

Polymers

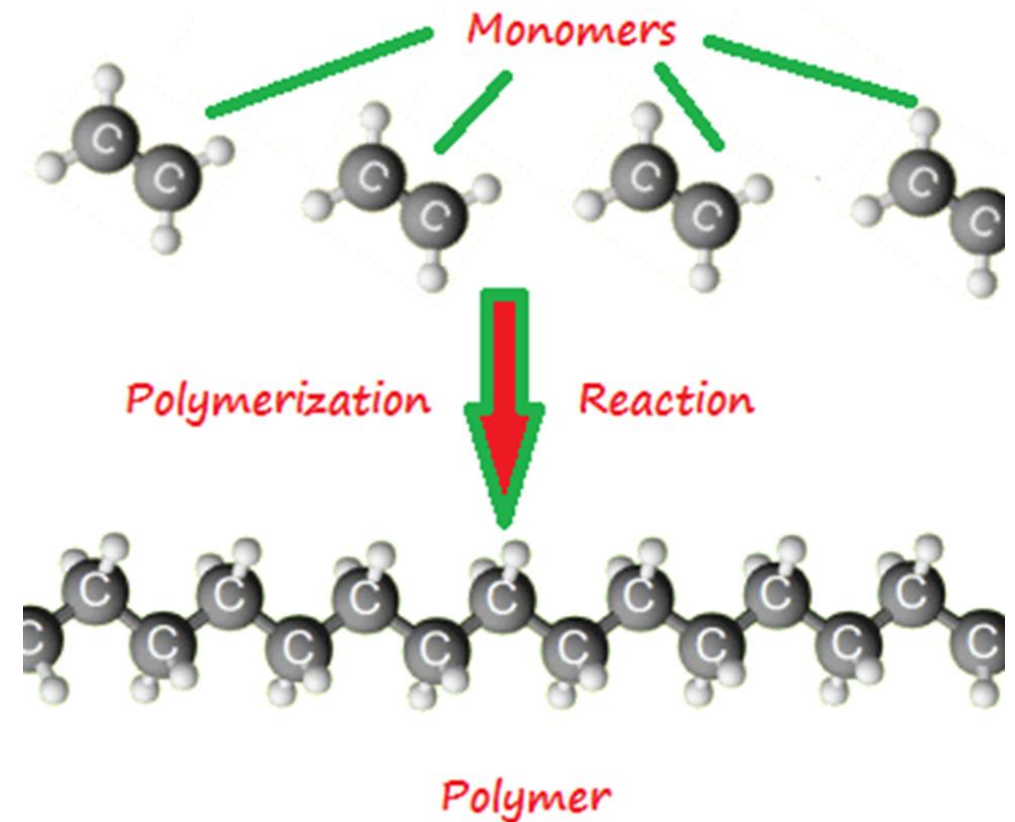
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Definitions

Polymer:

It is a high molecular weight molecule that is composed of many repeating units. (poly = many, mer = unit).



Definitions

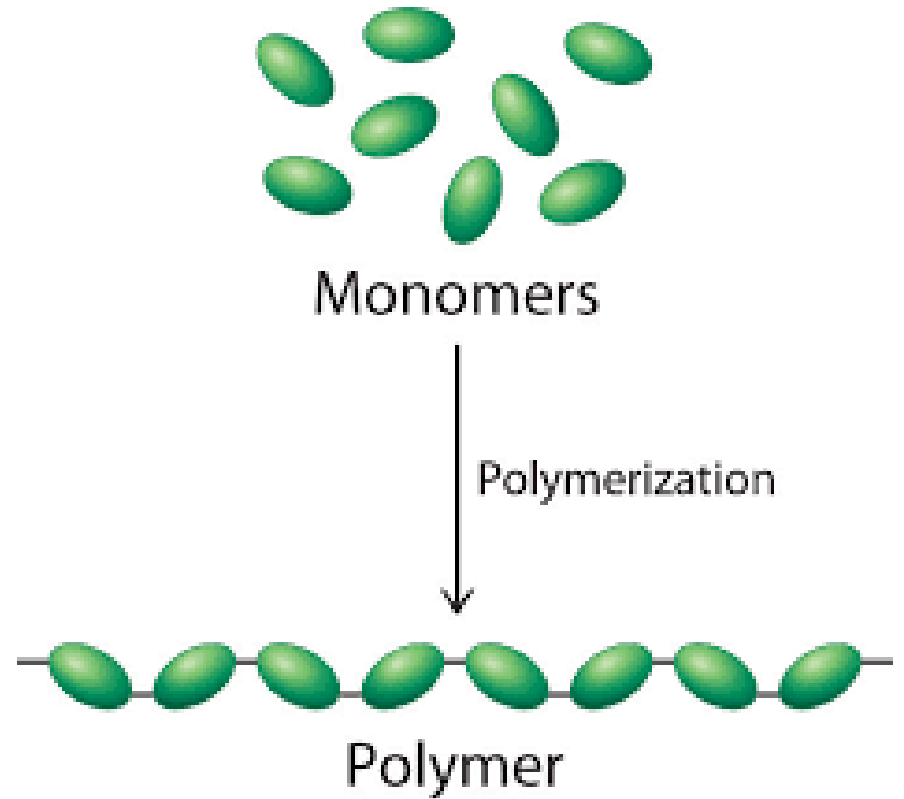
Monomer:

It is the smallest repeated building unit of the polymer chain. (mono = single).

Definitions

Polymerization reaction:

It is the reaction by which the monomers form the polymeric chain.

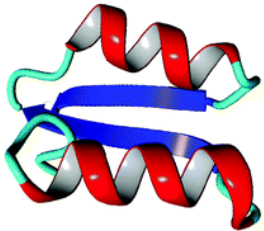
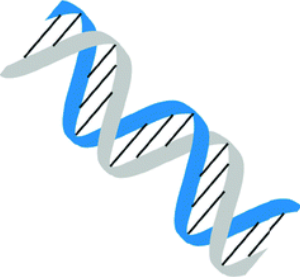

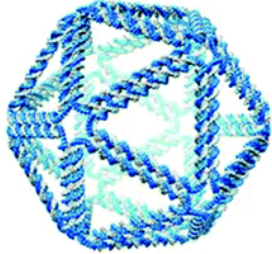
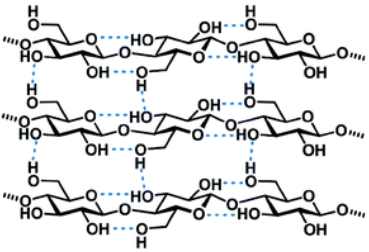


Classification of polymers:

1. According to origin:

a) Natural Polymers:

Synthesized by living cells. eg:
proteins, starch and
polysaccharides (**agar** and
alginate).

Polypeptides	Polynucleotides	Polysaccharides
		<p data-bbox="2277 588 2333 676">?</p> <ul data-bbox="2135 722 2474 833" style="list-style-type: none"><input type="checkbox"/> Lack of pure material<input type="checkbox"/> Difficult synthesis<input type="checkbox"/> Flexibility of the system<input type="checkbox"/> Branched structures
		

Classification of polymers:

1. According to origin:

b) Synthetic polymers:

Synthesized by chemical reactions inside the laboratory. e.g: Acrylic resin.

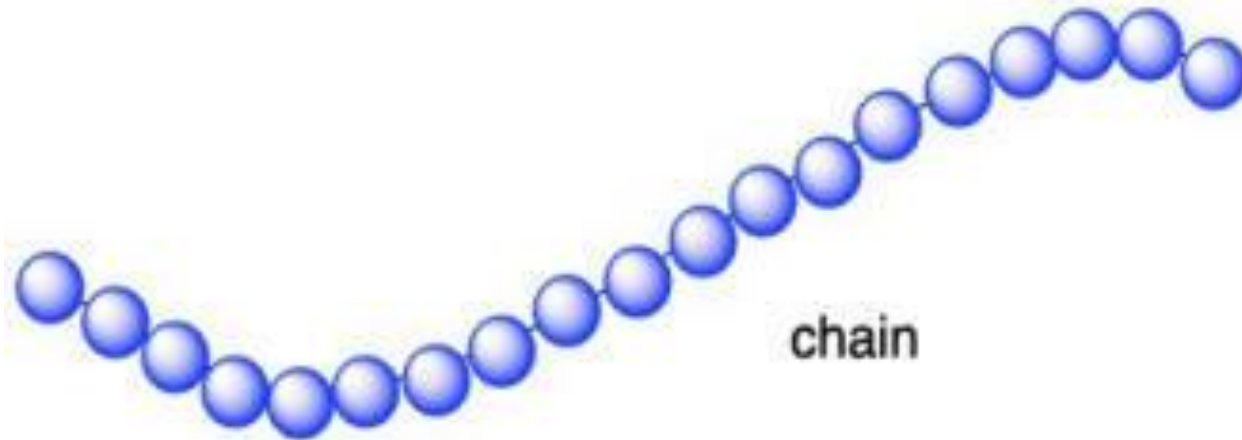


Classification of polymers:

2. According to arrangement in space (spatial configuration):

a) Linear Polymers:

The polymer molecule forms a thread without any branches.

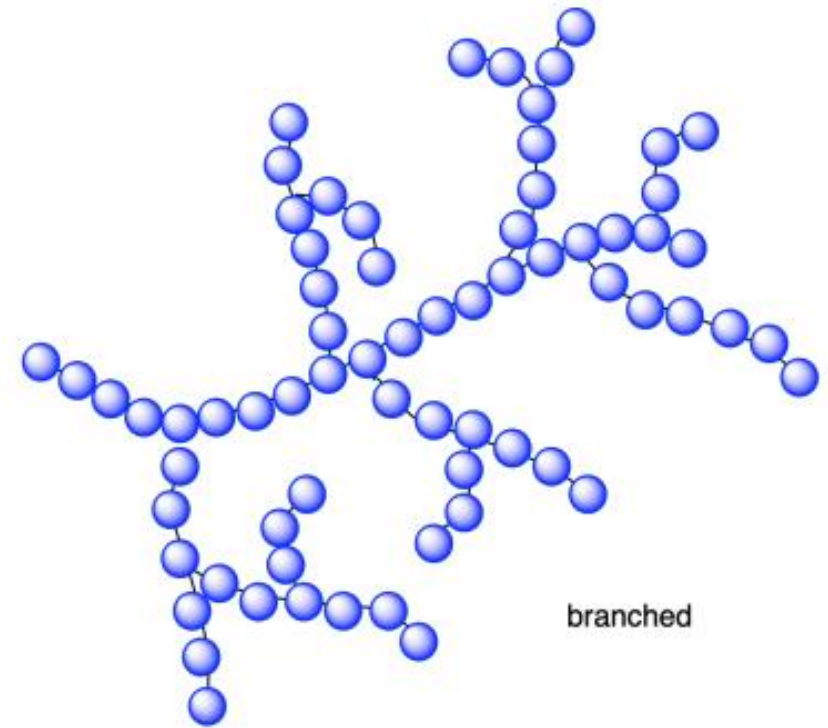


Classification of polymers:

2. According to arrangement in space (spatial configuration):

b) Branched Polymers:

In the polymer molecule, a shorter side chains are attached to the main backbone chain

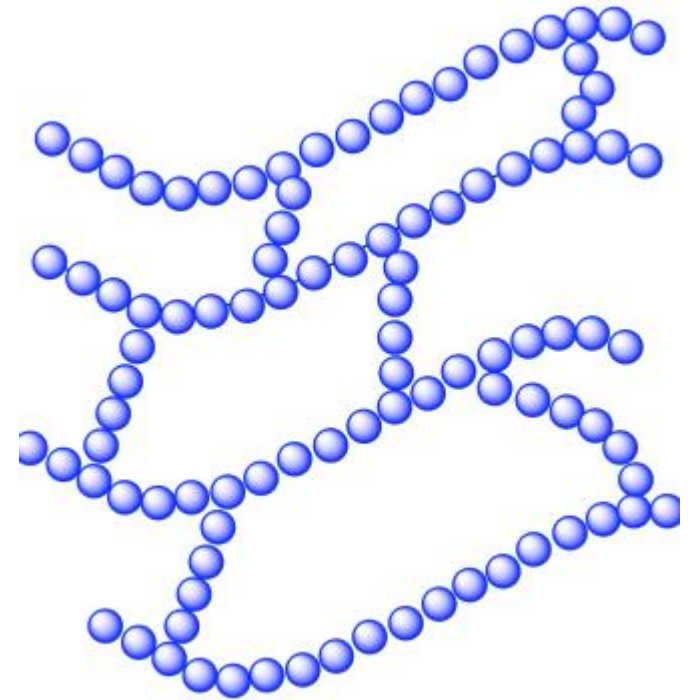
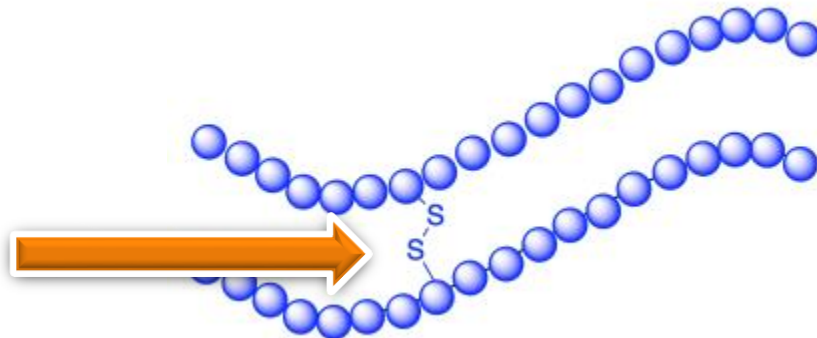


Classification of polymers:

2. According to arrangement in space (spatial configuration):

c) Cross-linked Polymers:

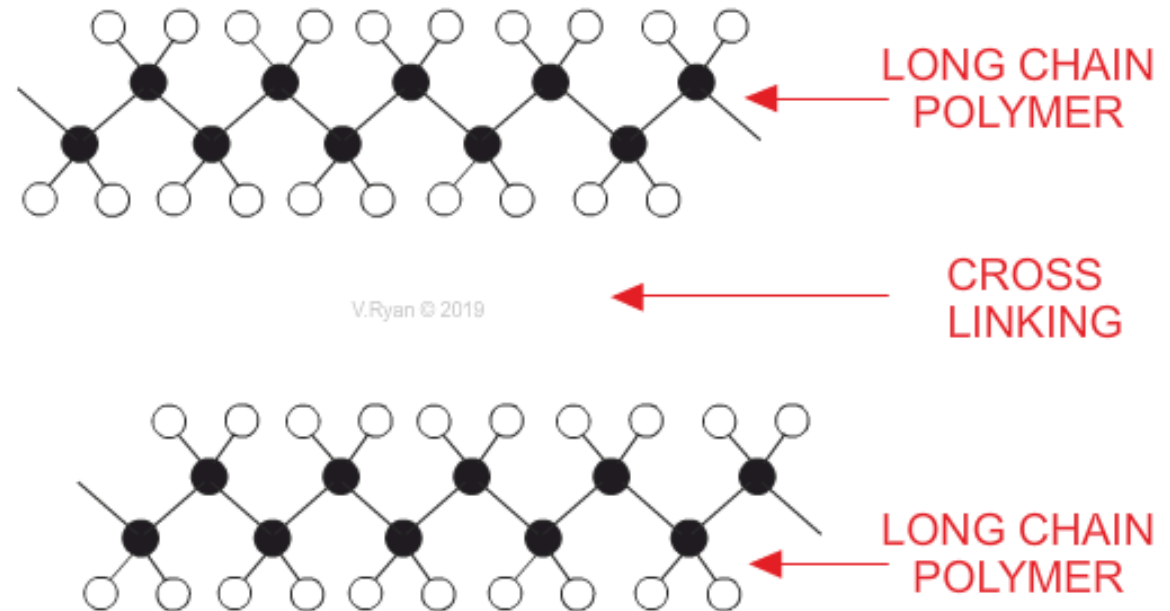
The main polymer chains are bonded by covalent bond



Classification of polymers:

2. According to arrangement in space (spatial configuration):

c) Cross-linked Polymers:



Classification of polymers:

3. According to Thermal behavior:

a) Thermoplastic Polymers.



b) Thermoset polymers.



Classification of polymers:

Thermoplastic polymers	Thermoset polymers
Linear Polymers	Cross-linked Polymers
Chains bonded by secondary bond and entanglement of chains	Chains bonded by Primary bond
Reversible reaction	Irreversible reaction

Classification of polymers:

Thermoplastic polymers	Thermoset polymers
Heat → softens the polymer then harden by cooling	Heat → decomposes (burn) the polymer
Molded by heat and pressure → temporary destroy secondary bond	Molded by heat and pressure during initial stages → forming primary bond

Classification of polymers:

Thermoplastic polymers	Thermoset polymers
Final product has the same chemical composition	Final Product is chemically different than original substances
Show Glass Transition Temperature (T_g)	Not show Glass Transition Temperature

Classification of polymers:

4. According to Mechanical Properties:

a) Elastomers (elastic Polymers).

They have wide range of elastic deformation and low modulus of elasticity.

e.g: rubber base impression materials.



Classification of polymers:

4. According to Mechanical Properties:

b) Plastic Polymers.

They have moderate range of elastic deformation and moderate modulus of elasticity.

e.g: Acrylic resin.

Classification of polymers:

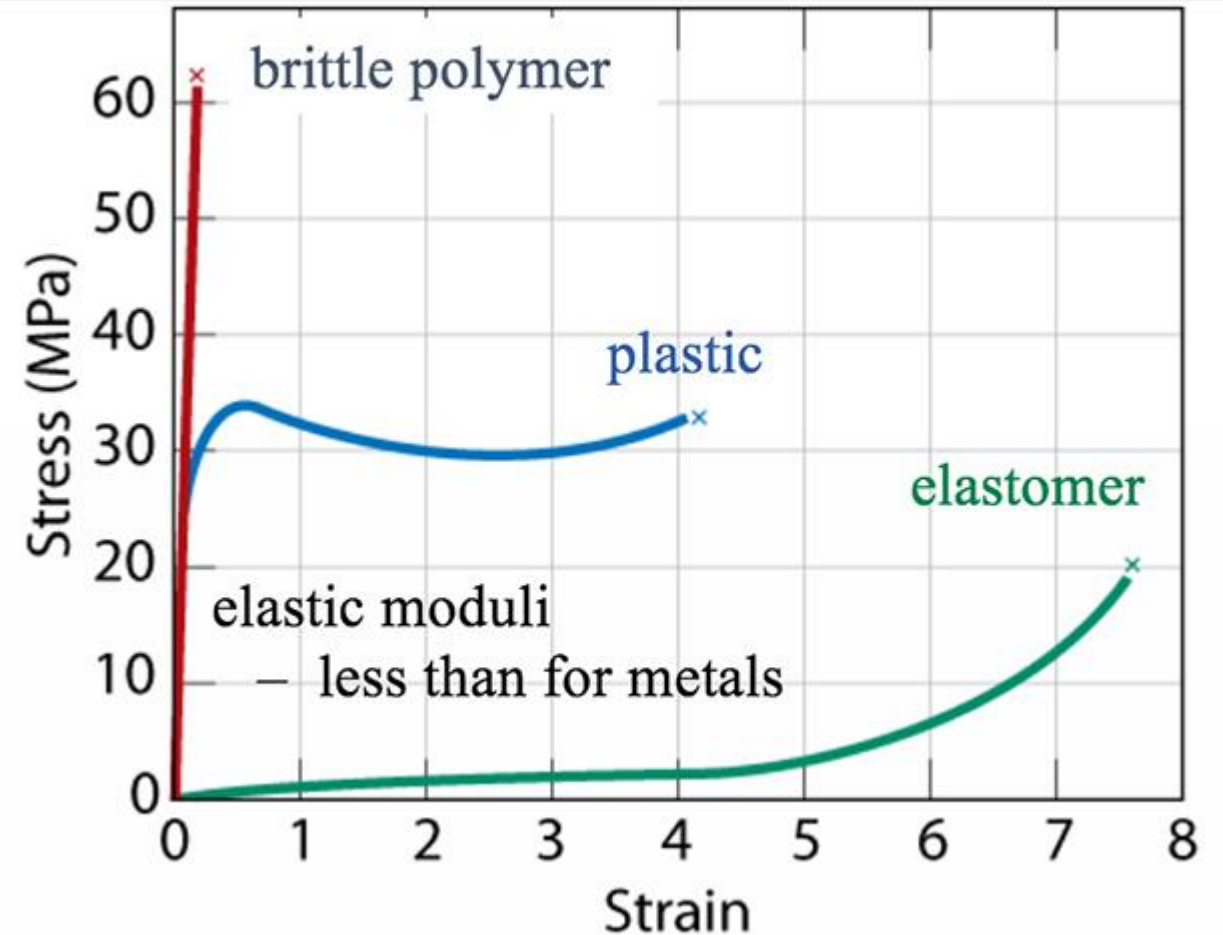
4. According to Mechanical Properties:

c) Brittle Polymers.

They have small range of elastic deformation and high modulus of elasticity.

Classification of polymers:

4. According to Mechanical Properties Stress-strain curve for polymers

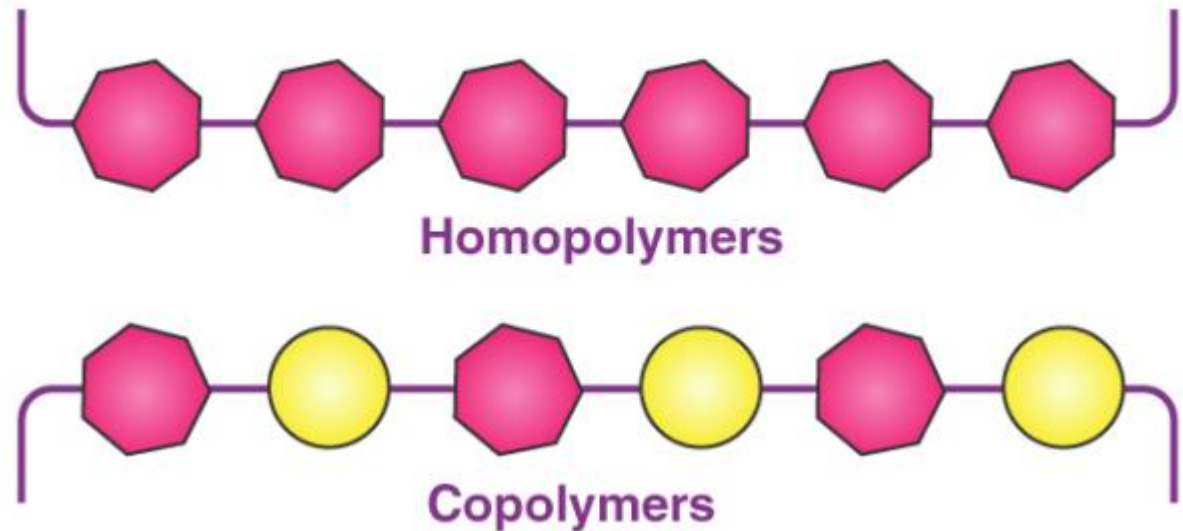


Classification of polymers:

5. According to chemical composition of monomers:

a) Homo-Polymers.

It is a polymer consists of single type of monomers



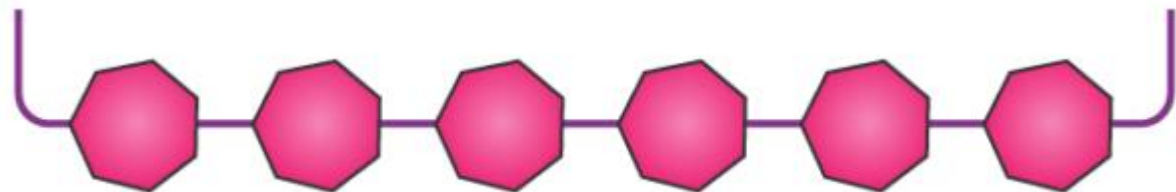
Classification of polymers:

5. According to chemical composition of monomers:

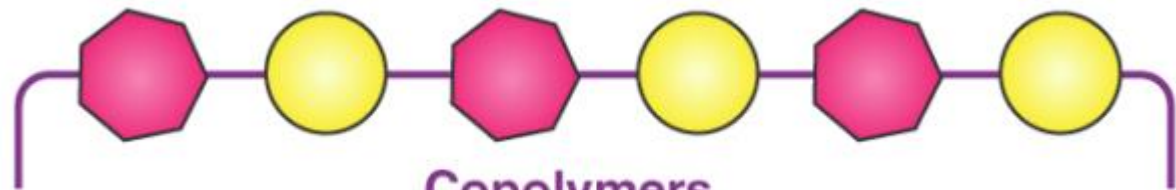
b) Co-Polymers.

It is a polymer consists of two or more different types of monomers.

They could be:



Homopolymers



Copolymers

Alternating



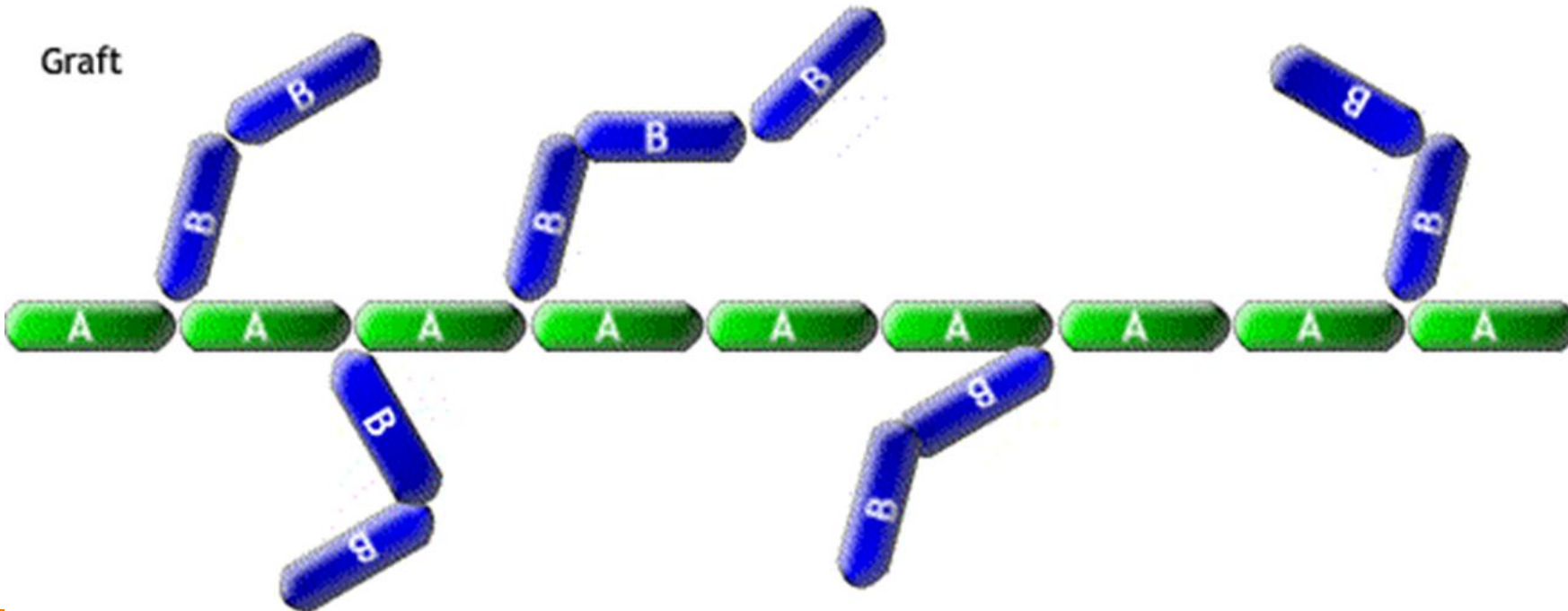
Block



Random



Graft



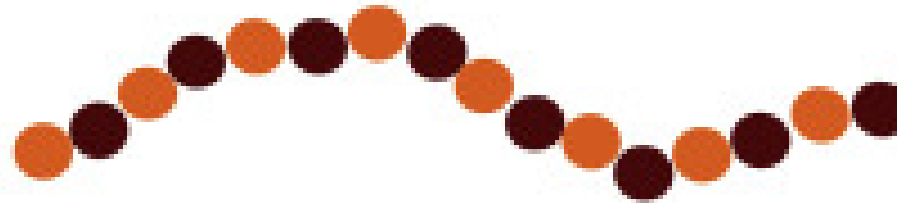
Classification of polymers:

5. According to chemical composition of monomers:

b) Co-Polymers:

1) Alternating copolymers:

Different monomers are arranged regularly in an alternative pattern.



Alternating Copolymer

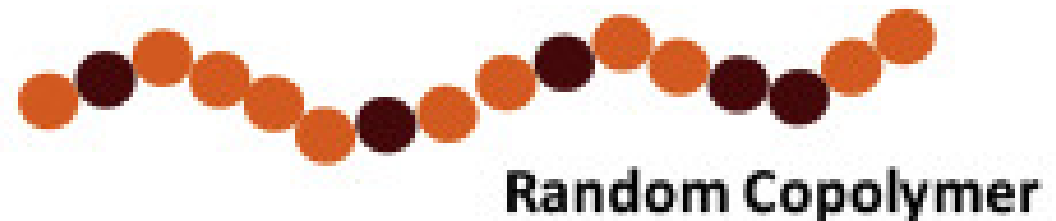
Classification of polymers:

5. According to chemical composition of monomers:

b) Co-Polymers:

2) Random copolymers:

Different monomers are arranged randomly.



Classification of polymers:

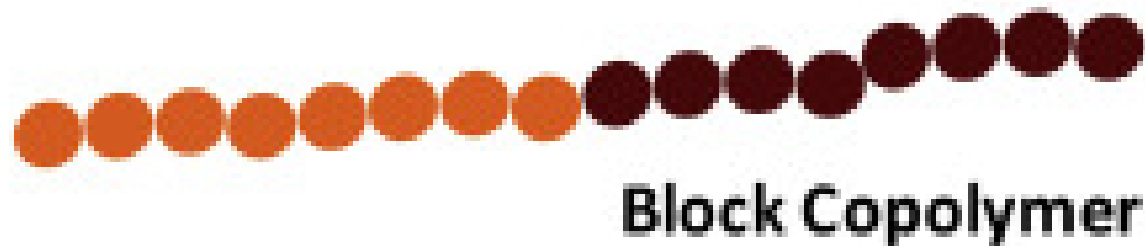
5. According to chemical composition of monomers:

b) Co-Polymers:

3) Block copolymers:

Each monomer forms a cluster.

The clusters are arranged alternatively.



Classification of polymers:

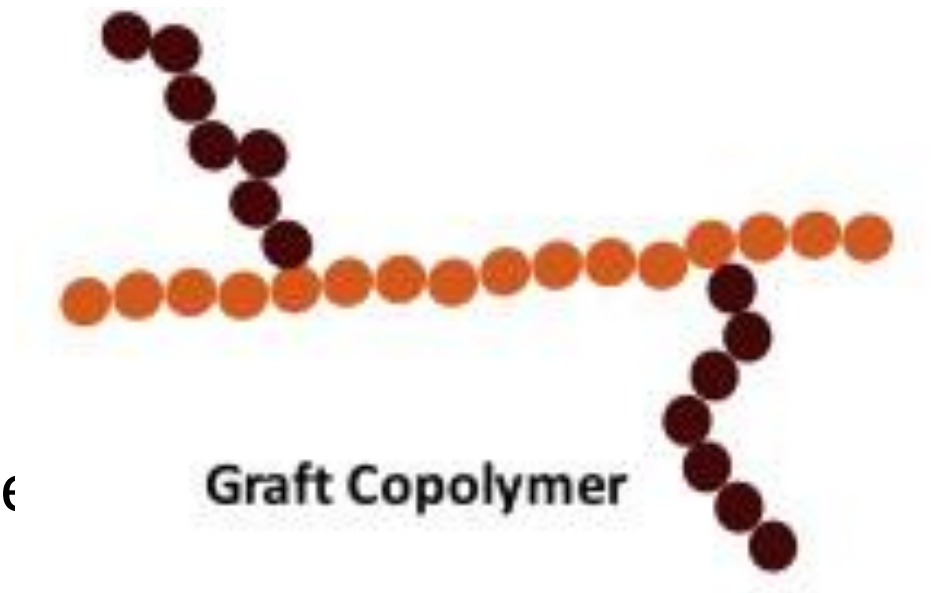
5. According to chemical composition of monomers:

b) Co-Polymers:

4) Graft copolymers:

One polymer forms a backbone.

The other monomer is attached as side chains to the backbone.



Classification of polymers:

6. **According to Polymerization Reaction:**
 - a) Condensation Polymerization Reaction.
 - b) Addition Polymerization Reaction.
 - i. Free radical
 - ii. Ring opening

Classification of polymers:

6. According to Polymerization Reaction:

a) Condensation Polymerization Reaction.

The monomers react together to form the polymer chains with elimination of a small molecule called by-product. eg: water, gas, etc.

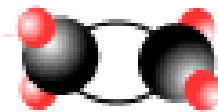
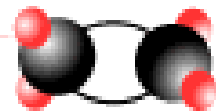


Classification of polymers:

6. According to Polymerization Reaction:

b) Addition Polymerization Reaction.

The monomers react together to form the polymer chains without elimination of a by-product.



Classification of polymers:

6. According to Polymerization Reaction:

b) Addition Polymerization Reaction.

The Addition polymerization reaction gives **more accurate** polymers than the condensation type as there is no elimination of by-products.

Stages of Free Radical Addition Polymerization Reaction

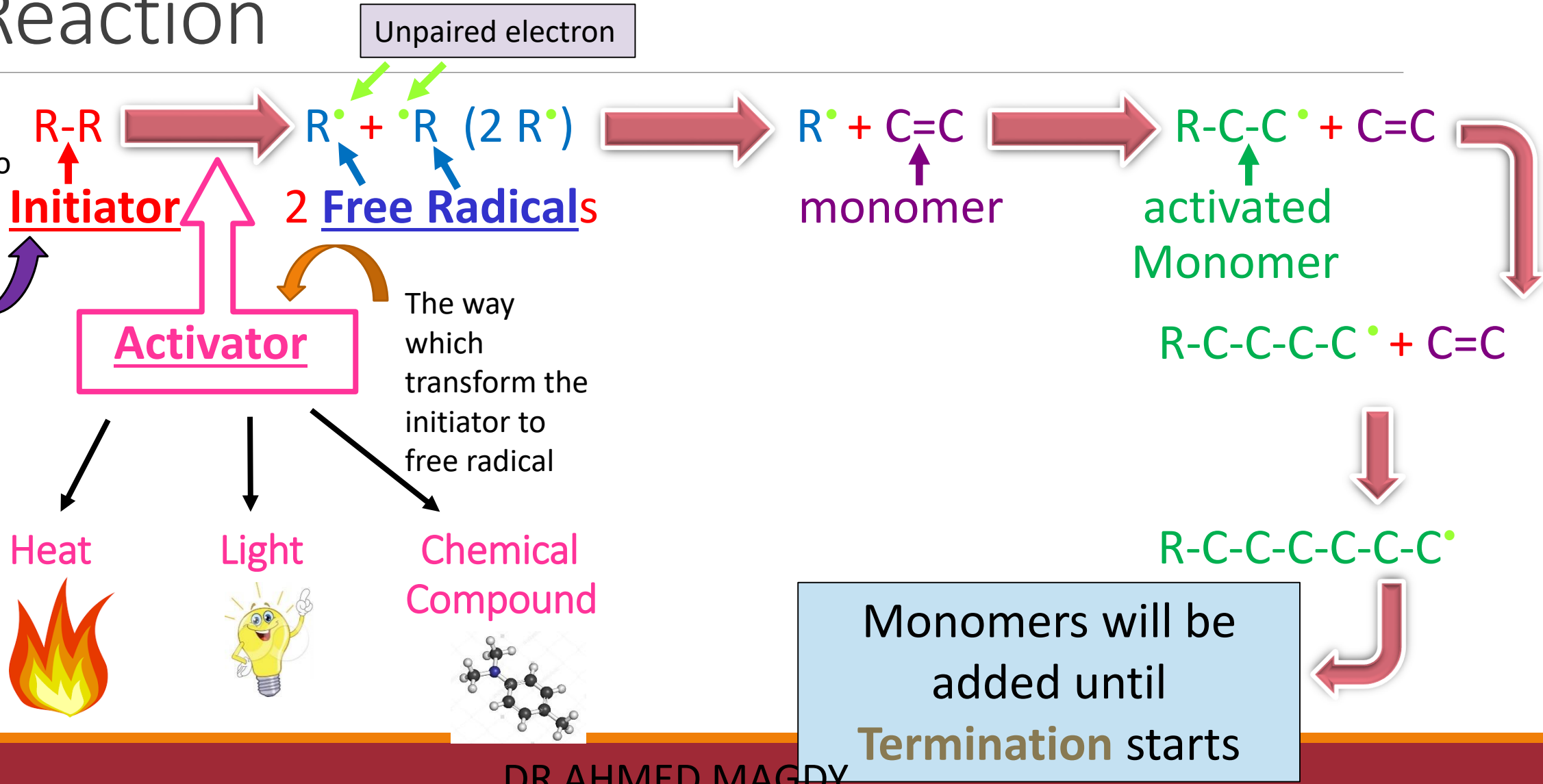
1. Activation
2. Initiation.
3. Propagation.
4. Termination

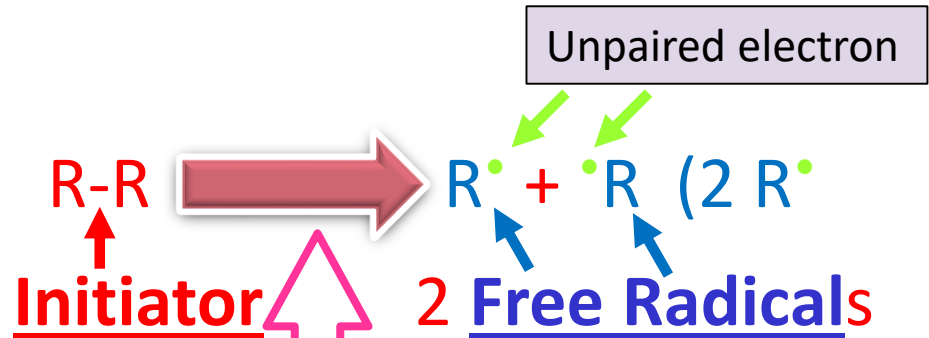
Stages of Addition Polymerization Reaction

1. Activation
2. Initiation.
3. Propagation.
4. Termination

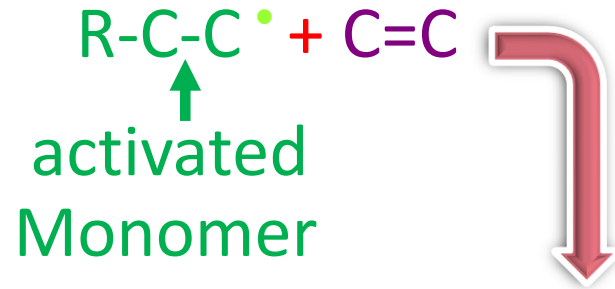
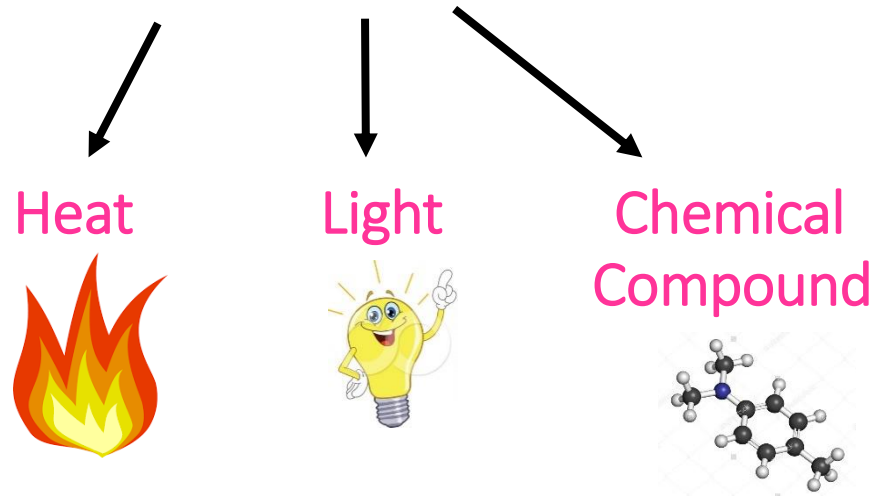
Stages of Addition Polymerization Reaction

Compound with weak bond to be transferred to Free Radical.

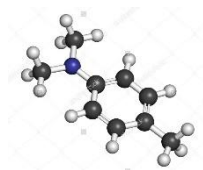
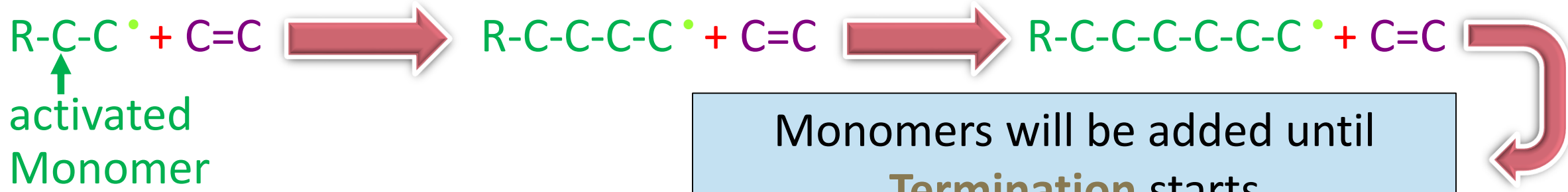




Activator



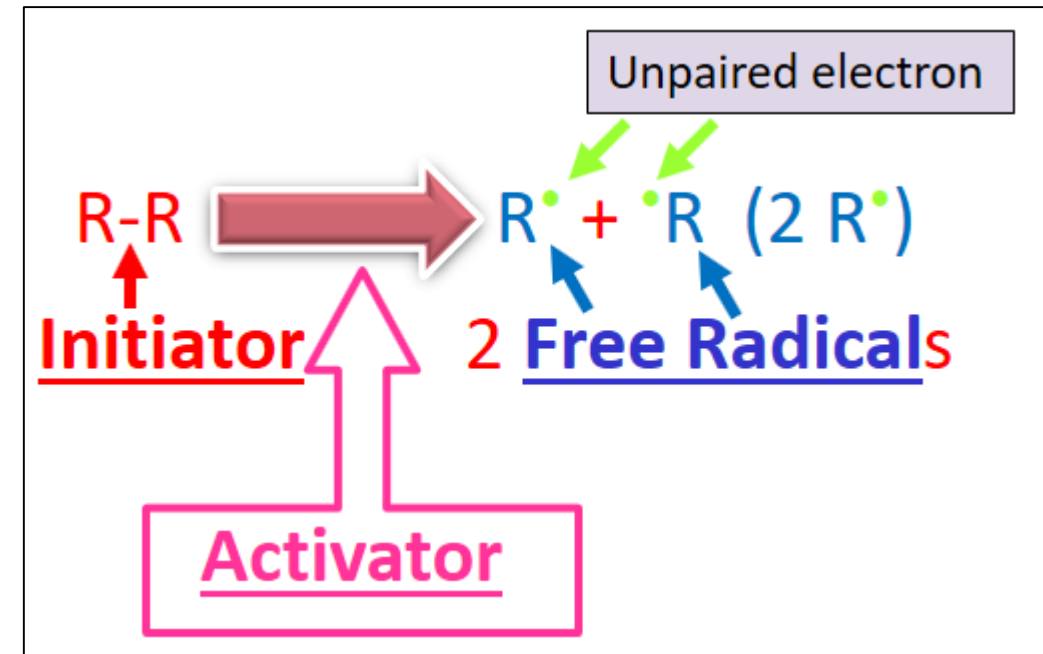
Monomers will be added until **Termination** starts



Stages of Addition Polymerization Reaction

1. Activation:

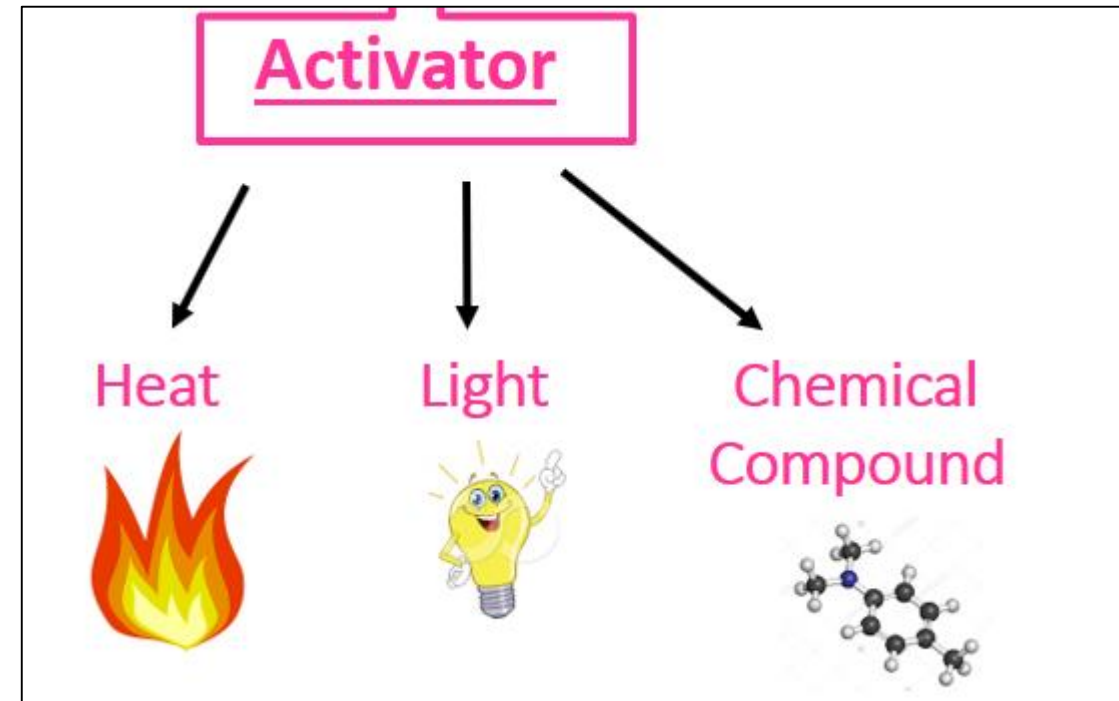
- It is the process of production of **free radicals**.
- Free radicals are the active form of the **initiators**.
- Free radical is highly reactive compound due to presence of **unpaired electron**.



Stages of Addition Polymerization Reaction

1. Activation:

- Initiator can be activated by:
 - a. Heat.
 - b. Light.
 - c. Chemical compound.



Stages of Addition Polymerization Reaction

2. Initiation:

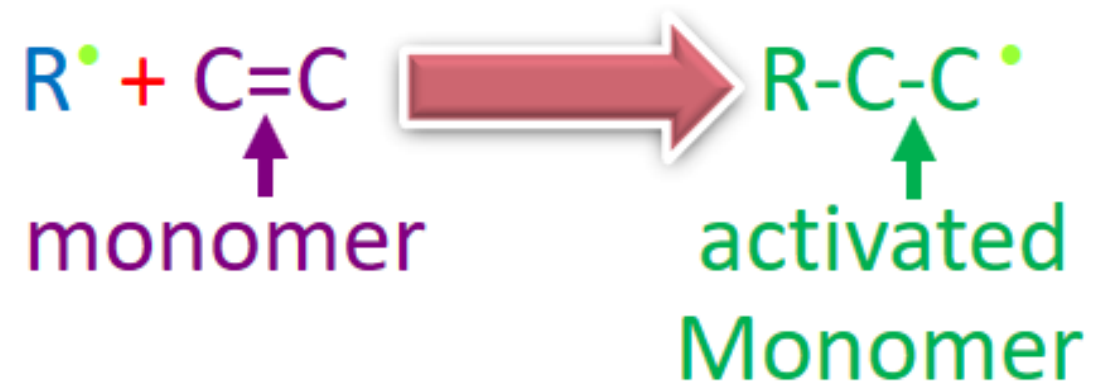
- It is the reaction of **free radical** with the first **monomer**.
- The free radical breaks the double bond of the monomer (C=C) and react with one carbon atom.



Stages of Addition Polymerization Reaction

2. Initiation:

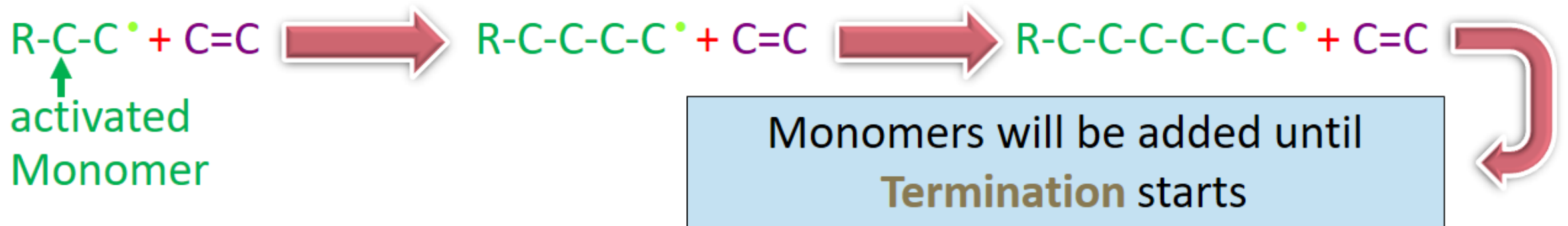
- The other carbon atom contains the unpaired electron making it very reactive.
- i.e: The reactivity of the free radical is transferred to the monomer (activated monomer)



Stages of Addition Polymerization Reaction

3. Propagation:

- It is the process of addition of the monomers to the growing chains.
- Each activated monomer attacks C=C of unreacted monomers transferring the active part to it.

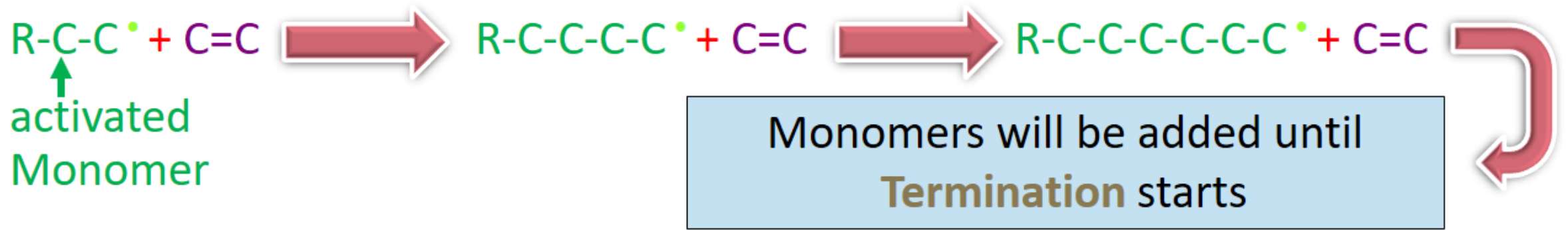


Stages of Addition Polymerization Reaction

3. Propagation:

Theoretically, the propagation step should be continued until all unreacted monomers are added.

Otherwise, the propagation step is stopped by termination



Stages of Addition Polymerization Reaction

4. Termination:

The termination process stops the growth of growing chains either by:

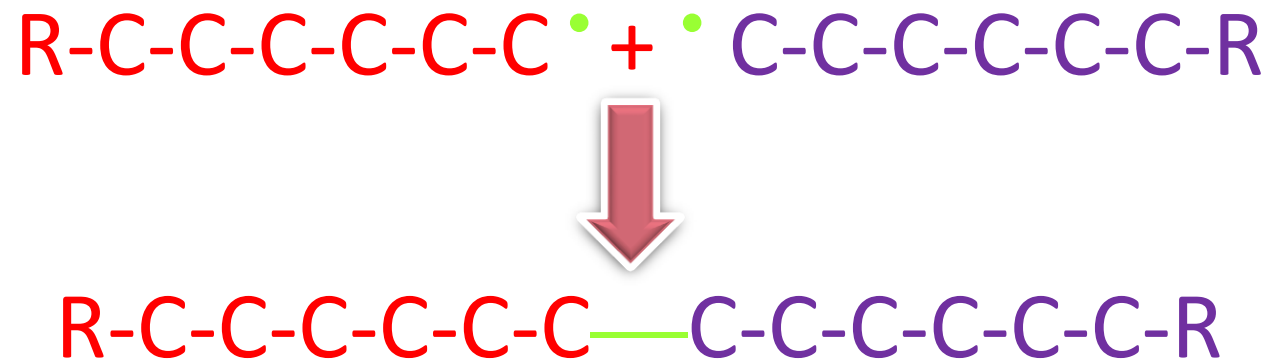
- a. Direct Coupling.
- b. Hydrogen atom transfer.

Stages of Addition Polymerization Reaction

4. Termination:

a. Direct Coupling.

Two growing chains reacts together to give one long stable chain.



Stages of Addition Polymerization Reaction

4. Termination:

a. Direct Coupling.

Two growing chains reacts together to give one long stable chain.

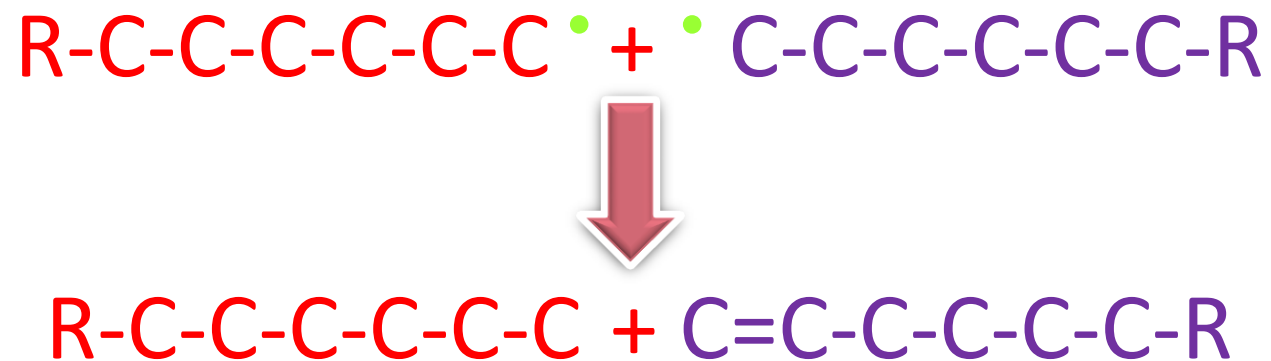


Stages of Addition Polymerization Reaction

4. Termination:

b. Hydrogen Atom Transfer.

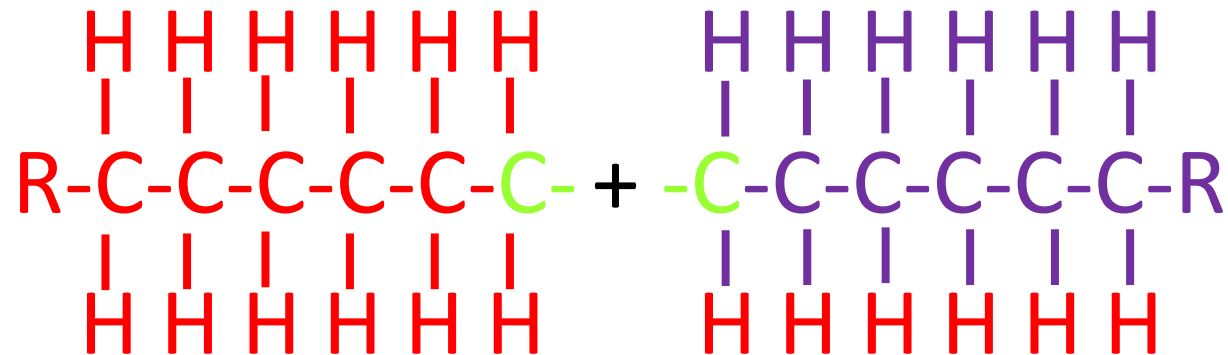
The Hydrogen atom transfers from active chain to another active chain to give two stable chains.



Stages of Addition Polymerization Reaction

4. Termination:

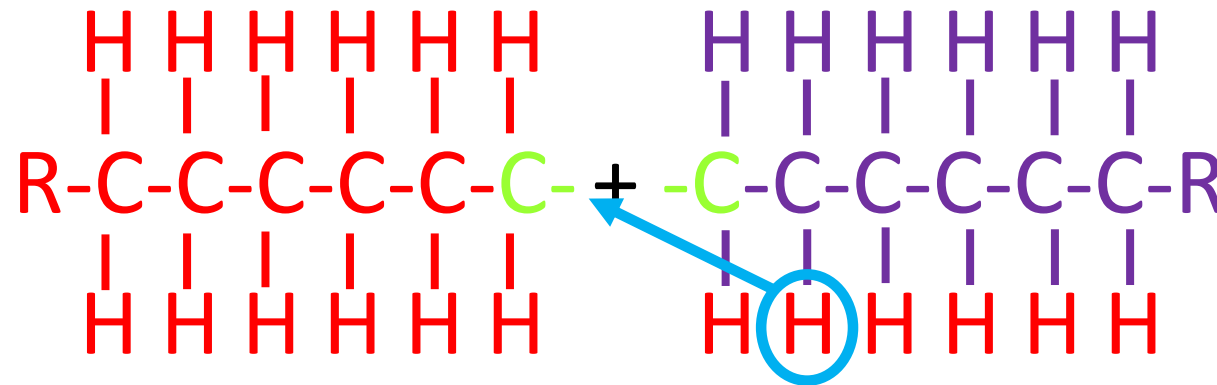
b. Hydrogen Atom Transfer.



Stages of Addition Polymerization Reaction

4. Termination:

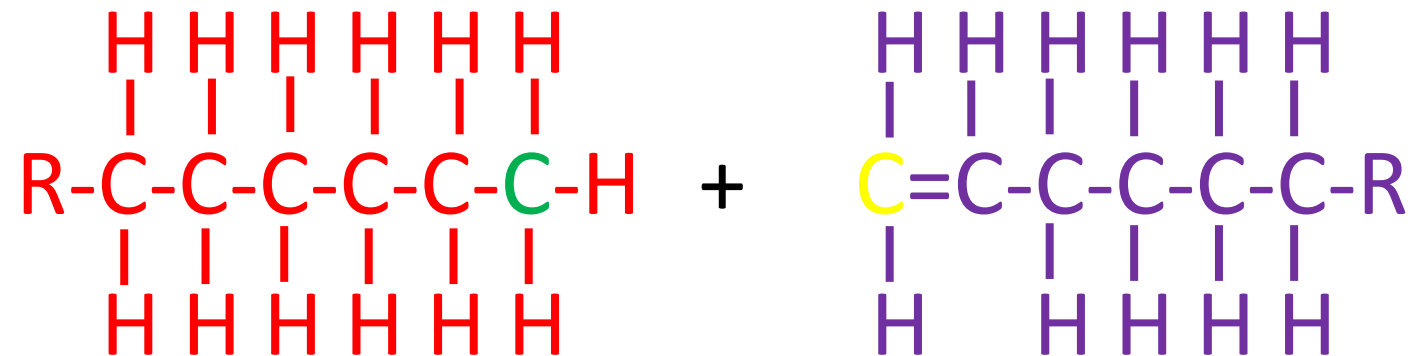
b. Hydrogen Atom Transfer.



Stages of Addition Polymerization Reaction

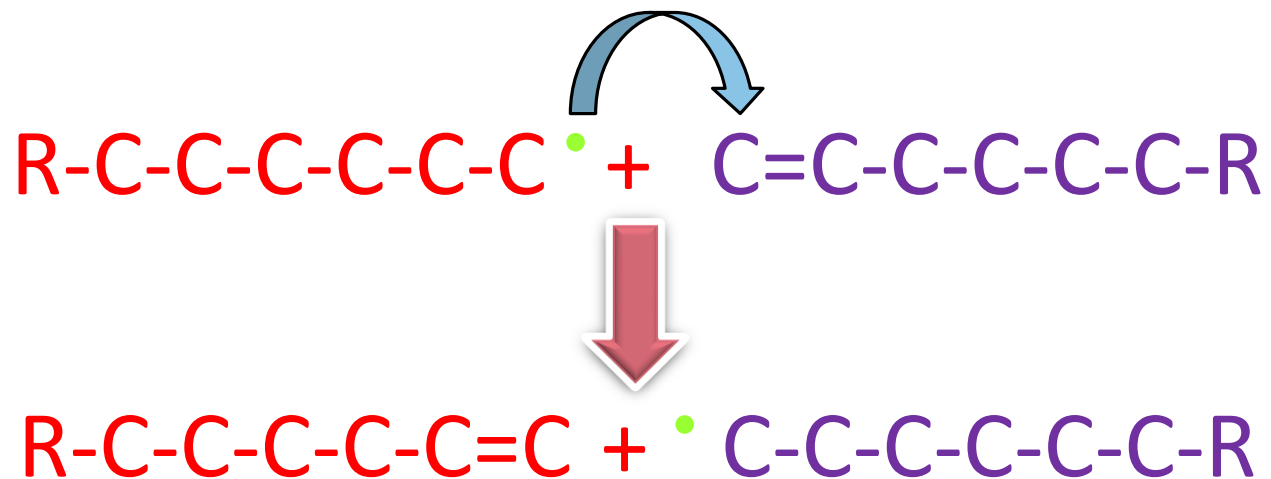
4. Termination:

b. Hydrogen Atom Transfer.



Chain Transfer

Chain transfer is a transfer reactivity from **active** chain to **inactive** chain.

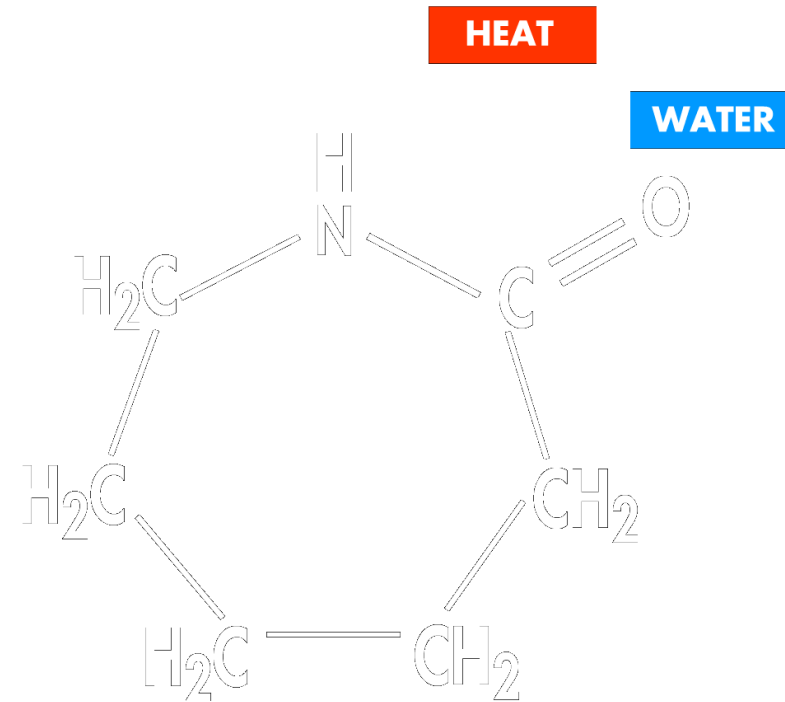


Termination

- The termination process occurs under normal conditions.
- This results in incompleteness of the polymerization reaction and presence of residual monomers

Ring opening polymerization reaction

The terminal group of the monomer is a ring.

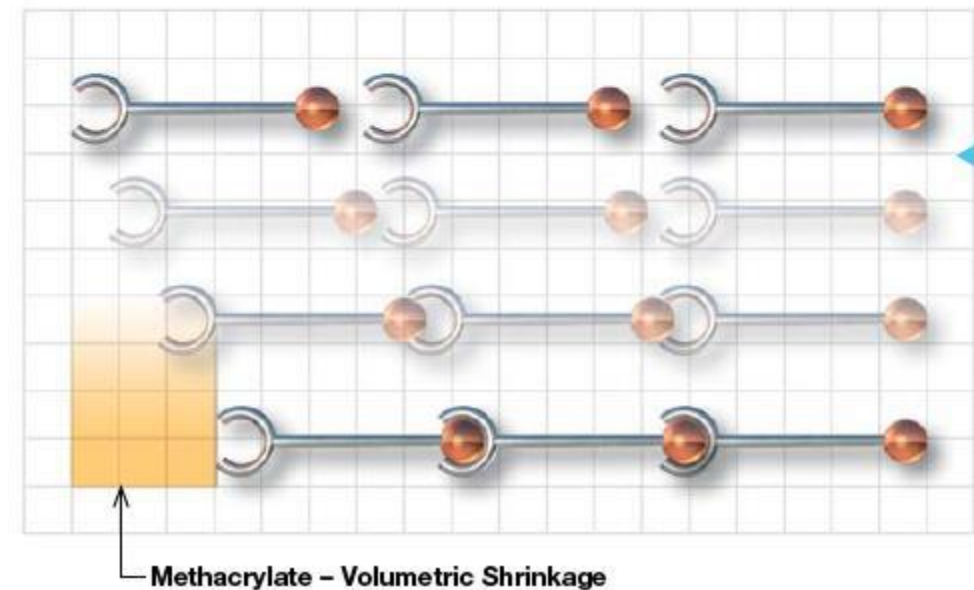
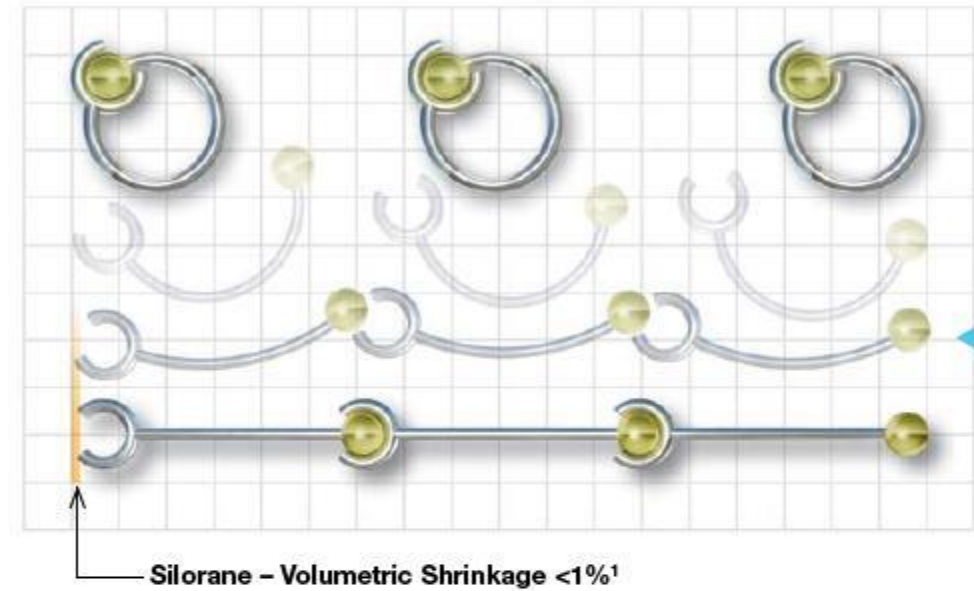


Caprolactam

Ring opening polymer

Advantages:

1. Less polymerization shrinkage
2. Less heat evolution



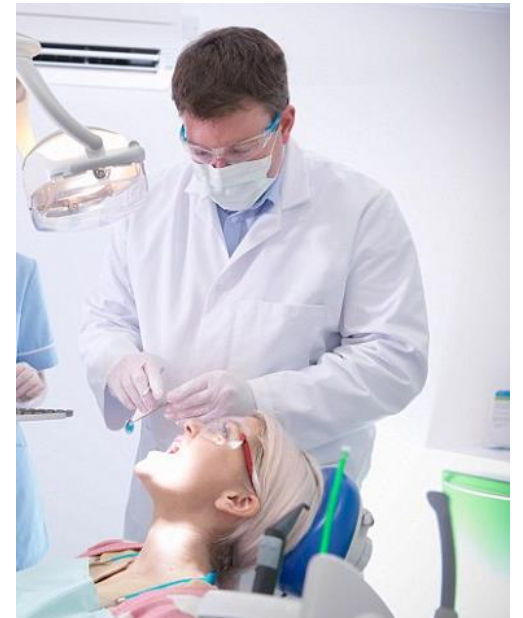
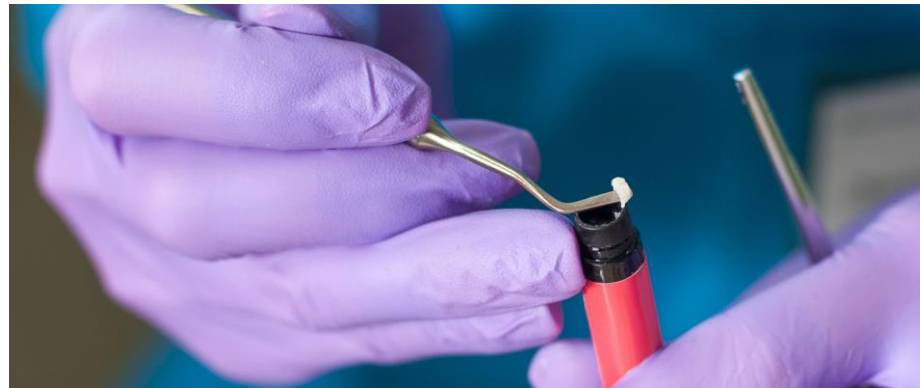
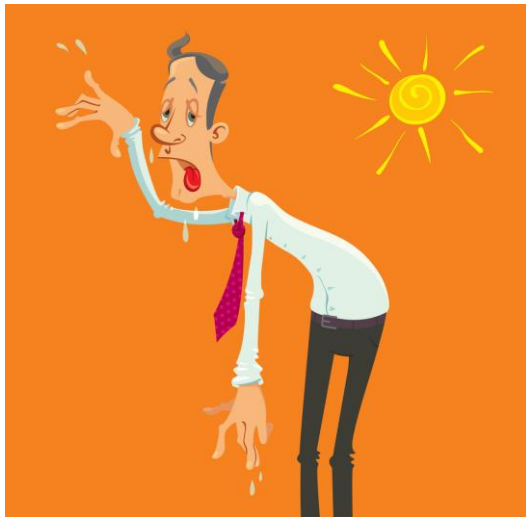
Inhibition and Retardation:

Inhibition → stopping

Retardation → lowering the rate

Inhibition and Retardation:

1. Hydroquinone are added to the monomers to inhibit the **premature polymerization** reaction of the monomers during **storage** or **accidental** exposure to heat or light.



Inhibition and Retardation:

2. **Eugenol** inhibits the polymerization reaction of **resin composite**.

So bases containing eugenol should not be used as a base under composite resin restorations.



Inhibition and Retardation:

- 3. Oxygen** inhibits the polymerization reaction of **resin composite**. So the surfaces of the restorations (in contact with oxygen during polymerization) should be polished to remove the unreacted surface layer or covered by a matrix band.



Factors Associated with polymerization reaction:

1. Evolution of **heat** due to the breaking of the covalent bonds of the monomers.
2. Reduction in the volume (**Polymerization shrinkage**).
3. Presence of **residual monomers**. Because not all the monomers participate in the reaction.

General Properties of the Polymers

- Polymers is molecular solids.
- Polymers is amorphous solids.

Factors affecting polymers properties



Strength and hardness

Rigidity

Glass transition temperature



Water sorption

Crazing

Ductility

Factors affecting polymers properties

1. Molecular weight (M.W) and Degree of polymerization (DP):

M.W of polymer molecule = Weight of mers X Number of mers.

The higher the M.W, the higher the degree of polymerization

Factors affecting polymers properties

1. Molecular weight (M.W) and Degree of polymerization (DP):

Degree of conversion (Degree of polymerization): is the total number of monomers in the polymer chain

$$D.P = M_w \text{ of polymer} / M_w \text{ of mer}$$

Factors affecting polymers properties

1. Molecular weight (M.W) and Degree of polymerization (DP):

Effect on properties:

The longer the polymer chain → the more the entanglement
between chains occurs → more secondary bonds

Factors affecting polymers properties

1. Molecular weight (M.W) and Degree of polymerization (DP):



Strength and hardness

Rigidity

Glass transition temperature



Water sorption

Crazing

Ductility

Factors affecting polymers properties

2. Copolymerization:

Copolymer is a polymer consists of two or more different types of monomers

Factors affecting polymers properties

2. Copolymerization:

Effect on properties:

Copolymerization allows the chemists to synthesize a polymer with desired properties (Tailor-make effect).

Factors affecting polymers properties

2. Copolymerization:

Effect on
properties:



Factors affecting polymers properties

3. Cross-linking:

It is the bonding of the polymer chains with primary covalent bond.

This leads to forming a network structure.

Factors affecting polymers properties

3. Cross-linking:

The cross linking agent is a chemical compound with two double bonds per molecule can bond **covalently** different chains.

Cross linking of rubbers is called vulcanization.

Factors affecting polymers properties

3. Cross-linking:

Effect on Properties:

a) Small degree of cross linking:

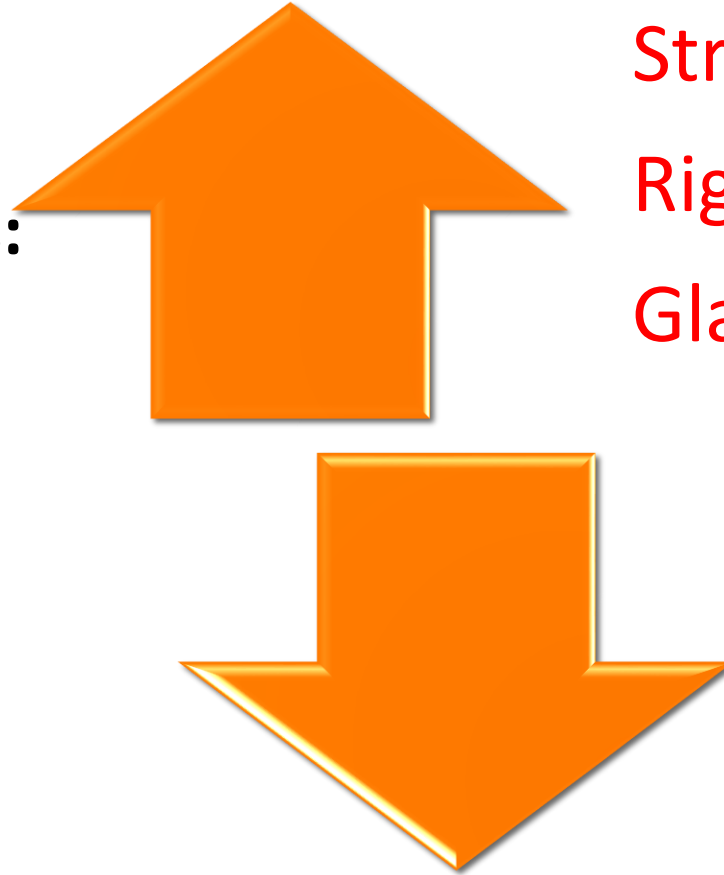
It limits the movement of polymer chains past each other

Factors affecting polymers properties

3. Cross-linking:

Effect on Properties:

- a) Small degree
of cross linking:



Strength and hardness

Rigidity

Glass transition temperature

Water sorption

Crazing

Ductility

Factors affecting polymers properties

3. Cross-linking:

Effect on Properties:

b) Extensive cross linking:

It Leads to brittleness of the polymer

Factors affecting polymers properties

4. Plasticizer:

It is the partially neutralization of the secondary Van der Waal forces between the polymer chains.

Factors affecting polymers properties

4. Plasticizer:

Types of plasticizers:

- a) Internal plasticizer.
- b) External plasticizer.

Factors affecting polymers properties

4. Plasticizer:

a) Internal plasticizer.

- Incorporated by copolymerization.
- It is a part of the polymer.

Factors affecting polymers properties

4. Plasticizer:

b) External plasticizer.

- It is a compound added to the polymer.
- It penetrates between the polymer chains to partially neutralize the secondary forces between the chains.

Factors affecting polymers properties

4. Plasticizer:

Effect on properties:

- It partially neutralizes the secondary forces between polymer.

Factors affecting polymers properties

4. Plasticizer:

Effect on properties:



Strength and hardness

Rigidity

Glass transition temperature



Water sorption

Crazing

Ductility

Factors affecting polymers properties

5. Addition of Inorganic Fillers:

Like composite resin

Effect on properties:

- The fillers improve the properties.

Factors affecting polymers properties

5. Addition of Inorganic Fillers:

Effect on properties:



Strength and hardness

Rigidity

Glass transition temperature



Water sorption

Crazing

Ductility

Factors affecting polymers properties

6. Rate of Loading:

Polymers are viscoelastic materials → sensitive to rate of loading:

- At slow rate of loading → behave in a ductile manner.
- At high rate of loading → behave in a brittle manner.

Factors affecting polymers properties

7. Degree of Crystallinity:

- Polymers are generally amorphous solids.
- In certain polymers, the chains can be aligned to form different degrees of ordered crystalline structure.

Factors affecting polymers properties

7. Degree of Crystallinity:

Degree of crystallinity depends on:

1) Chain configuration: (it should be simple)

Side branching and network → decrease crystallinity

Copolymerization → decrease crystallinity.

Factors affecting polymers properties

7. Degree of Crystallinity:

Degree of crystallinity depends on:

2) Monomer chemistry: (it should be simple)

High molecular weight → decrease crystallinity

Additives (plasticizers) → decrease crystallinity.

Factors affecting polymers properties

8. Spatial configuration:

Cross linking improve polymers properties.



Strength and hardness

Rigidity

Glass transition temperature

Water sorption

Crazing

Ductility

Factors affecting polymers properties

9. Temperature:

Polymers softens when they heated near their glass transition temperature

Elastomers

- They are polymers that display wide range of elastic deformation.
- They are formed of highly coiled and twisted polymeric chains that are uncoiled and straightened with tensile load.
- After removal of load, the chains spring back to their previous shape.

Elastomers

Elastomers are characterized by:

- a. Low modulus of elasticity.
- b. Their glass transition temperature is below room temperature.
- c. Have few cross linking.

Uses of polymers in dentistry:

Denture base material.

Artificial teeth.

Teeth restorative materials.

Dental cements.



Uses of polymers in dentistry:

Temporary crown materials.

Endodontic filling and sealers.

Maxillo-facial prosthesis.

Impression materials.



Thank You



DR AHMED MAGDY