Unit V

Polymers

Introduction Polymers form the backbone of modern civilisation are the chief products of the modern chemical industries. We know the significance of natural polymers like polysaccrides and proteins in our daily life. No less important are the man made polymers ~~are~~ or synthetic polymers too. These polymers may be synthetic rubbers for automobile tyres, synthetic fibres for clothing, plastic films for packing materials, plastic resins like bakelite for electrical switches etc, plastics for toys, kitchenware etc. These synthetic polymers have substantially replaced traditional materials such as natural fibres (say, cotton, wool etc.) natural rubber, construction material (say wood, metals, etc),

Classification Since polymers are numerous in number with different ~~bd~~ behaviours and can be naturally found or synthetically created, they can be classified in various ways. The following below are some basic ways in which we classify polymers

a) Classification based on source

i) Natural polymers : The easiest way to classify polymers is their source of origin. Natural polymers are polymers which occur in nature and are existing in natural sources like plants and animals. Some common examples are proteins (which are found in humans and animals alike), cellulose and starch (which are found in plants) or rubber (which we harvest from the latex of tropical plant).

ii) Synthetic polymers : Synthetic polymers are polymers which humans can artificially create/ synthesize in a lab. These are commercially produced by industries for human necessities.

commonly produced polymers which we use day to day are polyethylene (a mass produced plastic which we use in packaging) or nylon fibres (commonly used in our clothes, fishing nets etc.)

iii) Semi-synthetic polymers are polymers obtained by making modification in natural polymers artificially in a lab. These polymers formed by chemical reaction (in a controlled environment) and are of commercial importance, e.g. Vulcanised rubber (sulphur is used is cross bonding the polymer chains found in natural rubber) cellulose acetate (rayon) etc.

b) Classification based on structure of polymers Classification of polymers based on their structure can be of three types:

i) Linear polymers: These polymers are similar in structure to a long straight chain which identical links connected to each other. The monomers in these are linked together to form a long chain. These polymers have high melting points and are of higher density. A common example of this is PVC (polyvinyl chloride). This polymer is largely used for making electrical cables and pipes.

ii) Branch chain polymers: The structure of these polymers is like branches originating at random points from a single linear chain. Monomers join together to form a long straight chain with some branched chains of different lengths. As a result of these branches, the polymers are not closely packed together. They are of low density having low melting points. Low-density polythene (LDPE) used in plastic bags and general purpose

containers is a common example.

iii) Crosslinked or Network polymers: In this type of polymers, monomers are linked together to form a 3-D network. The monomers contain strong covalent bonds as they are composed of bi-functional and tri-functional in nature. These polymers are brittle and hard, e.g. bakelite (used in electrical insulators), melamine etc.

c) Classification based on mode of polymerisation: Polymerisation is the process by which monomer molecules are reacted together in a chemical reaction to form a polymer chain (or three-dimensional networks). Based on the type of polymerisation polymers can be classified as:

i) Addition polymers: These type of polymers are formed by the repeated addition of monomer molecules. The polymer is formed by polymerisation of monomers with double or triple bonds (unsaturated compounds). In this process, there is no elimination of small molecules like water or alcohol etc (no by-product of the process). Addition polymers always have their empirical formulas same as their monomers. e.g. ethene ($CH_2=CH_2$) to polyethene $\left(CH_2-CH_2\right)_n$.

ii) Condensation polymers: These polymers are formed by the combination of monomers, with the elimination of small molecules like water, alcohol etc.. The monomers in these types of condensation reactions are bi-functional or tri-functional in nature. A common example is the polymerisation of hexamethylenediamine ($H_2N-(CH_2)_6-NH_2$) and adipic acid ($HOOC-(CH_2)_4-COOH$) to give Nylon-66, where molecules of water are eliminated in the process.

d) Classification based on molecular forces : Intramolecular forces are the forces that hold atoms together within a molecule. In polymers, strong covalent bonds join atoms to each other in individual polymer molecules. Intermolecular forces (between the molecules) attract polymer molecules towards each other. Properties exhibited by solid materials like polymers depend largely on the strength of the forces between these molecules. Using this, polymers can be classified into four types :

i) Elastomers : Elastomers are rubber-like solid polymers, that are elastic in nature. When we say elastic, we basically mean that the polymer can be easily stretched by applying a little force.

The most common example of this can be seen in rubber bands (or hair bands). The polymers chains are held by the weakest ~~intra~~ intermolecular forces, hence allowing the polymer to be stretched. But as we notice removing that stress also results in the rubber band taking up its original form. This happens as we introduce crosslinks between the polymer chains which help it in retracting to its original position, and taking its original form. Our car tyres are made of vulcanized rubber. This is when we introduce sulphur to cross bond the polymer chains.

ii) Thermoplastics : Thermoplastics polymers are long-chain polymers in which inter-molecules forces (Van der Waal's forces) hold the polymer chains together. These polymers when heated are softened (thick fluid like) and hardened when they are allowed to cool down, forming a hard mass. They do not contain any cross bond can easily be shaped by heating and using moulds. A common example is polystyrene

iii) Thermosetting : Thermosetting plastics are polymers which are semi-fluid in nature with low molecular masses. When heated, they start cross-linking between polymer chains, hence becoming hard and infusible. They form a 3-D structure on the application of heat. This reaction is irreversible in nature. The most common example of a thermosetting polymer is that of bakelite, which is used in making electrical insulation.

iv) Fibres : In the classification of polymers, these are a class of polymers which are a thread like in nature, and can easily be woven. They have strong inter-molecules forces between the chains giving them less elasticity and high tensile strength. The intermolecular forces may be hydrogen bonds or dipole-dipole interaction. Fibres have sharp and high melting points. A common example is that of Nylon-66, which is used in carpets and apparels.

We can also classify polymers as di-block, tri-block and amphiphilic polymers

A diblock copolymer is a polymer cosisting of two types of monomers A and B. The monomers are arranged such that there is a chain of each monomer, and those two chains are grafted together to form a single copolymer chain.

Triblock copolymers have three blocks - one central block flanked by two blocks containing a different repeating unit. e.g. AAAAAAAAAA BBBBBBBBBB AAAAAAAAAA. Segmented block copolymers are comprised of many alternating small

blocks of different types of repeating unit.

Amphiphilic polymers are macromolecules that simultaneously contain hydrophobic and hydrophilic components. These molecules not only attract much attention in academic research but also are important materials in industry.

Polymerisation Reactions

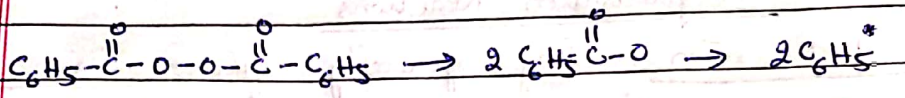
1. **Addition polymerisation** : They generally follow **Chain Mechanism**. Depending on the nature of chain-carrying species (free radicals, cations or anions) in these reactions, they have been classified as free radical addition polymerisation, cationic addition polymerisation and anionic addition polymerisation.

2. **Condensation polymerisation** : There is a wide variety of condensation reactions which have been used to initiate the formation of high polymers. These reactions generally involve the intermolecular condensation between different functional group containing molecules with the liberation of simple molecules like water, ammonia etc from the reaction molecule(s). In other words, a multistage polycondensation reactions takes place, which is composed of several separate reactions. Since no chain reaction is involved in these polycondensation reaction, only a few condensations can actually take part in such polymerisations.

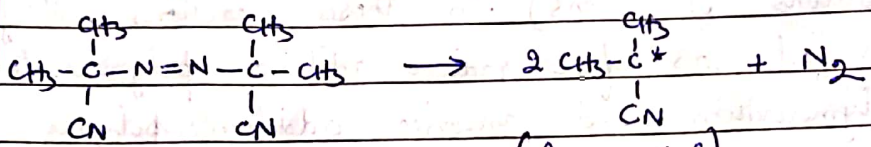
The relevent aspect of the mechanisms of these addition polymerisation reactions are summarised below

A. Free radical addition polymerisation Its free radical mechanism involves the usual three steps as shown below:

i) Initiation Radical initiators such as benzoyl peroxide, azobisisobutyronitrile, etc. generate free radicals which initiate the reactions with the vinyl monomer

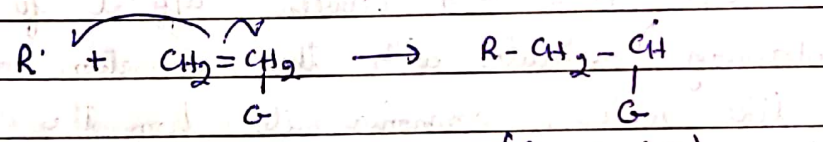


Benzoyl peroxide



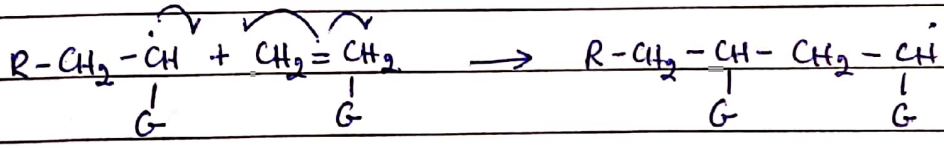
(free radical)

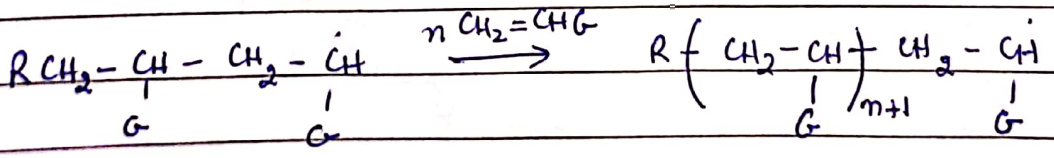
These radicals, which may be represented as R, add to a molecule of the vinyl monomer (say $CH_2=CH_2-G$) to produce another free radical



(free Radical)

ii) Propagation The radical ($R-CH_2-\dot{C}H-G$) produced in step (i) adds to another monomer molecule forming yet another radical. Successive addition of monomer to such radicals leads to the formation of long-chain radicals

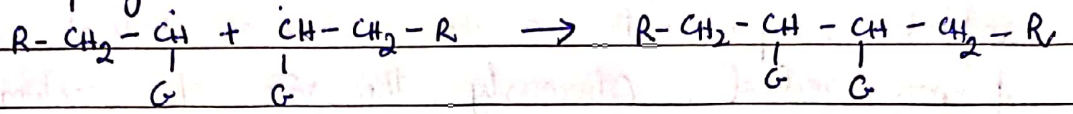




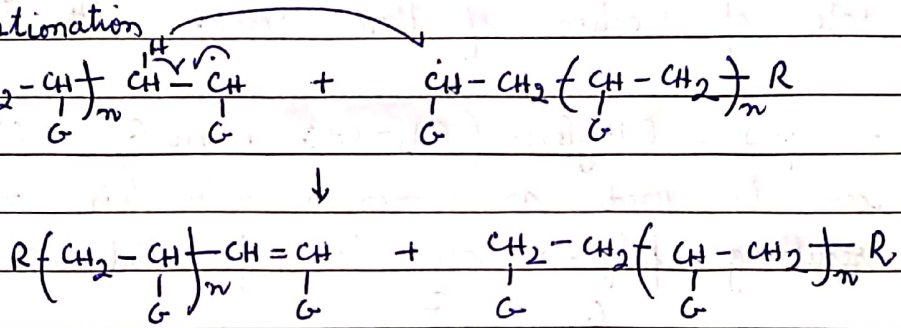
It may be noted that in this step radicals attack the monomer at the methylene group because (a) the resulting radical is the more stable secondary radical, and (b) the methylene group is sterically less hindered than the other carbon.

iii) Termination It occurs by any of the following processes:

a) Coupling

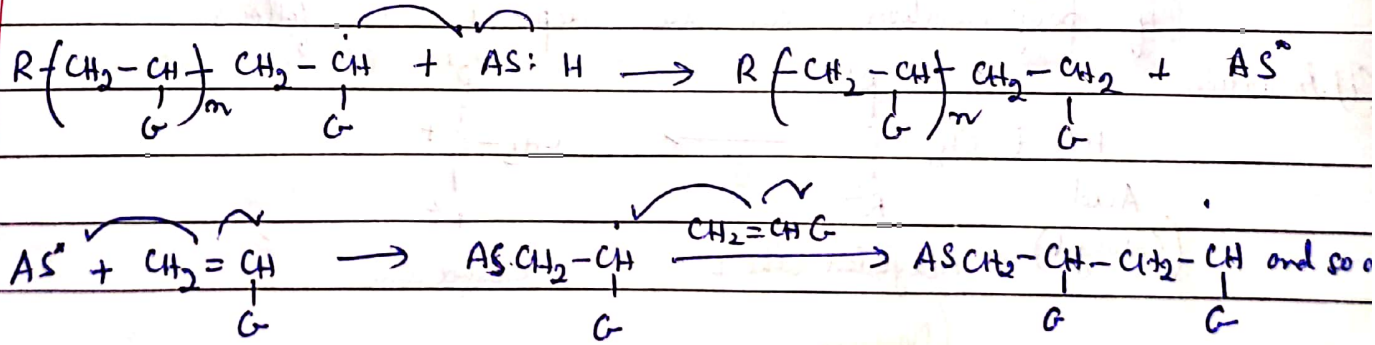


b) Disproportionation



That the presence of initiator residue (R) at chain ends in step (iii) has actually been demonstrated in a convincing evidence in support of this mechanism. The radicals actually formed in intermediate steps (i) and (ii) were also evident from E.S.R. (Electron Spin Resonance) spectroscopy.

c) Chain transfer: A growing polymer chain in step (ii) may abstract an atom from impurity ASH (say, in the monomer). This will terminate the original polymer chain although a new radical will be produced to start a new polymer chain



Role of inhibitors or retarders Substances which prevent the production of high polymers are called inhibitors, and substances which reduce the rate of polymerisation are known as retarders. Phenols are commonly used as inhibitors or retarders in such radical reactions. Phenoxy radical ($ArO^{\cdot}$) derived from phenol ($ArOH$) are highly resonance stabilised and hence too unreactive to add to the monomer to continue the chain. Such radicals couple with another inhibitor radical or a polymer radical. Obviously, the rate of reaction of these radicals with inhibitors is much greater than the rate of reaction of their reaction with the monomer.

examples : Ethylenes ($CH_2=CHG$ where $G = H, Cl, CN, C_6H_5, OCOCH_3$ etc) can be used as monomers under this reaction, and the resulting polymers can be represented as shown below

$$\left(CH_2-\underset{G}{CH}-CH_2-\underset{G}{CH}\right)_n$$

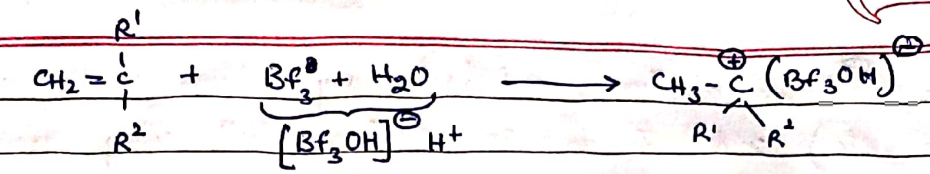
Propylene and isobutylene do not polymerise satisfactorily by free radicals mechanism. Polymers obtained by free radical mechanism are generally atactic in nature.

B. Cationic addition polymerisation : These reactions are catalysed by protonic acids such as haloacids, sulphuric acid, perchloric and lewis acids like $AlCl_3$, BF_3, $TiCl_4$ and carbocation salts. The generalised mechanism of this type of polymerisation can be depicted as follows :

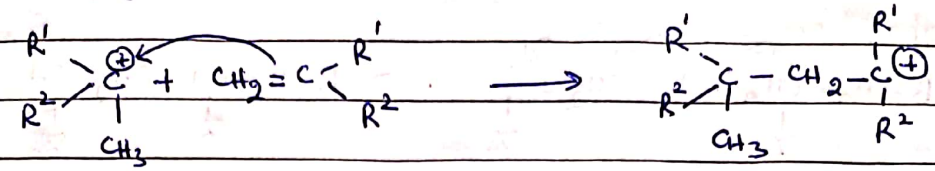
(i) Initiation

$$H^+ + CH_2=\underset{R^2}{\overset{R'}{C}} \longrightarrow CH_3-\overset{R'}{\underset{R^2}{C^+}}$$

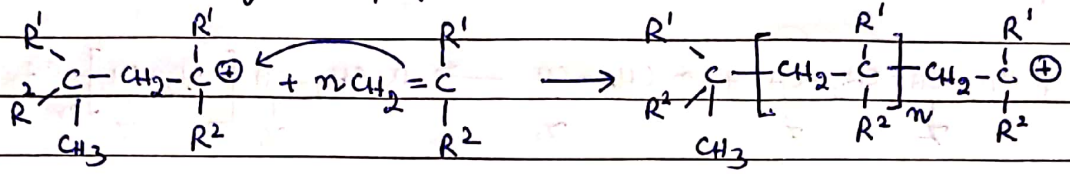
Acid (Catalyst) — Alkylated alkene (Monomer) — Carbocation



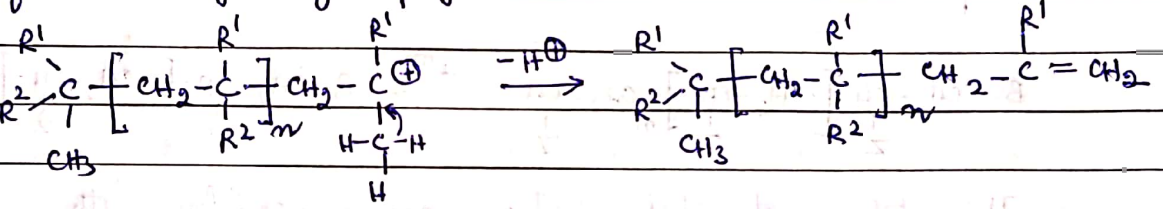
ii) Propagation :



This step repeats itself several times to continue the polymer chain and form polymer.

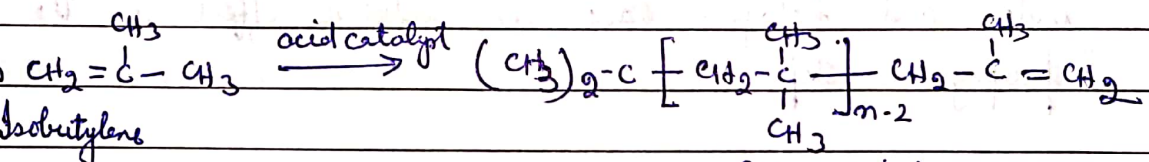


iii) Termination : It usually occurs by abstracting a proton from the growing polymerise carbocatine



$(R^2 = CH_3)$

examples : This type of polymerisation usually occurs with monomers which are alkenes containing electron-releasing substituent(s) such as alkyl groups, alkoxy groups etc. e.g.

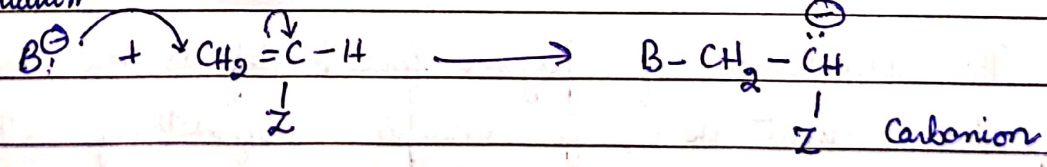


Isobutylene

Polyisobutylene

C. Anionic addition polymerisation : The generalised mechanism this reaction, catalysed by a Base $(:B^{\ominus})$ is as follows :

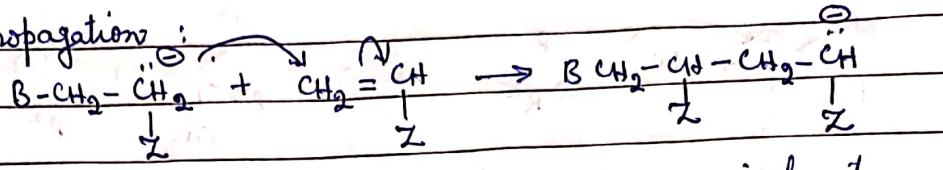
i) Initiation



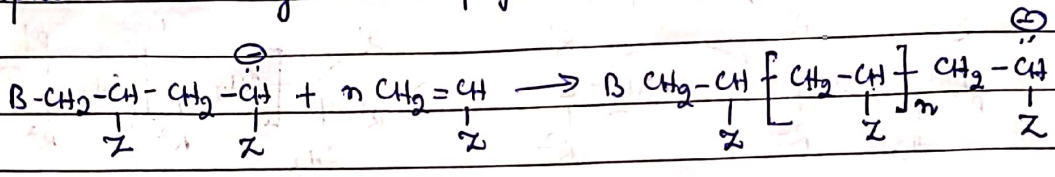
Carbanion

Where $\overset{\ominus}{B}:$ is a basic catalyst (say lithium amide, n-butyl lithium etc) and Z is an electron-withdrawing group such as $-CN$, $-C_6H_5$, $-COOR$ etc.)

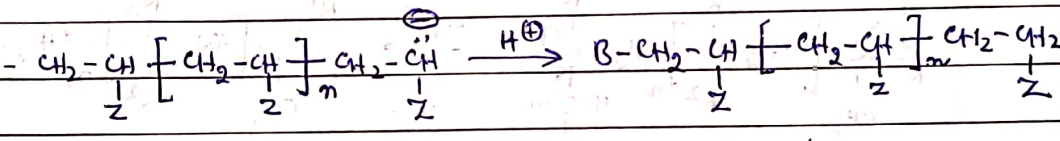
ii) Propagation :



The carbanion attacts the monomer successively to produce the long chain polymeric carbanion



iii) Termination : It usually occurs by combination with a proton some other lewis acid in the reaction mixture.



This type of polymerisation occurs readily with ethylene substituted powerful electron-withdrawing groups to facilitate the nucleophilic attack. Certain additive like ether and amines have a strong influence on the course of anionic polymerisation. The presence of oxygenated compound water and halogen have an adverse effect on the propagation step.

examples : The monomers take part in such polymerisation are usually substituted alkenes such as acrylonitrile ($CH_2=CH-CN$), stypene ($C_6H_5CH=CH_2$), methyl methacrylate ($CH_2=C(CH_3)COOCH_3$) etc.

The orientation of polymer formed depends on the nature of the solvent used, for example methyltriethoxy methyl

methacrylate forms isotactic polymer in hydrocarbon solvents and syndiotactic polymer is polar solvents at low temperatures.

Free-radical versus Ionic mechanisms: We have seen ~~above~~ above the alkene monomers can undergo addition polymerisation by chain involving free-radicals or ions (cations or anions). Nature of monomers, experimental conditions etc determine the precise mechanism followed in specific cases. Under suitable conditions, the same monomer can be made to undergo free-radical polymerisation or ionic polymerisation.

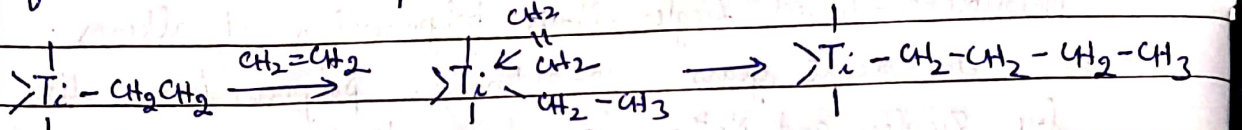
Metallocene-based Ziegler-Natta polymerisation of alkenes:

In recent years, co-ordination polymerisation, discovered by Ziegler and Natta has been finding increasing popularity over the free radical induced addition polymerisation. Here, the polymerisation is effected by using complex solid catalyst (Ziegler-Natta catalysts) consisting of transition metal chlorides (e.g. titanium chloride) and an alkyl aluminium compound (say $TiCl_4$-$AlEt_3$) in an inert solvent such as heptane. These reactions can be brought about under relatively mild conditions. Further, they lead to linear polymers with a high order of stereochemical control in the polymers produced by this process. For example, polymers commercially obtained by this method are crystalline isotactic polypropylene; 100% cis 1,4-polybutadiene (formed by 1,4-addition) and 100% cis 1,4-polyisoprene. (1,4-addition)

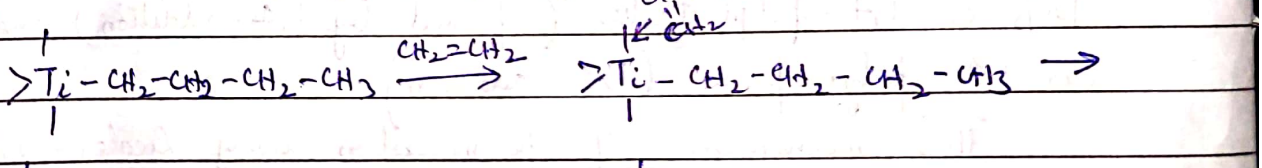
The mechanism of polymerisation using Ziegler-Natta catalyst is not fully understood as yet. However, it is believed that the transition metal compound is reduced by metal alkyls to a lower valency state which is capable of ~~coordination~~ coordinating the monomer by a π-bond or an allylic bond.

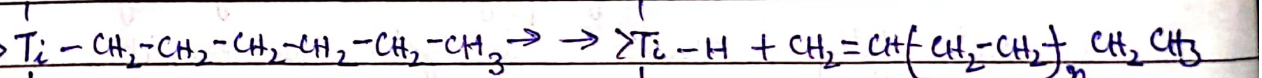
This results in the formation of a highly stereospecific polymer. The well-known polymer, polyethene, produced by Ziegler-Natta process is linear. Obviously, the Ziegler-Natta polyethene should be, and actually is, mechanically stronger than the free-radical induced polyethylene.

Mechanism: When triethylaluminium and titanium trichloride are mixed, they form a titanium complex holding an ethyl group. When an alkene, say, ethene is added to this mixture, it forms a coordination complex with the transition metal titanium by donating its π-electrons, i.e., the π-cloud of the alkene overlaps with an empty d-orbital of titanium



Now both ethyl and ethylene molecule are held by the metal, an insertion reaction occurs is which the ethylene molecule is inserted between the metal and ethyl group. In other words instead of ethyl there is now n-butyl group attached to titanium. The binding site where the ethylene was held earlier is now vacant. Another ethylene molecule gets π-bonded to the metal, and then inserts itself between the metal and the n-butyl group to form, this time, a n-hexyl group. So the process continues over and over again with the alkyl group growing two carbon atoms at a time





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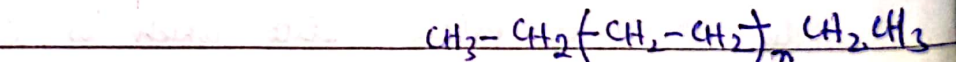

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Ultimately, insertion of hydrogen occur either by hydrogenation of or by β-elimination and the molecule of polyethene gets separated from the metal.

List of Ziegler-Natta catalysts used for preparing different polymers:

Catalyst used	Polymer formed
$R_2AlCl + TiCl_4$	Polyethylene
$R_3Al + TiCl_3$	cis-1,4- polyisoprene
$Et_3Al + TiCl_3$	Polypropylene (Isotactic)
$Et_3Al + VCl_3$	Trans-1,4- polybutadiene
$AlEt_2Cl \cdot H_2O + CoX_2$	cis-1,4- polybutadiene

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