FREE RADICAL

POLYMERIZATION

March 2015

- **Free radical can be formed if there are unpaired electron.**

Generation of Free Radicals

- Thermal decomposition

$$R{-}R \xrightarrow{\Delta} 2R^{\cdot}$$

- Photochemical decomposition
- Oxidation-Reduction reaction
- High energy particle radiation

（1）Activity of The Free Radical

- **The activity of a free radical is determined by its structure.**
  - **The stronger the conjugative effect of a free radical, the more stable it is.**
  - **Polar group lessens the activity of the free radical.**
  - **Bulky group lessens the activity of reaction, because it prevents the nearing of the reagent.**

The Order of the Relative Activity of Radicals

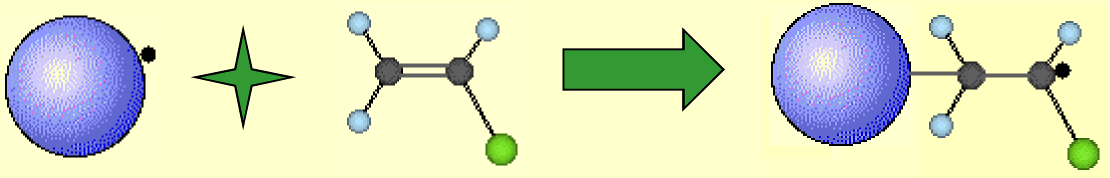
$H^{\cdot} > {}^{\cdot}CH_3 > {}^{\cdot}C_6H_5 > R\dot{C}H_2 > R_2\dot{C}H > R_3C^{\cdot} >$

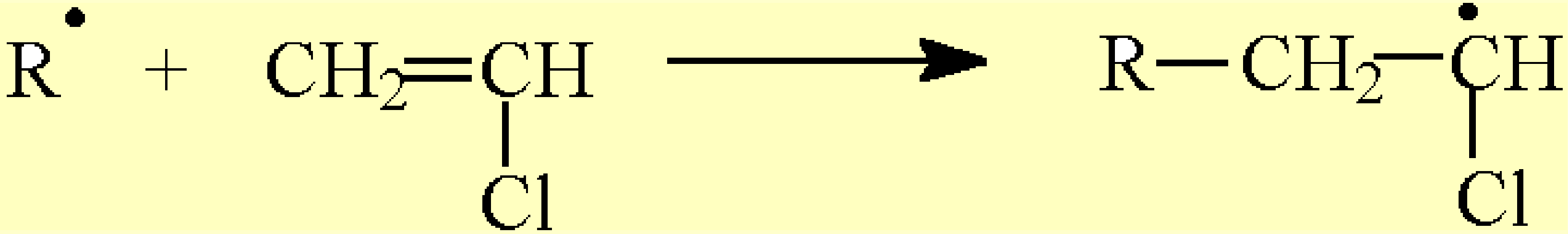
$R\dot{C}H{-}OR > R\dot{C}H{-}CN > R\dot{C}H{-}COOR > CH_2{=}CH{-}\dot{C}H_2 >$

$C_6H_5{-}\dot{C}H_2 > (C_6H_5)_2\dot{C}H > (C_6H_5)_3C^{\cdot}$

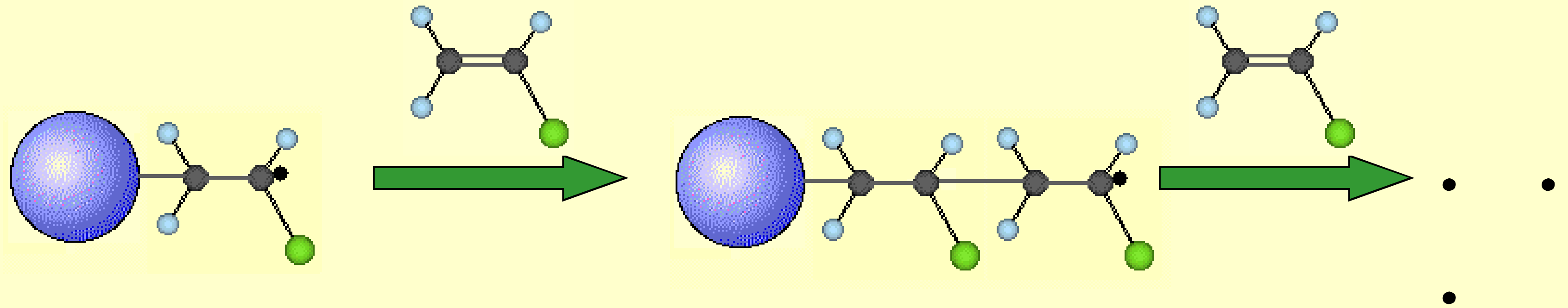
The Radicals in the last line are the inert radicals that have no ability of initiating olefinic monomers' polymerization

① Radical Addition Reaction

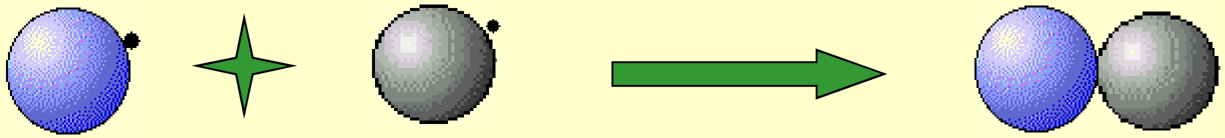




$$R^{\bullet} + CH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow R{-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{\overset{\bullet}{C}H}}$$



② Radical Coupling Reaction



$$R^{\bullet} + R'^{\bullet} \longrightarrow R-R'$$

3.1.2 Monomer Structure and Polymerization Types

- **Most of the mono olefin, conjugated diolefin, alkyne, and carbonyl compounds, and some of the heterocyclic compounds can be polymerized from the thermodynamic viewpoint.**

- **However, the selectivity of the various monomers to different polymerization mechanisms varies greatly.**

Examples

Vinyl chloride only can undergo radical polymerization.

Isobutylene only can undergo cationic polymerization.

Methyl methacrylate can undergo radical as well as anionic polymerization.

Styrene can undergo radical, anionic, cationic, and coordination polymerization.

Ethylene, the most simple alkene, with a symmetric structure, can undergo radical polymerization under high pressure, and coordination polymerization by particular initiator systems.

What makes the differences is mainly decided by the structure of the substituent on the carbon-carbon double bond, and is also decided by the electronic effect and the steric effect of the substituent.

Monosubsitituted Alkene Double Bond Monomers

- $CH_2{=}CH{-}X$, the electronic effect of the substituents X involves the inductive or resonance effect.

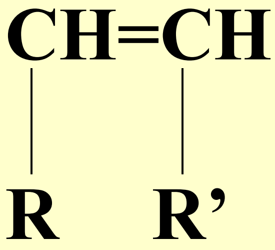
  - The effect of substituent manifests itself by its alteration of electron-cloud density on the double bond and it has the ability to affect the stability of the active center.

- **Whether an alkene polymerizes by radical, anionic, or cationic initiators depends on the inductive and resonance characteristics of the substituents present.**

1，2—disubstituted monomers

- **Owing to strong steric effect, this kind of monomers are usually hard to polymerize.**

- **For example, maleic anhydride is hard to homopolymerize, but can copolymerize with styrene or vinyl acetate.**



$$\underset{\mathrm{R}}{\mathrm{CH}}=\underset{\mathrm{R'}}{\mathrm{CH}}$$

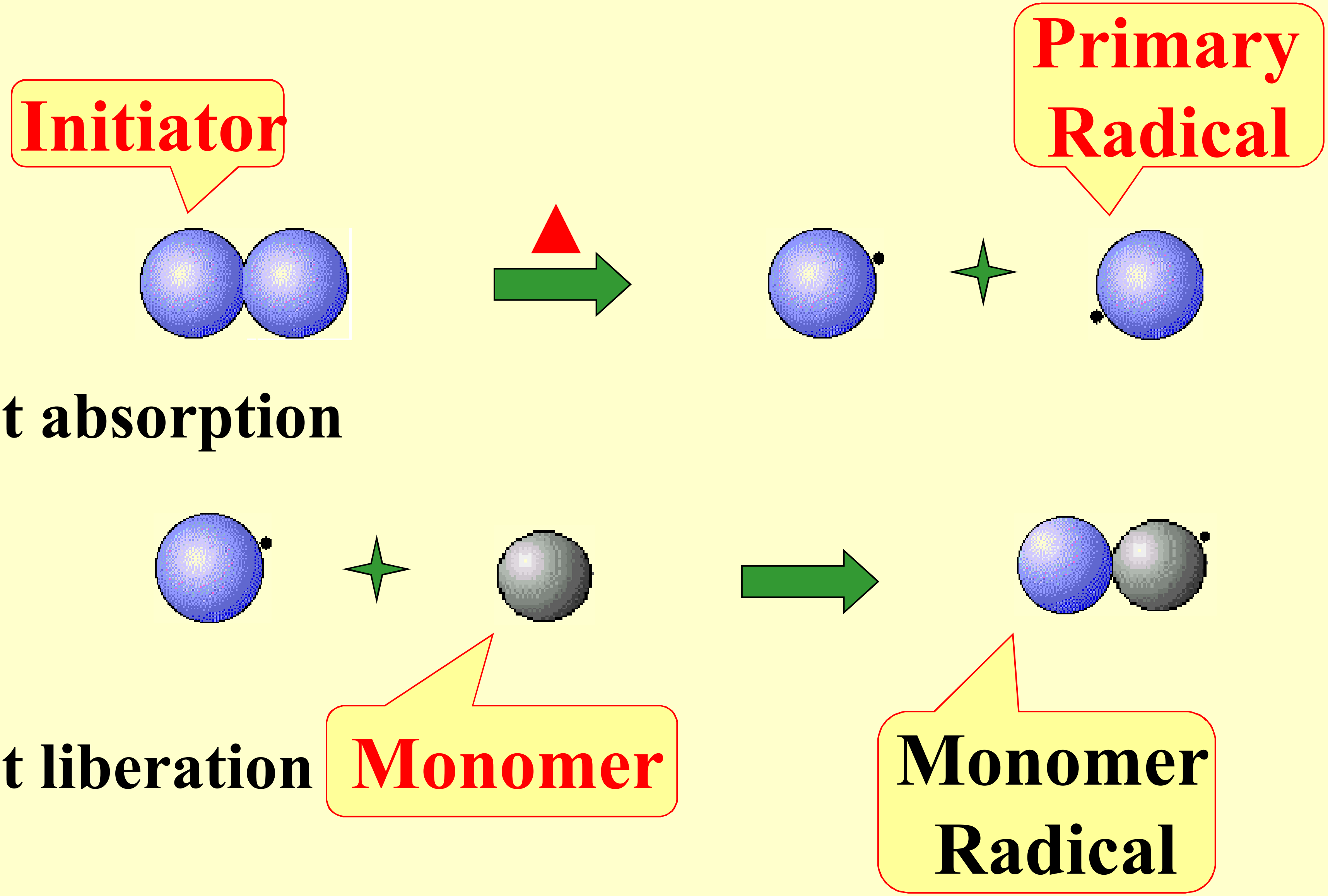
Tri or tetrasubstituted ethylene

- **They usually cannot polymerize.**
- **But, there are an exception when the substituent is fluorin.**
- **Owing to the small radius of the fluorin, all of them , from mono to tetrasubstituted fluoroethylene, can polymerize well.**

3.1.3 Elementary Reactions of Radical Polymerization

- Radical polymerization is chain polymerization
- Composed by at least three elementary reactions
  - Chain initiation
  - Chain propagation
  - Chain termination
  - Perhaps accompanied by chain transfer reaction and so on

（1）Chain Initiation Reaction



Initiator

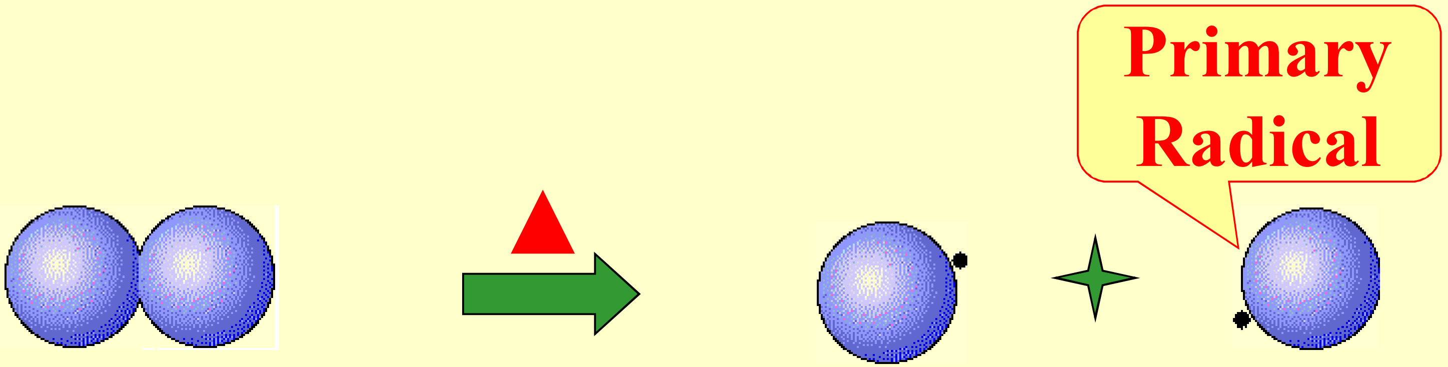
Primary Radical

heat absorption

heat liberation

Monomer

Monomer Radical



$I \longrightarrow 2R\cdot$ $R\cdot$ **Primary Radical**

- **The decomposition of initiators is a heat absorption reaction.**
- **With a relatively high activation emergy, about 100～170 KJ/mol**

- **The reaction rate is relatively slow.**

Decomposition rate constant is usually $10^{-4} \sim 10^{-6}$/s

Initiator decomposition reaction-----
controls the overall rate of the chain initiation.

Monomer

Monomer Radical

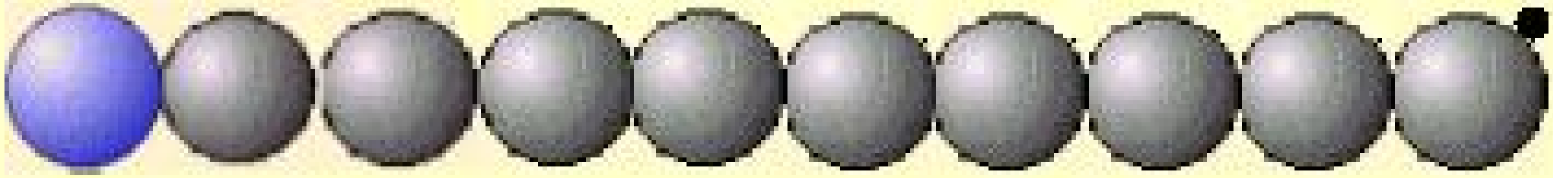
$$R^{\bullet} + M \longrightarrow RM^{\bullet}$$

$RM^{\bullet}$ **Monomer Radical**

- **The primary radicals add to monomers to produce monomer radicals.**
- **The process of opening a π-bond, and producing a σ-bond is a exothermal reaction.**

- **With a low activation energy, about 20～34 kJ/mol**
- **And a great reaction rate constant. This is a very fast reaction.**

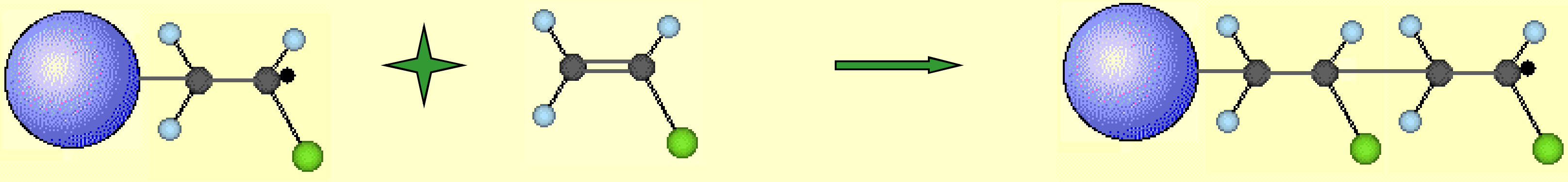
(2) Chain Propagation Reaction



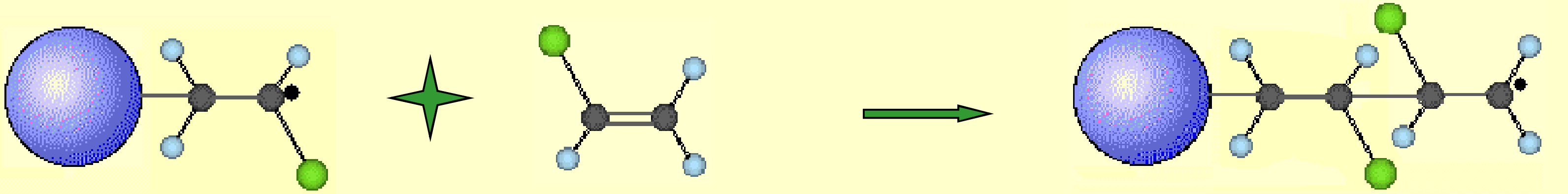
$$RM^{\bullet} \xrightarrow{M} RMM^{\bullet} \xrightarrow{M} RMMM^{\bullet} \xrightarrow{M} \ldots$$

$$M_n^{\bullet} + M \longrightarrow M_{n+1}^{\bullet}$$

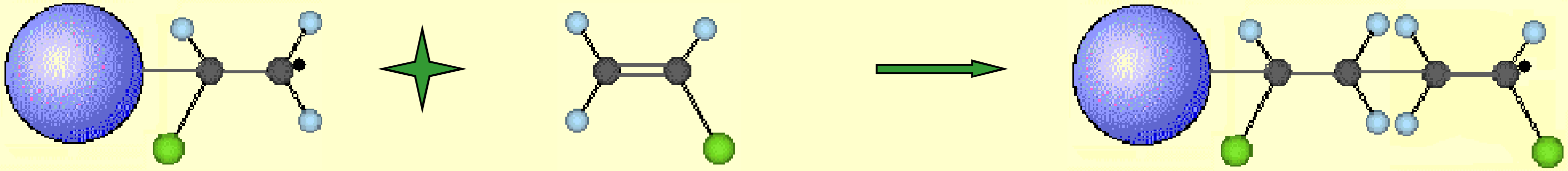
Head-to-Tail structure



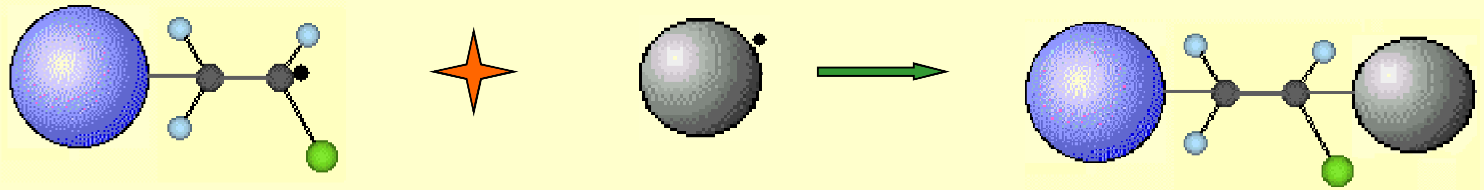
Head-to-Head structure



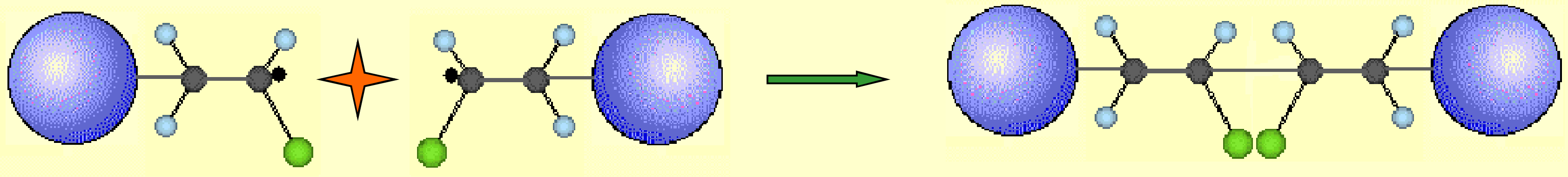
Tail-to-Tail structure



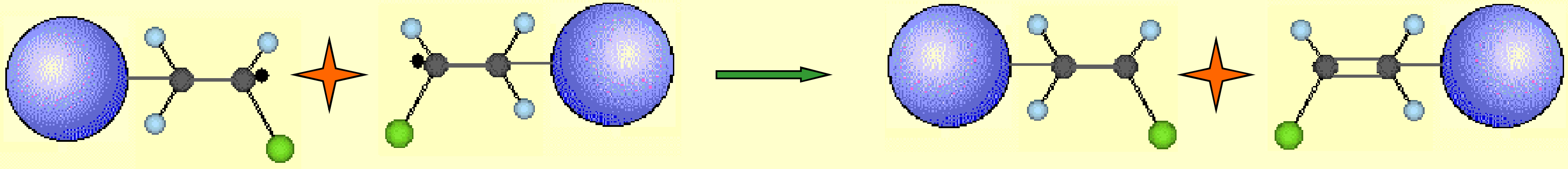
（3）Chain Termination Reaction



Radical Exhaustion

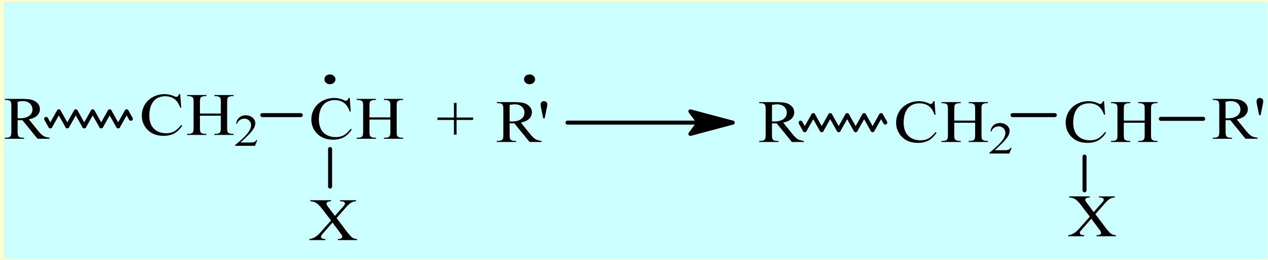


Coupling Termination



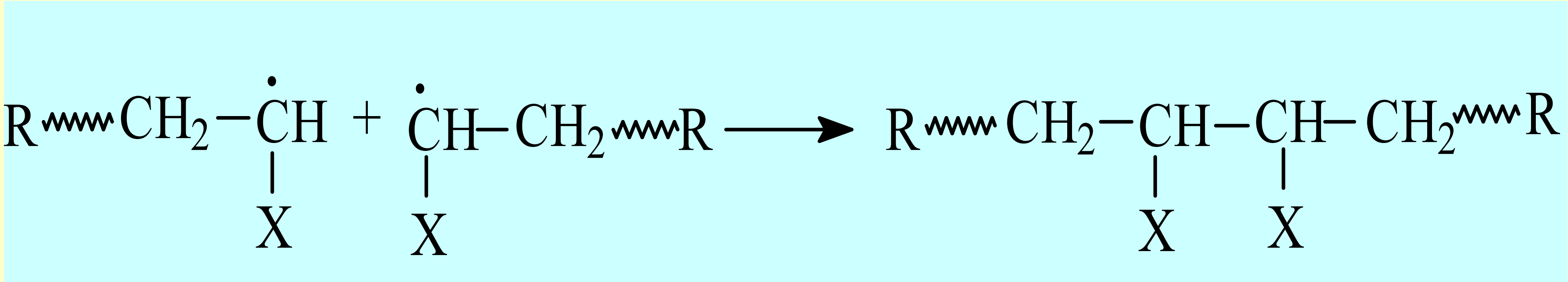
Disproportionation Termination

- **Monoradical termination------ Exhausts one radical initiator**

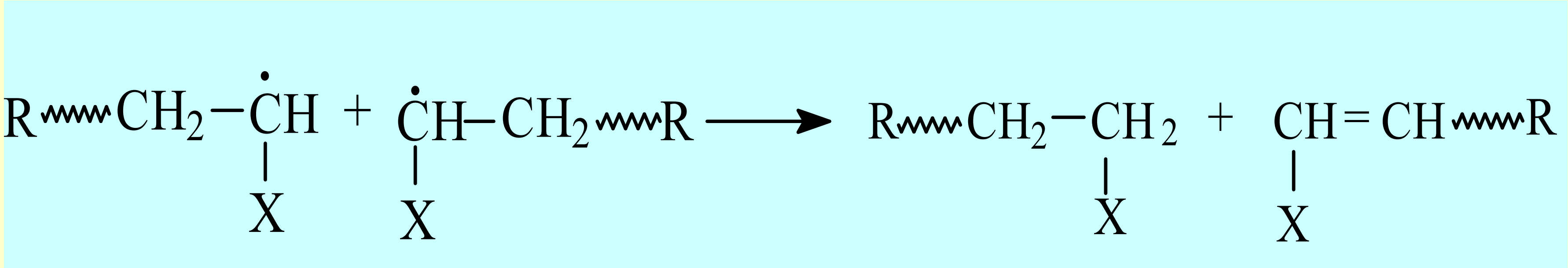


$$R\sim\!\sim CH_2-\underset{X}{\underset{|}{\dot{C}H}} + \dot{R}' \longrightarrow R\sim\!\sim CH_2-\underset{X}{\underset{|}{CH}}-R'$$

- **Biradical termination------coupling termination; disproportionation termination**



$$R\sim\!\sim CH_2-\underset{X}{\underset{|}{\dot{C}H}} + \underset{X}{\underset{|}{\dot{C}H}}-CH_2\sim\!\sim R \longrightarrow R\sim\!\sim CH_2-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH}}-CH_2\sim\!\sim R$$



$$R\sim\!\sim CH_2-\underset{X}{\underset{|}{\dot{C}H}} + \underset{X}{\underset{|}{\dot{C}H}}-CH_2\sim\!\sim R \longrightarrow R\sim\!\sim CH_2-\underset{X}{\underset{|}{CH_2}} + \underset{X}{\underset{|}{CH}}=CH\sim\!\sim R$$

Biradical termination ------

coupling termination;

disproportionation termination

- **Coupling Termination ----**
  - The degree of polymerization is the sum of the monomeric units of the two radical chains.
  - The two ends of the molecule are the residues of the initiators.

Termination of disproportionation ----

- The Degree of Polymerization is the number of the monomeric units of the radical chain.
- Each molecule contains a initiator residues end.
- However, the terminated chemical structures of the two molecules are different, one saturated, and the other unsaturated.

- **The modes of termination reactions are determined by the monomer structure and the polymerization temperature.**

The modes of termination------
monomer structure
polymerization temperature

- **With bulk substituents-----the possibility of disproportionation termination increases.**

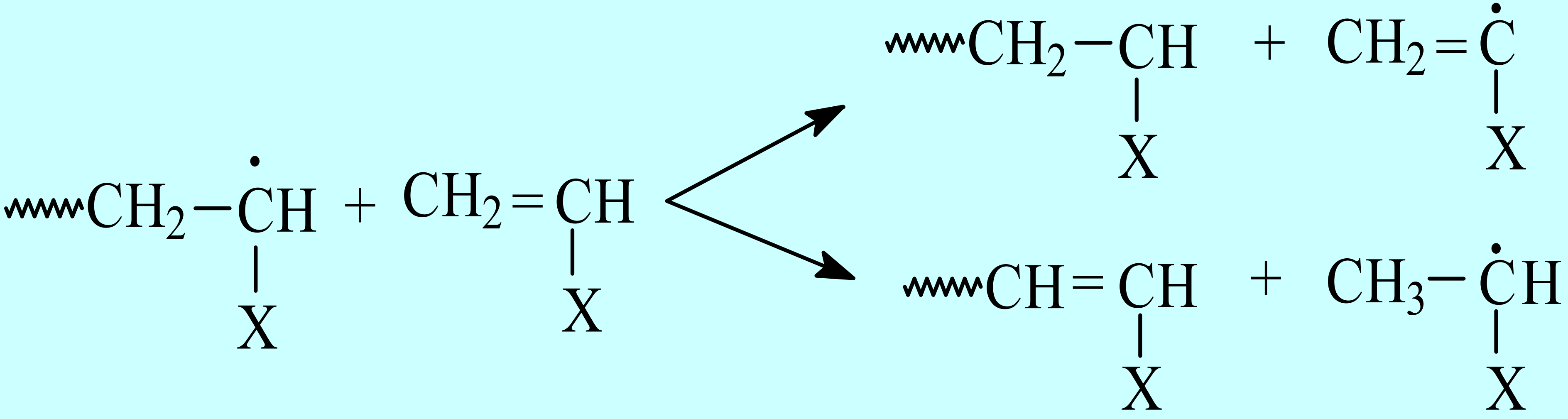
- **At low polymerization temperature----tending to coupling termination.**

（4）Chain Transfer Reaction

- **To monomer**
- **To solvent**

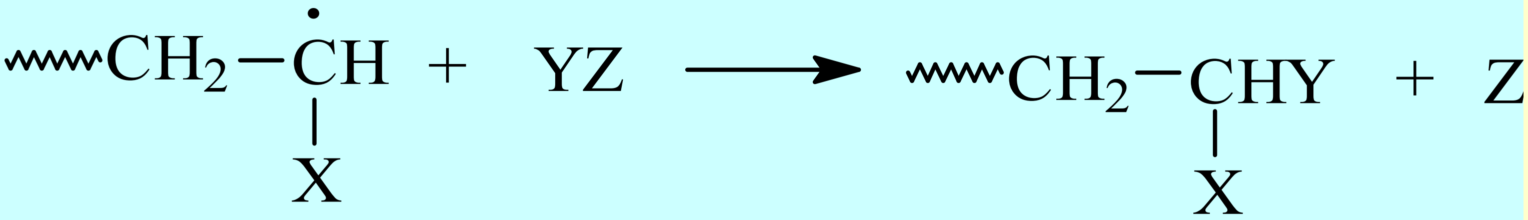
  (or to chain transfer agent）
- **To initiator**
- **To polymer**

[1] to monomer



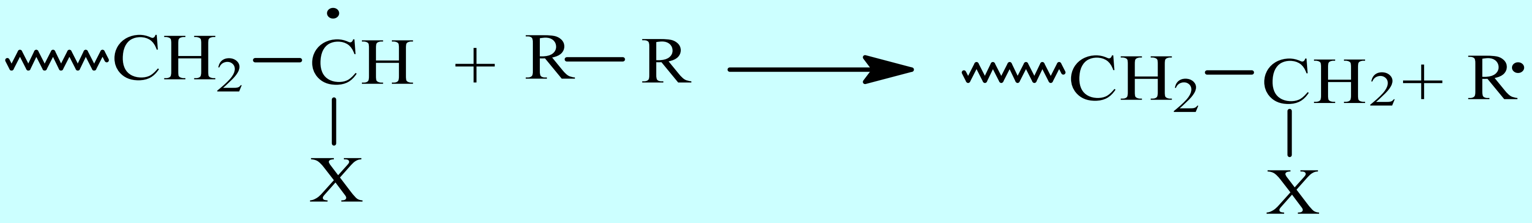
$$\sim\!\sim\!\sim CH_2-\underset{X}{\dot{C}H} + CH_2=\underset{X}{CH} \rightarrow \begin{cases} \sim\!\sim\!\sim CH_2-\underset{X}{CH} + CH_2=\underset{X}{\dot{C}} \\ \sim\!\sim\!\sim CH=\underset{X}{CH} + CH_3-\underset{X}{\dot{C}H} \end{cases}$$

[2] To solvent(or to chain transfer agent）



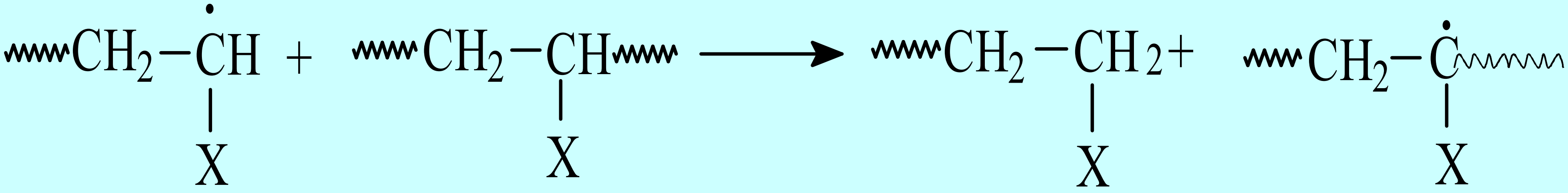
$$\sim\!\sim\!\sim CH_2-\underset{X}{\dot{C}H} + YZ \longrightarrow \sim\!\sim\!\sim CH_2-\underset{X}{CHY} + Z$$

[3] to initiator



$$\sim\sim CH_2-\underset{X}{\dot{C}H} + R-R \longrightarrow \sim\sim CH_2-\underset{X}{CH_2} + R\cdot$$

[4] to molecule



$$\sim\sim CH_2-\underset{X}{\dot{C}H} + \sim\sim CH_2-\underset{X}{CH}\sim\sim \longrightarrow \sim\sim CH_2-\underset{X}{CH_2} + \sim\sim CH_2-\underset{X}{\dot{C}}\sim\sim$$

Characteristics of Radical Polymerization

- **From microscopic view, radical reaction consists of four elementary reactions--initiation, propagation, termination, and transfer.**
- **The rate of initiation is the lowest one, which controls the overall rate of polymerization. In conclusion, the characteristics of radical polymerization are slow initiation, fast propagation, fast termination, and easy transfer.**

- **The degree of polymerization increases only in the propagation process.**

- **In the system there are only monomers and polymers, no intermediate compounds.**

- **Prolonging the reaction time is mainly to increase the conversion rate, with little effects on the molecular-weight. However, gel effect will increase the molecular-weight.**
- **A small amount（0.01 % ～ 0.1 %）of inhibitors is enough to terminate the radical polymerization.**