymers. Some polymers, on the other hand, undergo some chemical change on heating and convert themselves into an infusible mass. They are like the yolk of egg, which on heating sets into a mass, and, once set, cannot be reshaped. Such polymers, that become infusible and insoluble mass on heating, are called 'thermosetting' polymers.

### 1.3.4 Plastics, Elastomers, Fibres and Liquid Resins

Depending on its ultimate form and use, a polymer can be classified as plastic, elastomers, fibre or liquid resins. When, *e.g.*, a polymer is shaped into hard and tough utility articles by the application of heat and pressure, it is used as a 'plastic'. Typical examples are polystyrene, PVC and polymethyl methacrylate.

When vulcanised into rubbery products exhibiting good strength and elongation, polymers are used as 'elastomers'. Typical examples are natural rubber, synthetic rubber, silicone rubber.

If drawn into long filament like material whose length is at least 100 times its diameter, polymers are said to have been converted into 'fibre' *e.g.* nylon and terylene.

Polymers used as adhesives, potting compound sealants, etc. in a liquid form are described liquid resins. Commercially available epoxy adhesives and polysulphide sealants are typical examples.

### 1.3.5 Atactic, Isotactic and Syndiotactic Polymers

On the basis of the configurations, (stereochemistry) polymers can be classified into three categories viz., atactic, isotactic (cis-arrangement) and syndiotactic (trans-arrangement).

Those polymers in which arrangement of side groups is at random around the main chain, are termed as atactic polymers.

Those polymers in which the arrangement of side groups are all on the same side are known as isotactic polymers.

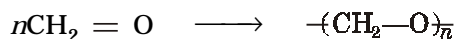
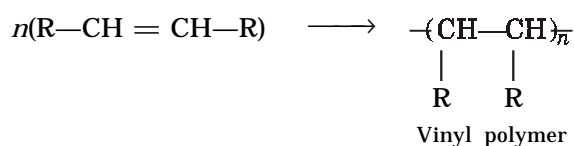
Whereas, those polymers in which the arrangement of side groups is in alternating fashion is termed as syndiotactic polymers.

## 1.4 TYPES OF POLYMERS

There are two types of polymers; viz. (i) addition polymer, and (ii) condensation polymer.

### 1.4.1 Addition Polymers

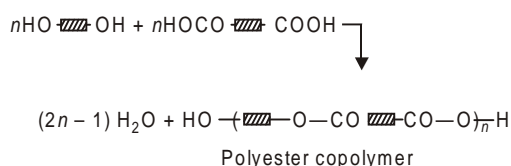
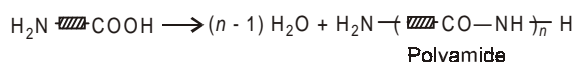
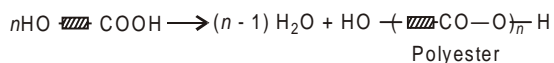
The addition polymer is one in which the monomers are molecules with multiple bonds which undergo true addition reactions with each other, *e.g.*,



Polystyrene, PVC, polyethylene, polychlorostyrene etc. are the examples of addition polymers.

### 1.4.2 Condensation Polymers

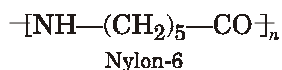
The condensation polymer is one in which a small molecule (usually water) is eliminated in the condensation of any two monomer units. It is clear, therefore, the monomers for condensation polymers must be (at least) bifunctional molecules in which one function on one monomer molecule reacts with the other function on another molecule, *e.g.*,



The last example implies a variant in which two bifunctional units are present on each of two kinds of monomers to create a condensation polymer.

Polymers which possess only long sequential strands like those listed are called linear polymers.

Nylon is the main example of condensation polymer



## 1.5 STRUCTURE OF POLYMERS

### 1.5.1 Elastomers or Rubbers

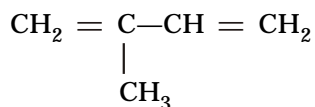
An elastomer is a linear polymer which exhibits elasticity and other rubber-like properties. Rubbers are of two types:

- (i) Natural rubber, and
- (ii) Synthetic rubber.

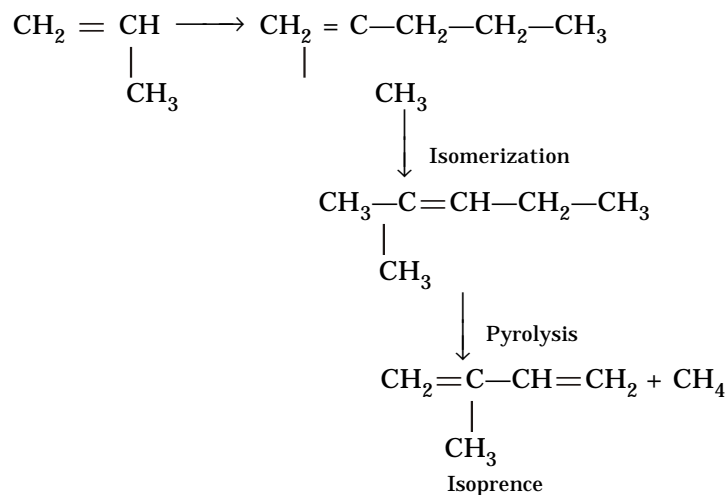
#### 1.5.1.1 Natural Rubber

Natural rubber is obtained in the form of latex from rubber trees (*Hevea brasiliensis*). The latex normally contains 30-60% rubber. It can be used, as such, in the latex form or the solid rubber can be coagulated from the latex using 1% acetic acid solution. Natural rubber is a highly soft and elastic material.

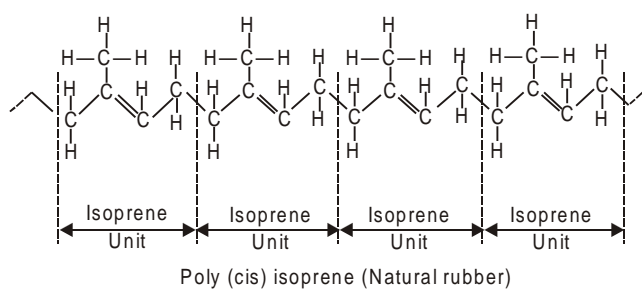
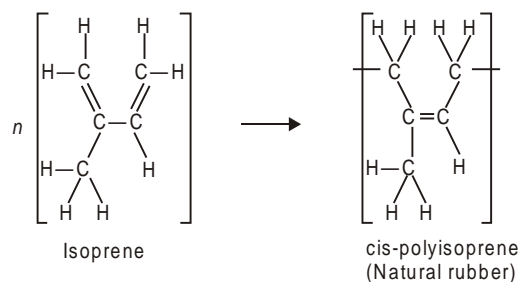
Natural rubber is a polymerized form of isoprene (2, Methyl-1,3-butadiene):



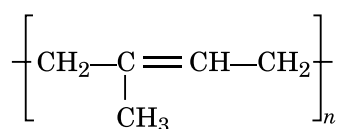
Isoprene is synthesized from propylene, as follows:



Polymerization of isoprene yields polymers containing varying degrees of cis-1,4- and trans-1,4 as well as 1,2 or 3,4-vinyl units in the molecule, depending upon the initiator and the solvent systems employed. Under controlled conditions, polyisoprene containing upto 96% cis-configuration can be obtained by using a lithium alkyl initiator and anhydrous oxygen free aliphatic hydrocarbon solvents.

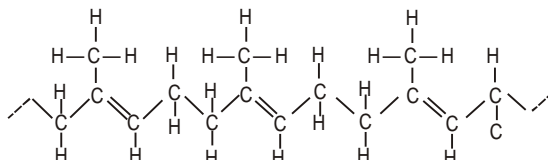


The general structure of polyisoprene is as follows:



### Gutta Percha

It is obtained from the mature leaves of *dichopsis gutta* and *palagum gutta* trees. Gutta percha may be recovered by solvent extraction, when insoluble resins and gums are separated. Alternatively the mature leaves are ground carefully; treated with water at about 70°C for half an hour and then poured into cold water. When gutta percha floats on water surface and is removed. The structure of gutta is as follows:



Both the cis- as well as trans-varieties occur in nature as natural rubber and gutta percha, respectively. Natural rubber is a highly soft and elastic material. It is soluble in carbon disulphide and petrol. Whereas Gutta-percha is a hard thermoplastic solid and dissolves in petrol only on heating and is thrown out of solution when cooled. Structurally, gutta-percha is trans-polyisoprene; whereas natural rubber is cis-polyisoprene

#### 1.5.1.2 Synthetic Rubbers

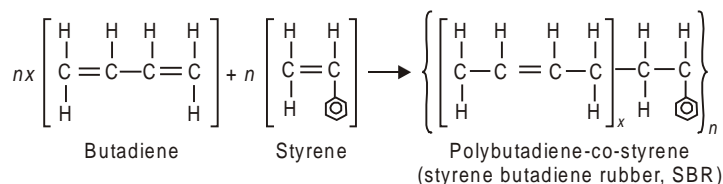
It is also known as artificial rubber. Synthetic rubbers are of following types:

- |   |                     |
|---|---------------------|
| (i) Styrene rubber                          | (GR-S or Buna-S)    |
| (ii) Nitrile rubber                         | (GR-A or Buna-N)    |
| (iii) Neoprene                              | (GR-M)              |
| (iv) Butyl rubber                           | (GR-I)              |
| (v) Polysulphide rubber                     | (GR-P or Thiocol)   |
| (vi) Polyurethane rubber                    | (isocyanate rubber) |
| (vii) Chlorosulphonated Polyethylene rubber | (Haplon)            |
| (viii) Silicone rubber.                     |                     |

#### (i) Styrene Rubber (Buna-S)

Styrene butadiene rubber (SBR) is prepared by the copolymerization of butadiene (75%) and styrene (25%) in an emulsion system at 50°C in the presence of catalyst such as cumene hydroperoxide.

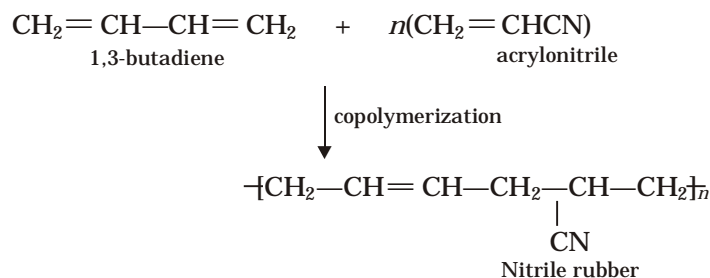
SBR is also known as Buna-S or GR-S. Styrene rubber has high abrasion resistance, high load bearing capacity, low oxidation resistance, swells in oil and solvents, like natural rubber SBR also vulcanised and produce cold rubber, which has greater tensile strength and greater abrasion resistance.



SBR is used in motor tyres, shoes soles, footwear components, insulation of wire and cables, carpet backing, gaskets, adhesives, etc.

### (ii) Nitrile Rubber (Buna-N/NBR)

It is a copolymer of acrylonitrile and butadiene. It is prepared by the copolymerization of acrylonitrile and butadiene in emulsion systems.

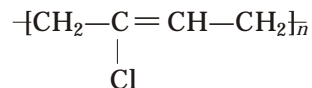


Nitrile rubber (GR-A) has low swelling, low solubility, good tensile strength and abrasion resistance even after immersion in gasoline or oils. It has good heat resistance.

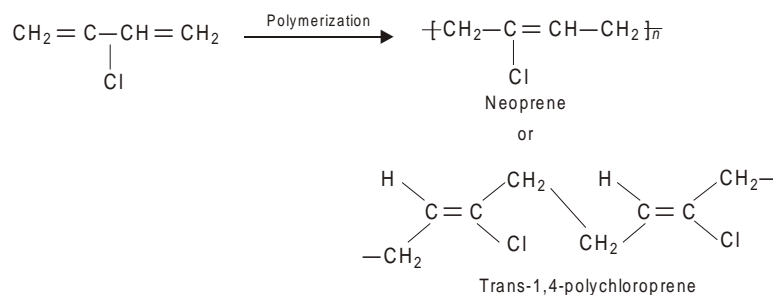
It is used in fuel tanks, gasoline hoses, as an adhesive and in the form of latex for impregnating paper, leather and textiles.

### (iii) Neoprene (GR-M)

Neoprene, also known as polychloroprene, has the following structure:



It is prepared by the free radical polymerization of chloroprene (2-chloro-1, 3-butadiene) in an emulsion system.

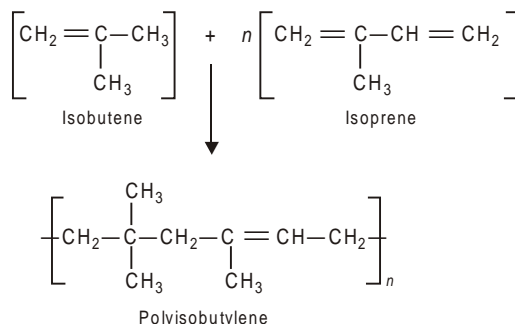


Neoprene can be vulcanised to a considerable extent by heat alone. Its physical properties are enhanced by compounding it with metallic oxides, such as ZnO or MgO. They have a higher oil resistance than many rubbers including nitrile rubbers. Due to the Trans-1, 4,-structure, it is therefore, an easily crystallisable elastomer. The vulcanized products are found to have excellent tensile strength.

This elastomer is principally used for providing oil resistant insulation coatings to wires and cables and for producing shoe soles, solid tyres, gloves and industrial hoses, tubing for carrying corrosive gases and oils.

**(iv) Butyl Rubber (GR-I)**

Butyl rubber, also known as polyisobutylene, is prepared by the copolymerization of isobutene with isoprene and methylchloride as solvent.

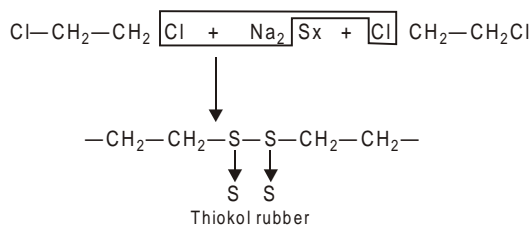


Butyl rubber is amorphous under normal conditions but gets crystallized on stretching. It has excellent resistance to heat, abrasion, ageing, chemicals (such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$  or  $\text{HF}$ ), polar solvents (like alcohol and acetone) but is soluble in hydrocarbon solvents like benzene.

Butyl rubber is used as inner tubes because its superior impermeability to gases. It is used for wire and insulation. It is used in the production of tyres.

**(v) Polysulphide Rubber (GR-P)**

Polysulphide rubber, also known as Thiokol, is prepared by the reaction between sodium polysulphide ( $\text{Na}_2\text{S}$ ) and ethylene dichloride ( $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ ).

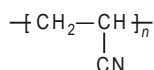


Thiokols are those elastomers in which sulphur forms a part of the polymer chain. It has extremely good resistance to mineral oils, fuel oxygen, ozone and sunlight. It is also impermeable to gases. It cannot be vulcanized and hence does not form hard rubber. It has poor strength and abrasion resistance.

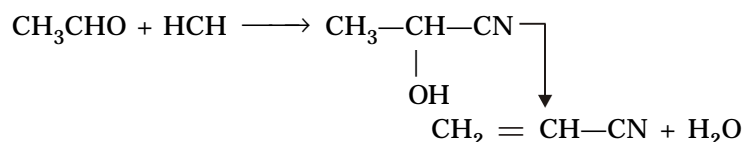
Polysulphide rubbers are mainly used to make sealants, gaskets, balloons, fabric coatings and gasoline hoses. Polysulphides form excellent fuel material and, upon mixing with inorganic oxidisers such as ammonium perchlorate, they become solid propellants for rockets.

**1.5.2 Polyacrylonitrile (PAN)**

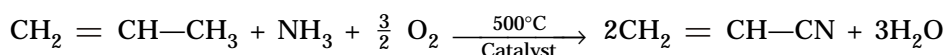
Polyacrylonitrile (PAN), also known as Polyvinyl cyanide, has the following structure:



Acrylonitrile can be made either by the direct catalytic addition of HCN to acetylene, or by the addition of HCN to ethylene oxide to give ethylene cyanohydrin, followed by dehydration.



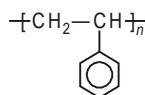
It can also be produced by ammonoxidation of propylene:



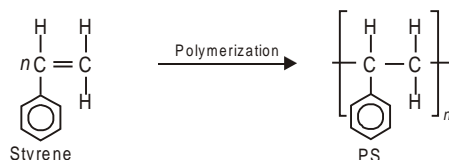
PAN has a remarkable resistance to heat upto around 220°C and exhibits very good mechanical properties. PAN is used to produce fibres known as PAN fibres. The copolymers of PAN with butadiene (nitrile rubber) is a material of great industrial importance.

### 1.5.3 Polystyrene (PS)

Polystyrene, also known as polyvenyl benzene has the following structure:



Polystyrene is prepared by the free radical addition polymerization of styrene monomer (dissolved in ethyl benzene) in the presence of benzoyl peroxide as a catalyst.

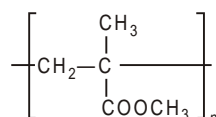


It is a transparent, light, excellent moisture resistant. It can be nitrated and sulphonated by fuming nitric acid and cone.  $\text{H}_2\text{SO}_4$  respectively. It yields water soluble emulsion at 100°C. It is highly electric insulating, highly resistant to acids and goods and is chemical resistant. It has low softening range (90-100°C) and brittle. However, it has the unique property to transmitting light through curred sections.

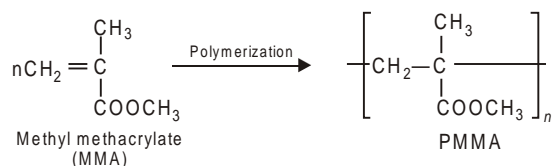
It is used in moulding of articles like comb, toys, buttons, buckels, radio and television parts, refrigerator parts, battery cases, high frequency electric insulators, lenses, etc.

### 1.5.4 Polymethyl Methacrylate (PMMA)

Polymethyl Methacrylate, also known as Lucite or Plexiglass has the following structure:



PMMA is prepared by radical polymerization (in bulk or suspension) of methyl methacrylate in the presence of acetyl peroxide or  $\text{H}_2\text{O}_2$  as catalyst.

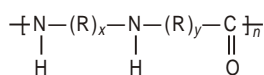


PMMA is a hard, fairly rigid material with a high softening point of about 130-140°C, but it becomes rubber like at a temperature above 65°C. It has high optical transparency, high resistance to sunlight and ability of transmitting light accurately. However, it has low chemical resistance to hot acids and alkalis and has low scratch resistance.

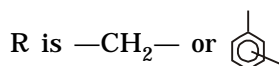
It is used to make attractive signboards and durable lenses for automobile lighting, TV screens, artificial eyes, paints, adhesives, etc.

### 1.5.5 Polyamides

Polyamides are prepared by the melt polycondensation between dicarboxylic acids and diamines. They have the general structure as follows:



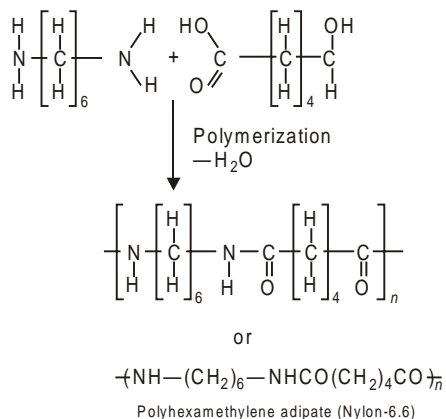
where



The aliphatic polyamides are generally known as NYLONS. There are different types of nylons and are usually indicated by a numbering system. This number gives the number of carbon atoms present in the monomer molecules. Aliphatic Nylon have M.P. of 250-300°C.

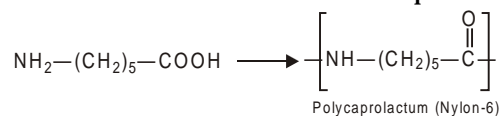
#### Nylon-6:6

It is obtained by the polymerization of adipic acid with hexamethylene diamine.



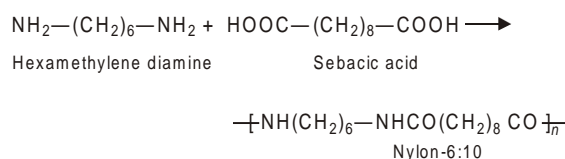
### Nylon-6

It is prepared by the self condensation of  $\epsilon$ -amino caproic acids.



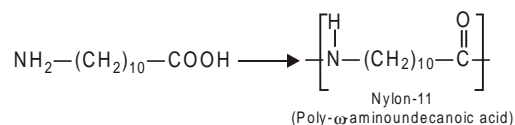
### Nylon-6:10

It is prepared by the reaction between hexamethylene diamine and sebacic acid. The product formed is hexamethylene diammonium sebacate (Nylon-6:10) which on further polymerization forms ribbon of Nylon-6:10. This is not used as a fibre. It is used in brushes, bristles, sports equipment, etc.



### Nylon-11

It is produced by the self condensation of  $\omega$ -aminoundecanoic acid.



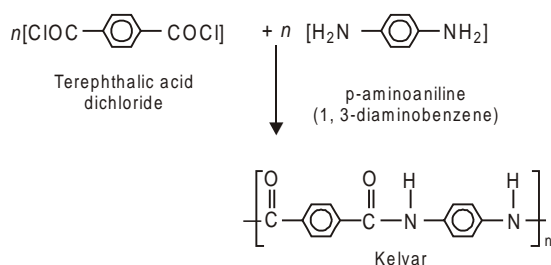
Nylon-11 is less water sensitive than other nylons because of its greater hydrocarbon character. It is used as textile fibre.

Nylon-6:6 is used as plastic as well as a fibre. It has good tensile strength, abrasion resistance and toughness upto 150°C. Also, it offers resistance to many solvents. However, formic acid, cresols and phenols dissolve this polymer. It is used to produce tyre cord, monofilament of ropes, substitute of metal in gears and bearings.

### Kelvar

It is a aromatic polyamide similar to nylons, but in benzene rings rather than aliphatic chains linked to the amide groups —CONH—.

It is prepared by the condensation polymerization of terephthalic acid dichloride and 1, 4-diaminobenzene

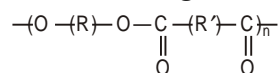


Kelvar is exceptionally strong. This is due to the stronger intermolecular forces between neighbouring chains. It also has high heat stability.

Kelvar is used in tyres, brakes, clutches lining and other car parts, bullet proof vests, motor cycle helmets, aerospace and aircraft industries.

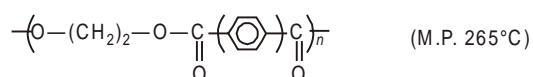
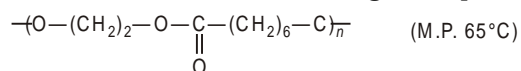
### 1.5.6 Polyester Resins

Polysters have the structure with ester linkages as follows:

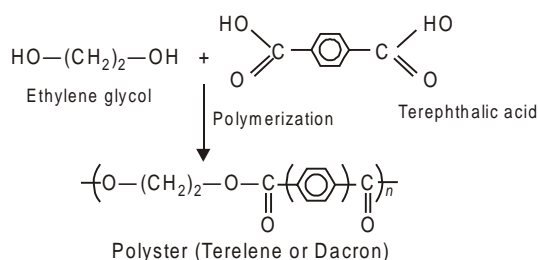


where R and R' are aliphatic.

They are prepared by a polycondensation reaction between a dicarboxylic acid and a diol. Aliphatic polysters were not of much industrial importance, mainly because of their low M.P. *e.g.*, the polyster with a degree of polymerization comparable to the commercial polyethylene melts somewhere in the range of 50-80°C, whereas the M.P. of polyethylene is around 120°C. This problem of low M.P. was overcome by introducing aromatic rings into the polyster chain. This is evident from the following examples:



Polyster (*e.g.*, terene or terelene or dacron) is prepared by the condensation polymerization of dicarboxylic acid with dihydroxy alcohols.



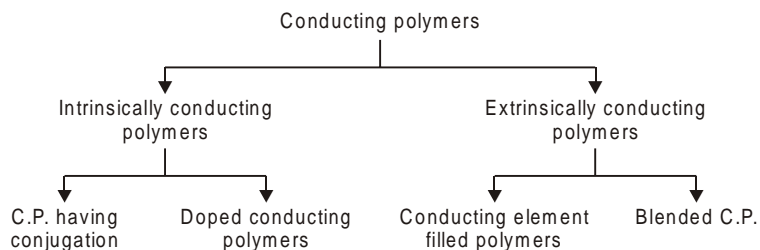
Polyster is a good fibre forming material. This is due to the presence of numerous polar groups and symmetrical structures. Such fibres have high stretch resistance. Polyethylene terephthalate (PET) is highly resistant to mineral and organic acids but is less resistant to alkalis.

It is used in making synthetic fibres like terelene, dacron etc., for blending, with wool to provide better crease and wrinkle resistance. It is also used as glass reinforcement material in safety helmets, battery boxes, etc.

## 1.6 CONDUCTING POLYMERS AND THEIR APPLICATIONS

Ordinary polymers are purely insulators. Conducting polymers (CP) are long chain having current flowing properties. To make the polymer materials conductive they are doped with atoms that donate negative or positive charges (oxidizing or reducing agents) to each unit, enabling current to travel down the chain. Depending on the dopant, conductive polymers exhibit either p-type or n-type conductivity.

Conducting polymers can be classified into the following types:



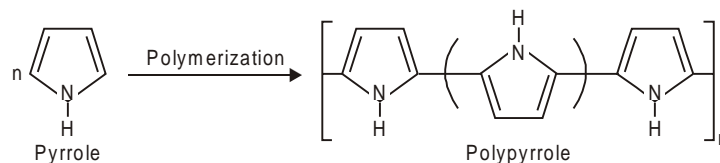
These are briefly discussed below :

### 1.6.1 Intrinsically Conducting Polymers

(a) C.P. having conjugated  $\pi$ -electrons in the backbone :

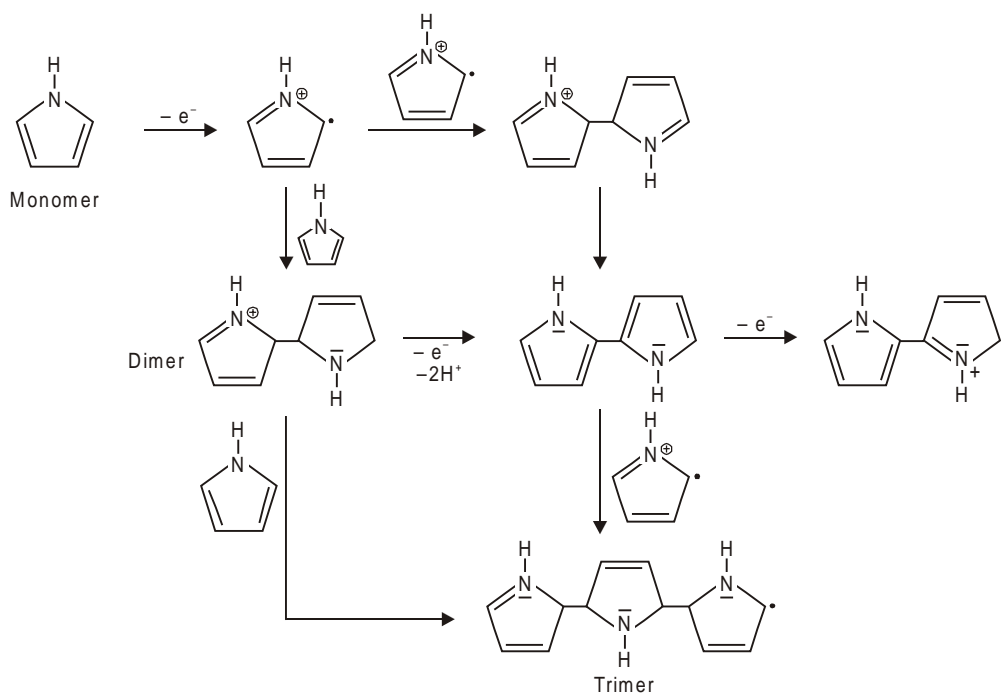
Such polymers contains conjugated  $\pi$ -electron in the back bone which increases their conductivity to a large extent. This is because overlapping of conjugated  $\pi$ -electrons over the entire backbone results in the form of valence bonds as well as conduction bonds, which extends over the entire polymer molecule.

**For example—Polypyrrole:** It is obtained by electropolymerization of pyrrole



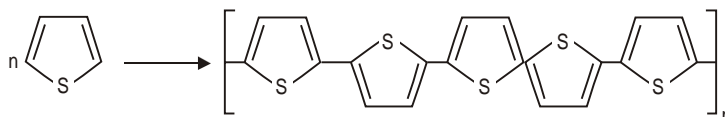
Polypyrrole is an inherently conducting polymer due to inter chain doping of electrons. It can be easily prepared by oxidative polymerization of the monomer pyrrole.

#### Mechanism



## Polythiophene

Polythiophenes consist of a chain of alternating double and single-bonds like poly acetylene, however, each first and fourth carbon atom are connected by a sulphur atom forming a thionyl ring.



Therefore, bond between the second and the third carbon atom get more single bond character than other C–C bonds and consequently also the bonds connecting the thionyl rings are more of single-bond character.

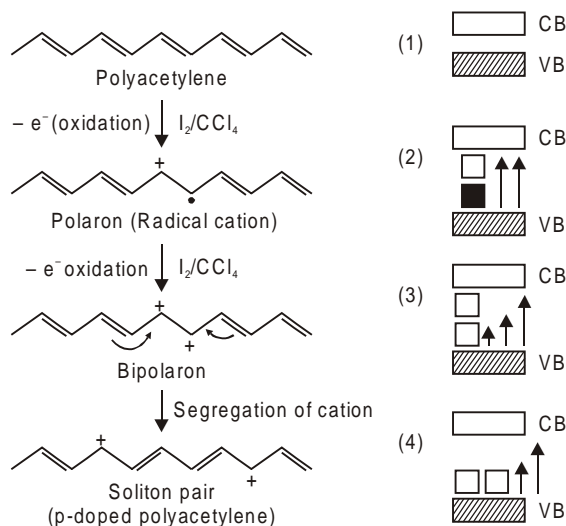
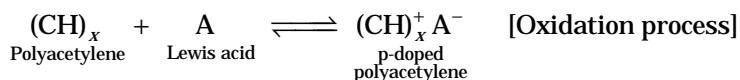
Due to this weaker mesomerization than in polyacetylene the band gaps of polythiophenes are shifted to the blue and UV. Beside of their structure defining function the sulphur atoms will have also a direct influence on the electronic and optical properties of a polythiophene.

**(b) Doped Conducting Polymers:** It is of two types

- (i) *p*-doping (oxidative doping).
- (ii) *n*-doping (reductive doping).

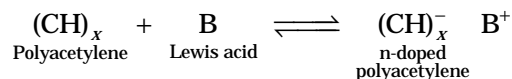
### *p*-doping

It is done by oxidation process. (i.e., removal of  $e^-$  from the polymer pi – back bone). This formation is known as polaron. A second oxidation of this polaron, followed by radical recombination yields two positive charge carriers on each chain which are mobile.

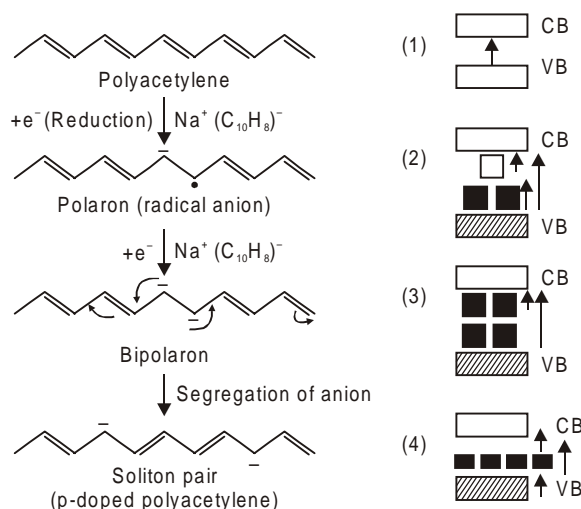


### n-doping

It is done by reduction process (addition of an  $e^-$  to the polymer).



It forms polaron and bipolaron in two steps. This followed by recombination of radicals yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction.



[Here VB = Valence bond, CB = Conduction bond, ▨ = Donal level].

### 1.6.2 Extrinsicly Conducting Polymers

It is of two types

- Conductive Element filled polymers.
- Blended conducting polymers.

**(a) Conductive Element Filled Polymer:** In this, the polymers act as the binder to hold the conducting element (such as carbon black, metallic fibers, metallic oxides etc.) together in the solid entity.

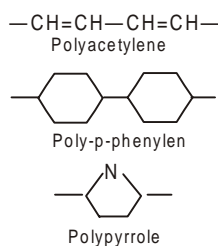
Minimum concentration of conductive filler which should be added so that polymer starts conducting is known as percolation threshold. Carbon black is very used as filler which has very high surface area ( $1000\text{m}^2/\text{gm}$ ) more porosity and more of a filamentous properties. It bears good conductive properties and low in cost, light in weight, as well as durable.

It is used in hospital operating theatres where it was essential that static charges did not build up leading to explosion involving on aesthetics.

**(b) Blended Conducting Polymers:** It obtained by blending a conventional polymer with a conducting polymer. Such polymers possess better physical, chemical, electrical and mechanical properties and they can be easily processed.

For example: up to 40% of polypyrrole will have little effect on tensile strength and also give a much higher impact strength than obtained with a carbon-black filled compound at only 10% loading. Such compounds are used in electromagnetic shielding.

A polymer which conduct electricity is termed as 'conducting polymer'. Most polymeric materials are poor conductor of electricity, because of the non-availability of large number of free electrons in the conduction process. Although no commercial products are yet known, there is considerable interest in polymers with a wide range of electrical conductive properties, produced for the most part by doping with inorganics such as arsenic, pentafluoride or iodine, polymers such as polyacetylene and the polyphenylene sulfide, *e.g.*,



Electrical conductivity of some important polymers are as given below in Table 1.1.

**Table 1.1**

Sl. No.	Polymers	Electrical conductivity in $\text{Ohm}^{-1} \text{m}^{-1}$
1	Nylon 6, 6	$10^{-12} - 10^{-13}$
2	Polystyrene	$< 10^{-14}$
3	Phenol formaldehyde	$10^{-9} - 10^{-10}$
4	Polyethylene	$10^{-15} - 10^{-17}$
5	Polytetrafluoroethylene	$< 10^{-17}$
6	Poly-methyl methacrylate	$< 10^{-12}$

The phenomenon of conduction is observed in a number of polymers such as polypyrrole, polythiophene, polyacetylene, polyparaphenylene and polyaniline which have been doped with appropriate impurities. These polymers may be made either *n*-type, *i.e.*, free electrons dominant or *p*-type, *i.e.*, holes dominant, depending upon the type of dopant used. However, unlike semiconductors, the dopant atoms or molecules do not substitute or replace any of the polymer atoms, *n* and *p* doping polymers are produced in the following ways :

*n*-doping : Polymer + A  $\longrightarrow$  (Polymer)<sup>*n*-</sup> A<sup>*n*+</sup> where A is Na, Li etc.

*p*-doping : Polymer + B  $\longrightarrow$  (Polymer)<sup>*n*+</sup> B<sup>*n*-</sup> where B is I<sub>2</sub>, Br<sub>2</sub>, AsF<sub>5</sub> etc.

Since  $\pi$  electrons can easily be removed or added to the polymeric chains, so unsaturated polymers with  $\pi$  electrons are mostly employed for producing high conducting polymers by the process of doping. In general, the polymer can be made conductive in the following ways:

- (i) Conductivity by doping
- (ii) Conductive element filled polymer

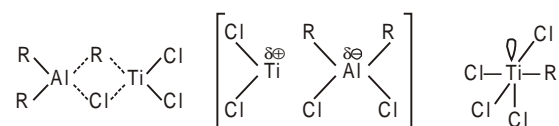
- (iii) Conjugated  $\pi$  electron conducting polymer
- (iv) Blended conducting polymer
- (v) Decreasing in band gap
- (vi) Coordination conducting polymer
- (vii) Photoconductive polymers.

### 1.6.3 Applications of Conducting Polymers

- (1) Polythiophene is marketed under the trade name Baytron. It can be used to make plastics paintable by adding the conductive agent first, and also in the electrodes of small, high performances tantalum capacitors found in telecommunications, computer and automobile products.
- (2) Contex, a fiber is coated with a conductive polymer polypyrrole can be woven to create an antistatic fabric which can be used in carpet industry.
- (3) These can be used in producing photovoltaic devices, *e.g.*, in Al/polymer Au photovoltaic cells.
- (4) It used in making button type batteries. These batteries are long lasting, rechargeable and can produce current density up to 50 mA/cm<sup>2</sup>.
- (5) Used as conductive paints.
- (6) Used as electro-chemical accumulators.
- (7) An emerging application for electrically conductive polymeric materials is biosensors and chemical sensors, which can convert chemical information into measurable electrical response.  
(Aptech has developed a range of enzyme biosensors.)
- (8) Used for making sensors for pH, O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> and glucose as analytical sensors.
- (9) Used in rechargeable lead-acid battery in automotive.
- (10) Used in optically display devices based on polythiophene.
- (11) Used in solar cells.
- (12) Used in photovoltaic systems.
- (13) Used in electronic devices such as transistors and diodes.
- (14) Used in telecommunication systems.
- (15) Used in the wiring in aircraft and aerospace components.
- (16) Used in antistating coatings for clothing.
- (17) Used in variable transmission (smart) windows etc.

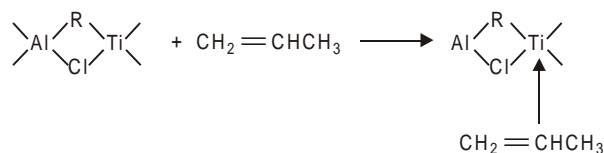
### 1.7 ZEIGLER-NATA CATALYSTS

These are a special type of coordination catalysts, comprising two components, which are generally referred to as the catalyst and the cocatalyst. The catalyst component consists of halides of IV-VIII group elements having transition valence and the cocatalysts are organometallic compound such as alkyls, aryls and hydrides of group I-IV metals (Zeigler-Nata Catalysts). Although there are organo aluminium compounds such as triethyl aluminium ( $\text{AlEt}_3$ ) or diethyl aluminium chloride ( $\text{AlEt}_2\text{Cl}$ ) in combination with titanium chlorides—both tri and tetra ( $\text{TiCl}_3$  and  $\text{TiCl}_4$ )—are, by far, the most commonly used. Aluminium alkyls act as the electron acceptor whereas the electron donor is titanium halides and the combination, therefore, readily forms coordination complexes. The complex formed is insoluble in the solvent and is, hence, heterogeneous in nature. Many structures have been proposed for these complexes are:

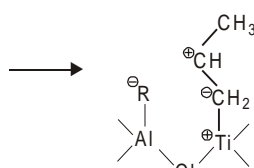


The active centres, from where the polymer chain growth propagates are formed at the surface of the solid phase of the catalyst complex, and the monomer is complexed with the metal ion of the active centre before its insertion into the growing chain.

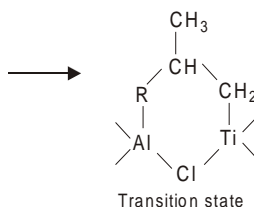
The complex formed, now acts as the active centre. The monomers then attached towards the Ti—C bond (C from the alkyl group R) in the active centre, when it forms a  $\pi$  complex with the Ti ion.



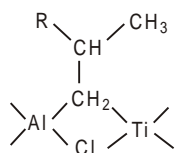
The bonds between R and Ti opens up producing an electron deficient Ti and a carbanion at R.



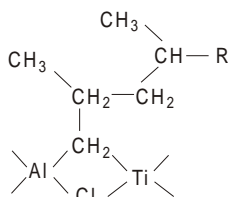
The Ti ion attracts the  $\pi$  electrons pair or the monomer and forms  $\sigma$  bond



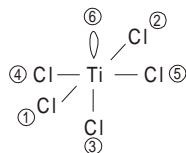
This transition state now gives rise to the chain growth at the metal carbon bond, regenerating the active centre:



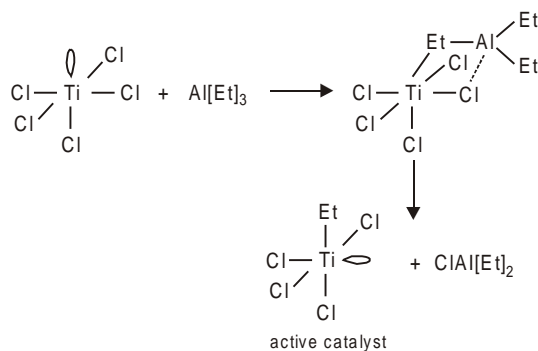
Repeating the whole sequence, with the addition of second monomer molecule, we will get the structure of the resultant chain growth as:



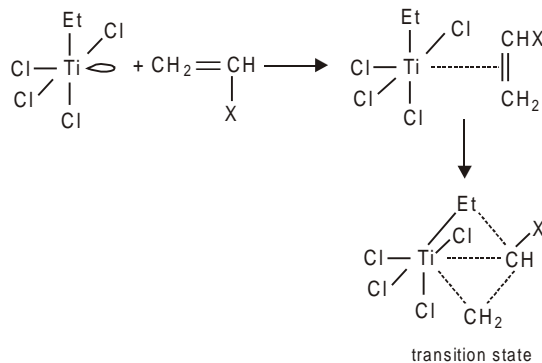
The five coordinated titanium ions on the surface of the catalyst is assumed to have a vacant orbital as shown at 6 in the following structure:



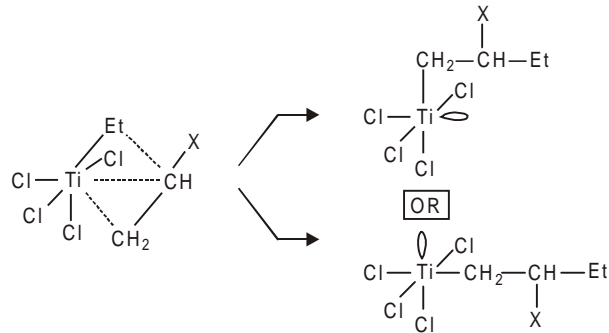
After the chemisorption of aluminium alkyl on the  $\text{TiCl}_3$  crystal,  $\text{Ti}^{3+}$  is alkylated by an exchange mechanism, as follows:



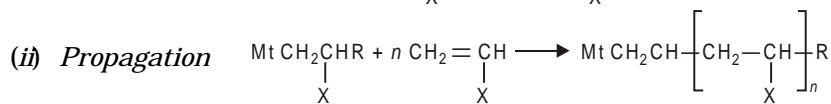
Once the active catalyst is formed, the monomer is attached towards the vacant orbital which then forms a transition  $\pi$  complex with the Ti.



The transition state quickly gives rise to the growth of the polymer chain by the monomeric insertion at the Ti-Et bond.

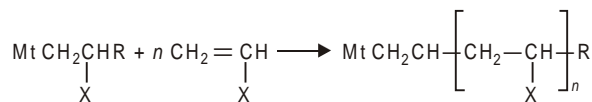


Therefore, on the basis of the above, polymerization is characterised by the initiation propagation and termination reaction as follows:

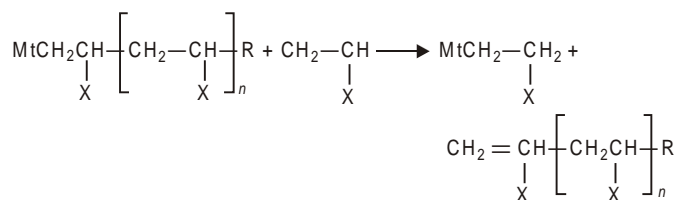


(iii) *Termination*

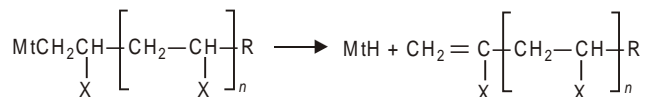
By an active hydrogen compound



By Transfer with monomer



By spontaneous internal transfer



Here Mt denotes transition metals such as Ti, Mo, Cr, V, Ni, or Rh. Ziegler-Natta polymerization is used to prepare polypropylene, polyethylene, polydiene, etc.



8. What are organic polymers? Give the structure of five organic polymers.
9. What are vinyl monomers? Give four examples.
10. Give the mechanism of free radical polymerization of vinyl monomers.
11. What are initiators? Name four free radical initiators.
12. What are inhibitors? Give examples.
13. What is Ziegler Natta catalyst? Give two examples. What is the significance of a catalyst in polymerization?
14. What are condensation polymers? Give four examples of condensation polymers.
15. What are bio-polymers? Give three examples.
16. Classify the polymers on the basis of stereochemistry.
17. If average degree of polymerization of polymethyl methacrylate is  $10^3$ , calculate its average molecular weight.
18. State the differences between addition and condensation polymerization.
19. Write two uses of the following polymers; low density polyethylene; polystyrene, polymethylmethacrylate, Nylon 66, epoxy resins.
20. State the differences between RNA and DNA,
21. What are proteins? Write any three tests for proteins.
22. What are polysaccharides? Write examples and their building unit.
23. What is a copolymer? Write structure of Buna—N, Buna—S. Classify the copolymers on the basis of arrangement of two monomer units?
24. What are the characteristics of polymer? Why do polymers have an average molecular weight.
25. State the differences between free radical and ionic polymerization.
26. Write structure of phenol formaldehyde resin, urea formaldehyde resin, polyimides, polycarbonate and polyurethanes.
27. (i) If two polymers of molecular weight 10,000 and 1,00,000 are mixed together in equal parts by weight, determine the number average and weight average molecular weights.  
(ii) If the above polymers are mixed so that equal number of molecules are added, determine  $\bar{M}_n$  and  $\bar{M}_w$ .
28. A sample of polystyrene is composed of a series of fractions of different sized molecules.

<i>Fraction</i>	<i>Weight/fraction</i>	<i>Molecular weight</i>
A	0.10	12,000
B	0.19	21,000
C	0.24	35,000
D	0.18	49,000
E	0.11	73,000
F	0.08	1,02,000
G	0.06	1,22,000
H	0.04	1,46,000

Calculate the number average and weight average molecular weights of this polymer sample.

29. Fractions of a polymer when dissolved in an organic solvent gave the following intrinsic viscosity values at 25°C.

$M(g\ mol^{-1})$ :	34,000	61,000	1,30,000
$[\eta]$ :	1.02	1.60	2.73

30. What is polydispersity index? Give its importance. Write expressions for calculation of  $\bar{M}_w$ ,  $\bar{M}_v$ , and  $\bar{M}_z$  for polymers. Name the techniques to determine the above average molecular weight(s).
31. State whether true or false. If false, give the correct statement:
- Polyvinyl alcohol can be prepared by polymerization of vinyl alcohol.
  - $CH_4$  can be polymerised.
  - $C_2H_2$  and aniline cannot be polymerised.
  - Polymers have sharp melting point.
  - Ziegler-Natta catalyst is used for the preparation of syndiotactic polymer.
32. Explain in details about conducting polymers.
33. What are adhesives? Explain the synthesis and application of epoxy resin. [VTU 2006-07]
34. What are elastomers? Discuss the advantages of synthetic elastomers. [VTU 2006-07]
35. Give the synthesis and applications of butyl rubber. [VTU 2006-07]
36. Discuss the mechanism of conductance in polyacetylene. [VTU 2006-07]

### SOLVED NUMERICALS

**1.** Calculate the number average degree of polymerization of an equimolecular mixture of hexamethylenediamine and adipic acid for the extent of reaction 0.500, 0.800, 0.900, 0.950, 0.970, 0.990 and 0.995.

**Solution.**

$$\bar{D}_p = \frac{1}{1-p}$$

Then putting the value of  $p$

If  $p = 0.500$ , then  $\bar{D}_p = 2$

$$p = 0.800, \quad \text{then } \bar{D}_p = \frac{1}{1-0.800} = 5$$

$$p = 0.900, \quad \text{then } \bar{D}_p = \frac{1}{1-0.900} = 10$$

$$p = 0.950, \quad \text{then } \bar{D}_p = 1/1-0.950 = 20$$

$$p = 0.970, \quad \text{then } \bar{D}_p = 1/1-0.970 = 33.3$$

$$p = 0.990, \quad \text{then } \bar{D}_p = 1/1-0.990 = 100$$

$$p = 0.995, \quad \text{then } \bar{D}_p = 1/1-0.995 = 200$$

2. If two polymers of molecular weights 10,000 and 100,000 are mixed together in equal parts by weight, determine the number average and weights average molecular weights; and if the above polymers are mixed so that equal number of molecules are added, determine  $\bar{M}_n$  and  $\bar{M}_w$ .

**Solution.** If equal parts of the two polymers of molecular weight  $M = 10,000$  and  $1,00,000$  are mixed

$$\begin{aligned}\text{Then } \bar{M}_n &= \frac{(10,000 \times 10) + (1,00,000 \times 1)}{1 + 10} = 18181 \approx 18,200 \\ \bar{M}_w &= \frac{10 \times 10^8 + 1 \times 10^{10}}{10^4 + 10^5} = 91819 \approx 92,000.\end{aligned}$$

3. What is the percentage of sulphur present in vulcanised rubber? (Isoprene  $M.wt = 68$ ).

**Solution.** 2 monomer units of isoprene require 2 atoms for cross links

Hence  $2 \times 68$  gm of isoprene requires  $2 \times 32$  gm of sulphur

68 gm of isoprene requires 32 gm of sulphur

The vulcanised rubber (68 + 32) contains 32 gm of sulphur

Thus, 1 gm of vulcanised rubber contains =  $\frac{32}{100}$  gm

and 100 gm of vulcanised rubber contains =  $\frac{32}{100} \times 100 = 32\%$

4. A polymer sample consists of 10% by weight of macromolecules of molecular wt 19000 and 90% by wt of macromolecules with  $M.wt$  1,00,000. Calculate the  $\bar{M}_n$  and  $\bar{M}_w$ .

**Solution.**  $\bar{M}_n = \frac{\sum NiMi}{\sum Ni} = \frac{\sum Wi}{\sum Ni}$

As given  $W_1 = 10$  gm and  $W_2 = 90$  gm

Thus,  $\sum W_1 = W_1 + W_2 = 10 + 90 = 100$  gm

Since  $Ni = \frac{Wi}{Mi}$

Hence  $N_1 = 10/10,000$  and  $N_2 = 90/1,00,000$

Therefore,  $\bar{M}_n = \frac{\sum Wi}{\sum Ni} = \frac{W_1 + W_2}{N_1 + N_2} = \frac{10 + 90}{10/10,000 + 90/1,00,000} = 5.26$

and  $\bar{M}_w = \frac{\sum NiM_i^2}{\sum NiMi} = \frac{N_1M_1^2 + N_2M_2^2}{N_1M_1 + N_2M_2} = \frac{N_1M_1^2 + N_2M_2^2}{W_1 + W_2}$

$$= \frac{10/10,000 \times (10,000)^2 + 90/1,00,000 \times (1,00,000)^2}{10 + 90} = 9.1 \times 10^4$$

5. The  $\bar{M}_n$  of a polystyrene is  $10^5$  gm/mole. Find its  $\bar{D}p_n$ .

**Solution.** As we know that  $\bar{D}p_n = \frac{\bar{M}_n}{M_o}$

