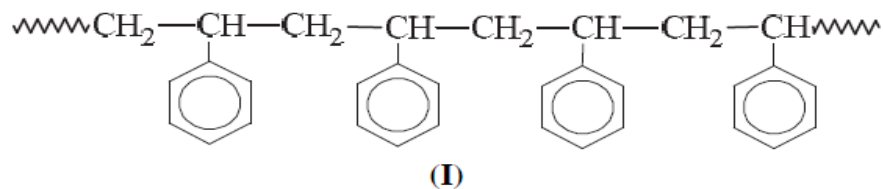


Basic concept and definitions

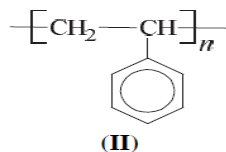
Polymer

- The term *polymer* stems from the Greek roots *poly* (many) and *meros* (part). The word thus means “many parts” and designates a molecule made up by the repetition of some simpler unit called a *mer*.

The structure of polystyrene, for example, can be written as



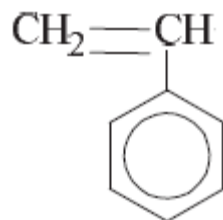
Or



n , represent the number of repeating units in the polymer molecule.

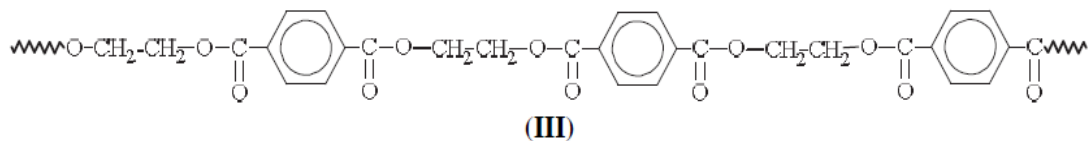
Monomer

- Monomers are generally simple organic molecules from which the polymer molecule is made. The structure of the repeating unit of a polymer is essentially that or closely related to that of the monomer molecule(s).

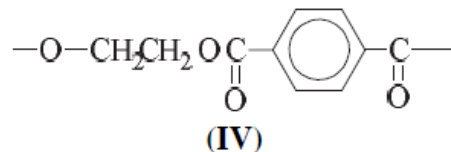


Styrene Monomer

- A repeating unit may be a single component such as **(II)** for the polymer **(I)**, or it may consist of the residues of several components, as in poly(ethylene terephthalate), which has the structure :



Or it can be written as:



Degree of polymerization

- This term refers to the number of repeating units that constitute a polymer molecule.
- The abbreviation DP usually used to refer to the degree of polymerization
- The subscript (n) used on the parentheses in the foregoing structural formulas for polymers represents this DP
- The relation between degree of polymerization and molecular weight M of the same macromolecule (polymer) is given by

$$M = (DP)M_o$$

Where M_o is the formula weight of the repeating unit.

Classifications of polymers

A- Origin of the polymer

- Polymers can be classified as Natural or Synthetic based on the origin of the polymer
- Nucleic acids, proteins, cellulose, silk etc... are naturally occurring polymers.
- Thousands of synthetic polymers are presented in different industries
- On the other hand, some naturally occurring polymers were made by synthetic methods (polyisoprene)

B- Functional groups presented in the monomer.

Polyamide, polyesters, polyimide, polycarbonate, polyethers and etc...

C- Polymer structure (Molecular Architecture)



(a) Linear



(b) Short branched



(c) Long branched



(d) Cross-linked



(e) Ladder



Star polymer

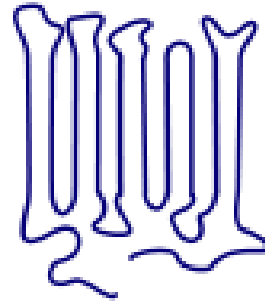


Comb polymer

Amorphous or crystalline



Amorphous



Semicrystalline

Homopolymers or copolymers

If a macromolecule is made from only one species of monomer, the product is a *homopolymer*.

A *copolymer* is a polymer derived from more than one species of monomer.

—**ABBABBBAABBAABAABBA**—

Random copolymer

—**ABABABABABABABABAB**—

Alternating copolymer

—**AAAAAAAAAABBBBBBBBBB**—

Block copolymer

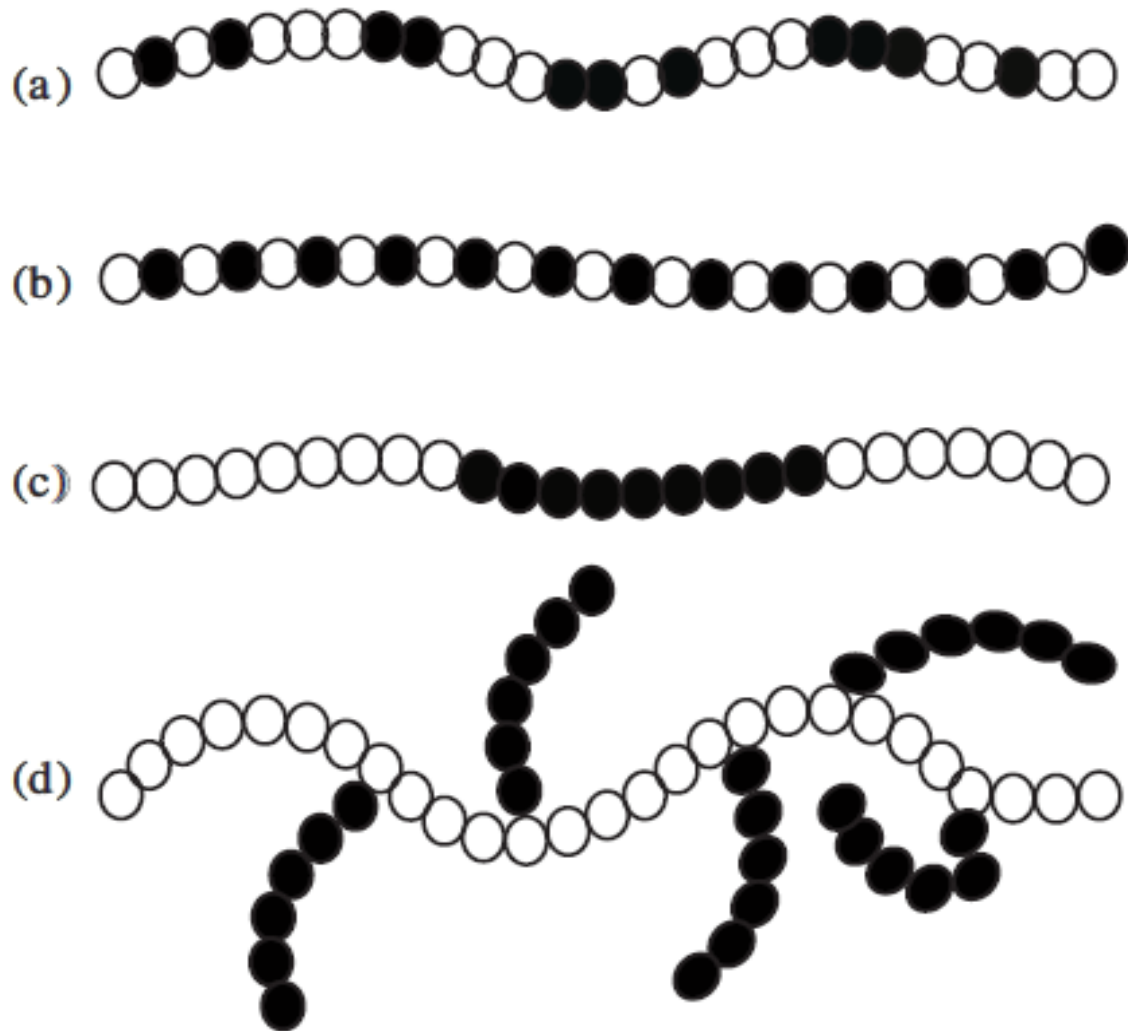
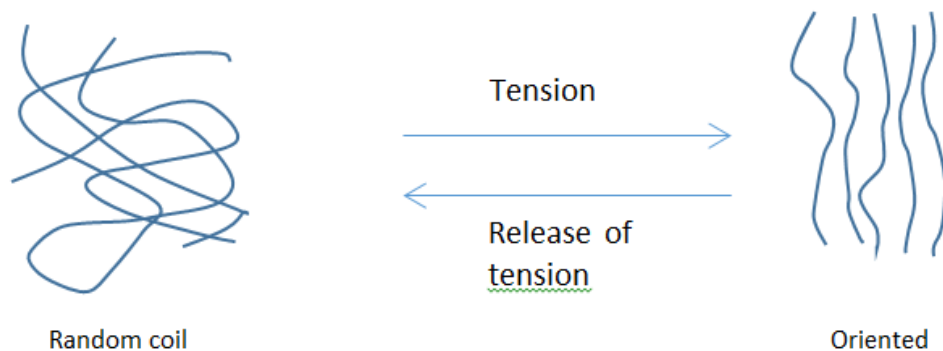


Figure: Copolymer arrangements: (a) two types of monomers(denoted by open and filled circles) are randomly placed. (b) the monomers are randomly arranged. (c) A block copolymer. (d) grafted copolymer

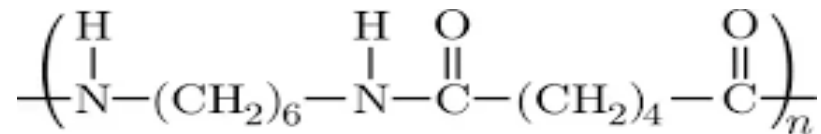
Elastomers, fibers and plastic

- **Elastomer**
- Irregular shape with weak intermolecular attractive forces.
- Capable of high extension (up to 1000%)
- It has elasticity due to the presence of chemical and/or physical crosslinks
- Usually has amorphous structure.
- i.e. natural rubber in addition to synthetic elastomers (polybutadien, polyisopren, polysiloxans, poly urethane and nitrile).

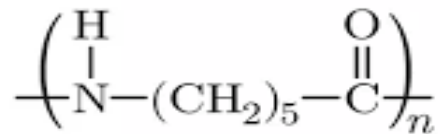


Fibers

- normally are linear polymers
- has no pendant or crosslinking groups
- highly crystalline
- long, thin, and threadlike making it suitable for textile applications
- i.e. esters, nylon, acrylic, cotton, wool and silk



Nylon 66



Nylon 6

Plastics

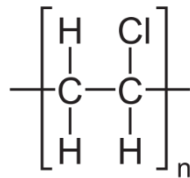
- has properties intermediate between elastomers and fibers
- some polymers can be used as fibers and plastics depending on the processing conditions
- used as sheet, pipes, paint

Thermoplastic and thermosets

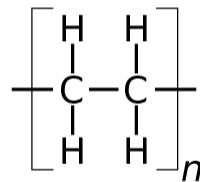
Thermoplastic

- soften and flow under heat and pressure
- up on cooling, the polymer hardened and take the shape of the mold (container)
- can stand for several heating and cooling cycles without suffering any structural breakdown
- polystyrene, polyvinyl chloride, polyethylene, and polypropylene
- It is used for packaging, beverage and trash containers, automotive parts

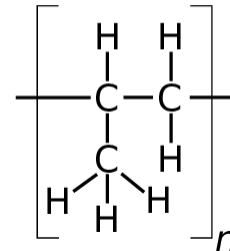
Polyvinyl chloride



Polyethylene



Polypropylene



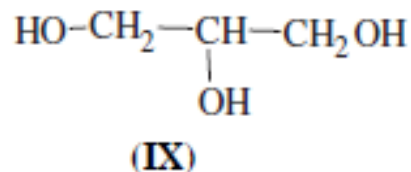
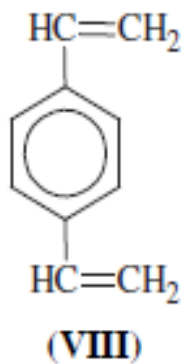
- **Thermoplastic Advantages:**

- * Highly recyclable
- * High-Impact resistance
- * Reshaping capabilities
- * Chemical resistant
- * Aesthetically superior finishes

Polymerization and Functionality

The **functionality** of a molecule is the number of sites it has for bonding to other molecules *under the given conditions of the polymerization reaction*.

Bifunctional polymers are polymers with 2 active sites. i.e styrene
A *polyfunctional* monomer is one that can react with more than two molecules under the conditions of the polymerization reaction.
divinyl benzene **(VIII)** is tetrafunctional , glycerol **(IX)** is trifunctional

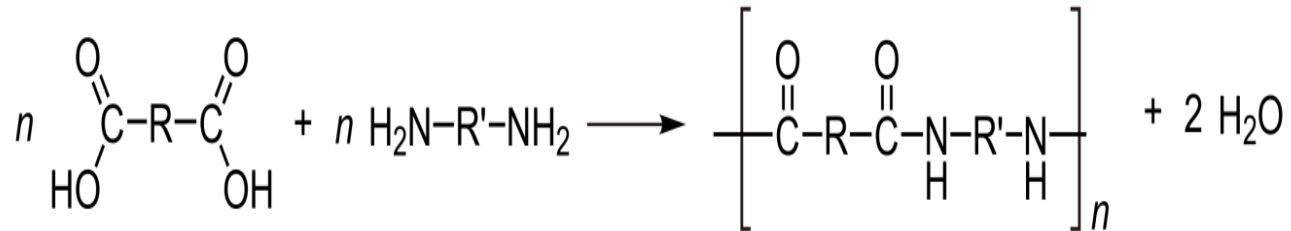


Q/ What is the functionality of the following monomers in reactions with (i) styrene, $C_6H_5CH=CH_2$ and (ii) adipic acid, $HOOC(CH_2)_4COOH$?

- (a)
$$\begin{array}{c} CH_3 \\ | \\ H_2C=C \\ | \\ O=C-OCH_3 \end{array}$$
- (b) $HOCH_2CH_2OH$
- (c) $H_2C=CH-CH_2OH$

Polymers synthesis

- Polymerization is the process of joining together small molecules by covalent bonds. The small molecules (monomer) must be at least difunctional.
- Polymerization reactions can be classified into two categories: condensation VS addition and stepwise VS chainwise
- Condensation reactions are those in which some parts of the reacting system is eliminated as a small molecules. i.e. polyamides, cellulose, starch, wood and silk.



- Addition polymers have the same number of atoms as the monomer in its repeating unit. mostly such polymers are derived from vinyl monomers such as styrene, vinyl chloride methyl methacrylate, vinyl acetate
- Backbone atoms in addition polymerization are usually carbon atoms in contrast to condensation polymers where backbone contains more than one atom.
- The second classification based on kinetic of polymerization
- Step reaction: the chain growth occurs in a slow, step wise manner. Two monomers reacts to form dimer. The dimer reacts with another monomer to form trimer or with another dimer to form tetramer.
- Thus the average molecular weight of the system increases slowly over a period of time.
- Chain polymerization requires ionic or radical initiator to begin chain growth
- The chain growth takes place by rapid addition of olefin molecules to the growing chain

TABLE 14.19 Comparison of Step-Reaction and Chain-Reaction Polymerization

Step-reaction polymerization	Chain-reaction polymerization
Growth occurs through the reaction of any two molecular units with proper functional groups.	Growth occurs only by addition of one unit at a time.
Monomer consumed early in the reaction.	Monomer concentration decreases steadily throughout the reaction.
At any stage all molecular species are present in a calculable distribution.	Reaction mixture contains almost only monomer, high polymers, and very little growing chains.
Polymer chain length increases steadily during the polymerization.	Polymer chains are formed from the beginning of the polymerization and throughout the process.
\overline{DP} is low to moderate.	\overline{DP} can be very high.
Polymerization rate decreases steadily as functional groups consumed.	Polymerization rate increases initially as initiator units generated; remains relatively constant until monomer is depleted.
Long reaction times and high extents of reactions are essential to obtain high molecular weight.	Long reaction times give high yields but have little effect on molecular weight.

Addition polymerization

- The reaction involve 3 kinetic steps reaction
 - 1- initiation (anion, cation, free radical)
 - 2- propagation
 - 3- termination

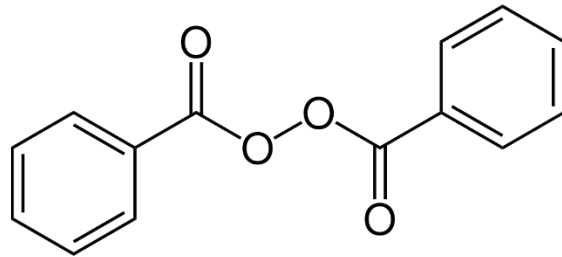
(see table 14.21)

Free radical polymerization

- **Initiators**

- Peroxides (**ROOR**) AND HYDROPEROXIDES (**ROOH**)
THERMALLY UNSTABLE ($\text{RO}\cdot$, $\text{HO}\cdot$)

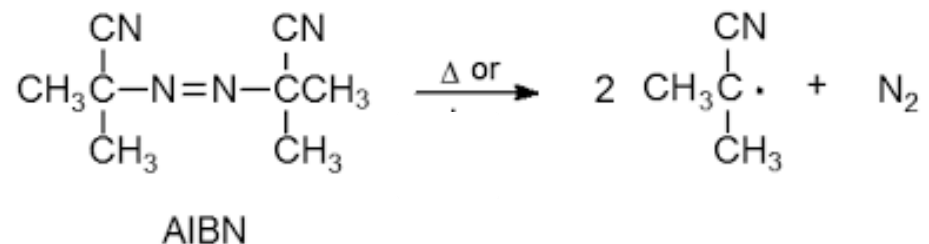
benzoyl peroxide, diacetyl peroxide, cumyl peroxide, di-t-butyl peroxide



benzoyl peroxide

Azo compounds

- THERMALLY decompose



- **Redox initiator**
- Low temp. initiation
i.e. Persulfate and hydrogen peroxide

Photo-initiator



Free radical polymerization

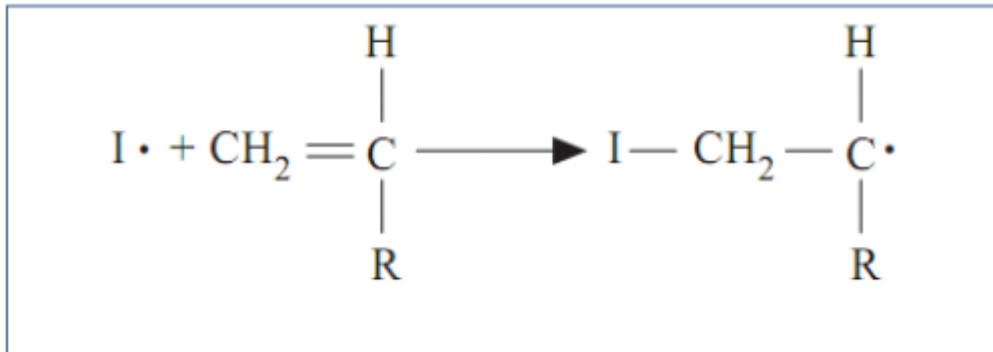
A. INITIATION:

a) Homolysis of the relatively weak covalent bond in the initiator.



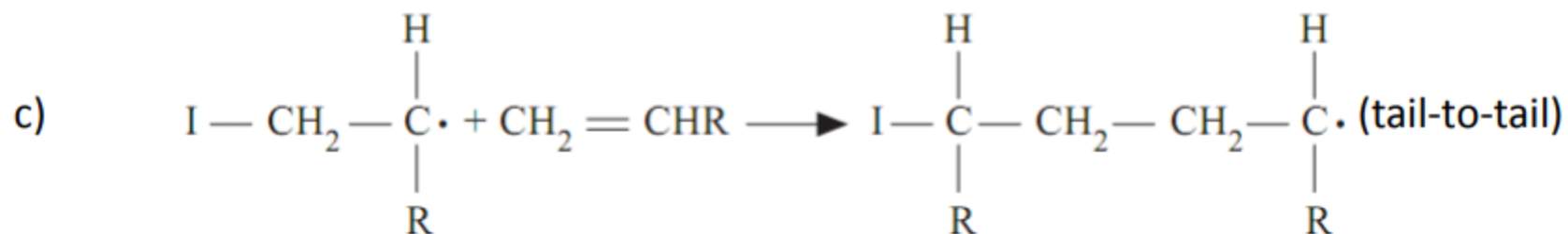
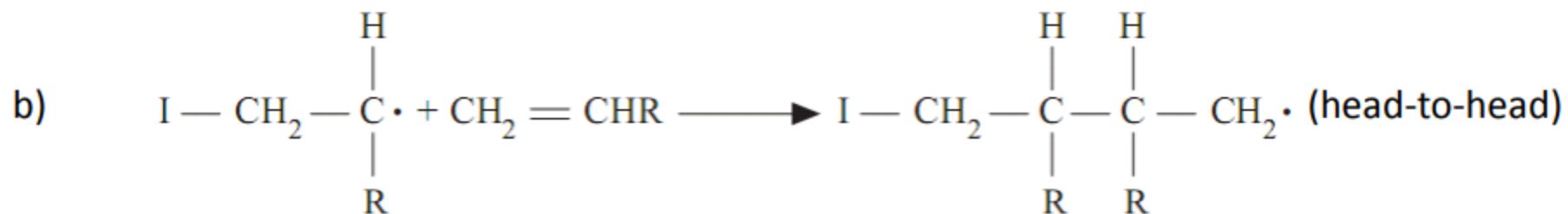
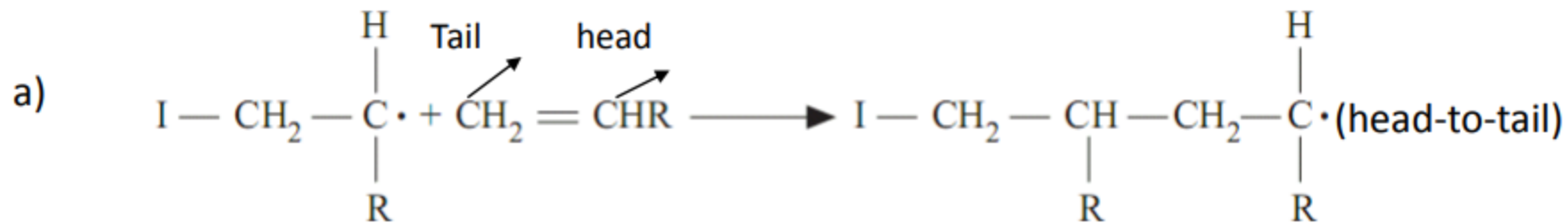
primary radical

b) The free radical created adds to one of the electrons of the one of the bonds constituting the double bonds in the monomer in the presence of the vinyl monomer



Monomeric active center (**initiated monomer**)

B. PROPAGATION: During propagation, the initiated monomer adds other monomers, usually thousands of monomer molecules, in rapid succession. Propagation continues until the growing chain radical is deactivated by chain termination or transfer.

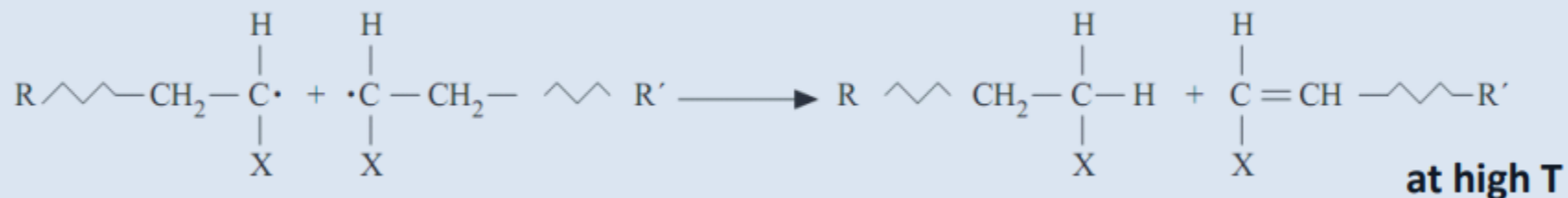


C. TERMINATION: The growth activity of the polymer chain radical is destroyed by reaction with another free radical in the system to produce polymer molecule(s)

Combination or coupling:

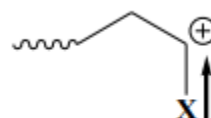
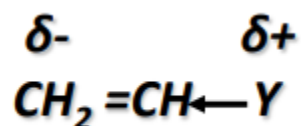


Disproportionation:



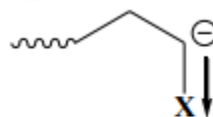
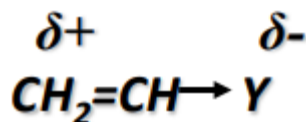
Ionic polymerization

Cationic polymerization: Electron donating substituent increasing the electron density on the double bond and facilitate the attack of cationic species such as alkoxy, alkyl, alkenyl, and phenyl



cationic

Anionic polymerization: Electron withdrawing substituent decreasing the electron density on the double bond and facilitate the attack of anionic species such as cyano and carbonyl



anionic

Cationic polymerization

- Catalysts for cationic polymerization; AlCl_3 , AlBr_3 , BF_3 , TiCl_4 , SnCl_4 , H_2SO_4 (all Lewis acids with strong electron acceptor capacity) To be effective, they need presence of a Lewis base such as H_2O , ROH , acetic acid as a cocatalyst

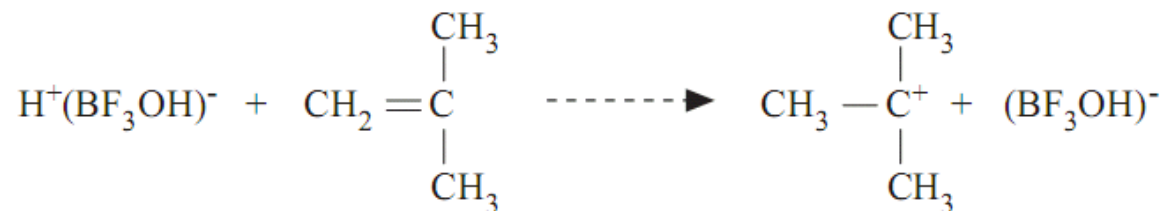
MECHANISM

Initiation

First, the catalyst and cocatalyst (e.g., water) form a complex:

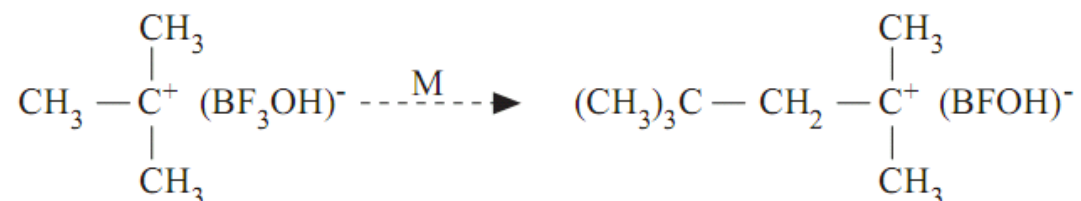


The complex then donates a proton to an isobutylene molecule to form a carbonium ion:

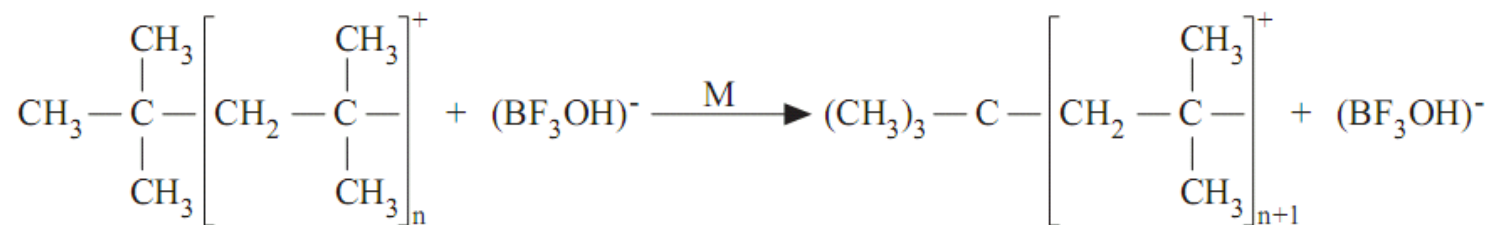


Propagation

The carbonium ion reacts with a monomer molecule in the propagation step.



In general, the propagation reaction can be written as

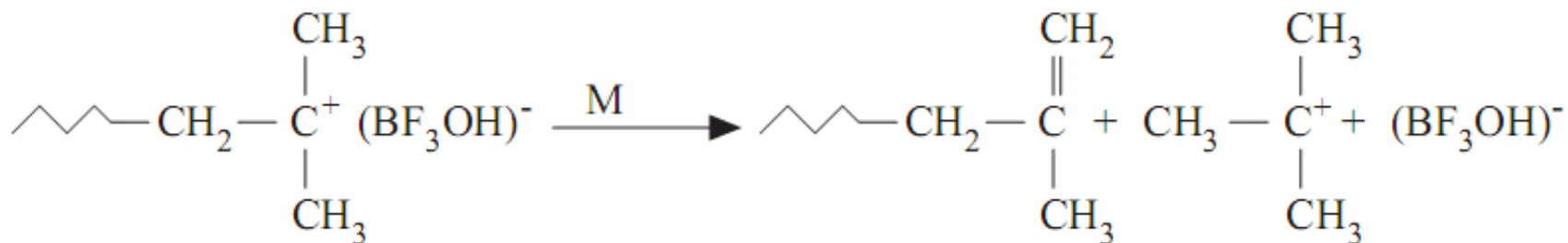


Termination

1- dissociation



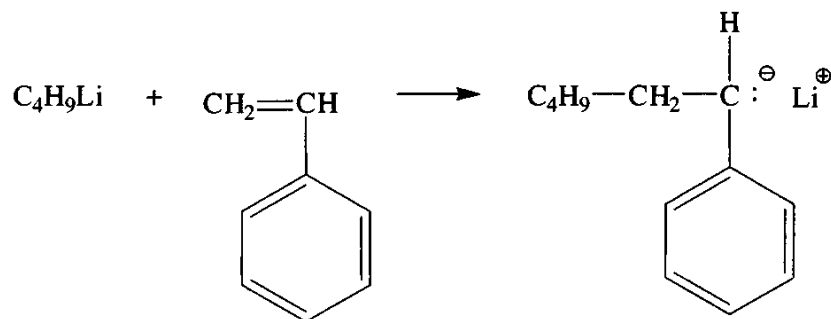
2- Chain transfer



Anionic polymerization

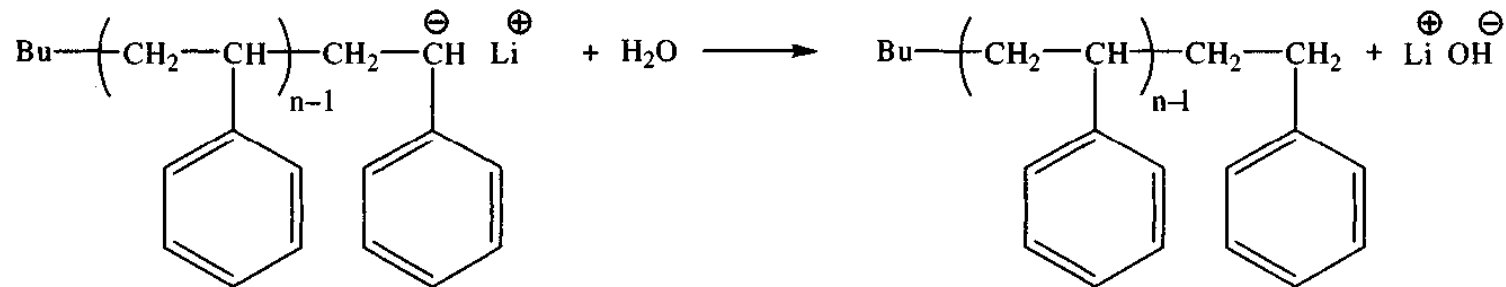
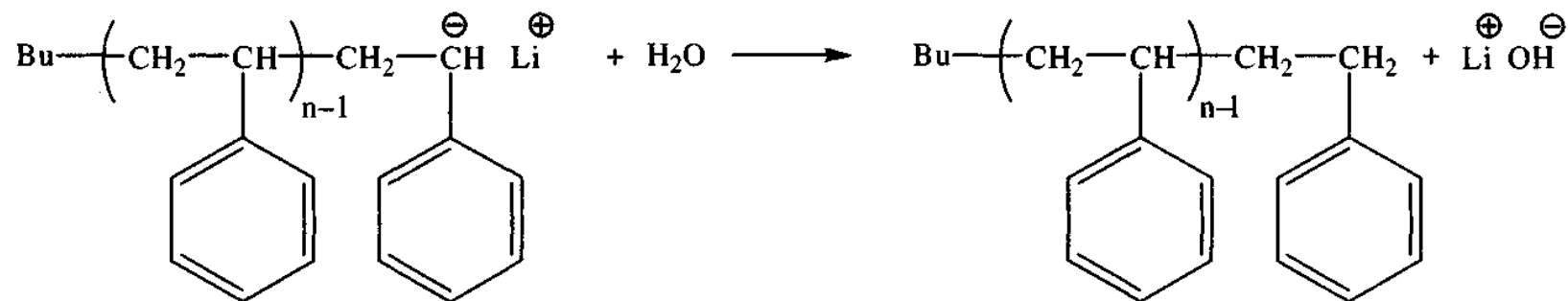
- **Initiation.**

- *Nucleophilic initiators*/NaNH₂ and LiN(C₂H₅)₂, alkoxides, hydroxides, cyanides, phosphines, amines

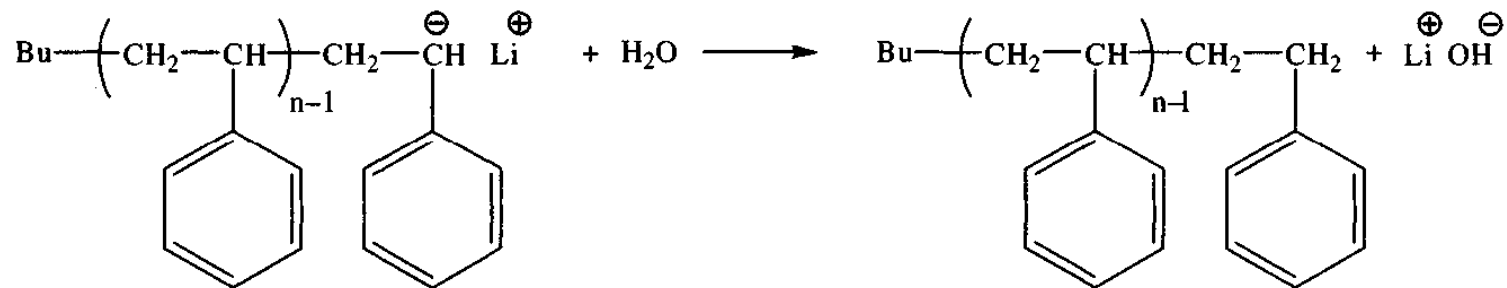


Electron transfer initiators such as free alkali metals (e.g., Na, Li) or complexes of alkali metals and unsaturated or aromatic compounds (e.g., sodium naphthalene)

Propagation



- Termination
- *living* polymerization
- termination occurs only by the deliberate introduction of oxygen, carbon dioxide, methanol or water as follows:



Polymer Structure-Property Relationships

- properties and the final uses of the polymer :
 - 1- chemical composition and 2- structure
 - physical properties of polymers
 - 1- strength of the covalent bonds,
 - 2- the stiffness of the segments in the polymer backbone,
 - 3- the strength of the intermolecular forces between the polymer molecules
- other factor
- a- distribution of crystallinity
 - b- molecular weight
 - c- molecular weight distribution,
 - d- the nature and amount of additives such as fillers,
 - e- reinforcing reagents, and
 - f- plasticizers

Thermal properties

Thermal stability

- **Not** decompose below 400 °C
- presence of aromatic moieties –common feature-
(Thermal degradation or decomposition occurs as a result of the temperature causing the bonds to vibrate to the rupture point. In the case of cyclic repeating units, breaking of one bond in a ring does not lead to decrease in molecular weight)

Glass transition temperature T_g

transition from the glassy state (hard and brittle amorphous state) to the rubbery or flexible state

- temperatures below T_g , there is no segmental motion,
- The melting point (T_m): temperature range where total or whole polymer chain mobility occurs
- T_g is approximately one-half to two-thirds of T_m
- flexible backbone and small substituent groups have low T_g , whereas those with rigid backbones, have high T_g
- Bulky substituent groups hinder rotation and therefore raise T_g

Polymer	Structure	T _g (°C)	T _m (°C)
Polydimethylsiloxane (silicon rubber)	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---O---} \\ \\ \text{CH}_3 \end{array} \right]$	-123	-29
Polyethylene	$\left[\text{---CH}_2\text{---CH}_2\text{---} \right]$	-120	135
Polypropylene (<i>atactic</i>)	$\left[\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{CH}_3 \end{array} \right]$	-20	176
Polypropylene (<i>isotactic</i>)		100	
Poly(vinyl chloride)	$\left[\begin{array}{c} \text{---CH}_2\text{---CH---} \\ \\ \text{Cl} \end{array} \right]$	89	285

Solubility

- **General rules for polymer solubility**

1. *Chemical structure*: (like dissolves like)

Ex: ethanol can dissolve poly(vinyl alcohol) & toluene can dissolve polystyrene

2. *Molecular weight* : solubility of a polymer decreases as its molecular weight increases.

3. *Cross-linking*

4. *Crystallinity*: solubility of a polymer decreases with an increase in the degree of crystallinity

5. *Branching increases the solubility in general*

Viscosity

- *Poise* = dyne seconds per square centimeter (1 poise = 10^{-1} Nsm⁻²).
Or *Pascal* = Newton seconds per square centimeter (1 Pas = 10 poise)

Impeded factor

- chain entanglement
- high intermolecular forces
- presence of reinforcing agents
- cross-links

Viscosity measurements = determining *relative* molecular weights of polymers

rapid, easy, and requires only minimal instrumentation.

- the viscosity of a polymer solution increases with the polymer molecular weight

Factors that control the viscosity of a polymer

- particular polymer
- and solvent,
- solute concentration,
- and temperature