TYPES OF POLYMERIZATION

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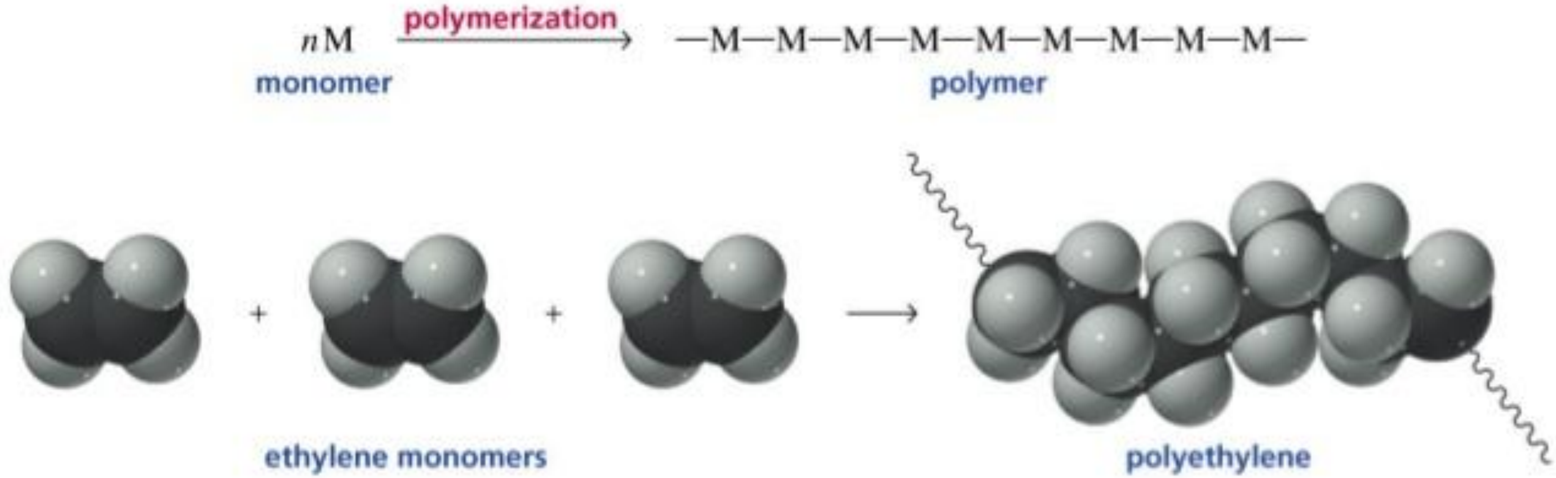
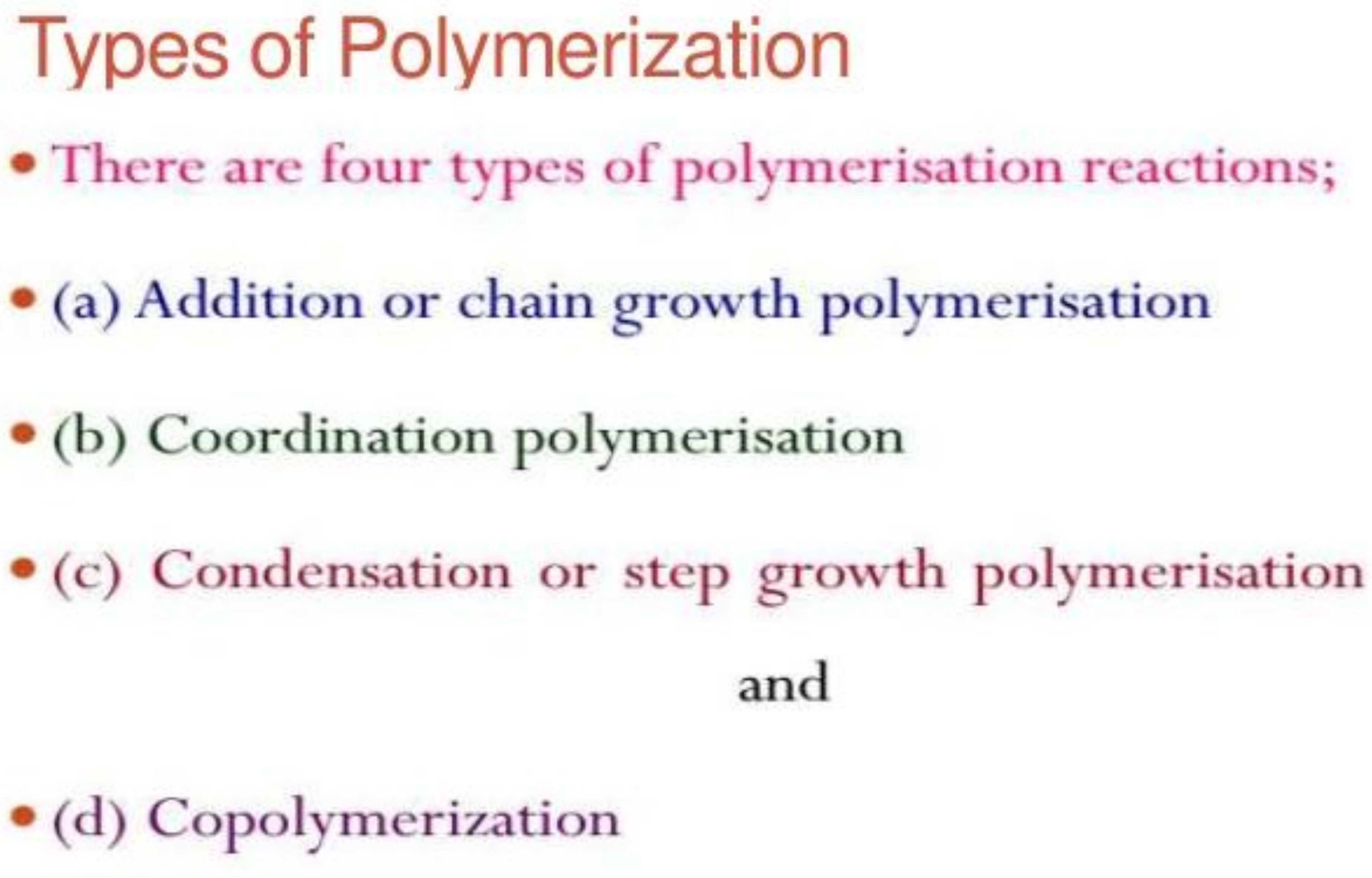
For 6th Sem

Introduction



Monomers has to be two functionality for polymerization.



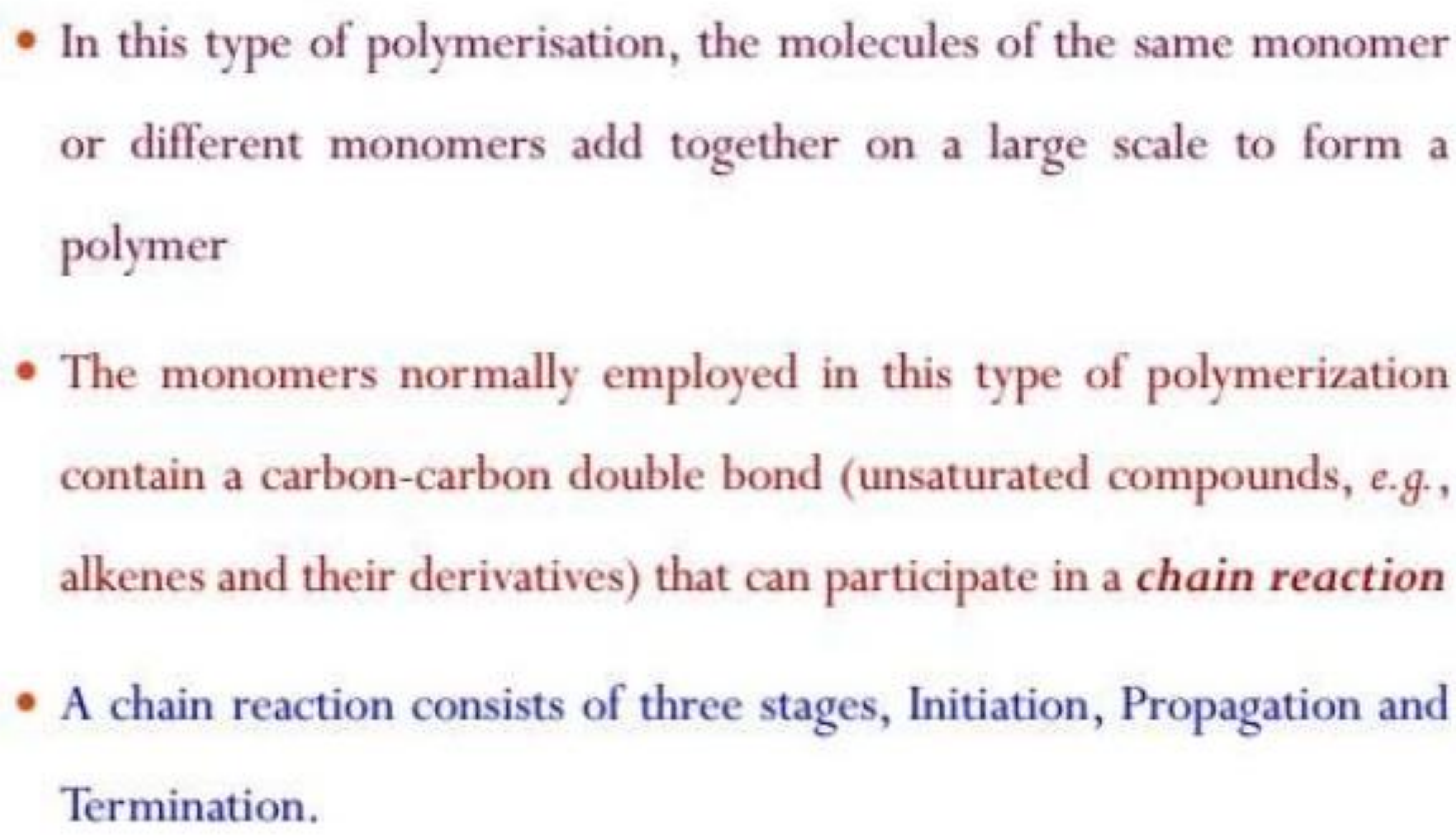
Types of Polymerization

- There are four types of polymerisation reactions;
- (a) Addition or chain growth polymerisation
- (b) Coordination polymerisation
- (c) Condensation or step growth polymerisation

and

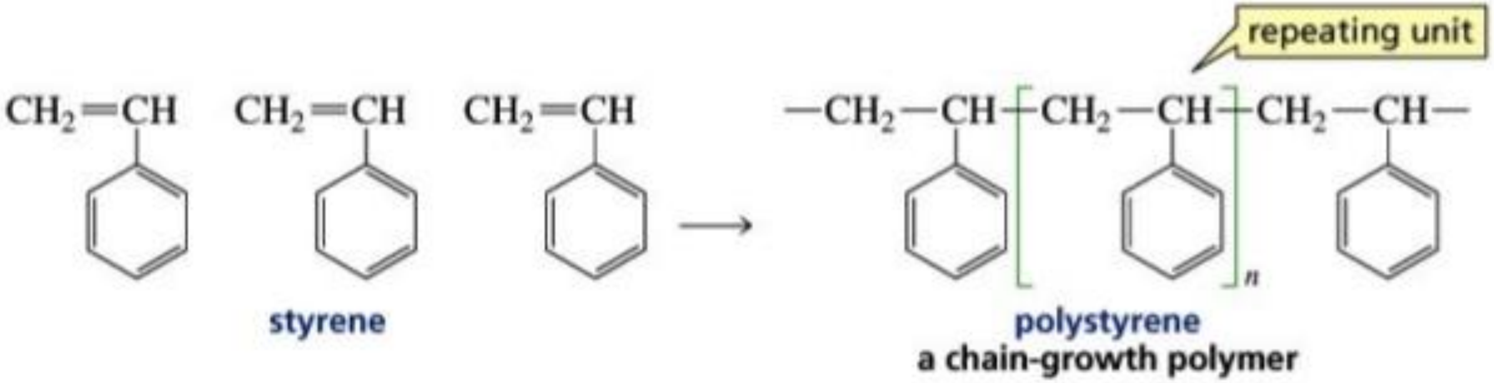
- (d) Copolymerization

Addition/Chain Growth Polymerization



- In this type of polymerisation, the molecules of the same monomer or different monomers add together on a large scale to form a polymer
- The monomers normally employed in this type of polymerization contain a carbon-carbon double bond (unsaturated compounds, *e.g.*, alkenes and their derivatives) that can participate in a ***chain reaction***
- A chain reaction consists of three stages, Initiation, Propagation and Termination.

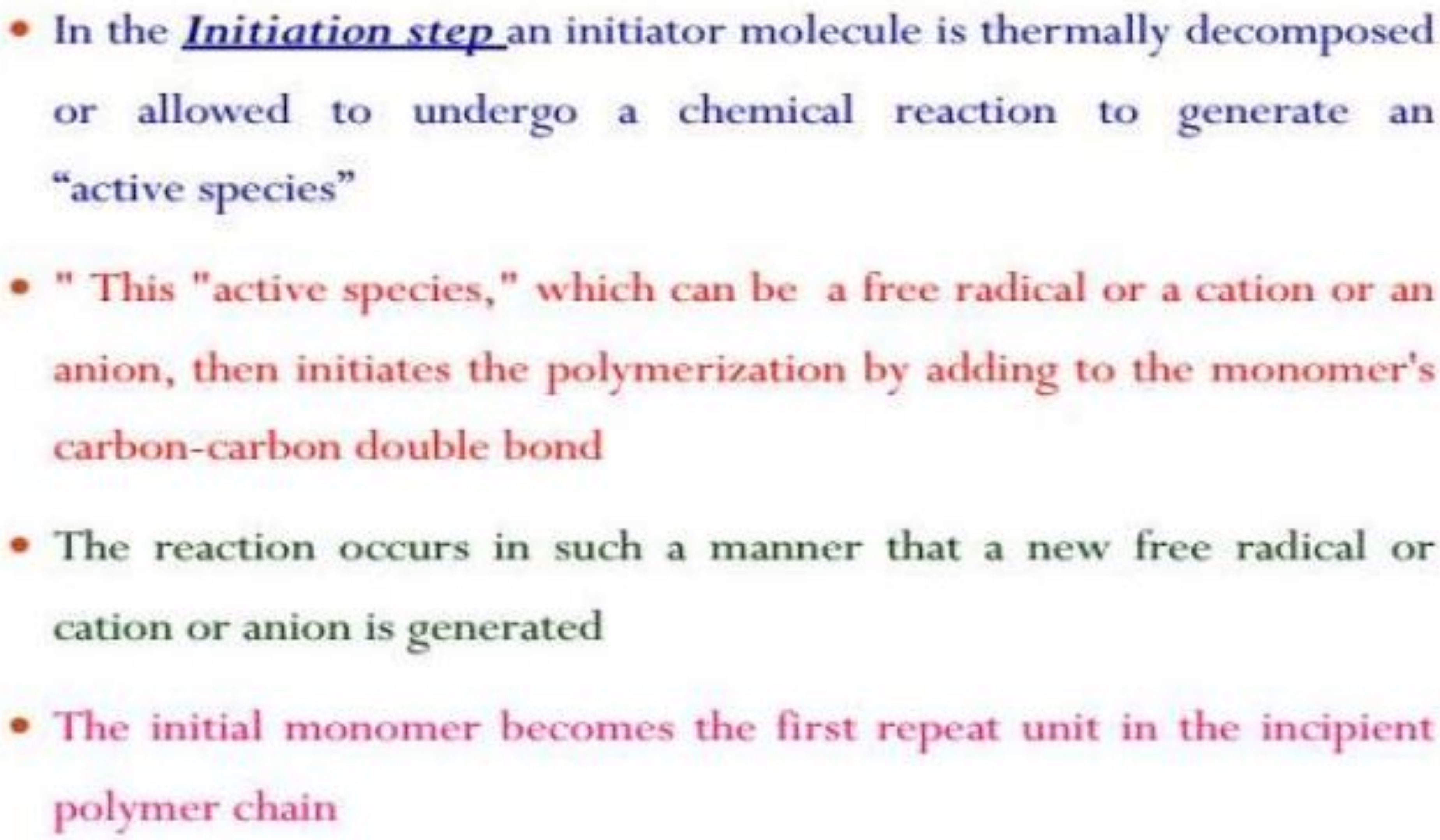
Chain-growth Polymerization



styrene

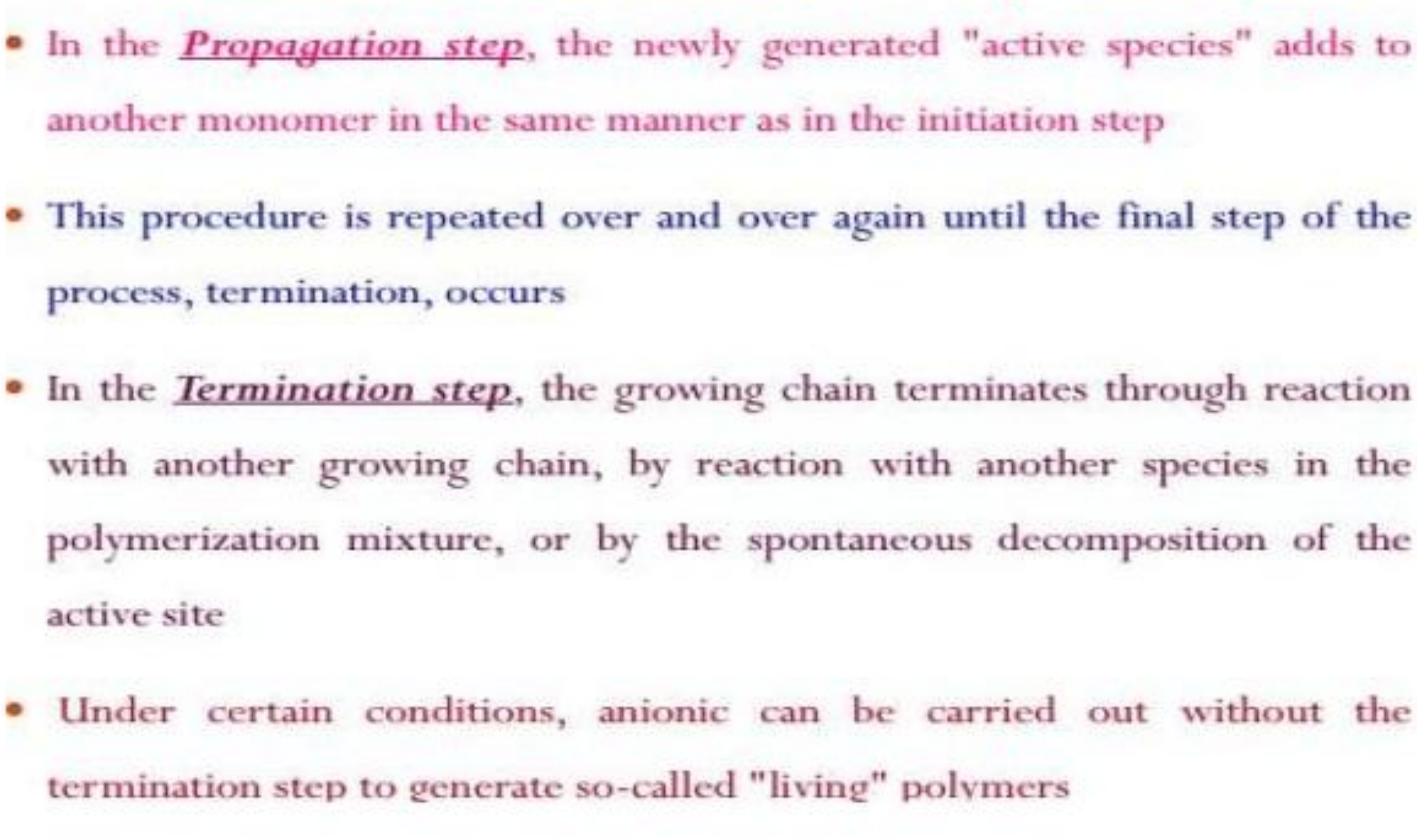
polystyrene
a chain-growth polymer

Addition/Chain Growth Polymerization



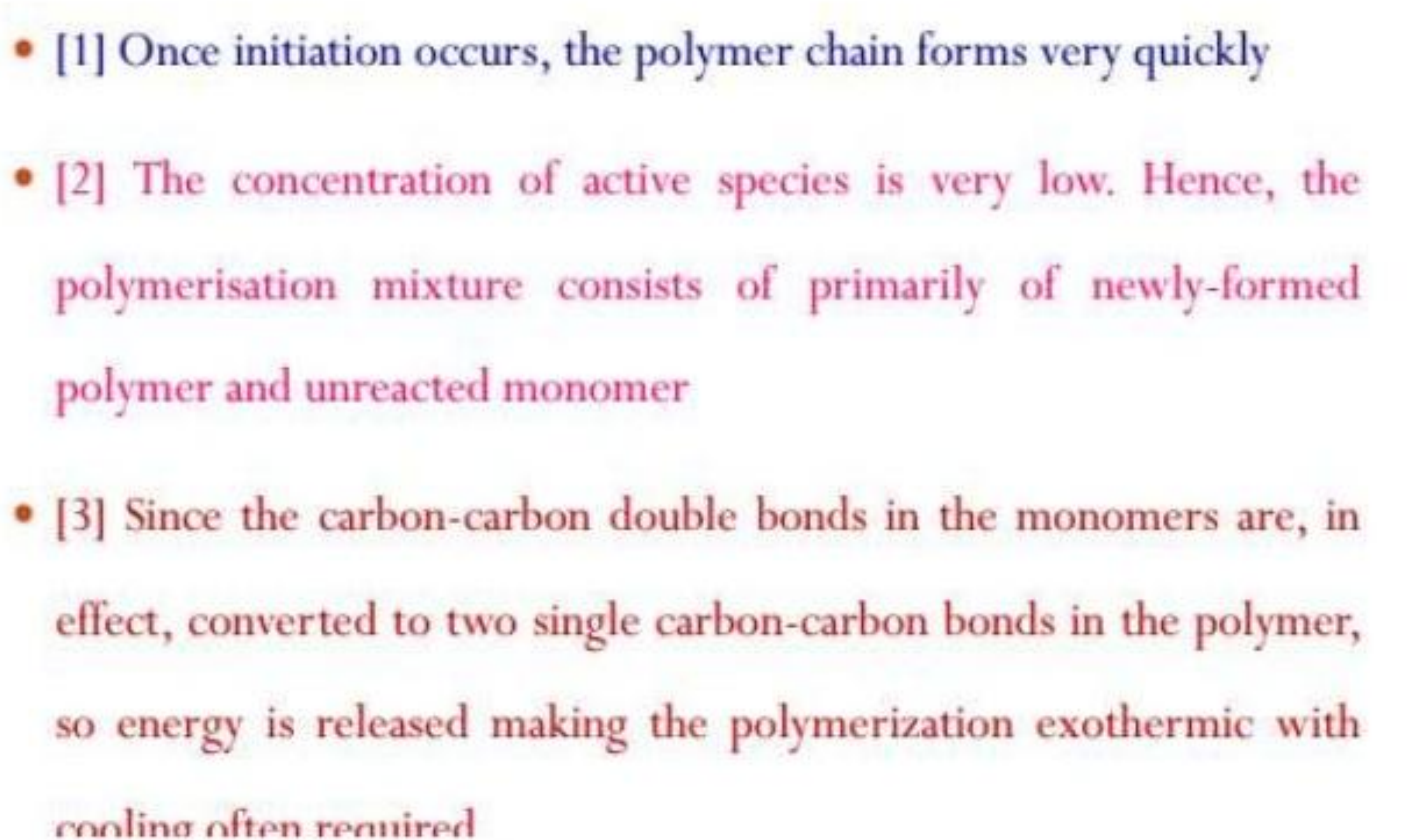
- In the ***Initiation step*** an initiator molecule is thermally decomposed or allowed to undergo a chemical reaction to generate an “active species”
- " This "active species," which can be a free radical or a cation or an anion, then initiates the polymerization by adding to the monomer's carbon-carbon double bond
- The reaction occurs in such a manner that a new free radical or cation or anion is generated
- The initial monomer becomes the first repeat unit in the incipient polymer chain

Addition/Chain Growth Polymerization

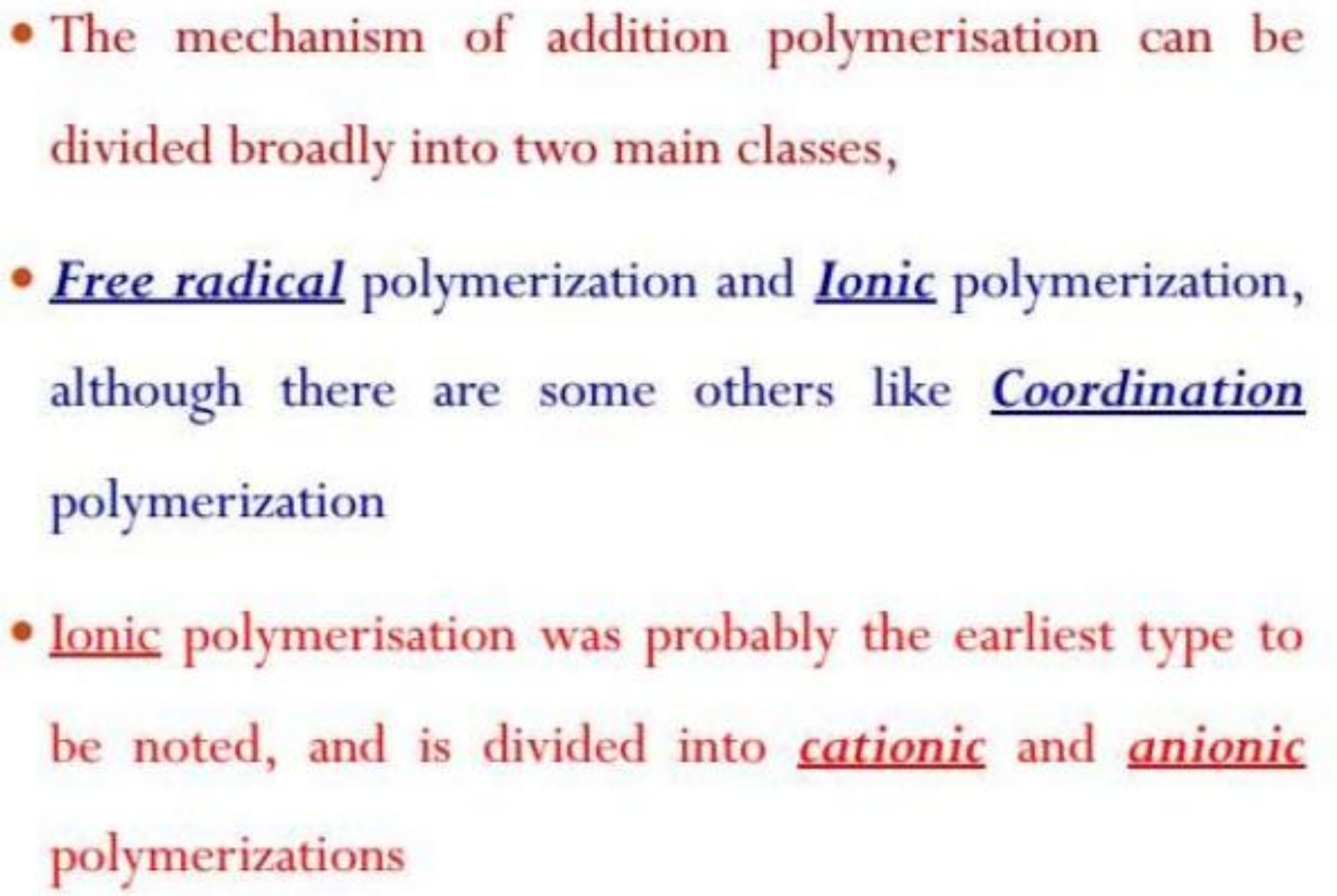


- In the ***Propagation step***, the newly generated "active species" adds to another monomer in the same manner as in the initiation step
- This procedure is repeated over and over again until the final step of the process, termination, occurs
- In the ***Termination step***, the growing chain terminates through reaction with another growing chain, by reaction with another species in the polymerization mixture, or by the spontaneous decomposition of the active site
- Under certain conditions, anionic can be carried out without the termination step to generate so-called "living" polymers

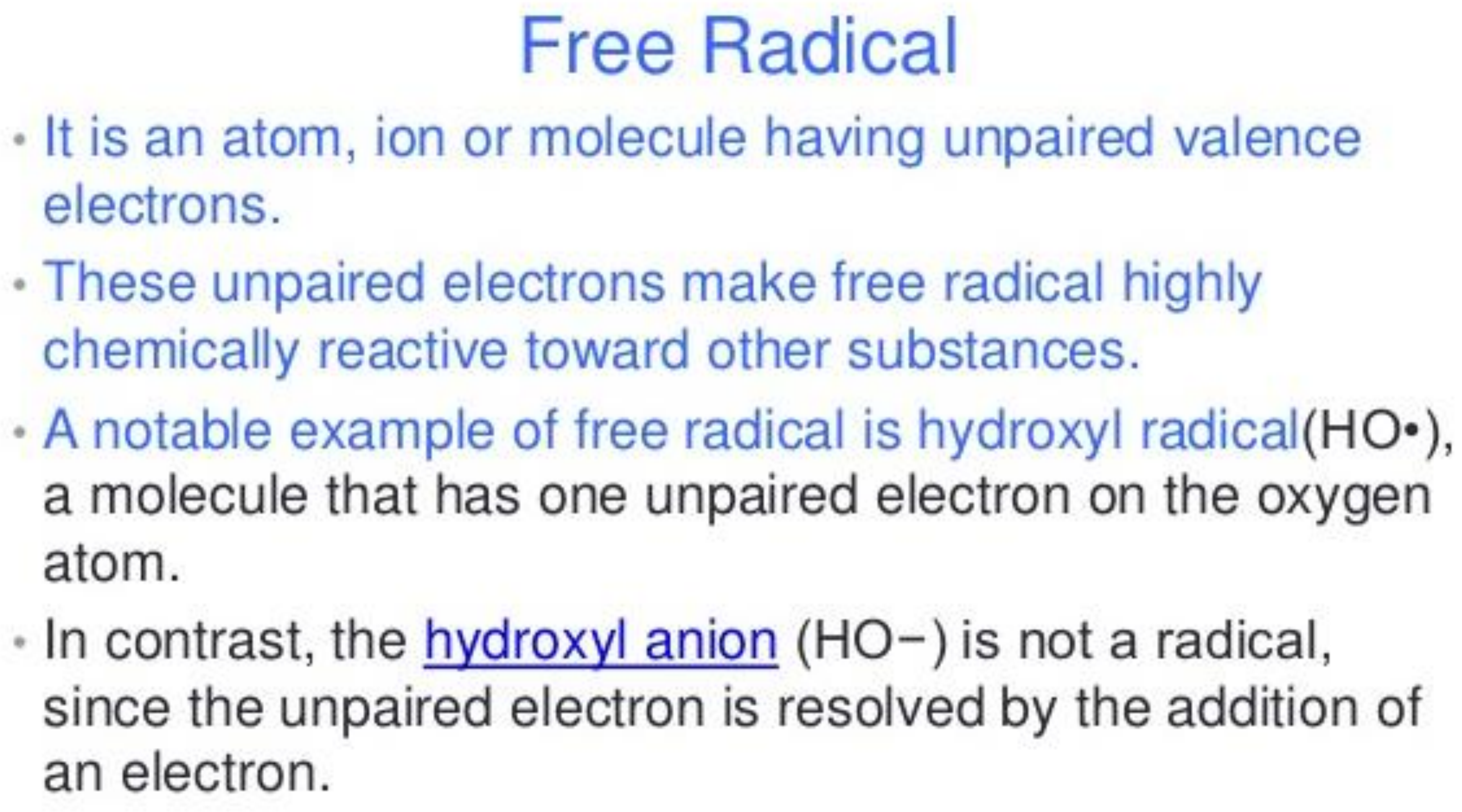
General Characteristics of Addition/Chain Growth Polymerization



- [1] Once initiation occurs, the polymer chain forms very quickly
- [2] The concentration of active species is very low. Hence, the polymerisation mixture consists of primarily of newly-formed polymer and unreacted monomer
- [3] Since the carbon-carbon double bonds in the monomers are, in effect, converted to two single carbon-carbon bonds in the polymer, so energy is released making the polymerization exothermic with cooling often required



- The mechanism of addition polymerisation can be divided broadly into two main classes,
- ***Free radical*** polymerization and ***Ionic*** polymerization, although there are some others like ***Coordination*** polymerization
- Ionic polymerisation was probably the earliest type to be noted, and is divided into ***cationic*** and ***anionic*** polymerizations



Free Radical

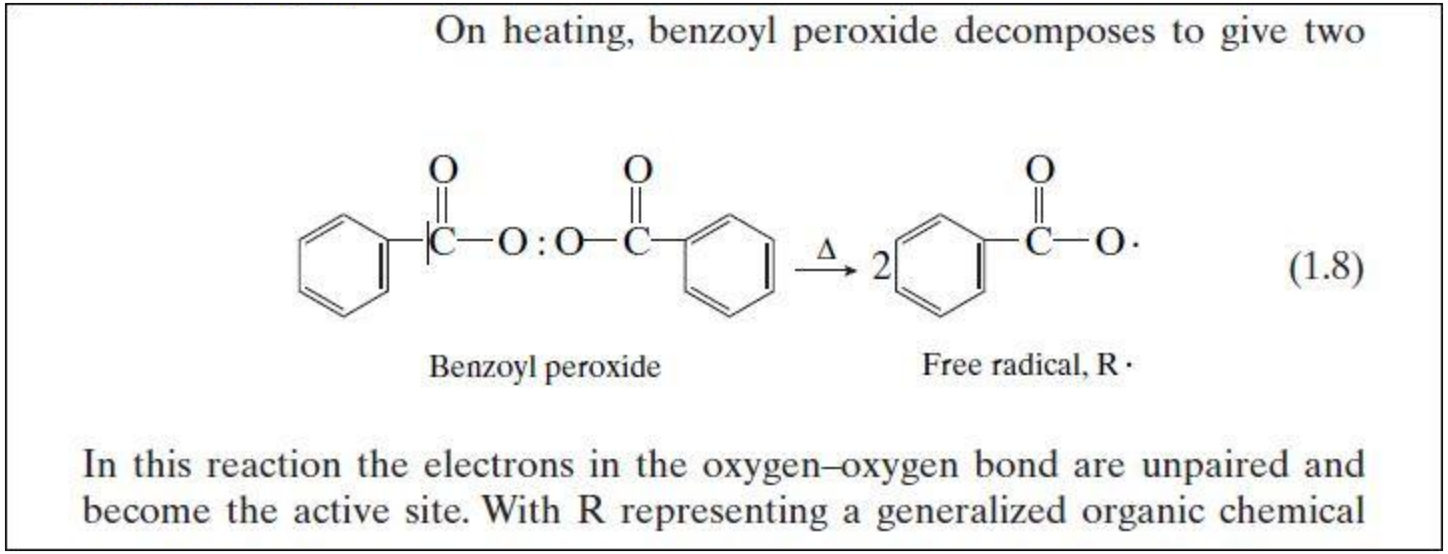
- It is an atom, ion or molecule having unpaired valence electrons.
- These unpaired electrons make free radical highly chemically reactive toward other substances.
- A notable example of free radical is hydroxyl radical(HO•), a molecule that has one unpaired electron on the oxygen atom.
- In contrast, the hydroxyl anion (HO−) is not a radical, since the unpaired electron is resolved by the addition of an electron.

Free Radical

- Free radicals may be created in a number of ways, including synthesis with very dilute or reactions at very low temperatures, or breakup of larger molecules.
- Free radicals play an important role in combustion, polymerization, plasma chemistry, biochemistry, and many other chemical processes.

FREE RADICAL POLYMERISATION

- A variety of alkenes or dienes and their derivatives are polymerized in the presence of a free radical generating initiator (catalyst) like benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc
- A free radical may be defined as an intermediate compound containing an odd number of electrons, but which do not carry an electric charge and are not free ions



On heating, benzoyl peroxide decomposes to give two

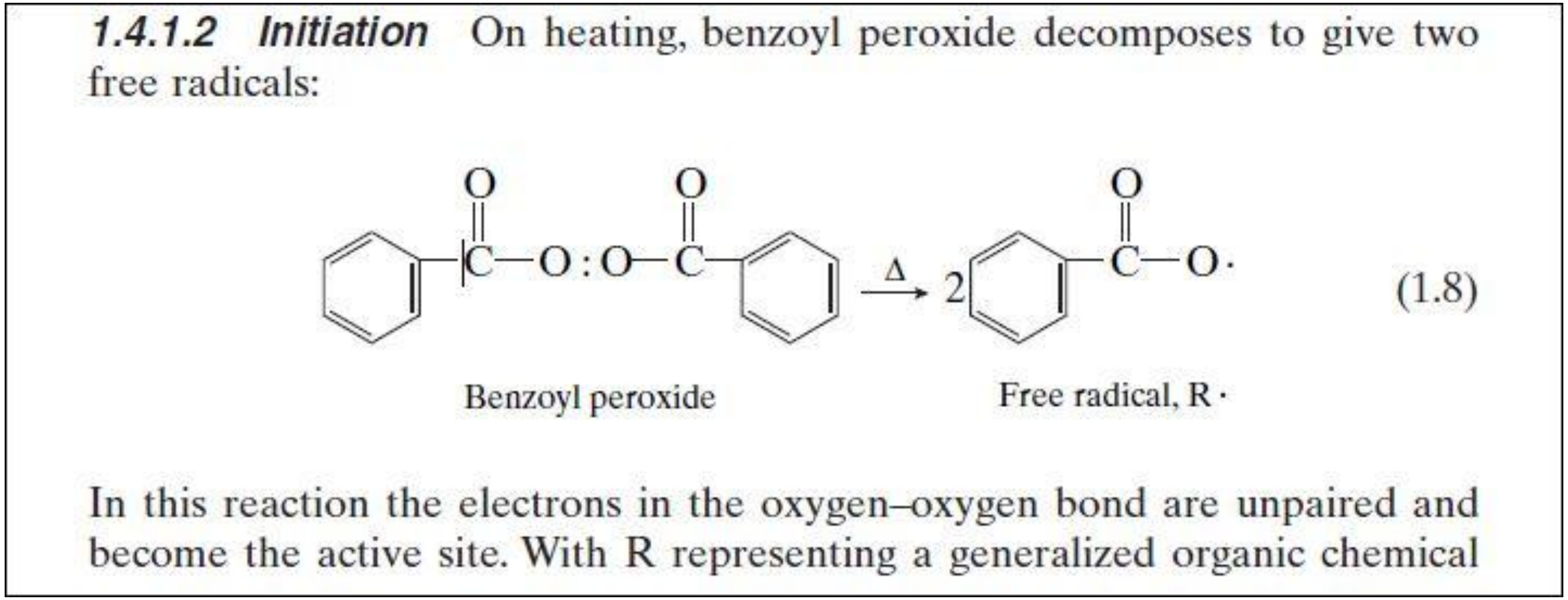
(1.8)

Benzoyl peroxide

Free radical, R·

In this reaction the electrons in the oxygen–oxygen bond are unpaired and become the active site. With R representing a generalized organic chemical

INITIATION



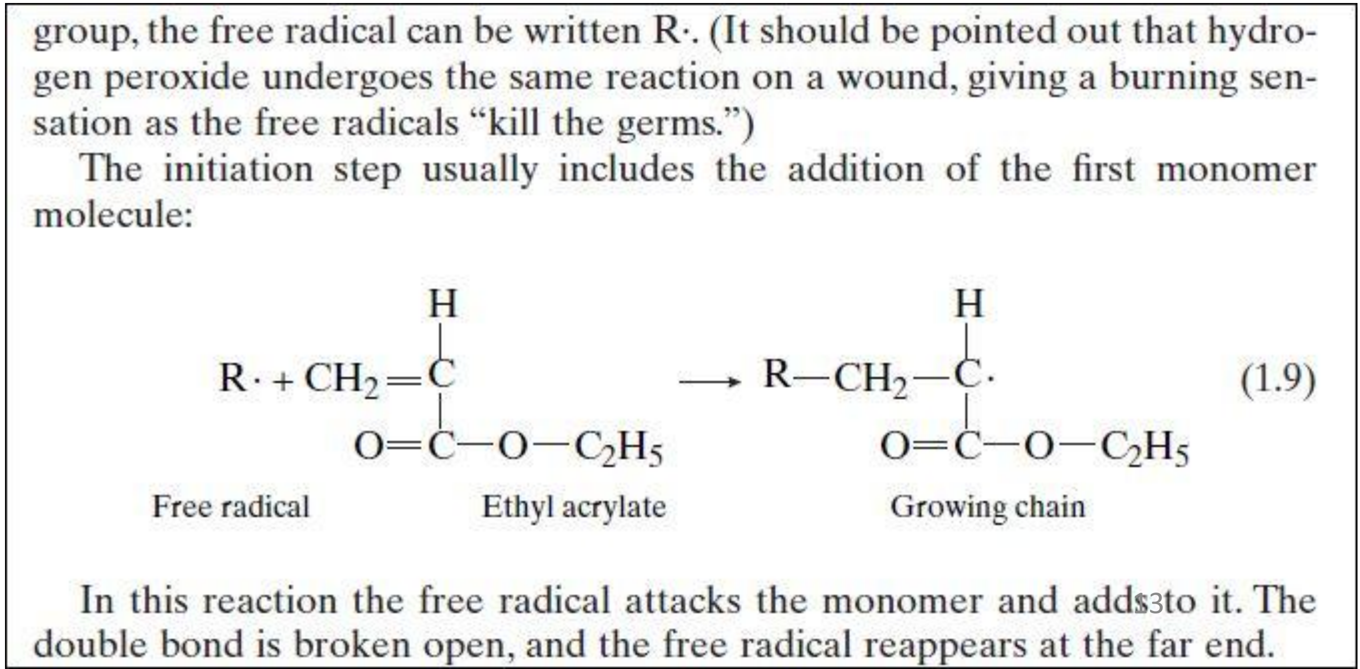
1.4.1.2 ***Initiation*** On heating, benzoyl peroxide decomposes to give two free radicals:

(1.8)

Benzoyl peroxide

Free radical, R ·

In this reaction the electrons in the oxygen–oxygen bond are unpaired and become the active site. With R representing a generalized organic chemical



group, the free radical can be written R·. (It should be pointed out that hydrogen peroxide undergoes the same reaction on a wound, giving a burning sensation as the free radicals "kill the germs.")

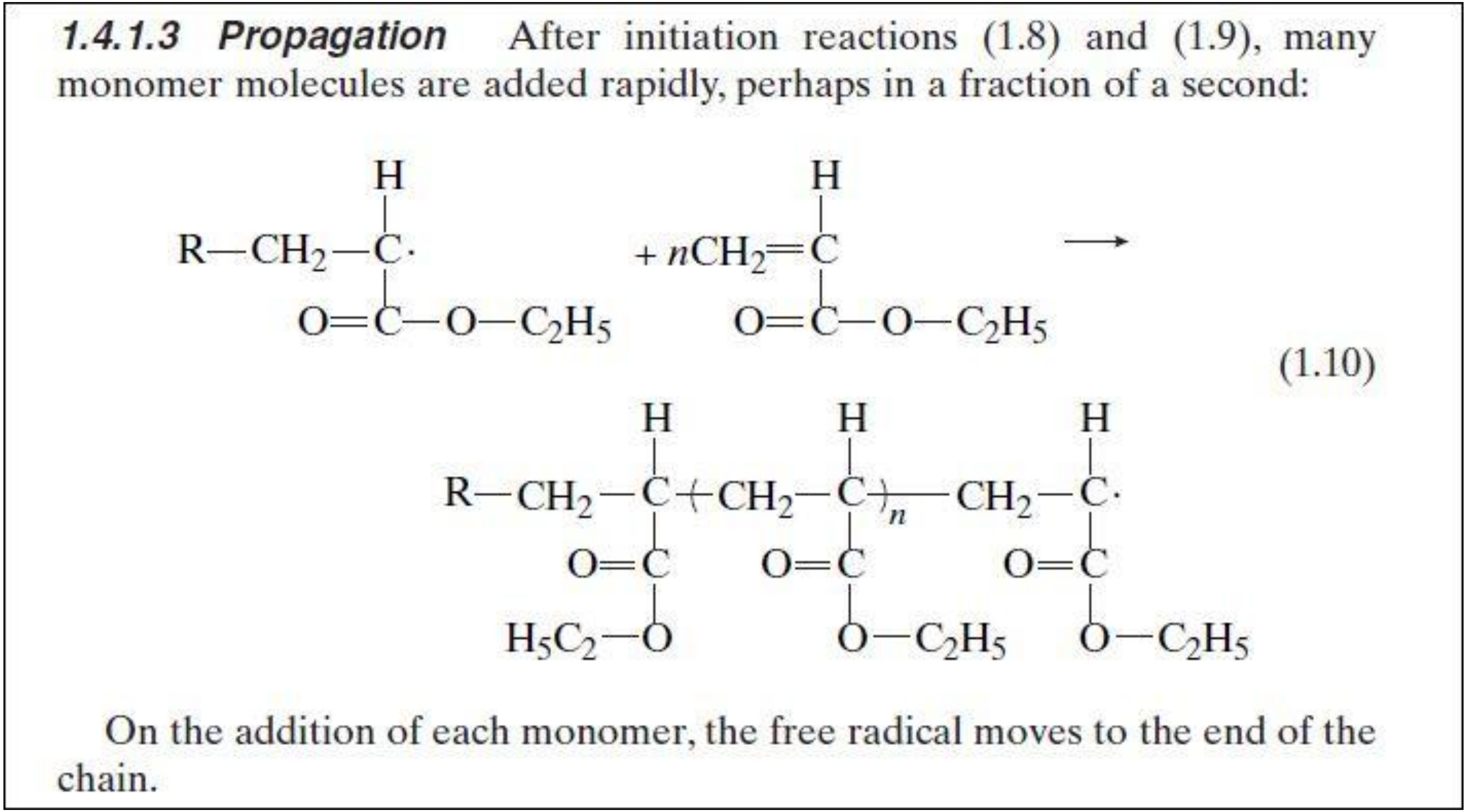
The initiation step usually includes the addition of the first monomer molecule:

$$\mathrm{R\cdot + CH_2{=}\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{\overset{\displaystyle H}{C}} \longrightarrow R{-}CH_2{-}\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{\overset{\displaystyle H}{C}}\cdot} \qquad (1.9)$$

Free radical Ethyl acrylate Growing chain

In this reaction the free radical attacks the monomer and adds to it. The double bond is broken open, and the free radical reappears at the far end.

PROPAGATION



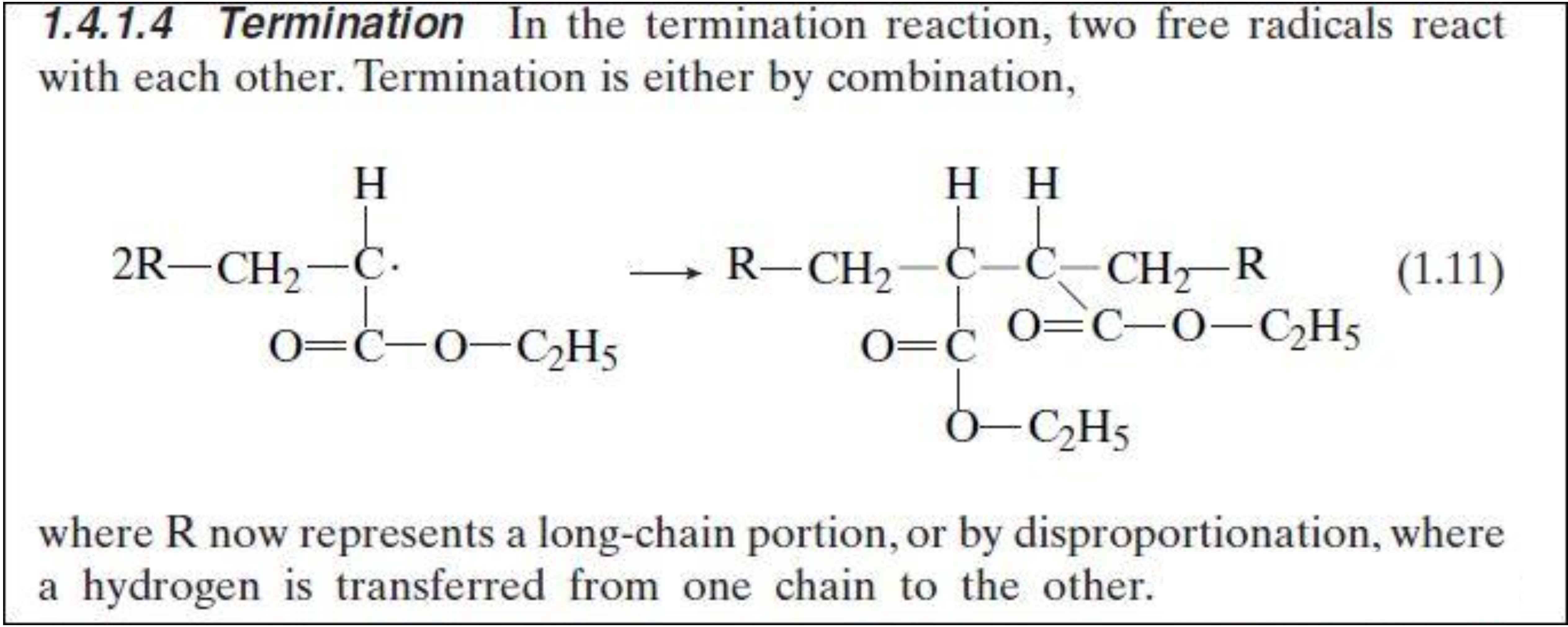
1.4.1.3 Propagation After initiation reactions (1.8) and (1.9), many monomer molecules are added rapidly, perhaps in a fraction of a second:

$$R{-}CH_2{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{|}}{C}}\cdot \;+\; nCH_2{=}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{|}}{C}} \longrightarrow$$

$$R{-}CH_2{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{|}}{C}}{+}CH_2{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{|}}{C}}{+}_n{-}CH_2{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O{=}C{-}O{-}C_2H_5}{|}}{C}}\cdot \qquad (1.10)$$

On the addition of each monomer, the free radical moves to the end of the chain.

TERMINATION

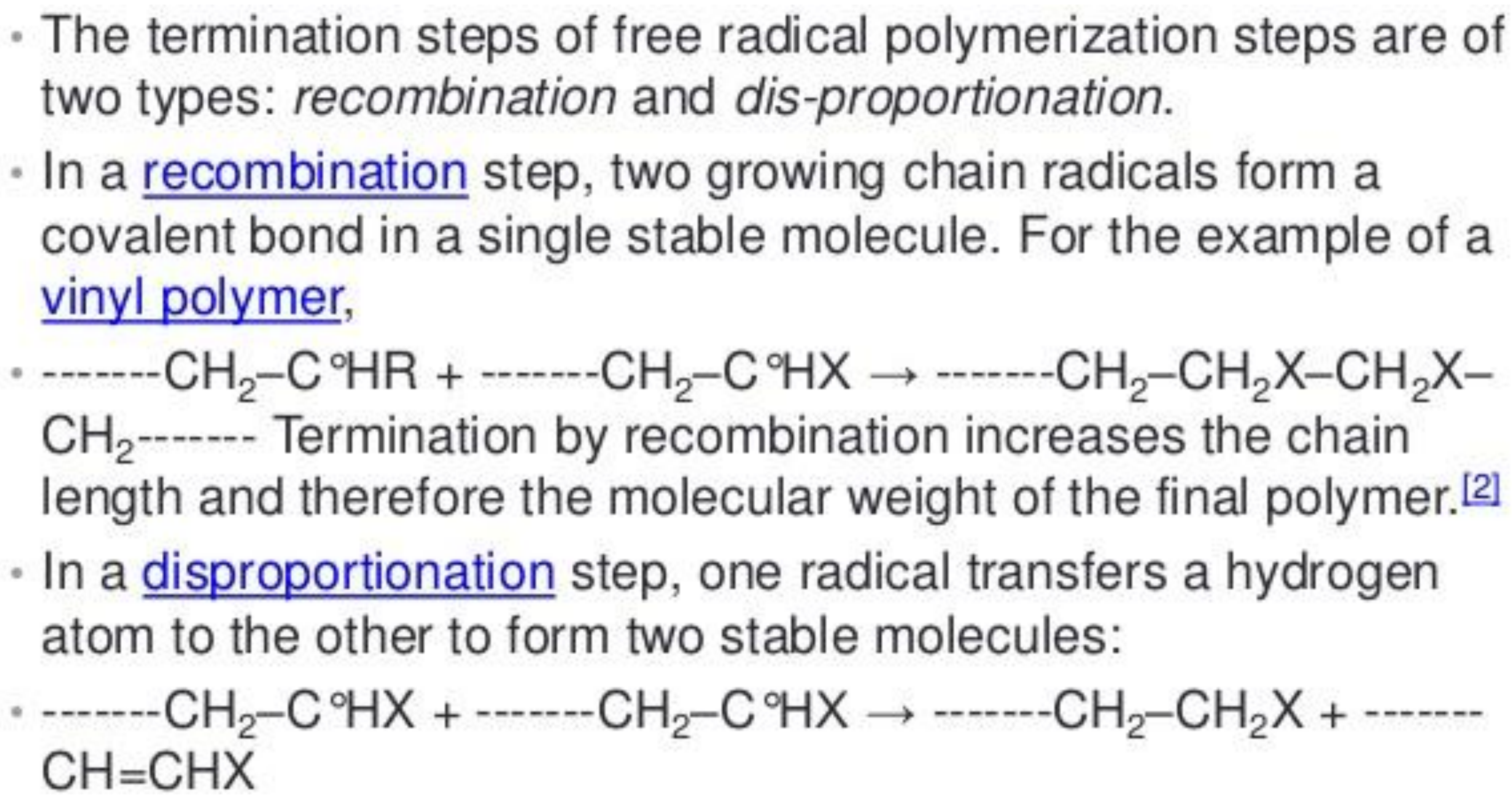


1.4.1.4 *Termination* In the termination reaction, two free radicals react with each other. Termination is either by combination,

$$2R{-}CH_2{-}\underset{\substack{|\\ O=C-O-C_2H_5}}{\overset{\substack{H\\ |}}{C}}\cdot \longrightarrow R{-}CH_2{-}\underset{\substack{|\\ O=C\\ |\\ O-C_2H_5}}{\overset{\substack{H\\ |}}{C}}{-}\underset{\substack{\backslash\\ O=C-O-C_2H_5}}{\overset{\substack{H\\ |}}{C}}{-}CH_2{-}R \qquad (1.11)$$

where R now represents a long-chain portion, or by disproportionation, where a hydrogen is transferred from one chain to the other.

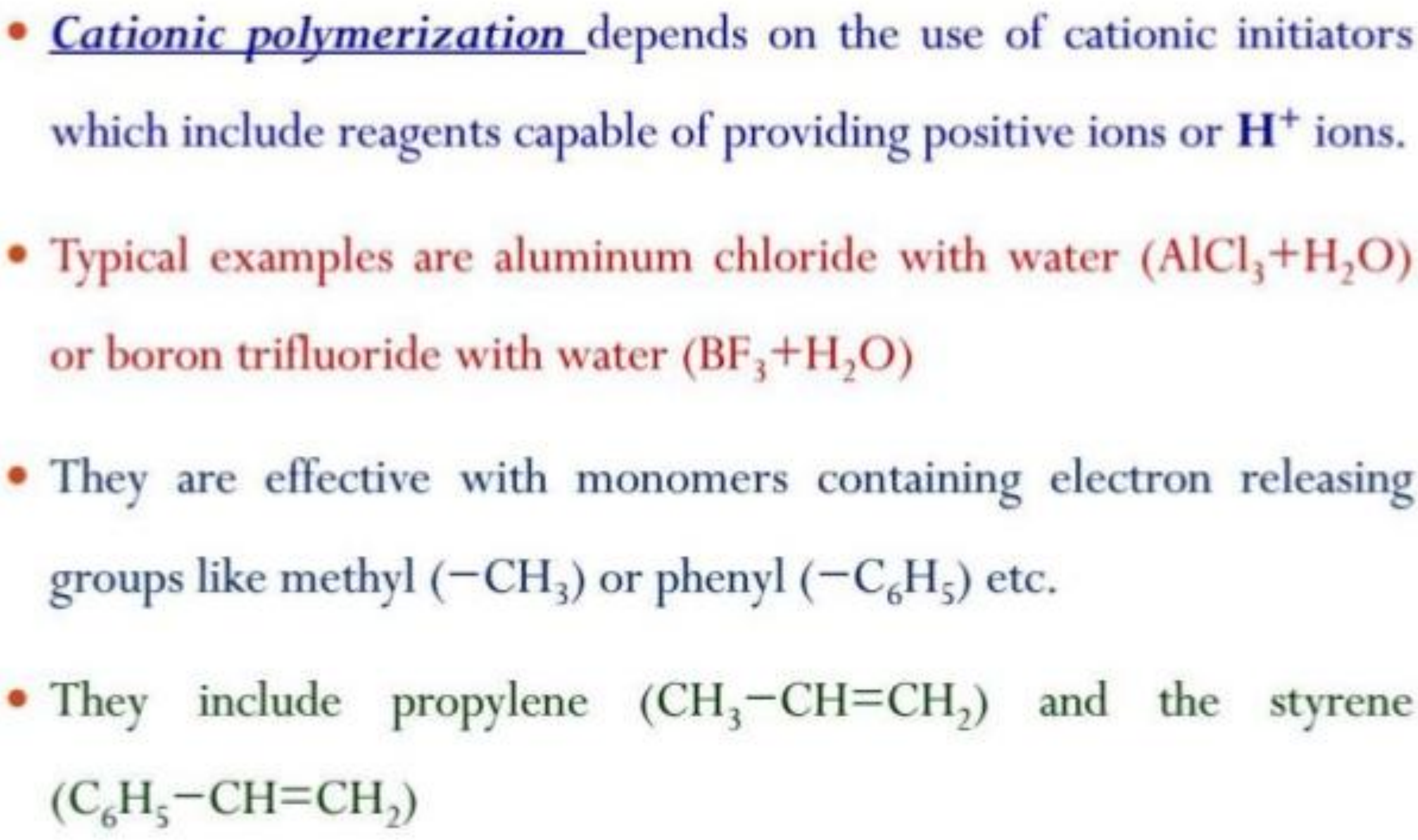
REMEMBER



- The termination steps of free radical polymerization steps are of two types: *recombination* and *dis-proportionation*.
- In a recombination step, two growing chain radicals form a covalent bond in a single stable molecule. For the example of a vinyl polymer,
- -------CH_2–C°HR + ------CH_2–C°HX → ------CH_2–CH_2X–CH_2X–CH_2------- Termination by recombination increases the chain length and therefore the molecular weight of the final polymer.[2]
- In a disproportionation step, one radical transfers a hydrogen atom to the other to form two stable molecules:
- -------CH_2–C°HX + ------CH_2–C°HX → ------CH_2–CH_2X + ------CH=CHX

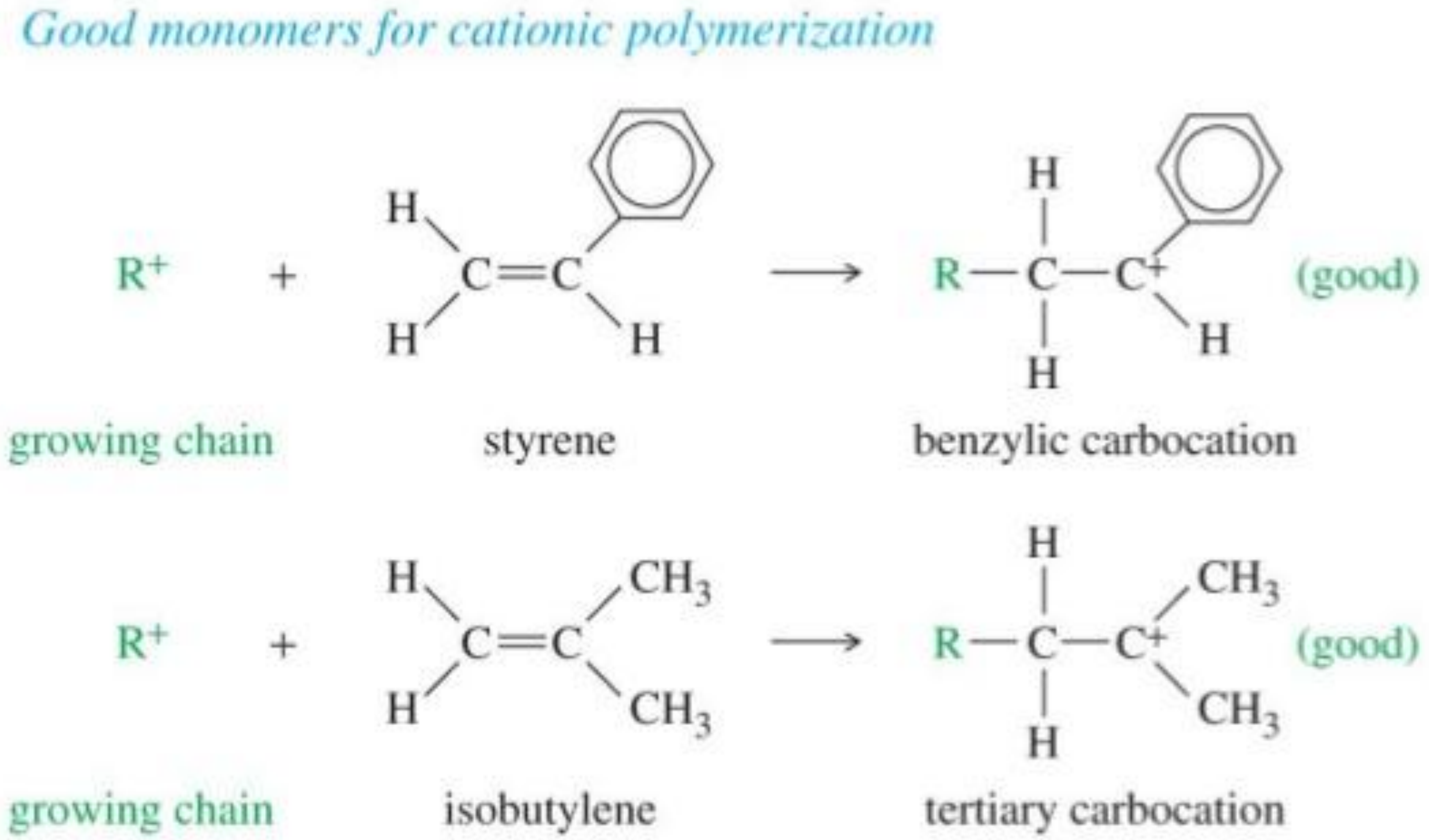
➢Ionic Polymerisation

- The addition polymerization that takes place due to ionic intermediate is called ionic polymerization
- Based on the nature of ions used for the initiation process ionic polymerization classified into two types;
- (a) Cationic polymerization and
- (b) Anionic polymerization



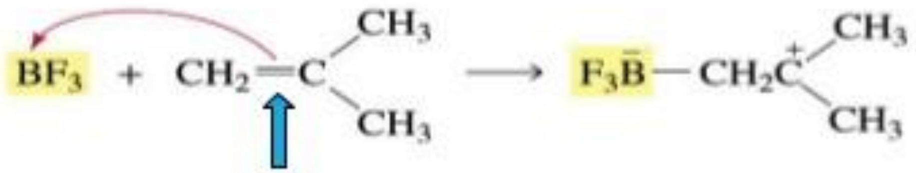
- ***Cationic polymerization*** depends on the use of cationic initiators which include reagents capable of providing positive ions or $\mathbf{H^+}$ ions.
- Typical examples are aluminum chloride with water ($AlCl_3+H_2O$) or boron trifluoride with water (BF_3+H_2O)
- They are effective with monomers containing electron releasing groups like methyl ($-CH_3$) or phenyl ($-C_6H_5$) etc.
- They include propylene ($CH_3-CH=CH_2$) and the styrene ($C_6H_5-CH=CH_2$)

Good Monomers for Cationic Polymerization



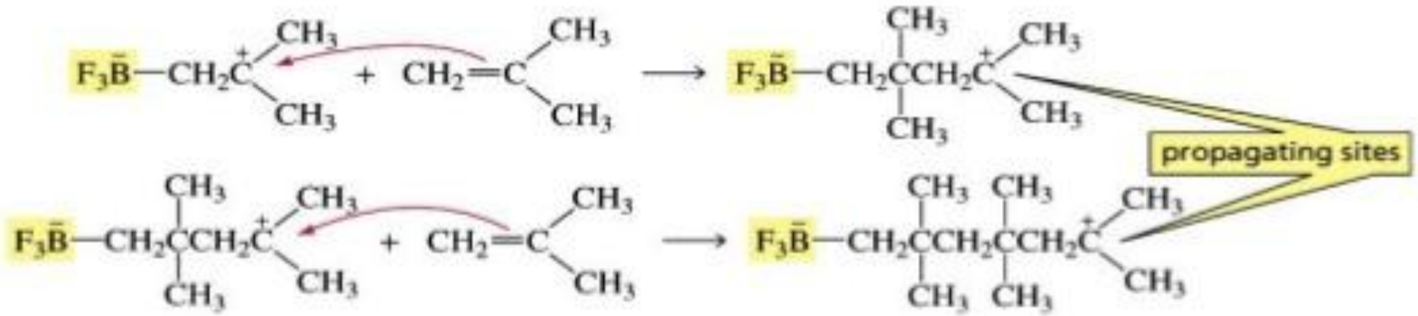
Cationic Polymerization

chain-initiating step

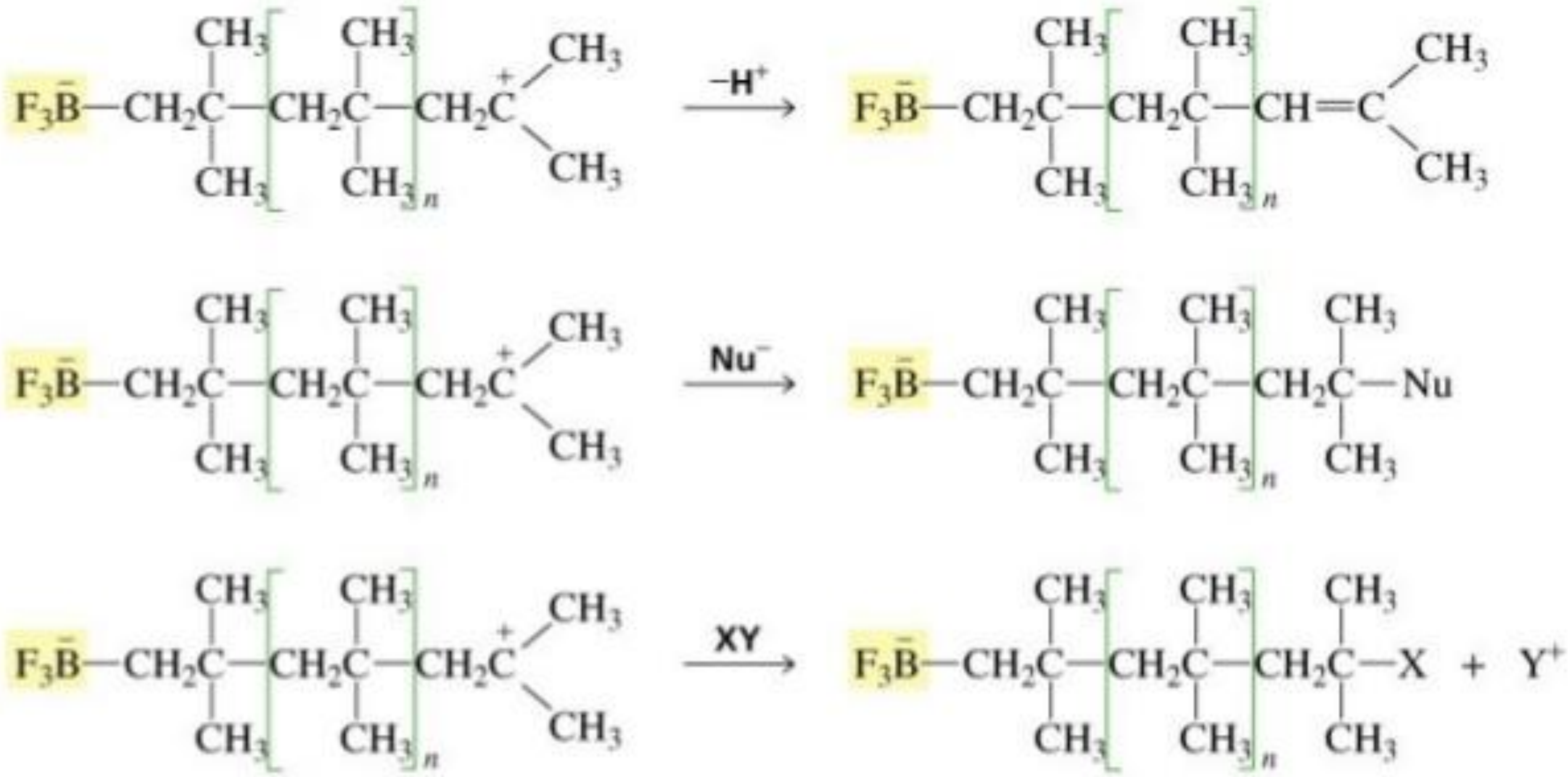


the alkene monomer
reacts with an electrophile

chain-propagating steps



chain-terminating steps



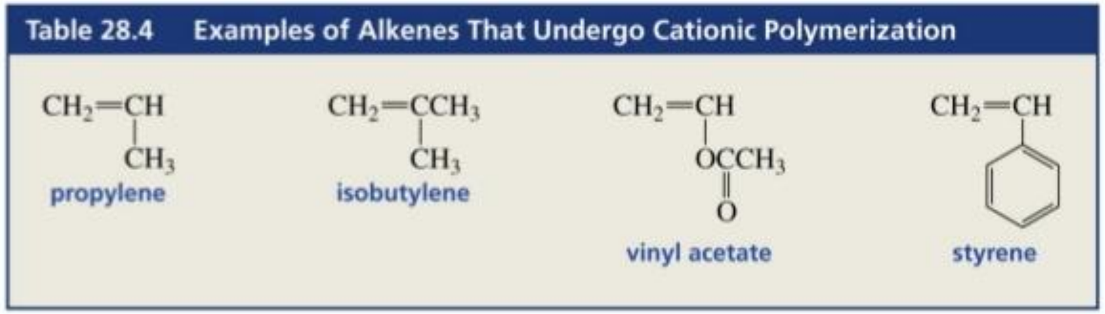
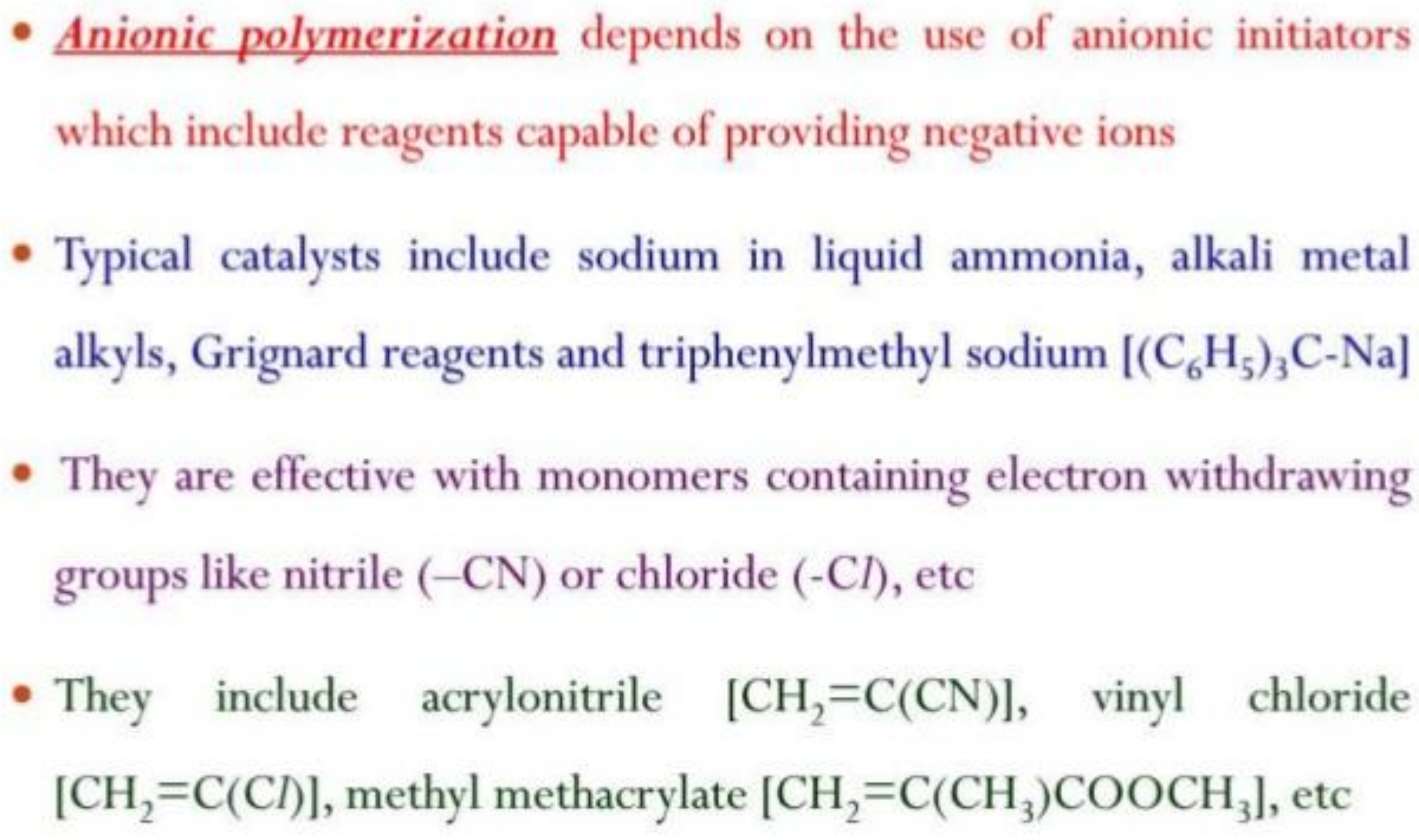


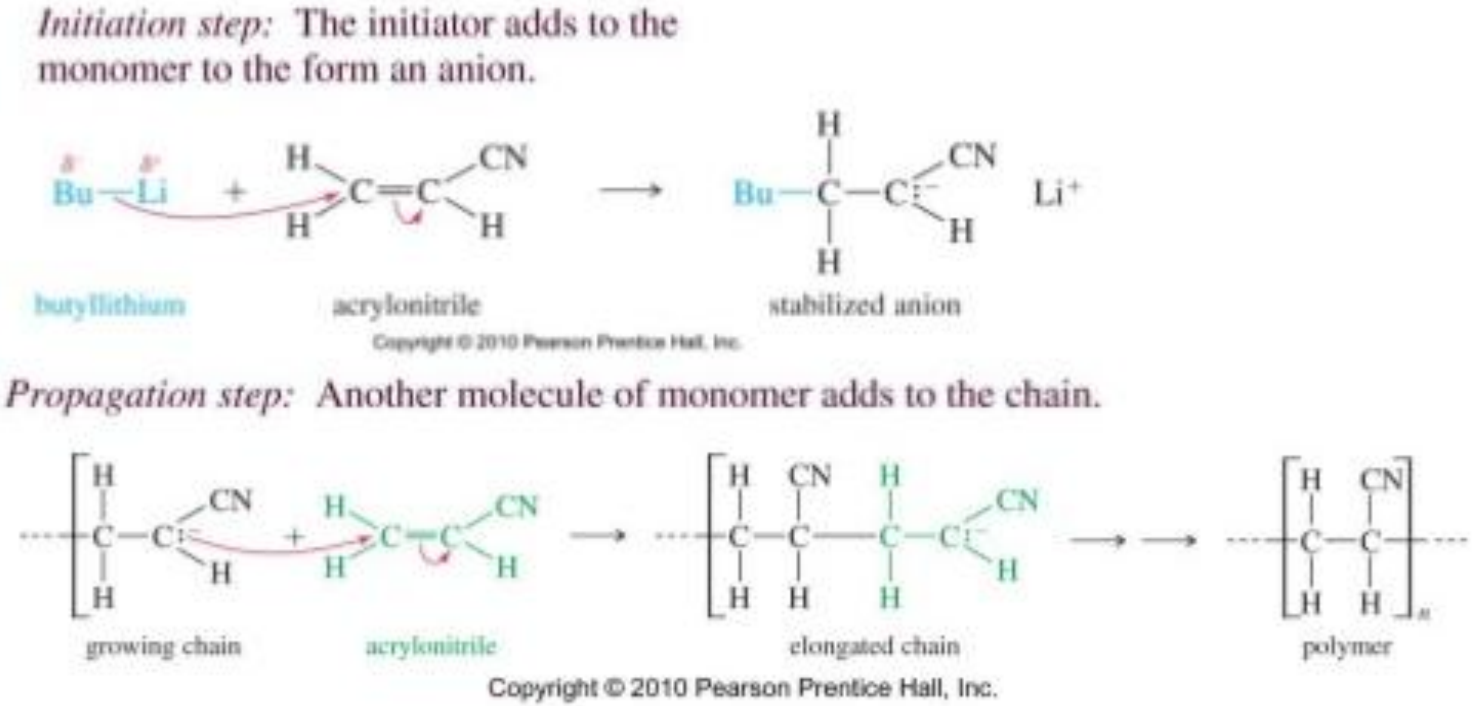
Table 28.4 Examples of Alkenes That Undergo Cationic Polymerization

$\underset{CH_3}{CH_2{=}CH}$	$\underset{CH_3}{CH_2{=}CCH_3}$	$\underset{\underset{O}{\overset{\|}{OCCH_3}}}{CH_2{=}CH}$	$CH_2{=}CH$
propylene	isobutylene	vinyl acetate	styrene



- ***Anionic polymerization*** depends on the use of anionic initiators which include reagents capable of providing negative ions
- Typical catalysts include sodium in liquid ammonia, alkali metal alkyls, Grignard reagents and triphenylmethyl sodium $[(C_6H_5)_3C\text{-}Na]$
- They are effective with monomers containing electron withdrawing groups like nitrile ($-CN$) or chloride ($-Cl$), etc
- They include acrylonitrile $[CH_2{=}C(CN)]$, vinyl chloride $[CH_2{=}C(Cl)]$, methyl methacrylate $[CH_2{=}C(CH_3)COOCH_3]$, etc

Anionic Polymerization

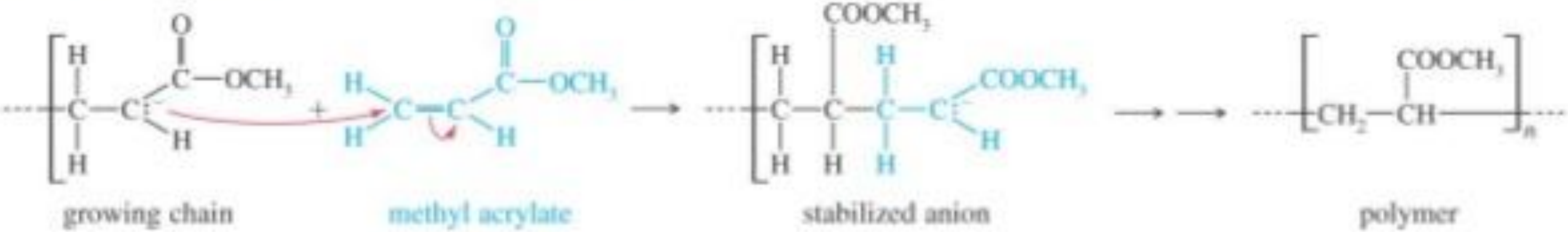


Initiation step: The initiator adds to the monomer to the form an anion.

Propagation step: Another molecule of monomer adds to the chain.

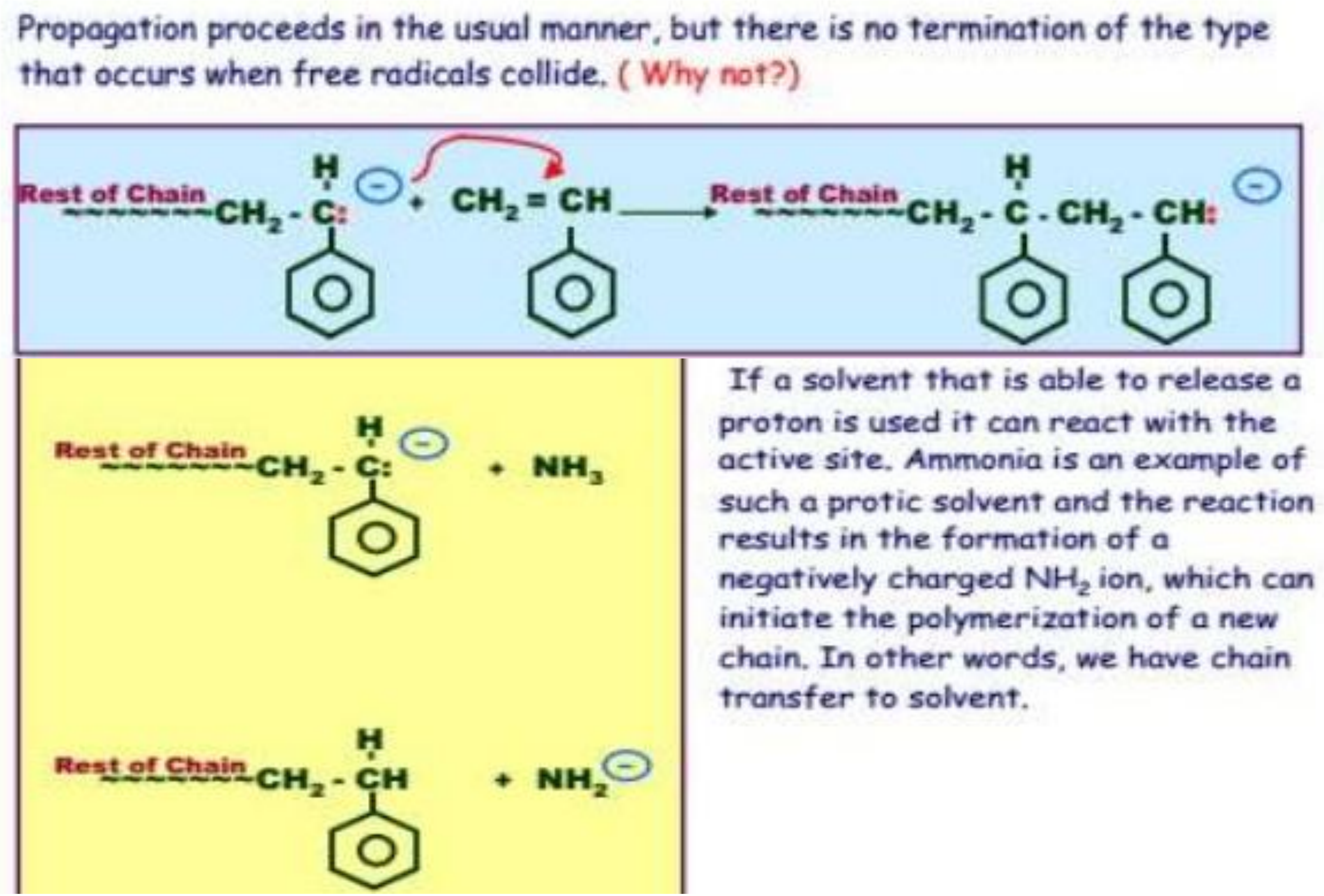
- Alkene must have an electron-withdrawing group like C═O, C≡N, or NO_2.
- The reaction is initiated by a Grignard or organolithium reagent.

Chain-Growth Step in Anionic Polymerization



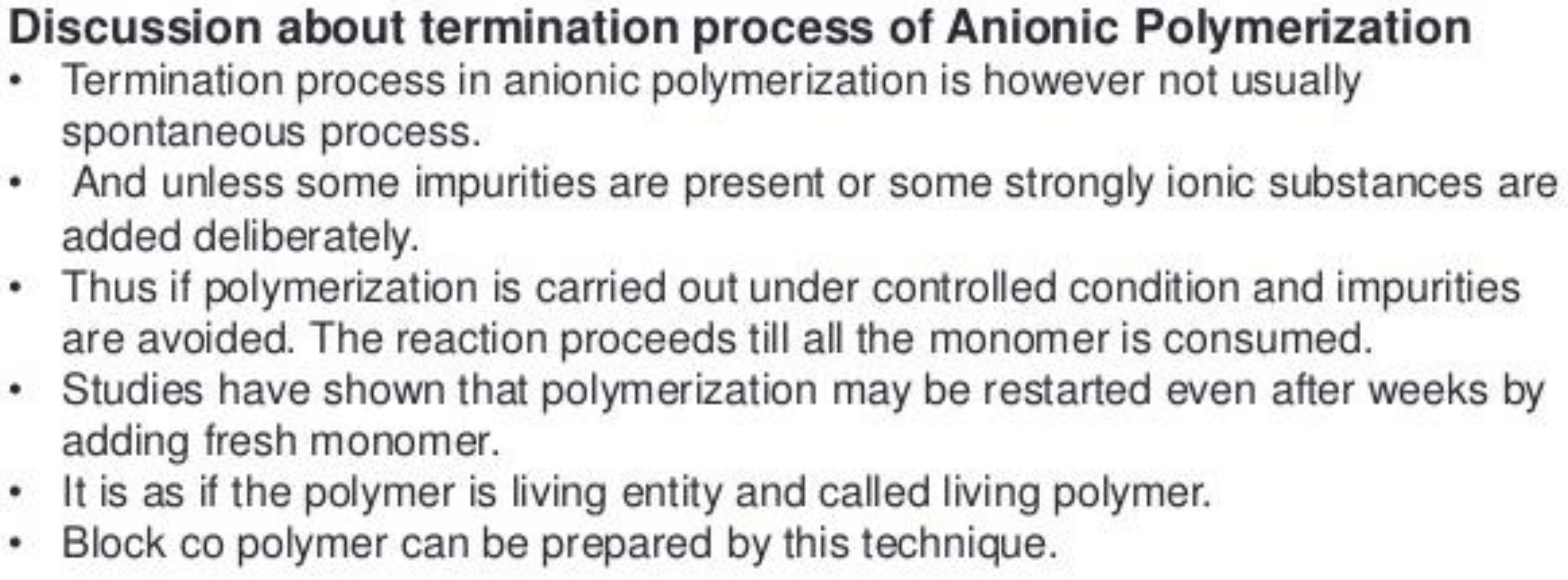
Chain-growth step in anionic polymerization

- Effective anionic polymerization requires a monomer that gives a stabilized carbanion when it reacts with the anionic end of the growing chain.



Propagation proceeds in the usual manner, but there is no termination of the type that occurs when free radicals collide. (Why not?)

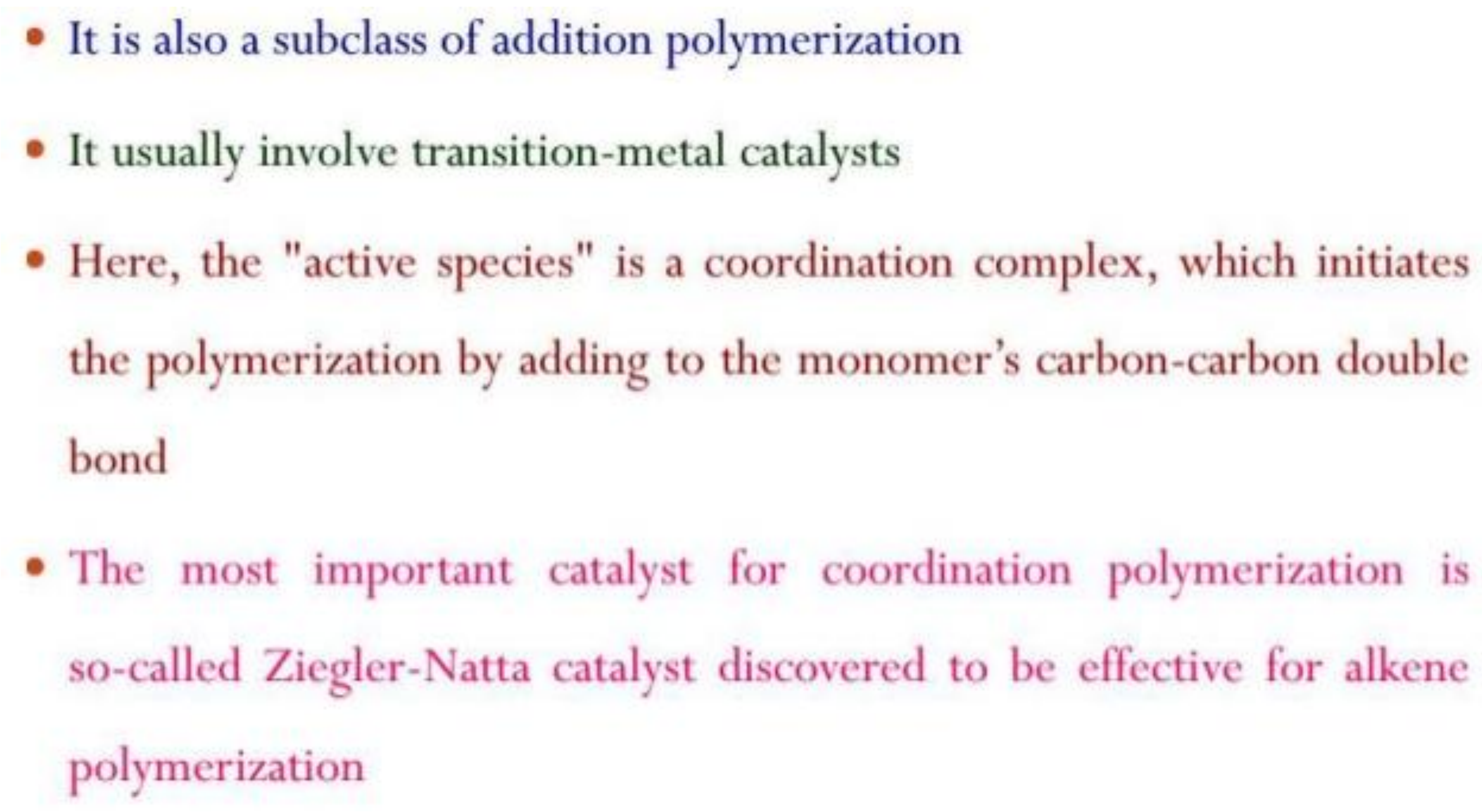
If a solvent that is able to release a proton is used it can react with the active site. Ammonia is an example of such a protic solvent and the reaction results in the formation of a negatively charged NH_2 ion, which can initiate the polymerization of a new chain. In other words, we have chain transfer to solvent.



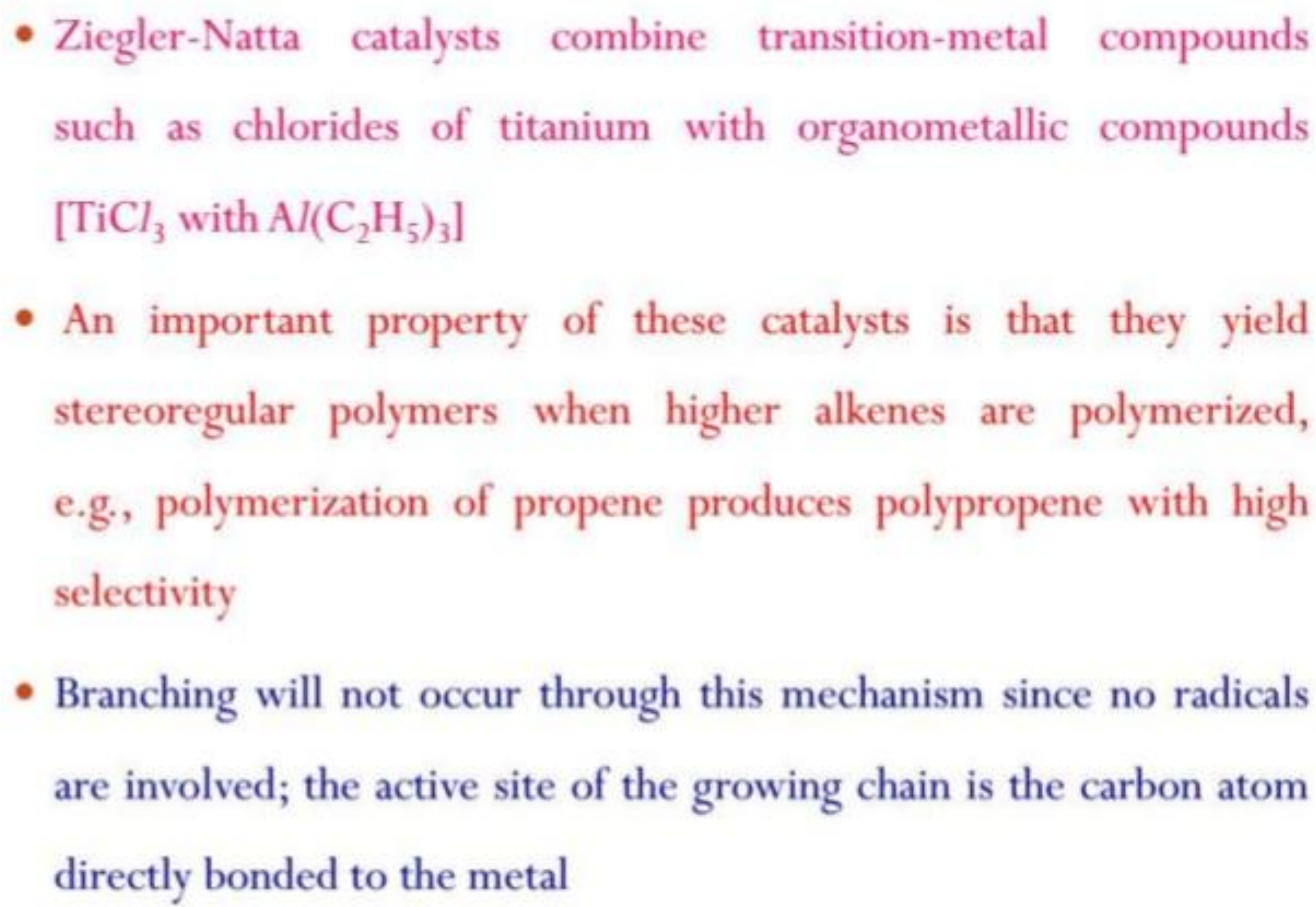
Discussion about termination process of Anionic Polymerization

- Termination process in anionic polymerization is however not usually spontaneous process.
- And unless some impurities are present or some strongly ionic substances are added deliberately.
- Thus if polymerization is carried out under controlled condition and impurities are avoided. The reaction proceeds till all the monomer is consumed.
- Studies have shown that polymerization may be restarted even after weeks by adding fresh monomer.
- It is as if the polymer is living entity and called living polymer.
- Block co polymer can be prepared by this technique.

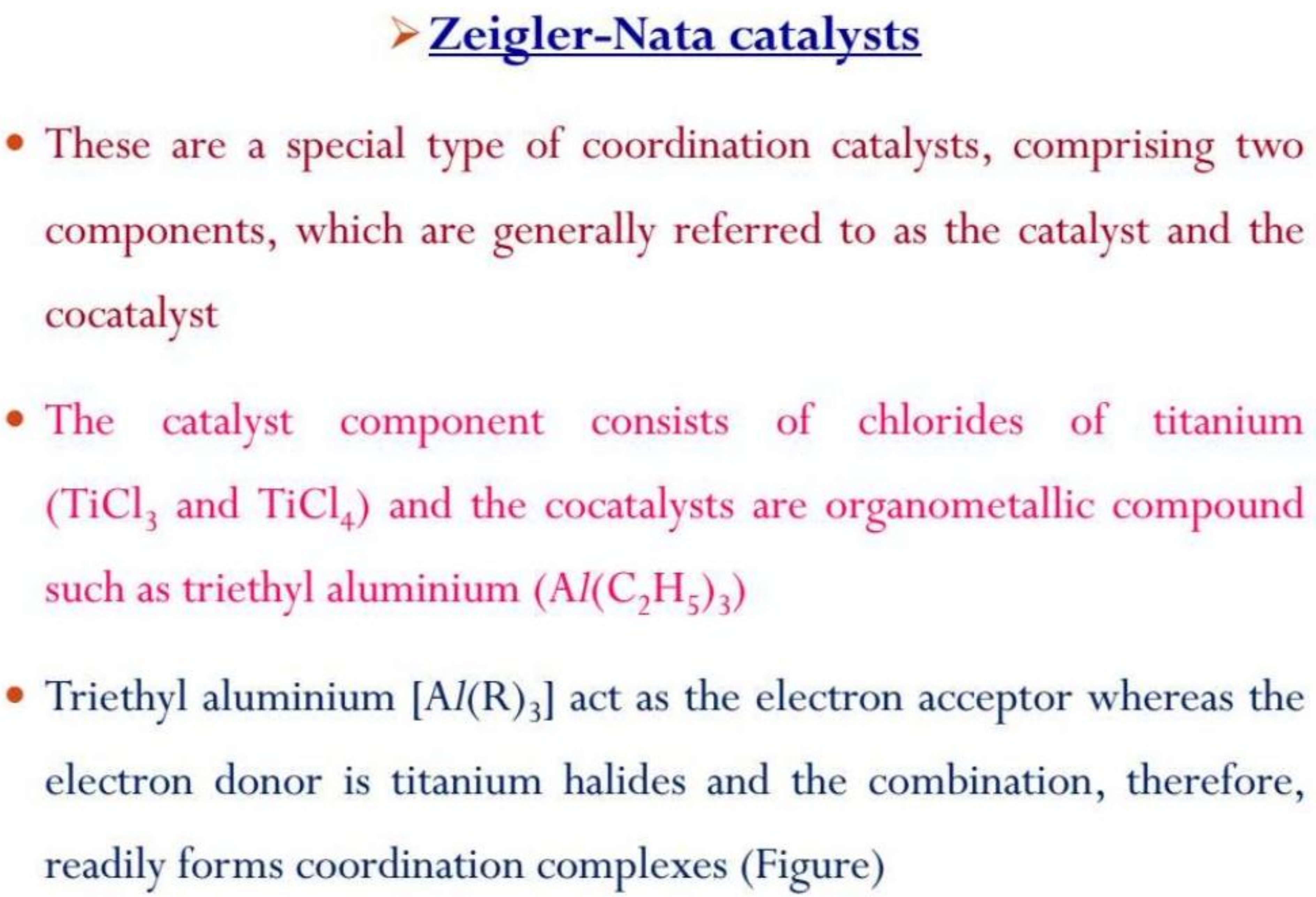
CO ORDINATION POLYMERIZATION



- It is also a subclass of addition polymerization
- It usually involve transition-metal catalysts
- Here, the "active species" is a coordination complex, which initiates the polymerization by adding to the monomer's carbon-carbon double bond
- The most important catalyst for coordination polymerization is so-called Ziegler-Natta catalyst discovered to be effective for alkene polymerization



- Ziegler-Natta catalysts combine transition-metal compounds such as chlorides of titanium with organometallic compounds $[\mathrm{TiC}l_3 \text{ with } \mathrm{A}l(\mathrm{C}_2\mathrm{H}_5)_3]$
- An important property of these catalysts is that they yield stereoregular polymers when higher alkenes are polymerized, e.g., polymerization of propene produces polypropene with high selectivity
- Branching will not occur through this mechanism since no radicals are involved; the active site of the growing chain is the carbon atom directly bonded to the metal



➢ Zeigler-Nata catalysts

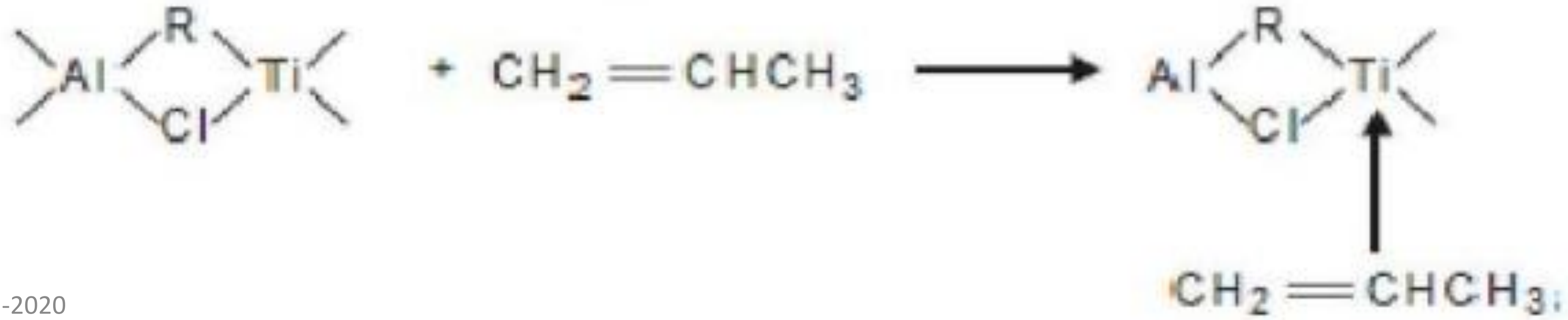
- These are a special type of coordination catalysts, comprising two components, which are generally referred to as the catalyst and the cocatalyst

- The catalyst component consists of chlorides of titanium ($TiCl_3$ and $TiCl_4$) and the cocatalysts are organometallic compound such as triethyl aluminium ($Al(C_2H_5)_3$)

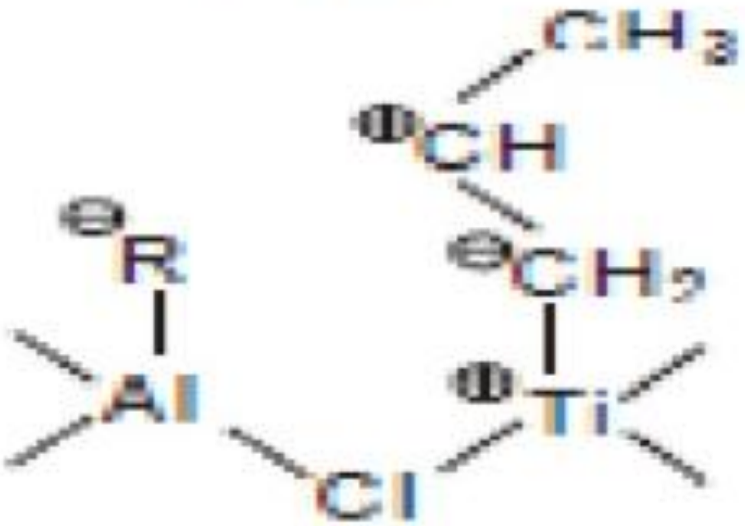
- Triethyl aluminium [$Al(R)_3$] act as the electron acceptor whereas the electron donor is titanium halides and the combination, therefore, readily forms coordination complexes (Figure)

- The complex formed, now acts as the active centre

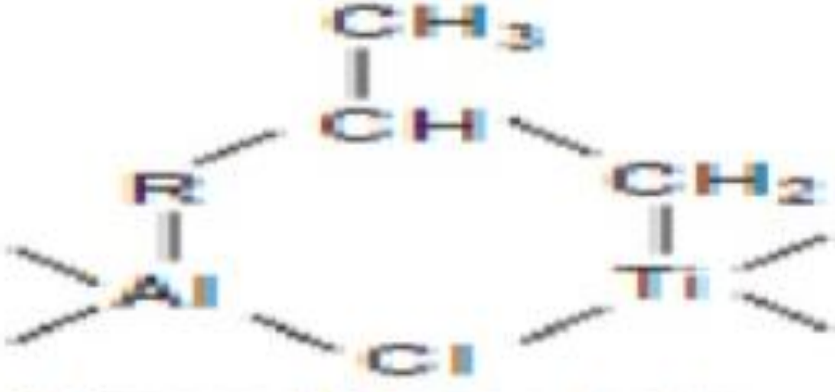
- The monomer is complexed with the metal ion of the active centre in a way that the monomers attached towards the Ti—C bond (C from the alkyl group R) in the active centre, when it forms a π complex with the Ti ion (Figure)



- The bonds between R and Ti opens up producing an electron deficient Ti and a carbanion at R (Fig. 3)

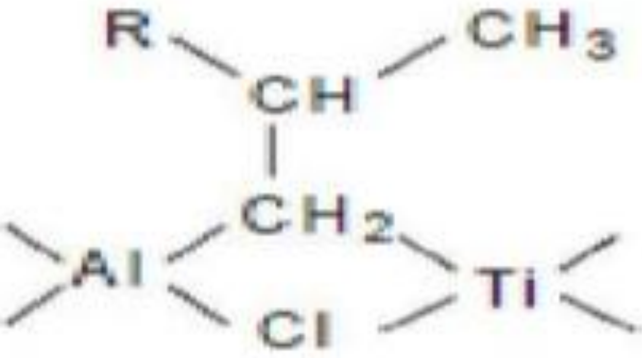


- The Ti ion attracts the π electrons pair or the monomer and forms σ bond (Fig. 4)

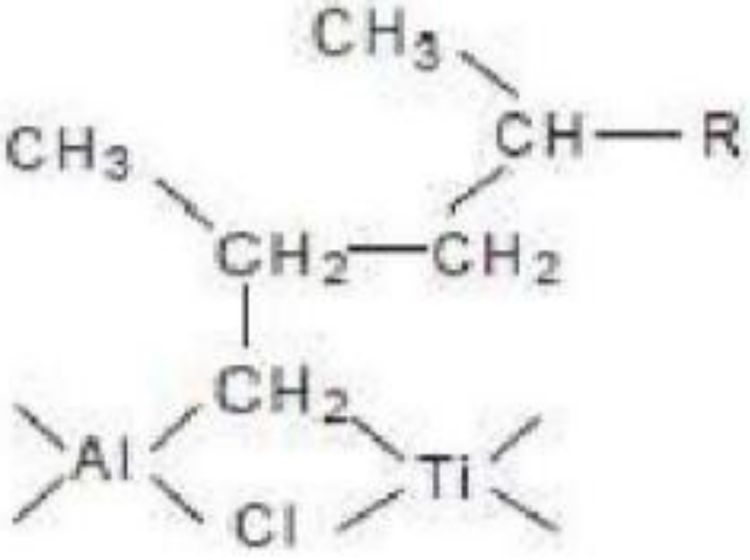


Transition state

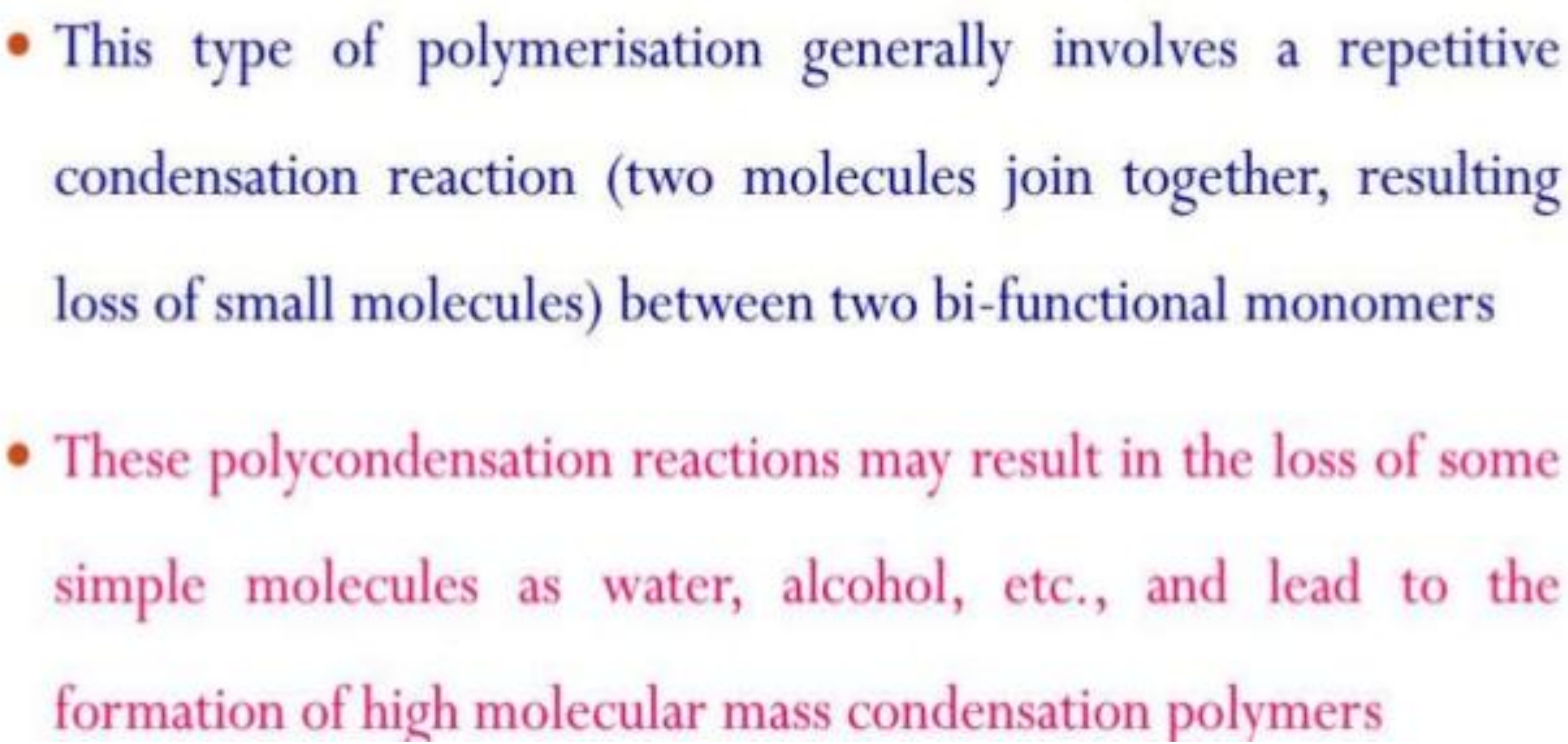
- This transition state now gives rise to the chain growth at the metal carbon bond, regenerating the active centre (Fig. 5)



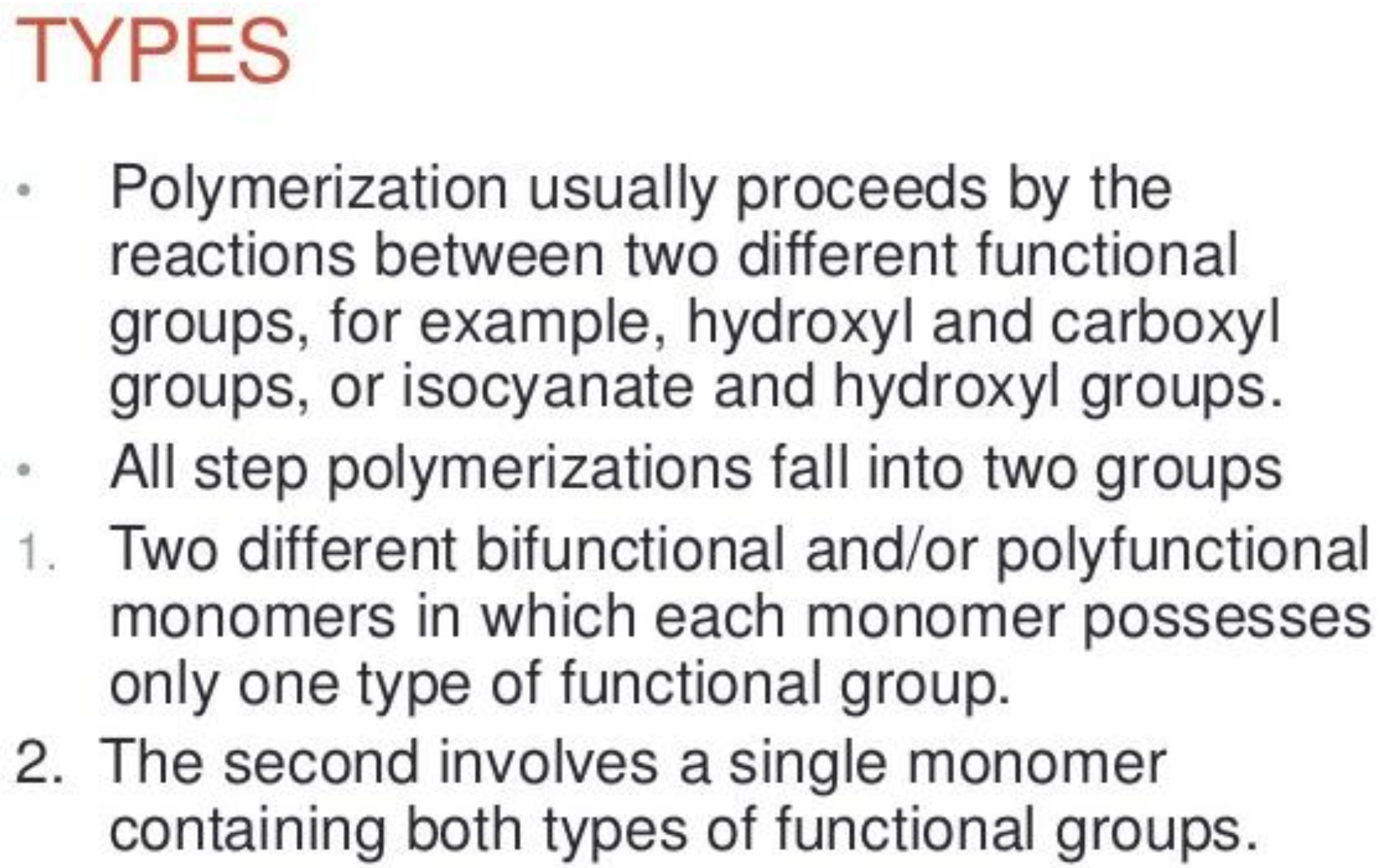
- Repeating the whole sequence, with the addition of second monomer molecule, we will get the structure of the resultant chain growth as shown in Fig. 6



CONDENSATION POLYMERIZATION



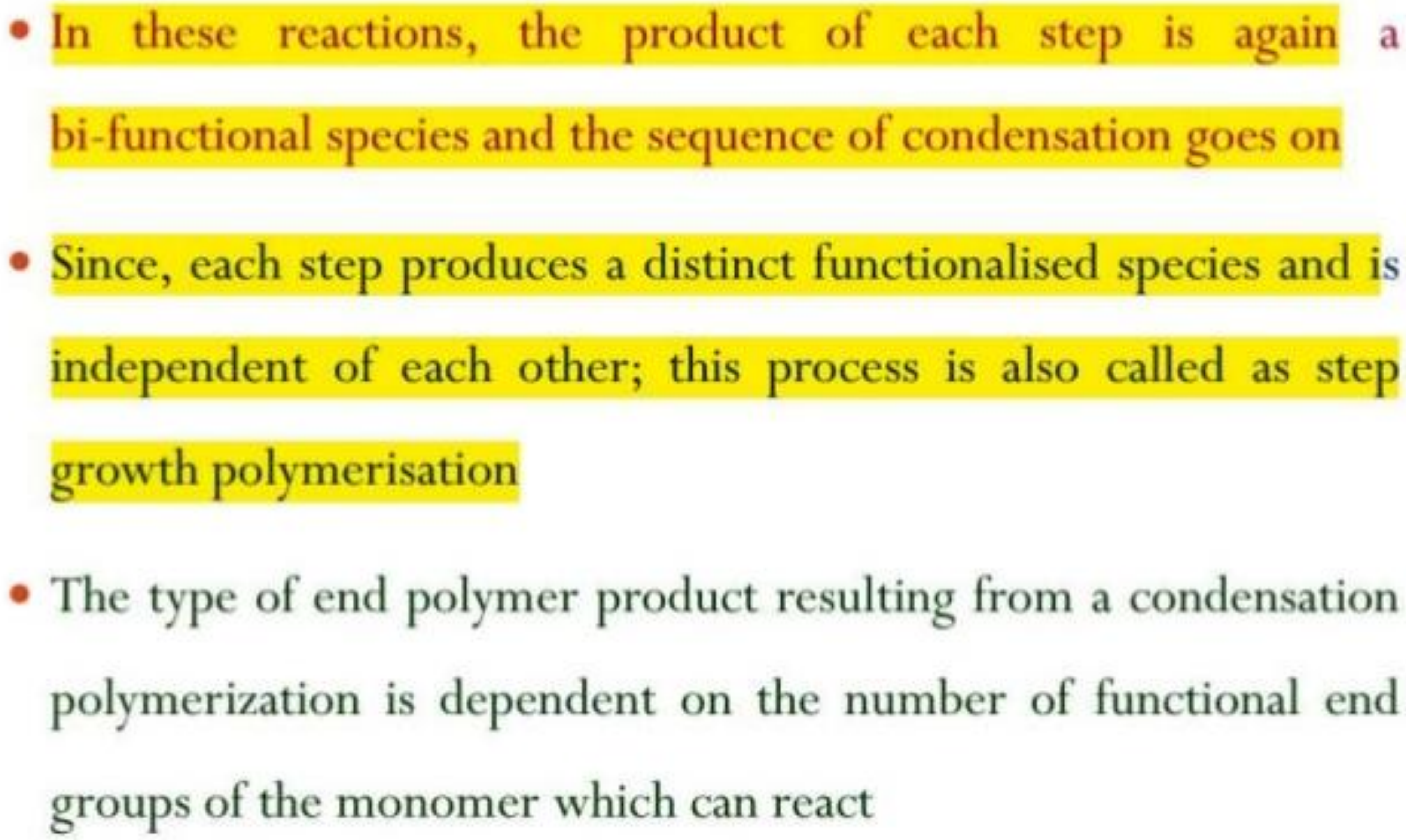
- This type of polymerisation generally involves a repetitive condensation reaction (two molecules join together, resulting loss of small molecules) between two bi-functional monomers
- These polycondensation reactions may result in the loss of some simple molecules as water, alcohol, etc., and lead to the formation of high molecular mass condensation polymers



TYPES

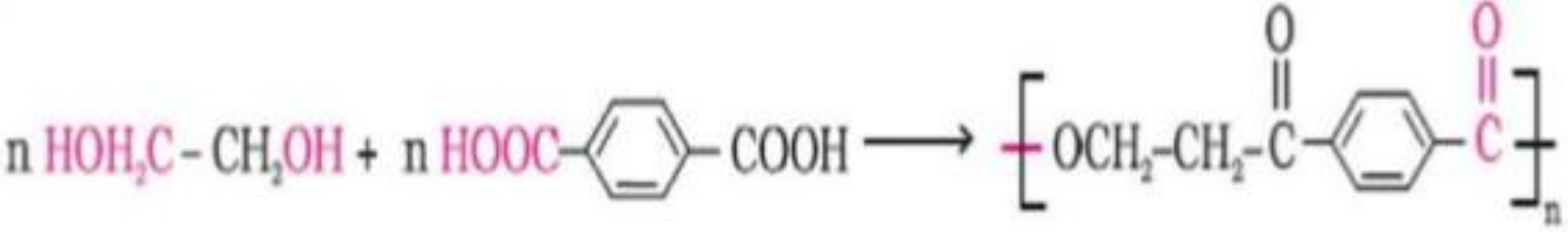
- Polymerization usually proceeds by the reactions between two different functional groups, for example, hydroxyl and carboxyl groups, or isocyanate and hydroxyl groups.
- All step polymerizations fall into two groups

1. Two different bifunctional and/or polyfunctional monomers in which each monomer possesses only one type of functional group.
2. The second involves a single monomer containing both types of functional groups.

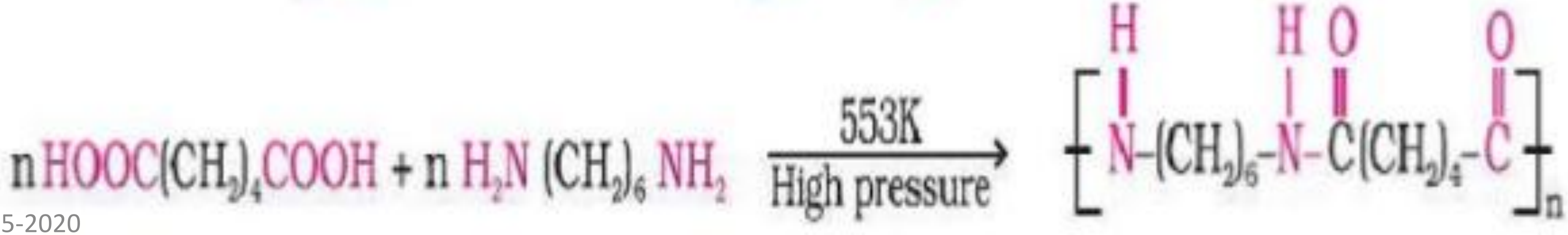


- In these reactions, the product of each step is again a bi-functional species and the sequence of condensation goes on
- Since, each step produces a distinct functionalised species and is independent of each other; this process is also called as step growth polymerisation
- The type of end polymer product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react

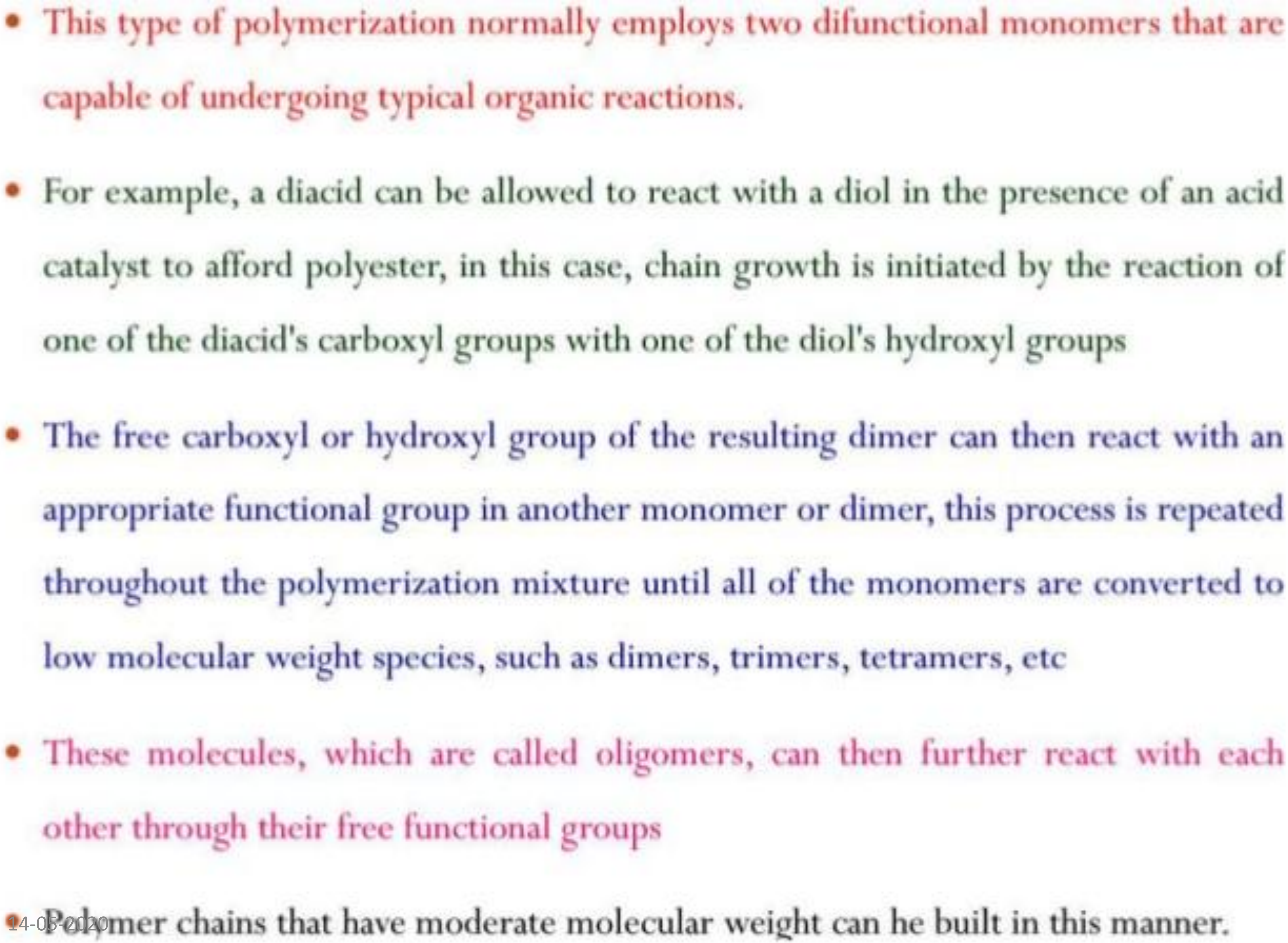
- Monomers with only one reactive group terminate a growing chain, and thus give end products with a lower molecular weight
- Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three dimensional polymers which are cross linked.



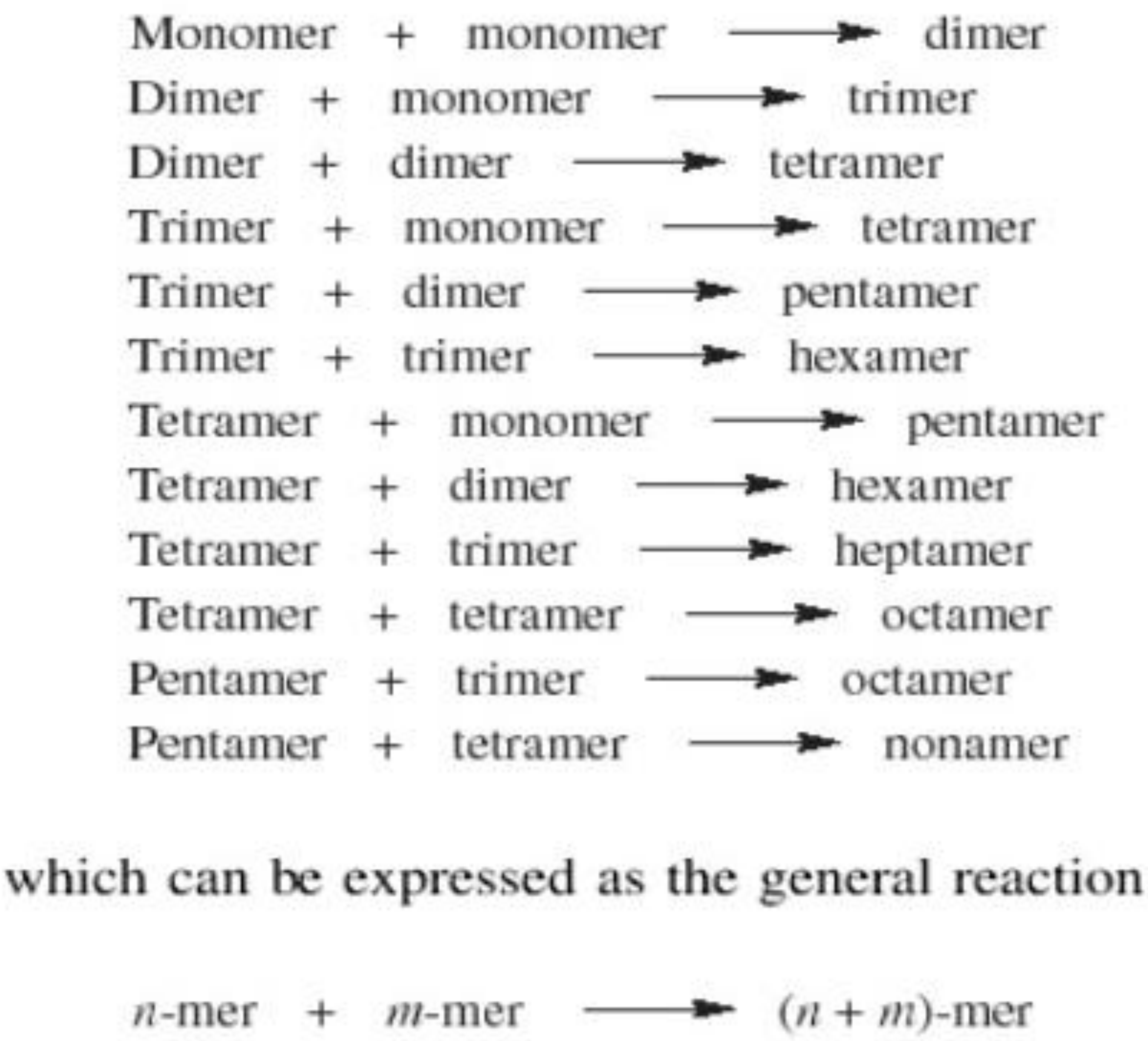
- Polyamide is created through amide linkages between monomers, which involve the functional groups carboxyl and amine (an organic acid and an amine monomer)
- Nylon-6 is an example which can be manufactured by the condensation polymerisation of hexamethylenediamine with adipic acid under high pressure and at high temperature.



$$n\,HOOC(CH_2)_4COOH + n\,H_2N\,(CH_2)_6\,NH_2 \xrightarrow[\text{High pressure}]{553K} \left[\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{C}(CH_2)_4-\overset{O}{C} \right]_n$$



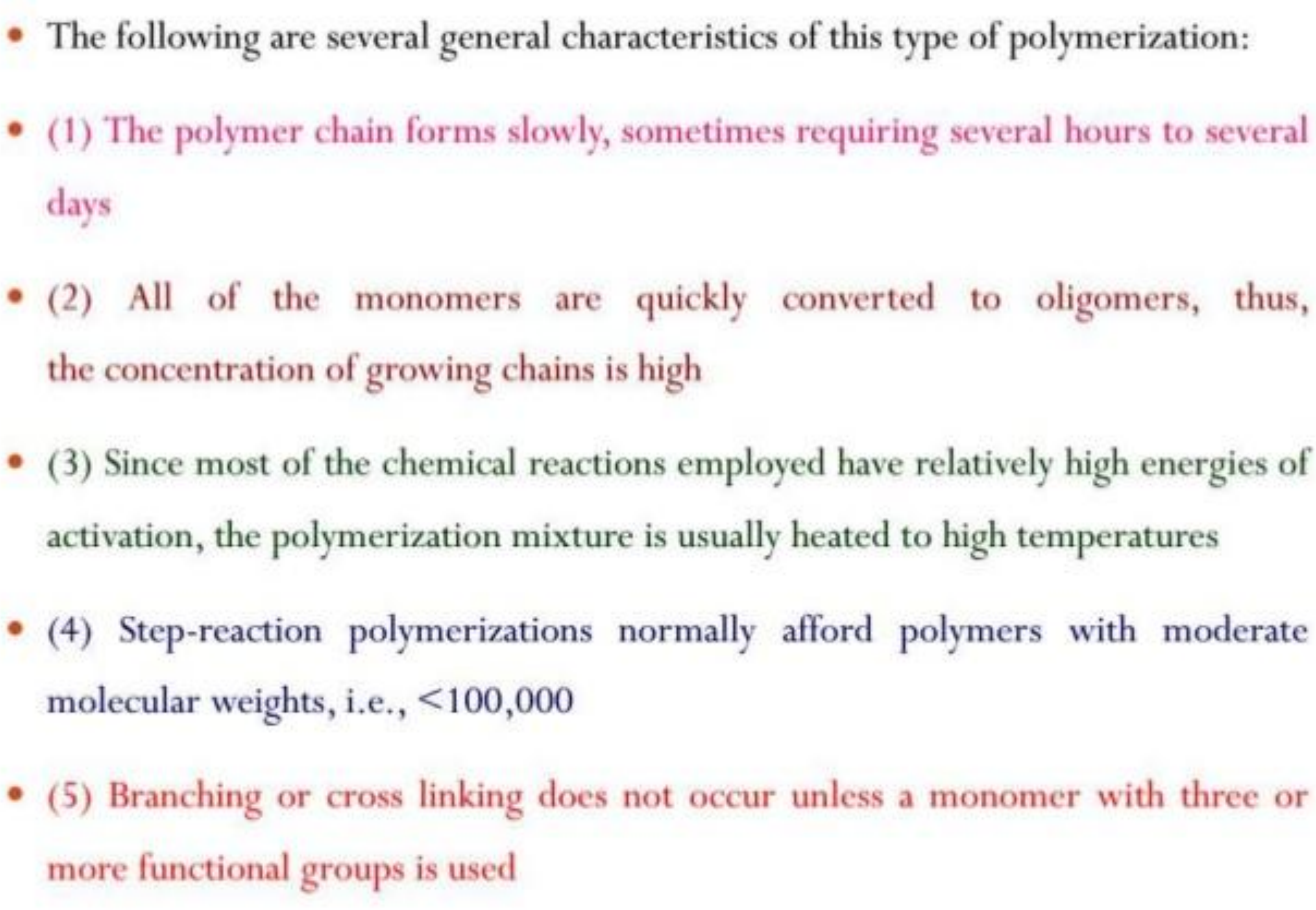
- This type of polymerization normally employs two difunctional monomers that are capable of undergoing typical organic reactions.
- For example, a diacid can be allowed to react with a diol in the presence of an acid catalyst to afford polyester, in this case, chain growth is initiated by the reaction of one of the diacid's carboxyl groups with one of the diol's hydroxyl groups
- The free carboxyl or hydroxyl group of the resulting dimer can then react with an appropriate functional group in another monomer or dimer, this process is repeated throughout the polymerization mixture until all of the monomers are converted to low molecular weight species, such as dimers, trimers, tetramers, etc
- These molecules, which are called oligomers, can then further react with each other through their free functional groups
- Polymer chains that have moderate molecular weight can he built in this manner.



Monomer + monomer ⟶ dimer
Dimer + monomer ⟶ trimer
Dimer + dimer ⟶ tetramer
Trimer + monomer ⟶ tetramer
Trimer + dimer ⟶ pentamer
Trimer + trimer ⟶ hexamer
Tetramer + monomer ⟶ pentamer
Tetramer + dimer ⟶ hexamer
Tetramer + trimer ⟶ heptamer
Tetramer + tetramer ⟶ octamer
Pentamer + trimer ⟶ octamer
Pentamer + tetramer ⟶ nonamer

which can be expressed as the general reaction

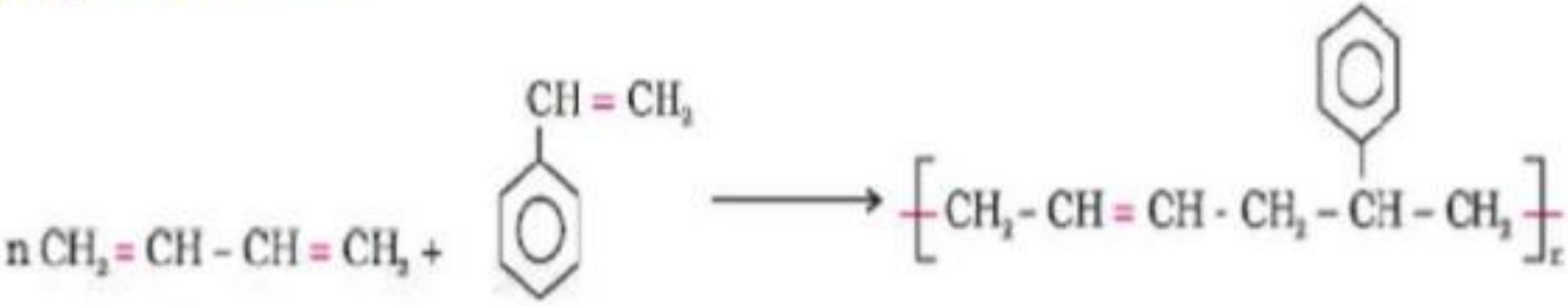
$$n\text{-mer} + m\text{-mer} \longrightarrow (n + m)\text{-mer}$$



- The following are several general characteristics of this type of polymerization:
- (1) The polymer chain forms slowly, sometimes requiring several hours to several days
- (2) All of the monomers are quickly converted to oligomers, thus, the concentration of growing chains is high
- (3) Since most of the chemical reactions employed have relatively high energies of activation, the polymerization mixture is usually heated to high temperatures
- (4) Step-reaction polymerizations normally afford polymers with moderate molecular weights, i.e., <100,000
- (5) Branching or cross linking does not occur unless a monomer with three or more functional groups is used

CO POLYMERIZATION

- It is a polymerisation reaction in which a mixture of more than one monomeric species is allowed to polymerize and form a copolymer
- The copolymer can be made not only by chain growth polymerisation but by step growth polymerisation also
- It contains multiple units of each monomer used in the same polymeric chain



1, 3-Butadiene Styrene Butadiene - styrene copolymer

EXAMPLES

- The synthesis of polyamides illustrates both groups of polymerization reactions. Thus polyamides can be obtained from the reaction of diamines with diacids

$$n\mathrm{H_2N{-}R{-}NH_2} \;+\; n\mathrm{HO_2C{-}R'{-}CO_2H} \longrightarrow$$
$$\mathrm{H{-}\!\left(NH{-}R{-}NHCO{-}R'{-}CO\right)_{\mathit{n}}\!OH} \;+\; (2n-1)\mathrm{H_2O}$$

- or from the reaction of amino acids with themselves:

$$n\mathrm{H_2N{-}R{-}CO_2H} \longrightarrow \mathrm{H{-}\!\left(NH{-}R{-}CO\right)_{\mathit{n}}\!OH} \;+\; (n-1)\mathrm{H_2O}$$

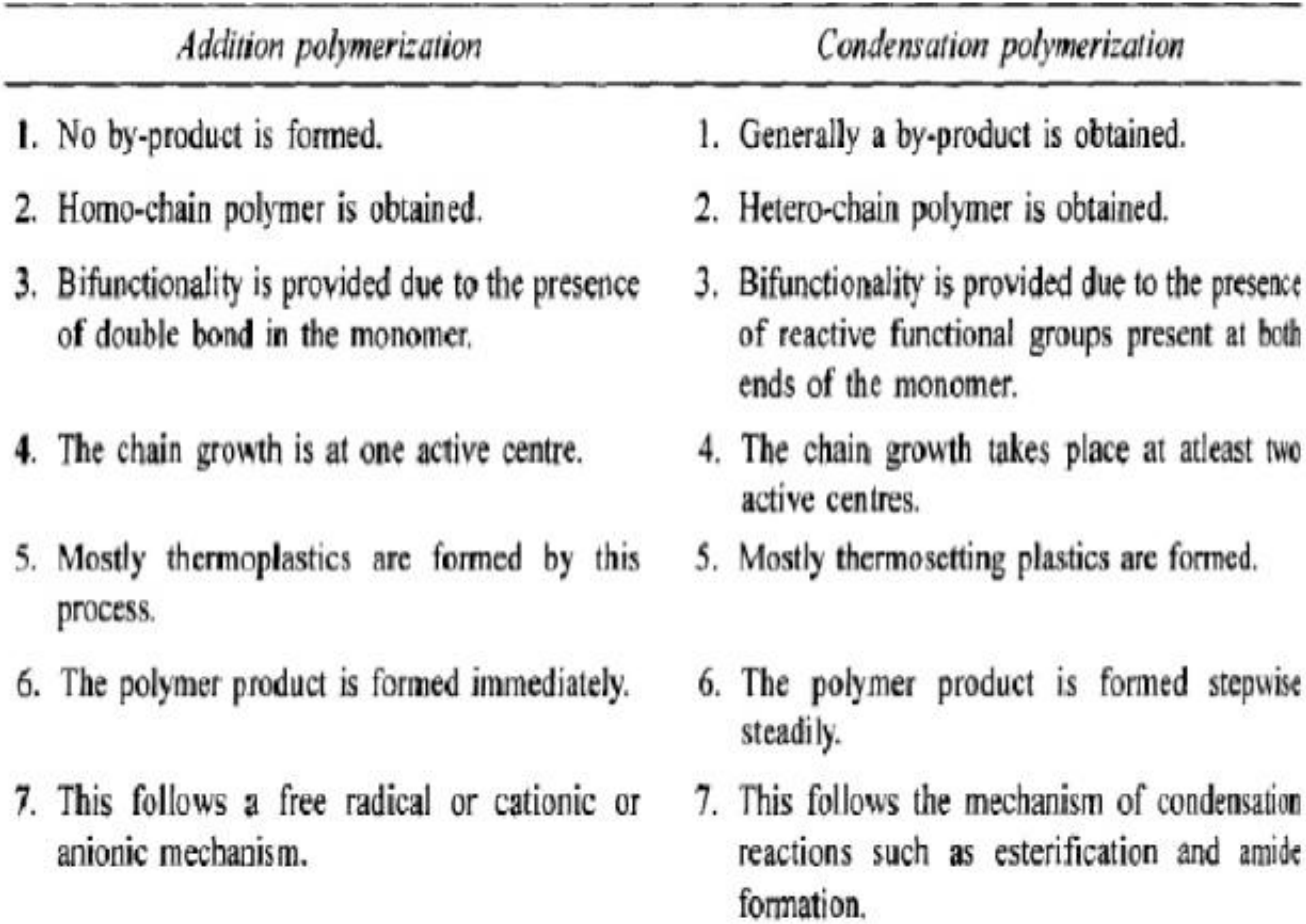
GENERAL DESCRIPTION

- The two groups of reactions can be represented in a general manner by the equations

$$nA{-}A + nB{-}B \longrightarrow \left(A{-}AB{-}B \right)_n$$

$$nA{-}B \longrightarrow \left(A{-}B \right)_n$$

- where A and B are the two different types of functional groups.



Addition polymerization	*Condensation polymerization*
1. No by-product is formed.	1. Generally a by-product is obtained.
2. Homo-chain polymer is obtained.	2. Hetero-chain polymer is obtained.
3. Bifunctionality is provided due to the presence of double bond in the monomer.	3. Bifunctionality is provided due to the presence of reactive functional groups present at both ends of the monomer.
4. The chain growth is at one active centre.	4. The chain growth takes place at atleast two active centres.
5. Mostly thermoplastics are formed by this process.	5. Mostly thermosetting plastics are formed.
6. The polymer product is formed immediately.	6. The polymer product is formed stepwise steadily.
7. This follows a free radical or cationic or anionic mechanism.	7. This follows the mechanism of condensation reactions such as esterification and amide formation.