



# Polymer Chemistry

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# Polymer Chemistry

# Polymers

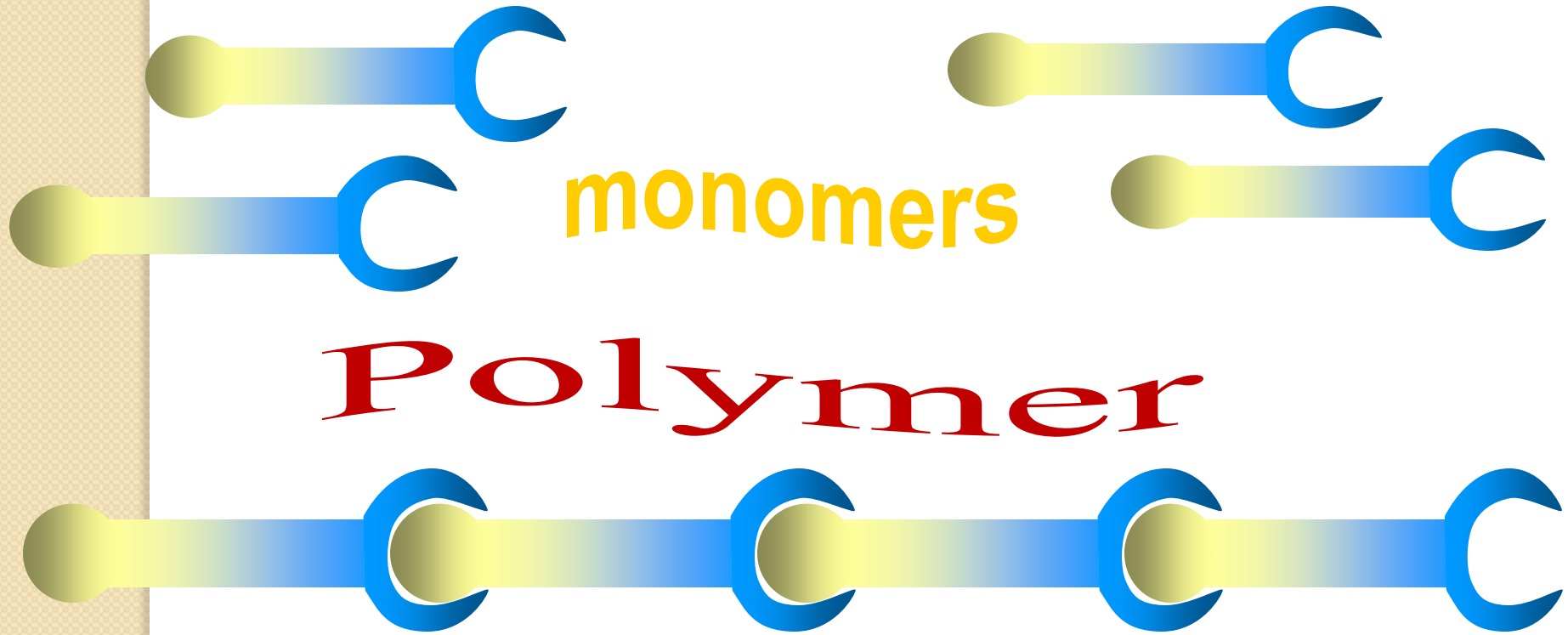
◦ **What is a polymer?**

**Very Large molecules structures chain-like in nature.**

**Poly mer**

**many repeat unit**

# Introduction



The word, **polymer**, implies that polymers are constructed from pieces (**monomers**) that can be easily connected into long chains (**polymer**). When you look at the above shapes, your mind should see that they could easily fit together.

➤ **Polymer:** High molecular weight molecule made up of a small repeat unit (monomer).

– A-A

➤ **Monomer:** Low molecular weight compound that can be connected together to give a polymers.

➤ **Oligomer:** Short polymer chain

➤ **Copolymer:** Polymer made up of 2 or more monomers

– **Random copolymer:** A-B-B-A-A-B-A-B-A-B-B-B-A-A-B

– **Alternating copolymer:** A-B-A-B-A-B-A-B-A-B-A-B-

# Types of Polymers

Polymers have different chemical structures physical properties, mechanical behavior, thermal characteristics, etc.

**Natural and synthetic polymers:** Proteins, DNA, cotton, silk, wool and rubber.

**Organic and inorganic polymers:** A polymer whose backbone is essentially made of carbon atoms is an organic polymer ;e.g. synthetic polymers like polyaniline etc. The inorganic polymers contain no carbon atom in their chain backbone ; e.g. glass and silicone.

## **Thermosetting and Thermoplastic polymers:**

Thermosetting : cross-linked polymer that undergo chemical change on heating and convert themselves into infusible mass.(tyres, rubber bands)

Thermoplastic: Polymers on heating and can be converted into any shape on cooling ;e.g. polyethelene, PVC, nylon, etc.

## **Plastics, elastomers, fibers and liquid resins.**

Plastics: polystyrene, PVC, polymethacrylate, etc.

elastomers: natural rubber, synthetic rubber, silicone rubber, etc.

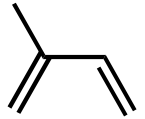
Fibers: nylon and terylene.

Resins : adhesives, sealants etc.

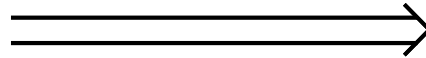


# Natural Polymers

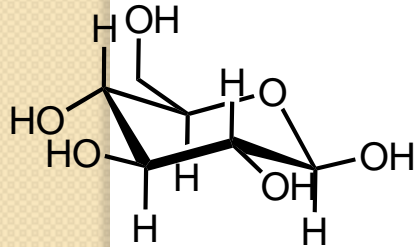
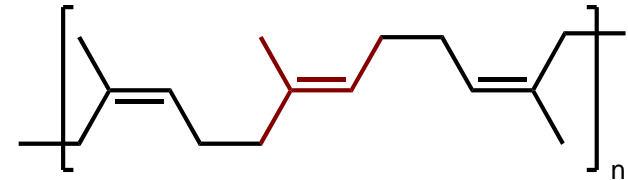
## Monomer



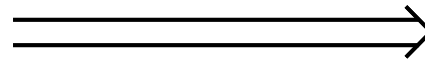
Isoprene



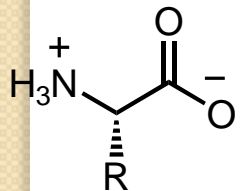
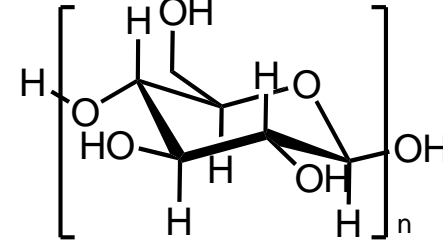
Polyisoprene:  
Natural rubber



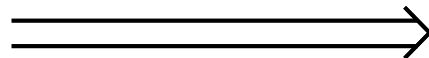
$\beta$ -D-glucose



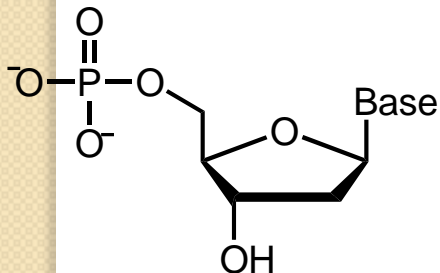
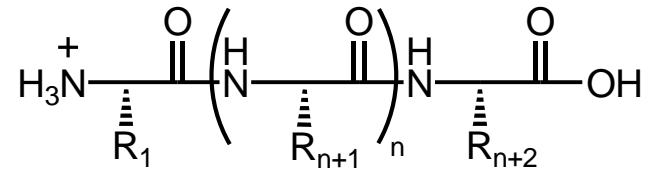
Poly( $\beta$ -D-glycoside):  
cellulose



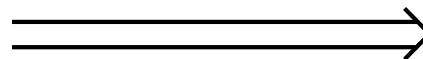
Amino Acid



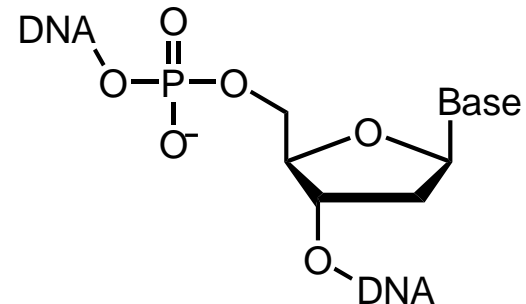
Polyamino acid:  
protein



Nucleotide  
Base = C, G, T, A



oligonucleic acid  
DNA



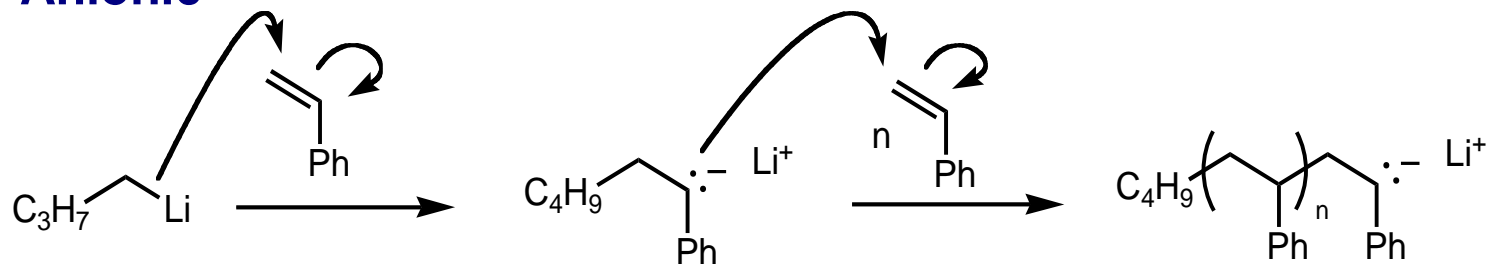


# Polymer Synthesis

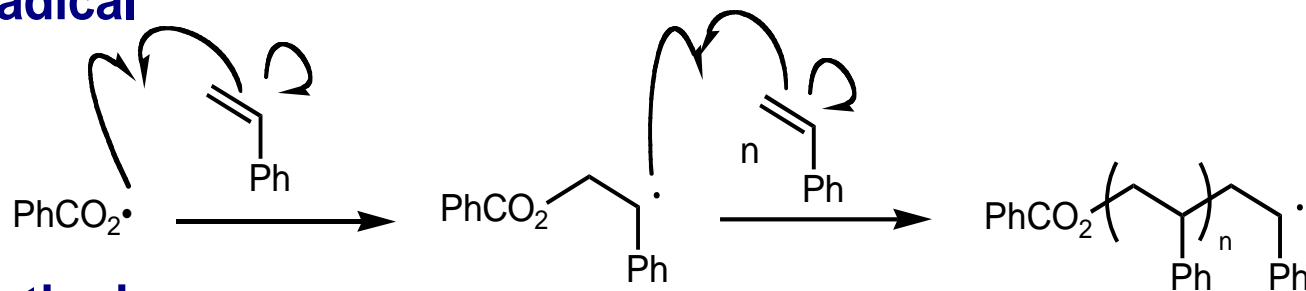
- There are two major classes of polymer formation mechanisms
  - **Addition polymerization:** The polymer grows by sequential addition of monomers to a reactive site
    - Chain growth is linear
    - Maximum molecular weight is obtained early in the reaction
  - **Step-Growth polymerization:** Monomers react together to make small oligomers. Small oligomers make bigger ones, and big oligomers react to give polymers.
    - Chain growth is exponential
    - Maximum molecular weight is obtained late in the reaction

# Types of Addition Polymerizations

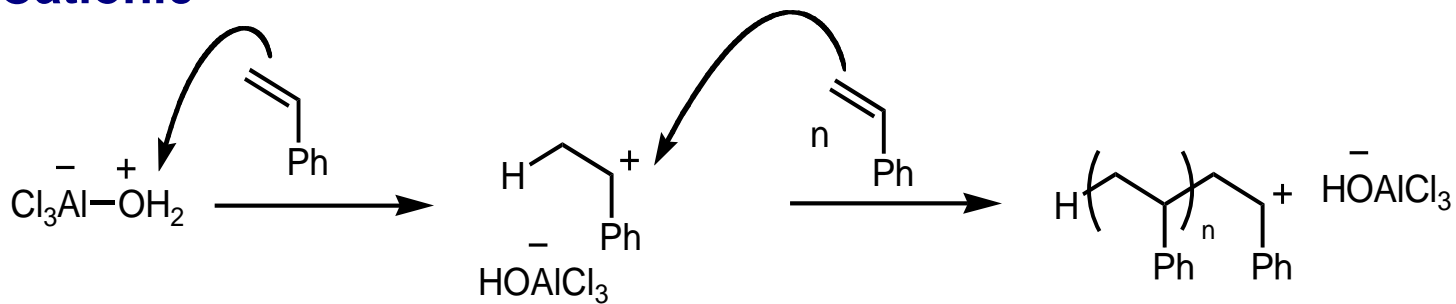
## Anionic



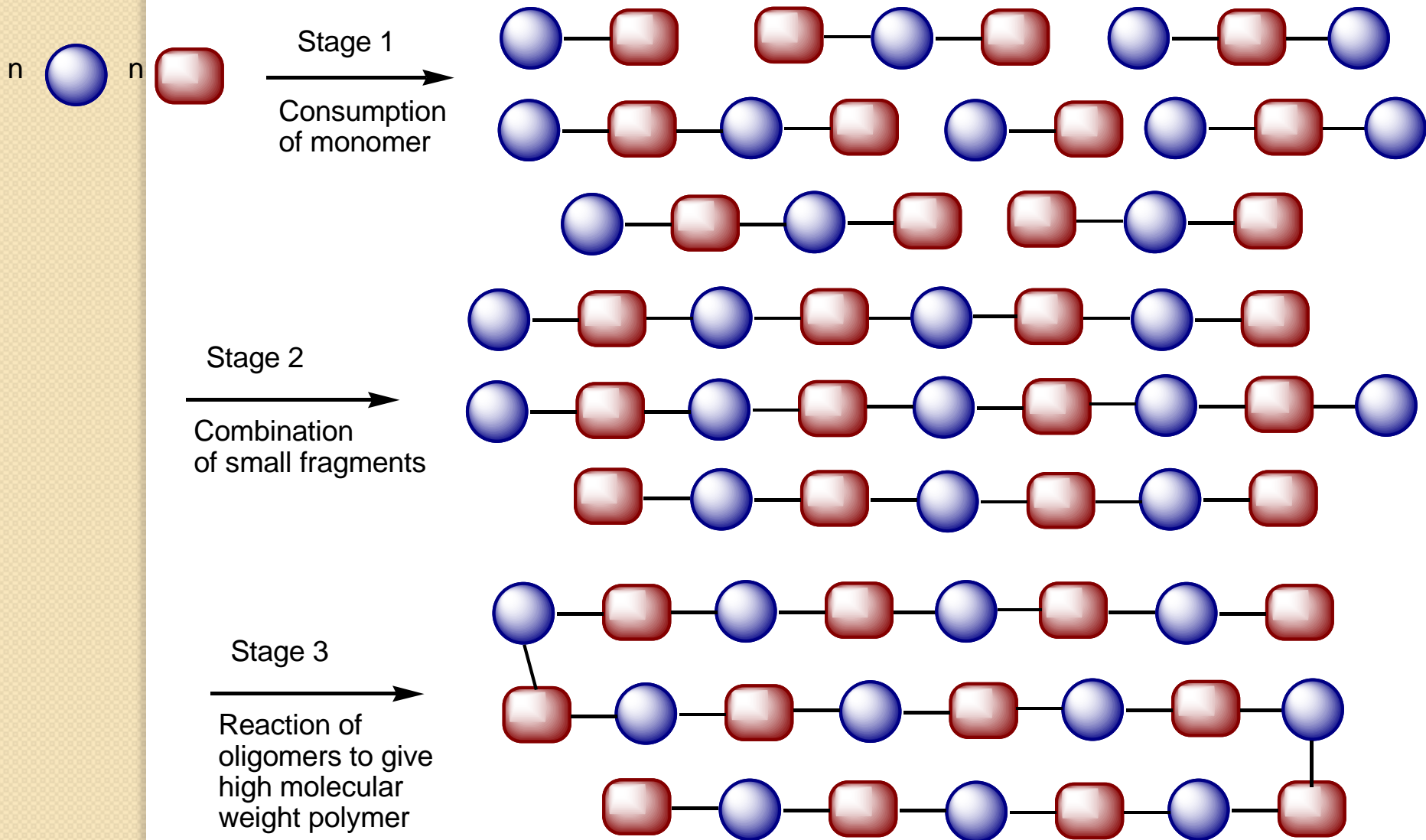
## Radical



## Cationic



# Step-Growth Polymerization



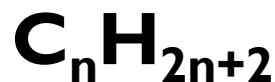
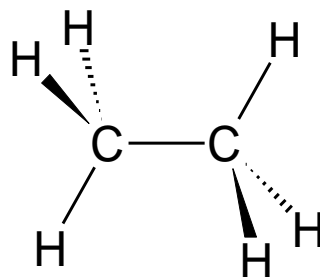
# Polymer Composition

**Most polymers are hydrocarbons**

– i.e. made up of **H** and **C**

- **Saturated hydrocarbons**

– Each carbon bonded to four other atoms



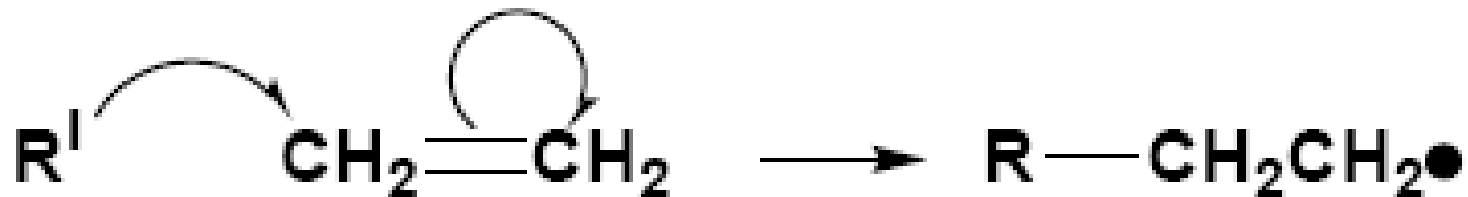
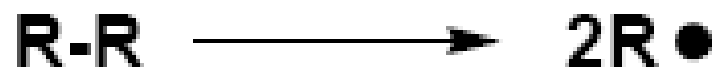
# CHAIN POLYMERIZATION

## Free Radical Polymerization

- **Free radical are independently-existing species that have unpaired electron. Normally they are highly reactive with short life time.**
- **Free radical polymerization's are chain polymerization's in which each polymer molecules grows by addition of monomer to a terminal free-radical reactive site known as active center.**
- **After each addition the free radical is transferred to the chain end.**
- **Chain polymerization is characterized by three distinct stages, Initiation, propagation and termination.**

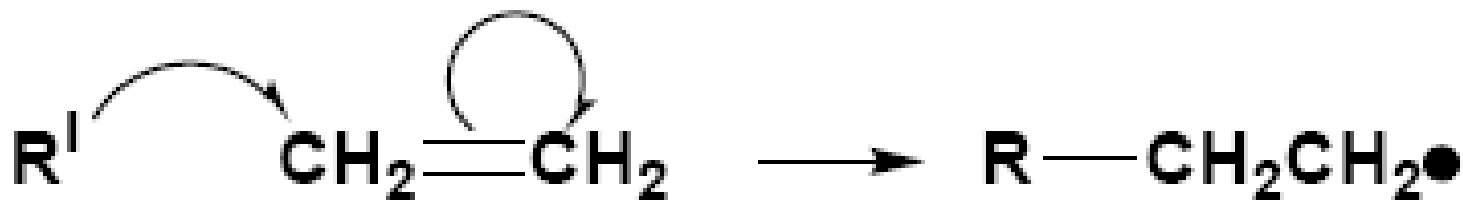
# Free Radical Polymerization

## step 1: Initiation



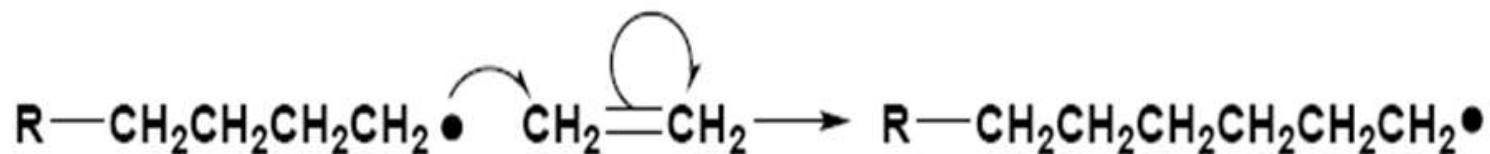
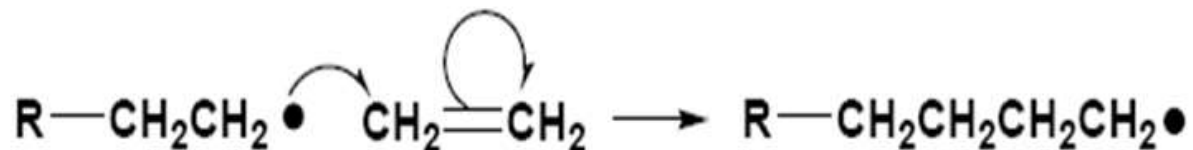
# Free Radical Polymerization

## step 1: Initiation



# Free Radical Polymerization

step 2: Propagation





# Free Radical Polymerization

## step 3: Termination



# Ionic Polymerization

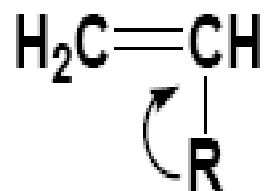
- Ionic polymerization is more complex than free-radical polymerization
- Whereas free radical polymerization is non-specific, the type of ionic polymerization procedure and catalysts depend on the nature of the substituent (R) on the vinyl (ethenyl) monomer.
- Cationic initiation is therefore usually limited to the polymerization of monomers where the R group is electron-donating
- This helps stabilise the delocation of the positive charge through the p orbitals of the double bond

# Ionic Polymerization

- Anionic initiation, requires the R group to be electron withdrawing in order to promote the formation of a stable carbanion (ie, -M and -I effects help stabilise the negative charge).

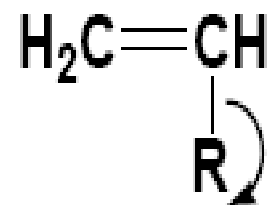
# Ionic Polymerization

**Cationic**



**R - Electron donating**

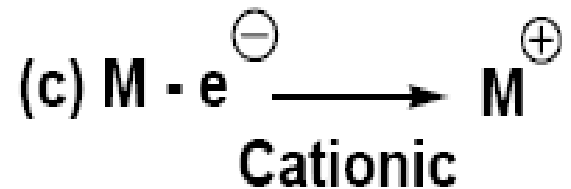
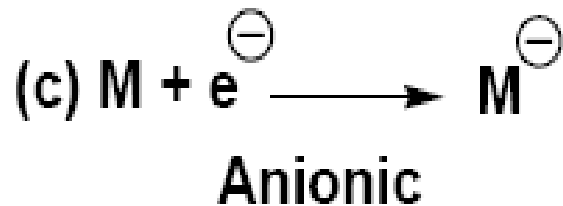
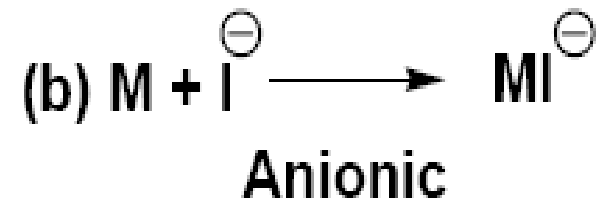
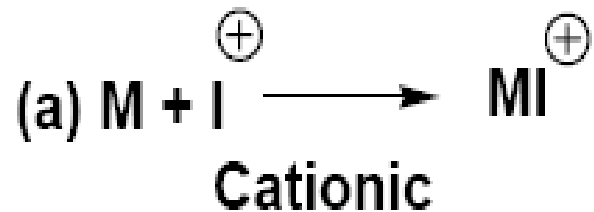
**Anionic**



**R - Electron withdrawing**

# Ionic Polymerization

(i) Initiation can occur in one of the four following ways:



# Ionic Polymerization

- M is a Monomer Unit.
- As these ions are associated with a counter-ion or gegen-ion the solvent has important effects on the polymerization procedure.

# Ionic Polymerization

## **(ii) Chain Propagation depends on :**

- Ion separation
- The nature of the Solvent
- Nature of the counter Ion

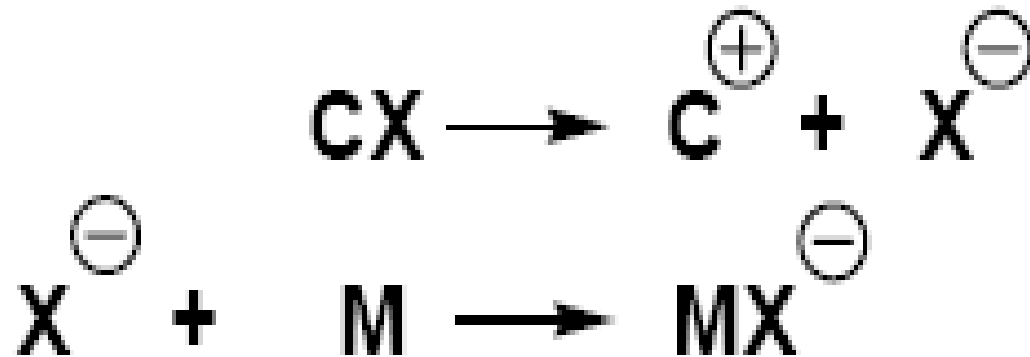
# Anionic Polymerization

- Involves the polymerization of monomers that have strong electron-withdrawing groups, eg, acrylonitrile, vinyl chloride, methyl methacrylate, styrene etc. The reactions can be initiated by methods (b) and (c) as shown in the sheet on ionic polymerization



# Anionic Polymerization

- eg, for mechanism (b)



# Anionic Polymerization

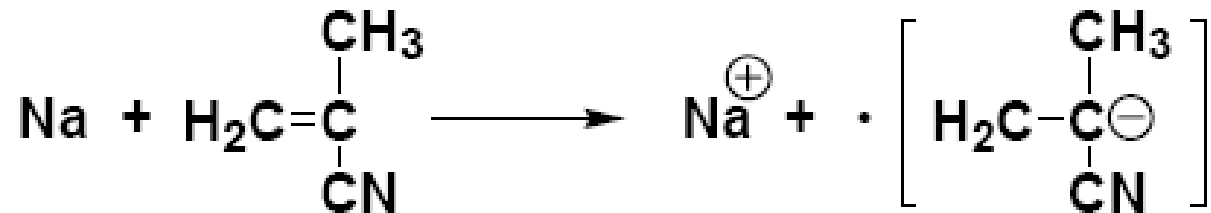
- The gegen-ion may be inorganic or organic and typical initiators include  $\text{KNH}_2$ ,  $n\text{-BuLi}$ , and Grignard reagents such as alkyl magnesium bromides

# Anionic Polymerization

- If the monomer has only a weak electron-withdrawing group then a strong base initiator is required, eg, butyllithium; for strong electron-withdrawing groups only a weak base initiator is required, eg, a Grignard reagent.

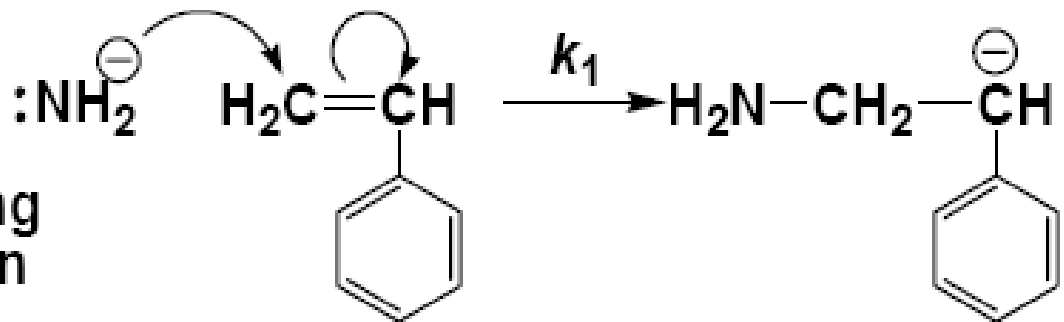
# Anionic Polymerization

- Initiation mechanism (c) requires the direct transfer of an electron from the donor to the monomer in order to form a radical anion.
- This can be achieved by using an alkali metal eg.,



# Anionic Polymerization of Styrene

## (i) Initiation

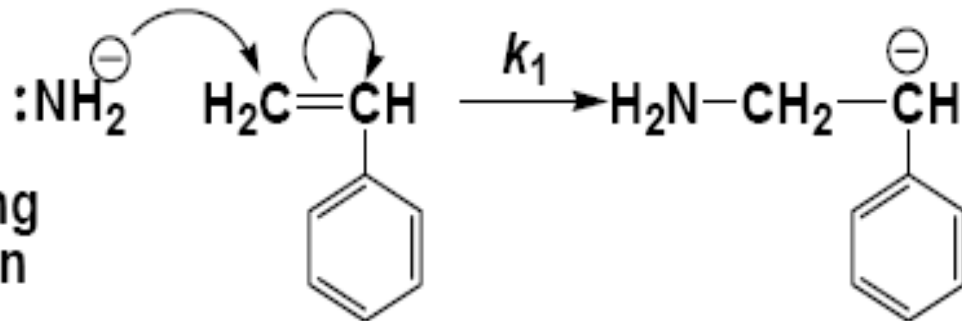


Rate determining  
step in initiation

$$\text{Rate } v_1 = k_1 [\text{NH}_2^{\ominus}] [\text{M}]$$

# Anionic Polymerization of Styrene

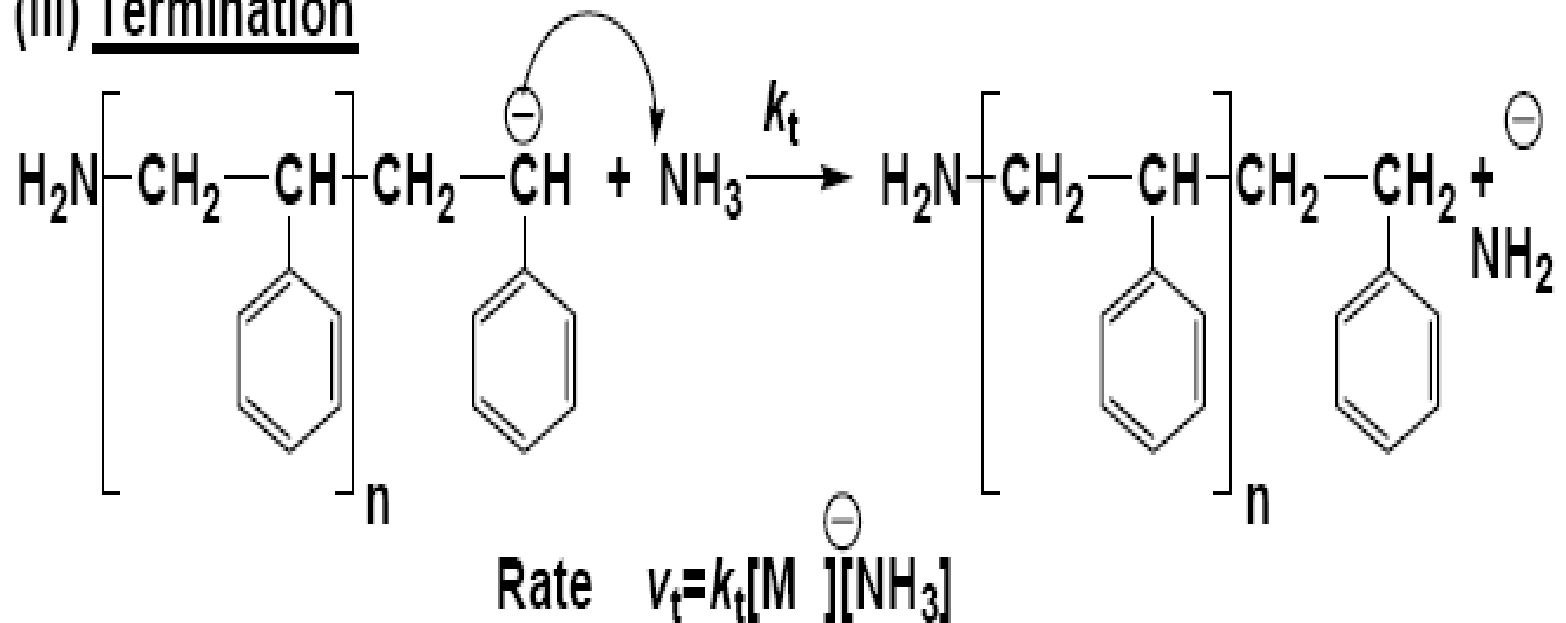
(i) Initiation



$$\text{Rate } v_1 = k_1 [\text{NH}_2^-] [\text{M}]$$

# Anionic Polymerization of Styrene

## (iii) Termination



# Anionic Polymerization of Styrene

Assuming steady state conditions, the concentration of propagating species is:

$$[M^{\ominus}] = \frac{k_1[NH_2^{\ominus}][M]}{k_t[NH_3]} \quad \text{which gives} \quad v_p = \frac{k_p k_1[NH_2^{\ominus}][M]^2}{k_t[NH_3]}$$

and the length of the polymer chains depends on the number of initiations



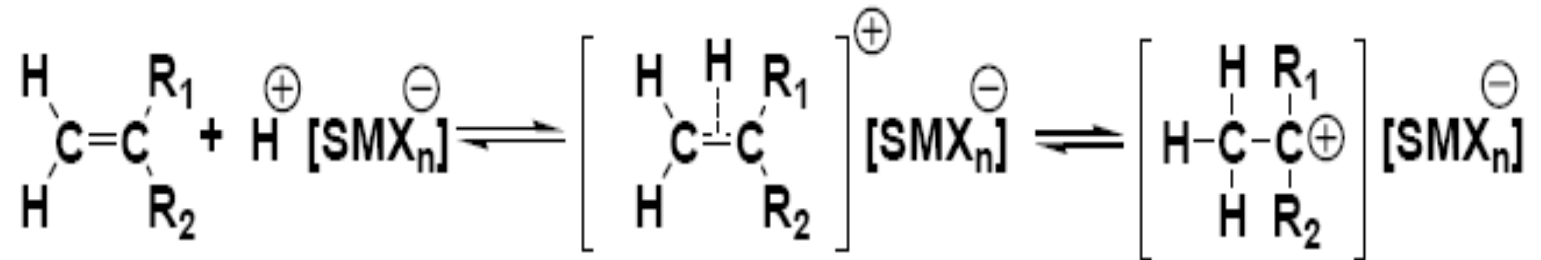
# Anionic Polymerization of Styrene

Thus 
$$\langle x_n \rangle = \frac{k_p[M]}{k_t[NH_3]}$$

The activation energy for transfer is larger than for propagation, and so the chain length decreases with increasing temperature.

# Cationic Polymerization

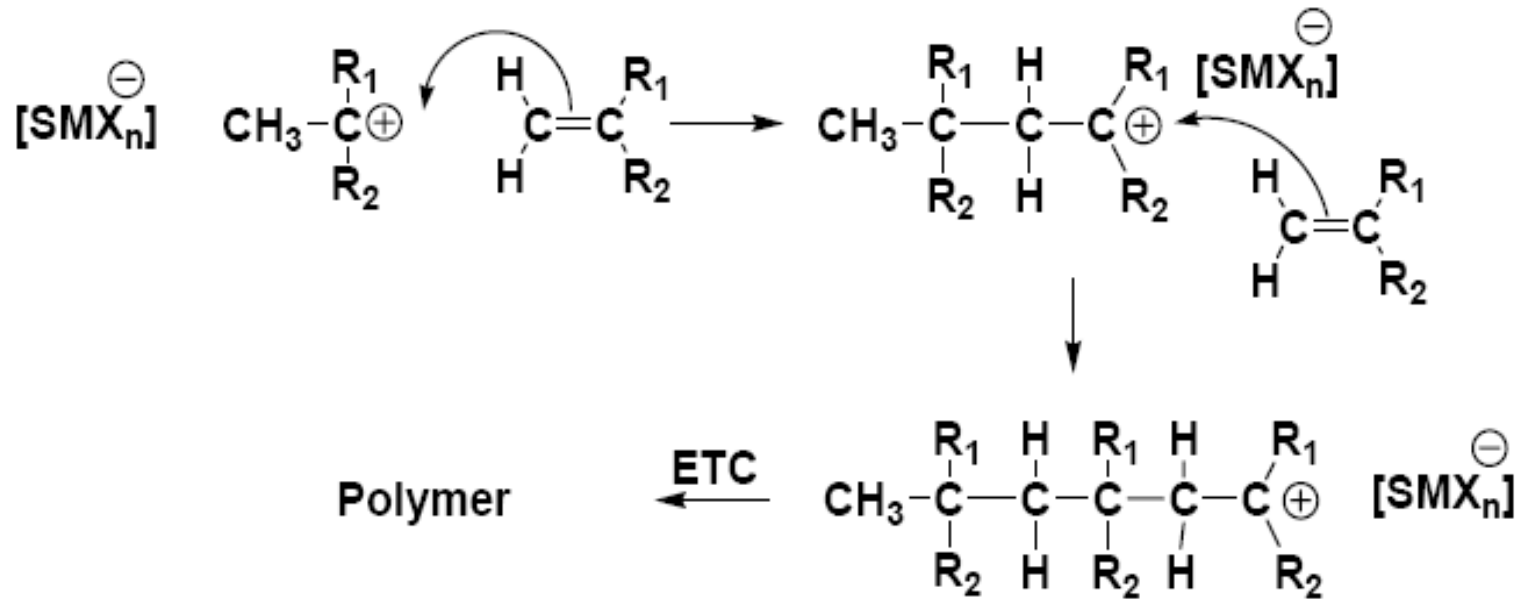
## (i) Initiation



# Cationic Polymerization

- (ii) PropagationChain growth takes place through the repeated addition of a monomer in a head-to-tail manner to the ion with retention of the ionic character throughout

# Cationic Polymerization



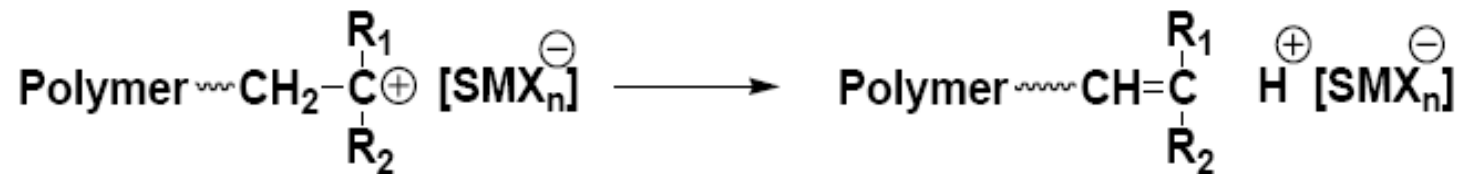
# Cationic Polymerization

## **(iii) Termination**

Termination of cationic polymerization reactions are less well-defined than in free-radical processes. Two possibilities exist as follows:

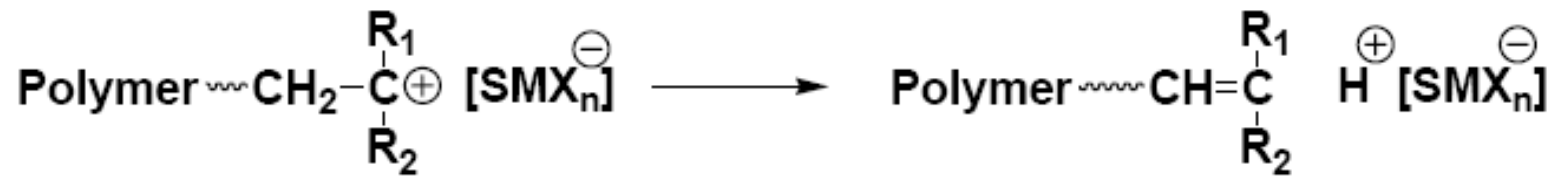
# Cationic Polymerization

(a) Unimolecular rearrangement of the ion pair



# Cationic Polymerization

- Hydrogen abstraction occurs from the  
(a) Unimolecular rearrangement of the ion pair



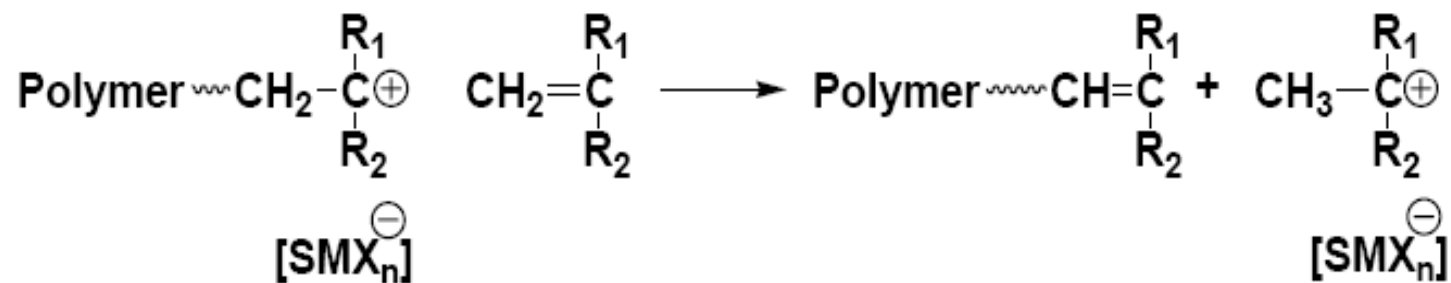
# Cationic Polymerization

- The kinetic chain is terminated and the initiator complex is reduced - a more effective route to reaction termination.



# Cationic Polymerization

(b) Bimolecular transfer reaction with the monomer



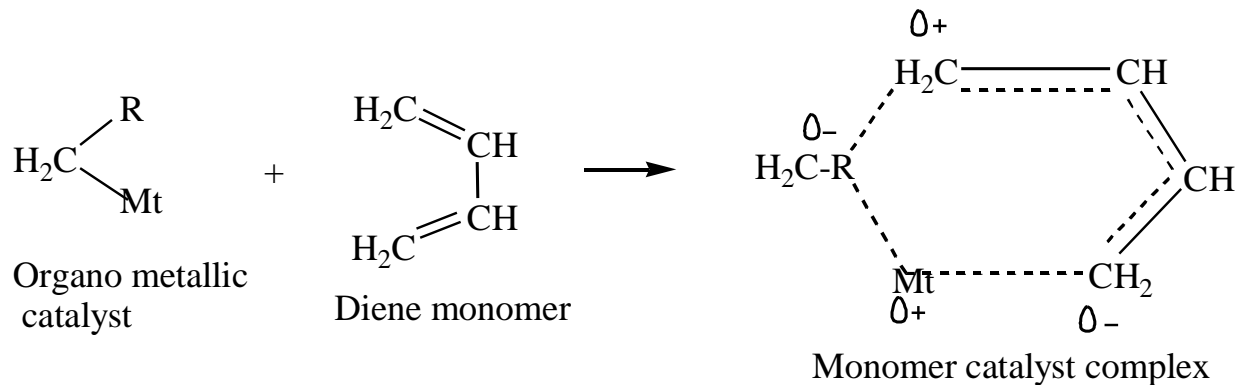
Reformation of the monomer-initiator complex, ensuring that the kinetic chain is not terminated by the reaction.

# Cationic Polymerization

- The kinetics of these reactions is not well understood, but they proceed very rapidly at extremely low temperatures.

# Ziegler Natta Polymerization

- Polymerization reactions especially of olefins and dienes catalysed by organometallic compounds is known as coordination polymerization.
- The first step in polymerization is the formation of a monomer – catalyst complex between the organometallic compound and the monomer.

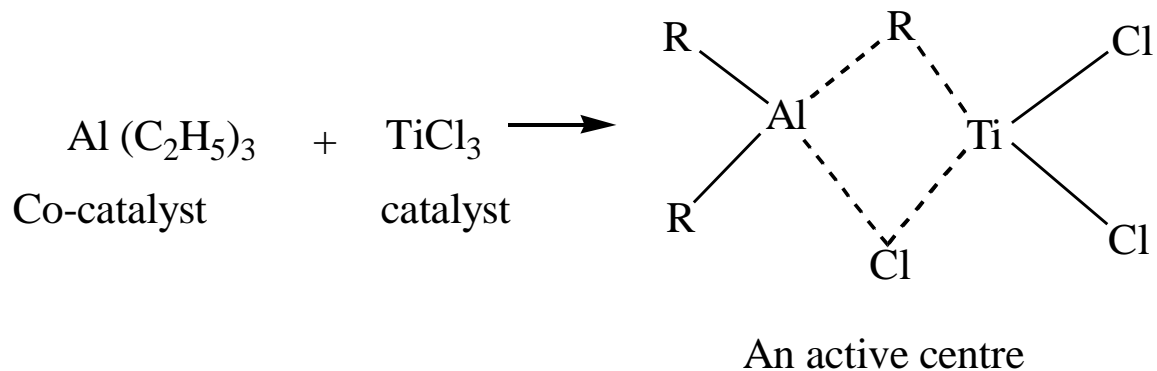


- Here Mt indicates metals like Ti, Mo, Cr, Ni.
- In the formation of monomer – catalyst complex, a coordination bond is involved in between a carbon atom of the monomer and the metal of the catalyst. Hence the polymerization effected by such catalyst systems is called coordination polymerization.

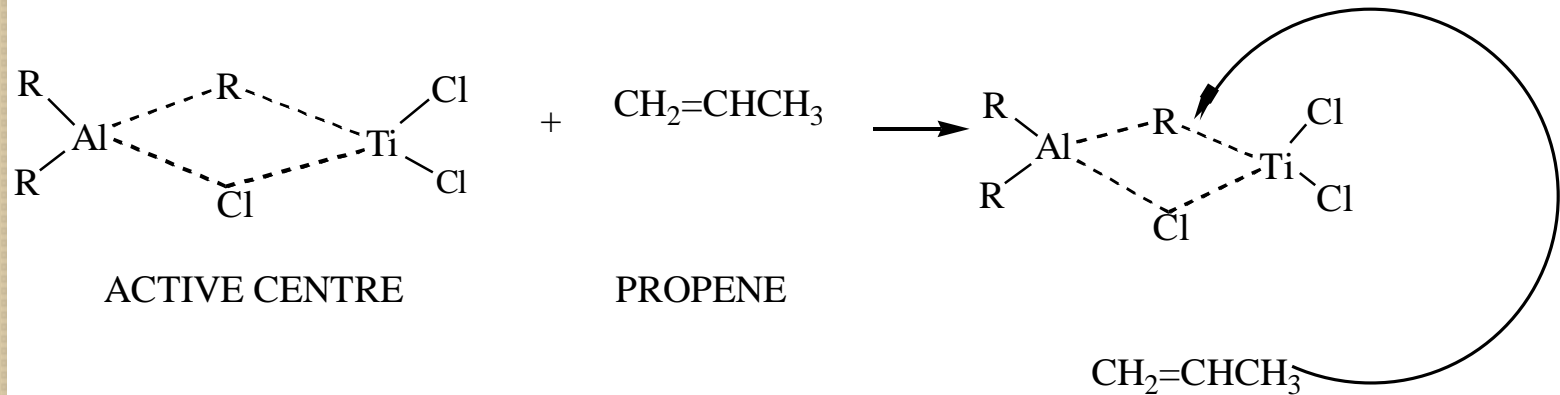
- Ziegler Natta catalysts are such type of catalyst as existed in coordination polymerization.
- It comprises of two components as against single component organo metallic component and other consisting of halides of IV-VIII group elements having transition valences.
- The co-catalysts are organo-metallic compound such as alkyls, aryls and hydrides of I-IV metals.
- The commonly used catalysts and co-catalysts are Titanium chlorides (both tri and tetrachlorides) and triethyl aluminium i.e.  $\text{Al}(\text{C}_2\text{H}_5)_3$ , diethyl aluminium chloride  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ .

- Aluminium alkyls acts as the electron acceptor and the titanium halide acts as electron donor. Therefore these two forms a coordination complex which is necessary for coordination polymerization.
- The formed complex is insoluble in the solvent .
- Many structures are proposed for these complexes

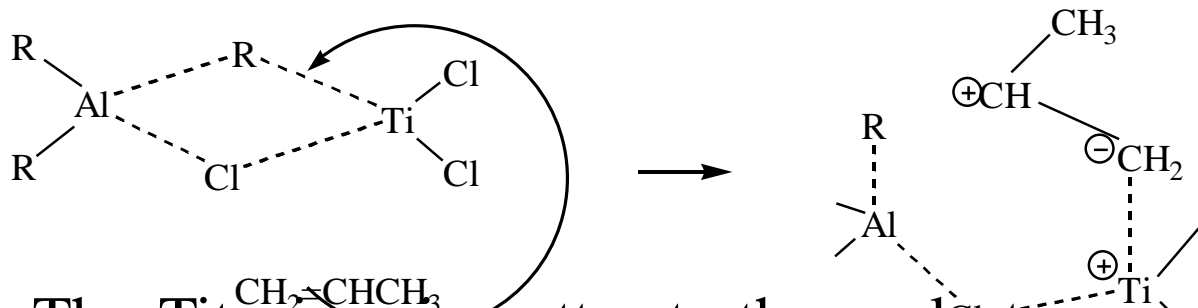
- From the active centre, the chain reaction propagates and form a solid surface of catalyst complex phase and the monomer is complexed with metal ion of the active centre before it inserts into growing chain.
- When catalyst and co-catalyst components are mixed , there occurs a chemisorption of the aluminium alkyl (electro positive in nature) on the Titanium Chloride solid surface, resulting in the formation of an electron deficient bridge complex as



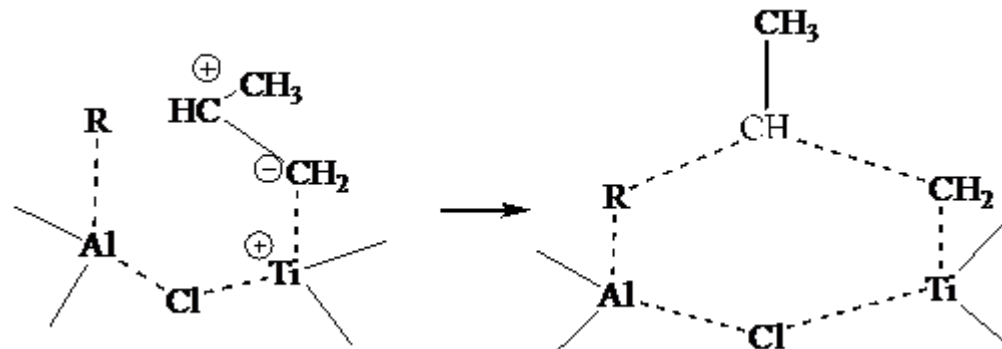
- The monomer is attracted towards Ti-C bond (C from alkyl group R) in the active centre. When it forms a  $\pi$ -complex with Titanium ion. The rate of reaction is influenced by the electrons present in the active centre.



The bond between R and Ti opens up producing an electron deficient Ti and a carbanion at R.

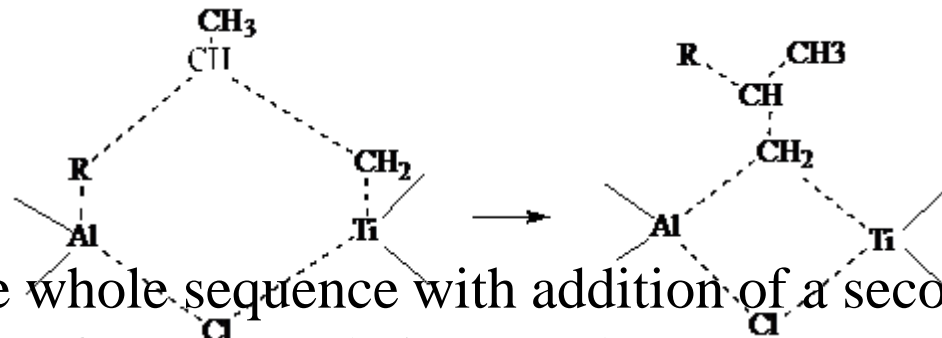


The Titanium ion attracts the  $\pi$  electron pair of monomer and forms a sigma bond. While the counter ion attracts electron-deficient centre of the monomer. The monomer is then inserted into a transition state ring structure.

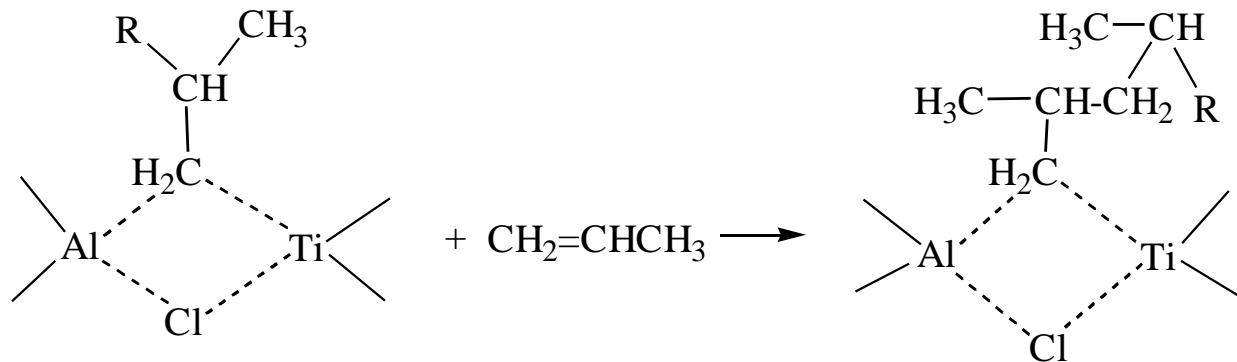




- This transition state now gives rise to the chain growth at the metal carbon bond regenerating the active centre.



Repeating the whole sequence with addition of a second monomer the structure of resultant chain growth as



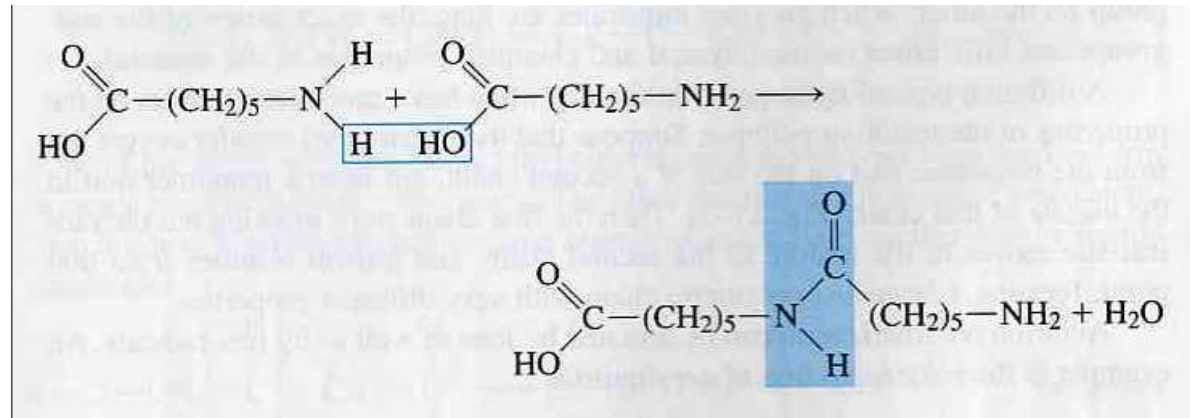
The monomer insertion is repeated in this manner and orientation of the substituent group of monomer is always taken from the metal ion end resulting a stereo regular polymer.

## Condensation polymerization

Condensation polymerization: the polymer grows from monomers by splitting off a small molecule such as water or carbon dioxide.

Example: formation of amide links and loss of water

Monomers



First unit of polymer +  $\text{H}_2\text{O}$

# CONDENSATION POLYMERIZATION

- Those which yield polymers with R.U. having less atoms than present in the monomers from which they formed (elimination of a small molecule).
- Example
- Polyester is a typical condensation reaction between bifunctional monomers with elimination of water.

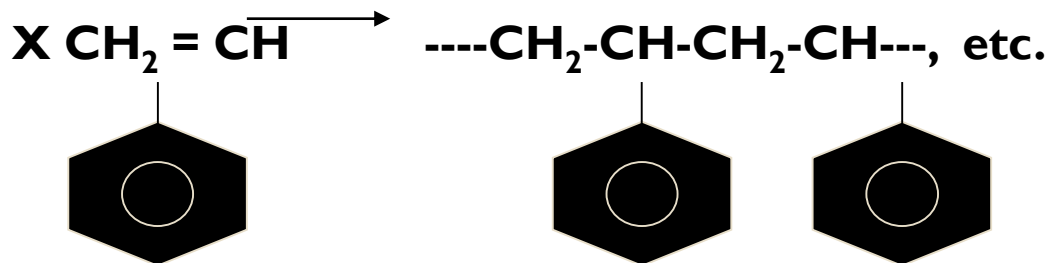


# ADDITION POLYMERIZATION

- Those which yield polymers with repeat units having identical molecular formula to those of monomers from which the one formed.

## Example

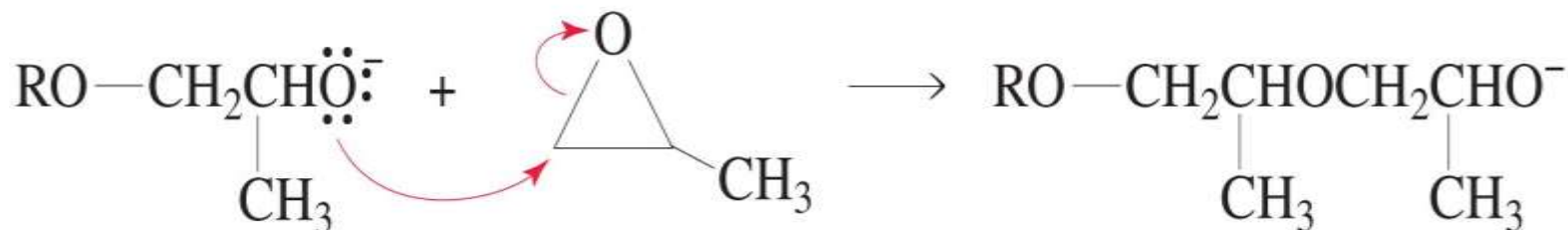
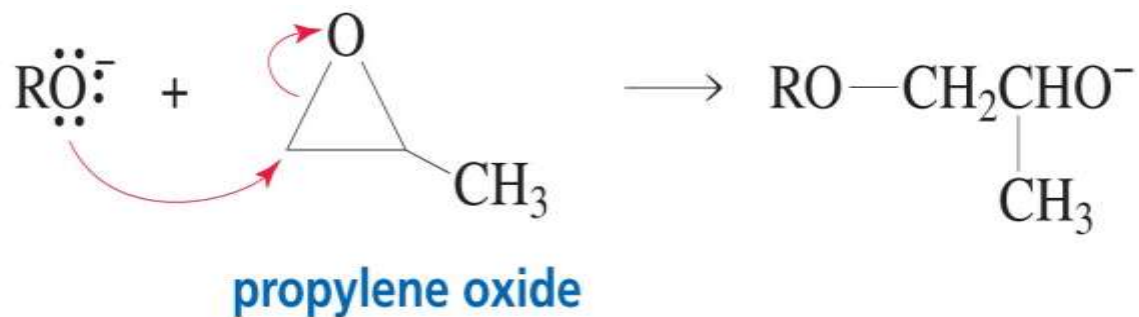
Polystyrene.

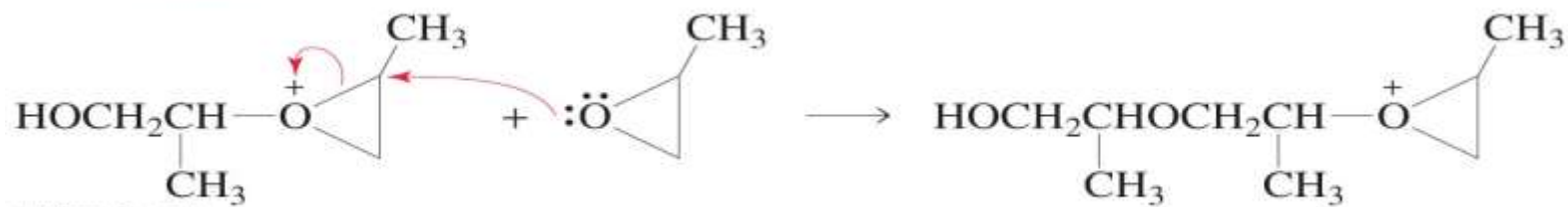
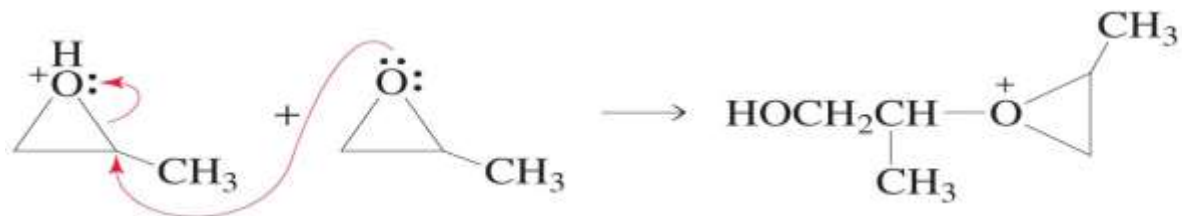
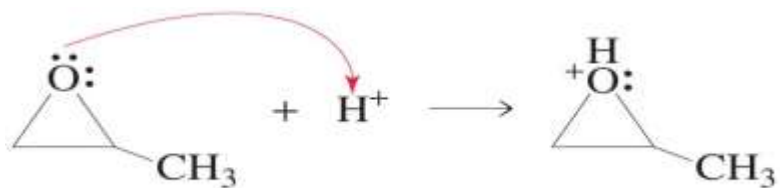


- The addition reaction mechanisms are result from chain reactions involving some sort of active center.
- Because condensation reaction mechanisms are usually formed by the step wise intermolecular condensation of reactive groups.
- And because some condensation process reacted in addition manner a new term is used to defined this process (step reaction or condensation polymer).

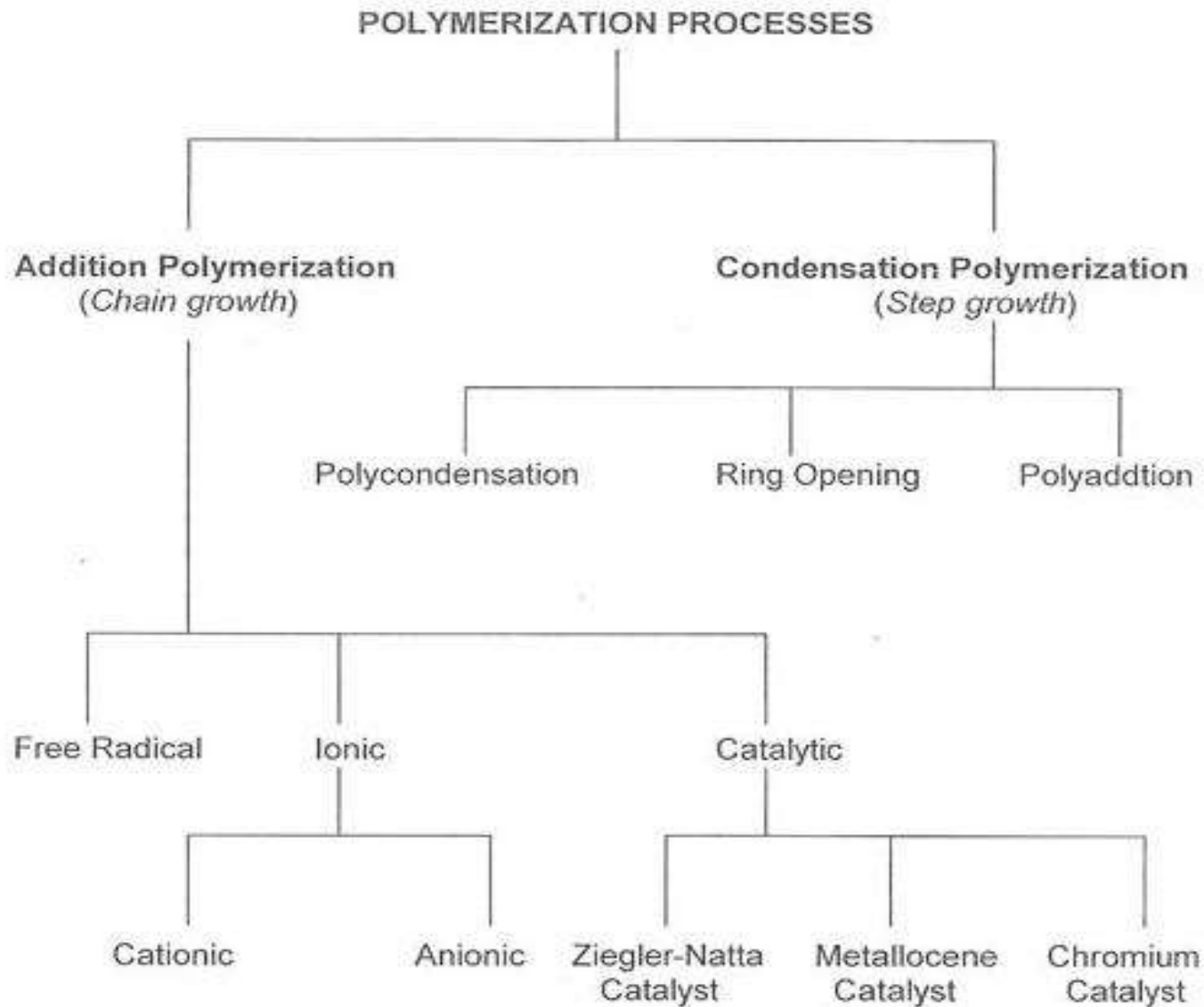
# Ring-Opening Polymerization

A ring-opening polymerization (ROP) is another form of chain-growth polymerization in which the terminal end group of a polymer chain acts as a reactive center where further cyclic monomers can be added by ring-opening and addition of the broken bond.





# Polymerisation techniques





# POLYMERIZATION TECHNIQUES

POLYMERIZATION TECHNIQUES 1. Addition polymerization, Bulk polymerization □ Solution polymerization, Suspension polymerization, Emulsion polymerization, Condensation polymerization, Melt polycondensation, Solution polycondensation .

Some of the techniques are given below

**BULK POLYMERIZATION** • Mass or block polymerization: Polymerization of the undiluted monomer. • carried out by adding a soluble initiator to pure monomer (in liquid state). • The mixture is constantly agitated & heated to polymerization temperature. • Once the reaction starts, heating is stopped as the reaction is exothermic. • The heat generated is dissipated by circulating water jacket. • Viscosity increases dramatically during conversion.

**BULK POLYMERIZATION** • The method is used for the polymerization of liquid state monomers. • It is usually adopted to produce polystyrene, polyvinyl chloride, polymethyl methacrylate and low density polyethylene.

**SOLUTION POLYMERIZATION:** Some disadvantages of bulk polymerization are eliminated in solution polymerization. Monomer along with initiator dissolved in solvent, formed polymer stays dissolved. The mixture is kept at polymerization temperature & constantly agitated. Depending on concentration of monomer the viscosity of solution does not increase.

**SOLUTION POLYMERIZATION:** After the reaction is over, the polymer is used as such in the form of polymer solution or the polymer is isolated by evaporating the solvent. Polymer so formed can be used for surface coating. It is used for the production of Polyacrylonitrile, PVC, Polyacrylic acid, Polyacrylamide, Polyvinyl alcohol, PMMA, Polybutadiene, etc

**SUSPENSION POLYMERIZATION:** Liquid or dissolved monomer suspended in liquid phase like water. Initiators used are monomer soluble e.g. dibenzoyl peroxide. Thus, polymer is produced in heterogeneous medium. Initiator The size of monomer droplets is 50-200  $\mu\text{m}$  in diameter. The dispersion is maintained by continuous agitation and the droplets are prevented to coalesce (unite or merge) by adding small quantity of stabilizers.

**SUSPENSION POLYMERIZATION:** The stabilizers used are PVA, gelatin, cellulose are used along with inorganic stabilizers such as kaolin, magnesium silicate, aluminum hydroxide, calcium/magnesium phosphate, etc if necessary. As it concerns with droplets, each droplet is tiny bulk reactor. The polymerization takes place inside the droplet & product formed being insoluble in water. The product separated out in the form of spherical pearls or beads of polymer. Hence the technique is also known as Pearl polymerization / Granular polymerization / Bead polymerization.

**EMULSION POLYMERIZATION:** The technique is used for the production of large number of commercial plastics & elastomers. The system consists of water insoluble monomer, dispersion medium & emulsifying agents or surfactants (soaps and detergents) and a water soluble initiator (potassium persulphate / H<sub>2</sub>O<sub>2</sub>, etc). The monomer is dispersed in the aqueous phase, not as a discrete droplets, but as a uniform emulsion. The size of monomer droplet is around 0.5 to 10 μm in diameter depending upon the polymerization temperature & rate of agitation.



# **CONDUCTING POLYMERS**

# Conducting Polymers



In 1906 very small but measurable electrical conductance was reported for anthracene. Single crystals of anthracene and other condensed aromatic ring systems formed interesting behaviour of electrical conductivity. It obviously follows that a high polymeric system obtained in semiconducting or conducting form would combine the electrical properties of condensed polynuclear aromatic compounds with the useful mechanical strength and thermal properties and good corrosion resistance.

- Introduction of Polymer
- Types of polymer
- Synthesis of Polymers
- What is conductivity?
- What makes a material conductive?
- How can plastic become conductive?
- Self-Doped conducting polymers
- Types of Self-Doped conducting polymers
- Doping Mechanism in Self-Doped polymers
- Doping process.
- Factors that affect the conductivity.
- Applications.

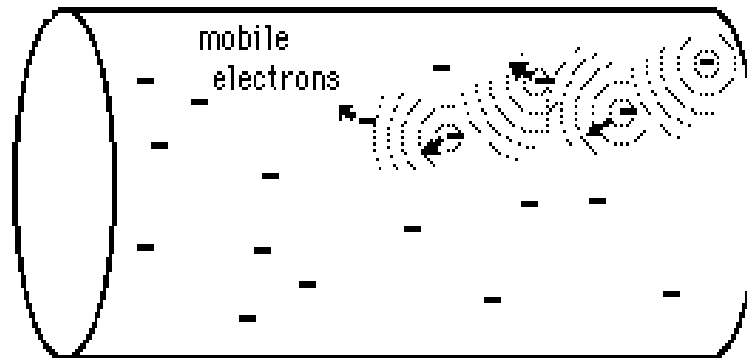
# What is conductivity?


Conductivity can be defined simply by Ohms Law.

$$V = IR$$

Where R is the resistance, I the current and V the voltage present in the material. The conductivity depends on the number of charge carriers (number of electrons) in the material and their mobility. In a metal it is assumed that all the outer electrons are free to carry charge and the impedance to flow of charge is mainly due to the electrons "bumping" in to each other.

Cross-section of copper wire



An external influence  repels a nearby electron

The electron's neighbors find it repulsive. If it moves toward them, they move away, creating a chain of interactions which propagates through the material at the speed of light.

Insulators however have tightly bound electrons so that nearly no electron flow occurs so they offer high resistance to charge flow. So for conductance free electrons are needed.

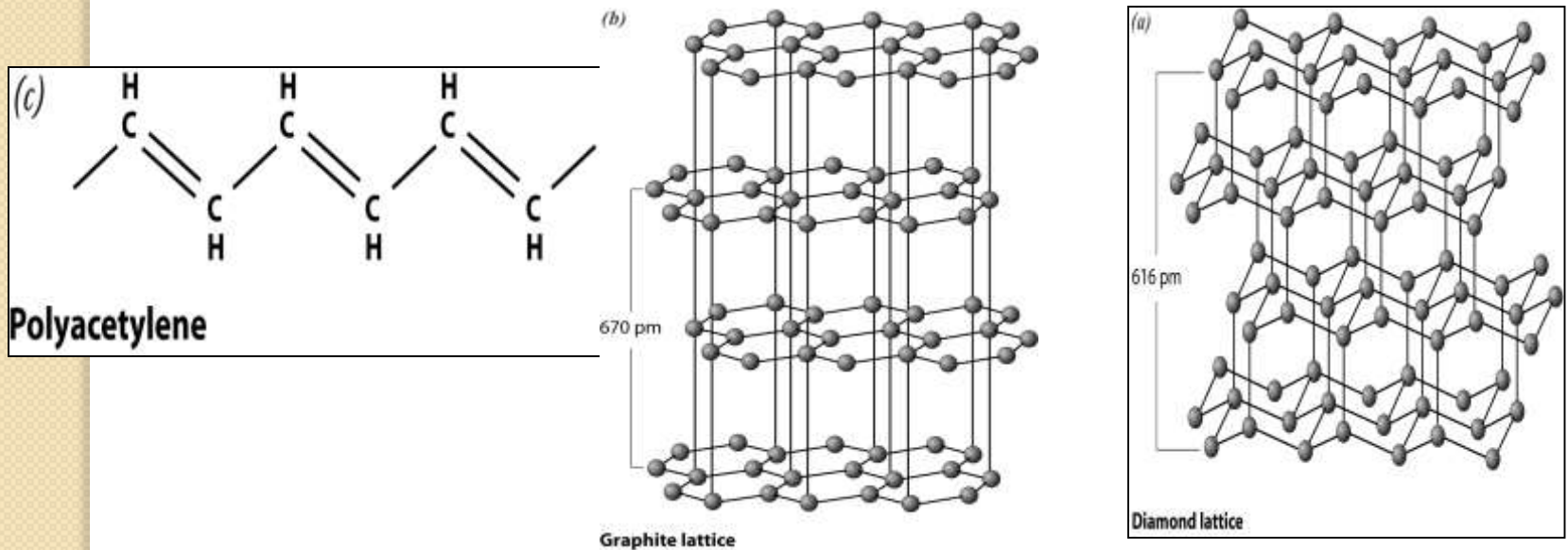


# Conducting Polymer

- ❖ Polymers are generally insulators because the organic molecules of which they are composed have **no free electrons** to carry current ; all the electrons are held firmly by atoms forming the molecules.
- ❖ In Conducting Polymers the carbon atoms are backbone linked by double bonds have the potential to **conduct electricity**, especially when a number of such bonds occur in the vicinity of each other.

# What makes the material conductive?

Three simple carbon compounds are diamond, graphite and polyacetylene. They may be regarded as three- two- and one-dimensional forms of carbon materials .



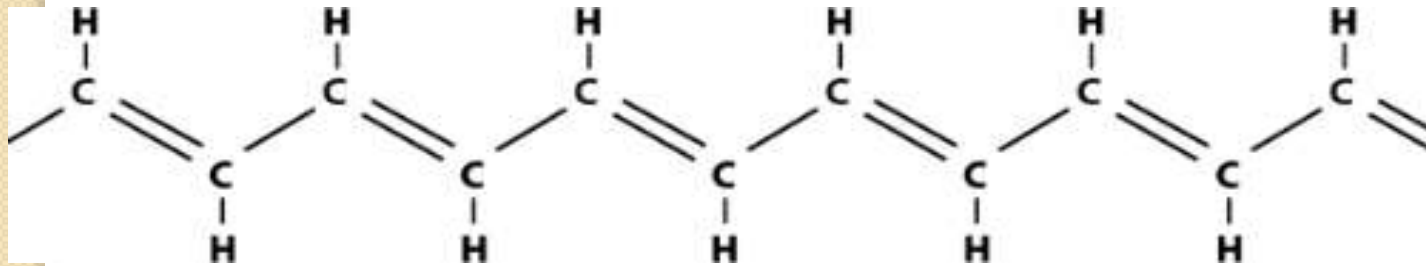
**Diamond**, which contains only  $\sigma$  bonds, is an insulator and its high symmetry gives it isotropic properties.

**Graphite** and **acetylene** both have mobile  $\pi$  electrons and when doped, are highly anisotropic and behave as metallic conductors.

# Two conditions to become conductive:

1-The first condition for this is that the polymer consists of alternating single and double bonds, called conjugated double bonds.

In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” ( $\sigma$ ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localised “pi” ( $\pi$ ) bond which is weaker.



2-The second condition is that the plastic has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. The process is known as doping.

# The Nobel Prize in Chemistry 2000

Yet Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa have changed this view with their discovery that a polymer, polyacetylene, can be made conductive almost like a metal by the reaction of conjugated polymers with Ziegler-Natta catalyst ( $\text{AlR}_3 + \text{TiCl}_4$ ) resulting in highly delocalized polycations and polyanions



**Alan G. MacDiarmid**

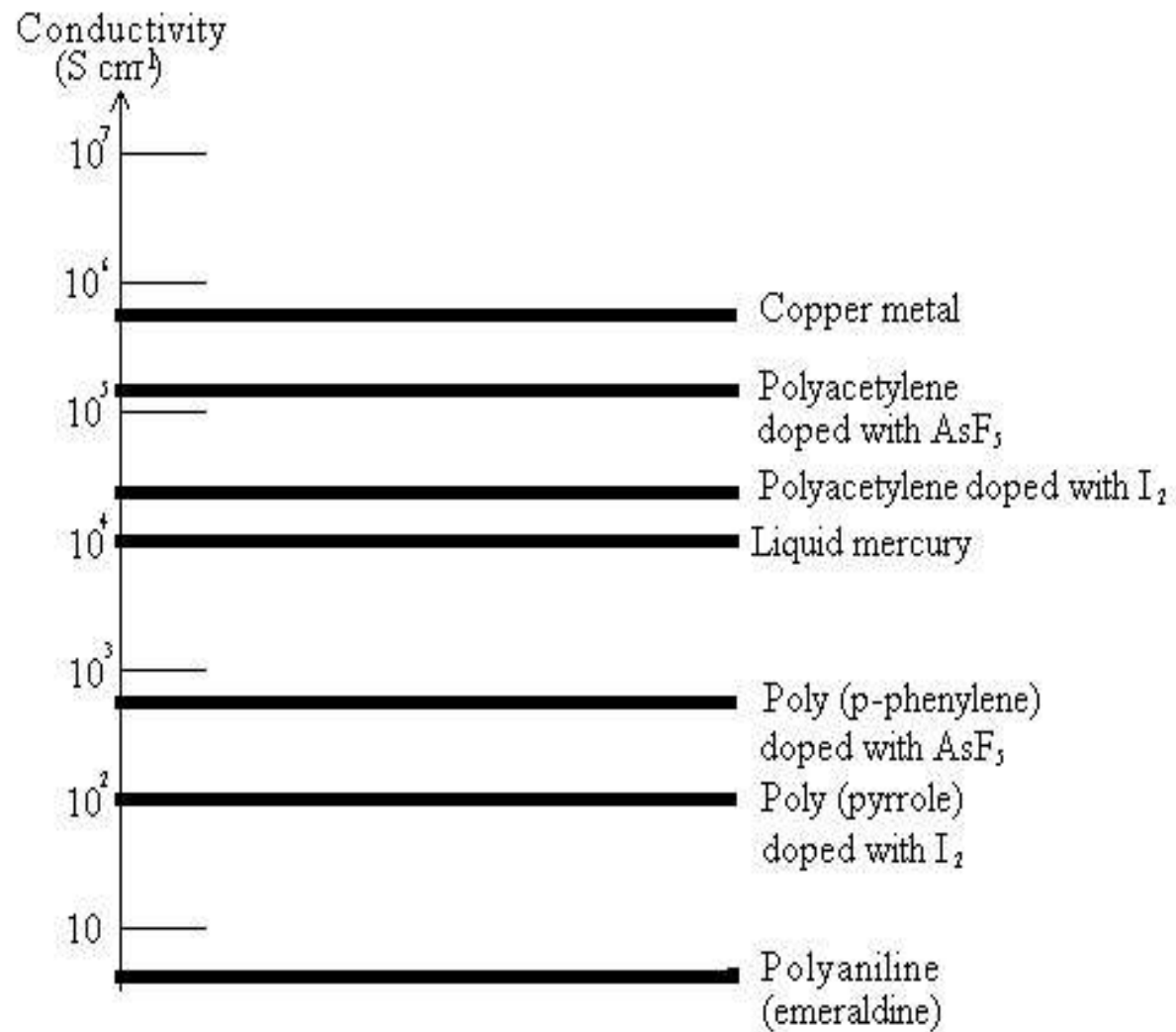
Professor at the University of Pennsylvania,  
Philadelphia, USA.

**Hideki Shirakawa**

Professor Emeritus,  
University of Tsukuba, Japan.

**Alan J. Heeger**

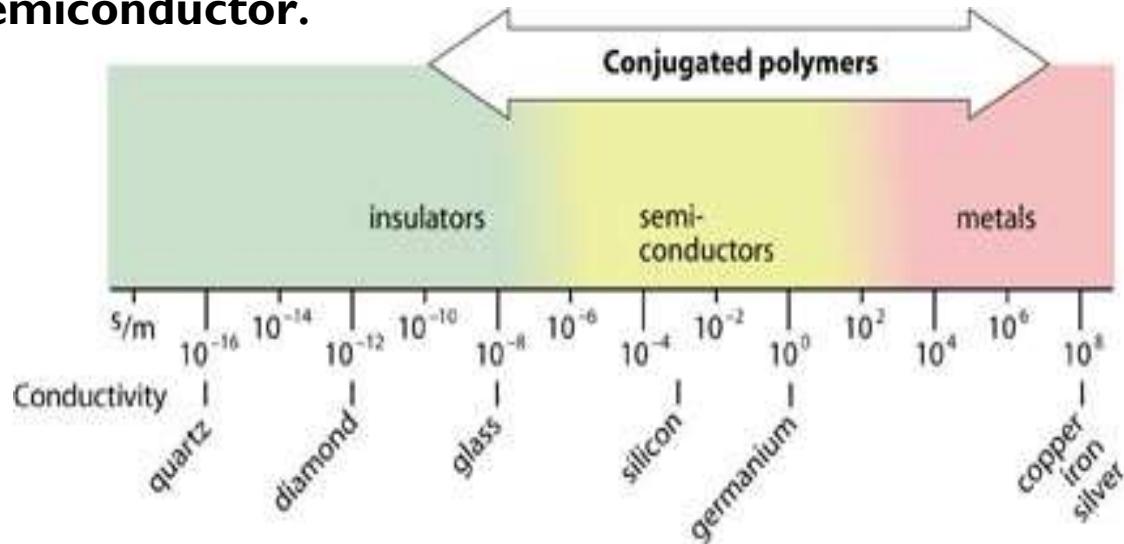
Professor at the University of California  
at Santa Barbara, USA.



Logarithmic conductivity ladder locating some metals and conducting polymers

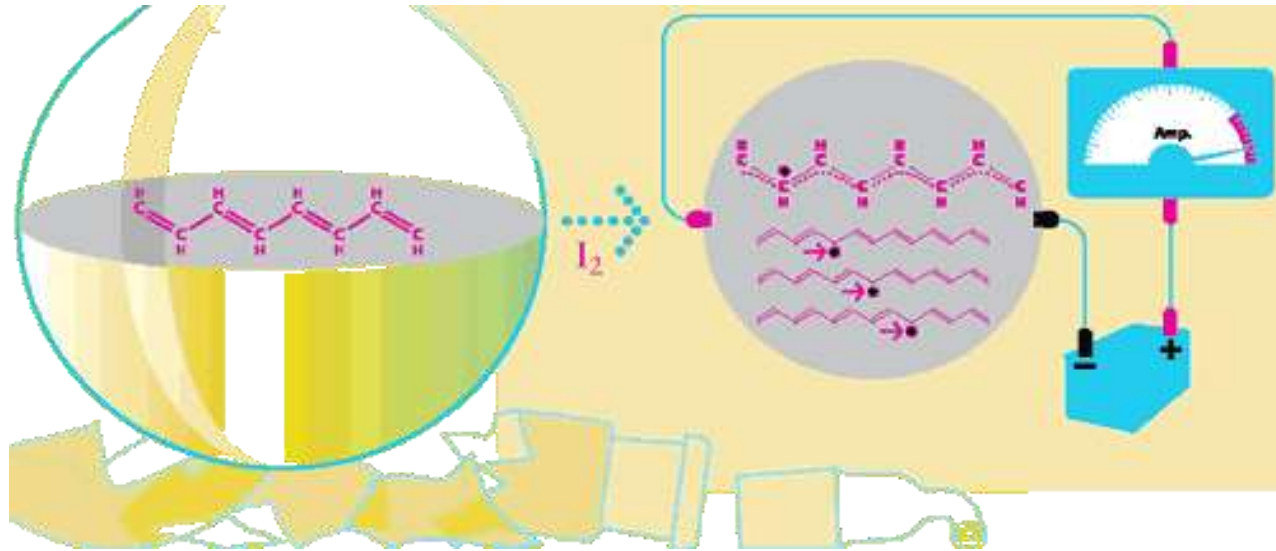
# DOPING - FOR BETTER MOLECULE PERFORMANCE

- Doped polyacetylene is, e.g., comparable to good conductors such as copper and silver, whereas in its original form it is a semiconductor.



**Conductivity of conductive polymers compared to those of other materials, from quartz (insulator) to copper (conductor). Polymers may also have conductivities corresponding to those of semiconductors.**

- The halogen doping transforms polyacetylene to a good conductor.

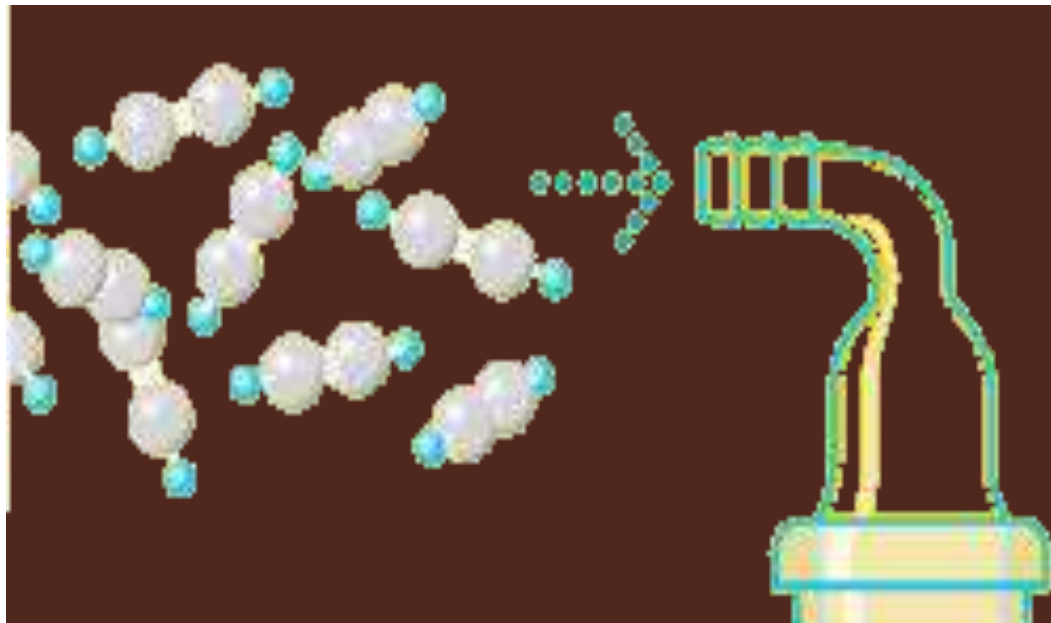


Oxidation with iodine causes the electrons to be jerked out of the polymer, leaving "holes" in the form of positive charges that can move along the chain.



# How can plastic become conductive?

Plastics are *polymers* that form long chain of molecules of repeating units. In becoming electrically conductive, a polymers imitate a metal, that is, its electrons need to be free to move and not bound to the atoms. *Polyacetylene* is the simplest possible conjugated polymers. It is obtained by polymerisation of acetylene, shown in the figure.





## What is doping?

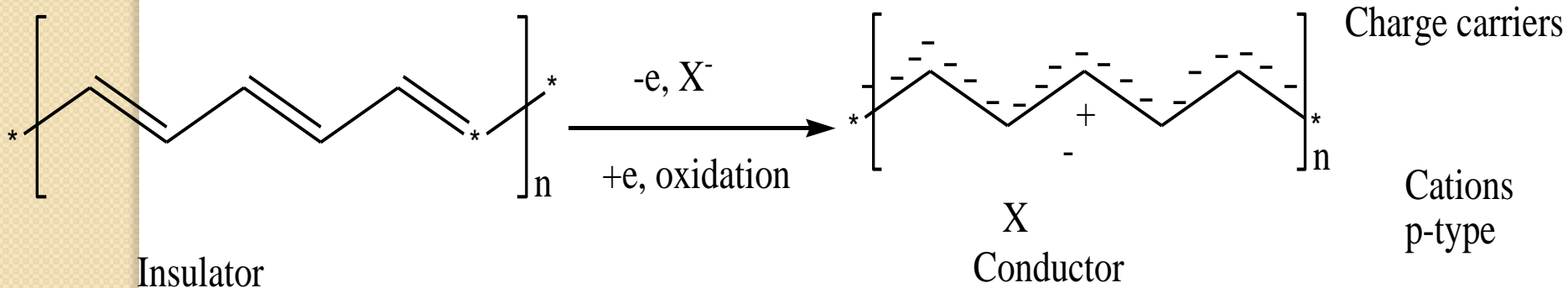
Doping is addition of controlled amounts of specific impurity atoms for the purpose of changing the conductivity of a material by increasing either the electron or hole concentration.

Donors (Electron-increasing Dopants)	Acceptors (Hole-increasing Dopants)
$\left. \begin{array}{l} P \leftarrow \\ As \\ Sb \end{array} \right\}$ Column V elements	$\left. \begin{array}{l} B \leftarrow \\ Ga \\ In \\ Al \end{array} \right\}$ Column III elements

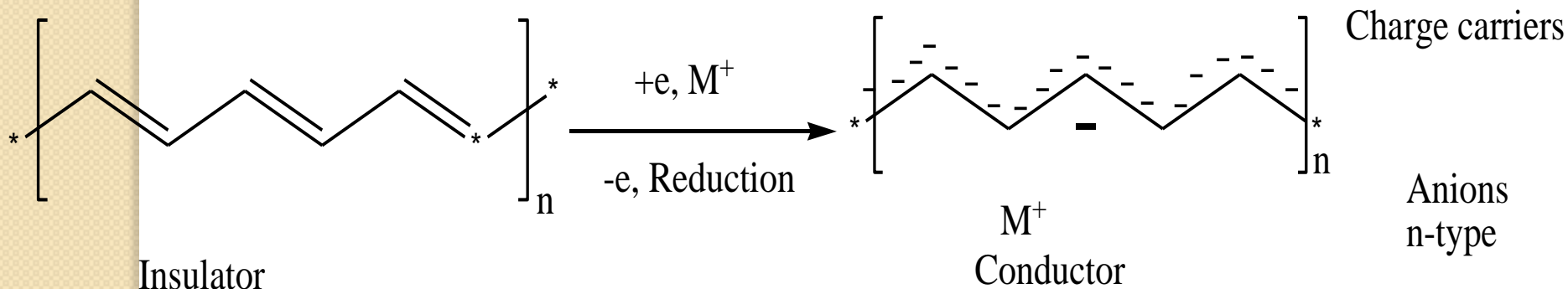
Dopant atoms can either be "donors" or "acceptors." Donors increase the electron concentration, whereas acceptors increase the hole concentration. This is due to the fact that an element from Column IV of the Periodic Table has four valence electrons which are shared with its four nearest neighbors via covalent bonding.

# Doping.

- There are two types of doping:
- 1-oxidation with halogen (or *p*-doping).



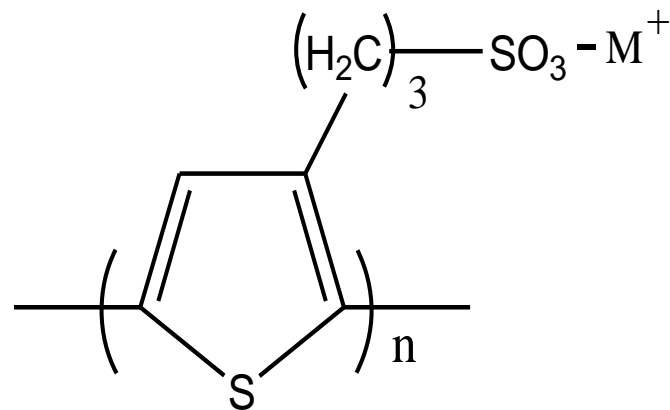
2- Reduction with alkali metal (called *n*-doping).



**Oxidant :FeCl<sub>3</sub>, Fe(OTs)<sub>3</sub>,AsF<sub>5</sub>, I<sub>2</sub>, Br<sub>2</sub>, Cl<sub>2</sub> Reductant :RLi, Naph<sup>-</sup>Li<sup>+</sup>**

# Self-Doped conducting polymers

- ❖ In 1987 Wudl first reported novel concept of self doping in conducting polymer
- ❖ Self-doping useful for increasing the solubility of conducting polymers in aqueous media.
- ❖ When **ionizable** functional groups that form **negatively** charged sites are attached to the polymers chains to make conducting, referred as '**Self-Doping**'. Or When the groups is an **acid**, referred as '**Self-Acid-Doping**'.



**Chemical structure of self-doped Polythiophene derivatives**

# Types of Self-Doped conducting polymers

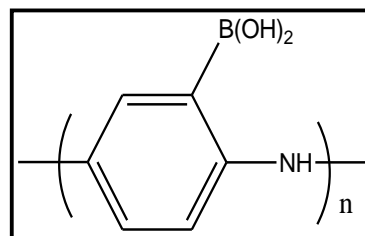
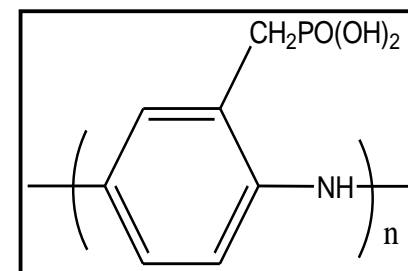
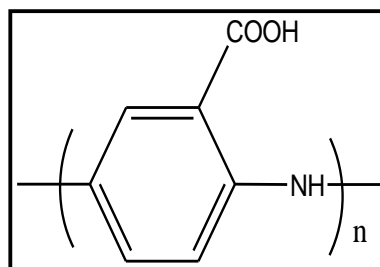
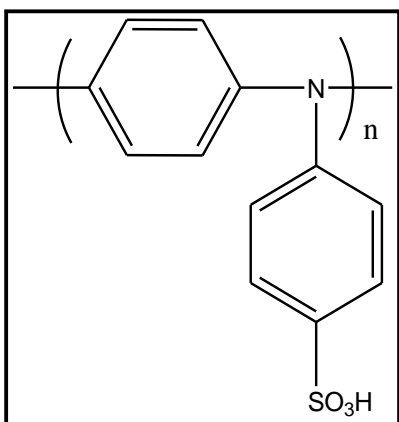
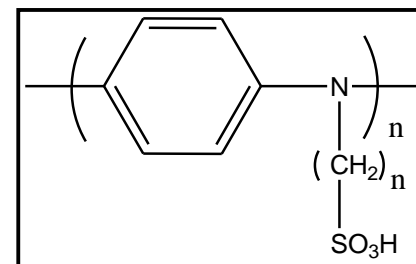
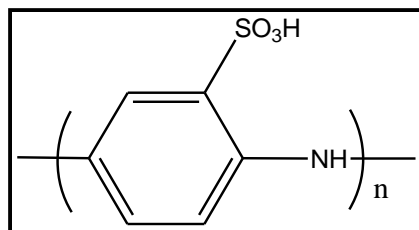
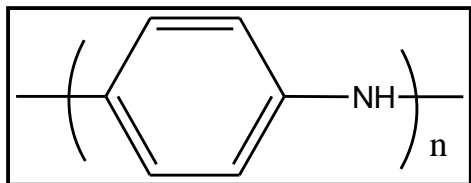
Self-Doped conducting polymers have been functionalizing the monomer and polymers with ionizable, negatively charged moieties.

It is prepared with various functional groups such as Sulfonic acid, alkyl and alkoxy-sulfonic acid, Carboxylic acid, Phosphonic acid, Acetic acid and boronic acid.

Two types of Self-Doped conducting polymer derivatives.

- 1. It contains ionizable functional groups attached directly to the aromatic ring of polymers backbone.**
- 2. It contains ionizable functional groups bound through a spacer consisting of alkane or aromatic groups of heteroatoms in conjugated backbone.**

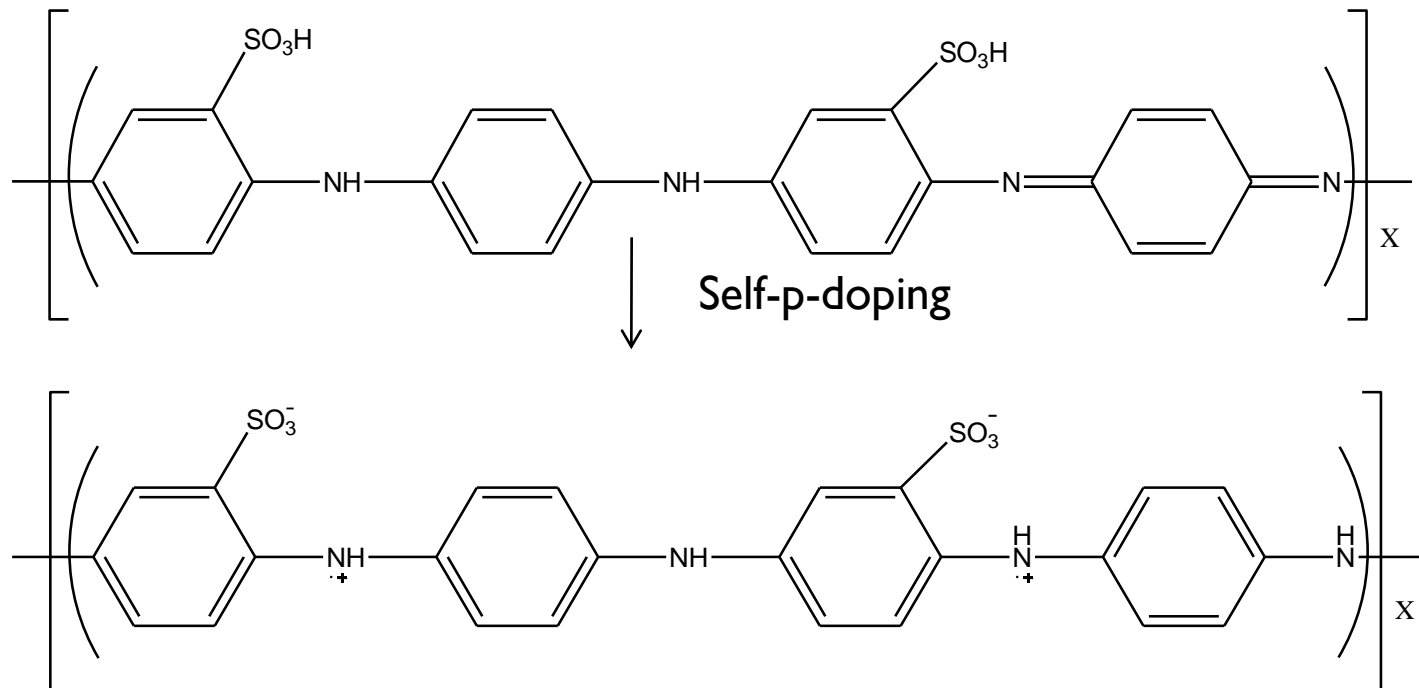
# ❖ Various self-doped polyaniline derivatives



## ❖ Doping Mechanism in Self-Doped polymers

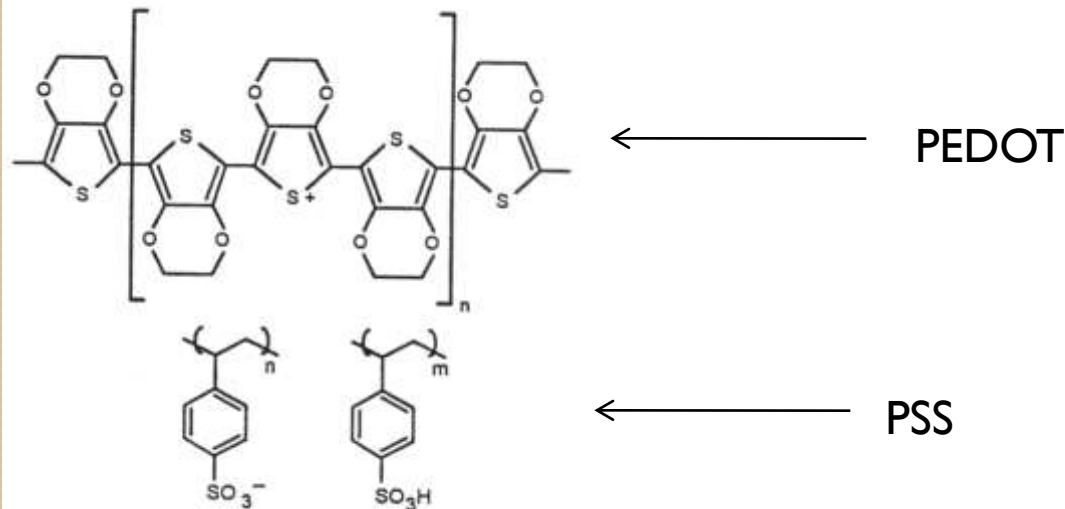
### • p- Type Doping

When sulphonated polyanilines are oxidized by ejection of electrons from nitrogen and reduction of protons. The removal of protons produces negative charges on  $\text{SO}_3^-$  which compensate positive charges of nitrogen. In the oxidized state of sulphonated polyanilines the positive charge carriers are more localised on nitrogen than on the parent polyaniline salt.



# p-type doping

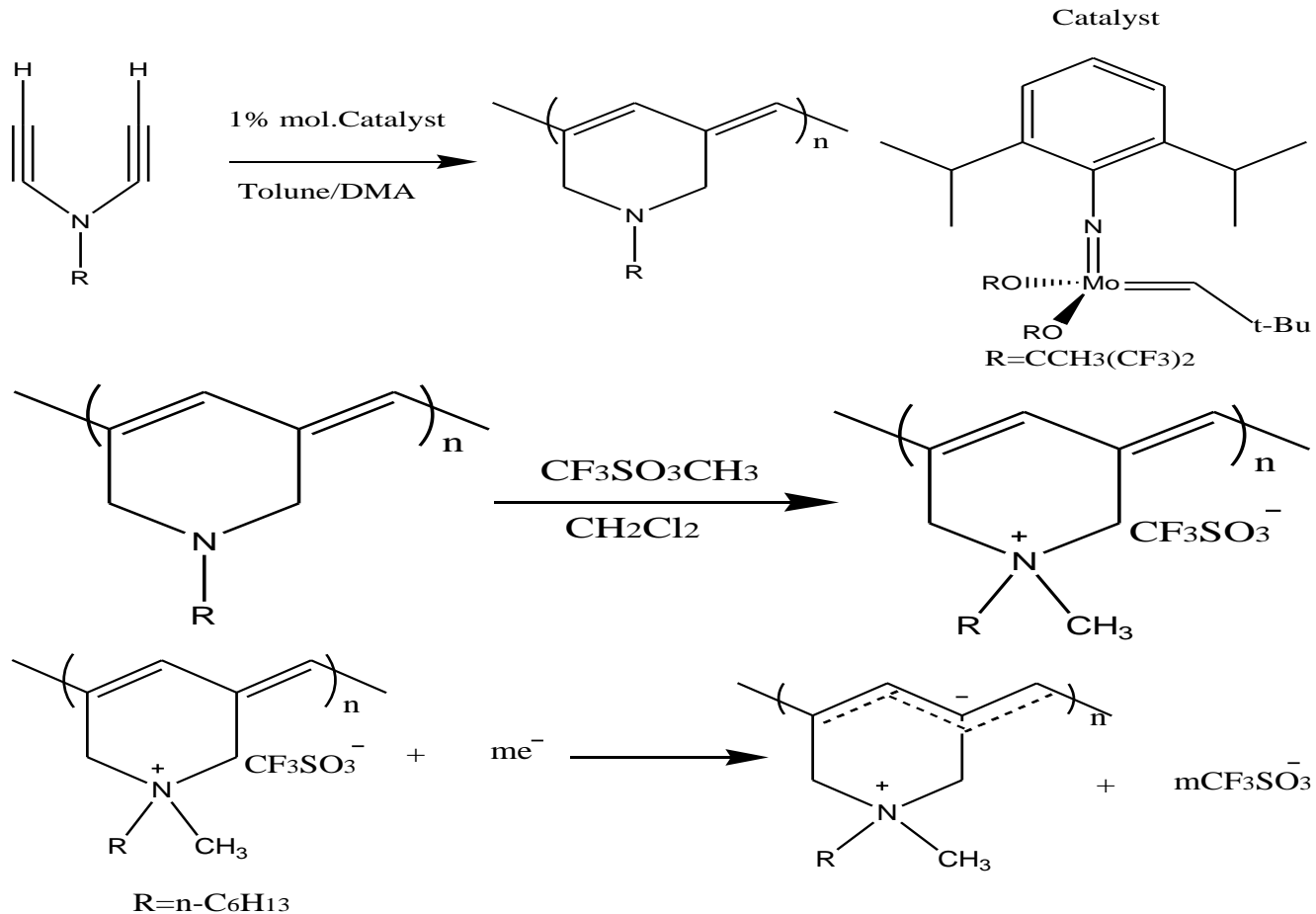
Polyethylene dioxythiophene polystyrene sulphonate (PEDOT/PSS) can be bought from Bayer as an aqueous solution. The sulphonic acid group on the PSS dopes the PEDOT to make it conductive.



The thin layer of PEDOT:PSS is virtually transparent and colorless, prevents electrostatic discharges during film rewinding, and reduces dust build up on the negatives after processing. The electrochromic properties of PEDOT are used to manufacture windows and mirrors which can become opaque or reflective upon the application of an electric potential. Widespread adoption of electrochromic windows could save billions of dollars per year in air conditioning costs.

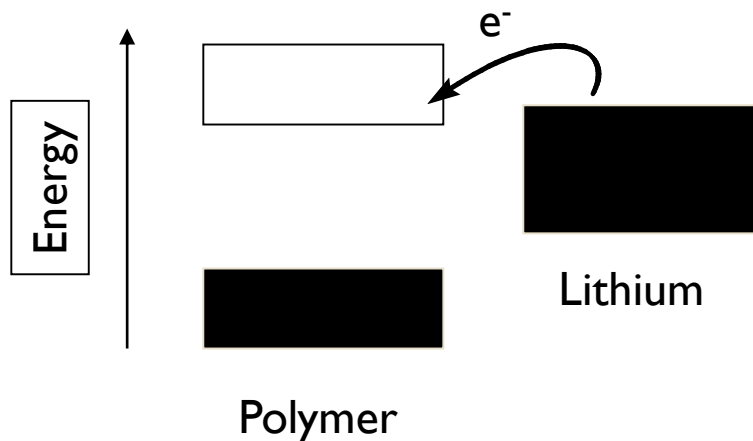
# ❖ n-Type Doping

Self-n-doped polymers, cationic sites act as dopant and are incorporated into the polymers. The polymer poly(dipropargylhexylamine) was prepared from cyclopolymerization of N-hexyldipropargylamine.

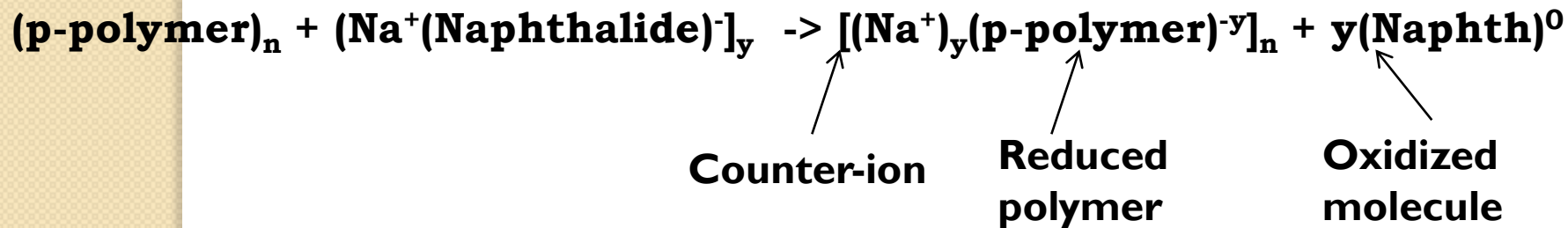




# n-type doping



Reducing agents donate electrons to the conduction band. Solids like calcium, lithium and sodium tend to dope the polymer only near the surface since they cannot diffuse into the film. Electrolytes (see below) can be used to dope an entire film.

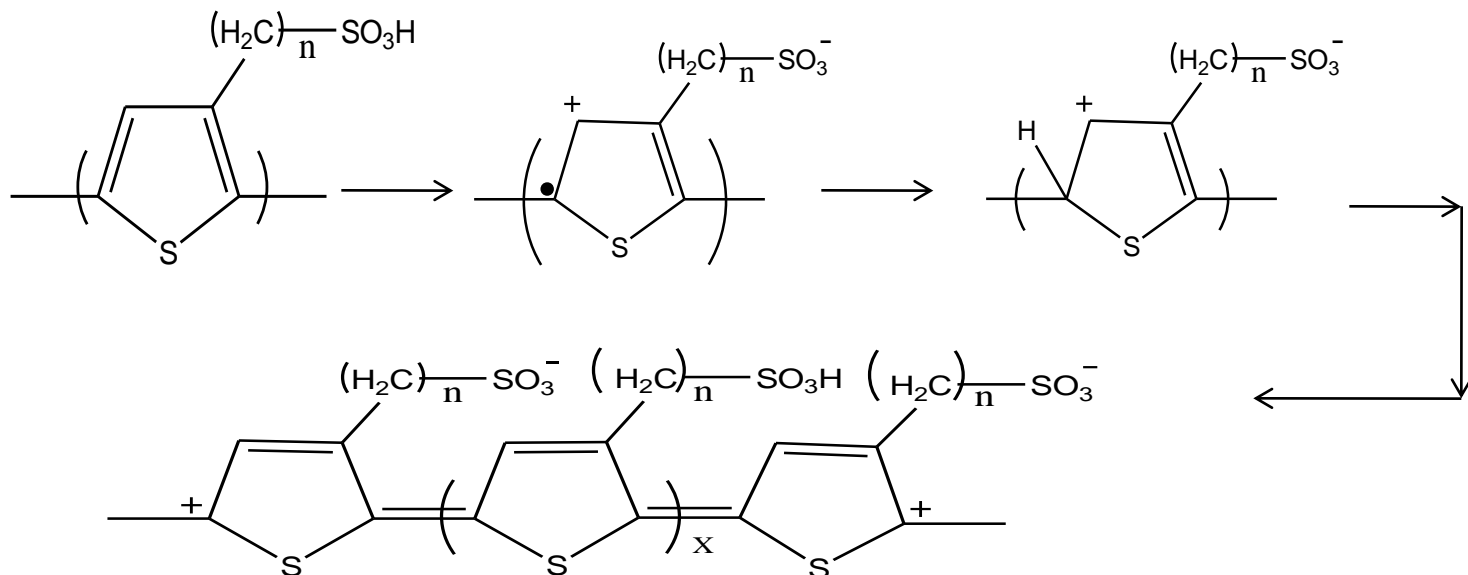


## ❖ Auto Doping

The term 'auto-doping' or self-acid-doping first introduced by Ikenoue, Wudl and Heeger. In presence of water the acidic proton is solvated by water molecules.

Protonation of backbone creates a polaron/ bipolaron and proton addition on the polymer chain.

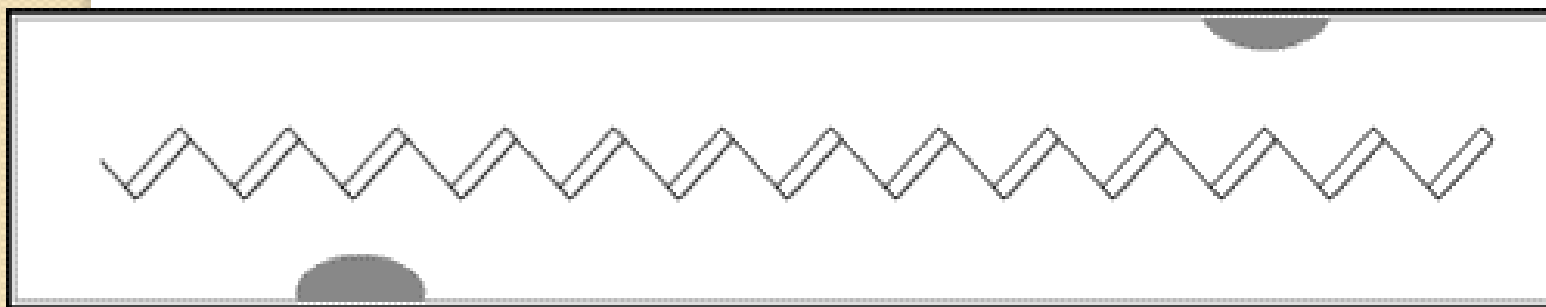
Auto-doping or Self-acid-doping is redox process.





- The game offers a simple model of a doped polymer. The pieces cannot move unless there is at least one empty "hole". In the polymer each piece is an electron that jumps to a hole vacated by another one. This creates a movement along the molecule - an electric current.

- The iodine molecule attracts an electron from the polyacetylene chain and becomes  $I_3^-$ . The polyacetylene molecule, now positively charged, is termed a radical cation, or **polaron**.



- The lonely electron of the double bond, from which an electron was removed, can move easily. As a consequence, the double bond successively moves along the molecule.
- The positive charge, on the other hand, is fixed by electrostatic attraction to the iodide ion, which does not move so readily.
- Doping is performed as much higher level (20-40%) in conducting polymers than in semiconductors (<1%). The polaron moves as a unit up and down the polymer chain and is responsible for the macroscopically observed conductivity of the polymer.

# Factors that affect the conductivity

1-Density of charge carriers.

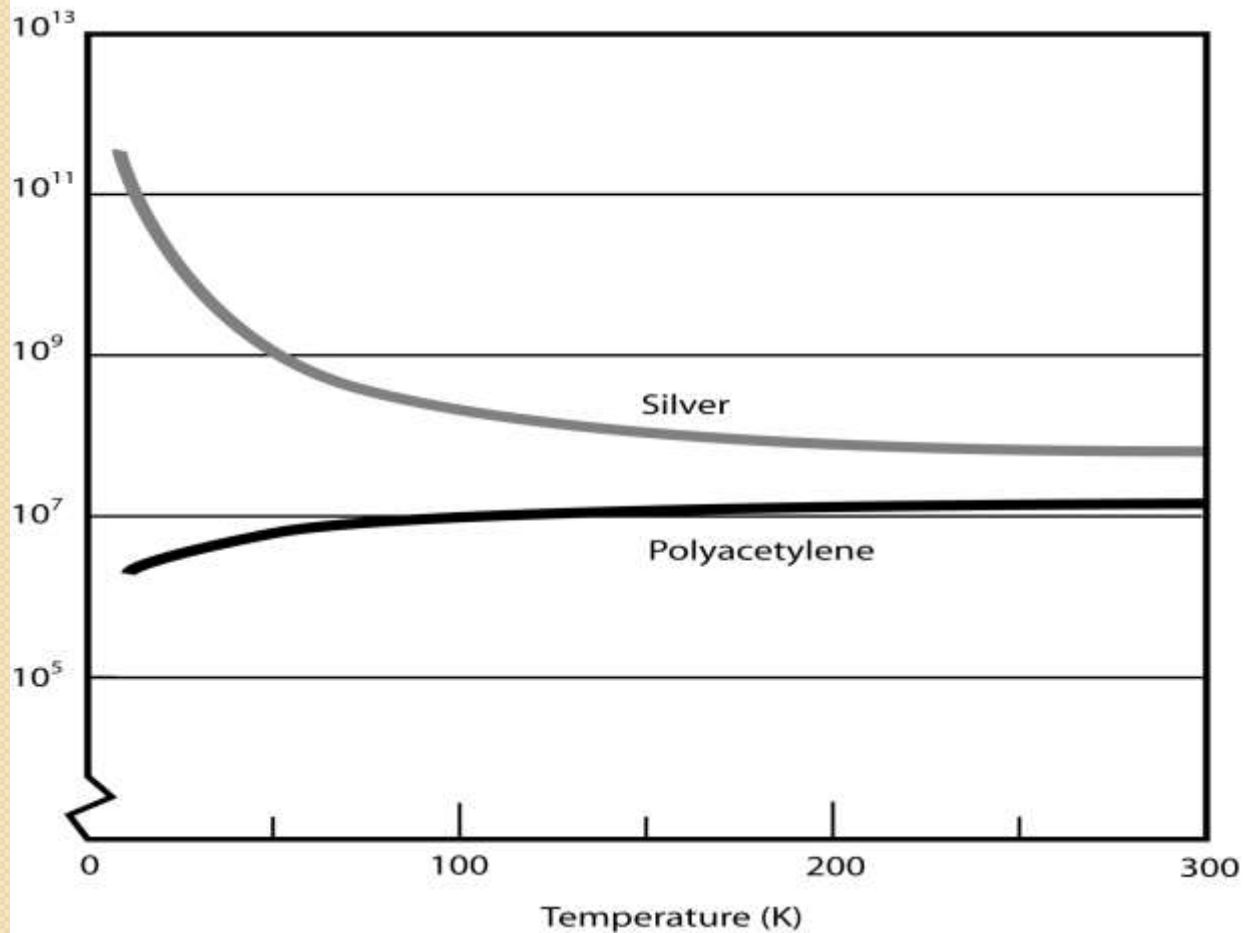
2- Their mobility.

3-The direction.

4-presence of doping materials (additives that facilitate the polymer conductivity)

5-Temperature.

### Conductivity (Siemens per m)



The conductivity of conductive polymers decreases with decrease in temperature in contrast to the conductivities of typical metals, e.g. silver, which increase with decreasing temperature.

## **Photoconducting polymers:**

Enhancement of electrical conductivity on exposure to light or irradiation is called photoconductivity. Photoconductive polymers are commonly insulators in the dark and they behave as semiconductors when exposed to light.

Photoconductors do not contain free charge carriers; in fact, the charge carriers are generated in them by the action of light. The electrical charge carriers may also be photo-generated extrinsically in an adjacent photo-conductor and then transferred to the polymer that would act as a charge transporting medium.

Poly(N-vinyl carbazole) (PNVC), exhibit high level of photoconductivity when sensitized with suitable electron acceptors.

# **Metal-filled conducting polymer composites:**

Metals may be used in the form of powders, flakes, whiskers, filaments and cords, wire and wire mesh as filler or reinforcing agent in a polymer matrix for making various moulded, formed or coated objects. The advantage of metal powders over other particulate fillers is that they impart good electrical and thermal conductivity into the composite. Uniform dispersion of metal powders etc. (particulate fillers) are achieved by shear mixing using the matrix polymer. For use of liquid polymer or resin intermediate, the metallic powders are normally dispersed in the liquid resin/polymer by continuous stirring which is then further continued with addition of suitable chain extenders or curatives before transferring the mix to a moulding or forming equipment for ultimate conversion into a useful end-product.



# Transistors:

The metal oxide semiconductor field effect transistor (MOSFET) is the most important device for microprocessors and memory device. Much research has explored the use of conducting polymers as an active material in field effect transistors devices. However, the performance of these organic devices has not been comparable with that of their inorganic counterparts due to low charge carrier mobility and relatively poor stability. Experiments have shown that the field effect mobility can be increased by two to three orders of magnitude by additional doping, confirming the fact that the carrier mobility in conjugated polymers depends strongly on doping.

# Biosensors:

Polyaniline is the conducting polymer most commonly used as an electrocatalyst and immobilizer for biomolecules. However for biosensors applications, a nearly neutral pH environment is required, since most biocatalyst (enzymes) operate only in neutral or slightly acidic or alkaline solution. Therefore, it has been difficult or impossible to couple enzyme catalyzed electron transfer processes involving solution species with electron transport or electrochemical redox reactions of mostly polyaniline and its derivatives. Polyaniline is conducting and electroactive only in its protonated form i.e. at low pH values. At pH values above 3 or 4 polyaniline is insulating and electrochemically inactive. Self doped polyaniline exhibit redox activity and electronic conductivity over an extended pH range, which greatly expands its applicability towards biosensors. Therefore the use of self doped polyaniline and its derivatives could in principle, enable the direct or mediated electron transfer between the polymer matrix and active centers of biocatalyst.

# Rechargeable batteries:

Lithium secondary batteries are one of the most important applications of electronically conducting polymer. Conducting polymers such as polyaniline, polypyrrole, and polythiophene are expected to be promising materials for the electrodes of secondary batteries because they are relatively stable in air and have good electrochemical properties.

In the discharging cycle of these batteries, the electrons flowing from the lithium anode (negative pole) through an external electric circuit must be consumed at the cathode (positive pole). When used as the active mass of a positive electrode, a conducting polymer ensures efficient utilization of electrons by converting the oxidized form of the conducting polymer into the reduced form. Conversely, electrochemical oxidation of the reduced form takes place in the reverse charging cycle.

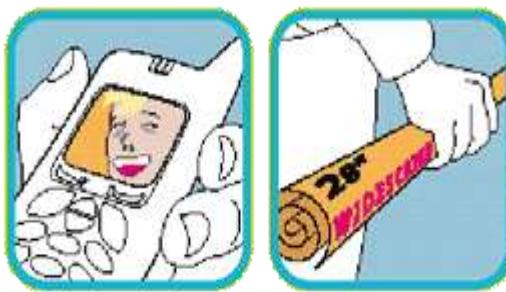
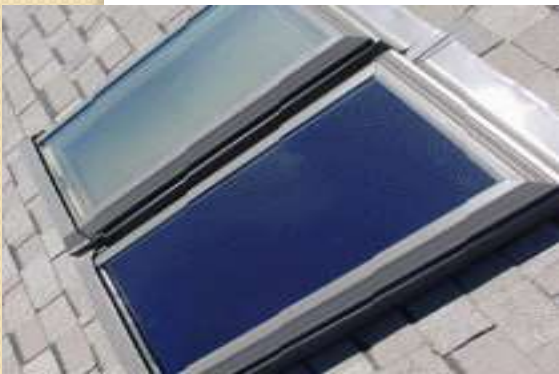
# APPLICATIONS

Conducting polymers have many uses. The most documented are as follows:

- × Anti-static substances for photographic film
- × Corrosion Inhibitors
- × Compact Capacitors
- × Anti Static Coating
- × Electromagnetic shielding for computers "Smart Windows"

A second generation of conducting polymers have been developed these have industrial uses likes:

- × Transistors
- × Light Emitting Diodes (LEDs)
- × Lasers used in flat televisions
- × Solar cells
- × Displays in mobile telephones and mini-format television screens
- × Sensors
- × Rechargeble Batteries



smart" windows

Shield for computer screen  
against electromagnetic  
"smart" windows  
radiation

Photographic Film

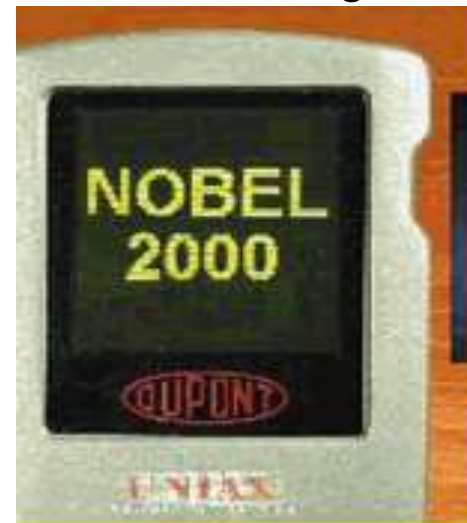
Solar cell

Light-emitting diodes



Film anticatic coating

Video anticatic coating



*By varying the molecular structure, light of different colours can be obtained.*

THANK YOU...