

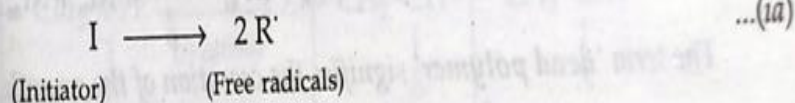
Mechanism of Polymerisation

6 MECHANISM OF ADDITION POLYMERIZATION

Polymerization reaction involve union of two or more small molecules to form a single large molecule, called *polymer*. Polymerization of ethylene and its substituted compound, $\text{CH}_2 = \text{CHX}$ can be carried out by using any of the *four* mechanisms :

(1) **Free radical polymerization mechanism** involves the following steps :

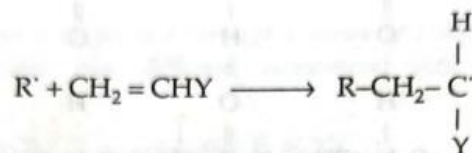
(i) **Initiation step** is considered to involve two reactions. The first is the production of free radicals, usually, by the homolytic dissociation of an initiator (or catalyst) to yield a pair of radicals R^\cdot



The second part of initiation involves the addition of this radical to the first monomer molecule (M) to produce the chain initiating species, M_1^\cdot

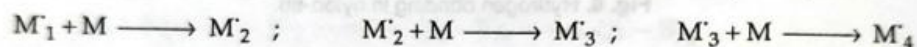


Thus, the polymerization of monomer, $\text{CH}_2 = \text{CHY}$, takes in the form :



(The radical R^\cdot is often referred as an *initiator radical* or a *primary radical*).

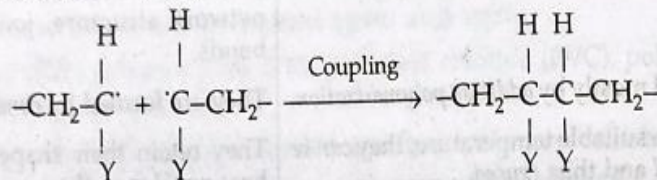
(ii) **Propagation step** consists of the growth of M_1^\cdot by successive additions of large numbers (hundreds, and perhaps, thousands) of monomer molecules according to equations :



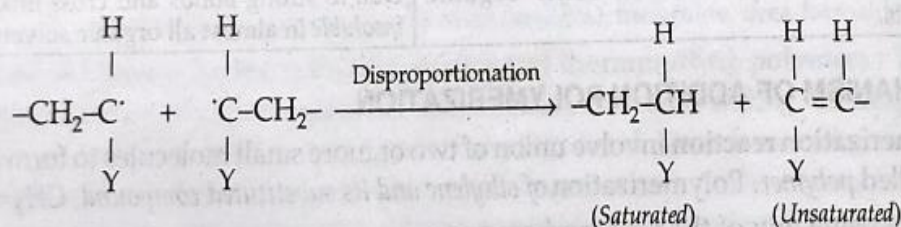
or in general terms : $\text{M}_n^\cdot + \text{M} \longrightarrow \text{M}_{n+1}^\cdot$

(iii) *Termination step* : At some point, the propagating polymer chain stops growing and terminates.

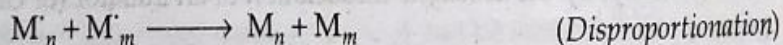
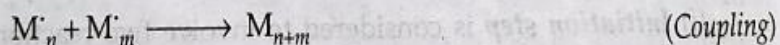
(i) By coupling or combination, e.g.,



or (ii) more rarely, by *disproportionation* in which a hydrogen atom of one radical centre is transferred to another radical centre. This results in the formation of two polymer molecules, one saturated and one unsaturated, e.g.,



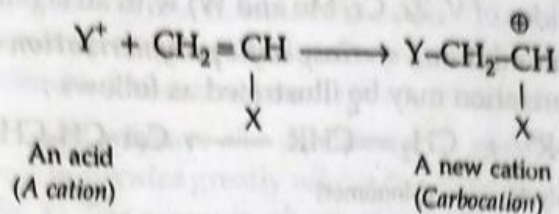
The two different modes of termination can be represented in general terms by :



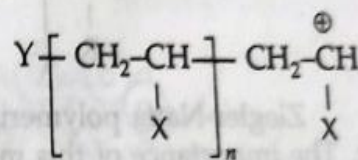
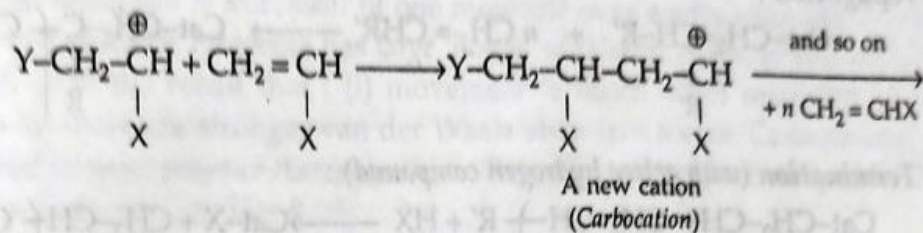
The term '*dead polymer*' signifies the cessation of the growth of the propagating radical.

(2) Cationic mechanism of polymerization involves the following steps :

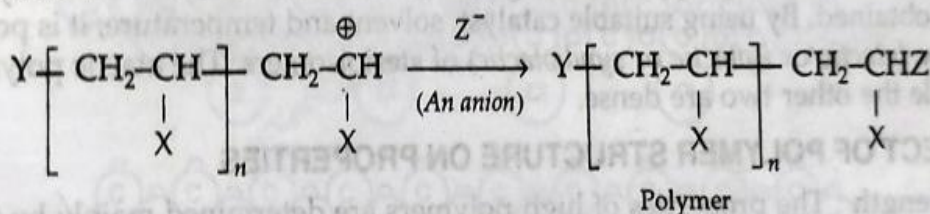
(i) **Initiation :**



(ii) **Propagation :**

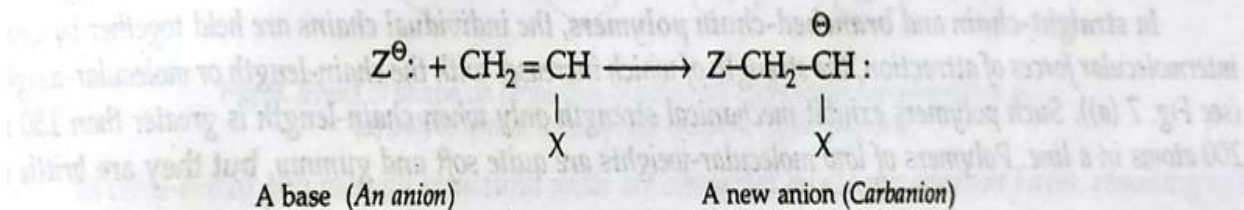


(iii) **Termination :**

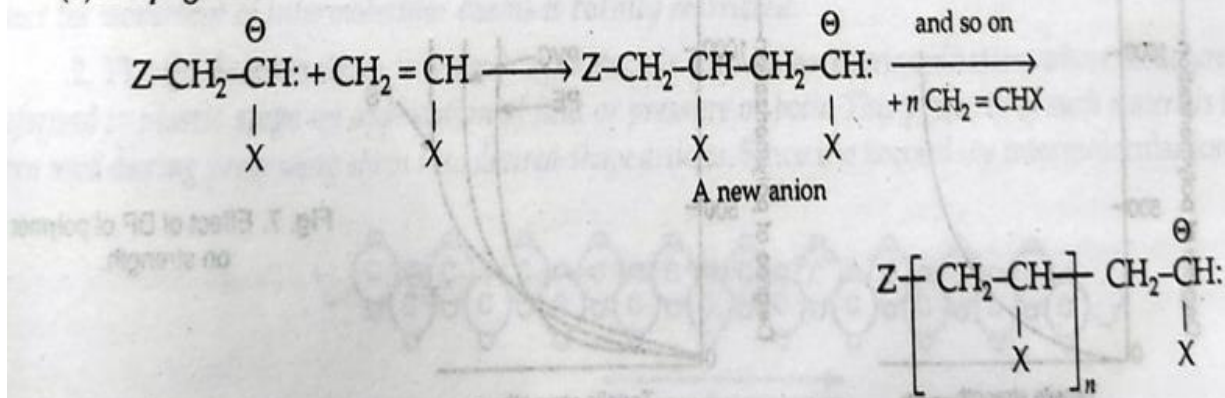


(3) **Anionic mechanism of polymerization** involves the following steps :

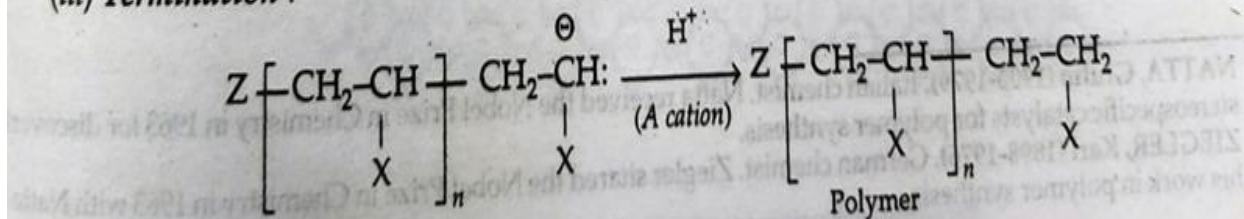
(i) **Initiation :**



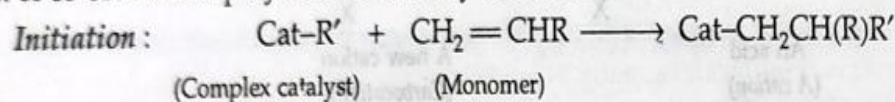
(ii) **Propagation :**



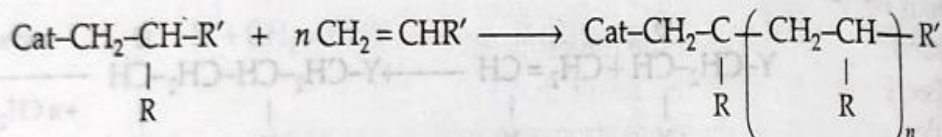
(iii) **Termination :**



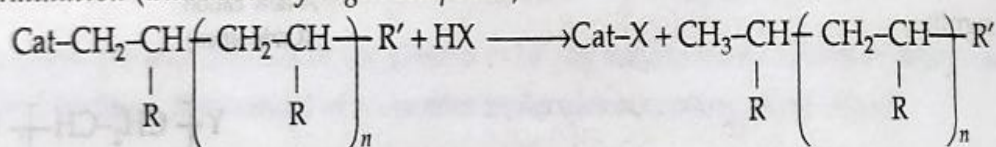
(4) Coordination polymerization or Ziegler-Natta polymerization. Ziegler (1953) and Natta (1955) discovered that in the presence of a combination of a *transition-metal halide* (like TiCl_4 or TiCl_3 , ZrBr_3 , TiCl_2 , halides of V, Zr, Cr, Mo and W) with an *organo-metallic compounds* (like triethyl aluminium, trimethyl aluminium), *stereospecific polymerization* can be carried out. Mechanism of co-ordination polymerization may be illustrated as follows :



Propagation :



Termination (with active hydrogen compound) :



Ziegler-Natta polymerization is used to prepare polypropylene, polyethylene, polydiene, etc. The importance of this method lies in the fact that *stereospecific polymers* are obtained. Thus, during polymerization of propylene, using the conventional catalysts, normally *random* or *atactic* polymer is obtained. By using suitable catalyst, solvent and temperature, it is possible to produce desired type (*atactic* or *isotactic* or *syndiotactic*) of stereoisomers. The atactic polymers are soft and elastic ; while the other two are dense.

Conductive polymers:

33. CONDUCTING POLYMERS

Most polymeric materials are poor conductor of electricity, because of the non-availability of large number of free electrons in the conduction process.

Within the past several years, polymeric materials has been synthesized which possess electrical conductivities on par with metallic conductors. Such polymers are called **conducting polymers**. Conductivities as high as $1.5 \times 10^7 \text{ ohm}^{-1} \text{ m}^{-1}$ have been attained in these polymeric materials. On a volume basis, this value is equal to *one-fourth* of the conductivity of copper, or is *twice* its conductivity on the basis of weight.

Table 6. Electrical conductivity of some polymers.

Polymers	Electrical conductivity ($\text{ohm}^{-1} \text{ m}^{-1}$)
1. Phenol formaldehyde	$10^{-9} - 10^{-10}$
2. Poly-methyl methacrylate	$< 10^{-12}$
3. Nylon 6,6	$10^{-12} - 10^{-13}$
4. Polystyrene	$< 10^{-14}$
5. Polyethylene	$10^{-15} - 10^{-17}$
6. Polytetrafluoroethylene	$< 10^{-17}$

Different types of conducting polymers are discussed below :

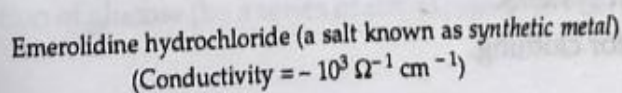
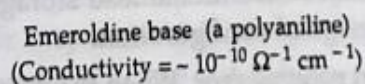
1. Intrinsically conducting polymer (ICP) or conjugated π -electrons conducting polymer
is a polymer whose backbones or associated groups consist of delocalized electron-pair or residual charge. Such polymers essentially contain conjugated π -electrons backbone, which is responsible for electrical charge. In an electric field, conjugated π -electrons of the polymer get excited, thereby can be transported through the solid polymeric material. Overlapping of orbitals (of conjugated π -electrons) over the entire backbone results in the formation of valence bands as well as conduction bands, which extends over the entire polymer molecule. Presence of conjugated π -electron in a polymer increases its conductivity to a larger extent.

Important commercially produced conducting polymers : (i) Polyacetylene polymers e.g., poly-*p*-phenylene, polyquinoline, polyphenylene-co-vinylene, poly-*m*-phenylene sulphide, etc.

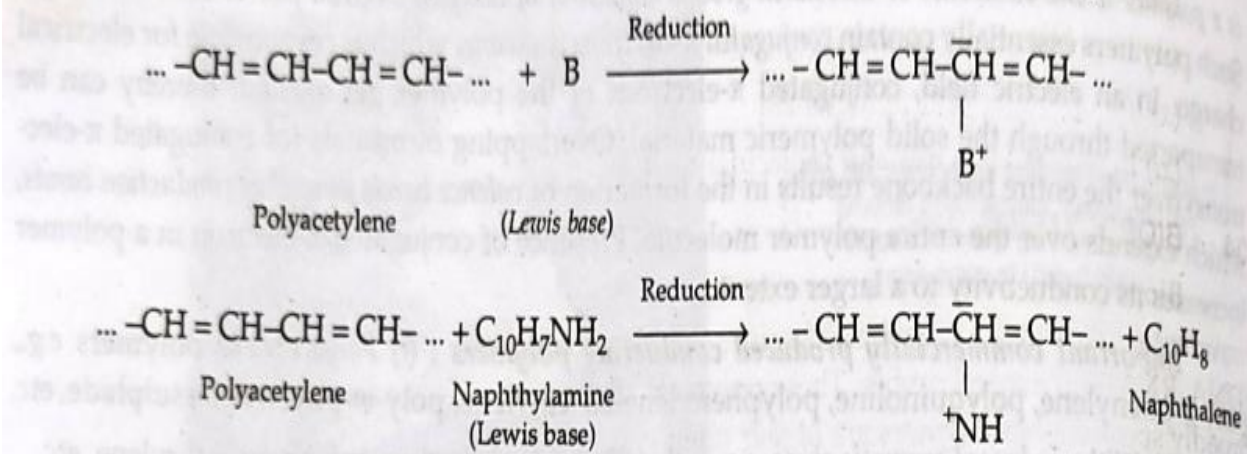
(ii) With condensed aromatic rings, e.g., polyaniline, polyanthrylene, polyphenanthrylene, etc.

(iii) With aromatic heteroaromatic and conjugated aliphatic units, e.g., polypyrrole, polythiophene, polyazomethine, polybutadienylene, etc.

(i) **P-doping** involves treating an intrinsically conducting polymer with a Lewis acid, thereby oxidation process takes place and positive charges on the polymer backbone are created. Some of the common P-dopant used are I_2 , Br_2 , AsF_5 , PF_6 , naphthylamine, etc. used For example :



(ii) **N-doping** involves treating an intrinsically conducting polymer with a Lewis base thereby reduction process takes place and negative charges on the polymer backbone are created. Some of the common N-dopant used are Li, Na, Ca, tetrabutyl ammonium, FeCl_3 , etc. For example :



3. **Extrinsically conducting polymers** are those polymers whose conductivity is due to the presence of "externally" added ingredient in them. These are of the following two types :

(i) **Conductive element-filled polymer** is a resin or polymer filled with conducting elements such as carbon black, metallic fibres, metal oxides, etc. In this, the polymer acts as the binder to hold the conducting elements together in the solid entity. These polymers possess reasonably good bulk conductivity ; and are, generally, low in cost, light in weight, mechanically durable and strong, and easily processable in different forms, shapes and sizes.

Generally, special grade conducting *carbon black* is used as a filler, due to its : (a) very high surface area (1,000 m/g), (b) high porosity, and (c) filamentous properties, Minimum concentration of conductive filler in the polymer to start the conduction process is known as *percolation threshold*.

Note : Mouldings obtained by adding even 10% of carbon black to a conducting polymer reduces drastically the tensile strength impact strength, and elongation-at-break.

(ii) **Blended conducting polymer** is product obtained by blending a conventional polymer with a conducting polymer either by physical or chemically change. Such polymers can be easily processed and possess better physical, chemical and mechanical properties.

4. Coordination conducting polymer (inorganic polymer) is a charge transfer complex containing polymer obtained by combining a metal atom with a polydentate ligand. Although the degree of polymerization in such polymers is small (≤ 18), yet they exhibit corrosion characteristics, and are usually indoubtable in most solvents.

Applications : Conducting polymers are finding increased use because they are light weight, easy to process and have good mechanical properties. Some of the important applications of conducting polymers are :

(i) In rechargeable light weight batteries based on perchlorate doped polyacetylene – lithium system. These are about 10 times lighter than conventional lead storage batteries. Such batteries are sufficiently flexible to fit a variety of designed configuration.

(ii) In optically display devices based on polythiophene. When the structure is electrically biased (1 to 3 V), the optical density of the film changes, i.e., its colour changes. Such electrochromic systems produce coloured displays with faster switching time and better viewing than conventional liquid crystal display devices (LED).

(iii) In wiring in aircrafts and aerospace components.

(iv) In telecommunication systems.

(v) In antistatic coatings for clothing.

(vi) In electromagnetic screening materials.

(vii) In electronic devices such as transistors and diodes.

(viii) In solar cells, drug delivery system for human body, etc.

(ix) In photo voltaic devices, e.g., Al/polymer/Au photovoltaic cells.

(x) In non-linear optical materials.

(xi) In molecular wires and molecular switches.

Polymer- Questions

- Q.1. Define the term polymer. Distinguish between thermoplastic and thermosetting polymers.
- Q.2. Explain with examples the process of step-growth polymerization.
- Q.3. Differentiate between homopolymer and copolymer.
- Q.4. Explain: (i) Co-polymerization (ii) Condensation polymerization with examples
- Q.5. Differentiate between addition polymerization and condensation polymerization with suitable examples.
- Q.6. Explain with examples conducting polymers.
- Q.7. Explain addition and condensation polymerization reactions. How structure of a polymer affects its properties.
- Q.8. what are polymers? Classify them on the basis of structure i.e., Linear, Branched and Crosslinked polymers. Give suitable examples.
- Q.9. Explain Atactic, Isotactic and Syndiotactic polymers.
- Q.10. explain the free radical, cationic and anionic polymerization with suitable Examples.
- Q.11. Discuss the effect of cross-linking and branching on polymer properties.
- Q.12. write short notes on the following
- (i) Crystallinity in polymers
 - (ii) Glass transition temperature (T_g)
- Q.13. Differentiate following:
- (i) Addition (Chain growth) and Condensation (step growth) polymerization.
 - (ii) Thermoplastic and Thermosetting
 - (iii) Free radical and Ionic polymerization
 - (IV) Homopolymers and Co-polymers.