

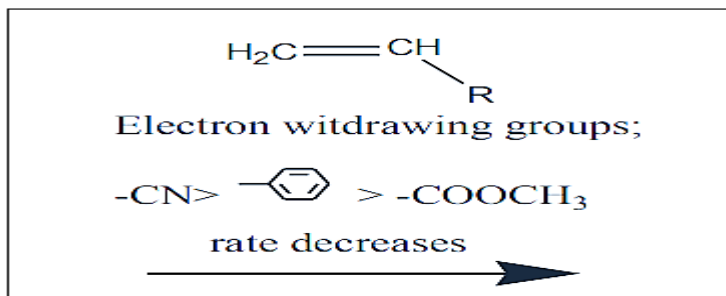
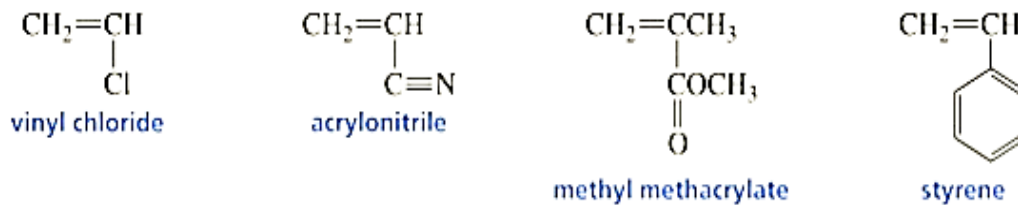
## b) Ionic polymerizations

Ionic polymerizations are more selective than radical processes due to strict requirements for stabilization of ionic propagating species.

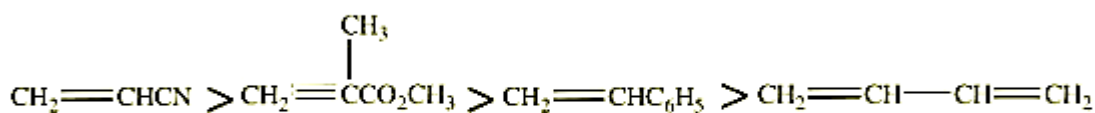
## I) Anionic Polymerization

The active center here is an anion

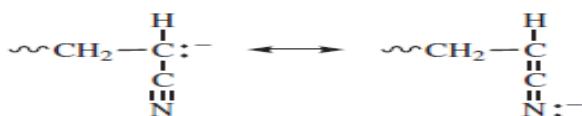
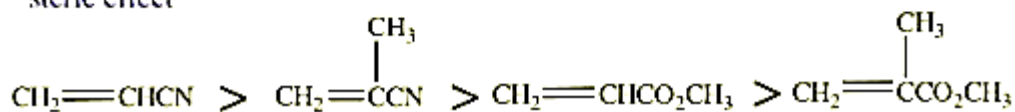
**Monomer:** monomers should have electron-withdrawing groups



inductive destabilization of the carbanion



steric effect



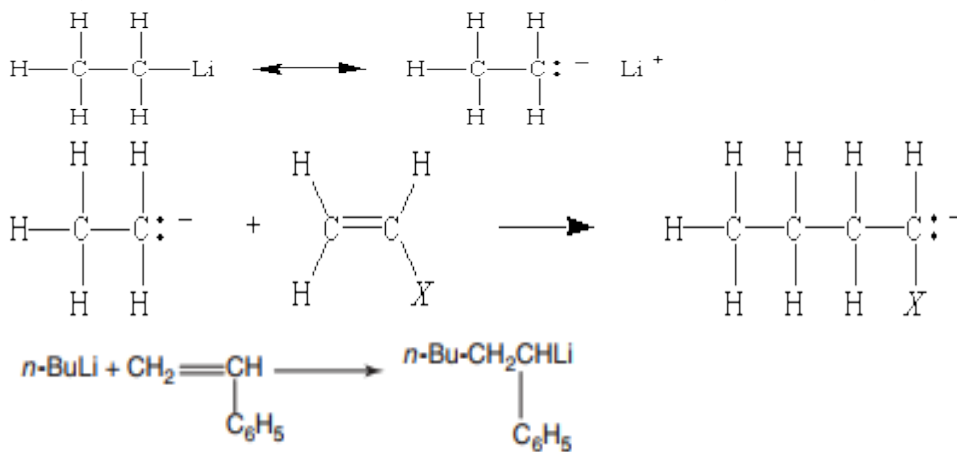
**Initiators:** has the ability to create negative charge on the monomeric molecule.

Types of Initiators: in anionic polymerization Initiators are often

1• Initiation by Nucleophilic Addition bases transfer (monofunctional):

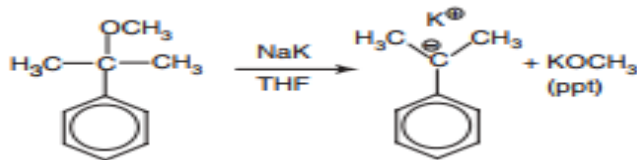
- Alkyl amides: sodamide  $\text{NaNH}_2$  or potassiumamide  $\text{KNH}_2$

- Organolithium: n-BuLi, s-BuLi, t-BuLi and Grignard reagents RMgX.



- Alcoholates or alcoxides(t-BuO-Li, t-BuO-K, ...)

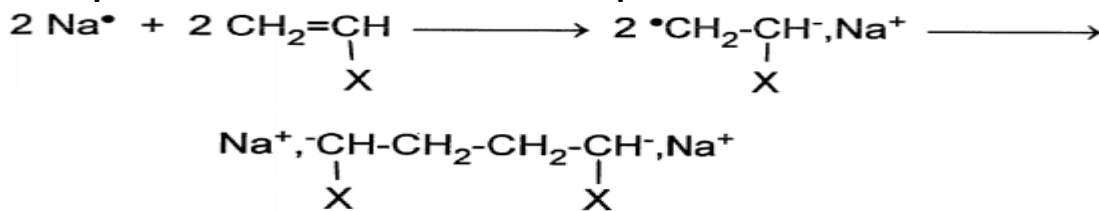
- Alkali salts of aromatic hydrocarbons: benzyl-Na, cumyl-K, ...



2. Electron transfer agents (bifunctional):

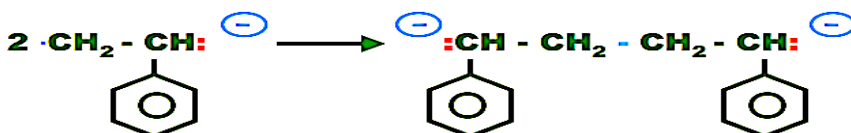
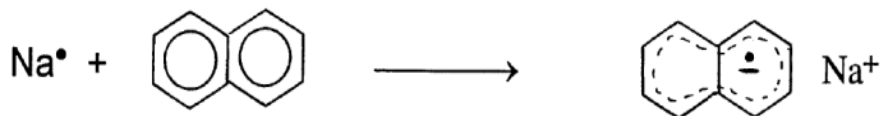
- Alkali metals (heterogeneous): such as an alkali metal in liquid ammonia

Examples: Potassium or sodium with liquid ammonia.



- radical anions: naphthalene sodium (homogeneous):

• Stable alkali metal complexes may be formed with aromatic compounds (e.g. Na/naphthalene) in ether.



• Sodium metal in tetrahydrofura

**Solvent:**

Due to the high nucleophilicity of the initiators (and propagating chain ends) it is absolutely necessary to avoid oxygen, water and protic

impurities: This implies - aprotic solvents: polar: THF, ... non-polar: toluene, cyclohexane, hexane, ... - rigorous purification of reagents - handling of reagents in vacuum or under inert gas

### Anionic Polymerization MECHANISM

#### Initiation

1) It performs by either a direct attack of a base on the monomer to form carbanion



Or by 2) Transfer of an electron from a donor molecule to the monomer to form anion radical



two radical anion combine together to form bi-anion



#### Propagation

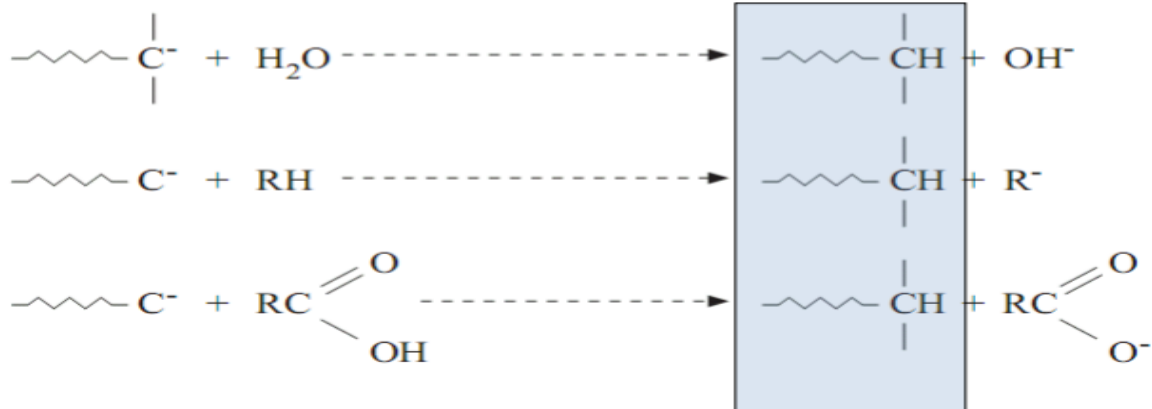


#### Termination:

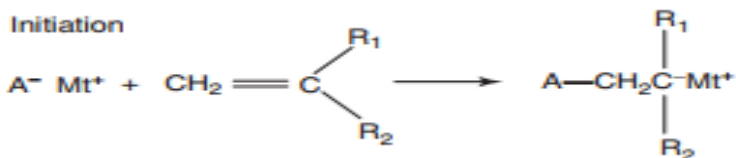
There is no termination so it is known as Living Polymers

In carefully controlled systems (pure reactants and inert solvents), anionic polymerization does not exhibit termination reactions. Such systems are referred to as living systems. Polymer molecules remain active even after all the monomer molecules are consumed. When fresh monomer is added the polymerization resumes.

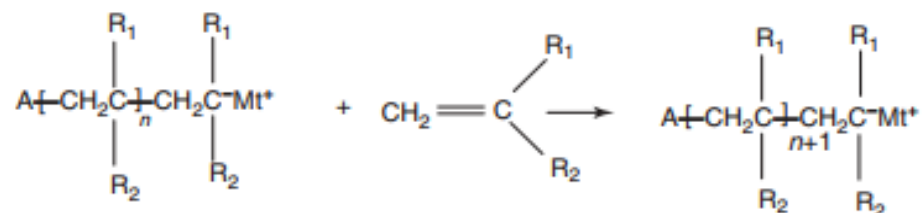
But it can terminate by addition of any substance has the ability to give  $H^+$  Such as ammonia, water etc. to form dead polymer as observed in the following equations



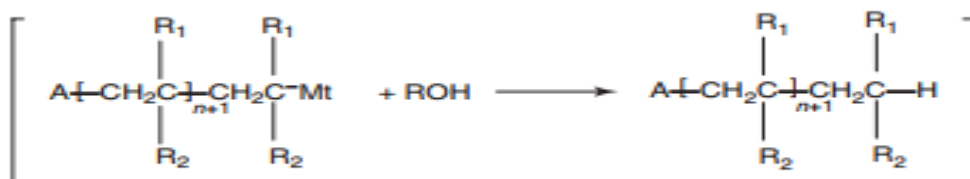
Or reacted with any impurities to form inactive anion



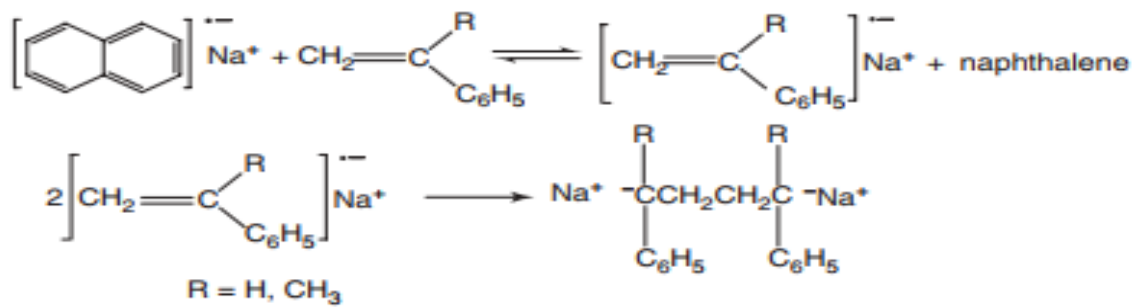
Propagation



Deliberate Termination (no spontaneous termination)



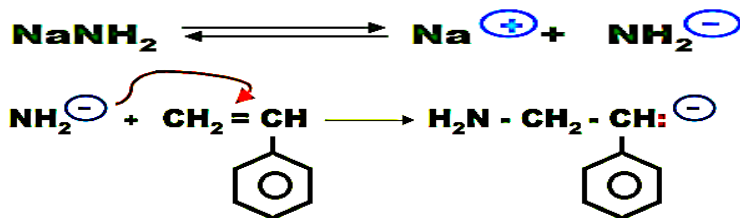
General mechanism for a living anionic polymerization.



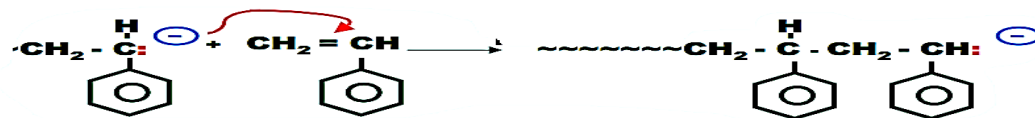
Initiation mechanism with aromatic radical anions by electron transfer.

Example of anionic polymerization is polymerization of styrene in presence of  $\text{NaNH}_2$  as shown in the following.

initiation



Propagation



Example of anionic polymerization of styrene using organometallic compounds, such as n-butyl lithium ( $n\text{-C}_4\text{H}_9\text{Li}$ ).

Initiation

The initiation involves a strong nucleophile, for example organometallic compounds, such as n-butyl lithium ( $n\text{-C}_4\text{H}_9\text{Li}$ ).

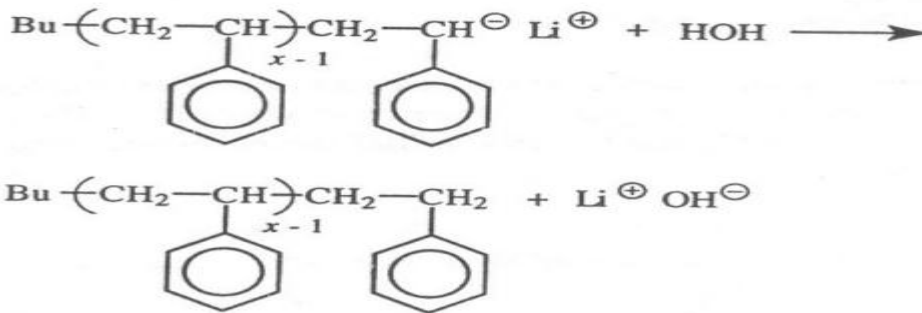


Propagation

The chain propagates by insertion of additional styrene monomers between the carbanion and counterion. If the reagents are pure and if the polymerization reactor is purged of water and  $\text{O}_2$ , the propagation proceeds indefinitely or until all monomer is consumed.

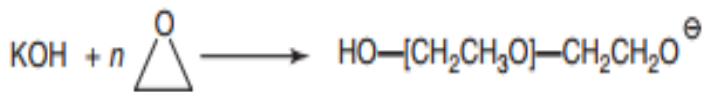
### Termination

Termination occurs only by the deliberate introduction of O<sub>2</sub>, CO<sub>2</sub>, methanol, or water.

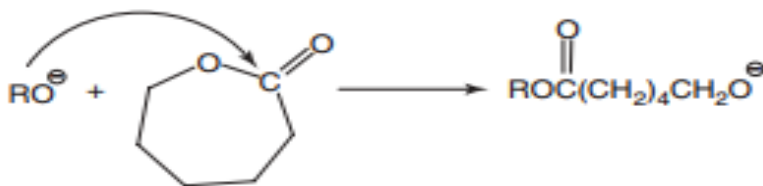


### Heterocyclic Monomers

A variety of heterocyclic monomers can be polymerized by anionic ring-opening polymerizations. The types of anionically polymerizable heterocyclic monomers include oxiranes (epoxides), thiacyclopropanes, thiacyclobutanes, lactones, lactides, lactams, anhydrides, carbonates, and silicones. Among these heterocyclic monomers, the anionic polymerizations of epoxides have been examined most extensively.



### Lactone example



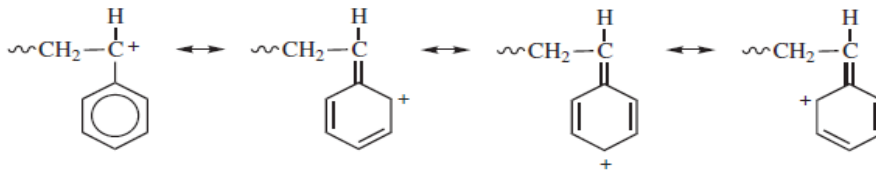
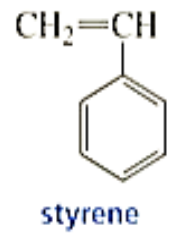
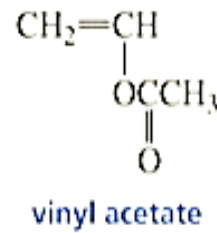
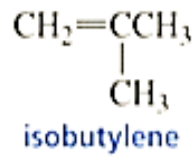
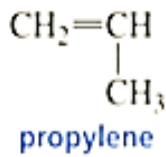
## II) Cationic Polymerization:

Polymerization in which the propagating chain carry or bearing positive charge.

### requirement for cationic polymerization

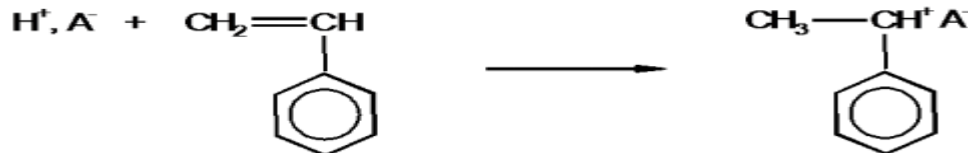
Monomers

Must contain electron donating substituent to increasing the electron density on the double bond and facilitate the attack of cationic species such as alkoxy, alkyl, alkenyl, and phenyl

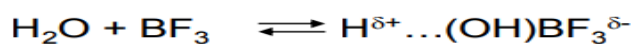


Catalysts for cationic polymerization;

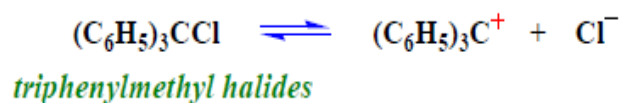
Protic Acids:  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HClO}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$ , ...

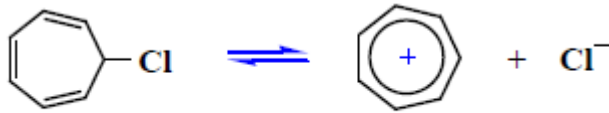


Lewis Acids:  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{BF}_3$ ,  $\text{TiCl}_4$ ,  $\text{SnCl}_4$ , (all lewis acids with strong electron acceptor capacity) To be effective, they need presence of a Lewis base such as  $\text{H}_2\text{O}$ ,  $\text{ROH}$ , acetic acid as a cocatalyst



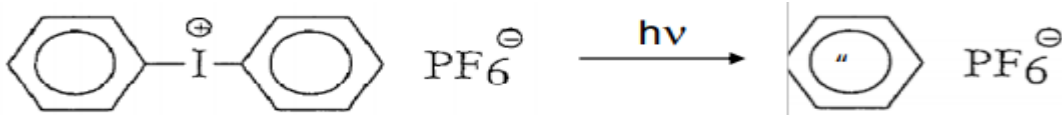
Ionizable initiator (Stable cations)





*tropylium halides*

Photoinitiator



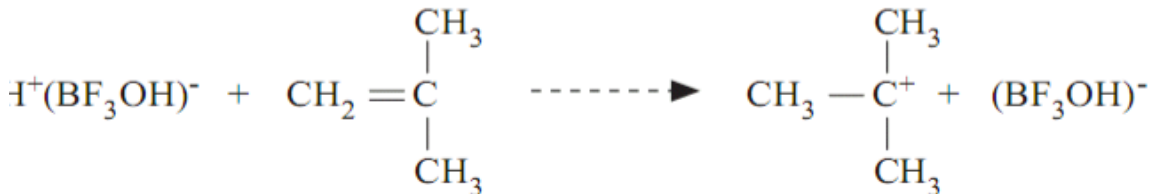
**Cationic Polymerization Mechanism:**

Initiation

First the catalysis and co-catalysis form complex

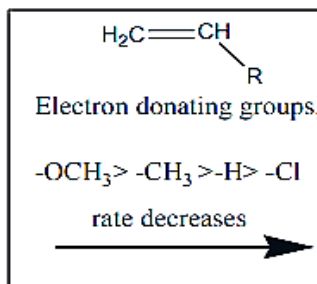
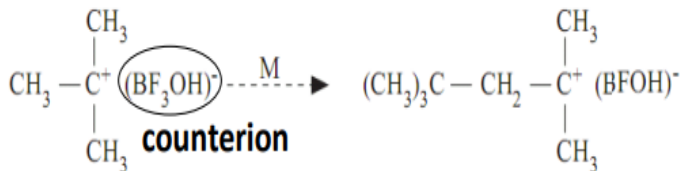


The catalysis donate the hydrogen proton to the isobutylene monomer to form carbonium ion



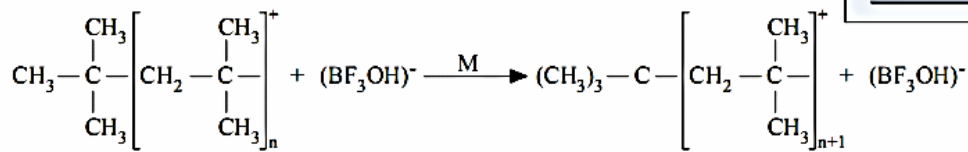
Propagation

The carbonium ion react with another monomers to form propagating chain carries positive charge



In general the propagation reaction can be written as





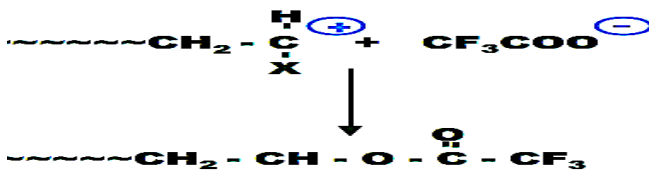
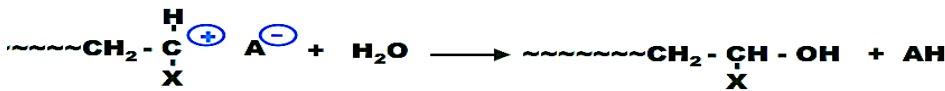
<p>Counterion</p> <p>-ClO<sub>4</sub>&gt;-TiClOH&gt;-I<sub>3</sub><sup>-</sup></p> <p>rate decreases</p> <p>→</p>
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The choice of solvent is important in CP.

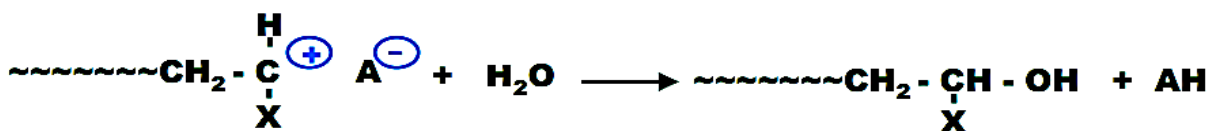
A linear increase in polymer chain length and an exponential increase in the reaction rate occur as the dielectric strength of the solvent increases.

Termination:

Termination occurs by rearrangement of ion pair to a polymer molecule with an unsaturated terminal unit end and the original complex or by transfer to the monomer.



termination can occur by anion- cation recombination



## Coordination Polymerization

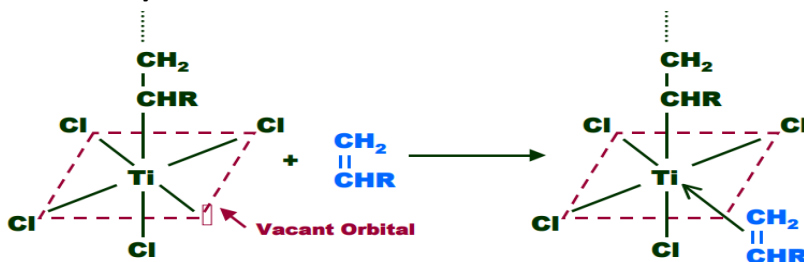
Coordination polymerizations, usually involve complexes formed between a transition metal and the p electrons of the monomer. (many of these reactions are similar to anionic polymerizations and could be considered under that category). These types of polymerizations usually lead to linear

and stereo-regular chains and often use so-called Ziegler - Natta catalysts, various metal oxides, or, more recently, metallocene catalysts.

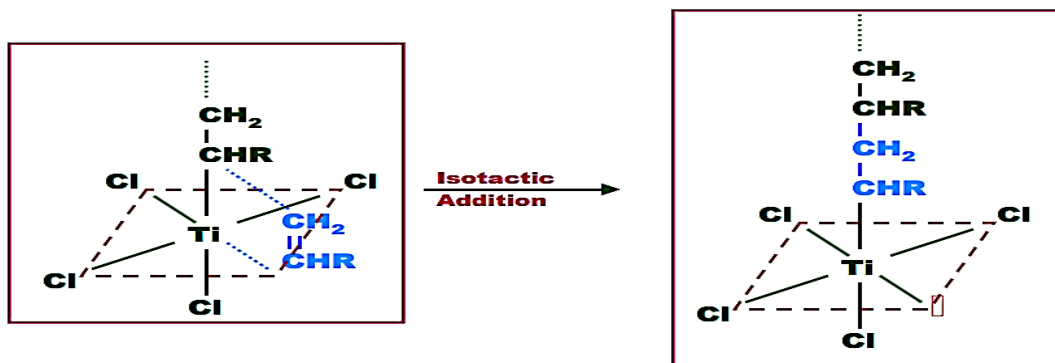
### III) Ziegler - Natta Catalysts

Ziegler-Natta catalysts generally consist of a metal organic compound involving a metal from groups I - III of the periodic table, such as triethyl aluminium, and a transition metal compound (from groups IV - VIII), such as titanium tetrachloride. The metal organic compound acts as a weak anionic initiator, first forming a complex whose nature is still open to debate.

Polymerization proceeds by a process of insertion. The transition metal ion (Ti in this example) is connected to the end of the growing chain and simultaneously coordinates the incoming monomer at a vacant orbital site. Two general mechanisms have been proposed and for simplicity here we simply illustrate the so -called monometallic mechanism ( the other is bimetallic)

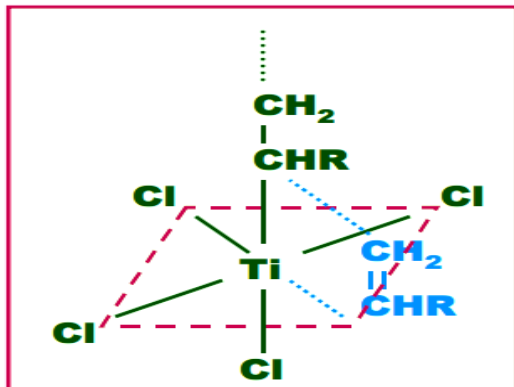


Isotactic placement can then occur if the coordinated monomer is inserted into the chain in such a way that the growing chain remains attached to the transition metal ion in the same position.

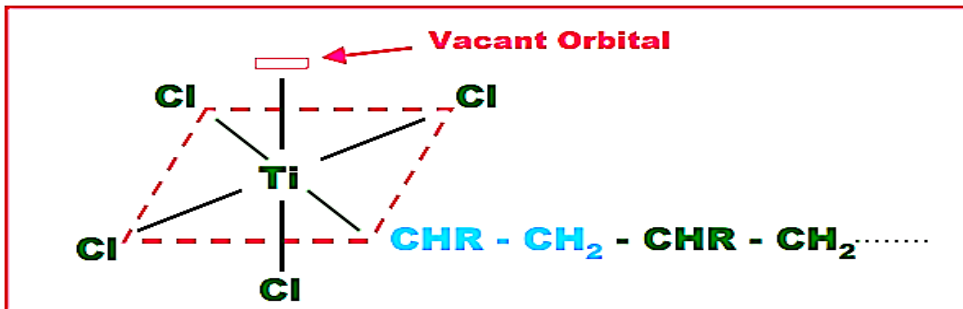


Or, if the chain becomes attached to the transition metal ion in the position of the orbital that was initially vacant, Syndiotactic addition will occur. This becomes more favored at lower temperatures, but vinyl monomers usually form isotactic chains with these catalysts. Because of the heterogeneous

nature of the geometry of the catalyst surface Atactic and stereoblock polymers can also be formed

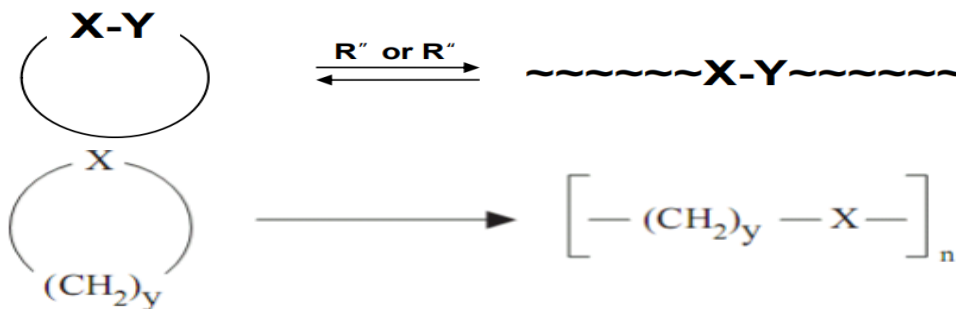


↓  
**Syndiotactic  
Addition**



Finally, Ziegler - Natta catalysts are used to polymerize a variety of  $\alpha$ -olefins (e.g. ethylene and propylene) and styrene, but many polar monomers cannot be polymerized this way as they inactivate the initiator, either through complexation or reaction with the metal components.

#### IV) Ring-Opening Polymerization (ROP)



- Ring-opening polymerization involves essentially an initial ring-opening of the cyclic monomer followed by polyaddition.

- The resulting polymers are normally linear. Their structural units usually have the same composition as the monomer.

### Monomers;

Epoxides such as ethylene and propylene oxides and epichlorohydrin and other cyclic ethers like trioxane and tetrahydrofuran. cyclic esters (lactones), cyclic amides (lactams), cycloolefins, and siloxane.

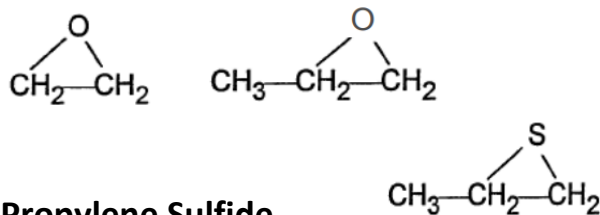
Applications; coatings, fibers, elastomers, adhesives, and thermoplastics- and thermoset-based composite system

There are three ring opening mechanisms :

- Anionic ROP (AROP)
- Cationic ROP (CROP)
- Ring-Opening Metathesis Polymerization (ROMP)

### •Anionic ROP (AROP)

Monomers (1): cyclic ethers such as Ethylene Oxide, Propylene Oxide

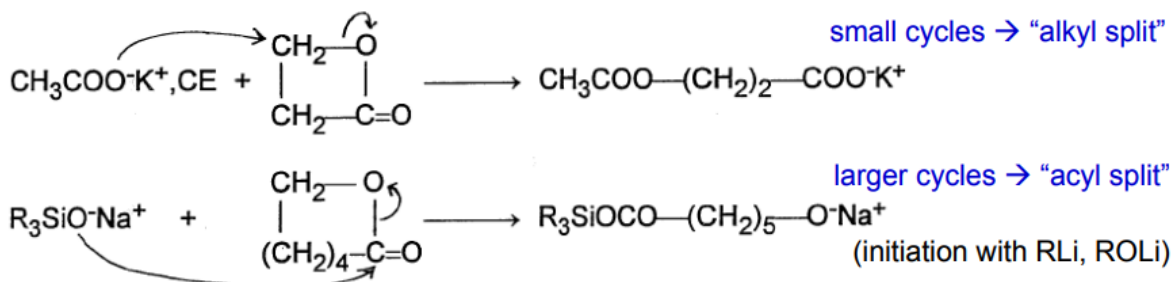


Propylene Sulfide

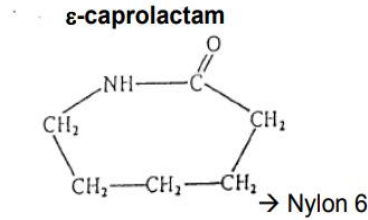
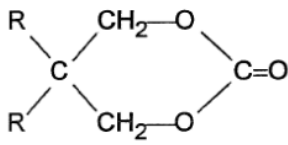
Nucleophilic Substitution Linear produce anionic chain end



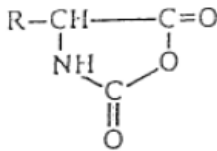
Monomers (2)



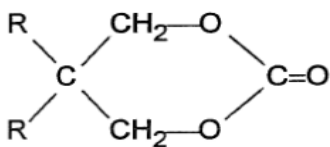
**Cyclic Carbonates:**



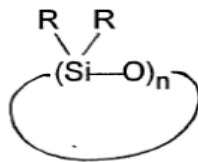
**N-carboxyanhydrides**



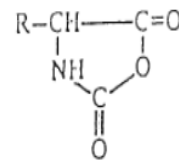
**Cyclic Carbonates:**



**Cyclic Siloxanes:**

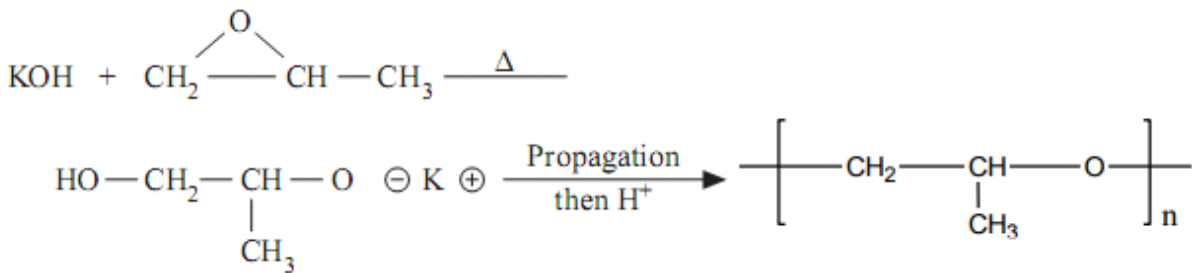


**N-carboxyanhydrides**



N-carboxyanhydrides

**1-Poly(propylene oxide) An important example of industrial ring opening polymerization**



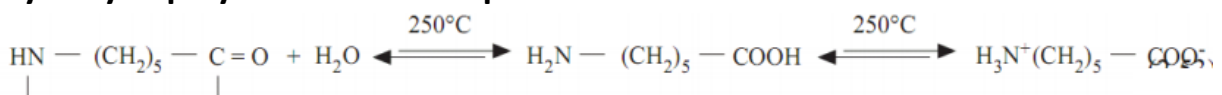
**Applications: Soft segments in polyurethane foams Automobile seats**

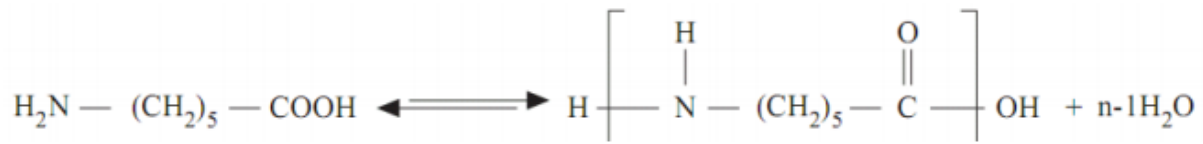
**2-POLYCAPROLACTAM (NYLON 6)**

The industrial manufacture of nylons involves either;

- a) water-initiated (hydrolytic) or
- b) a strong base-initiated (anionic) polymerization of caprolactam.

**Hydrolytic polymerization of caprolactam**

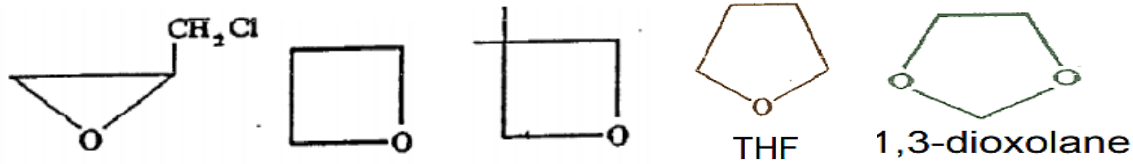




Polymerization by cationic initiation is also known, but mono-mer conversion and attainable molecular weights are inadequate for practical purposes and as such there is no commercial practice of this process.

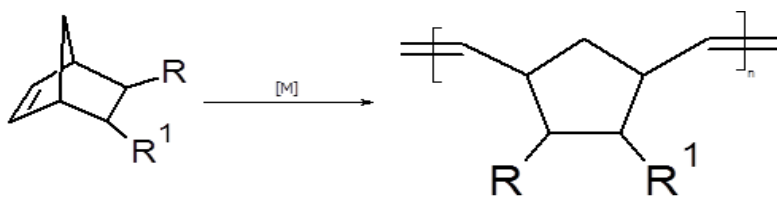
### Cationic Ring-Opening Polymerization (CROP)

Some monomers can perform CROP as shown in the following :

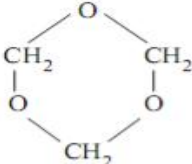
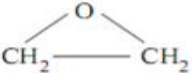
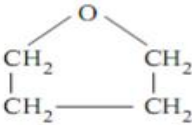


### Ring-Opening Metathesis Polymerization (ROMP).

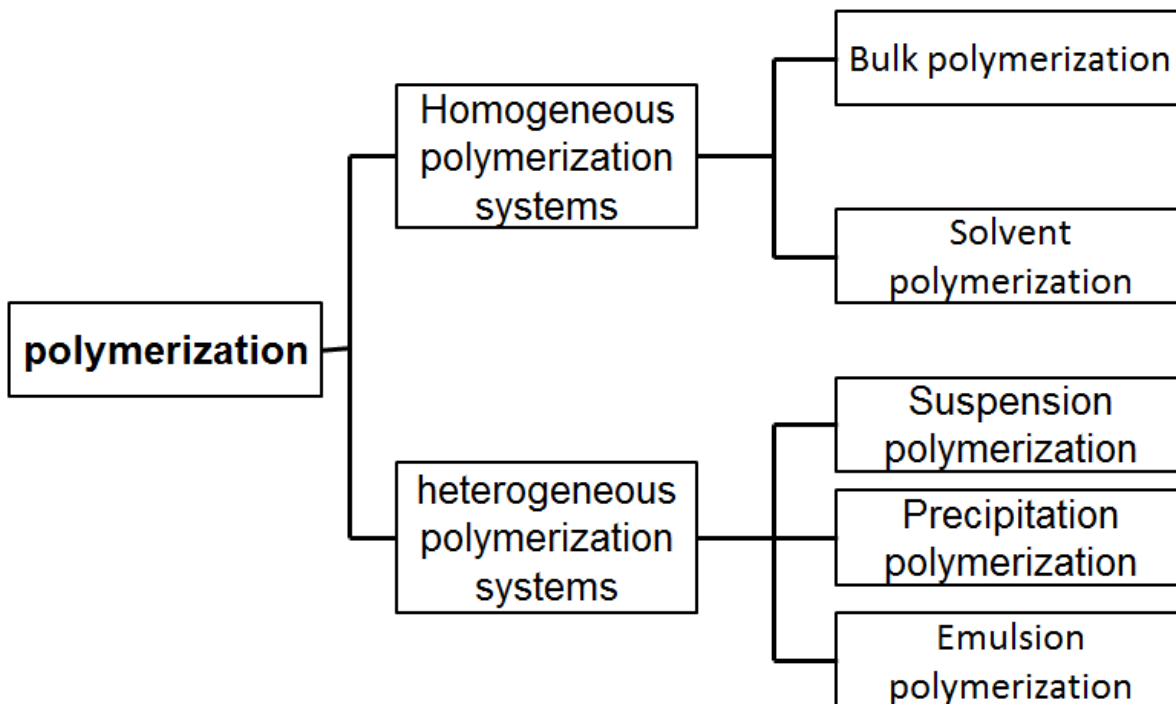
The metathesis polymerization reaction result in, the cyclic olefin as Ring Opening Metathesis Polymerization of a norbornene derivative



Examples of Commercially Important Ring-Opening Polymerizations

Monomer	Polymer	Mechanism
 trioxane	$[-CH_2-O-]_n$ polyoxymethylene	Cationic
 ethylene oxide	$-[CH_2-CH_2-O-]_n$ poly(ethylene oxide)	Anionic, cationic, coordination
 tetrahydrofuran ..	$-[(CH_2)_4-O-]_n$ poly(tetramethylene oxide)	Cationic

Process conditions



## [I] Homogeneous polymerization

### Bulk polymerization (mass polymerization)

- Involves pure monomer.
- Process difficult to control especially for highly exothermic reactions
- such radical chain polymerization
- Due to difficulties in controlling heat as the reaction medium becomes more

#### Viscous

- Local hot spots may occur resulting in degradation and discoloration
- Polymerization is carried out at low conversion to circumvent the above stated problems
- Typical application examples are polymerizations of ethylene, styrene and methacrylate.

### Solution polymerization

- Polymerization carried out in a solvent/solution
- Problems associated with bulk polymerization are reduced.
- Solvent acts as a diluent and aids in heat transfer.
- Thermal control is much easier
- Reaction mixture easy to stir due to reduced viscosity.

#### Disadvantages

- If solvent not carefully chosen, chain transfer to the solvent may occur.
- Problem of purity may arise as the solvent must be removed at the end of polymerization

#### Application

Polymerizations of vinyl acetate, acrylonitril and esters of acrylic acid

### Precipitation Polymerization

- A polymerization process in which a polymer is precipitated from solution.
- They are often referred to as powder or granular polymerization.
- Polymerization proceeds after precipitation by absorption of monomer and initiator in to polymer particles.

### Suspension polymerization

- Carried out by suspending monomer droplets in water



- The monomer droplets are prevented from coalescing by agitation in the presence of stabilizers
- Type of stabilizers:
  - Water-soluble polymers (often in the presence of an electrolyte)
  - Water-insoluble inorganic compounds

### Emulsion Polymerization

Polymerization of monomers in the form of (i.e. colloidal dispersed) system, which consist of water, emulsifier, the monomer. The reaction system is kept in an agitated state.

Components of an emulsion polymerization system

- Monomer and dispersing agent normally water
- Surfactants:
  - Ionic surfactants:
    - Fatty acid soaps:
      - sodium, potassium stearates, laurates, palmitate
    - Sulphates and sulphonates:
      - Sodium lauryl sulphate, sodium dodecyl sulphonate
  - Non-ionic surfactants
    - Poly(ethylene oxide)
    - Poly(vinyl alcohol)
    - Hydroxy ethyl cellulose