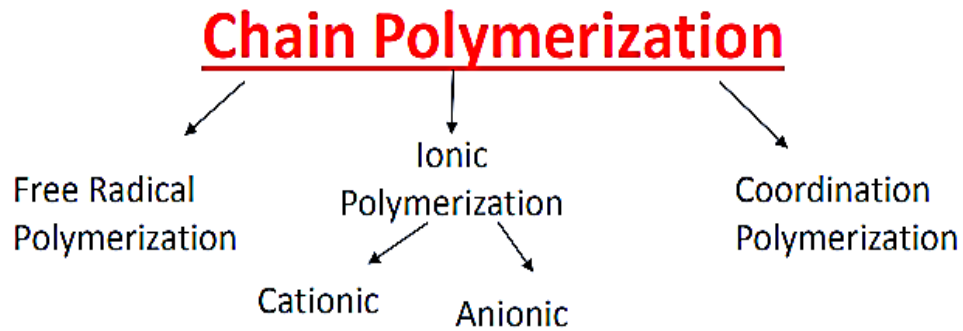


Chain growth polymerization

➤ Monomer with electron- withdrawing groups can proceed by an anionic pathway

➤ Monomer with electron-donating groups can proceed by a cationic pathway

**a) Free radical polymerization**

Free radical polymerization is the most economical process for use with vinyl monomers because the reaction mixture does not require the high-purity reactants and rigorous exclusion of moisture, air, and other impurities that is needed for successful operation of the alternative ionic or organometallic catalysis it also highly exothermic reactions.

Monomers used for free radical polymerization are olefin or  $\alpha$ -olefins

**Initiation**

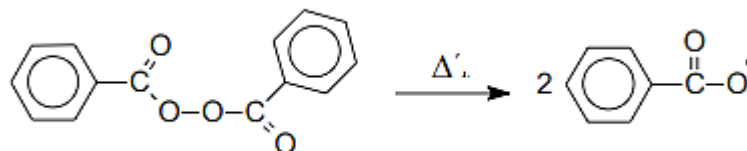
The initiation reaction is the formation or production of free radicals.

There are several ways to do this:

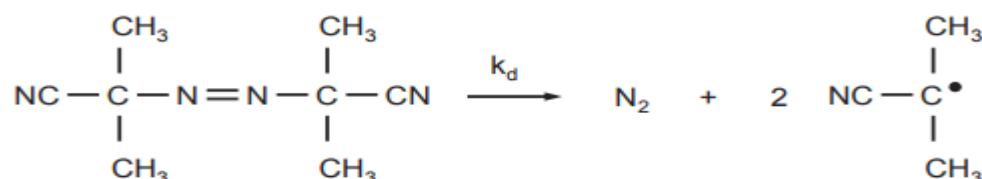
- Thermal initiator:

or homolytic decomposition of the weakly bonds The decomposition of the initiator

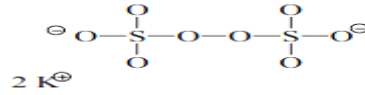
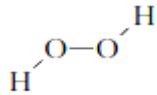
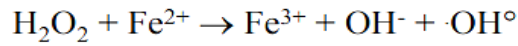
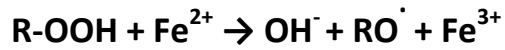
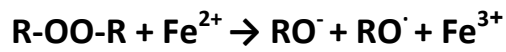
i) Peroxide such as Benzoylperoxide, hydrogen peroxide etc



ii) Azo-bis-isobutyronitrile (e.g. AIBN) forms free radicals:

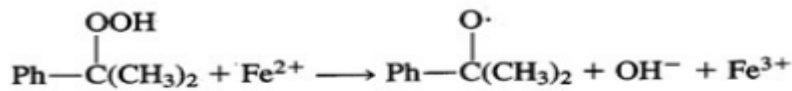


Redox-initiators Potassium persulfate, hydrogen peroxide or Fenton reagent These are normally generated by reacting peroxides with Fe<sup>2+</sup>

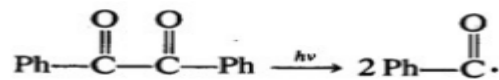
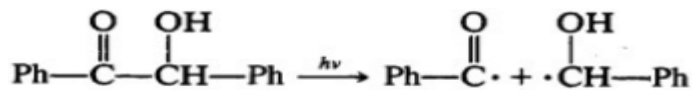
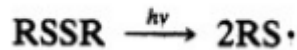


One electron transfer

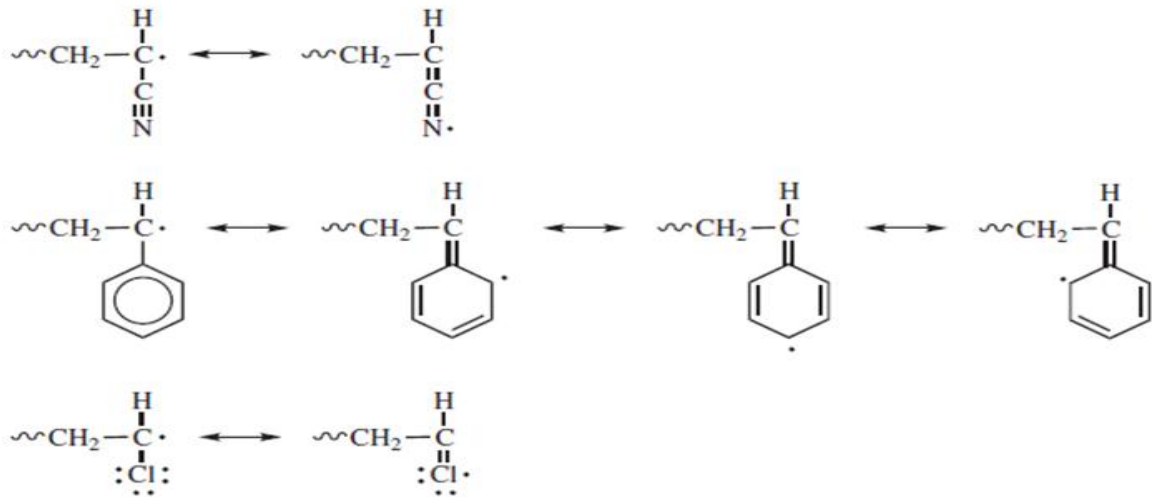
Making free radicals by one electron transfer by redox reaction .low temperature reaction



### Photolabile initiator



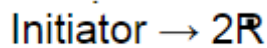
Resonance stabilization of the propagating radical occurs with almost all substituents (see below)



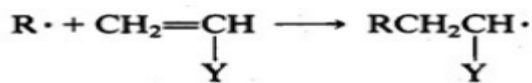
**Mechanism of polymerization:**

[1]Initiation: appearance of free radicalby

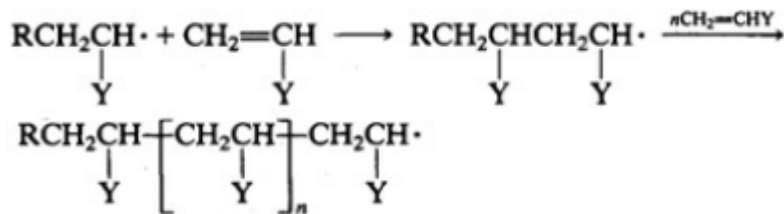
a)decomposition of initiator



b) Addition of imitator free radical to the monomer to form monomer free radical

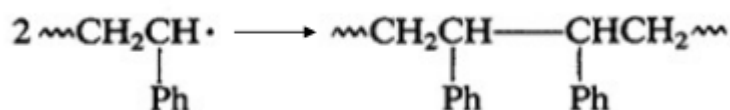


[2] Propagation



3] termination : is the disappearance of the free radical and formation of dead polymer this done by two pathway

Combination



## ii) Disproportionation



Factors favor Disproportionation

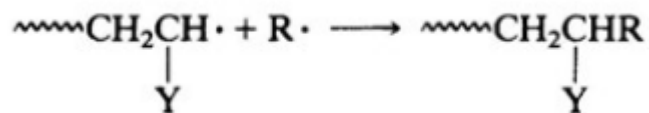
a) steric factor

b) viability of  $\alpha$  H for H transfer

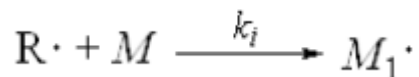
c) Electrostatic repulsion induced by of polar group (ester)



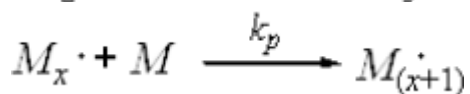
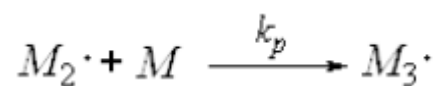
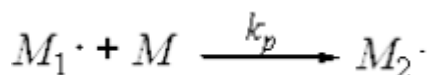
## iii) Combination with primary initiator radicals

Kinetic of the free radical mechanism :

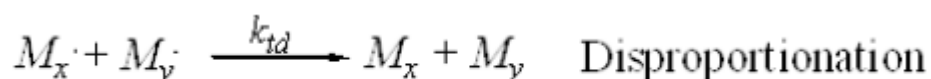
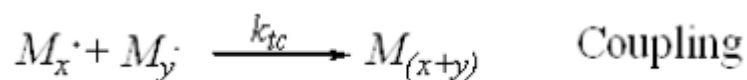
Initiation:



Propagation:



Termination:



- 1) The rates of initiation, propagation, and termination are all different.
- 2) Independent of chain length.
- 3) Negligible end group.
- 4) At steady state, **constant radical concentration** ( $-d[M\cdot]/dt = 0$ ).  
(steady state assumption)

b) initiation ( $R_i$ )

$$R_i = \frac{-d[M\cdot]}{dt} = 2fk_d[I]$$

f initiator efficiency (0.3-0.8):

$$f = \frac{\text{radicals that initiate a polymer chain}}{\text{radicals formed from initiator}}$$

$k_d$  : Decomposition rate constant.

[I] : molar concentration of initiator.

[M·] : molar concentration of radical.

## Termination rate

$$R_t = \frac{-d[M\cdot]}{dt} = 2k_t[M\cdot]^2$$

$$k_t = k_{tc} + k_{td}$$

## Propagation rate

$$R_p = \frac{-d[M]}{dt} = k_p[M][M\cdot]$$

$$2fk_d[I] = 2k_t[M\cdot]^2 \quad [M\cdot] = \sqrt{\frac{fk_d[I]}{k_t}}$$

$$R_p = \frac{-d[M]}{dt} = k_p[M] \sqrt{\frac{fk_d[I]}{k_t}}$$

## Steady state assumption

$R_i = R_t$  Formation and destruction of radical occur in the same rate (assuming the majority of polymers are formed at the steady state **[M·] remain constant**)

## Average kinetic chain

$$\bar{v} = \frac{R_p}{R_i} = \frac{R_p}{R_t} \quad (R_t = R_i \text{ at steady state})$$

$$\bar{v} = \frac{k_p [M] [M\cdot]}{2k_t [M\cdot]^2} = \frac{k_p [M]}{2k_t [M\cdot]} = \frac{k_p [M]}{2k_t \left( \frac{fk_d [I]}{k_t} \right)^{\frac{1}{2}}}$$

$$= \frac{k_p [M]}{2(fk_t k_d [I])^{\frac{1}{2}}}$$

Disproportionation :  $\overline{DP} = \bar{v}$

Combination :  $\overline{DP} = 2\bar{v}$

### Kinetics deviate from normal conditions

1. As viscosity becomes very high  
(bulk or concentrated solution polymerization)
2. when polymer precipitates
3. when chain transfer reaction occurs

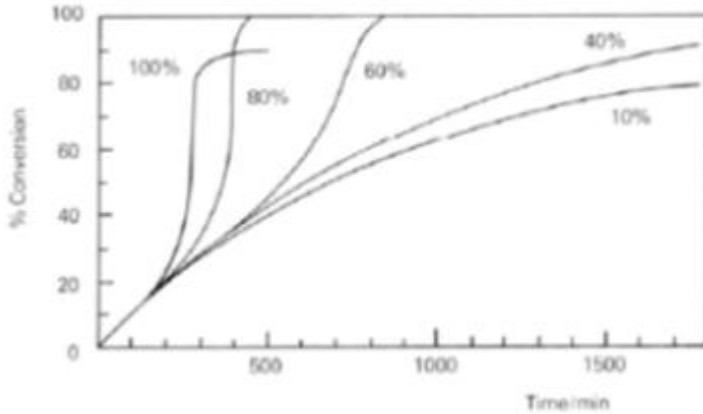
### As the viscosity becomes very high

- As viscosity become very high
  - Chain mobility reduce
  - Termination rate decrease (higher MW)
  - Polymerization rate autoaccelerate
  - Reaction exotherm increase
  - Gel forms

### Gel effect- Trommsdorff effect – Norris smith effect

At a certain stage in polymerization process, there is a considerable increase in both the reaction rate and the molecular weight. This is referred to as autoacceleration or gel effect as illustrated in the following figure. This is attributed to a decrease in the termination rate due to the increase of medium viscosity. So it is

- Difficult of termination reaction because of viscosity
- Ease of propagation because of small size of monomer even though high viscosity
- Autoacceleration by exothermic of propagation reaction .
- To obtain high molecular weight polymer like gel.



- Sharp increase in  $R_p$  as conversion of monomer increases
- Viscosity  $\uparrow$  Mobility of polymer chain radical  $\downarrow$
- $k_t \downarrow R_p \uparrow (R_p \propto k_t^{-1/2})$   $x_n \uparrow (x_n \propto k_t^{-1/2})$

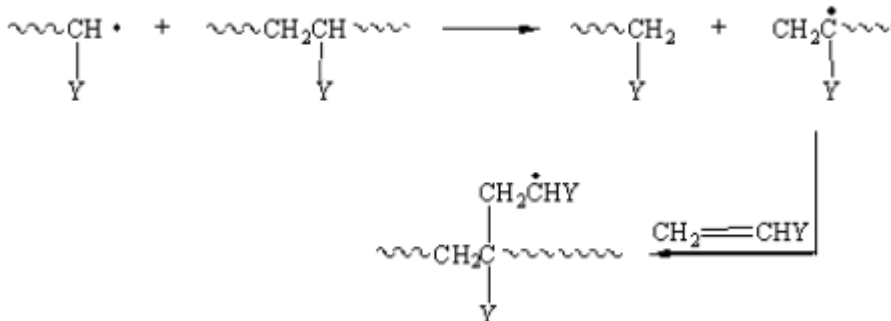
### Chain transfer reaction ;

It is transfer of reactivity from the propagating chain to other particle present in the reaction mixture

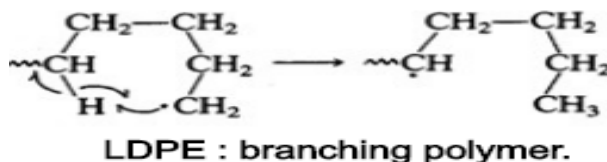
#### 1) Chain transfer to polymer

By hydrogen abstract this lead to lower the molecular weight, lower the molecular length and branching mostly contain 3 or 4 carbon length .

\* Growing radicals move to other polymer chain.

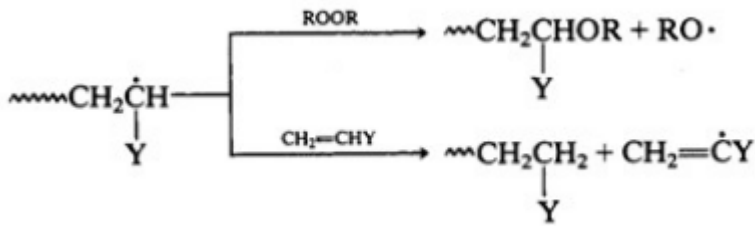


#### 2) Backbiting self-polymer chain ; branched mostly 5 or 6 member transition state

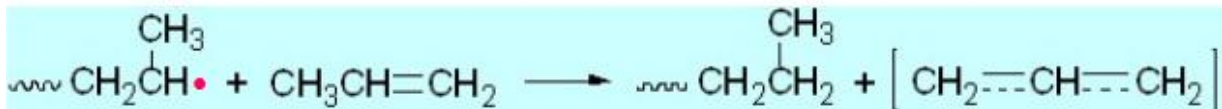


#### 2) chain transfer to monomer

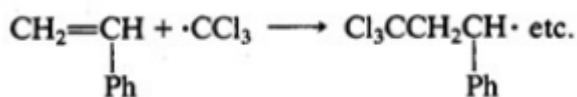
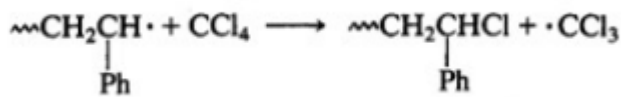
#### 3) chain transfer to initiator



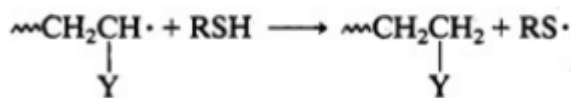
- Polypropylene cannot be prepared by free radical polymerization



#### 4) Chain transfer to the Solvent



#### Chain transfer to transfer agent



Telomerization :at high concentration of chain transfer agent ,low molecular weight polymer are obtained (Telomer)

#### Chain transfer agent.

A material deliberately added to the system to control the molecular weight by chain transfer is called a chain transfer agent.

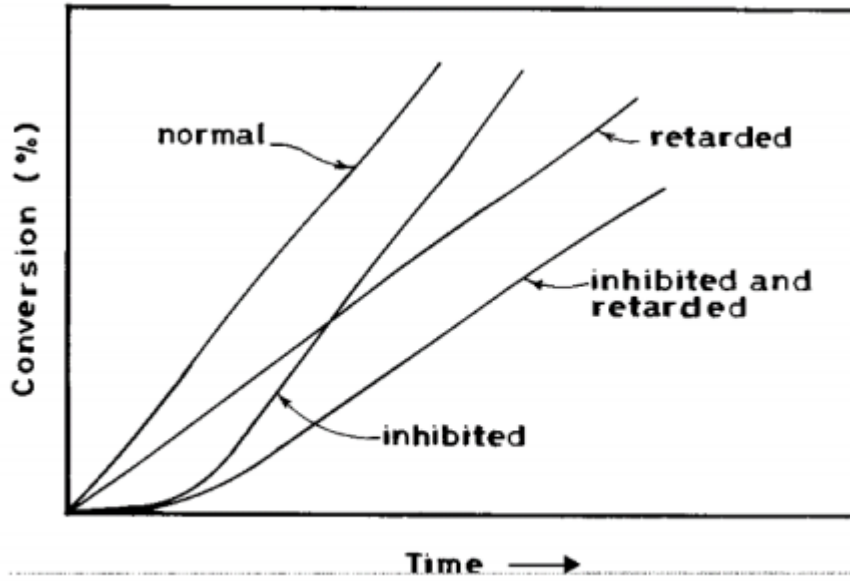
#### Retarder

A substance that reacts with the chain radicals to produce either nonradical products, or radicals with low reactivity as to incapable of adding monomer and reducing the polymerization rate is called retarder.

#### Inhibitor

If a retarder is so effective as to completely suppress the rate and degree of polymerization, it is called as an inhibitor.





*The influence of retarders and inhibitors on conversion.*