

Dr. Kalpana Singh

Topic- Synthetic polymers

Associate Professor

Sub topic- Addition polymer

Department of Chemistry

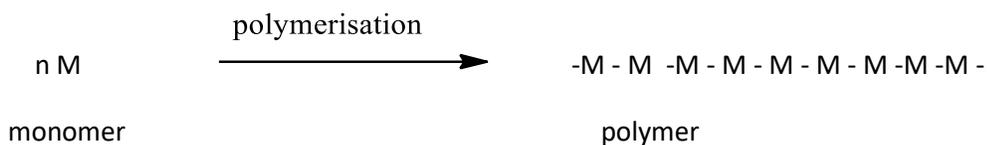
Shri J. N. P. G. College , Lucknow

Organic Chemistry - Paper 7 unit iv

B.Sc. V Semester

SYNTHETIC POLYMERS

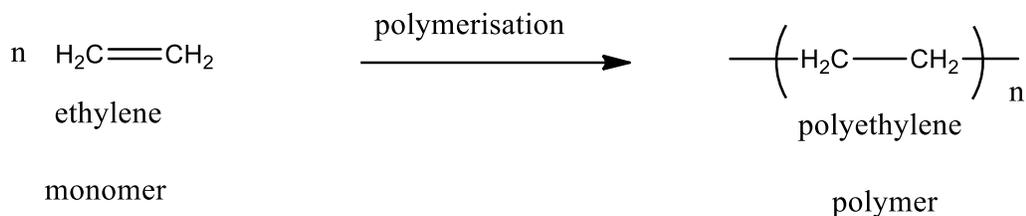
Polymer - a polymer is a large molecule made by covalently linking repeating units of small molecules called monomers. The process by which these simple molecules are converted into polymers is called **polymerization**.



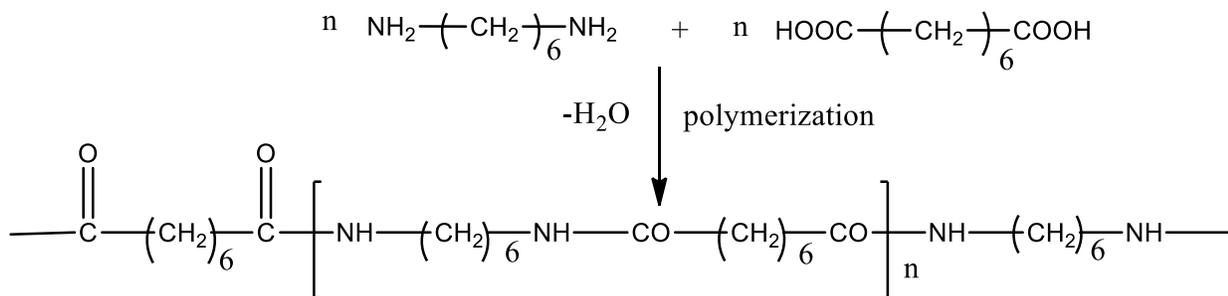
Classification of polymers based on

- *nature of repeating structural unit*

(i) **Homopolymer** - polymers that are formed from only one type of monomers.



(ii) **Copolymer**- polymers that are formed from two or more different monomers.



- *source of origin*

(i) biopolymers -biopolymers are synthesized by cells. examples -DNA , RNA, and polysaccharide

(ii) synthetic polymers - are synthesized by scientist
synthetic polymers can be divided into two classes

(a) chain growth polymers also known as addition polymers

(b)step growth polymers also known as condensation polymers

Chain growth polymers-

The most commonly used monomers in chain growth polymerization are ethylene and substituted ethylene ($\text{CH}_2=\text{CHR}$). Polymers formed from ethylene or substituted ethylene are called vinyl polymers. Chain growth polymerization take place by one of the three mechanism;

(i) radical polymerization

(ii) cationic polymerization

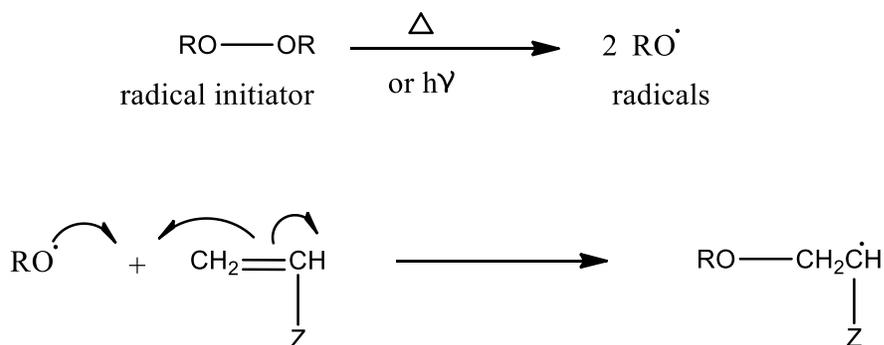
(iii) anionic polymerization

Each mechanism has an initiation step that starts the polymerization, propagation step that allow the chain to grow at propagating site and termination step that stop the growth of the chain. The choice of the mechanism depends on the structure of the monomer and the initiator used to activate the monomer.

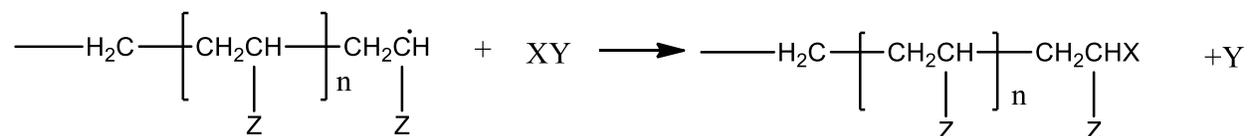
Radical polymerization

In this polymerization the initiator is a radical. In the initiation step radical initiator breaks homolytically into radicals and each of these radicals can react with a monomer.

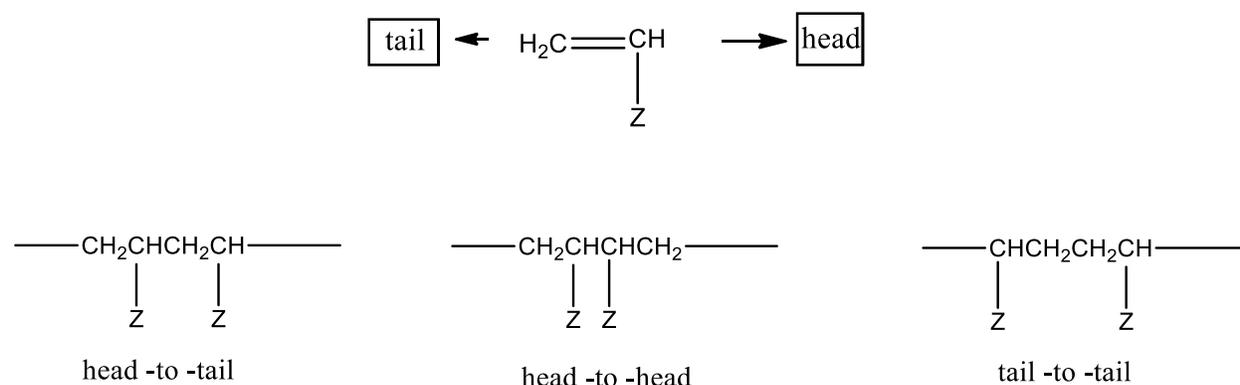
initiation step



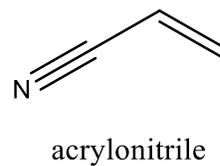
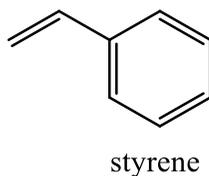
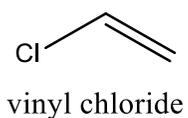
The molecular weight of the polymer can be controlled by the process known as **chain transfer**. In chain transfer, the growing chain reacts with a molecule XY in a manner that allows X to terminate the chain, leaving behind Y to initiate a new chain. Molecule XY can be a solvent, a radical initiator, or any molecule with a bond that can readily be cleaved homolytically.



Chain growth polymerization exhibit a preference for **head -to -tail** addition .



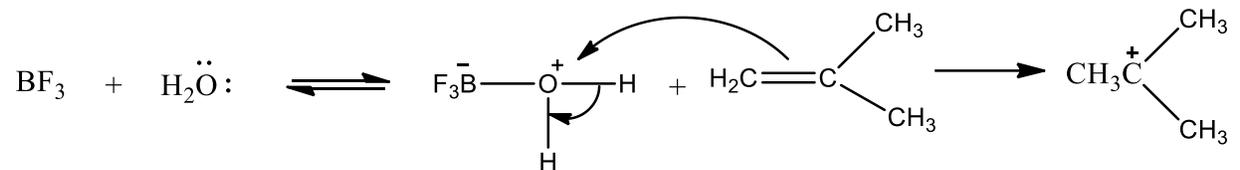
Monomers in which Z is either an electron withdrawing group or a group able to stabilize the growing radical species by electron delocalisation, undergo chain growth polymerization by radical mechanism.



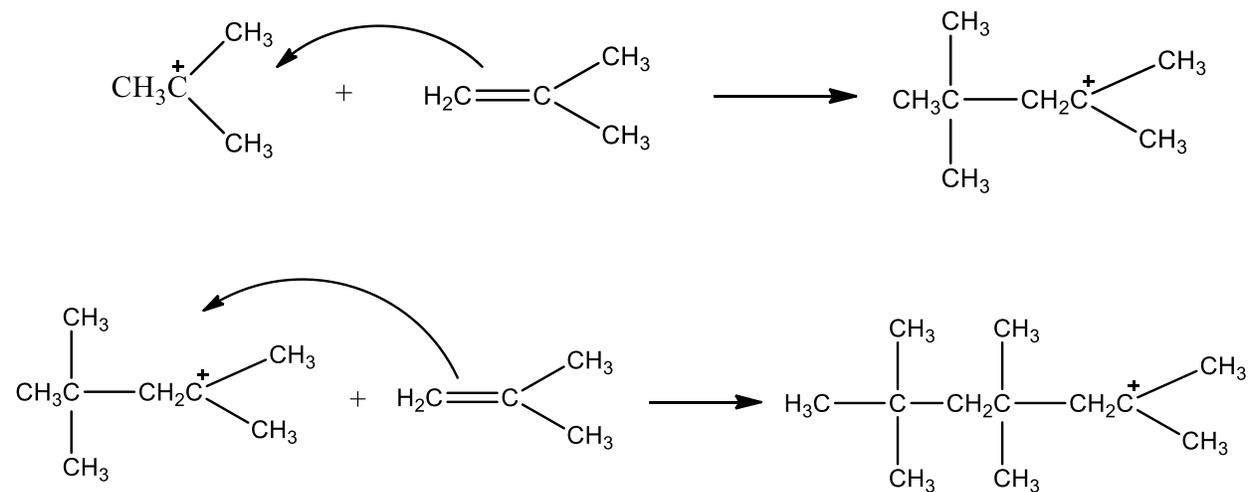
Cationic polymerization

- In this polymerization the initiator is an electrophile and propagation site is a cation. The initiator most often used is a Lewis acid, such as BF_3 together with a proton donating Lewis base such as water.

initiation step



propagation step

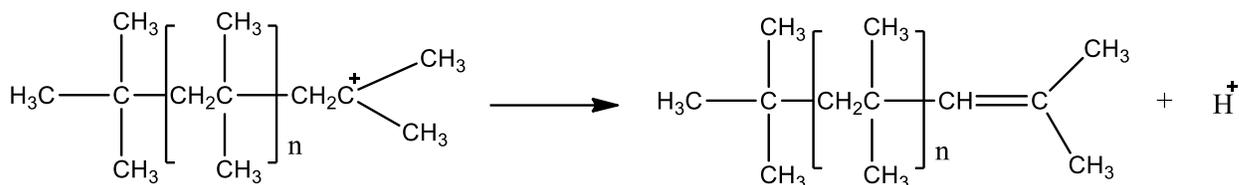


chain termination

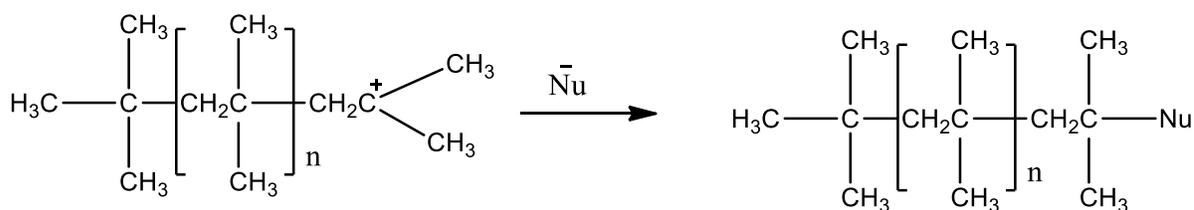
cationic polymerization is terminated by

- loss of proton
- addition of a nucleophile to the propagating site
- a chain-transfer reaction

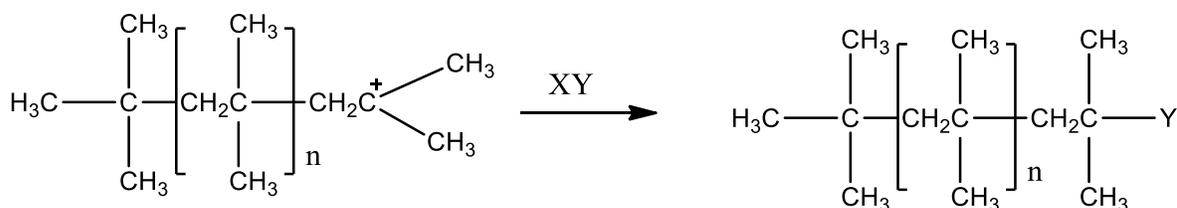
loss of proton



reaction with a nucleophile

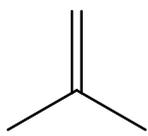


chain- transfer reaction

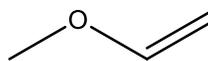


monomers with the substituent that can stabilize the positive charge at the propagating site either by hyperconjugation or by donating electron by resonance, undergo polymerization by cationic mechanism.

example-



isobutylene

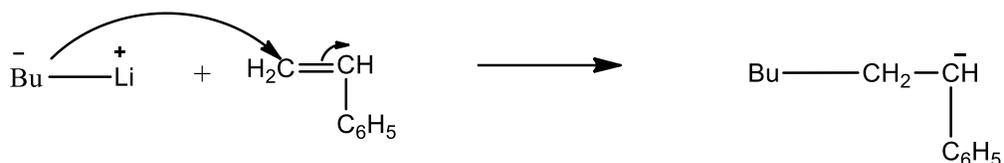


methyl vinyl ether

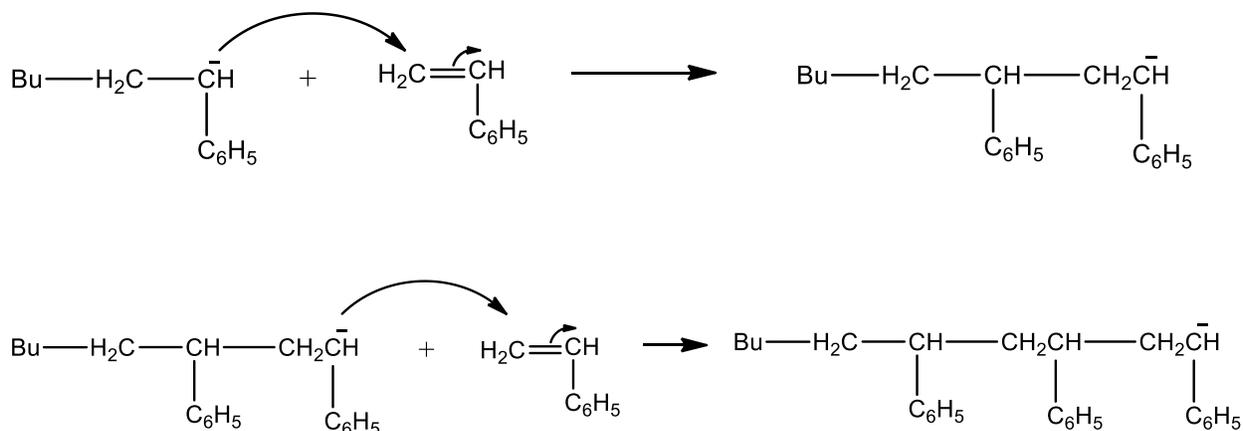
Anionic polymerization

In this polymerization the initiator is a nucleophile and propagation site is an anion. Nucleophile attack on an alkene does not occur readily so initiator must be a very good nucleophile such as sodium amide or butyllithium. The alkene must contain a substituent that can withdraw electron by resonance, which will decrease electron density of double bond.

initiation step

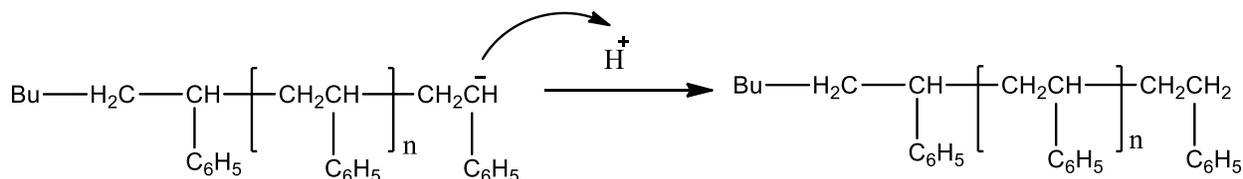


propagation step



chain termination

usually occurs by combination with a proton or some other lewis acid in reaction mixture.

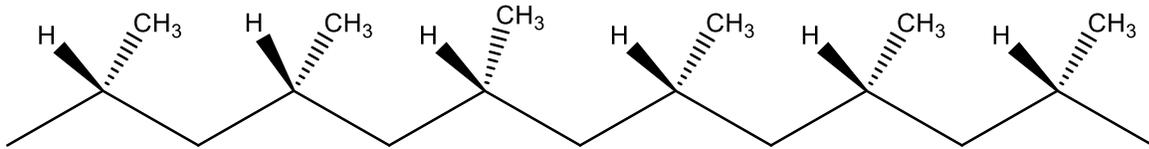


alkenes that undergo polymerization by an anionic mechanism are those that can stabilize the negatively charged propagating site by resonance electron withdrawal.

Stereochemistry of polymerization

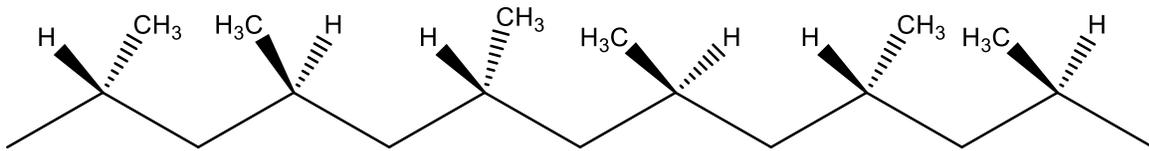
Polymers formed from monosubstituted ethylene can exist in three configurations:

Isotactic polymer - an isotactic polymer has all of its substituents on the same side of the carbon chain.



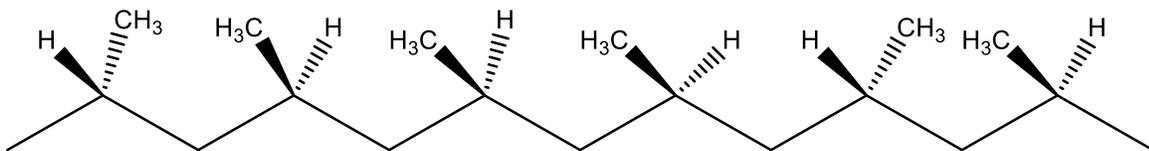
substituents are on the same side of carbon chain

Syndiotactic polymer - in this polymer substituents regularly alternate on both the sides of carbon chain.



substituents alternate on both the sides of carbon chain

Atactic polymer- A polymer in which substituents are randomly oriented on the extended carbon chain.



randomly oriented substituents on the carbon chain

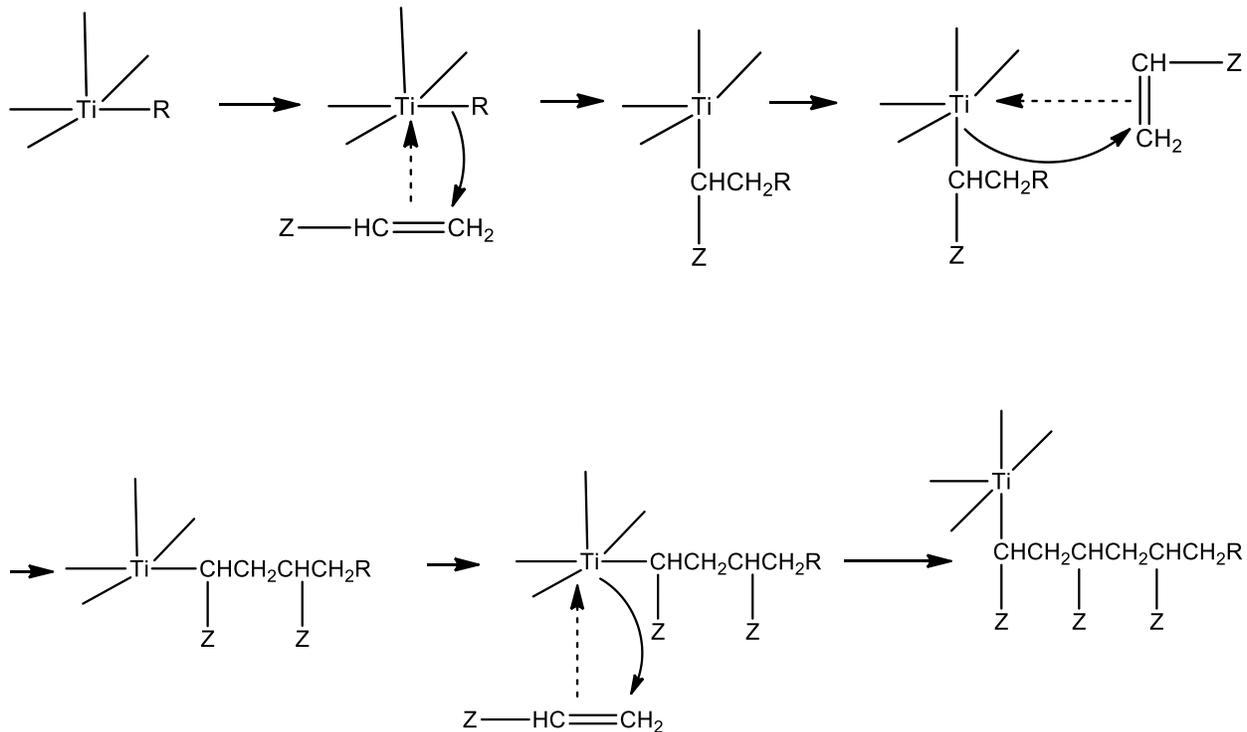
The configuration of polymer affects its physical properties. Isotactic and syndiotactic polymers are more likely to be crystalline solids. Polymers in atactic configuration are less rigid and therefore soft.

CO-ORDINATION POLYMERIZATION (ZIEGLER -NATTA POLYMERIZATION)

In 1953 Karl Ziegler and Giulio Natta found that the structure of a polymer could be controlled if the growing end of the chain and the incoming monomer were coordinated with an aluminium-titanium initiator. These initiators are now called **Ziegler -Natta catalysts**.

Mechanism

- The monomer forms a complex with titanium at an open coordination site.

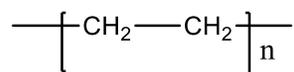


- The coordinated alkene is inserted between the titanium and the growing polymer, thereby lengthening the polymer chain.
- A new coordination site opens up during insertion of the monomer, the process can be repeated over and over.

Using **Ziegler -Natta catalyst** long unbranched polymers either isotactic or syndiotactic configuration can be prepared. **High density polyethylene is prepared using a Ziegler -Natta process.**

VINYL POLYMERS

(i) **Polyethylene**- Homopolymer of ethylene.

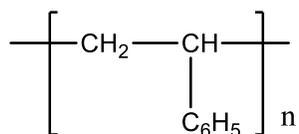


monomer $\text{---CH}_2\text{---CH}_2\text{---}$

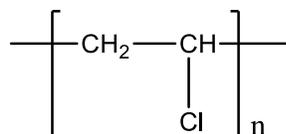
(a) **Low density polythene**-This type of polythene is branched and prepared by free radical polymerization . It has low density and low melting point.

(b)**High density polythene**-It is prepared by coordination polymerization(using Ziegler -Natta catalyst).It has high density and high melting point.

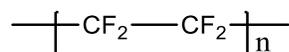
(ii) **Styron or Polystyrene**- Homopolymer of styrene used in refrigerator lining.(bad conductor of heat and electricity)



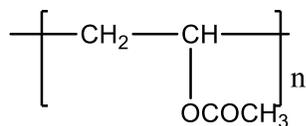
(iii)**Poly vinyl chloride, PVC**- Homopolymer of vinyl chloride used as adhesive and insulation covering for wires and cables.



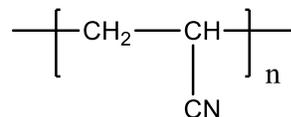
(iv) **Teflon or Poly tetrafluoroethylene (PTFE)**- Homopolymer of tetrafluoroethylene, used in coating of pans,pipes and electrical insulation.(due to chemical inertness and high thermal stability)



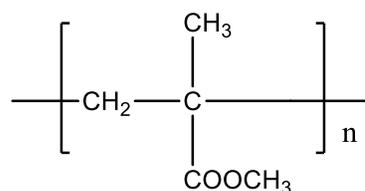
(v) **Polyvinylacetate, PVA**- Homopolymer of vinylacetate, used in making plastic emulsion paints and adhesives .



(vi) Polyacrylonitrile, PAN - Homopolymer of acrylonitrile (vinyl cyanide), forms water resistant and drying fibers .



(vii) Polymethylmethacrylate PMMA - Homopolymer of methyl methacrylate . Its commercial names are Plexiglas, Lucite, Acrylite and Perspex. used in manufacture of lenses, signboards and aircraft windows.



Saran is copolymer of vinylidene chloride(85%) and vinyl chloride (15%).

Orlon is homo polymer of acrylonitrile.

Vinyon is copolymer of vinylidene chloride (88%) and vinyl acetate (12%).

Super Glue is a polymer of **methyl α -cyanoacrylate**.

Styrene undergo polymerization by radical ,cationic and anionic mechanism. The mechanism depends on the nature of the initiator.