



## Classification of polymers , Types and mechanism of polymerization: A Review

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**Abstract** : Polymers are high molecular weight materials / macromolecules, composed of large number of low molecular weight species. The term polymer can be defined as a macromolecule with high molecular mass arising due to the joining of a large number of simpler / smaller molecules (called monomers).

ISSN 2454-308X



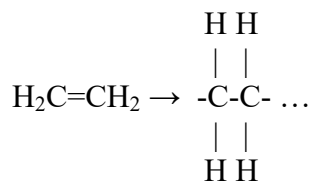
The polymers are characterized by variable molecular weight (depending on the source or mode of synthesis or extraction), low specific gravity, better resistance to erosion, corrosion, insects or fungi etc. The advantageous aspect of polymeric materials over other materials is that they can be tailor-made i.e. polymers can be synthesized as per our property requirement or soft to rigid / tough, transparent to opaque, light to heavy, crystalline to amorphous materials can be synthesized. To cite an example, there are different types of polyethylene  $\{(CH_2-CH_2)_n\}$  such as low density, medium density and high density polyethylene (abbreviated as LDPE, MDPE and HDPE). Polymers find applications as major class of materials such as plastics, fibres, rubbers, rexin (artificial leather) and explosives. Polymerization is the union of two or more simpler molecules (effected under the influence of heat, pressure, catalyst etc.), resulting in the formation of new macromolecule with the characteristic C-C linkages. The resultant macromolecule is called polymer and the original / parent simpler molecule is called monomer.

**Key Words** : Polymers, Polymerization, Step Polymerization, Chain Polymerization

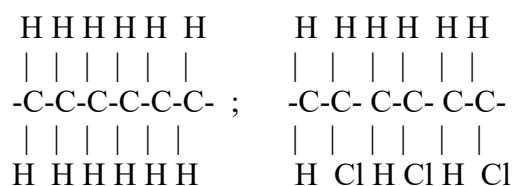
**Introduction** : The condition for a substance to be polymerized is the functionality. The functionality of a monomer is defined as the number of reactive / bonding sites available in the molecule such as carbon-carbon multiple bond, condensible functional groups such as



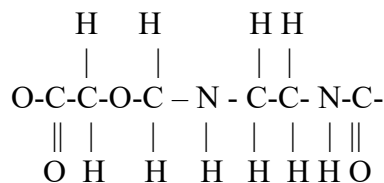
hydroxyl, carboxyl, amine, halo group etc. E.g. carbon – carbon double bond is termed as bi-functional, because when the double bond is broken, two single bonds become available for combination i.e. ethylene can be polymerized but not ethane.



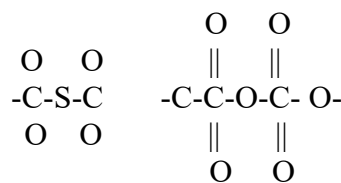
Polymers are classified based on their origin as natural and synthetic polymers. Natural polymers are the ones which are isolated from the natural sources. Cotton, silk, wool, rubber etc. belong to this type. There are also polymers modified from these natural polymers viz., cellophane, cellulose rayon, leather etc. Synthetic polymers are the polymers obtained from the low molecular weight compounds such as ethylene, phenol, formaldehyde etc. polyethylene, polyvinyl chloride (PVC), nylon, bakelite etc. are some of the synthetic polymers. Polymers are further classified as homochain and heterochain polymers based on whether the polymeric chain is made of only carbon atoms or also of heteroatoms such as oxygen, nitrogen, sulphur, silicon etc. e.g. polyethylene, Teflon, polystyrene, PVC (polyvinyl chloride) are homochain polymers since their polymeric chain is made of only carbon atoms.



Polyesters, polyamides, polysulfones, silicones are examples of heterochain polymers since their polymeric chain is also made of hetero-atoms such as oxygen, nitrogen, sulphur, silicon etc.

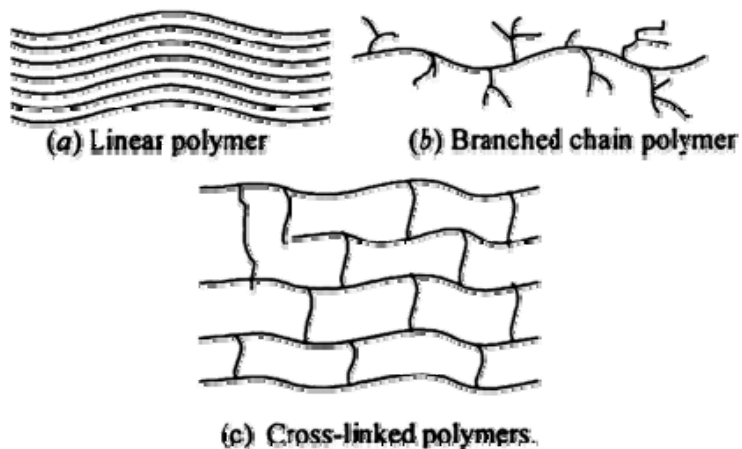


Polyamide



Polysulphone Polyester

Polymers are characterized by their variable molecular weight depending upon the source of extraction and synthetic route adopted. Synthetic polymers may be either straight chain polymers or branched chain polymers. The chain length of a polymer and the degree of polymerization are the parameters to be carefully understood in the case of a branched chain polymer. The degree of polymerization (DP) may be defined as the total number of repeating units / monomers present in the given polymer macromolecules whereas the chain length of a polymer is the number of monomer units present in the main polymeric chain.



Polymerization is classified based on (i) the mechanism of the process and (ii) practical aspects of the process. Based on the mechanism, polymerization is broadly classified into two types namely

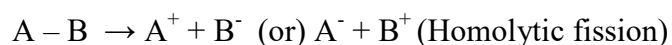
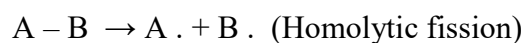
- (1) Addition or Chain polymerization and
- (2) Condensation or Step polymerization.

Based on practical considerations, polymerization is of types such as solution



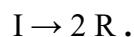
polymerization, emulsion polymerization, bulk polymerization etc.

Addition polymerization is the mechanism, which results in products, which are exact multiples of the original monomer molecule. Here, the monomer units, under the influence of heat, pressure, catalyst etc., add together with the conversion of C=C into C-C systems. Addition polymerization is also termed as chain polymerization as the reaction proceeds by chain mechanism. Some examples of addition polymers are polyethylene, polypropylene, polystyrene etc. It is obvious that any chain reaction involves three major steps namely chain initiation, chain propagation and chain termination. The chain initiation step is the decomposition of the initiator molecule to give rise to reactive species such as free radicals or cations or anion. Decomposition of initiator proceeds by homolytic or heterolytic fission. Consider the breaking of a covalent linkage between two atoms A and B. Homolytic fission of the covalent bond results in the formation of free radicals A. and B. i.e. the atoms A and B are separated with their unpaired electrons. In heterolytic fission, the covalent electron pair is transferred towards the more electronegative atom resulting in the formation of ions.



Addition or Chain polymerization is of types namely free radical polymerization, cationic polymerization and anionic polymerization based on whether the initiation of polymerization is caused by free radicals or cations or anions. Free radical polymerization is an important type, whose mechanism is discussed below:

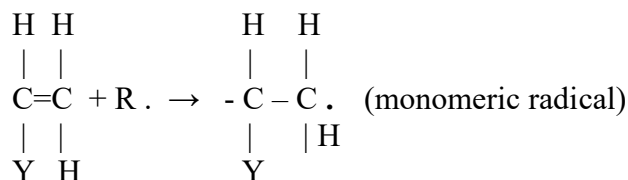
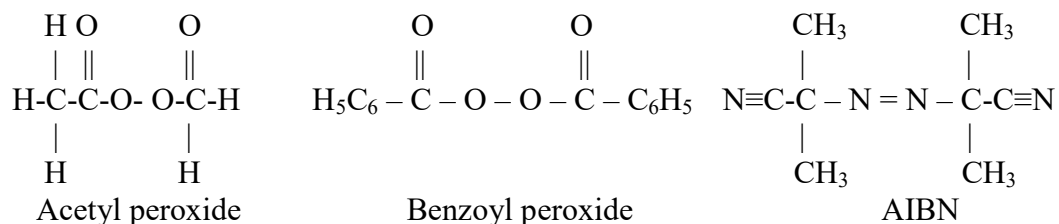
*Chain initiation:* The initiator molecule decomposes to give free radicals (highly reactive species).



Here, the initiator species has to be distinguished from the catalyst in that the initiator starts the reaction between various species whereas the catalyst just speeds up the reaction that is already taking place but slowly. Organic peroxides such as alkyl peroxides or acyl peroxides are used as initiators for polymerization e.g. acetyl peroxide -  $(CH_3CO)_2O_2$ , benzoyl peroxide



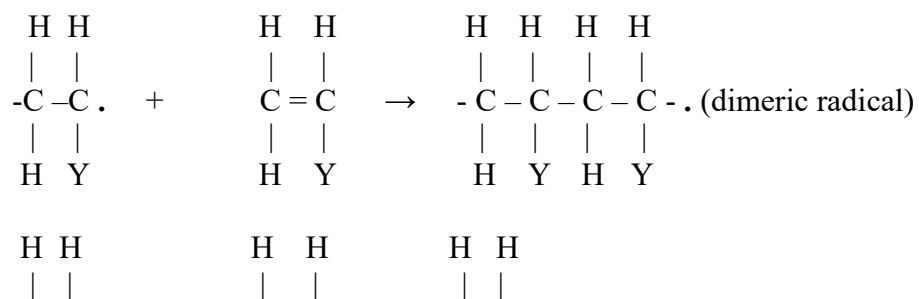
- (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>O<sub>2</sub> etc. Another important initiator used in free radical polymerization is AIBN – Azo bis (Iso Butyro Nitrile).

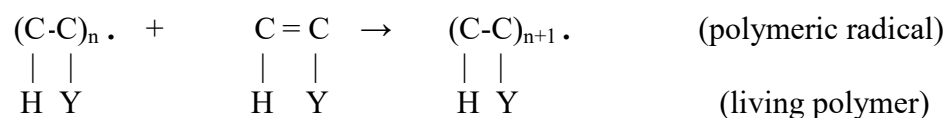


*Chain propagation:* The monomer molecule is attacked by the initiator radical to form a new reactive species monomeric radical; the monomeric radical, in turn, attacks another monomer molecule to form dimeric radical etc. this step proceeds continuously as long as polymeric radicals (reactive species) are available.

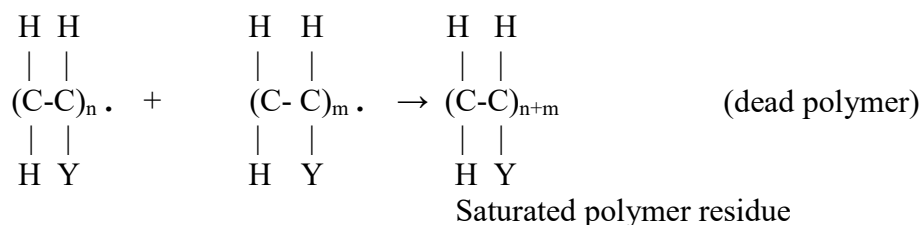


Here M<sub>n</sub> represents the polymer with degree of polymerization ‘n’. Thus, the degree of polymerization is the number of monomer units present in the polymer molecule. The polymeric radicals are also termed as living polymers as they can be further polymerized. Thus living polymers of various degrees of polymerization are formed in the chain propagation step.

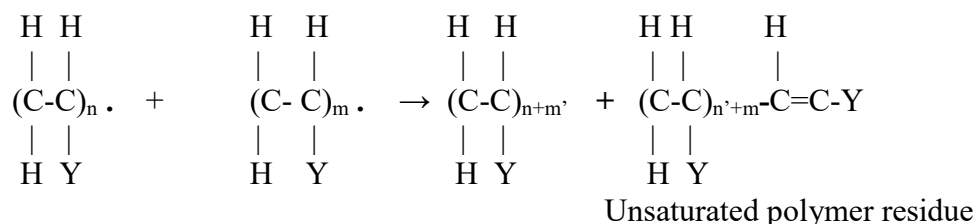




*Chain termination* involves the recombination of polymer radicals to form dead polymers, which cannot be further polymerized. Chain termination may take place either by disproportionation or by coupling process, both of which are explained below with the example of a vinyl monomer  $\text{H}_2\text{C}=\text{CHY}$  (Y is any group such as OH, X, COOH etc.).



(Recombination of polymeric radicals by coupling)



(Recombination of polymeric radicals by disproportionation)

The chain length is the number of monomers present in the main chain (carbon skeleton) of the polymer. (The term main chain signifies the chain with maximum carbon atoms, discarding the other chain branches). Another important salient feature of addition / chain polymerization is that the high molecular weight is formed at once / immediately.

Ionic polymerization is a type of chain reaction or addition polymerization involving cations or the anion intermediates as the chain initiators. The main steps are of course, chain initiation, chain propagation and chain termination. The type of polymerization reaction initiated by the proton and the chain propagated by the carbonium ion is called cationic polymerization.



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