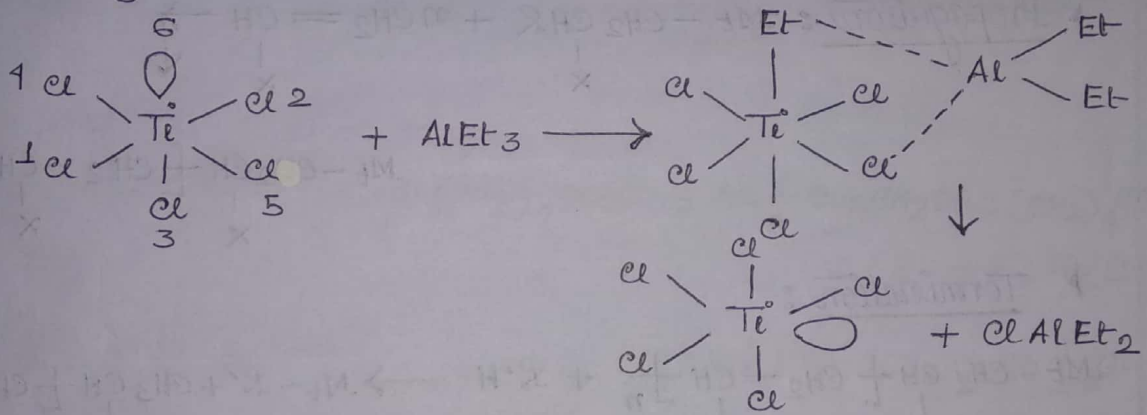
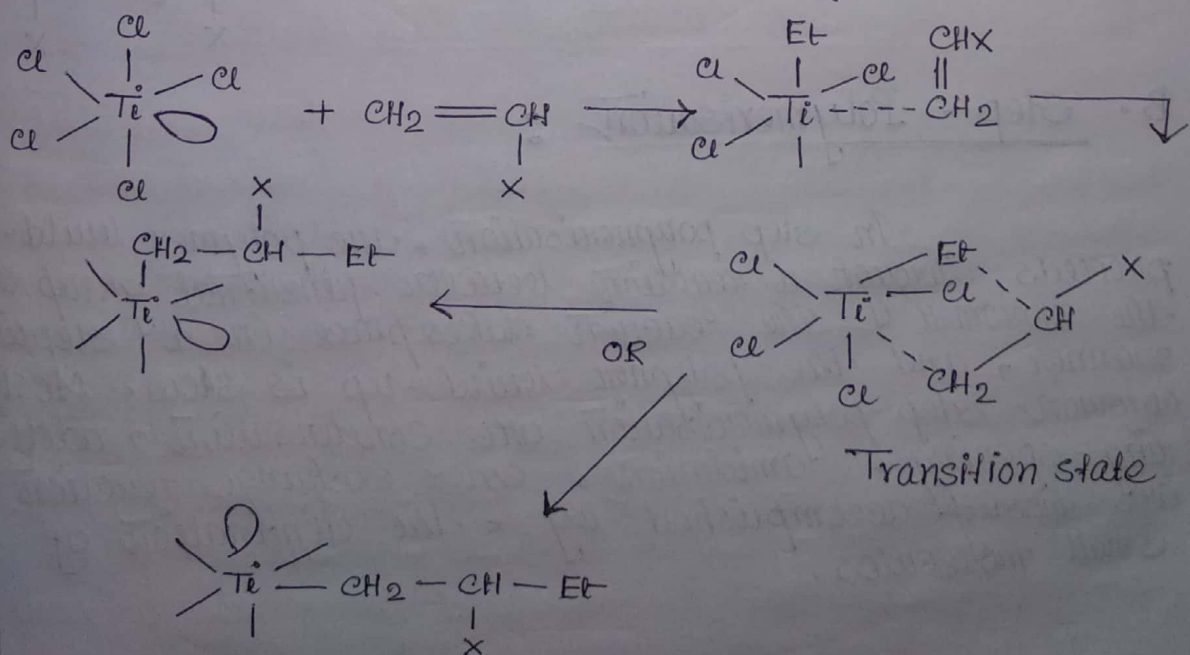


▶ Mono-metallic mechanism:

In case of mono-metallic mechanism, the active centre is at Ti-R part of the catalyst, while the Al-alkyl part performs only the function of alkylating the TiCl_3 .

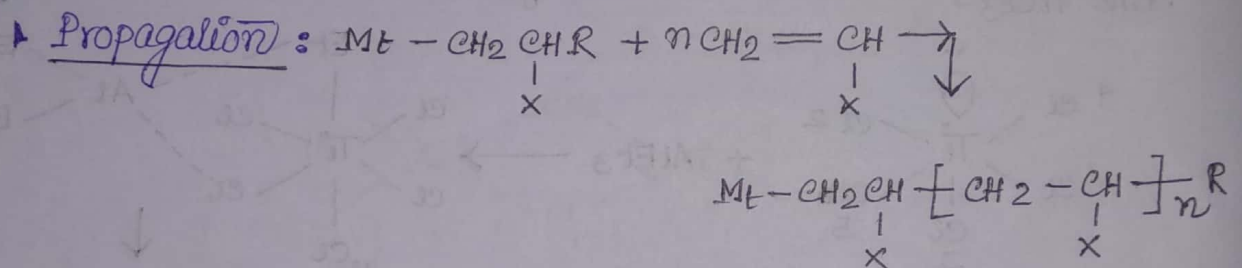
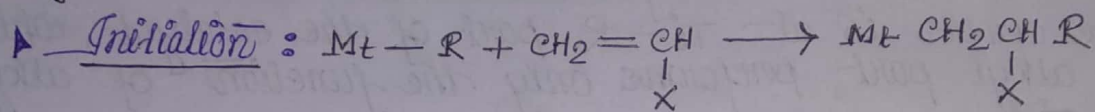


(The Cl at 1 & 2 are assume to be attached to another Ti in the crystal lattice of TiCl_3 . Except the Cl at 5 which can be replaced by an alkyl group, all the other four Cl are non-exchangeable.)

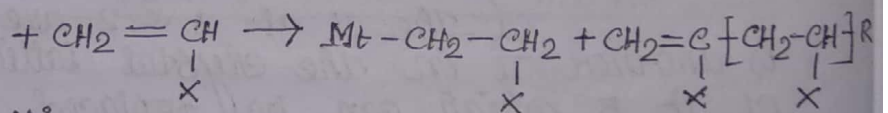
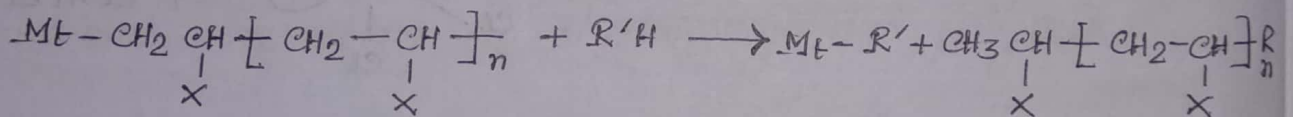


▶ N.B.: If the vacant d-orbital is regenerated at the same position all the time, the incoming monomer unit will be inserted with the same spatial arrangement, resulting in the formation of isotactic polymer. On the other hand, if the d-orbital migrates from one position to other alternately the monomer get inserted with alternating space spatial arrangement, resulting in the formation of a syndiotactic polymer.

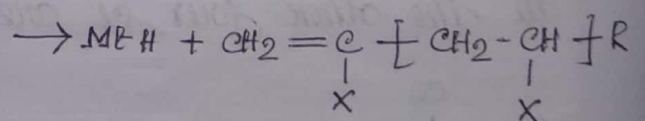
Whatever be the mechanism, the overall polymerisation can be represented as,



▶ Termination:



($Mt = Ti, Mo, Cr, V, Ni,$
Rh)

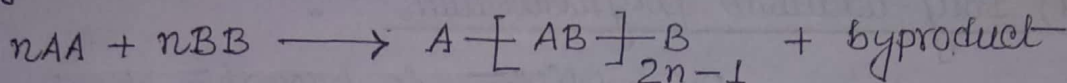


B. Step - Polymerisation :

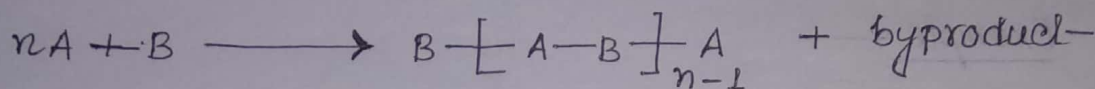
In step polymerisation, the polymer build-up proceeds through a reaction between functional group of the monomer. The reaction takes place in a stepwise manner, and the polymer build-up is slow. Most common step polymerisation are condensation, addition ring-opening, amidation, ester exchange reaction and are mostly accomplished by the elimination of small molecules.

i) Poly-condensation Polymerisation :

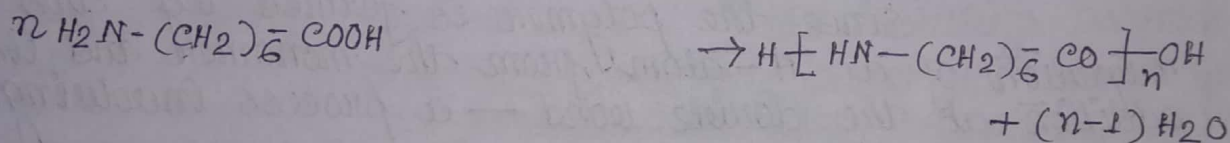
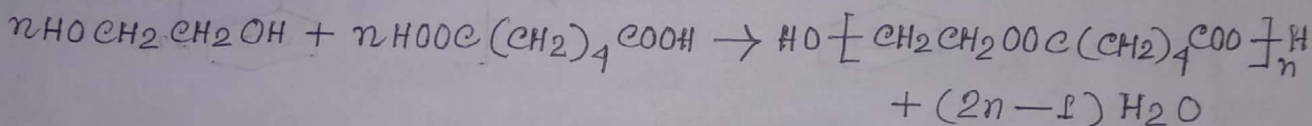
Poly-condensation is brought about by monomers containing two or more reactive functional groups condensing with each-other. When a pair of bifunctional monomers (such as dicarboxylic acid/dialcohol, dicarboxylic acid/di-amines or di-alcohol/di-halide) undergoes polycondensation, it is usually describes as an $AA-BB$ type poly-condensation.



When a single bifunctional monomer undergoes self-condensation, it is describes as $A-B$ type.

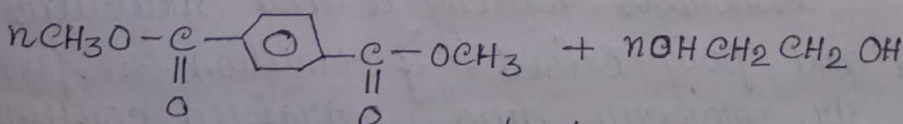


▶ Examples :



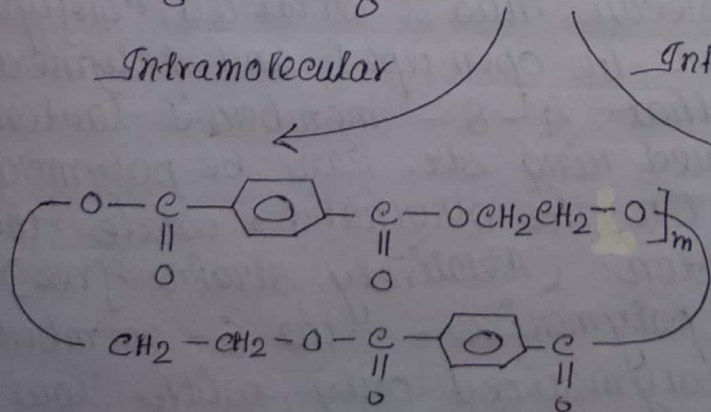
[See more example from condensation polymerisation]

If in both the $AA-BB$ and $A-B$ types, intramolecular condensation occurs, low M.W cyclic products will be formed.

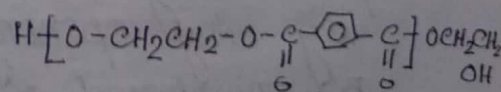


Intramolecular

Intermolecular



cyclic product
 $m = 2, 3 \text{ or } 4$



Required product
PETP

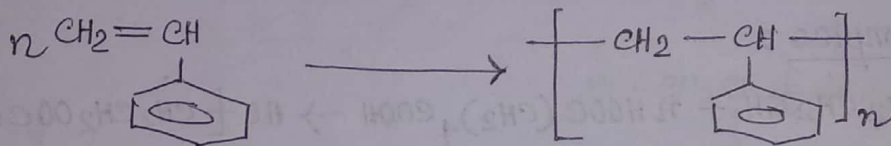
Polyethylene terephthalate

In AA-BB type, if one of the monomer is trifunctional the polymer develops a three-dimensional network. For example glycerol reacts with dibasic acid to give a complex str. When the three-dimensional network is just about to be formed, the whole polymer becomes an infusible & insoluble mass and this is call 'Gel'.

ii) Poly-addition polymerisation :

Polyaddition is brought about by the migration of atoms from one monomer to another, or to the intermediate product.

Example —

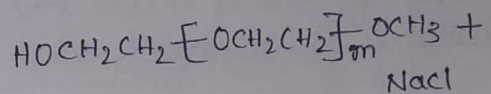
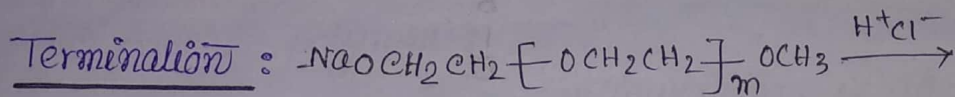
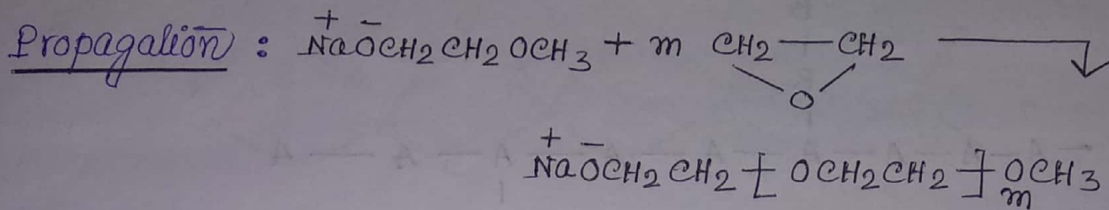
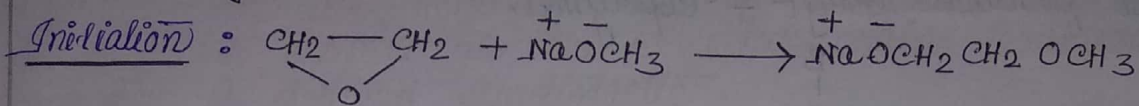


Since the polymer is formed by the migration of a H-atom from the monomer and its addition at the double bond — a process involving higher activation energy as compared to the free radical or ionic process — the polymer growth is rather gradual and step by step. The intermediate products are quite stable and can be isolated.

iii) Ring-Opening polymerisation :

Monomers having a ring structure can be opened and polymerised, if condition are favourable. When a ring str. molecule has a strained configuration, the same can be opened and polymerized. It may be noted that 4-8-membered lactones, possessing a strained ring str. can be polymerized by ring opening. On the otherhand, while the 5-membered γ -lacton (Relatively strain free) is rather difficult to polymerize, the 6-member δ -lacton can be polymerized only with low yield.

The mechanism of ring opening polymerization of oxirane system is shown below

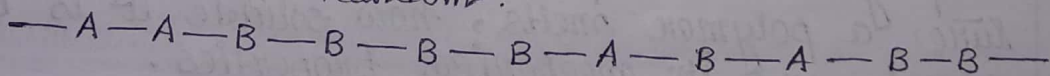


► Copolymers :

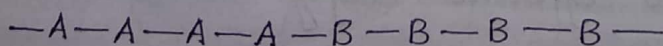
Polymers with two different repeating units in their chains, are called copolymers. When there are three chemically different units, the resulting polymer is termed a 'terpolymers'. Monomer placement may be totally random or perfectly alternating depending on their relative reactivities. Different types of copolymers are shown below

① Random copolymer :

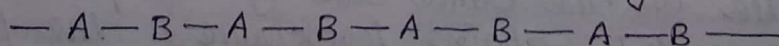
Placement of monomers A and B are random.



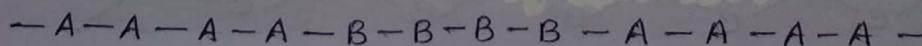
② AB-Block copolymer : It contains a long block of one monomer (A) followed by a block of other monomer (B)



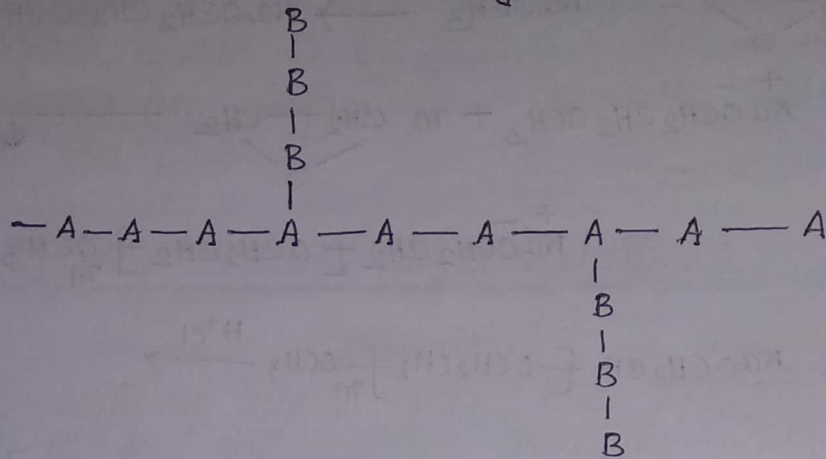
③ Alternating copolymer : It contains monomer A and B in alternating sequence.



④ ABA-Triblock copolymer : These copolymers have a central B-block joined by A-blocks at the end.



② Graft Copolymer : When a monomer is polymerized in the presence of a fully-formed polymer of another monomer, it produces Graft-copolymer.



▶ Tacticity : 'Tacticity' means arrangement or order. Tacticity is the stereochemical arrangement of the pendant groups (units) along the backbone chain of a polymer. In other words, it is the relative stereochemistry of adjacent chiral centres within a macromolecules.

The practical significance of tacticity rests on the effects on the physical properties of the polymer. The regularity of the macromolecular str. influences the degree to which it has rigid, crystalline long-range order or flexible, amorphous long-range disorder. Precise knowledge of tacticity of a polymer also helps understanding at what temperature a polymer melts, how soluble it is in a solvent and its mechanical properties.

The placements of the asymmetric group, are R (-CH₃, -Cl, -Ph) etc may be different kinds and therefore give rise to different configurations

③ Isotactic polymer :

In a configuration, if all the 'R' groups lie on the same side of the plane formed by the extended-chain backbone, the polymer is termed isotactic.

