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Unit - I

Polymerization Reaction

Polymerization Reactions — when a large number of similar or different molecules join together chemically, they produce a large molecule called polymer and the rxn is known as polymerisation.

Two types of polymerisation rxn given and described with their mechanism —

1. Addition polymerisation (chain growth polymerisation)
2. Condensation polymerisation (step growth polymerisation)

① Addition or chain growth polymerisation —

Addition type of polymerization, the molecules of the same or different monomers simply add on one another leading to the formation of a macromolecule in which the molecular formula of the repeating structural unit is the same as that of the starting monomer the polymers formed are called addition polymers.

Addition polymerisation rxn can be divided in two type depending upon the intermediates that are formed during the polymerisation.

Mechm of Chain polymerisation —

Addition polymerisation takes place either by a free radical mechm or Ionic mechm depending upon the Reagents used.

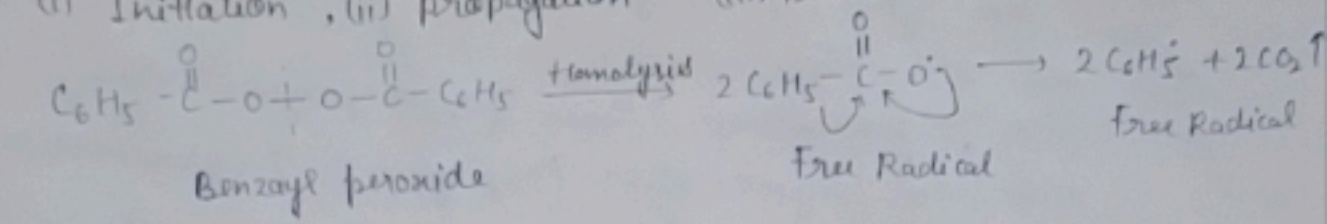
(A) Free - Radical vinyl Polymerisation -

Free - radical polymerisation is catalysed by organic peroxides or other reagents which decompose to give free radicals. addition polymers are vinyl polymers which are obtained by polymerization of alkene derivatives ($CH_2=CH-G$)

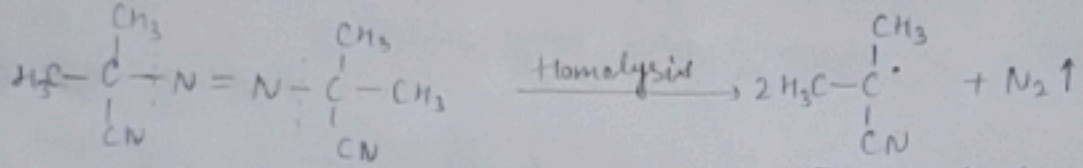
where G = H, CH_3, C_6H_5, Cl, CN, COOR etc)

This type of following three steps —

(i) Initiation, (ii) propagation (iii) termination



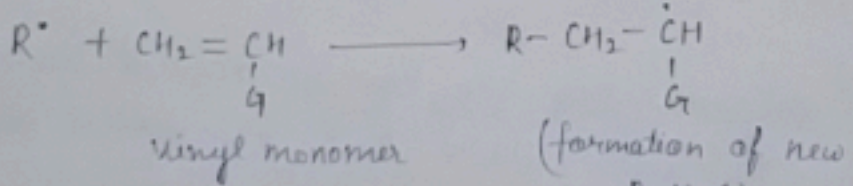
Benzoyl peroxide



Azo bis - isobutyronitrile

(I) Chain Initiation steps :—

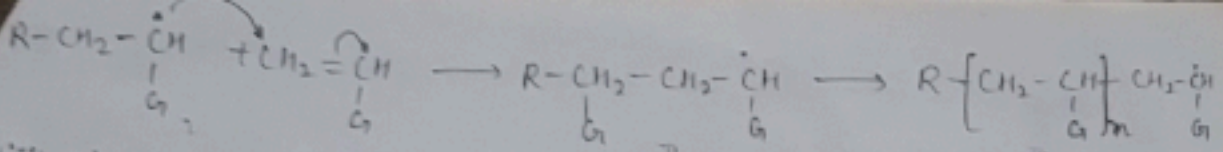
These radicals may be represented as (R) for simplification, add to a vinyl monomer ($H_2C=CH-G$) to produce another free radical.



vinyl monomer (formation of new Radical)

(ii) Chain propagation steps —

The Radical (I) produced in step (I) adds to another monomer to form yet another radical. Successive addition of monomers to such radicals leads to the formation of long chain radicals.

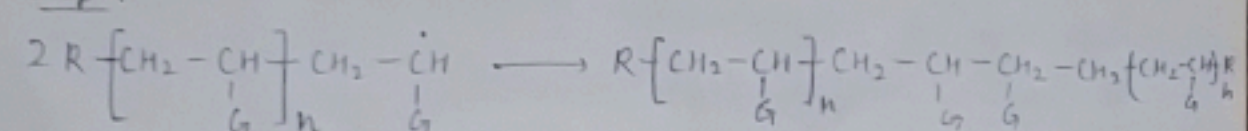


(iii) Chain Termination steps —

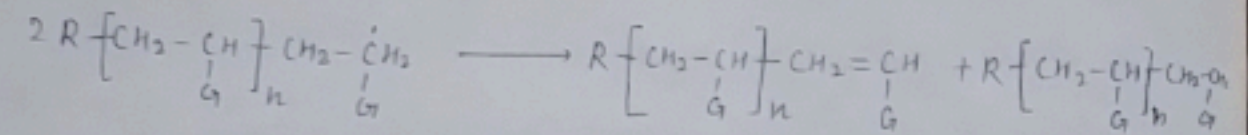
It occurs by any of the following two processes —

(a) Coupling step 1 :—

Step 1

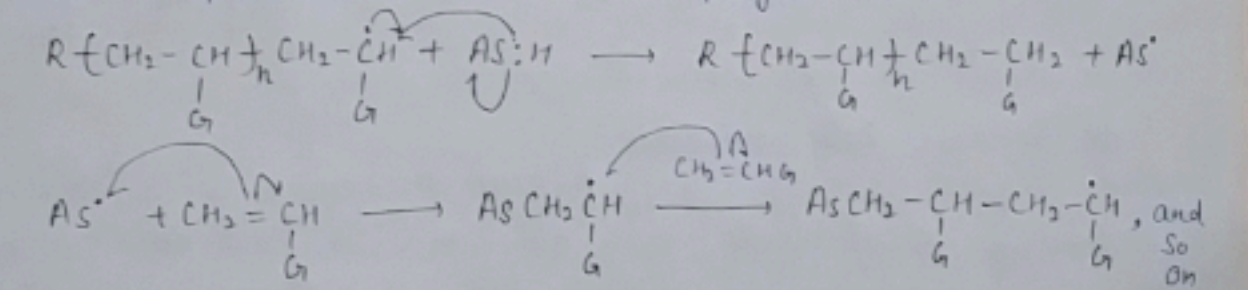


(b) Disproportionation step 2



(c) Chain transfer :—

A growing polymer chain in step (2) may also abstract an atom from some impurity ASH (monomer). This will terminate the original polymer chain, although a new radical will be produced to start a new polymer chain.



(B) Ionic vinyl polymerization —

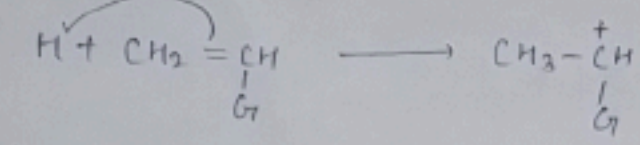
This type of vinyl polymerization proceeds through Ionic Intermediates (Carbocations or Carbanions) of free radicals. They are classified are cationic vinyl polymerization and anionic vinyl.

polymerization a/c as carbocations and carbanions respectively given below —

① Cationic addition :—

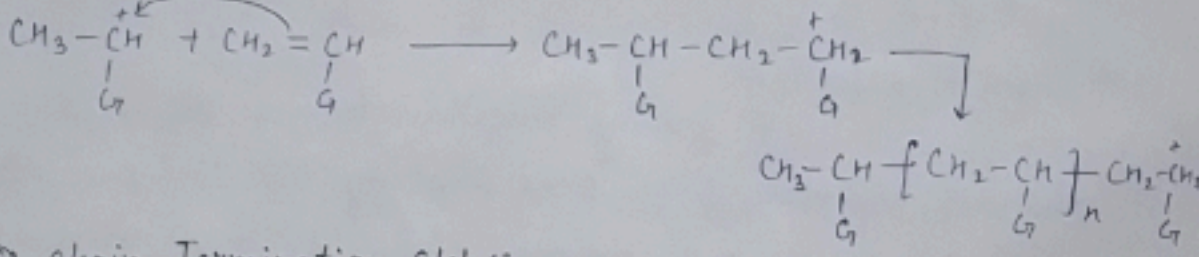
These rxn are catalysed by protonic acids such as halo acids, sulphuric acid and lewis acids like $AlCl_3$, BF_3, $TiCl_4$ and carbocation salts. The generalized mech^m of this type of polymerisation involves following steps—

ⓐ Chain initiation step—



(G = electron donating group)

ⓑ Chain propagation steps :—

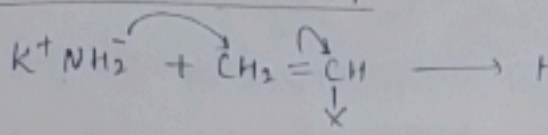


ⓒ Chain Termination steps :—

② Anionic Polymerization :—

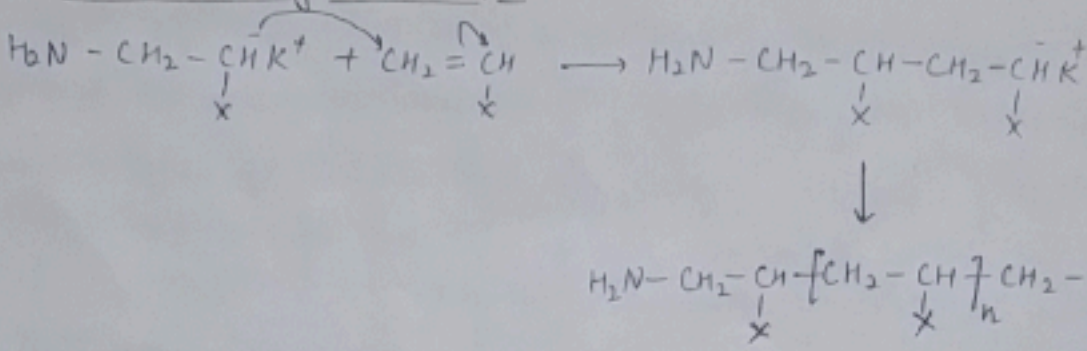
Alkene monomers with electrowithdrawing substituents such as C_6H_5, CN, COOR etc. can be polymerized by an anionic mech^m as well as by a free radical mech^m. Anionic polymerization, like free radical polymerization, occurs by a chain rxn in presence of strong bases such as Na, K, Li^+, NH_2^- etc. or organometallic compound such as n-butyllithium as initiators.

Chain Initiation steps:-

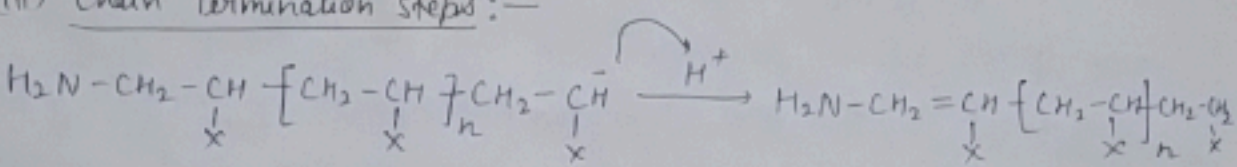


(where X = e⁻ withdrawing group)

(ii) Chain Propagation steps:-



(iii) Chain Termination steps:-



Living Polymers

The technique of emulsion polymerization applied to free-radical initiation overcomes to some degree of the problem of high termination rates which occurs when attempts are made to increase the rate of polymerization rxn by increasing the concentration of growing polymer chains.

A similar deterrent may also be effected in free-radical polymerization rxn initiated either in the gas phase or in the solid state, and in certain radical polymerization rxn which involve precipitation of the growing polymer chains in the rxn medium. For polymerization rxn initiated in the gas phase (that is, in the monomer vapor), it has been suggested that the fog formed very early in the rxn is composed of many fine droplets each containing only one active

growing chain very much like that in an emulsion polymer rxn. In a related manner, in solid-state polymerization rxn of crystalline monomers, termination is prevented by the presence of dislocations and grain boundaries within the crystals which prevent the radical endgroups of two growing polymer chains from coming into direct contact. Finally, in a precipitation polymerization, a radical endgroup can become protectively buried inside its own coiled-up polymer chain when the active polymer precipitates out of solution after reaching a certain molecular weight.

These four systems, emulsion, gas-phase, solid-state, and precipitation polymerization rxn, may, therefore, be considered to the free-radical counterparts of the living polymer polymerization rxn observed in most anionic and some cationic polymerization rxn, which have no inherent termination step. Long-lived polymer chains with active endgroups are also observed in heterogeneous polymerization rxn involving surface catalysis. In these systems, the active, growing end of the polymer chain is attached to the surface of the catalyst, and the chain will remain alive as long as it is attached. If the metal-carbon bond at the surface is not one which undergoes either a facile hydride elimination or an exchange rxn, then the active chain can have a very long lifetime.

② Condensation or step growth polymerization :-

This type of polymerization of large number of monomer molecules combine together usually with the loss of simple molecules like water, alcohol, ammonia, carbondioxide, hydrogen chloride etc. to form a macromolecule in which the molecular formula of the repeating structural unit is generally not same of the monomer. The polymers thus formed are called condensation polymers.

This process, the polymer is formed in a stepwise manner is called step growth polymer and the process is called step growth polymerization.

eg Polyester (Terylene), polyamide (Nylon 66), phenol-formaldehyde urea-formaldehyde resins, epoxy resin and poly urethanes etc.

Ring formation VS chain formation

Ring formation :-

(i) In Ring polymers, the monomer units are joined together in a cyclic structure, creating a closed loop.

(ii) This cyclic structure can lead to unique properties such as increased rigidity and decreased flexibility compared to linear chains.

(iii) Ring polymers often have higher thermal and chemical stability due to the absence of chain ends, which are vulnerable to degradation.

(iv) The synthesis of ring polymers usually requires specialized

-ed techniques such as ring-closure rxn or templat assisted polymerization.

Chain-formation:—

(i) In chain polymers, the monomer units are linked together in a linear or branched fashion, forming an extended chain.
(ii) Linear chain polymers are the most common and include materials like polyethylene, polystyrene, and polyvinyl chloride.
(iii) Branched chain polymers have side chains branching off from the main polymer backbone, altering prop^s such as crystallinity and melt viscosity.
(iv) Chain polymers typically exhibit more flexibility and can adopt various conformations depending on external conditions such as temp. and solvent.

Prop^s & Applications—

- Ring polymers tend to have higher densities and lower solubility compared to their linear counterparts.
- Due to their increased rigidity and stability, ring polymers find applications in areas such as drug delivery systems, nanotechnology, and materials science.
- Linear chain polymers are widely used in everyday materials such as plastics, fibers, coatings, and adhesives due to their versatility and processability.

Co-ordination or Zigler - Natta polymerization

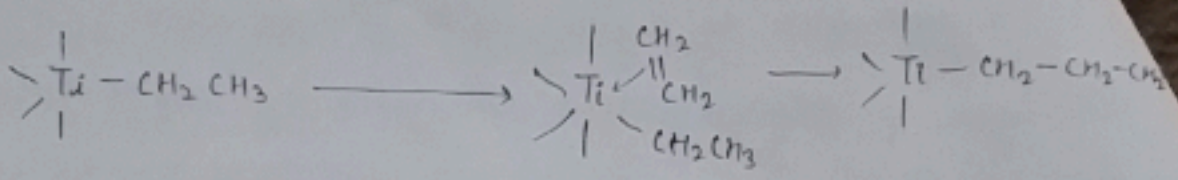
This type of polymerisation discovered by ziegler and Natta has been finding increasing popularity over the free radical induced addition polymerisation. The polymerisation is effected by using complex solid catalyst (Ziegler - Natta catalysts) which consisting of transition metal chlorides (eg. titanium chloride) and alkyl aluminium compounds [$TiCl_4 + Al(C_2H_5)_3$] in an inert solvent such as heptane.

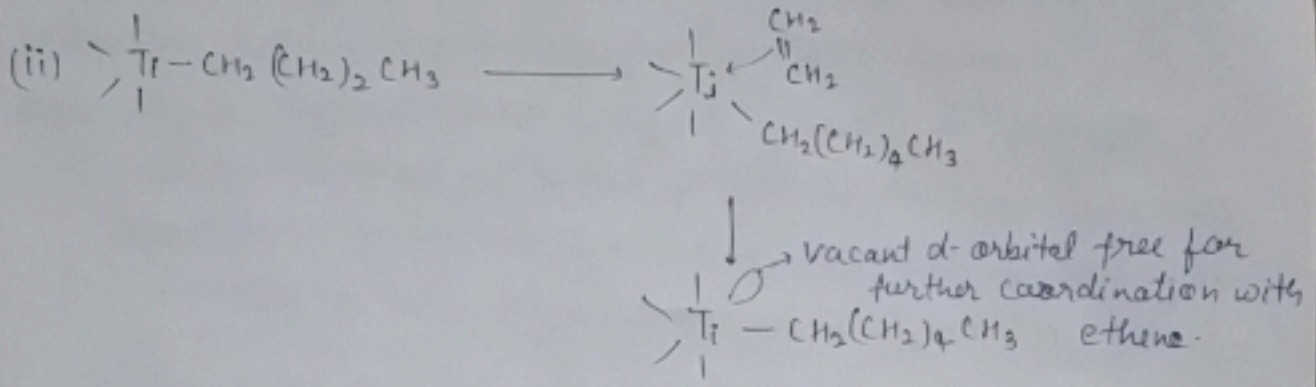
There are three main advantages of using Ziegler - Natta ~~Catalyst~~ catalysts such as —

(i) Polymerization takes place under relatively milder condition.
(ii) The polymers obtained are linear with no branching.
(iii) The polymerization occurs in a stereospecfic manner.

Mech^m —

Alkene (ethylene) attaches itself to titanium by π-bond. The π-cloud of ethylene overlaps an empty d-orbital of titanium. In next step, ethyl and ethylene both held by the metal. The ethylene unit inserts itself b/w titanium and ethyl group. In place of ethyl, there is n-butyl group attached to titanium. The bonding site ethylene was held is vacant again. The catalyst is ready to work again to repeat the entire process. This results to a highly stereospecific polymer. The well known polymer, polyethylene produced by Ziegler - Natta process is linear and mechanically stronger than free radical induced polyethylene. The mech^m follows following steps —

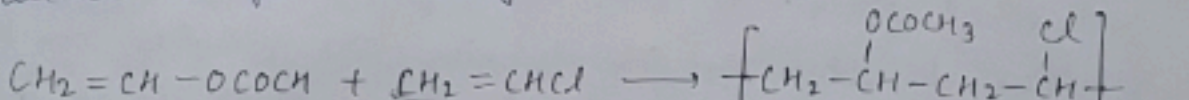
(i) 

(ii) 

Copolymerisation

Polymerisation of a single monomeric compound to form a homopolymer is known as homopolymerisation. Such a polymer is made up of identical units. polypropylene, polyisoprene, polyethylene etc.

In contrast, a copolymer results when two different kinds of monomers are polymerised together to give a product containing both the monomers. Such a process, known as copolymerisation, is of great importance as it allows to form a polymer possessing desired properties.



To a certain extent composition of a copolymer can be controlled by varying the proportions of the monomer in the polymerisation mixture. However, the composition of the polymer depends not only on the relative conch of the two monomers but also on the relative reactivities

of the monomers towards free radical addition.

In Copolymers the two monomers may be arranged in either of the following four way as shown –

A – A – B – A – B – B – A – B – A – A – A – B –

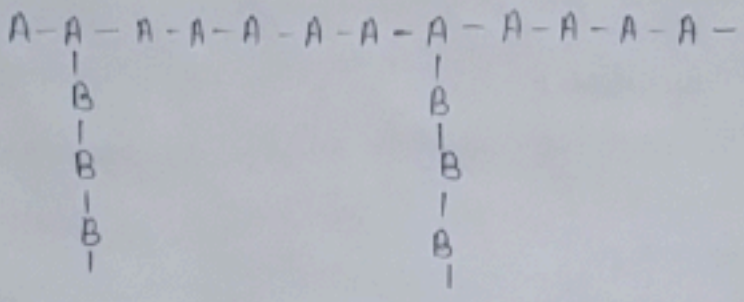
(a) Ramdom copolymer

A – B – A – B – A – B – A – B –

(b) Alternating copolymer

A – A – A – A – B – B – B – B – A – A – A – A – B – B – B – B –

(c) Block copolymer



(d) Graft copolymer

Three dimensional Network polymerisation

or

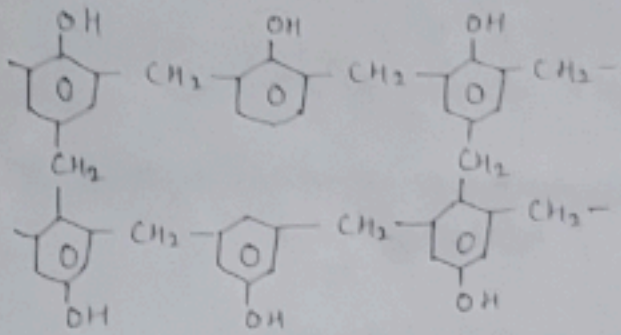
Cross linked Polymer

Cross linked polymer – They have long straight chain with different branched side chains. molecules are irregularly packed. eg. polyethylene HDPE High density polymer
LDPE Low density polymer.

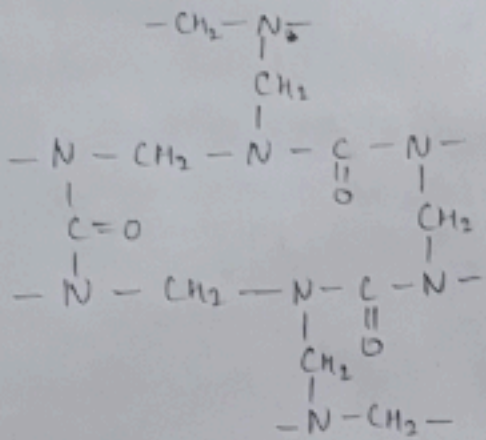
Network polymers :– Network polymers have trifunctional monomeric units that are formed by many interconnected polymer

chains. They are giant molecules in which movement of individual monomeric unit is prevented by strong cross linked. It is having three active covalent bonds. It should be in three dimensional network. Eg -

Bakelite, urea formaldehyde, melamine formaldehyde etc.



(Bakelite)



Urea formaldehyde Resin