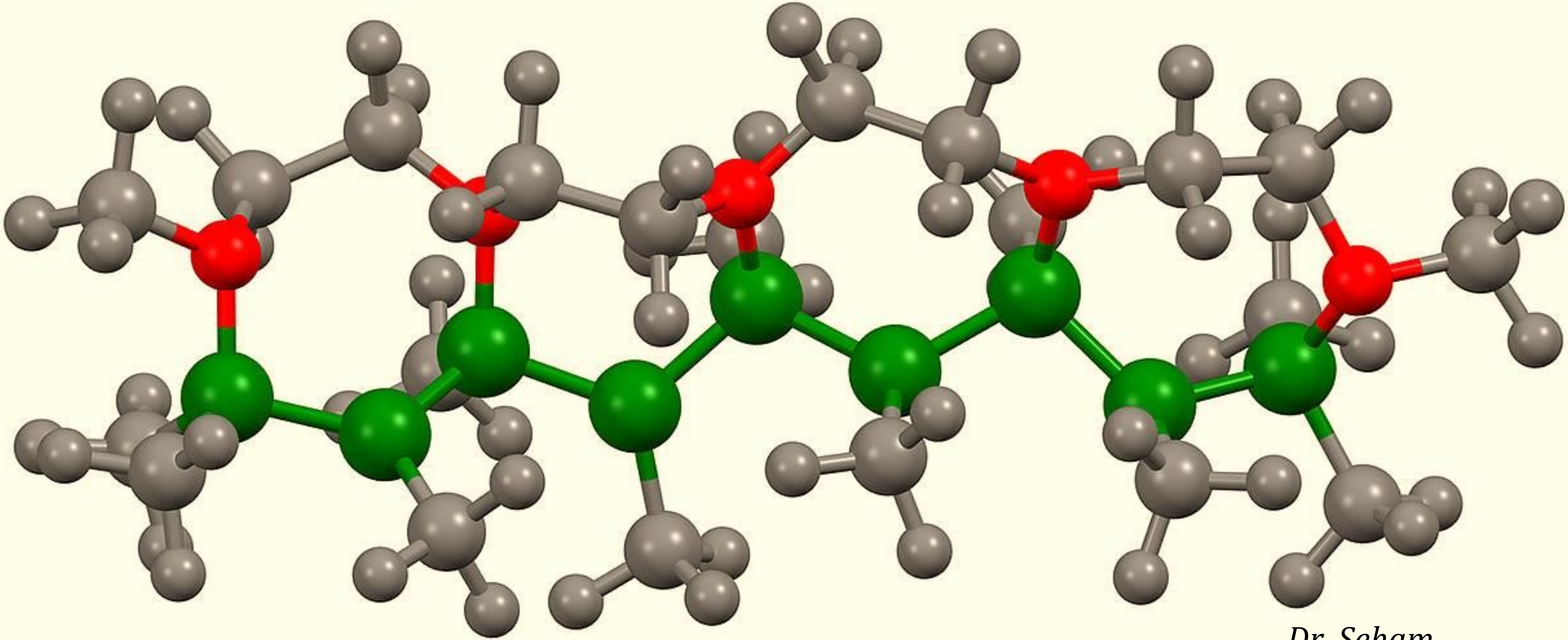
Chapter 2:

General Methods for preparing



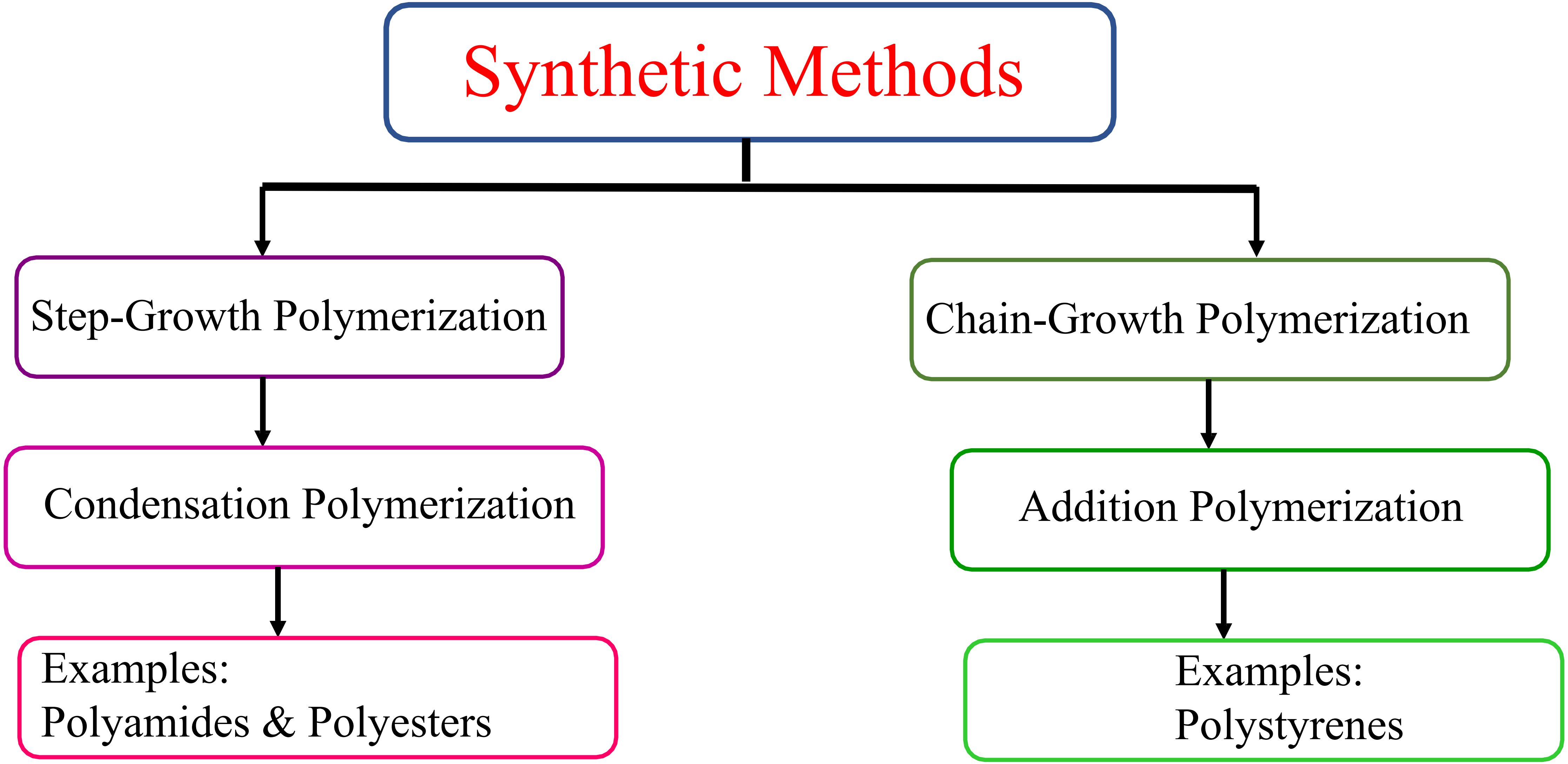
Dr. Seham
ALTERARY

By the end of this Chapter

You will be able to recognize

- Different types of polymerization mechanism
    - Condensation polymerization
        - Linear condensation polymers
        - Cross-linked condensation polymers
        - Synthetic fibers
    - Addition polymerization

There are two basic ways to form polymers:



Synthetic Methods

Step-Growth Polymerization

Condensation Polymerization

Examples:
Polyamides & Polyesters

Chain-Growth Polymerization

Addition Polymerization

Examples:
Polystyrenes

1. Condensation Polymerization

A ***Step-Growth Polymerization*** is a stepwise reaction between bi-functional or multi-functional monomers in which a high-molecular-weight polymer is formed after a large number of steps.

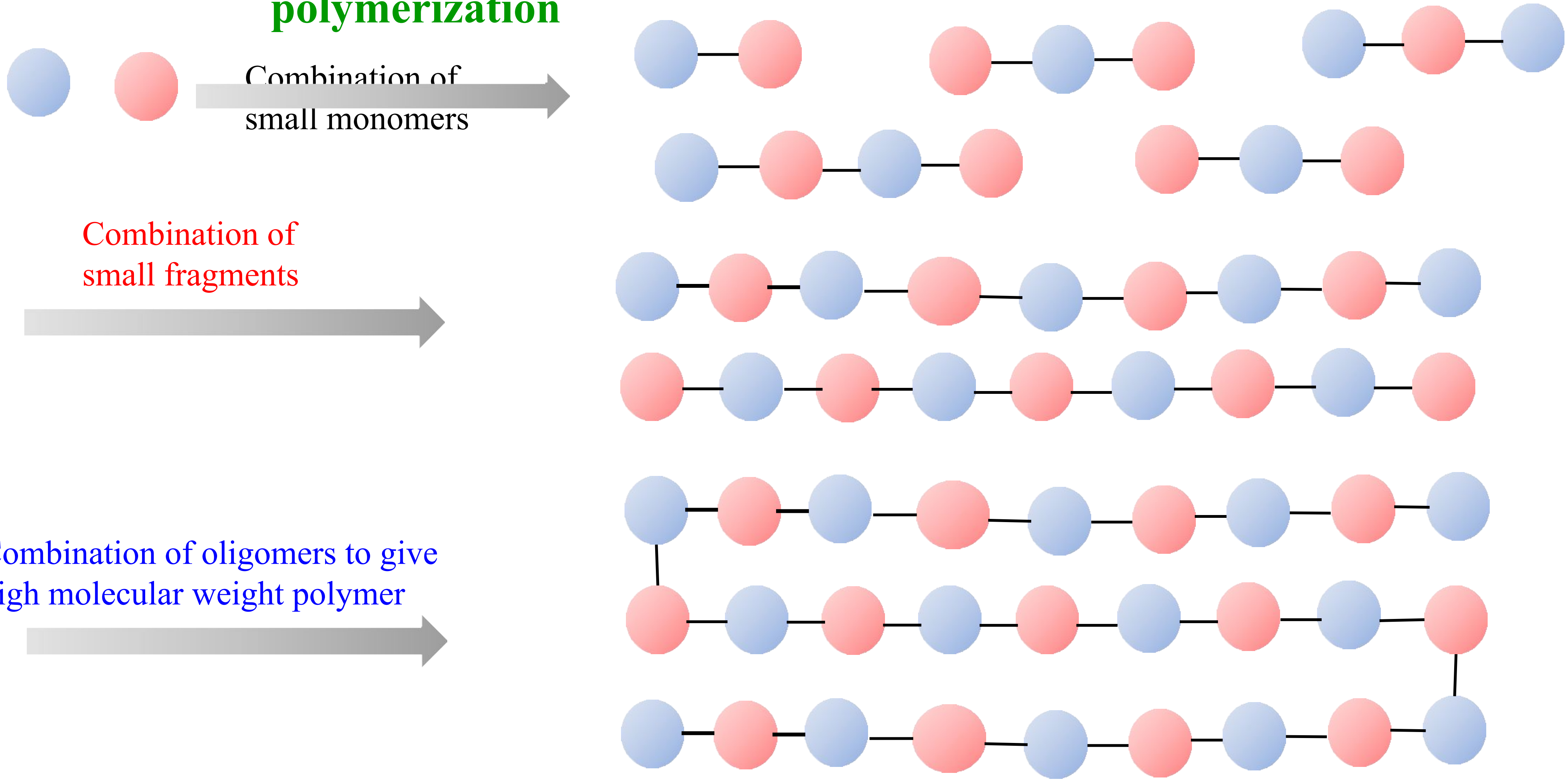
Characteristics of Condensation Polymers

Condensation polymers form more slowly **than** addition polymers, often requiring heat, and they are generally lower in molecular weight.

The terminal functional groups on a chain remain active, so that groups of shorter chains **combine** into longer chains in the late stages of polymerization.

According to the Step Growth Polymerization it may gives:
Linear Polymer Or *Cross linked polymer*.

A representation of step-growth polymerization



Combination of small monomers

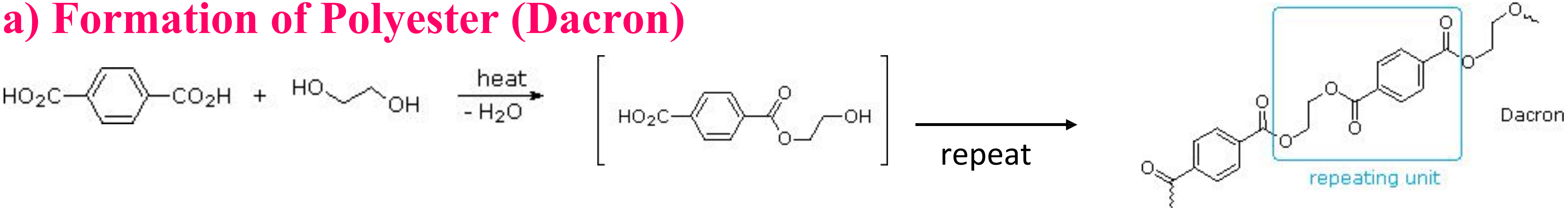
Combination of small fragments

Combination of oligomers to give high molecular weight polymer

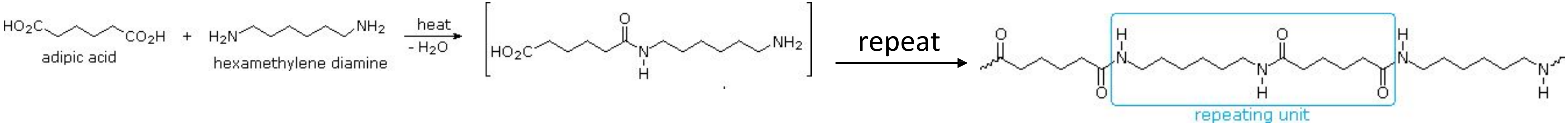
Examples of Condensation polymerization “step-growth polymerization”

The polyester **Dacron** and the polyamide **Nylon 66** are **two examples** of synthetic condensation polymers, also known as step-growth polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively).

a) Formation of Polyester (Dacron)



b) Formation of Polyamide (Nylon 66)



Condensation Polymerization

1. Linear Condensation Polymers

- Many **thermoplastic** polymers belongs to linear condensation polymers.

Thermoplastic

Plastic polymer material that becomes pliable or moldable at a certain elevated temperature and solidifies upon cooling.

- They may transfere into fiber polymer with **high degree of polymerization** because of the presence of polar groups.

Examples:

- Polyamides
- Polyesters
- Polycarbonate
- polyurethane

1. Linear Condensation Polymers

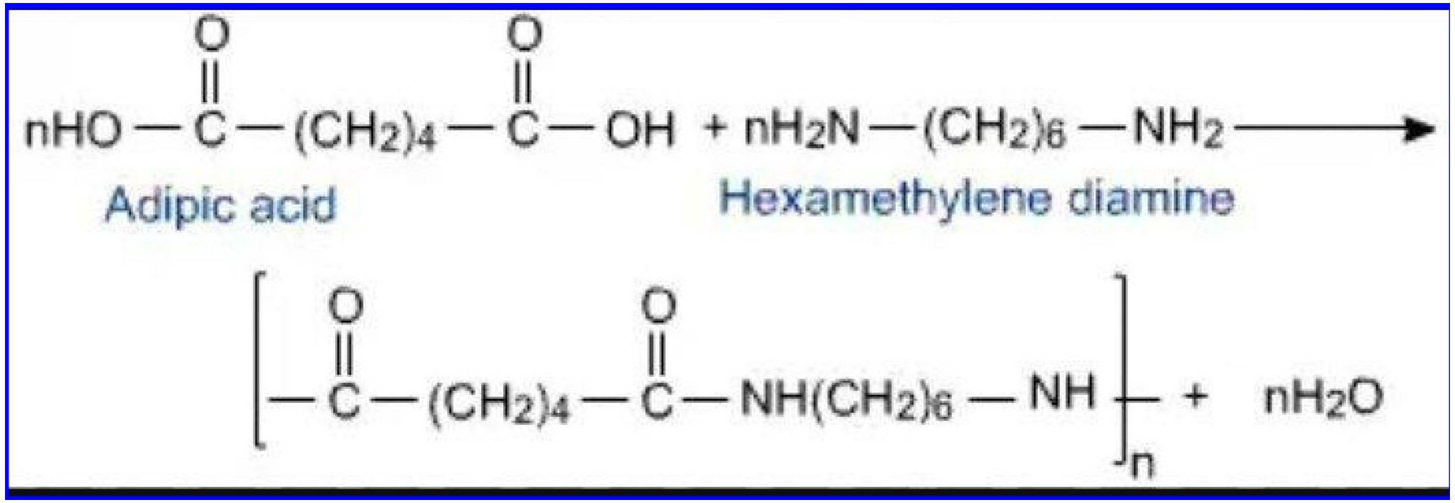
- Polyamides

1. They are called polyamides as they have an amide group –NHCO-
2. Preparation methods:
    A. Direct amidation between diacid & diamine
    B. Self amidation for amino acids
    C. Ring-opening polymerization reactions for cyclic amides

1. Linear Condensation Polymers

- **Polyamides**

Synthesis of Nylon 6,6



$$nHO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH + nH_2N-(CH_2)_6-NH_2 \longrightarrow \left[-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-NH(CH_2)_6-NH-\right]_n + nH_2O$$

Ammonium salt is formed in the beginning which is called Nylon salt,
By heating the salt water is lost and a polymer with 10,000 Mwt is formed.

Condensation Polymerization

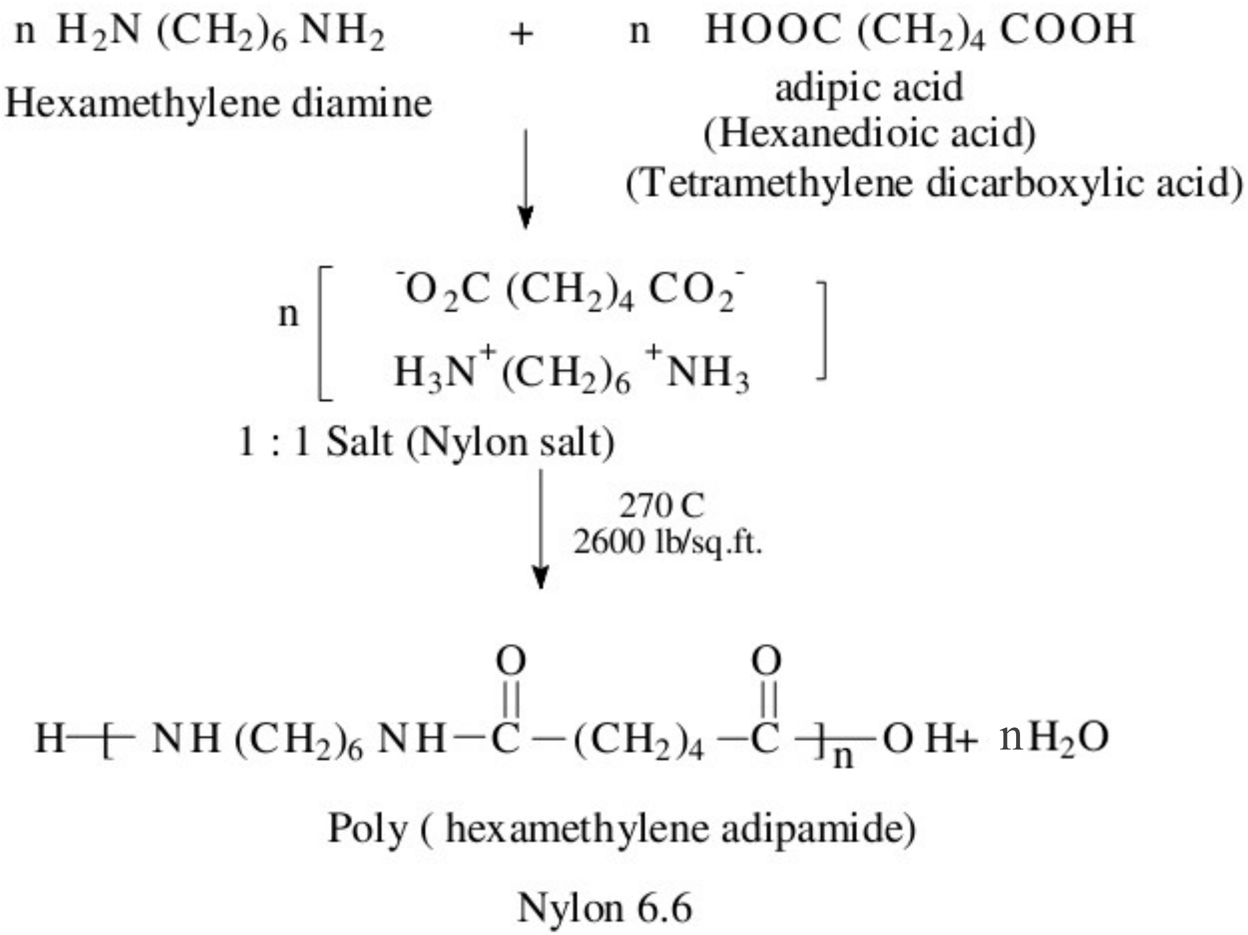
Growth Polymerization

1. Linear Condensation Polymers

- Polyamide

Direct Amidation

Synthesis of Nylon 6,6



$n\ H_2N\,(CH_2)_6\,NH_2 \quad + \quad n\ HOOC\,(CH_2)_4\,COOH$

Hexamethylene diamine

adipic acid
(Hexanedioic acid)
(Tetramethylene dicarboxylic acid)

$$n\left[\begin{array}{c} {}^{-}O_2C\,(CH_2)_4\,CO_2^{-} \\ H_3N^{+}(CH_2)_6\,{}^{+}NH_3 \end{array}\right]$$

1 : 1 Salt (Nylon salt)

$\xrightarrow[\text{2600 lb/sq.ft.}]{\text{270 C}}$

$$H{-}\!\!\left[NH\,(CH_2)_6\,NH{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}\right]_n\!{-}OH + nH_2O$$

Poly (hexamethylene adipamide)

Nylon 6.6

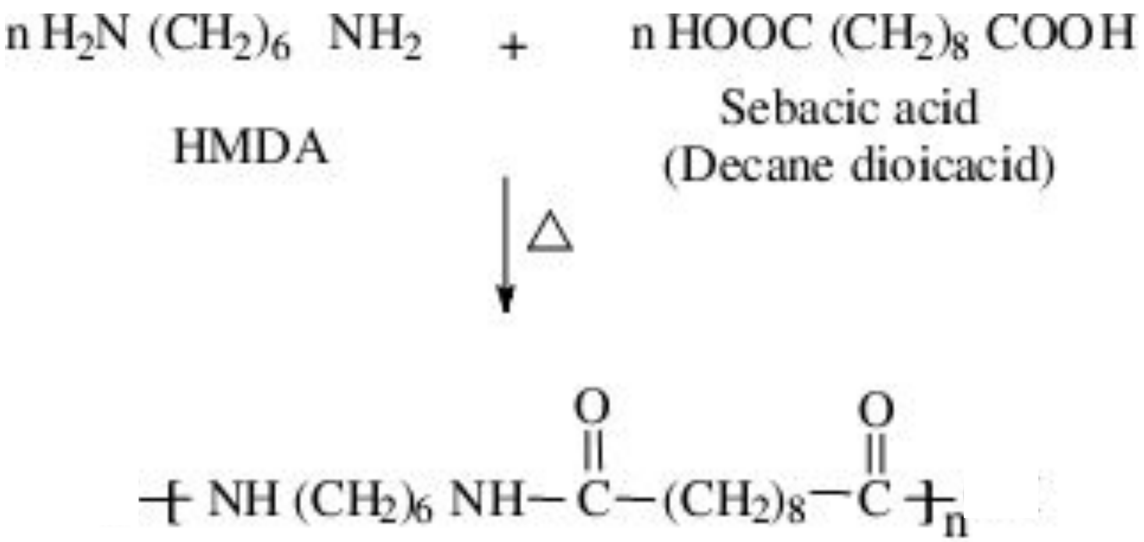
1. Linear Condensation Polymers

- Polyamides

Direct amidation

Synthesis of Nylon 6,10

The reaction takes place between hexamethylene diamine with sebacic acid



$$n\,H_2N(CH_2)_6NH_2 + n\,HOOC(CH_2)_8COOH \xrightarrow{\Delta} -\!\!\left[NH(CH_2)_6NH-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}} \right]\!\!-_n$$

Poly(hexamethylen esebasamide)
(Nylon 6.10)

Condensation Polymerization

Growth Polymerization

1. Linear Condensation Polymers

- Polyamides

B. Self amidation for amino acids

Synthesis of Nylon 11

Amino acid polymerization with different function groups

As the reaction of Amino undecanoic acid:

$$n\ H_2N(CH_2)_{10}COOH \longrightarrow [NH(CH_2)_{10}CO]_n + n\ H_2O$$

ω−Amino undecanoic acid

Nylon 11

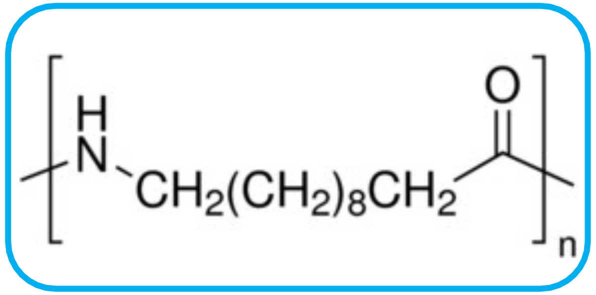
Condensation Polymerization

Growth Polymerization

B. Self amidation for amino acids

Reaction Mechanism of Nylon 11 Formation

Nylon 11 is produced by polymerization of 11-aminoundecanoic acid.



Nylon 11

Condensation Polymerization

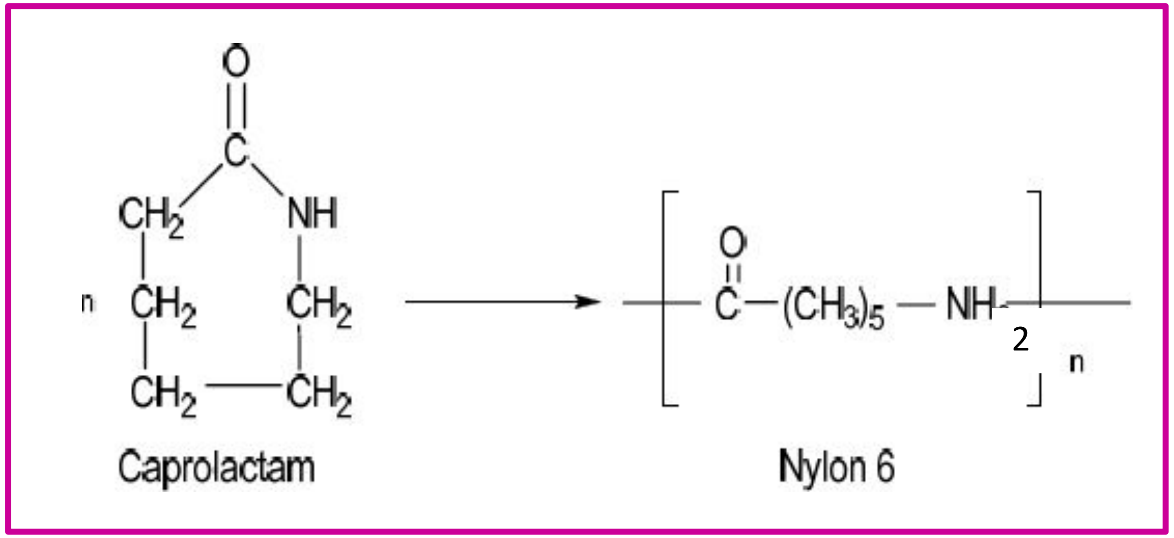
Growth Polymerization

C. Ring-opening polymerization reactions for cyclic amides

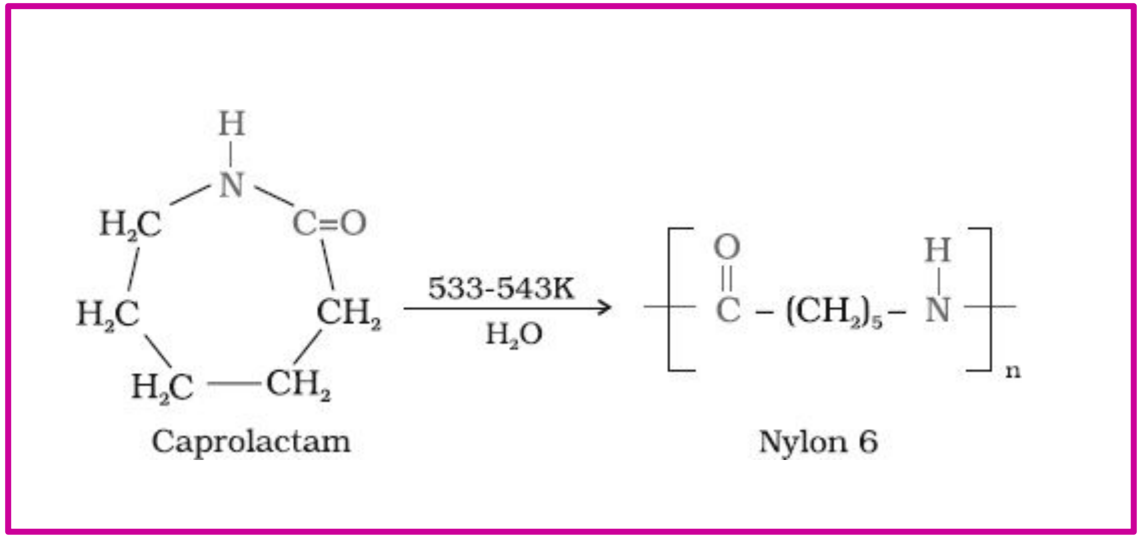
Example

Nylon 6

Nylon 6 is a linear addition polymerization of caprolactam (6-amino-caproic acid)



or



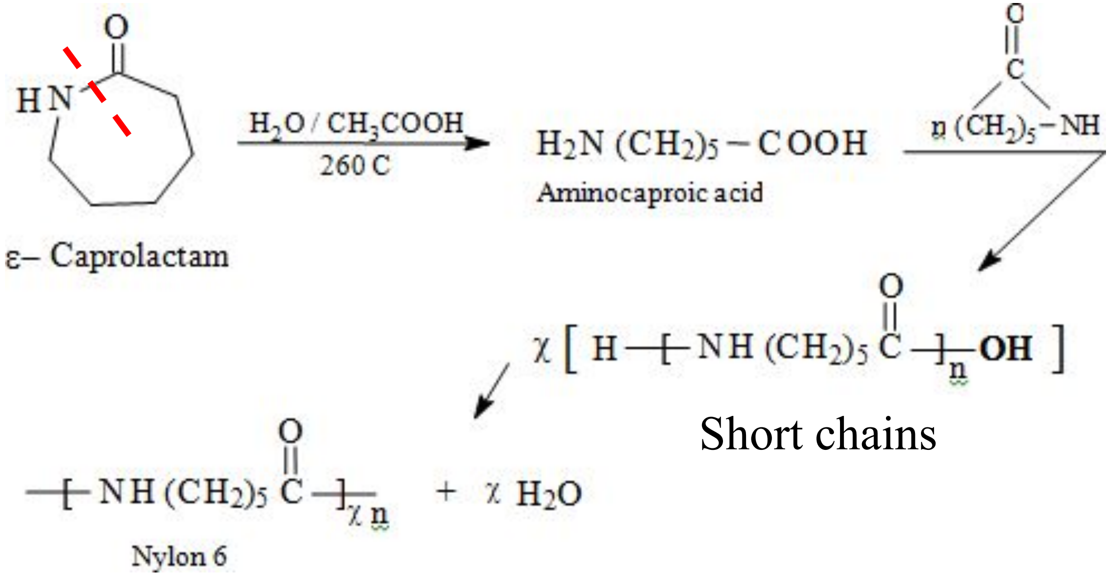
Condensation Polymerization

Growth Polymerization

C. Ring-opening polymerization reactions for cyclic amides

Reaction Mechanism of Nylon 6

- The mechanism starts with cleavage of amide linkage, Leading to the formation of the corresponding amino-carboxylic acid.
- The reaction proceed in short chains in the beginning.
- Although the reaction proceed with only caprolactam and water present, a material such as (phosphoric or acetic acid) at low concentration to act as a chain stabilizer and help to achieve the desired final viscosity.



Condensation Polymerization

C. Ring-opening polymerization reactions for cyclic amides

✔ Advantages of Polyamide Polymers

- Tough, strong, impact resistant
- Low coefficient of friction
- High temperature resistance
- Good solvent resistance
- Resistant to bases

Condensation Polymerization

Growth Polymerization

C. Ring-opening polymerization reactions for cyclic amides

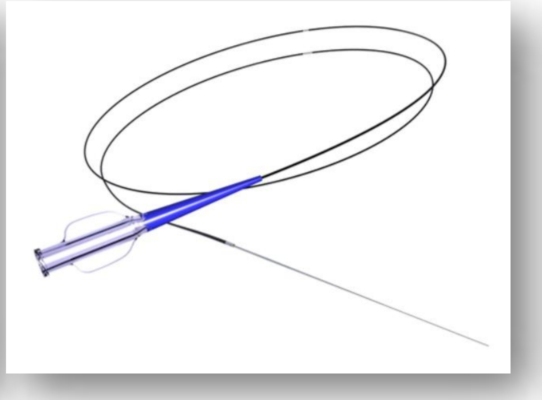
✔ Usages of Polyamide Polymers

Polyamide finds applications in fields ranging from the clothing business to the automotive industry. They are used in making, electrical appliances.

Carpets

Furniture fabrics

Women's socks



Medical instruments

Ex: hypotube

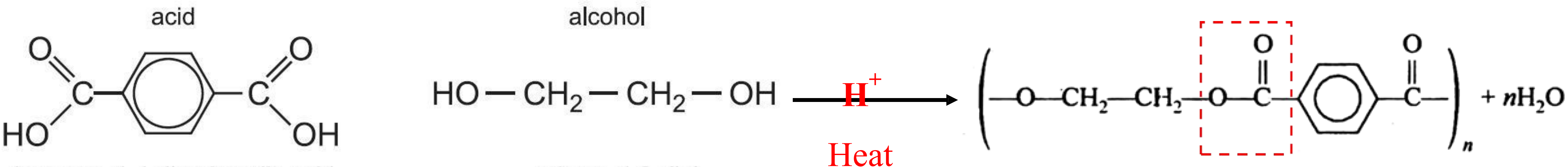
Openable double shell

Condensation Polymerization

Growth Polymerization

Polyesteres

- Polyesters are polymers formed from a dicarboxylic acid (Terephthalic acid) and a diol (Ethylene glycol).
- Polymers which are synthesized by similar manner usually have low Mwt, and easily decomposed during reaction heating.



benzene-1,4-dicarboxylic acid
(terephthalic acid)

ethane-1,2-diol
(ethylene glycol)

Poly(ethylene terephthalate) (Dacron)

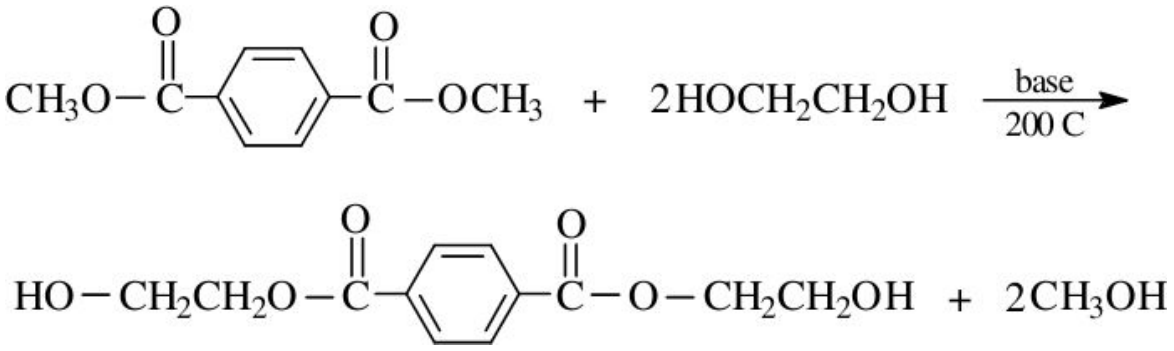
Condensation Polymerization

Growth Polymerization

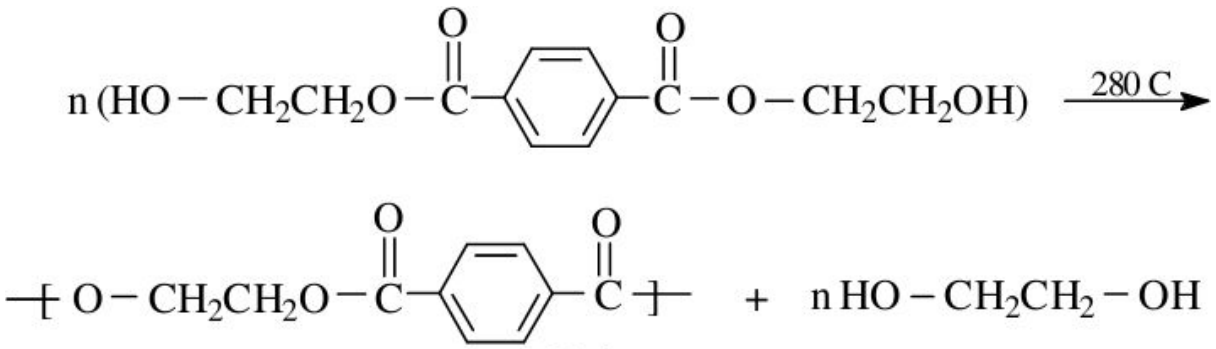
▪ Polyesteres

❖ Another way to synthesize polyesters from organic acid esters, in two steps as follow:

Step 1



Step 2



Polyester

Polyesteres

✔ Usages of Polyesters

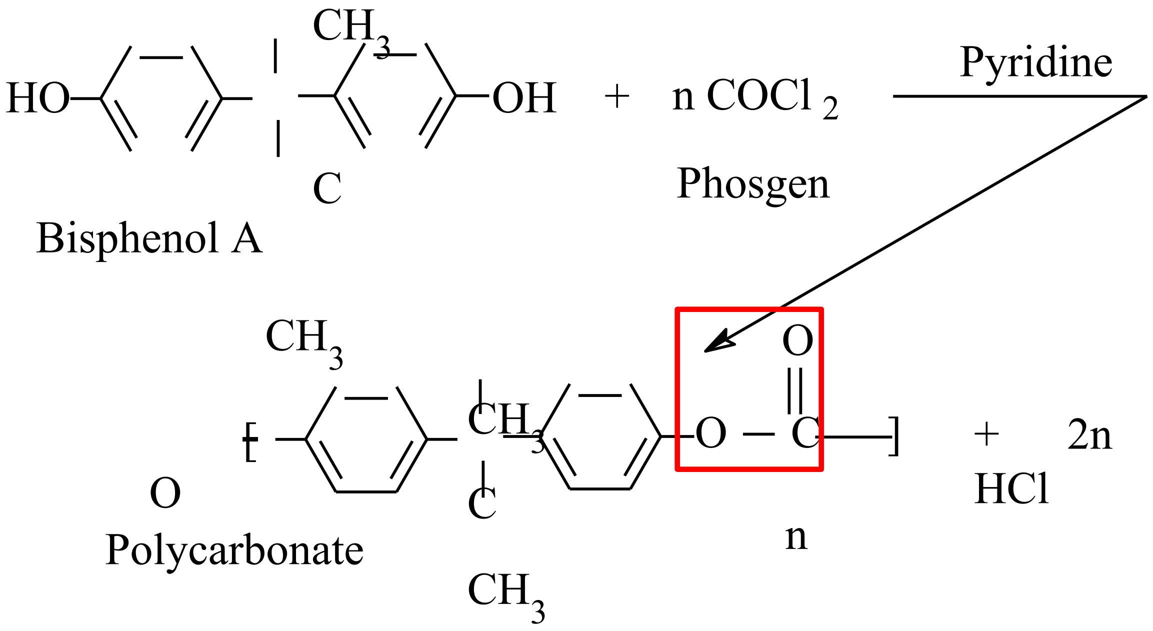
- ❑ **Polyester** is used in the manufacturing of all kinds of *clothes* and *home furnishings*, like *bedspreads*, *sheets*, *pillows*, *carpets* and even *curtains*.
- ❑ **PET:** The most common use of polyester today is to make the plastic bottles that store our much beloved beverages. Shatterproof and cheap these bottles are an absolute boon to the beverages industry.
- ❑ **Mylar:** An unusual and little known use of polyester is in the manufacturing of balloons. Not the rubber kind that you use for water balloons but the really pretty decorated ones that are gifted on special occasions. These are made of Mylar – a kind of polyester film manufactured by DuPont. The balloons are made of a composite of Mylar and aluminum foil.

Condensation Polymerization

Growth Polymerization

▪ Polycarbonates (PC)

- ❖ Are group of thermoplastic polymers containing carbonate group (-OCOO-) in their chemical structure.
- ❖ Polycarbonate used in engineering (**Engineering Plastics**) as they are **strong**, **tough** materials, and some grads are optically transparent.
- ❖ Polycarbonate is a relatively inexpensive material that is prepared via a multistep process from low-cost reagents.



Uses of Polycarbonates (PC)

- Some of the **common applications** are compact disc, safety helmets, bullet-proof glass, car headlamp lenses, baby feeding bottles, domes, roofing and glazing etc.

- Polycarbonate has been used safely in tubes and connectors for medical usage.

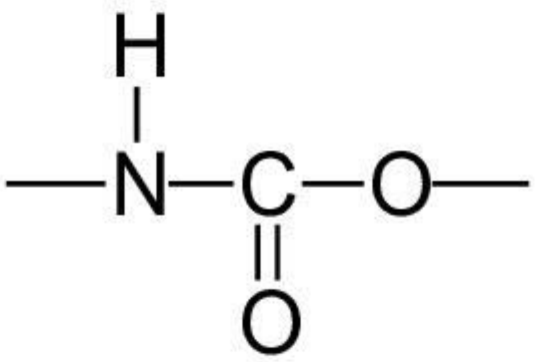
Condensation Polymerization

Growth Polymerization

Polyurethane

- Urethanes are also called carbamate esters.
- Carbamate are organic compounds derived from carbamic acid (NH_2COOH)

Chemical structure of the urethane group.

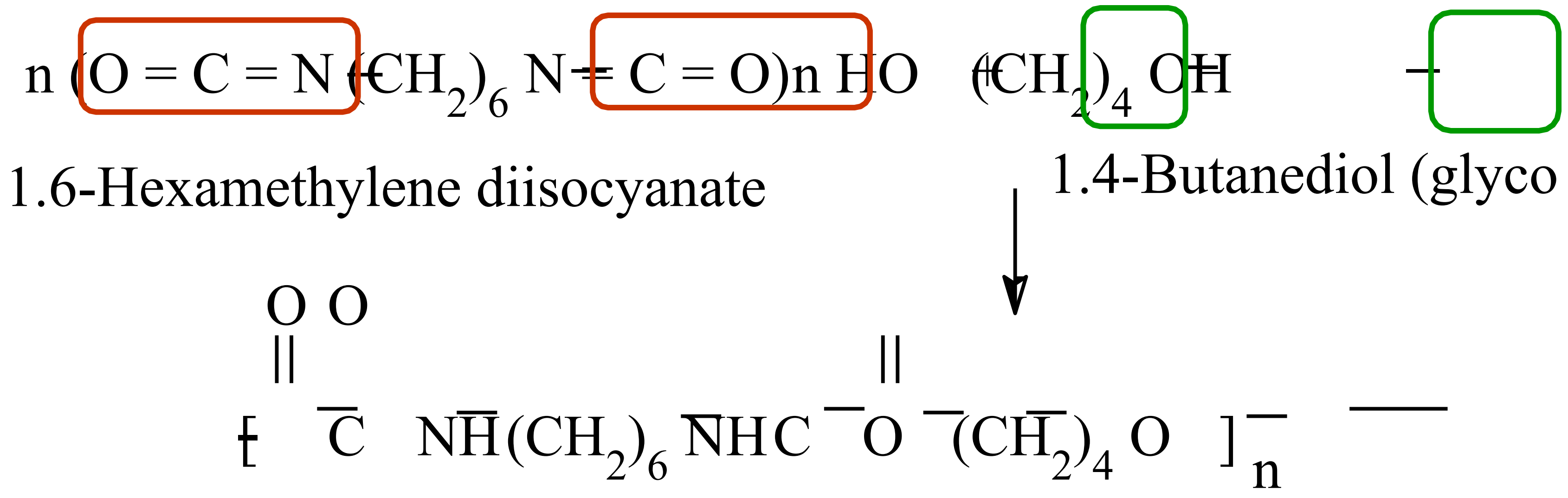


Condensation Polymerization

Growth Polymerization

Polyurethane

- Polyurethane polymers are formed through step growth polymerization, by reacting a monomer (with at least two isocyanate functional groups R−N=C=O) with another monomer (with at least two Hydroxyl or alcohol groups) in the presence of a catalyst.



$$n\,(O=C=N-(CH_2)_6-N=C=O)\quad n\,HO-(CH_2)_4-OH \longrightarrow \left[-\overset{\overset{O}{\|}}{C}-NH(CH_2)_6NH\overset{\overset{O}{\|}}{C}-O-(CH_2)_4O-\right]_n$$

Polyurethane

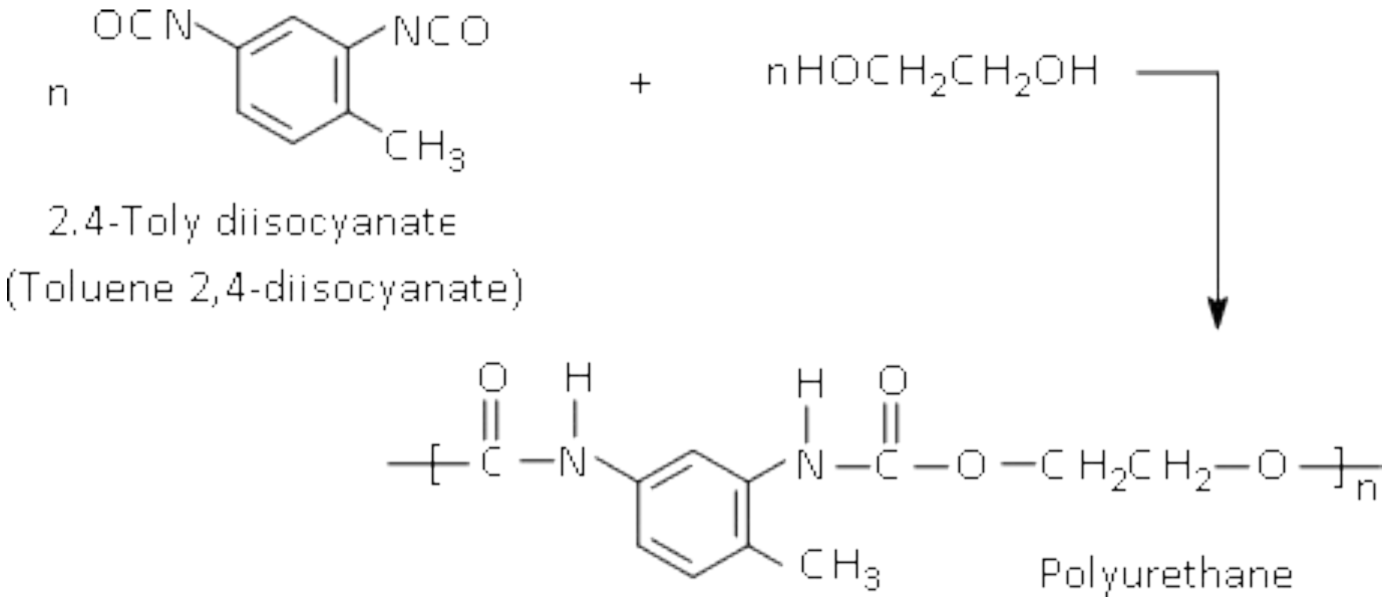
Condensation Polymerization

Growth Polymerization

- **Polyurethane**

Synthesis of Aromatic Polyurethane

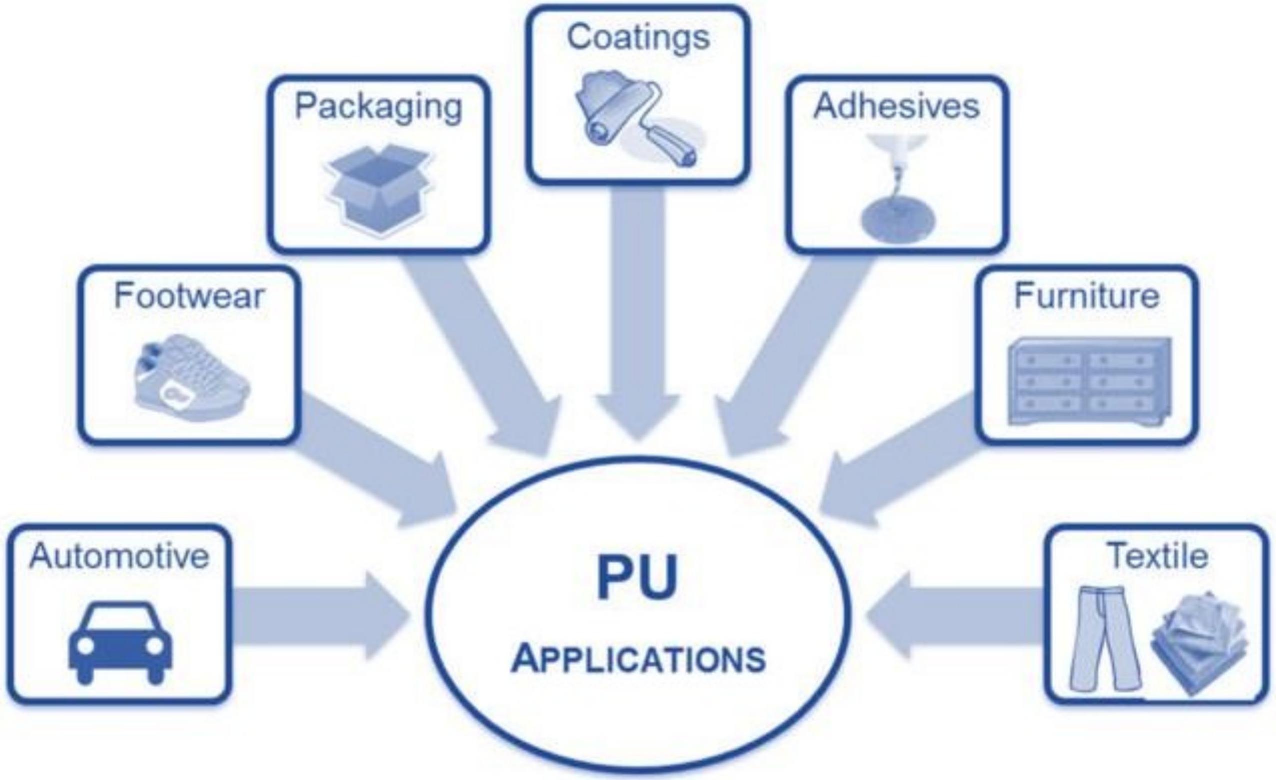
Primary aromatic diisocyanates: toluene diisocyanate (TDI) used in the production of Aromatic polyurethanes; as follow:



- This is a step-growth polymerization, but unlike other many polymerization such as; polyamides & polyesters ***no small molecule is eliminated***.

▪ Applications & Uses of Polyurethane

Polyurethanes are one of the most versatile families of polymers. They can be prepared from a wide variety of materials exhibiting extremely different properties and therefore, a high variety of applications.



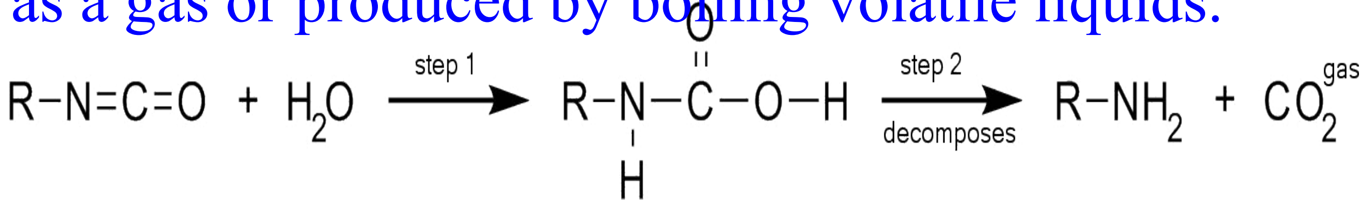
Condensation Polymerization

Growth Polymerization

- **Polyurethane Foam**

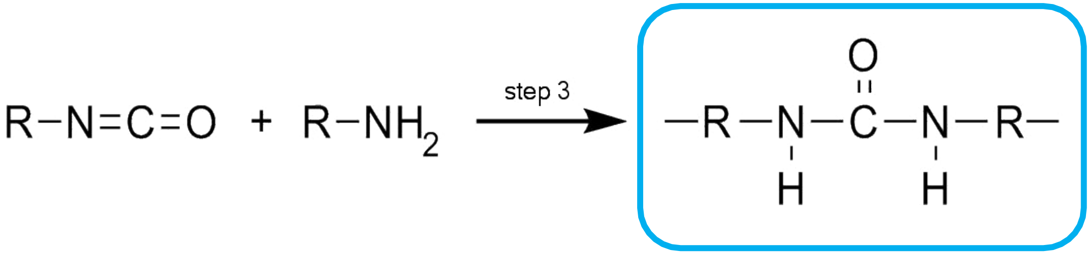
One of the most desirable attributes of polyurethanes is their ability to be turned into foam. Making a foam requires the formation of a gas at the same time as urethane polymerization is

occurring. The gas can be carbon dioxide, either generated by reacting isocyanate with water. Or added as a gas or produced by boiling volatile liquids.



$$R-N=C=O + H_2O \xrightarrow{\text{step 1}} R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[\text{decomposes}]{\text{step 2}} R-NH_2 + CO_2^{\text{gas}}$$

The amine reacts with more isocyanate to give a substituted urea which tends to form separate (Hard segment) phases consisting mostly of polyurethane.



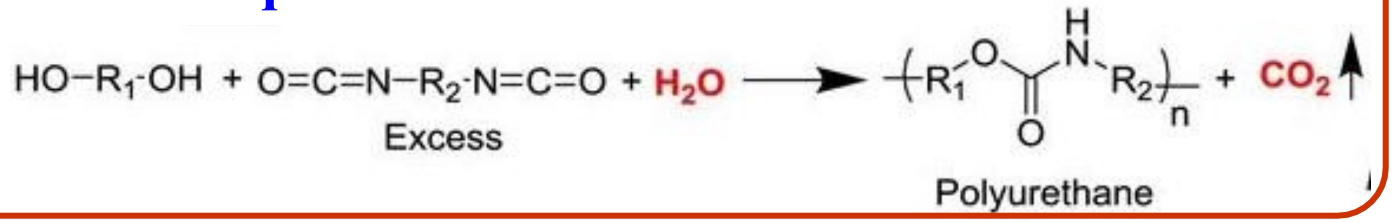
$$R-N=C=O + R-NH_2 \xrightarrow{\text{step 3}} \boxed{-R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-R-}$$

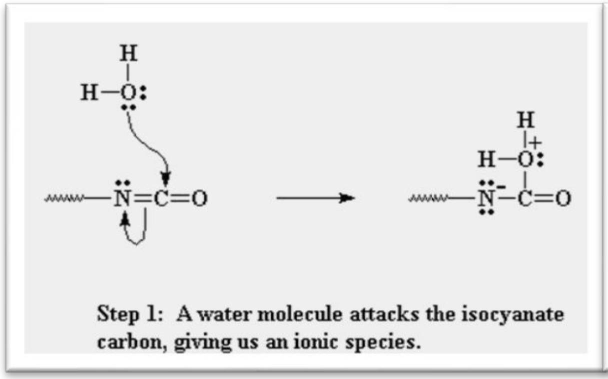
Condensation Polymerization

Growth Polymerization

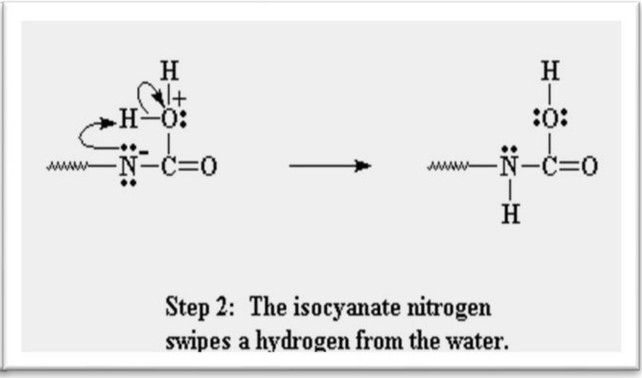
▪ Polyurethane Foam

General Equation

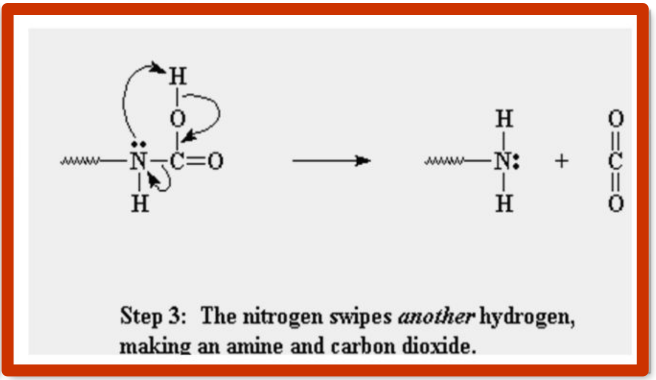




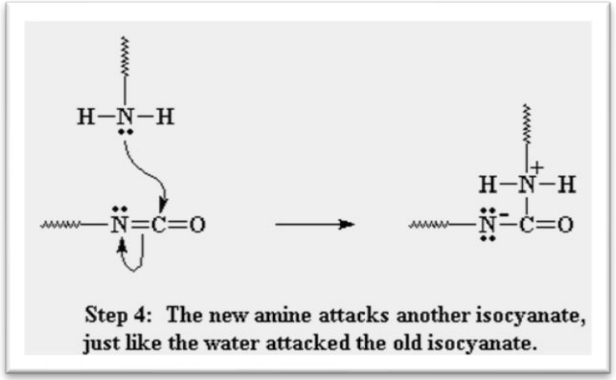
Step 1: A water molecule attacks the isocyanate carbon, giving us an ionic species.



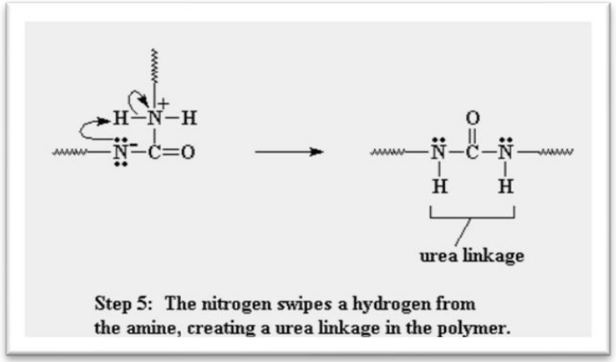
Step 2: The isocyanate nitrogen swipes a hydrogen from the water.



Step 3: The nitrogen swipes *another* hydrogen, making an amine and carbon dioxide.



Step 4: The new amine attacks another isocyanate, just like the water attacked the old isocyanate.



Step 5: The nitrogen swipes a hydrogen from the amine, creating a urea linkage in the polymer.

- When the polymerization reaction begins, the mixture is a liquid, and carbon dioxide produced is bubbled away.
- During the reaction progresses, and molecular weight increases, the mixture will become more and more viscous. As consequence, the carbon dioxide bubbles will be trapped in the viscous liquid.
- When the polymer finally solidifies, the CO_2 gas bubbles trapped and make the polymer a foam.

Condensation Polymerization

Growth Polymerization

Polyurethane Foam Application

❑ Building Insulation

Prevents air, moisture, vapor and sound infiltration, as well as reduce energy usage and heating and cooling costs.

polyurethane foam also, helps absorbing noise in sport halls but also in many other places of leisure such as theatres and cinemas.

❑ Transportation

The main applications of polyurethane foam in transport applications are for trimming, seats, headrests, (air-conditioning) filters and acoustic insulation

Condensation Polymerization

Growth Polymerization

▪ Polyurethane Foam Application

❑ paint rollers

Foam paint rollers are among the most popular paint application tools worldwide.

❑ Furniture and bedding

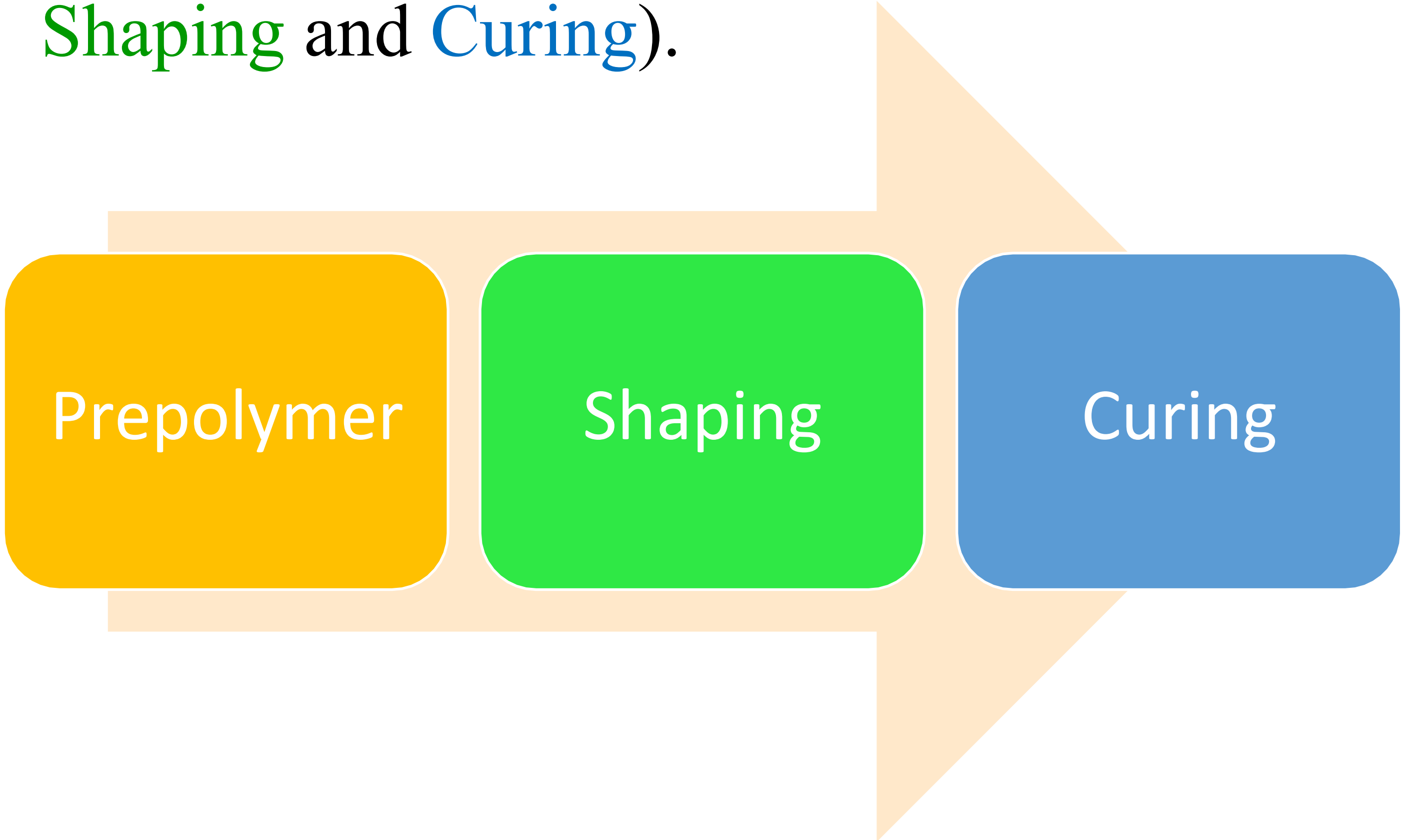
Polyurethane foams adapt to and support the body’s contours. They are an excellent and safe filling material for seating cushions and mattresses and can be produced to the density required by the manufacturer.

❑ Polyurethane Foam in Shoes & Clothing

Flexible polyurethane foam is used extensively by the clothing, Jackets, gloves and shoe industry.

NETWORK POLYMERS

Three steps are needed to prepare a network polymer. (Prepolymer- Shaping and Curing).



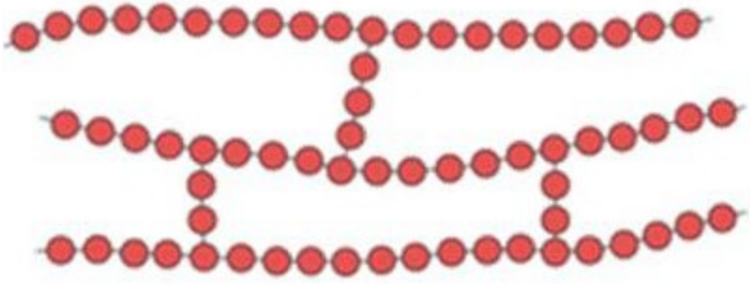
Condensation Polymerization

Cross-linked Polymerization

II. Crosslinked Polymers

- In these type of polymers, monomeric units are linked together to constitute 3D network.

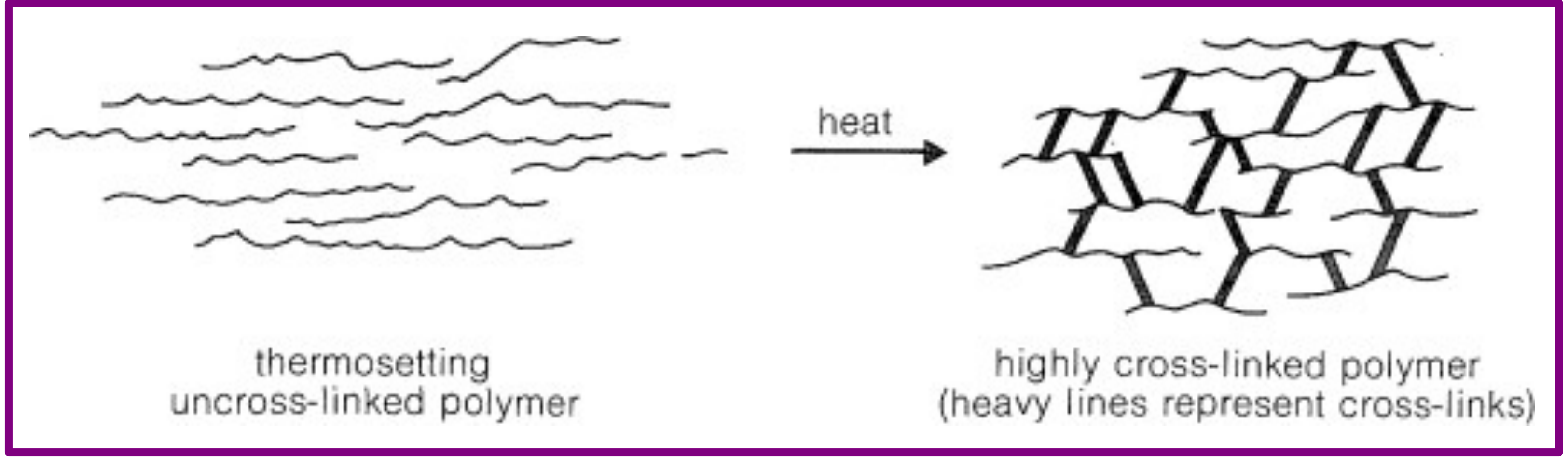
- The links involved are called cross links. And they are **hard**, **rigid** and **brittle** due to their network structure.



Condensation Polymerization

Cross-linked Polymerization

II. Crosslinked Polymers



Examples

1 Polyesters

2 Polyurethanes

3 Urea formaldehyde resins
4phenol formaldehyde resins

5-Epoxy resins

Condensation Polymerization

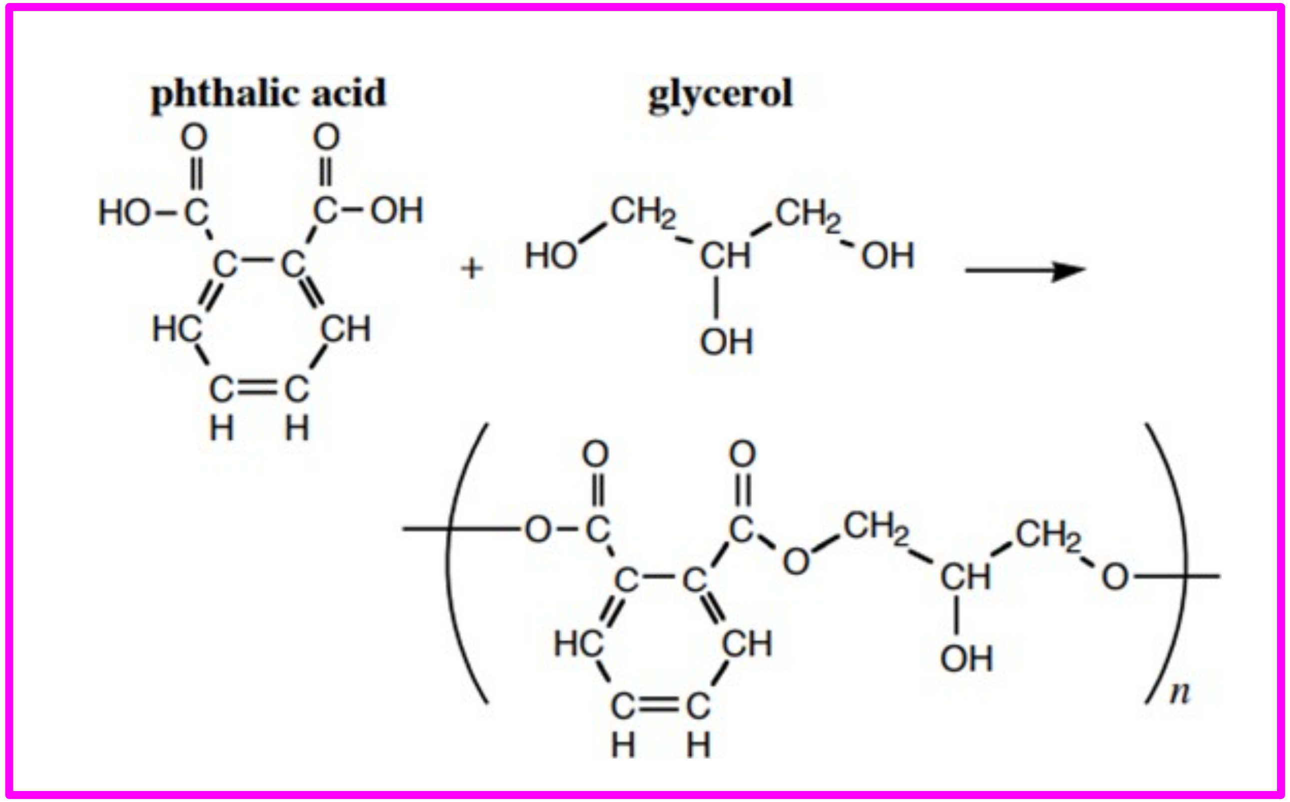
Cross-linked Polymerization

II. Crosslinked Polymers

1- Cross linked Polyesters

Cross linked polyesters can be obtained by reacting phthalic anhydride and glycerol in the presence of metal acetate.

Reaction scheme for the Preparation of Glypal



Glyptal resin

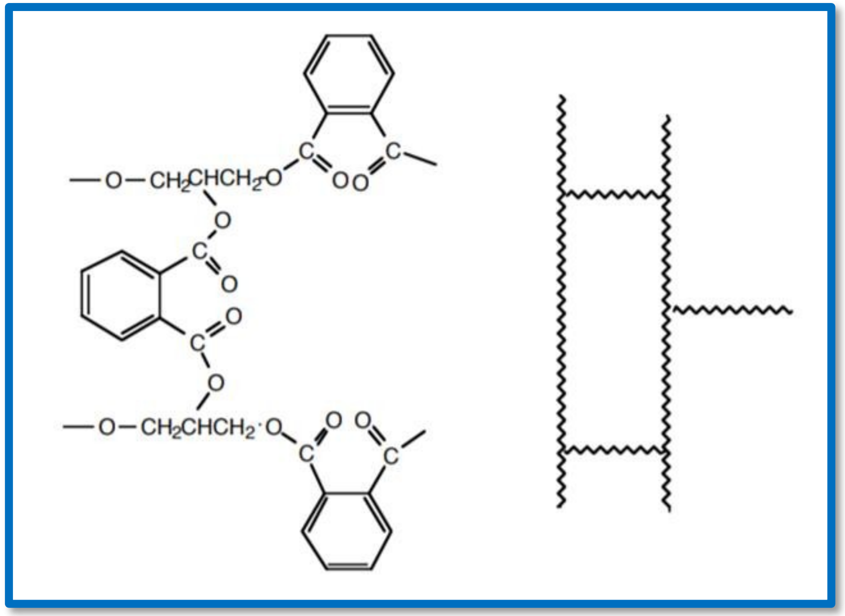
Glyptals are used in paints, lacquers and surface coatings.

II. Crosslinked Polymers

Cross-linked Polymerization

1- Cross linked Polyesters

Glyptal has an additional feature to it in that its properties can be modified by a process known as crosslinking. **A crosslinked polymer** *is one in which the long chains of molecules are joined to each other by covalent bonds*.

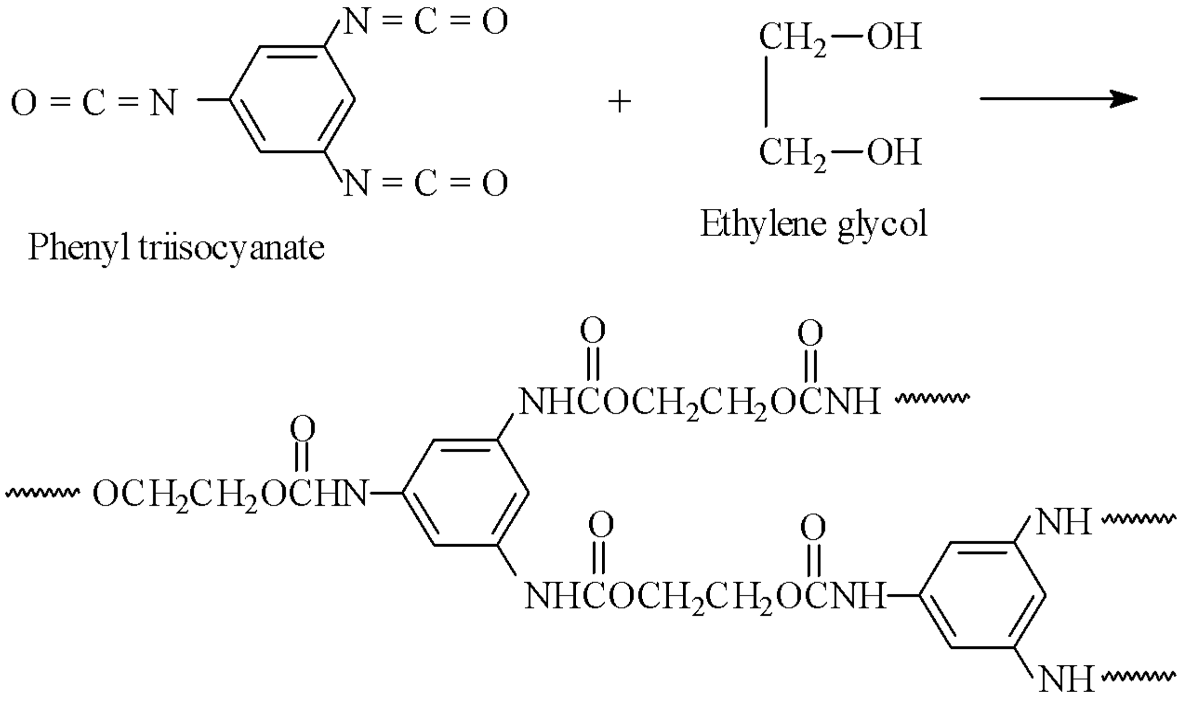


The link that is formed in Glyptal is shown above in the Figure, along with a diagram which illustrates the cross- linking of several polymer strands.

II. Crosslinked Polymers

2- Cross linked Polyurethane

- In such case using tri-isocyanate with ethylene glycol is a good way to form crosslinked Polyurethane.



Branching and crosslinking tends to increase by time .

What is resin?

- ❑ Resins and polymers are different because resins are compounds while polymers are macromolecules.
- ❑ The molecular weights of resins and polymers are also different; resins are smaller than polymers. polymers have longer chains than resins.
- ❑ Both resins and polymers, however, may occur as natural or synthetic, although polymers are formed by a particular process called polymerization.
- ❑ Resins can be molded into solid materials, they may be thick, viscous fluids or hard, brittle solids.

Natural Resins
Arabic Gum

Synthetic Resins

Cross-linked Polymerization

NETWORK POLYMERS

Formaldehyde prepared by polymerization in two stages.

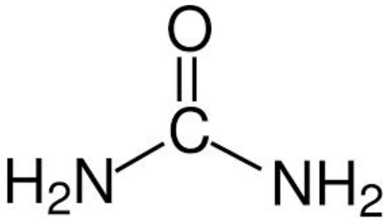
1. Formation of a prepolymer of low molar mass.
2. Prepolymer is forced to flow under pressure to fill a heated mold in which cross linking takes place. ===> highly crosslinked rigid polymer in the shape at the mold.

Since formaldehyde is a difunctional the co-reactants must have a functionality, f > 2.

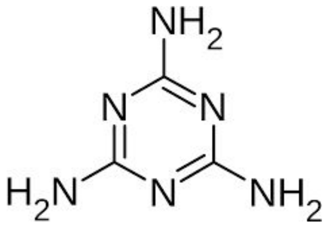
NETWORK POLYMERS

- The most commonly employed to form Network polymers are:

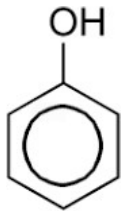
  - Urea (f = 4)



  - Melamine (f = 6)



  - Phenol (f = 3)

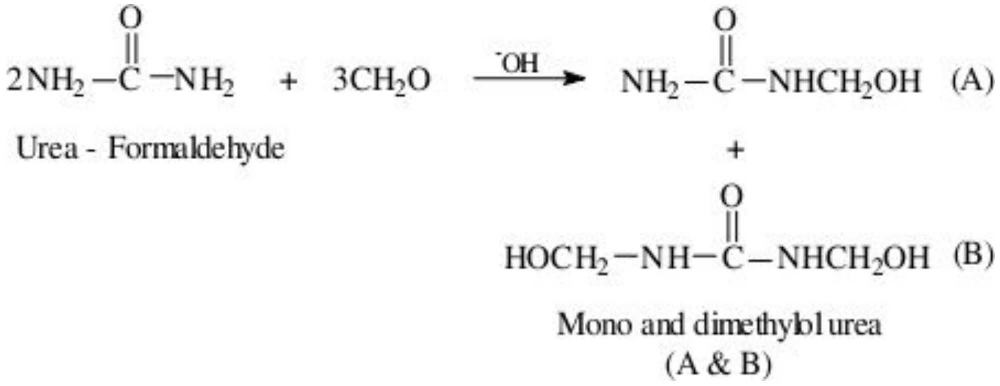


Cross-linked Polymerization

II. Crosslinked Polymers

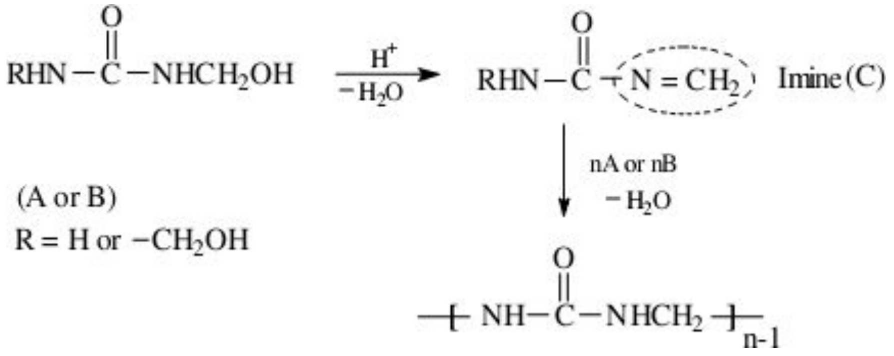
3- Urea Formaldehyde Resins

By Reaction of urea with formaldehyde in the presence of base to form **Methylol**



$$2NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + 3CH_2O \xrightarrow{^-OH} NH_2-\overset{O}{\overset{\|}{C}}-NHCH_2OH \ (A) + HOCH_2-NH-\overset{O}{\overset{\|}{C}}-NHCH_2OH \ (B)$$

Condensation reaction takes place in with formaldehyde in neutral medium or weak acid to give network structure polymer.



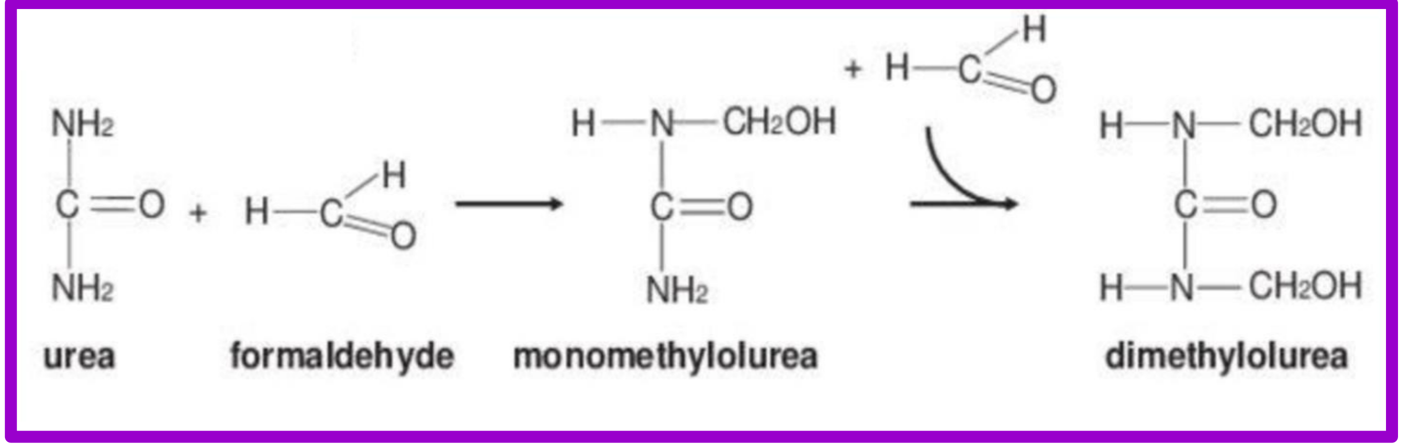
$$RHN-\overset{O}{\overset{\|}{C}}-NHCH_2OH \xrightarrow[-H_2O]{H^+} RHN-\overset{O}{\overset{\|}{C}}-N=CH_2 \ \text{Imine (C)} \xrightarrow[-H_2O]{nA \text{ or } nB} -\!\!\left[NH-\overset{O}{\overset{\|}{C}}-NHCH_2\right]\!\!-_{n-1}$$

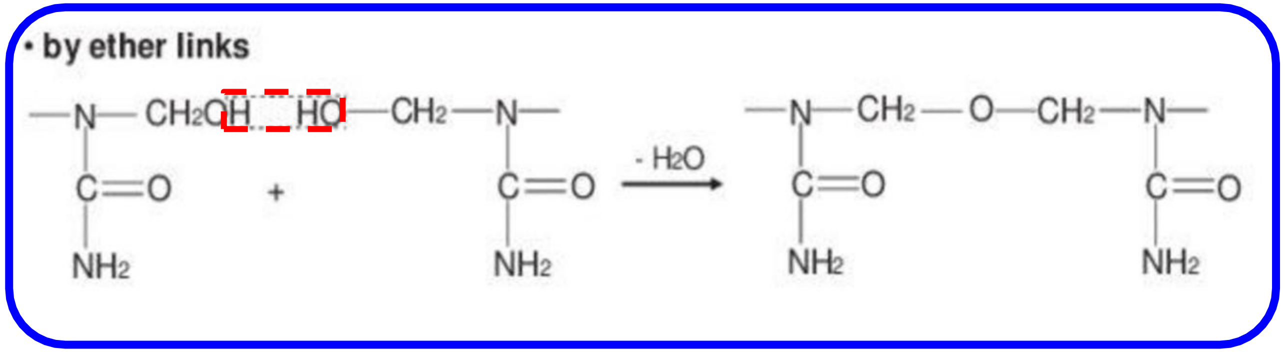
Cross-linked Polymerization

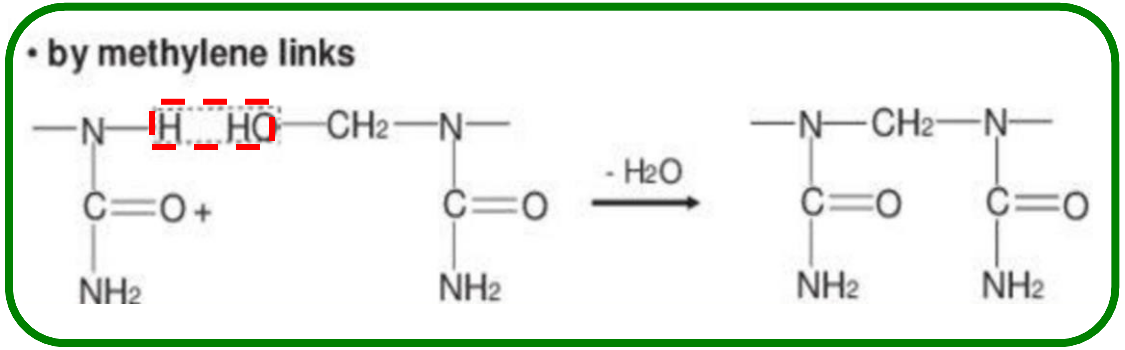
II. Crosslinked Polymers

3- Urea Formaldehyde Resins

By Reaction of urea with formaldehyde in the presence of base to form **Methylol**





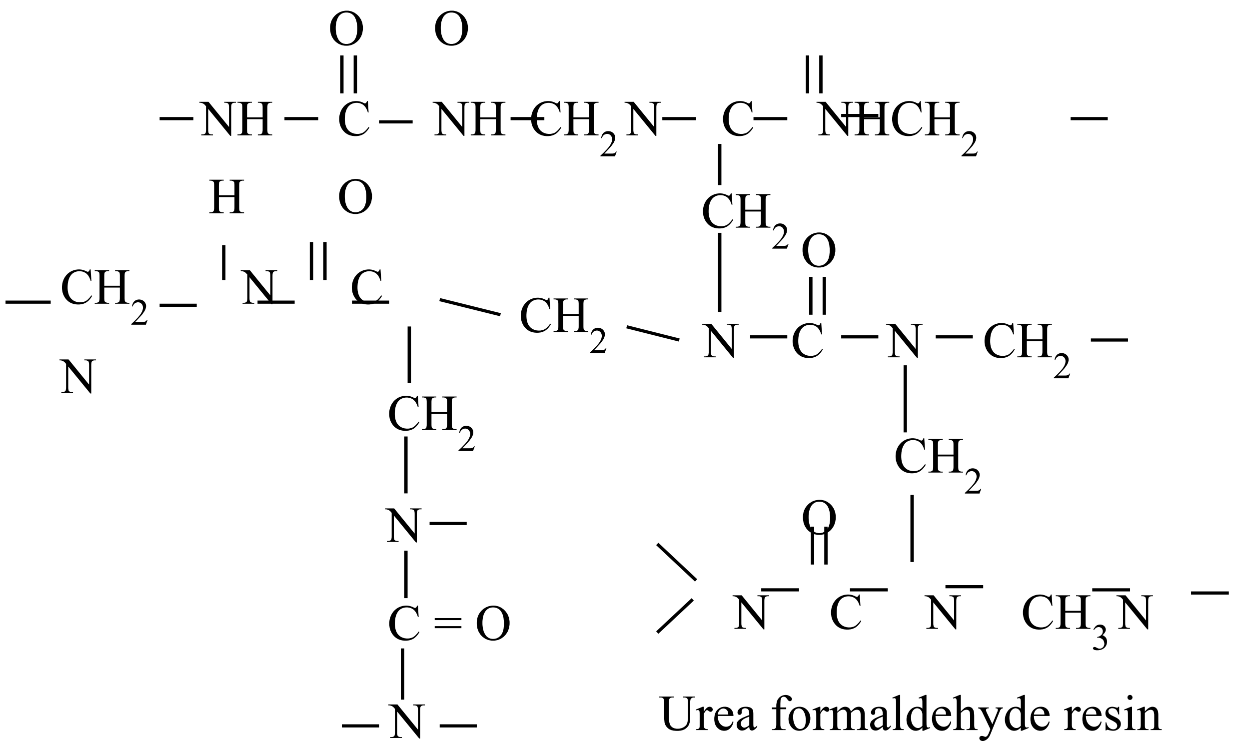


Cross-linked Polymerization

II. Crosslinked Polymers

3- Urea Formaldehyde Resins

The second stage after acid condensation of the methylolureas is to form insoluble cross-linked resins.



Urea formaldehyde resin

II. Crosslinked Polymers

3- Urea Formaldehyde Resins Uses & Applications

- Urea-formaldehyde (UF) resins are the main binders for wood composite boards, such as particleboards, fiberboards or hardwood plywood.

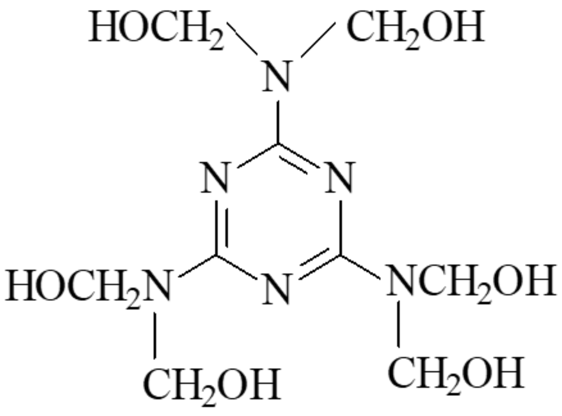
- In the use of UF resins, water solubility, good adhesion, high curing rate, and low cost are the attractive properties.

Cross-linked Polymerization

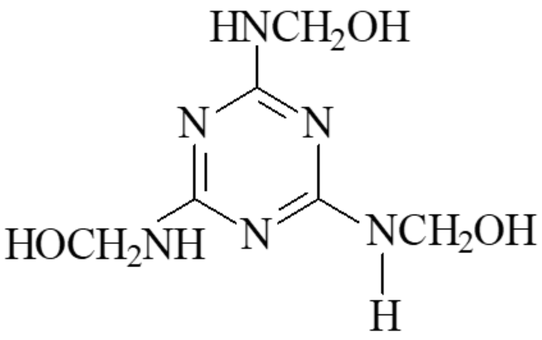
II. Crosslinked Polymers

4-Melamine-Formaldehyde Resins

By using trimethylol & hexamethylol



Hexamethylol



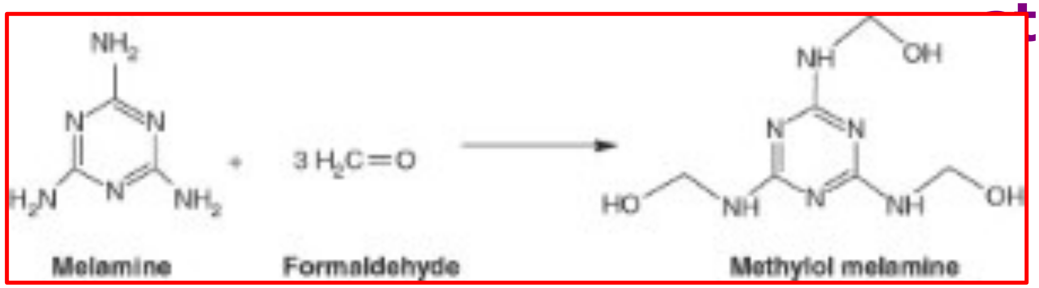
Trimethylol

Condensation Polymerization

II. Crosslinked Polymers

Cross-linked Polymerization

4-Melamine-Formaldehyde Resins

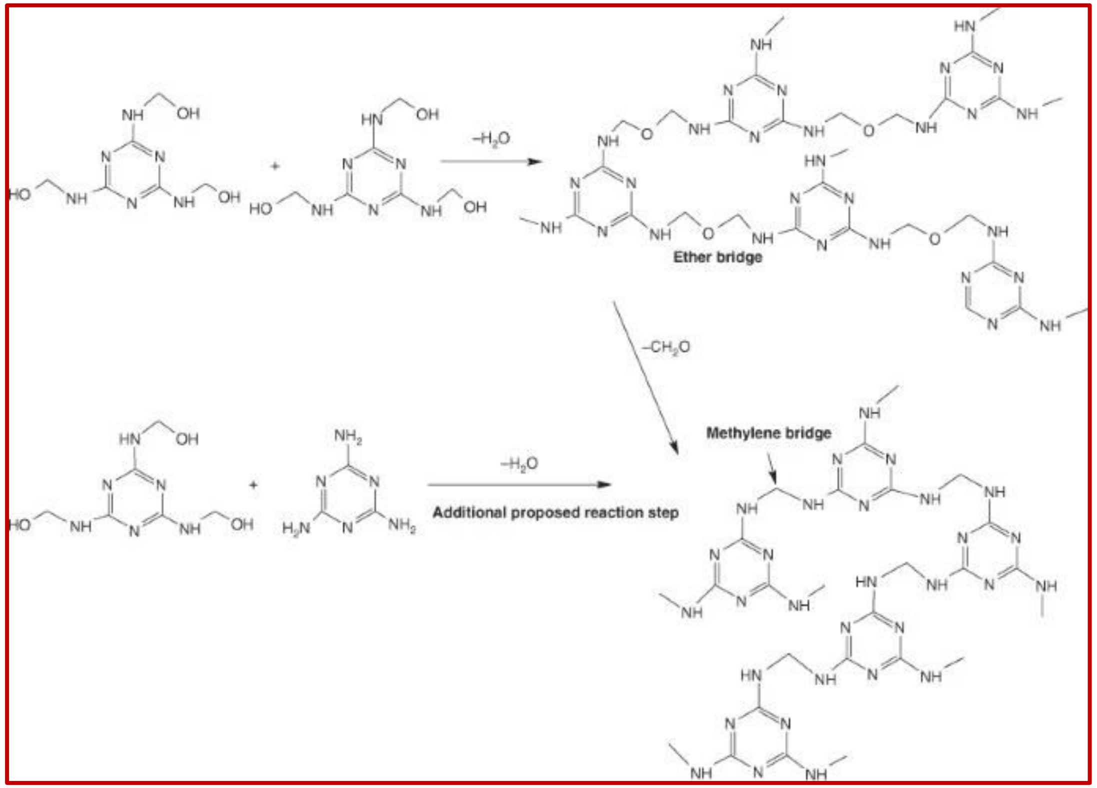


Methylolation step

This step involves direct reaction between melamine and formaldehyde to form methylolamine as follows

Condensation step

This step is more complex and involves multiple reactions that lead to intermediate ether-linkage-containing compounds. These ether linkages are transformed into methylene linkages by the elimination of formaldehyde as described by scheme.



II. Crosslinked Polymers

4 Melamine-Formaldehyde Resins

✔ It has advantage over urea –formaldehyde resins

Example of advantages:

- low cost,
- ease of use under a wide variety of curing conditions,
- low cure temperatures,
- water solubility,
- resistance to microorganisms and to abrasion,
- hardness, excellent thermally stable network.

II. Crosslinked Polymers

5-Phenol-Formaldehyde Resins

- The OH of the phenol activates the *O- & P-* position of the ring.
- Phenol formaldehyde are formed from **the condensation** of phenol with formaldehyde in the presence of alkaline or acidic medium in two stages.

In the first stage

polymer is formed (low molecular weight resin, which can be fused or melt)

In the second stage

the resin is treated to form network polymer

II. Crosslinked Polymers

5-Phenol-Formaldehyde Resins

There are two types of low molecular weight resin:

Resole phenols

Alkaline medium

Novolak phenols

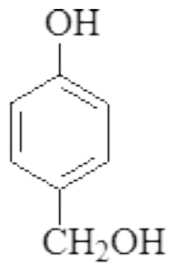
Acidic medium

Cross-linked Polymerization

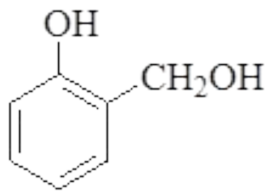
II. Crosslinked Polymers

5-Phenol-Formaldehyde Resins

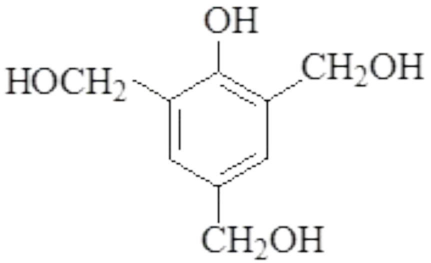
Type 1 **Resole phenols**



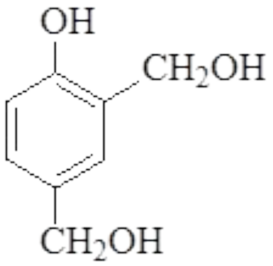
p-Methylol-Phenol



o-Methylol-Phenol



2.4.6- Tri-methylol-Phenol



2,4-Di-methylol-Phenol

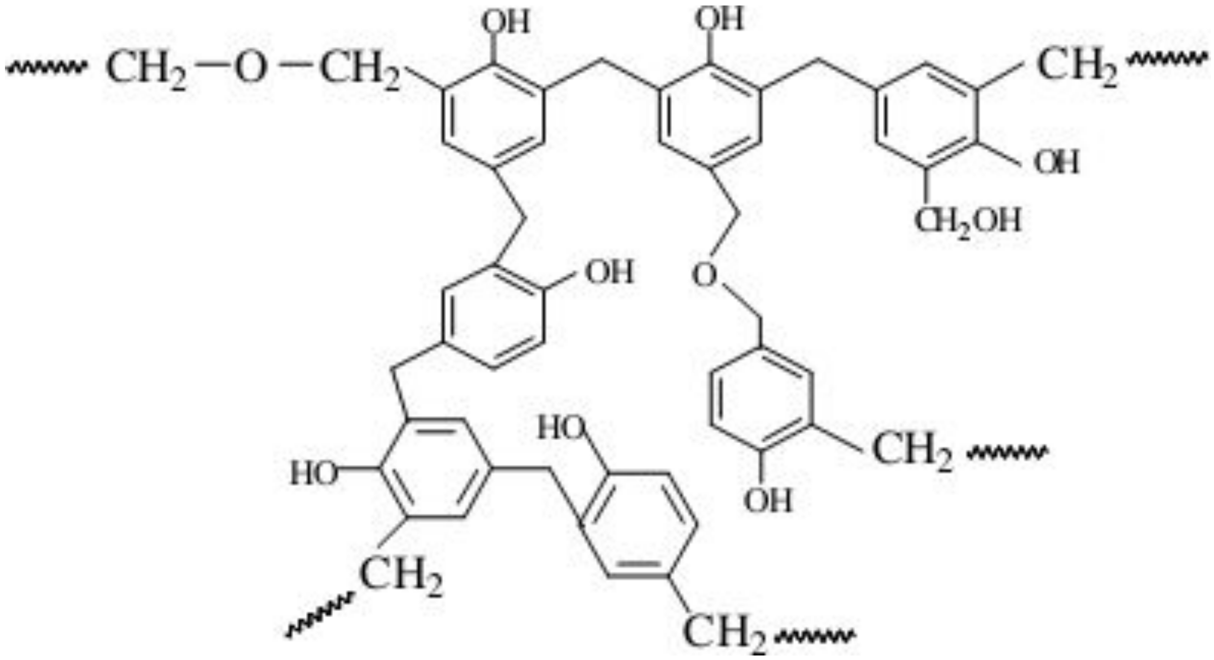
Cross-linked

Polymerization

II. Crosslinked Polymers

5-Phenol-Formaldehyde Resins

- Alkaline catalyst and excess formaldehyde methylene(-CH_2) bridge formation as well as (Oxygen) bridge formation may result in the release of water:

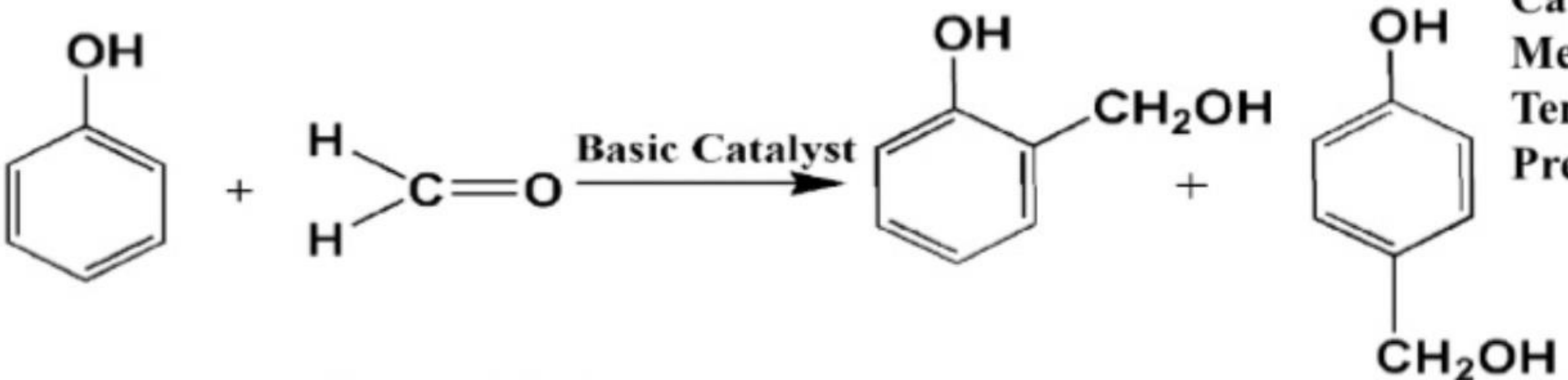


Chemical Structure of Resole Phenol-Formaldehyde Resin

Condensation Polymerization

II. Crosslinked Polymers

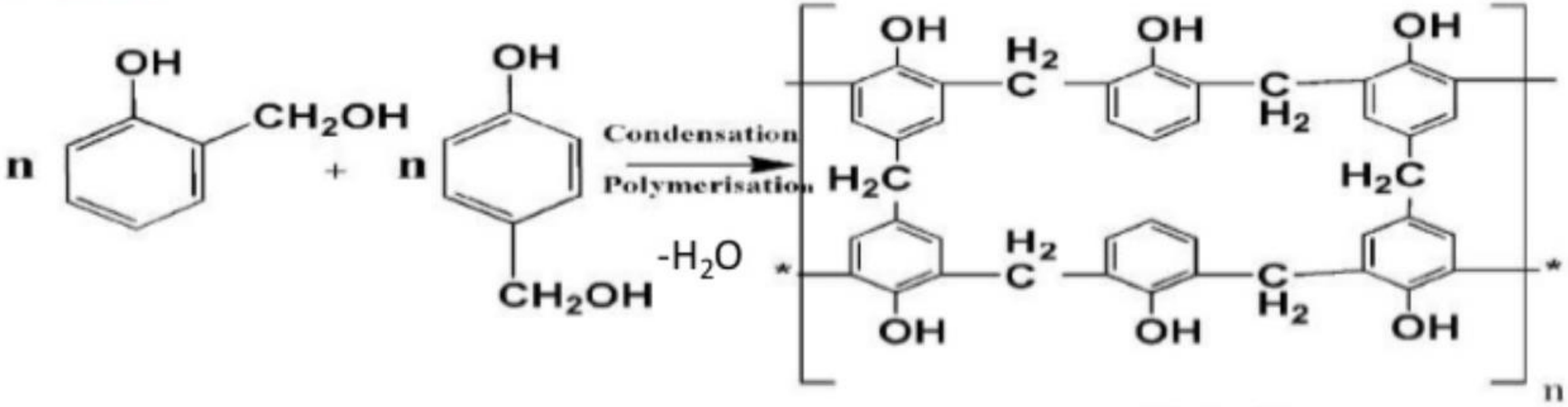
Cross-linked Polymerization



Catalyst: Sodium hydroxide (powdered)
Medium: Distilled Water
Temp: At around 70°C
Pressure: 1 atm

Heat of reaction: 180 cal/g

Resole:



Bakelite
(Cross-linked Polymer)

Temperature:
Hydroxymethyl phenols will crosslink on heating to around 120 °C
By product: Water

Cross-linked Polymerization

II. Crosslinked Polymers

5-Phenol-Formaldehyde Resins

Type 2: Novolak phenols

❑ An acidic catalyst and a molar excess of phenol to formaldehyde are conditions used to make Novolak resins, (formaldehyde to phenol molar ratio of less than one [F:P < 1]).

❑ A Novolak resin has no reactive methylol groups in its molecules, and therefor incapable of condensing with other novolak molecules in heating with out hardening agents.

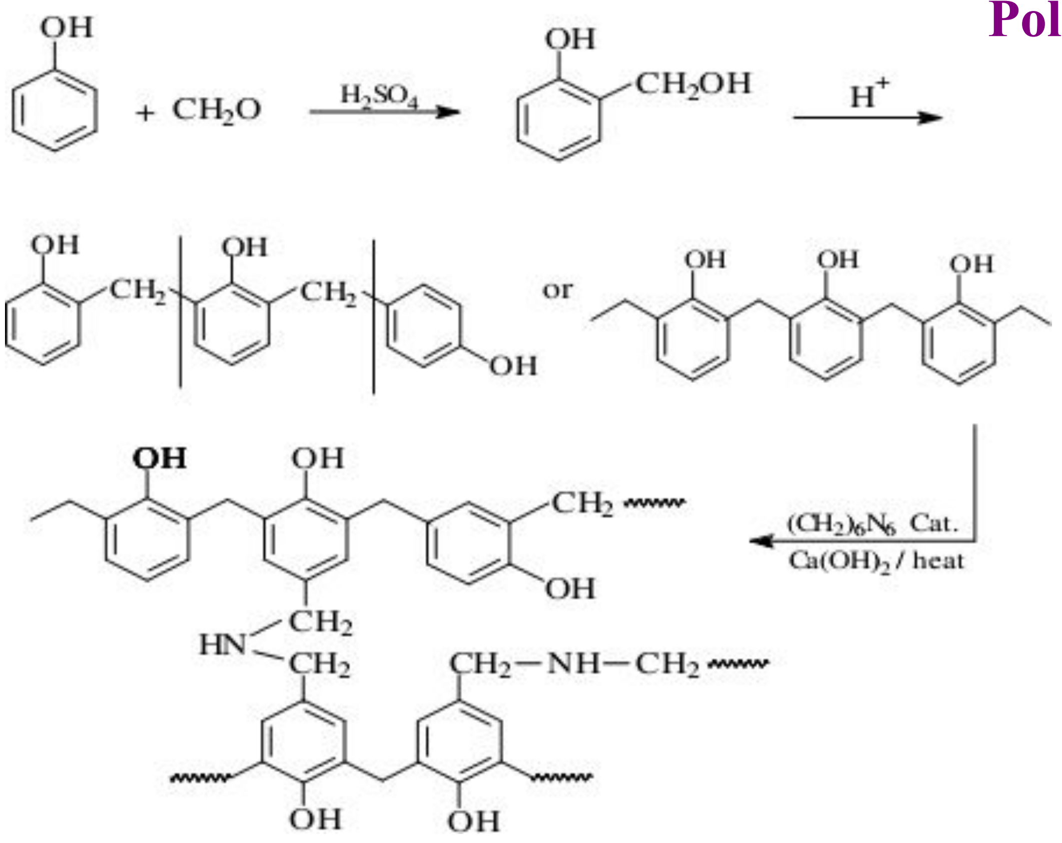
❑To complete resinification, additional formaldehyde is added to cross-link the Novolak resin. Phenolic rings are considerably less active as nucleophilic centers at an acid pH, due to hydroxyl and ring protonation.

Cross-linked Polymerization

II. Crosslinked Polymers

5-Phenol-Formaldehyde Resins

Type 2: Novolak phenols



- ❑ The protonated aldehyde is more effective electrophile. Thesubstitutionreaction proceeds slowly and condensation follows as a result of further protonation and the creation of a benzylcarbonium ion, which acts as a nucleophile.

- ❑ The final novolak resin is unable to react further without the addition of a cross-linking agent.
- ❑ The most common phenolic resin cross-linking agent (**hardener**) is hexamethylenetetramine, also known as hexamine,

II. Crosslinked Polymers

4-Phenol-Formaldehyde Resins

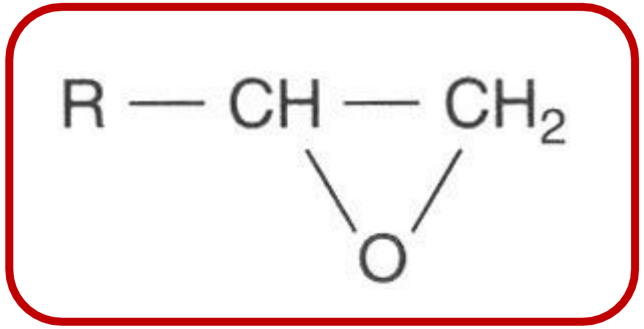
Resole	Novolak
Reaction is carried out in basic medium.	Usually obtain in acidic medium.
Phenol functionality is ortho, meta & para	Phenol functionality is ortho and para.
Phenol: formaldehyde is **1**:**1.2**	Phenol: formaldehyde is **1**:**0.8**
Already cross-linked	Can be cross-linked
Not soluble after complete cross-linking.	Soluble in alcohol, lower ester, ketone and dilute alkali.
Very high MW **due to** the three dimensional crosslinking structure	Average MW is between 600-1500
Melting point is starts at > 350° C	Melting point is between 100° C & 140° C
Thermoset polymer	Thermoplastic

Cross-linked Polymerization

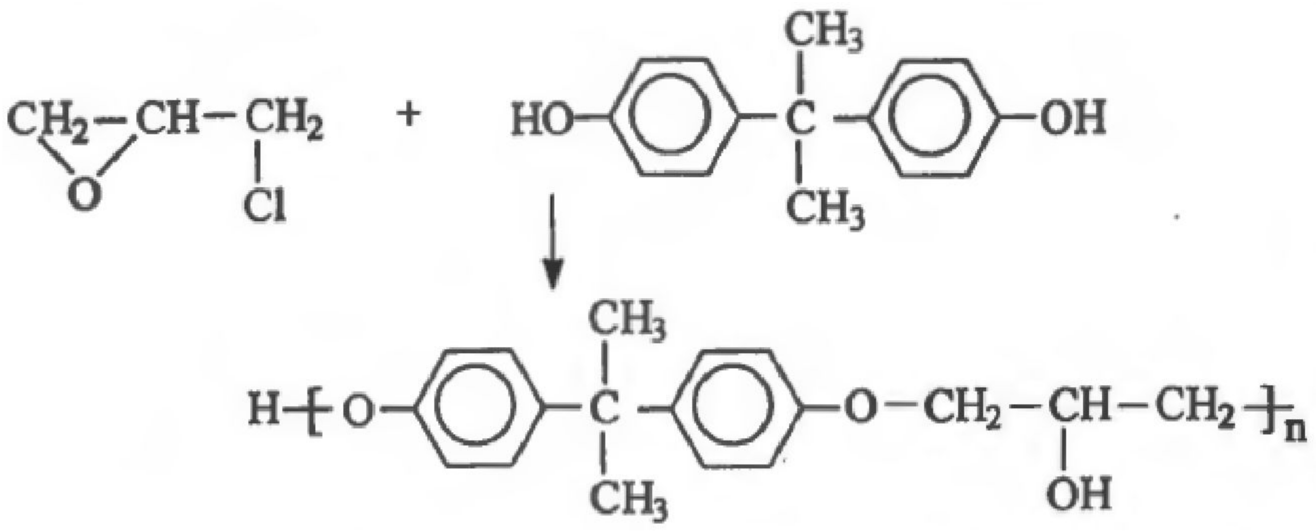
II. Crosslinked Polymers

6-Epoxy Resins

- They are formed from prepolymer containing the epoxide end group
- The reaction of **Epichlorohydrin** **with** **Bisphenol A** in alkali media gives a linear polymer.



Epoxide group

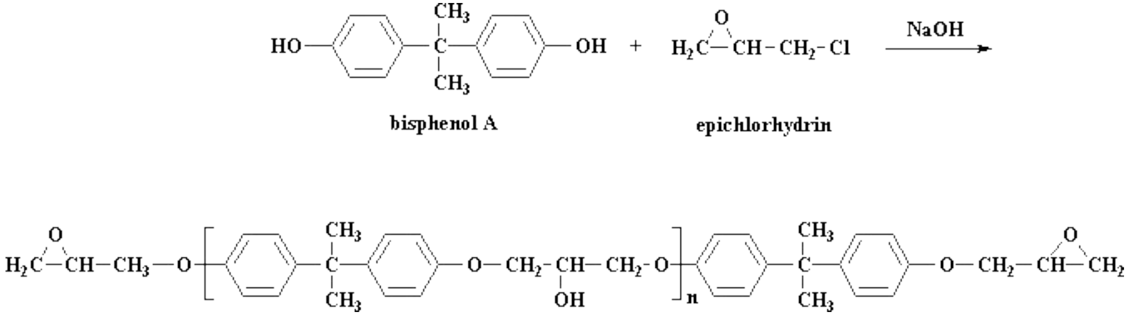


II. Crosslinked Polymers

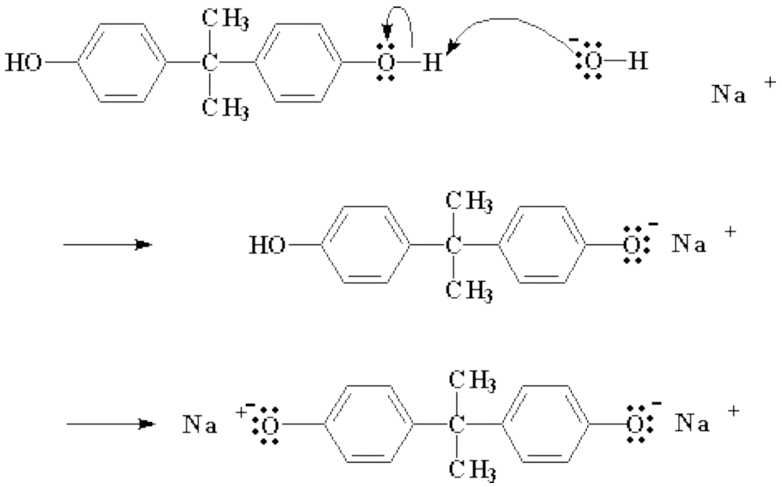
Reaction Mechanism of forming Epoxy Resins

Stage 1. **Making the Diepoxy**

- The following stage shows us how the prepolymer is obtained using **bisphenol A** and **epichlorohydrin**.



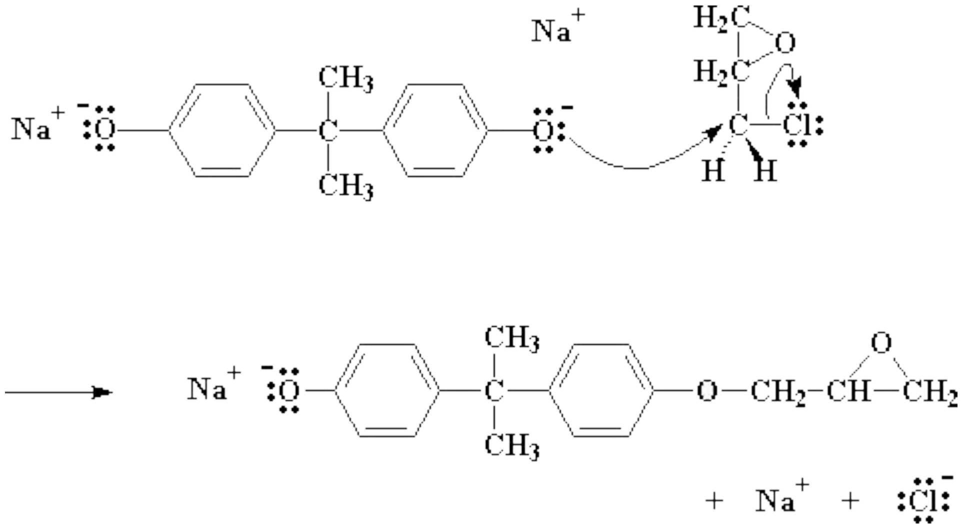
- First, Formation of **bisphenol A sodium salt** as with the help of **NaOH**.



II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

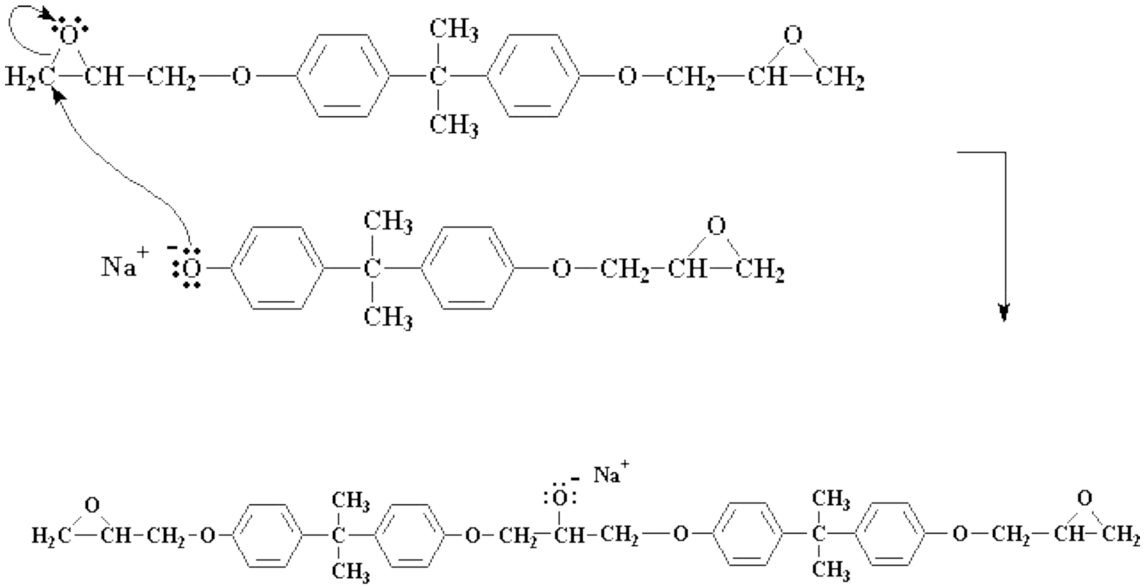
- The oxygen with three pairs of electrons will share its electrons with carbon atom on a nearby epichlorohydrin. The chlorine atom next to supposed to be sharing a pair of electrons with that carbon, but being electronegative as it is, tends to leave the molecule with electron pair.



II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

- The bisphenol A salt groups can react with epichlorohydrin in similar manner depending on the ratio between molecules.

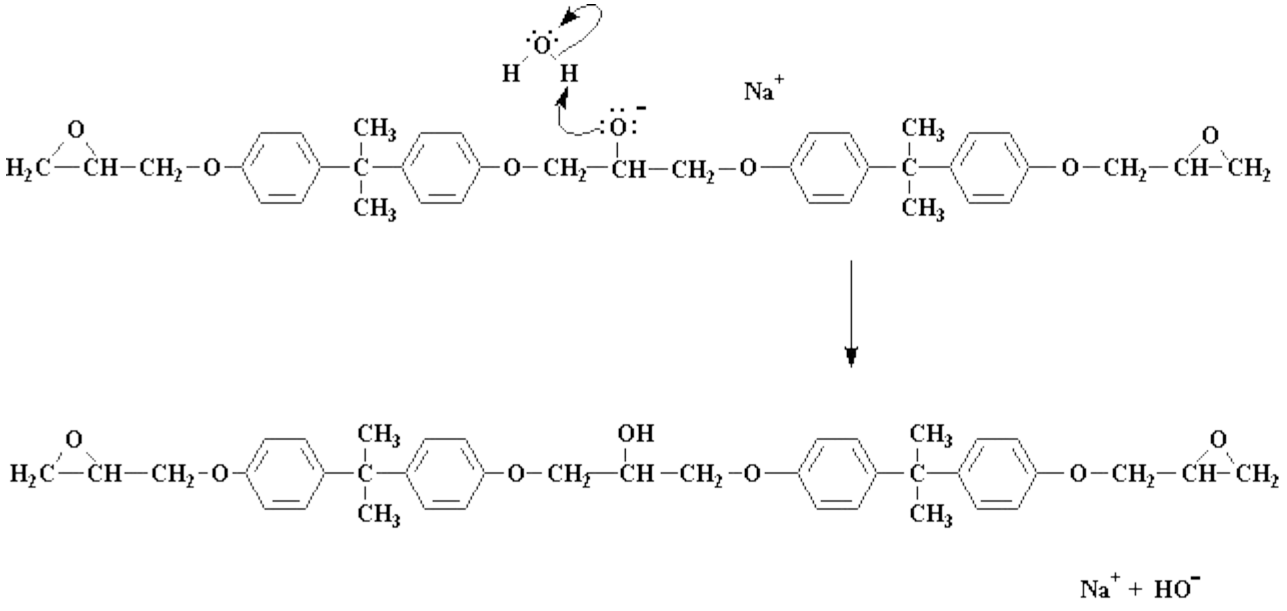


The sodium salt attacks the epoxide, giving a dimer. That dimer is a sodium salt.

II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

- If three molecules of epichlorohydrin for every two molecules of bisphenol A, a dimer is formed.



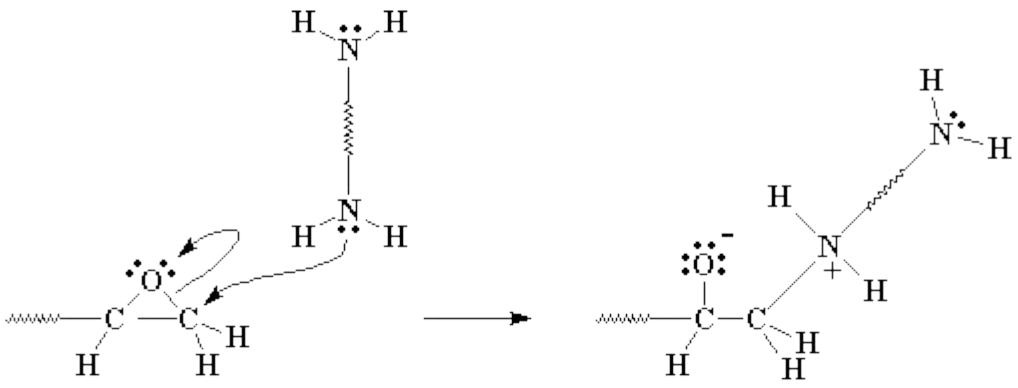
A water molecule comes along and the negative oxygen swipes a proton from it. This way we get an alcohol group, and we get our NaOH back.

II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

Stage 2. Curing the Diepoxy with a Diamine

- The lone pairs of electrons on the amine groups towards those epoxy groups, and they're going to share with the carbon near by the electronegative oxygen.

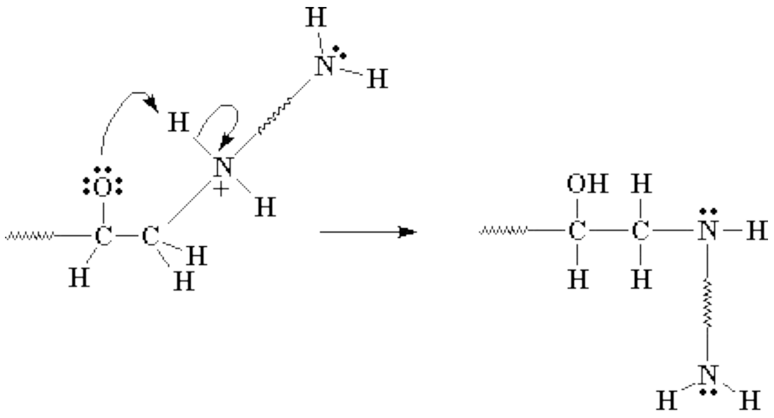


The diamine's electrons attack the carbon atom next to the epoxide oxygen, giving us a negative charge on the oxygen, and a positive charge on the nitrogen.

II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

- The bond between the carbon and the oxygen is broken, and a new bond forms between the carbon and the amine nitrogen, then a negative charge on the oxygen, and a positive charge on the nitrogen is obtained.
- one of those non-bonding electrons on the oxygen atom will attack the hydrogen attached to the positive nitrogen, as a result the hydrogen will separate from the nitrogen.



The oxygen's extra pair of electrons swipes a hydrogen from the ammonium nitrogen, making an alcohol group and an amine group.

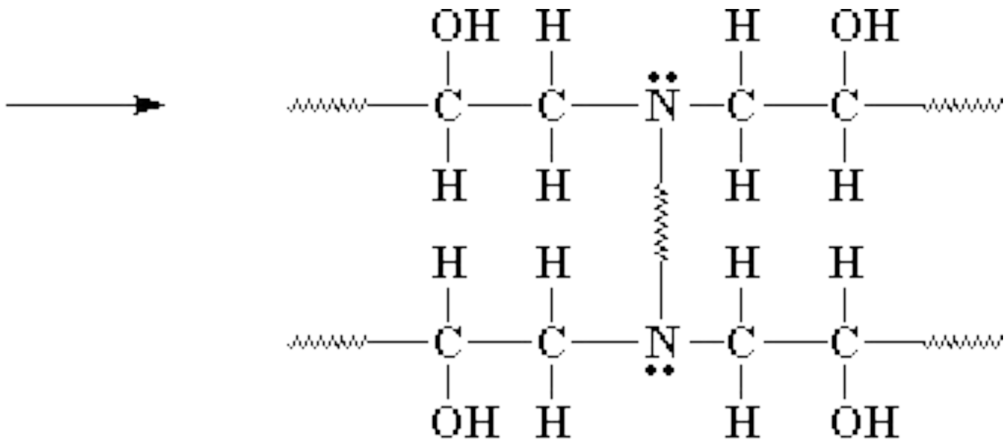
Condensation Polymerization

Cross-linked Polymerization

II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

- The amine group still has a hydrogen left on it, and can react with another epoxy group, in the exact same manner.



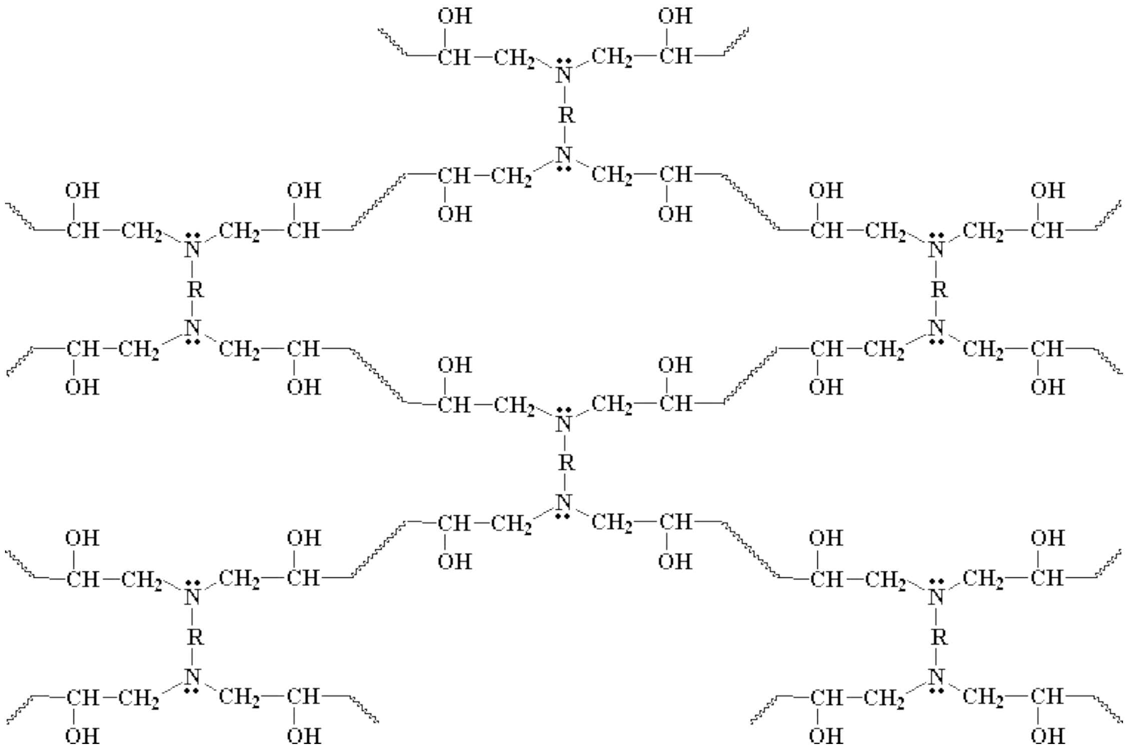
Then two more epoxide groups add to the amine at the other end of the diamine, eventually tying all the diepoxy oligomers into one big molecular network.

Cross-linked Polymerization

II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

- When all the diamine molecules and all the diepoxy molecules become tied together (in the same manner) giving finally the cross-linked resins.



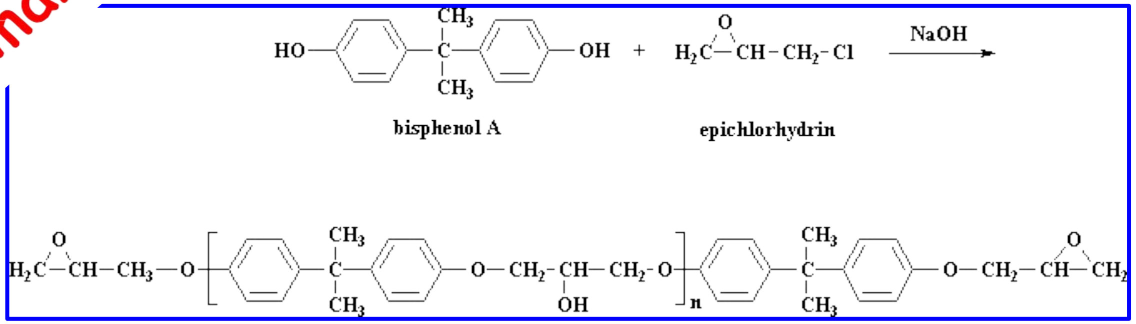
Condensation Polymerization

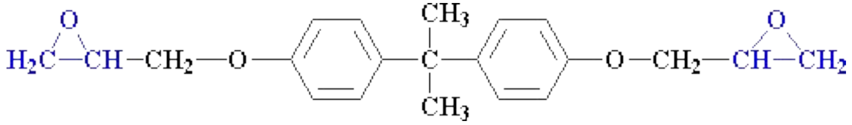
II. Crosslinked Polymers

Reaction Mechanism of forming Epoxy Resins

Cross-linked Polymerization

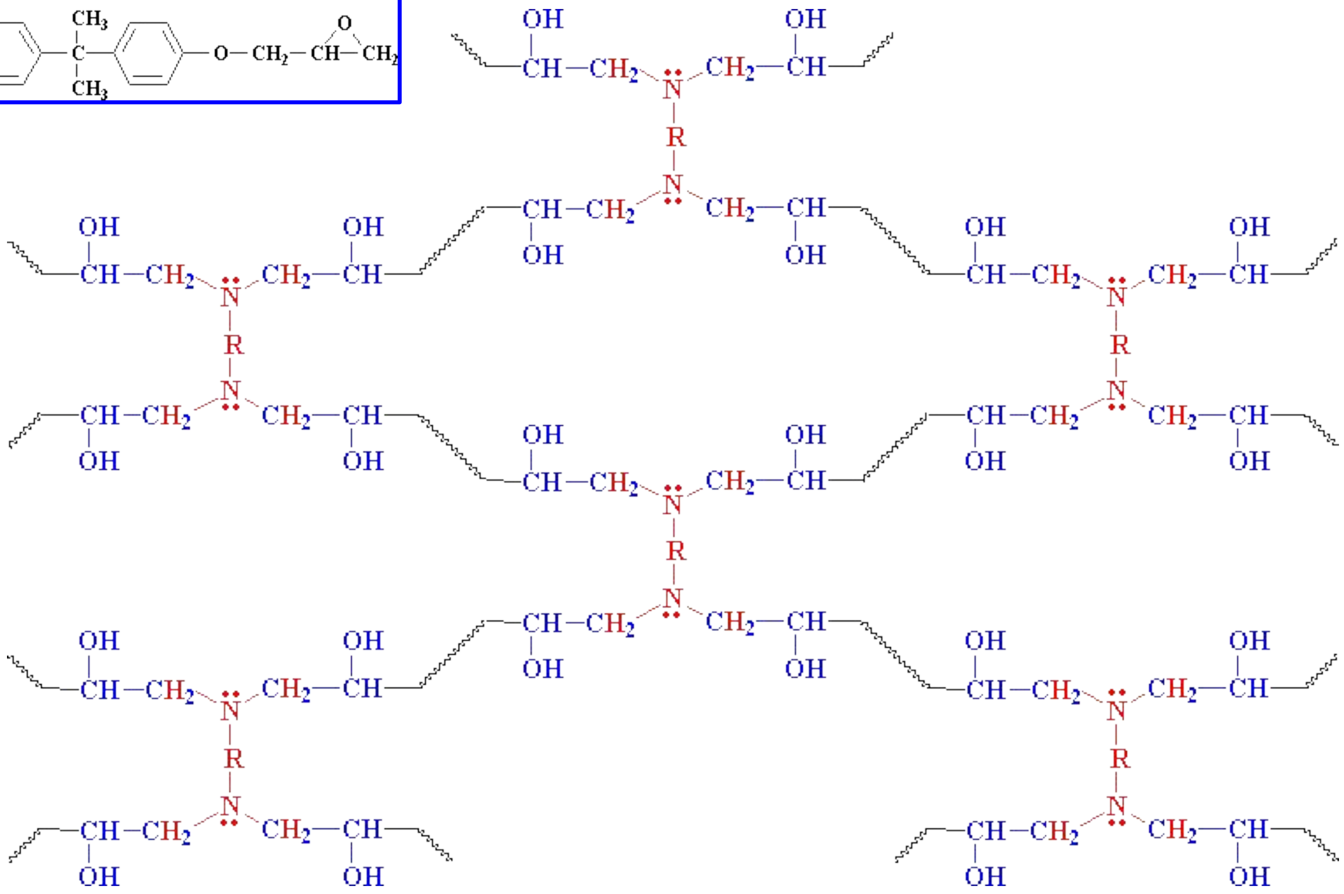
Reaction Summary





Diepoxy unit; n=1

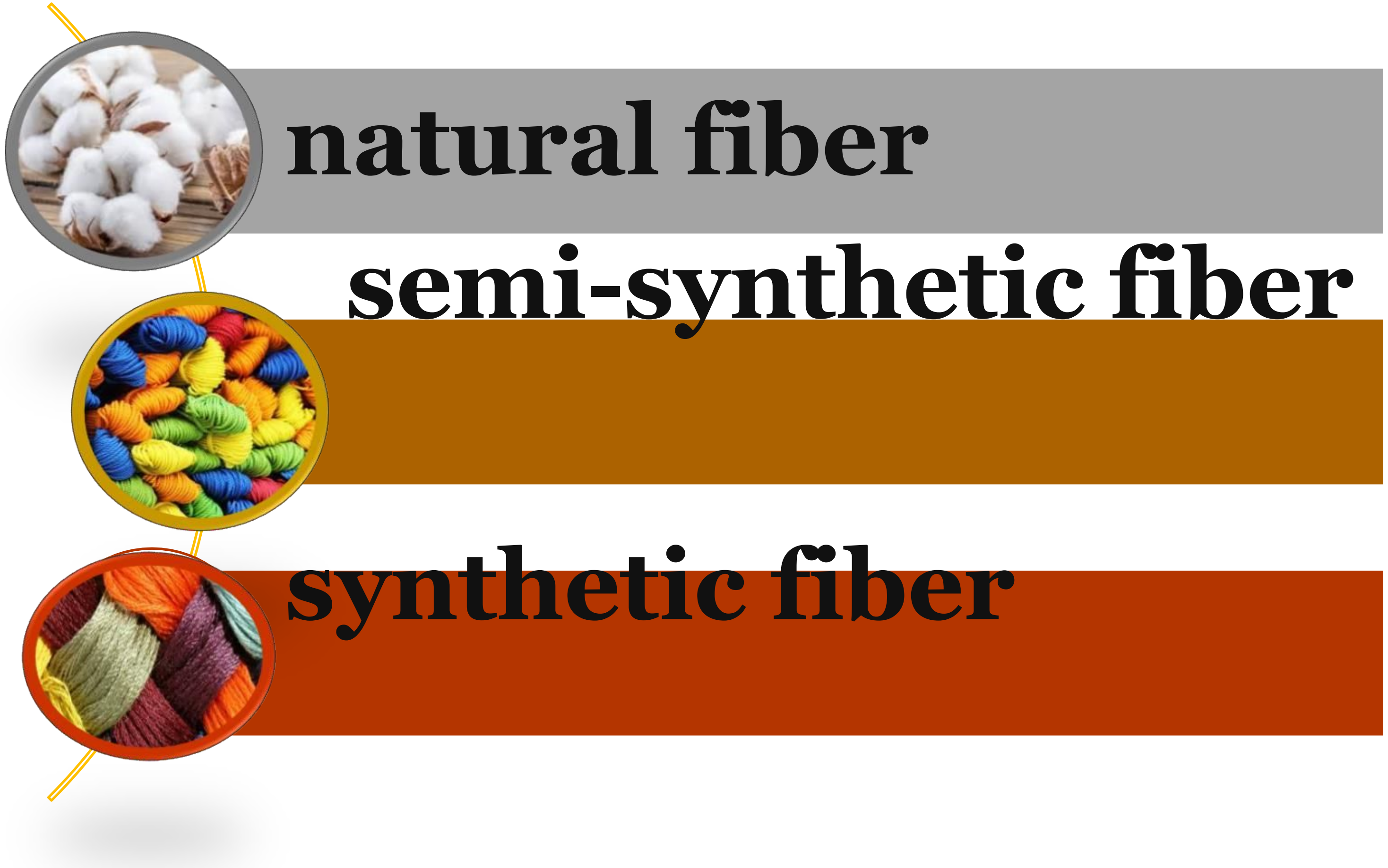
a diamine



Cross-linked Polymerization

III. Synthetic fibers Polymers

There are three types of fibers:



- **natural fiber**
- **semi-synthetic fiber**
- **synthetic fiber**

III. Synthetic fibers Polymers

Natural fiber

A natural fiber is collected from plants or animals. It’s that simple. Such as, silk, cotton, cashmere, sheep wool, and linen

Semi-synthetic fibers

Semi-synthetic fibers are made from natural raw materials with a naturally occurring **long-chain polymer structure** and are only modified and partially degraded by chemical processes. Most semi-synthetic fibers are cellulose regenerated fibers.

Synthetic fibers

All the synthetic fibers are prepared by a number of processes using raw materials of petrochemicals.

III. Synthetic fibers Polymers

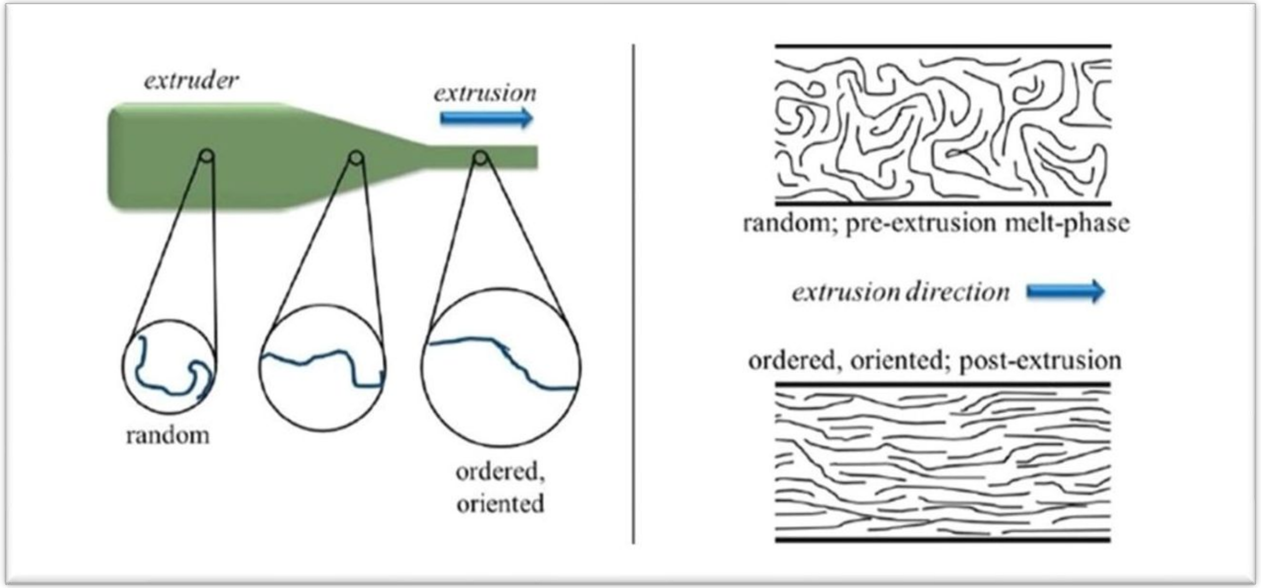
General Properties of Synthetic Fibers

Fibers are defined as filaments with a high ratio of polymer chain length to linear density. To achieve this, fibers must **possess three fundamental** and interrelated polymer properties: **orientation**, **chain length** and **crystallinity**.

1. Orientation

Linear polymer chains need to align to maximize intermolecular interactions for stability and flexibility. Alignment through orientation of the polymer chains is a key fiber property and an essential stage in the processing for all man-made fibers.

- The fiber orientation was found to depend on both the plaque thickness as well as the polymer type.



convergent vs. divergent flow

III. Synthetic fibers Polymers

General Properties of Synthetic Fibers

2. Chain length

- ☐ One parameter reflecting the length of a polymer chain is the degree of polymerization (DP).

(Their DP range for fibers is from around 500 to 10,000)

- ☐ The polymer chains need to be of the same appropriate mean length to allow sufficient intermolecular chain bonding to achieve desirable effects.

Staple fibers (short <7.6 cm)
e.g. cotton, wool

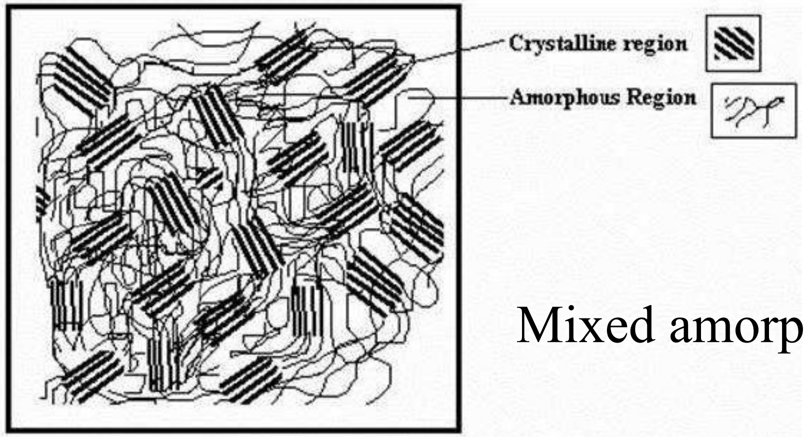
Filament fibers (7.6 cm< long <91.4)
e.g. silk, polyester

III. Synthetic fibers Polymers

General Properties of Synthetic Fibers

3. Crystallinity

- All polymers are part crystalline, part amorphous. For fibers, the crystalline regions need to dominate **because** they are necessary for fiber strength through intermolecular interaction between polymer chains.



Mixed amorphous crystalline macromolecular polymer structure

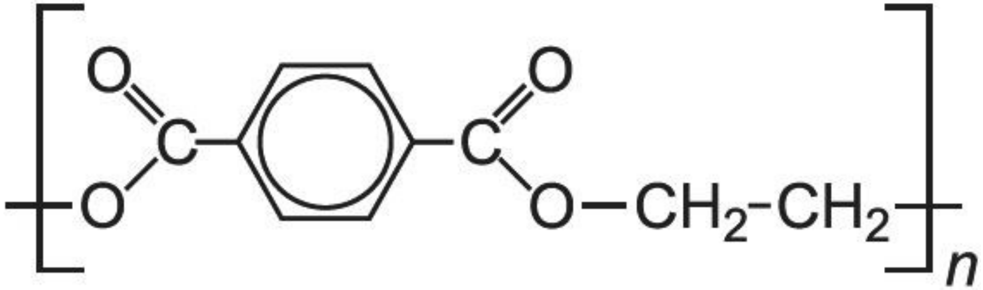
- Regular bifunctional repeating units in the polymer help crystallization, but not tri-functional groups which tend to cross-link to form more rigid networks.

III. Synthetic fibers Polymers

General Properties of Synthetic Fibers

3. Crystallinity

- Chain freedom can also be influenced by the chemistry of the side group, for instance poly(ester) has aromatic groups in its polymer, **resulting** in less flexible segments along the chain and a stiffer fiber.

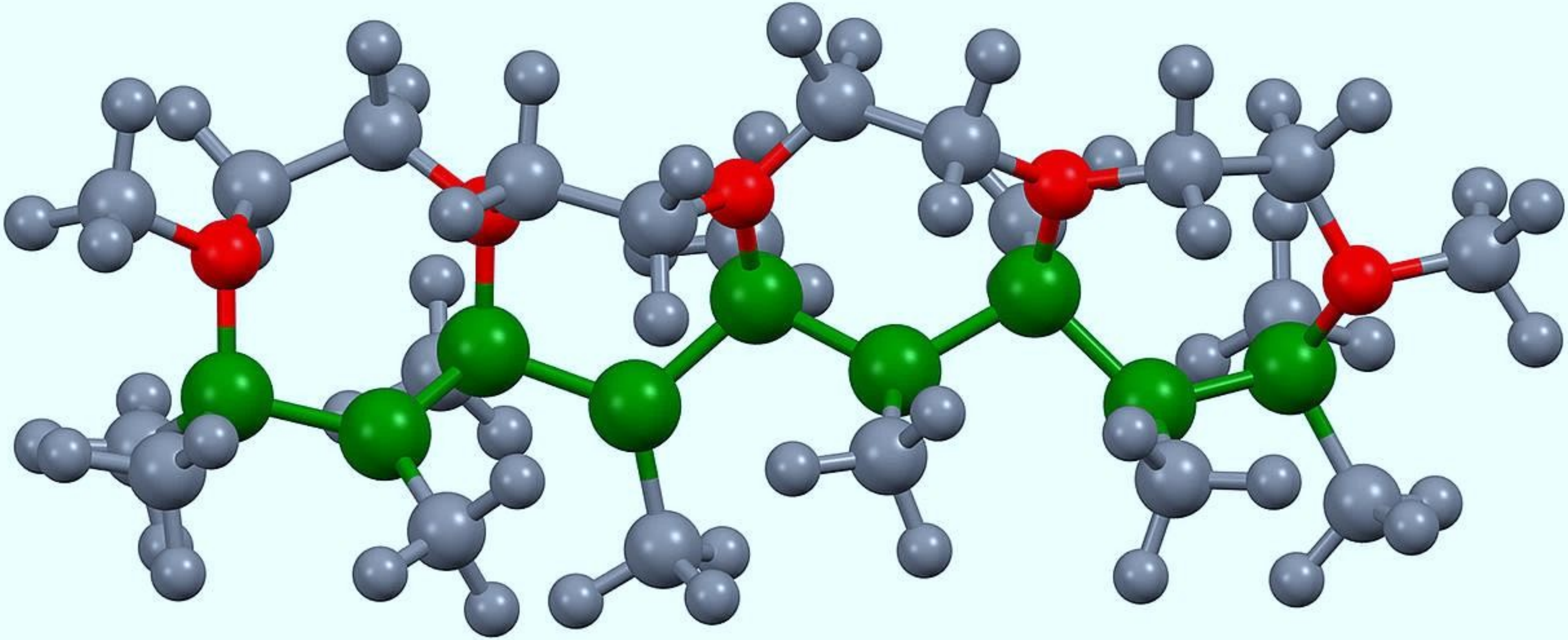


Polyethyleneterephthalate

- Bonds in the chain backbone and the side group chemistry affect the potential energy to change conformation, while intermolecular bonds that are stronger than van der Waals, i.e. dipole and hydrogen bonding, **increase bond strength**, affecting **fiber strength** and **fiber stiffness**.

Chapter 2: Part II

General Methods for preparing



By the end of this Chapter

You will be able to recognize

- ❖ Addition polymerization

  Through The following Reaction Types

  - **Radical Polymerization**
  - **Ionic Polymerization**
    - ✔ **Anionic Polymerization**
    - ✔ **Cationic Polymerization**
  - **Ziegler-Natta polymerization**
  - **Ring Opening Polymerization**

- ❖ Modification of Polymerization

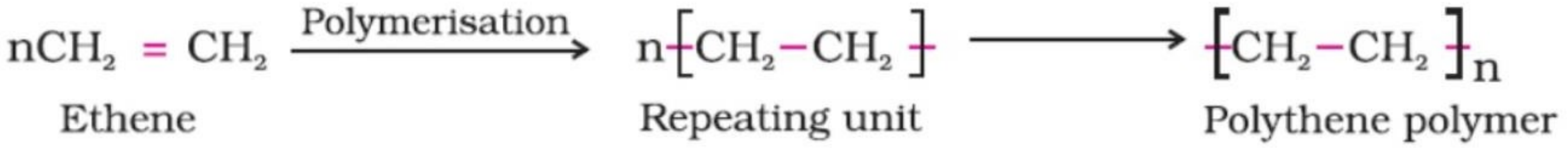
Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

Addition polymerization occurs by a chain reaction in which one carbon-carbon double bond adds to another. Monomers continue to react with the end of the growing polymer chain in an addition polymerization reaction until the reactive intermediate is destroyed in a termination reaction.

An addition polymer is a polymer which is formed by an **addition reaction**, where many monomers bond together via rearrangement of bonds without the loss of any atom or molecule.



$$nCH_2=CH_2 \xrightarrow{\text{Polymerisation}} n\left[CH_2-CH_2\right] \longrightarrow \left[CH_2-CH_2\right]_n$$

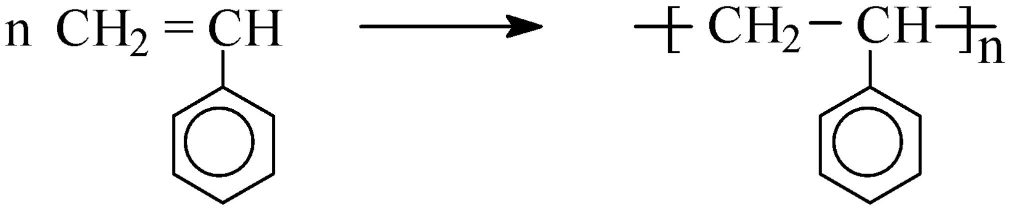
Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

- Homopolymer is produced when only one type of chemical repeated unit (monomer) is used make a polymer.

$$nA \longrightarrow A\text{-}A\text{-}A\text{-}A\text{-}A = \left[A\right]_n$$



- The combination of two or more chemically different repeating units (monomers), the polymer will have the characteristics of copolymer.

$$n\,A \quad + \quad n\,B \longrightarrow \text{-}A\text{-}B\text{-}A\text{-}B\text{-} \quad = \quad \left[A\text{-}B\right]_n$$

Addition Polymerization
(Polymerization through Double Bond)

Chain growth polymerization

Chain Growth Polymerization reaction consists of three stages:

1 **Initiation**

2 **Propagation**

3 **Termination**

Initiation step,
involves the formation
of active species.

Propagation step,
the growth of a polymer
chain by successive
addition
of monomers.

Termination step,
pairs of radicals also
have a tendency to react
with each other and thus
annihilate their activities.

Addition Polymerization

(Polymerization through Double Bond)

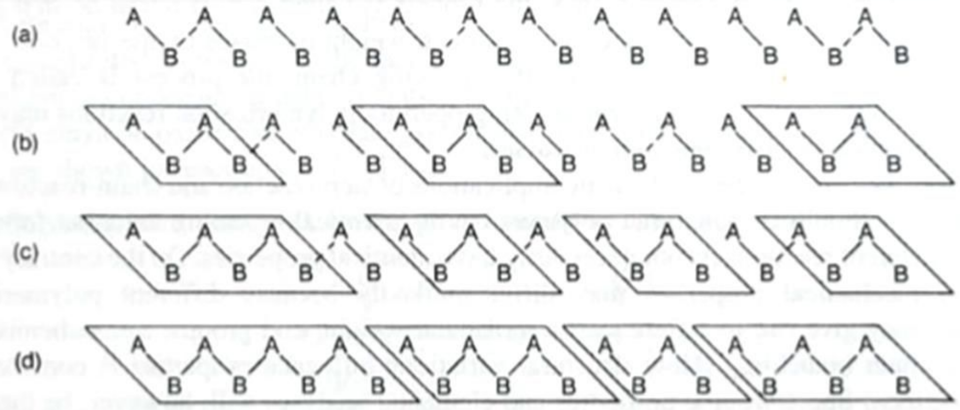
Chain growth polymerization

STEP-GROWTH (CONDENSATION) **VERSUS** CHAIN-GROWTH (FREE RADICAL)POLYMERIZATION

Step-Growth Polymerization	Chain-Growth Polymerization
Is the formation of a polymer from bi-functional or multifunctional monomers	Is the formation of polymers from unsaturated monomers.
Oligomers are formed at the beginning and are later combined together, forming the polymer chain.	A polymer chain is formed at the beginning by the attachment of one monomer at a time
Monomers are bi-functional or multifunctional	Monomers are unsaturated
A rapid loss of monomers can observed at beginning	There is no rapid loss of monomers at the beginning
All monomers are active themselves	An active site can be observed at the end of the polymer chain
Does not require initiators	Requires initiators to break the double bond in monomer molecule
Shows no termination	Show no growth of polymer after termination
Only monomers and polymers are observed	Any types of molecules can be observed

Comparison

Step-Growth Polymerization



IGURE 1.4. Step-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP}$ = 1.3; (c
5% reacted, $\overline{DP}$ = 1.7; (d) 100% reacted, $\overline{DP}$ = 3. (Broken lines represent reacting species.)

Chain-Growth Polymerization

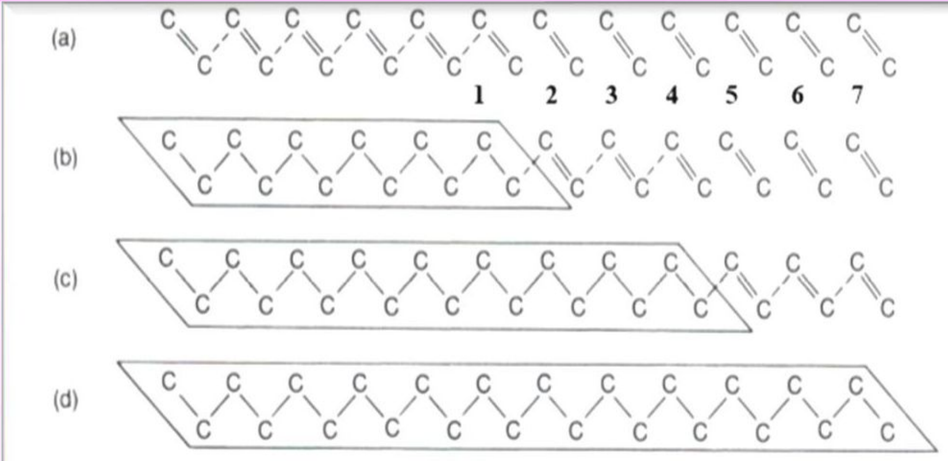


FIGURE 1.5. Chain-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP}$ = 1.
(c) 75% reacted, $\overline{DP}$ = 3; (d) 100% reacted, $\overline{DP}$ = 12. (Broken lines represent reacting species.)

Addition Polymerization

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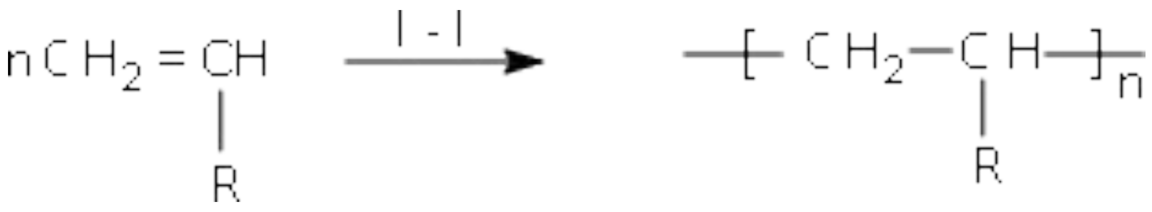
Chain growth polymerization

Vinyl Polymerization

General Equation



$$n\,CH_2=\underset{\displaystyle R}{\underset{|}{CH}} \xrightarrow{I-I} -\!\!\left[CH_2-\underset{\displaystyle R}{\underset{|}{CH}} \right]\!\!-_n$$

R can be atom or group ex; -Cl, -CN, $-C_6H_5$, $–OCH_3$, $-CH_3$

I-I represents the initiator

Note that:

The appropriate choice of catalysts or initiators depends on the substituent R and polymer type.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

Chain Growth Polymerization

- Free Radical
- Ionic
  - Anionic
  - cationic
- Coordination
- Ring Opening

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1 Free Radical Polymerization

❑ Free radical polymerizations are chain polymerizations in which each polymer molecules grows by addition of monomer to a terminal free-radical reactive site known as active center.

❑ In Radical Polymerization **the initiator** is a radical, and **the propagating site** of **reactivity** (*) is a carbon radical.

❑ Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1 Free Radical Polymerization

Initiators of Radical Chain Polymerization

Initiators should be relatively stable at room temperature but should decompose rapidly enough at polymer processing condition to ensure a practical reaction rate. A large number of free radical initiators are available.

They may be classified into three major types:

(a) thermal initiators including peroxides and azo compounds,

(b) photo initiators

(c) redox initiators

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1 Free Radical Polymerization

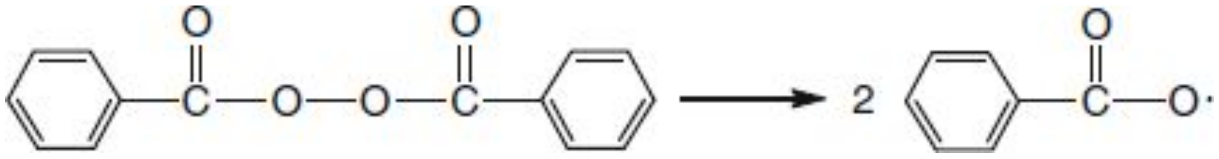
Types of initiators used

a) Thermal Initiators

A thermal initiator is an initiator which is **converted to a free-radical** by the action of heat/light.

Example 1

The most commonly used peroxide is benzoyl peroxide , which undergoes thermal hemolysis to form benzoyloxy radicals.



benzoyl peroxide

benzoyloxy radicals

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

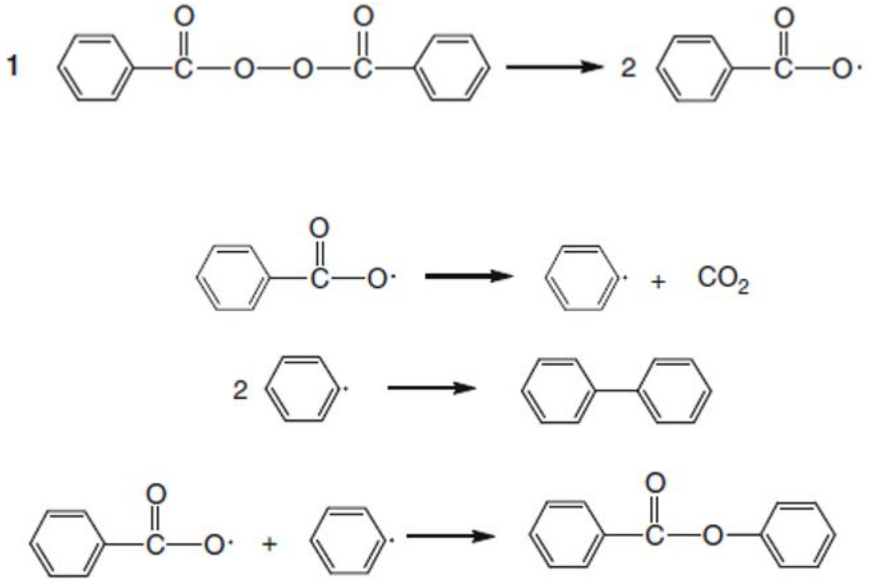
1- Free Radical Polymerization

Types of initiators

a) Thermal Initiators

Example 1 **Benzoyl peroxide** used

The benzoyloxy radicals may undergo a variety of reactions besides adding to monomer,



Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

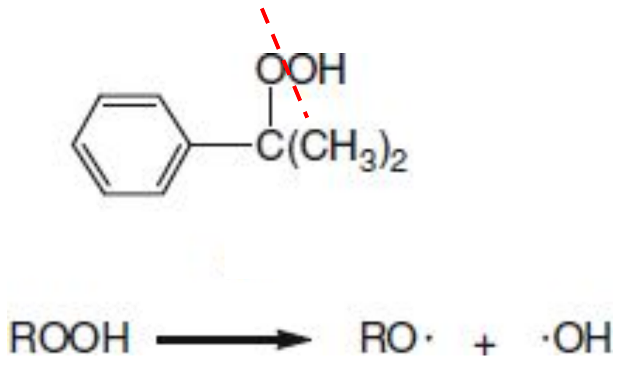
1 Free Radical Polymerization

Types of initiators used

a) Thermal Initiators

Example 2 Cumyl hydroperoxide

Hydroperoxides such as cumyl hydroperoxide decompose to form alkoxy and hydroxyl radicals.



Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

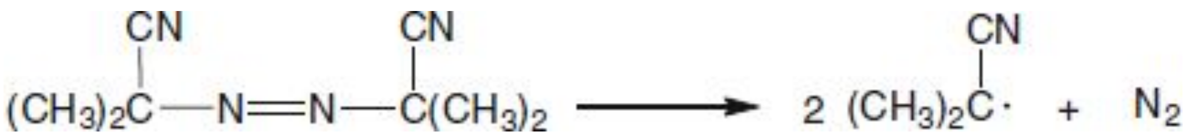
1 Free Radical Polymerization

Types of initiators used

a) Thermal Initiators

Example 3 Azo compound

α,ά-Azobis(isobutyronitrile), is the most widely used azo compound which decomposes at relatively low temperatures. The driving force for decomposition is the formation of nitrogen and the resonance-stabilized cyanopropyl radical.



$$(CH_3)_2\overset{CN}{\overset{|}{C}}-N{=}N-\overset{CN}{\overset{|}{C}}(CH_3)_2 \longrightarrow 2\ (CH_3)_2\overset{CN}{\overset{|}{C}}\cdot + N_2$$

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

b) Photo Initiators

- ❑ Photo-initiators are molecules that absorb photons upon irradiation with light and form reactive species out of the excited state, which initiate consecutive reactions. The initiating species may be radicals, cations, or anions.

- ❑ Radical photo-initiators are commercially available in large number from companies.

- ❑ A photo-initiator should exhibit several properties, from which the most important are:
  (i) high absorption at the exposure wavelength and high molar extinction coefficient,
  (ii) high quantum yield of formation of initiating species,
  and (iii) high reactivity of the radical towards the monomer.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

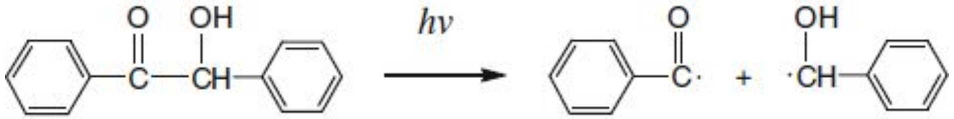
Types of initiators used

b-1) Photo Initiators

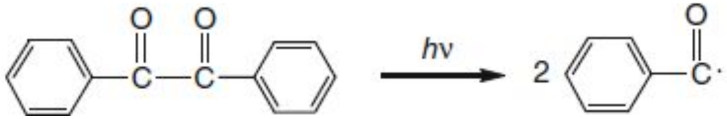
Peroxides and azo compounds dissociate photolytically as well as thermally. The major advantage of photoinitiation is that the reaction is essentially independent of temperature.

Examples

$RSSR \xrightarrow{h\nu} 2\ RS\cdot$



benzoin



benzyl

Addition Polymerization

(Polymerization through Double Bond)

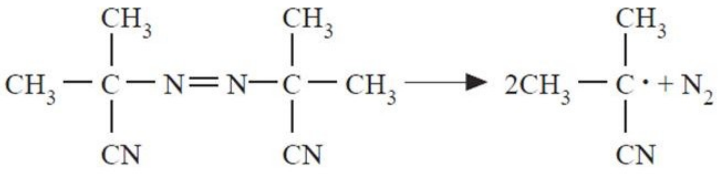
Chain growth polymerization

1- Free Radical Polymerization

Types of initiators used

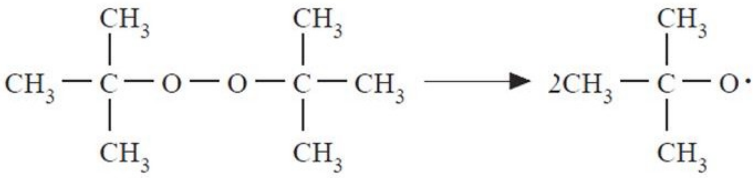
b-2) Photo Initiators

An example of photochemically induced free-radical formation is the decomposition of azo-bisisobutyronitrile by short-wavelength visible light or near-ultraviolet radiation at temperatures as low as 0 °C, where ***no thermal initiation occurs***.



$$CH_3-C(CH_3)(CN)-N=N-C(CH_3)(CN)-CH_3 \longrightarrow 2CH_3-\overset{CH_3}{\underset{CN}{C}}\cdot + N_2$$

azobisisobutyronitrile (AIBN)



$$CH_3-C(CH_3)_2-O-O-C(CH_3)_2-CH_3 \longrightarrow 2CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O\cdot$$

di-*t*-butylperoxide

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

c) Redox Initiators

A very effective method of generating free radicals under mild conditions is by one-electron transfer reactions, the most effective of which is redox initiation. This method has found wide application for initiating polymerization reactions and has industrial importance, e.g. in low-temperature emulsion polymerizations.

This narrow range of dissociation energies limits the types of useful compounds to those containing fairly specific types of covalent bonds, for example, oxygen–oxygen, oxygen–nitrogen and sulfur– sulfur bonds.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

c) Redox Initiators

C-1. Peroxide

- Fenton's reagent, the combination of H_2O_2 and ferrous salt, has been applied to the oxidation of many organic compounds, including alcohols, glycols, aldehydes, ethers, esters and amines.

- A mechanism for the reaction between hydrogen peroxide and ferrous ion involves **a one-electron transfer** from the ferrous ion to the peroxide **with the dissociation of** the oxygen–oxygen bond and the generation of one hydroxyl radical. and one hydroxyl ion.

$$\boxed{Fe^{2+} + H_2O_2 \rightarrow [HO\dot{-}OH]Fe^{3+} \rightarrow Fe^{3+} + OH^- + {\cdot}OH}$$

- In the presence of sufficient monomer, all of the $^{\cdot}OH$ radicals generated can initiate polymerization. Polymerization of several vinyl monomers, in aqueous media initiated by the H_2O_2–Fe^{2+} redox system, have been studied.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

c) Redox Initiators

C-1. Persulfate

- With disulphides persulfates and elemental halogens, analogous reactions occur

$$\boxed{RS\text{-}SR + Fe^{2+} \longrightarrow Fe^{3+} + RS^{\cdot} + RS^{-}}$$

- With persulfate initiator, several monomers (acrylonitrile, methacrylic acid, methacrylamide, methyl methacrylate and ethyl acrylate) have been grafted onto wool fibres with the aid of cysteine present in wool.

Addition Polymerization

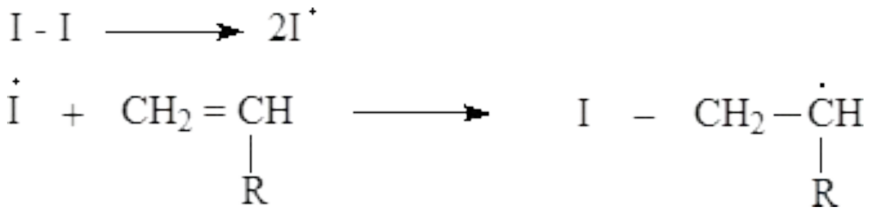
(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

1-Initiation Step

Chain polymerization is initiated by a reactive species I* produced from an initiator I.

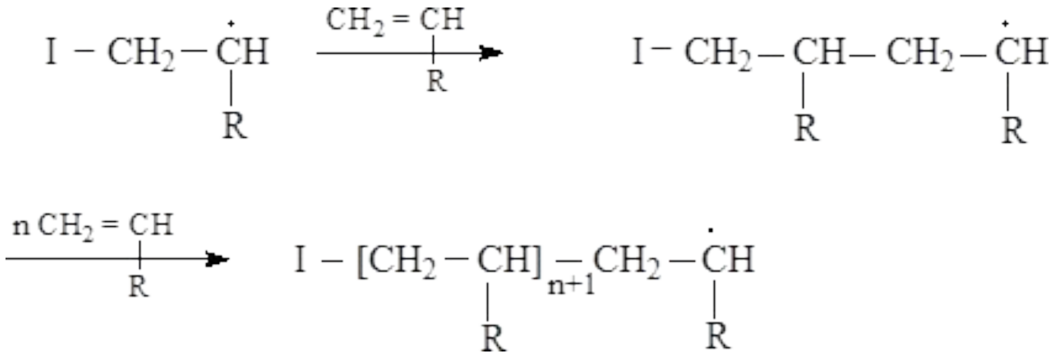


$$I-I \longrightarrow 2I^{\bullet}$$

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

2-Propagation Step

Each time a free radical hits a molecule a new free radical is formed.



$$I-CH_2-\underset{\underset{R}{|}}{\dot{C}H} \xrightarrow[R]{CH_2=CH} I-CH_2-\underset{\underset{R}{|}}{CH}-CH_2-\underset{\underset{R}{|}}{\dot{C}H}$$

$$\xrightarrow[R]{n\,CH_2=CH} I-[CH_2-\underset{\underset{R}{|}}{CH}]_{n+1}-CH_2-\underset{\underset{R}{|}}{\dot{C}H}$$

Addition Polymerization

(Polymerization through Double Bond)

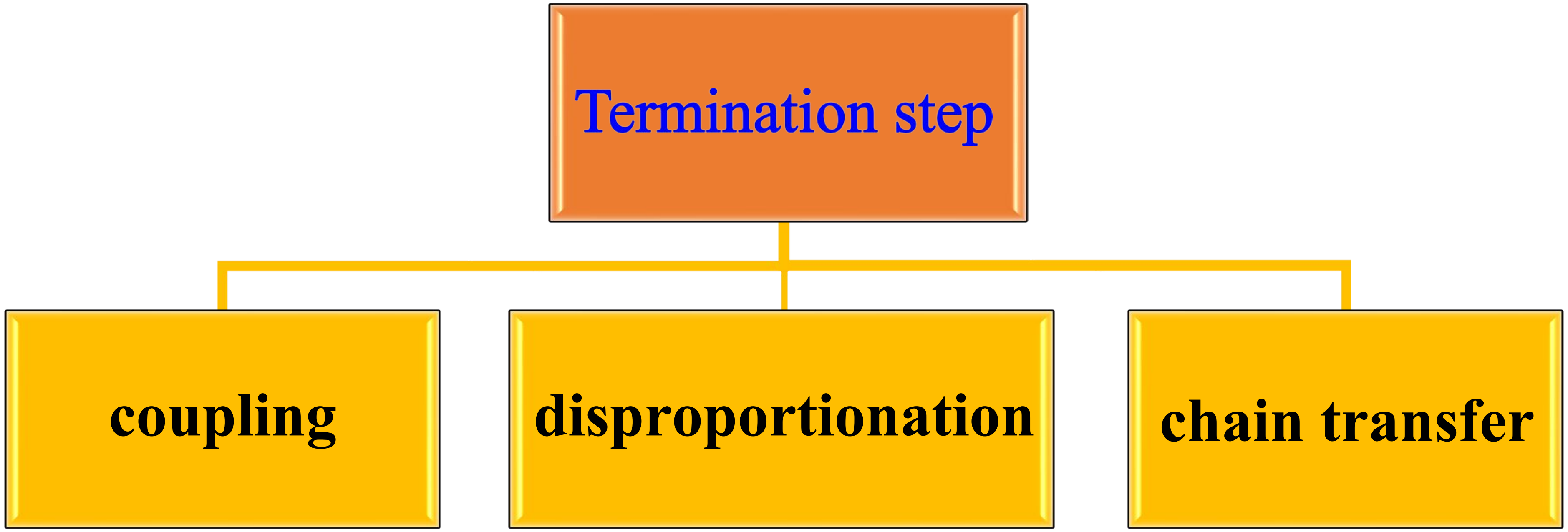
Chain growth polymerization

1- Free Radical Polymerization

3-Termination Step

The process stops here because no new free radicals are formed. The destruction of the reactive center can be done by:

There are basically **three ways** in which chains terminate



Termination step

coupling

disproportionation

chain transfer

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

3-Termination Step

1. coupling

The first is known as **coupling** and occurs when two free radicals join together. This can be
represented by the general equation.

$$\text{(polymer chain 1)} - RH\bullet + \bullet HR - \text{(polymer chain 2)}$$
$$\rightarrow \text{(polymer chain 1)} - RH - RH - \text{(polymer chain 2)}$$

Such a mechanism significantly increases molecular mass, if it results in two polymer chains joining. This is the main mechanism which terminates the polymerization of styrene.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

3-Termination Step

2.Disproportionation

An alternative mechanism that may occur when two radicals interact is known as **disproportionation**. In this case, one molecule abstracts a hydrogen atom from the other and the other molecule forms a double bond.

$$\begin{aligned}&(\text{polymer 1})-\mathrm{RH}\bullet+\bullet\mathrm{HR}-\mathrm{CH_2}(\text{polymer 2})\\&\rightarrow(\text{polymer 1})-\mathrm{RH_2}+\mathrm{R{=}CH}-(\text{polymer 2})\end{aligned}$$

Disproportionation has *no effect on molecular mass*. Poly(methyl methacrylate) (PMMA) terminates by a mixture of coupling and disproportionation.

Addition Polymerization

(Polymerization through Double Bond)

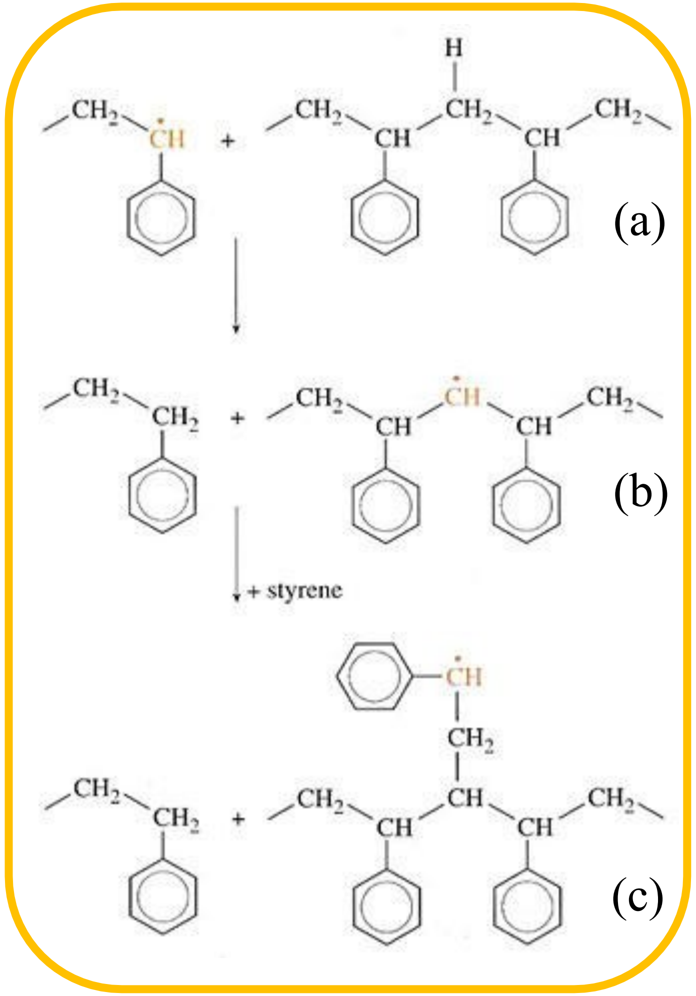
Chain growth polymerization

1- Free Radical Polymerization

3-Termination Step

3.Chain transfer

The third method of termination is **chain transfer** in which a radical abstracts a hydrogen atom from a neighbouring molecule. In the case of polystyrene the effect will be as shown in Figure; where (a) shows the situation before the interaction and (b) shows the structures after chain transfer in which the radical is transferred to one of the mid-chain carbon atoms. The new radical may now attack further styrene Figure(c) but, because it is not on the end of the chain, side branching occurs.



Addition Polymerization

(Polymerization through Double Bond)

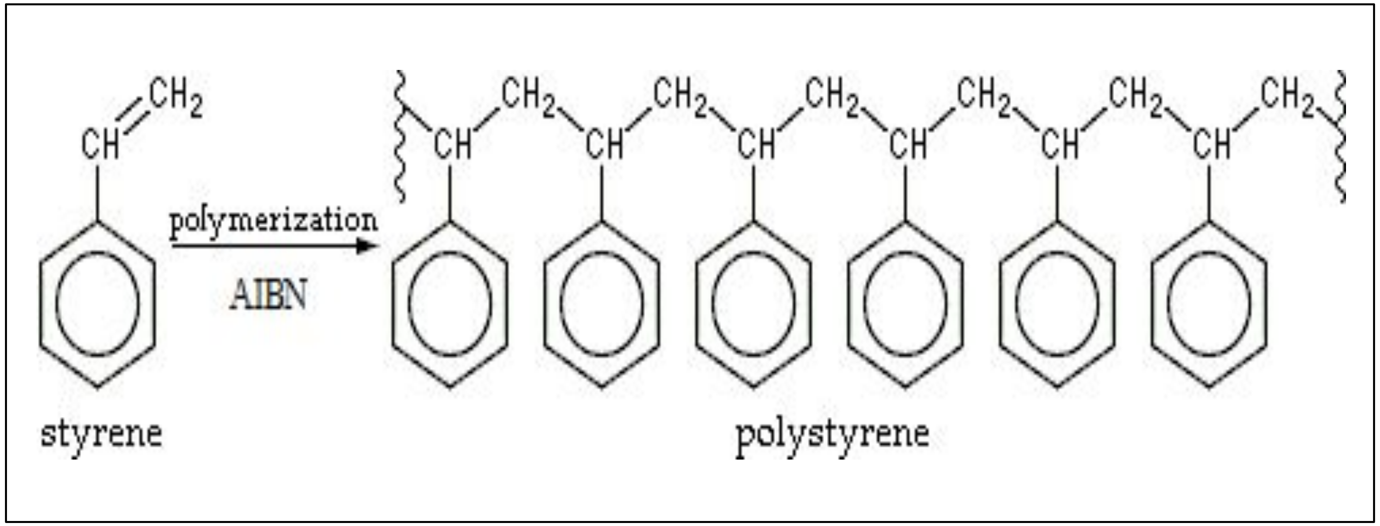
Chain growth polymerization

1- Free Radical Polymerization

Examples

polystyrene polymerization

The polystyrene is made by chain-growth polymerization. The longer reaction time will produce more a longer chain during polymerization.



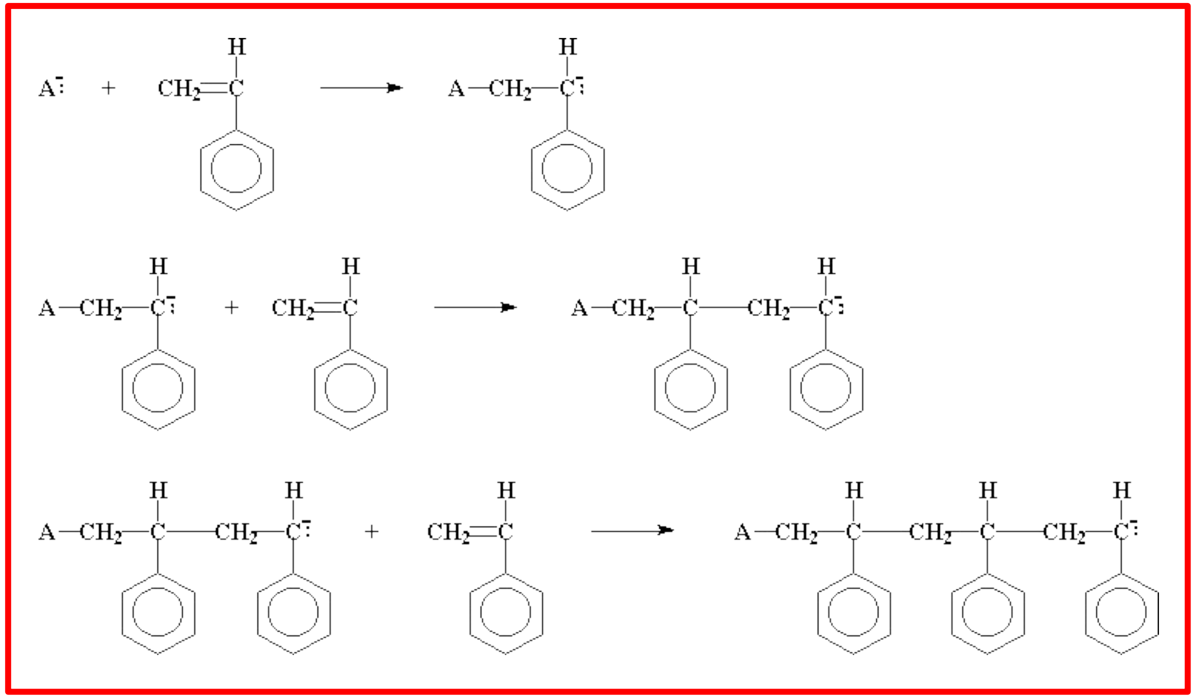
Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization

Polystyrene Polymerization Mechanism



- The first equation illustrates the initiation process.
- The second equations is an example of chain propagation. Each monomer unit adds to the growing chain in a manner that generates the most stable radical. (only styrene monomer can react with the growing polystyrene chain).
- Termination of two reactive radical sites are removed by simultaneous conversion to stable product(s). The termination step occurs mainly by *disproportionation* or *chain transfer*

Addition Polymerization

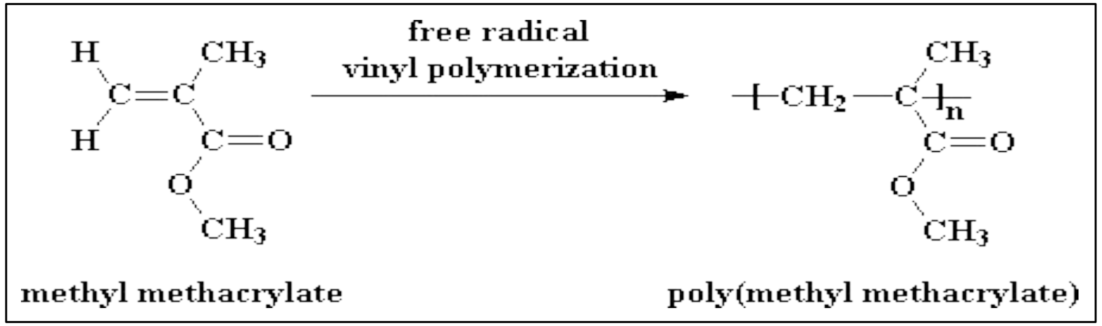
(Polymerization through Double Bond)

Chain growth polymerization

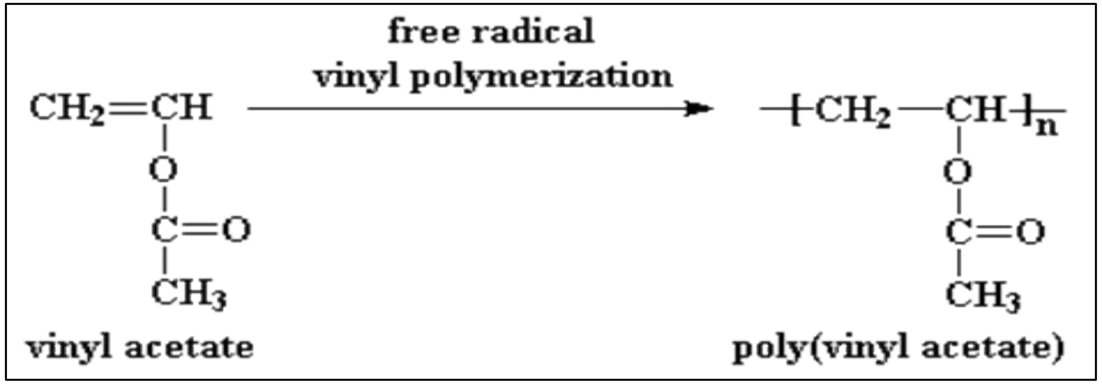
1- Free Radical Polymerization

Examples

- ❑ The most common technique is the free radical polymerization of MMA. The free radical polymerization of **acrylates** and **methacrylates** is a chain polymerization across the double bond of the monomer.



- ❑ The free radical polymerization of MMA can be performed homogeneously, by bulk or solution polymerization, or heterogeneously, by suspension or emulsion polymerization.

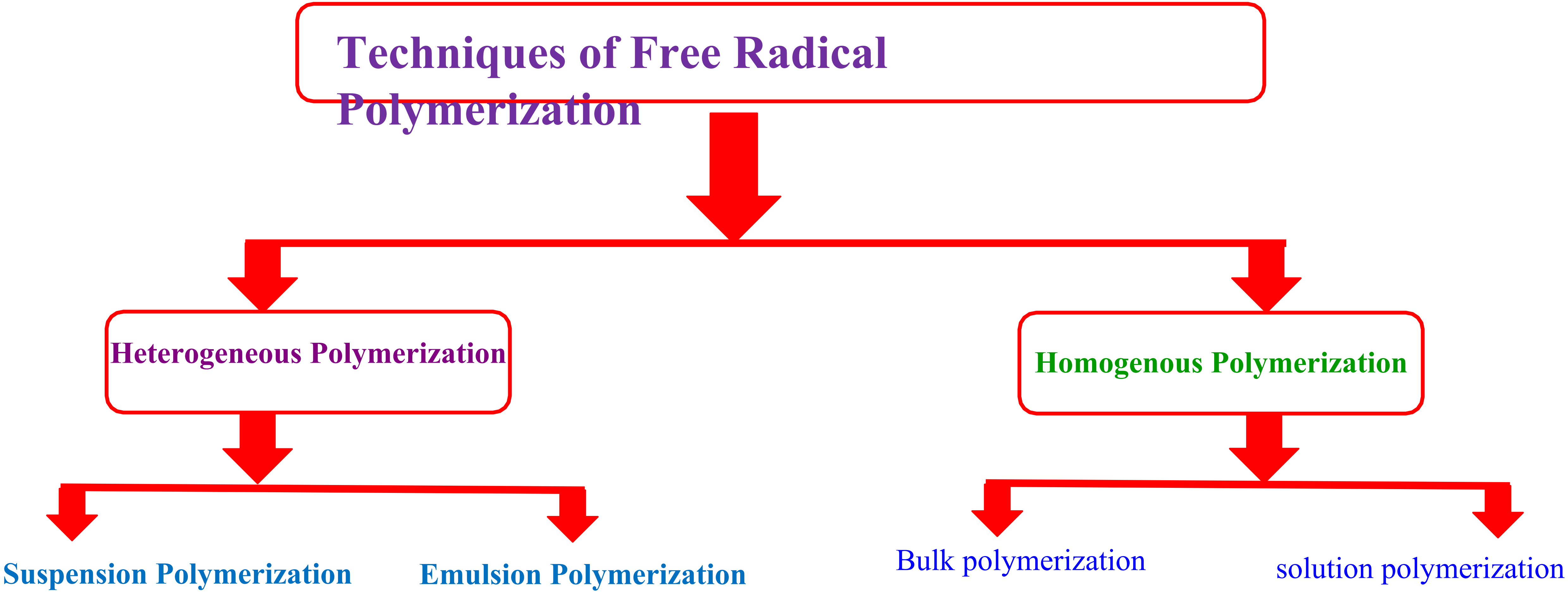


Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

1- Free Radical Polymerization



Techniques of Free Radical Polymerization

Heterogeneous Polymerization

Homogenous Polymerization

Suspension Polymerization

Emulsion Polymerization

Bulk polymerization

solution polymerization

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

I. Homogenous Polymerization

a) Bulk polymerization

Mass or Block Polymerization: Polymerization of undiluted monomer.

- Carried out by adding a soluble initiator to pure monomer in liquid state (**solvent is not required**).

- It is usually adopted to produce polystyrene, polyvinyl chloride, polymethyl methacrylate and low density polyethylene.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

I. Homogenous Polymerization

a) Bulk polymerization

Advantage	Disadvantage
This technique is simple requires no solvent.	Heat transfer is difficult
The obtained polymer is pure	Mixing becomes difficult as the viscosity of reaction mass increases.
The system requires thermal insulation.	The polymerization is obtained with a broad molecular weight distribution due to the high viscosity.
	Very low molecular weights are obtained.

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

I. Homogenous Polymerization

b) Solvent polymerization

- Solution polymerization is a method of industrial polymerization. In this procedure, a monomer is dissolved in a non-reactive solvent that contains a catalyst.

- The reaction results in a polymer which is also soluble in the chosen solvent.

Addition Polymerization

(Polymerization through Double Bond)

I-Homogenous Polymerization

b) Solvent polymerization

Advantage	Disadvantage
The solvent acts as a diluent & helps in facilitating continuous transfer of heat of polymerization, Therefore temperature control is easy.	To get pure polymer, evaporation of solvent is required
The solvent allows easy stirring as it decreases the viscosity of reaction mixture.	The method is costly since it uses expensive solvents
solvent also facilitates the ease of removal of polymer from the reactor.	
Viscosity built up is negligible	

Addition Polymerization
(Polymerization through Double Bond)

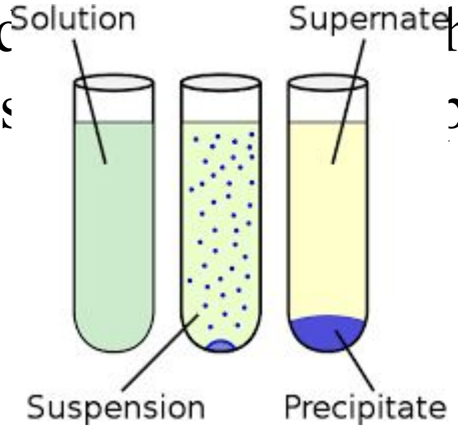
Chain growth polymerization

II. Heterogeneous Polymerization

a) Suspension Polymerization

What means by suspension solutions?

A suspension is a heterogeneous mixture in which the solute particles **do not dissolve**, but get suspended throughout the bulk of the solvent, left floating around freely in the medium. The internal phase (solid) is c hout the external phase (fluid) through **mechanical agitation**, with the us ɔients or **suspending agents**.

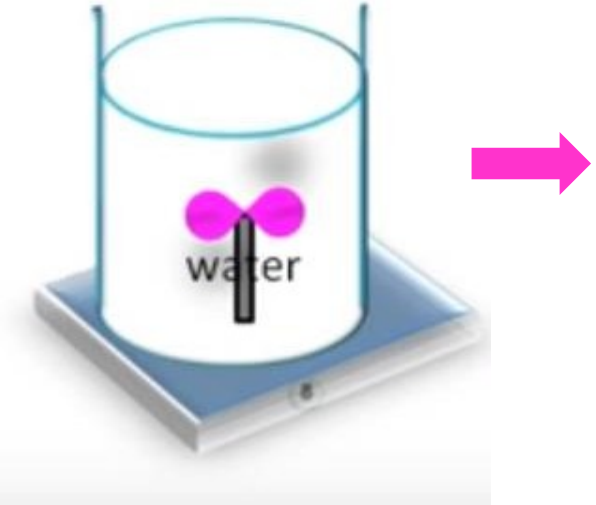


Addition Polymerization
(Polymerization through Double Bond)

Chain growth polymerization

II. Heterogeneous Polymerization

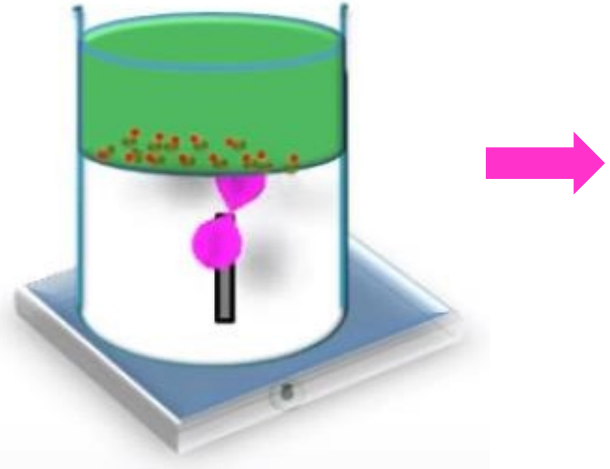
a) Suspension Polymerization



The figure shows a beaker above thermostat and agitator is used to prevent coagulation.

The monomer (green color is the organic phase)

The water below (white color is the aqueous phase)



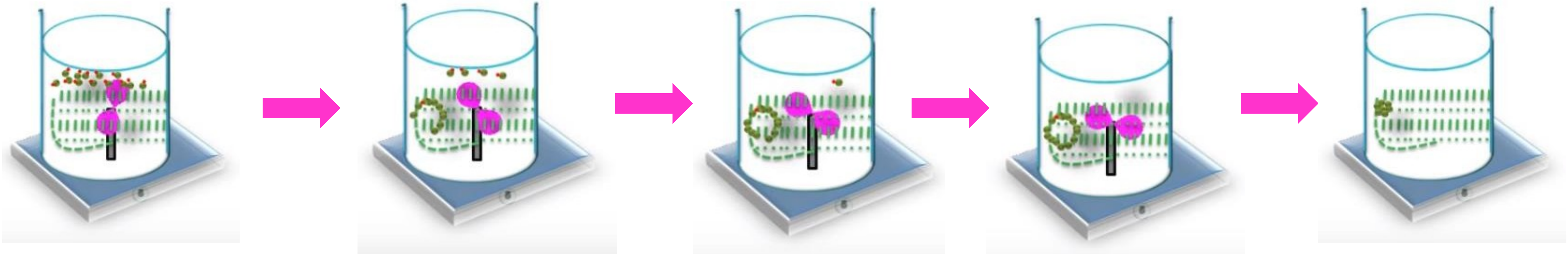
The monomer is water insoluble and contains initiators; initiators which are represented by red color

Addition Polymerization
(Polymerization through Double Bond)

Chain growth polymerization

II. Heterogeneous Polymerization

a) Suspension Polymerization



Addition of suspending agent which will help to keep the solid part as suspension.

Formation of polymer micro-droplet

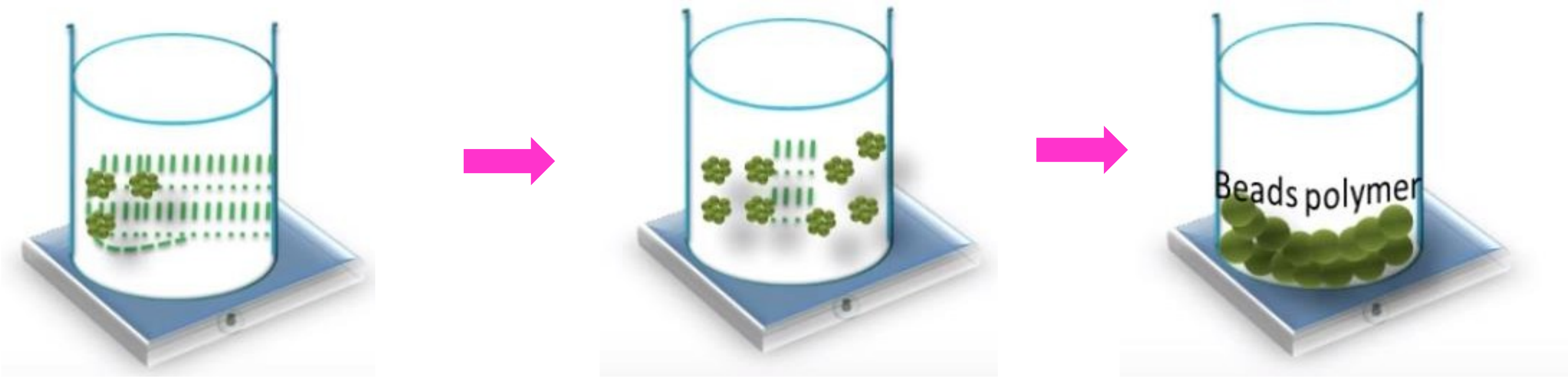
Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

II. Heterogeneous Polymerization

a) Suspension Polymerization



Formation of polymer beads

- The polymer is produced in heterogenous polymer

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

II. Heterogeneous Polymerization

a) Suspension Polymerization

Advantages

- ✔ using water as solvent making suspension polymerization technique an economic method
- ✔ Product isolation is very easy and the products are very pure.

Disadvantages

- ▯ This method is applicable only for water insoluble monomers.
- ▯ Control of particle size is difficult.

Applications

- ❑ Polystyrene beads are used as ion exchange resins.

Addition Polymerization

(Polymerization through Double Bond)

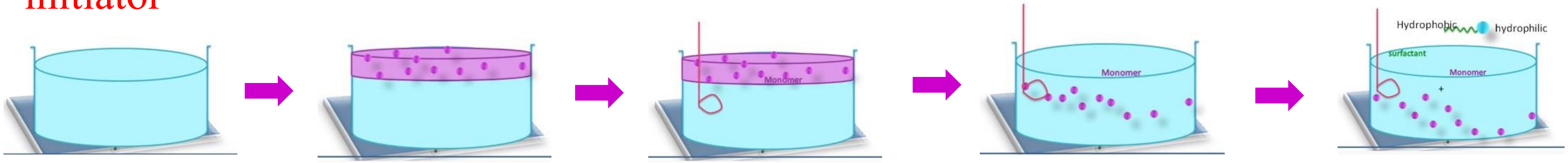
Chain growth polymerization

II-Heterogeneous Polymerization

b)Emulsion Polymerization

Emulsion Polymerization Process

❑ The main components of emulsion polymerization media involve monomer(s), dispersing medium, emulsifier, and water-soluble initiator



The beaker is filled with water and placed in the thermostat

Formation of heterogeneous solution by adding organic monomer

The dispersion medium is water in which hydrophobic monomers is emulsified by surface-active agents (surfactant).

Then surfactant is added; which combine with water to form micelles

Addition Polymerization

(Polymerization through Double Bond)

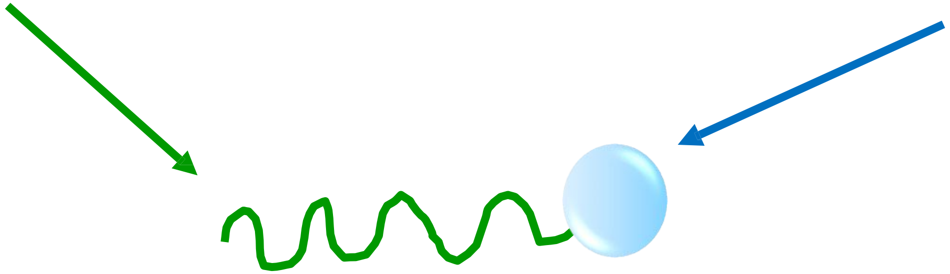
Chain growth polymerization

II-Heterogeneous Polymerization

b)Emulsion Polymerization

- In general, monomer droplets are not effective in competing with micelles in capturing free radicals generated in the aqueous phase due to their relatively small surface area, so the micelle act as a meeting site of water-soluble initiators and hydrophobic vinyl monomers. As polymerization continue inside micelle, the micelle grow by monomer addition from monomer droplets outside and latex are formed.

The structure of surfactant



Hydrophobic Part

Tail

Water
Hater

Hydrophilic Part

Head

Water
Lover

Addition Polymerization

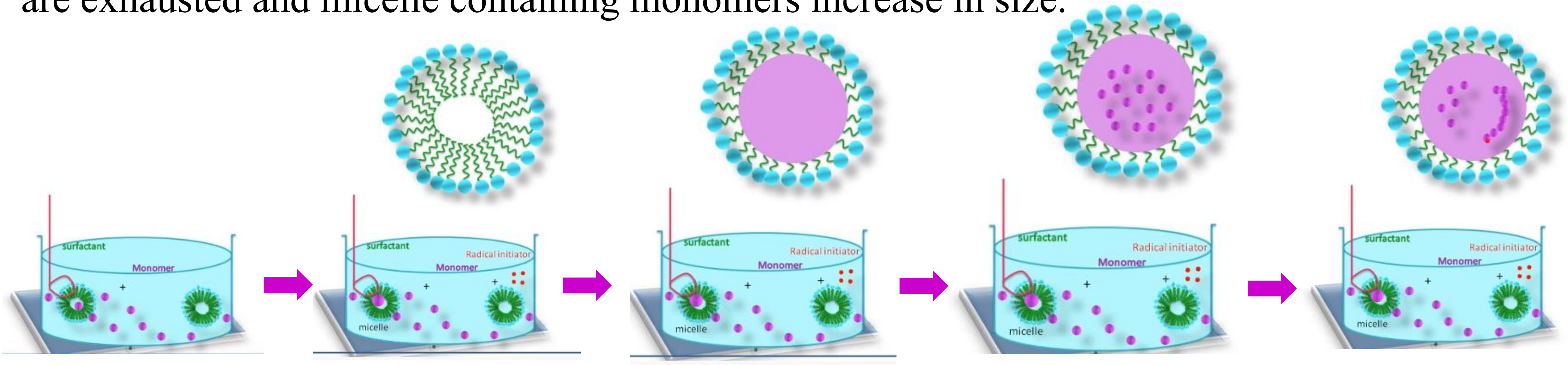
(Polymerization through Double Bond)

Chain growth polymerization

II-Heterogeneous Polymerization

b)Emulsion Polymerization

- When surfactant concentration exceeds critical micelle concentration (CMC) it aggregate in the form of spherical micelles, so surface tension at the surface decrease, as a result hydrophobic monomers enter in to the vicinity of micelle and reaction continue until all monomer droplets are exhausted and micelle containing monomers increase in size.



Water-soluble initiators enter into the micelle where free radical propagation start

Addition Polymerization

(Polymerization through Double Bond)

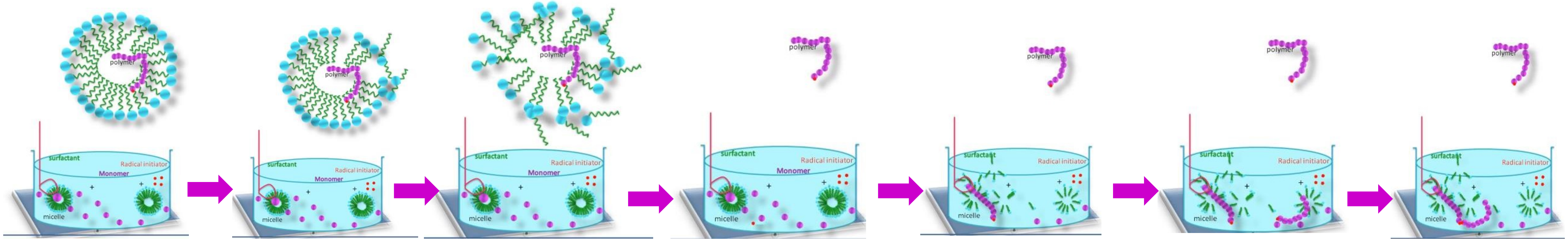
Chain growth polymerization

II-Heterogeneous Polymerization

b)Emulsion Polymerization

An emulsifier

An emulsifier or emulsifying agent is a compound or substance that acts as a stabilizer for emulsions, preventing liquids that ordinarily don't mix from separating.



The polymer chain radical is terminated by forming the macropolymer

Addition Polymerization

(Polymerization through Double Bond)

Chain growth polymerization

II-Heterogeneous Polymerization

b)Emulsion Polymerization

Advantages

- The rate of polymerization is high.
- Heat can be easily controlled and hence viscosity build up is low.

Disadvantages

- Polymer needs purification.
- It is difficult to remove entrapped emulsifier and de-emulsifier.

Applications

Emulsion polymerization is used in large scale production like water based paints,
Adhesives, plastics etc..,

Addition Polymerization
(Polymerization through Double Bond)

2-Ionic polymerization

2-1.*Anionic polymerization*

Anionic addition polymerization is a form of *chain-growth polymerization* or addition polymerization that involves the polymerization of monomers initiated with anions.

- Negative molecules are used in this type of polymerization, in low boiling point solvents.
- Strong bases are used in mono-vinyl polymerization with electron with drawn groups, which helps to stabilize the negative ions during the reaction.
- Anionic polymers shows **narrow molecular weight distribution** such as; polystyrene

Examples

-CN and –$COOCH_3$

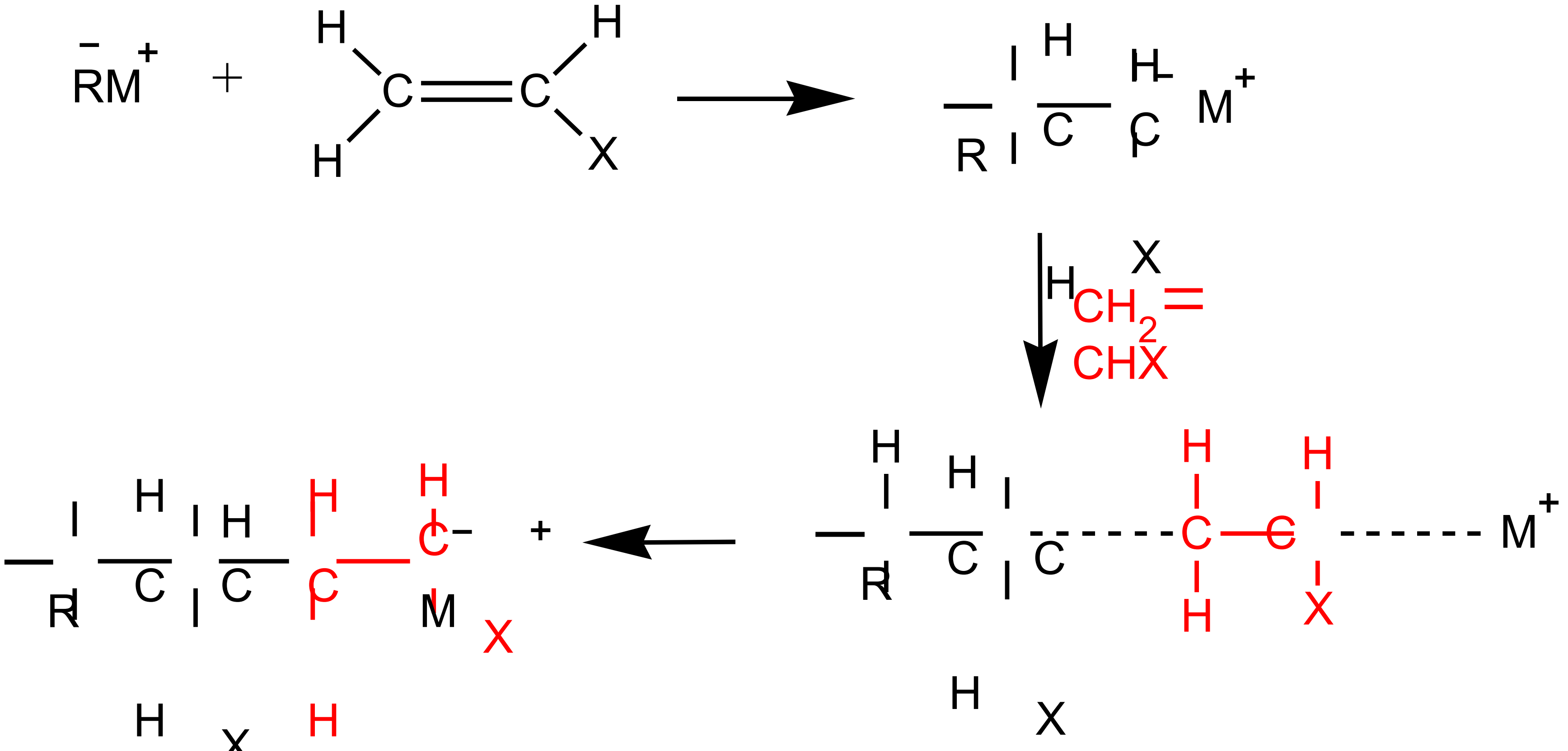
Addition Polymerization

(Polymerization through Double Bond)

Addition Polymerization

2-1.*Anionic polymerization*

Usually *n*-butyl lithium is a good strong base for anionic polymerization



Addition Polymerization

(Polymerization through Double Bond)

2-1. *Anionic polymerization*

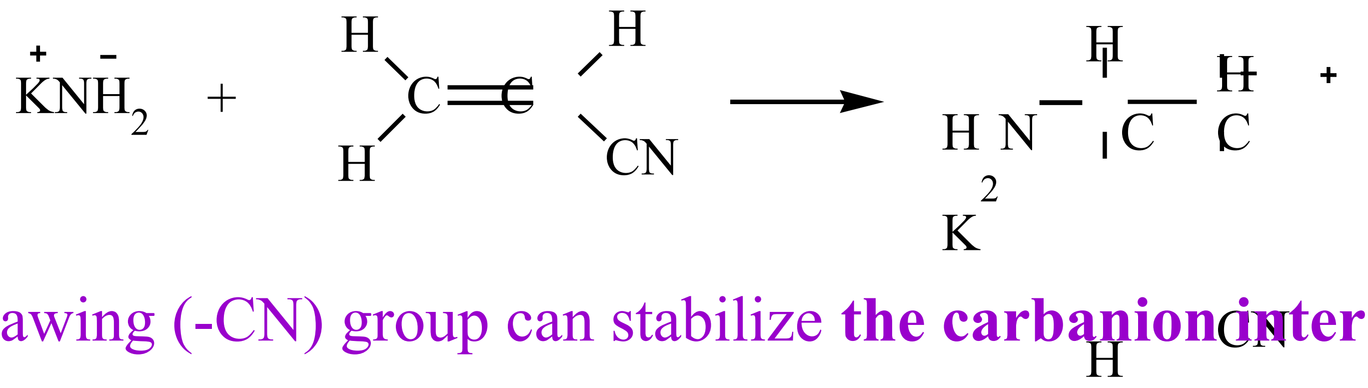
Example 1:

Anionic polymerization of acrylonitrile in ammonia, solvent at – 70° C

Initiation Step

$$K + NH_3 \longrightarrow \overset{+}{K}\overset{-}{NH_2} + 1/_2H_2\uparrow$$

Formation of Initiator



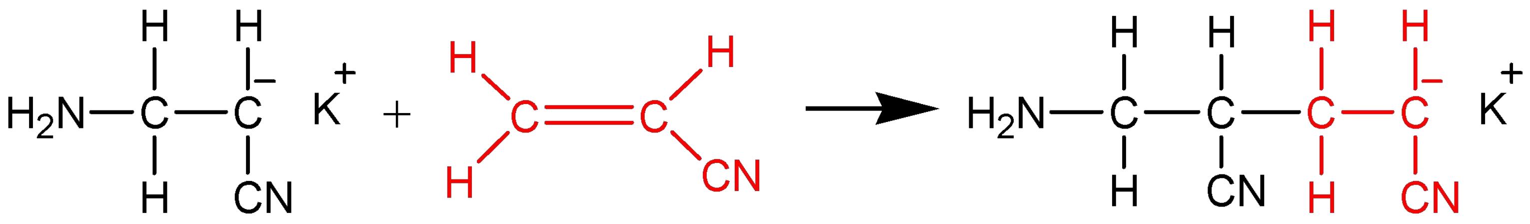
The electron with drawing (-CN) group can stabilize **the carbanion intermediate**.

Addition Polymerization
(Polymerization through Double Bond)

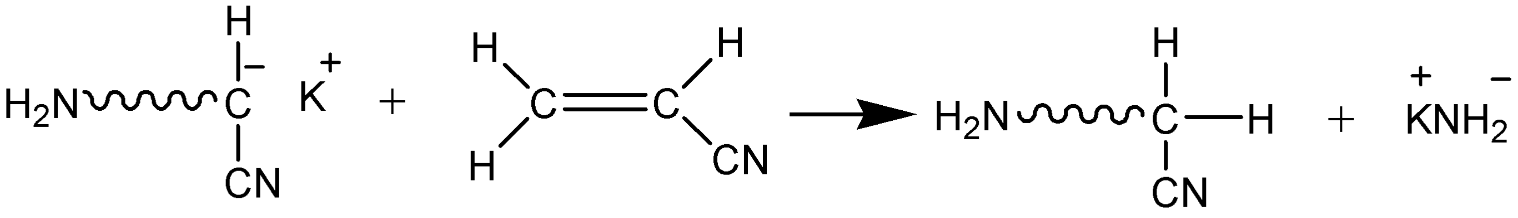
Addition Polymerization

2-1.*Anionic polymerization*

Propagation Step



Termination Step

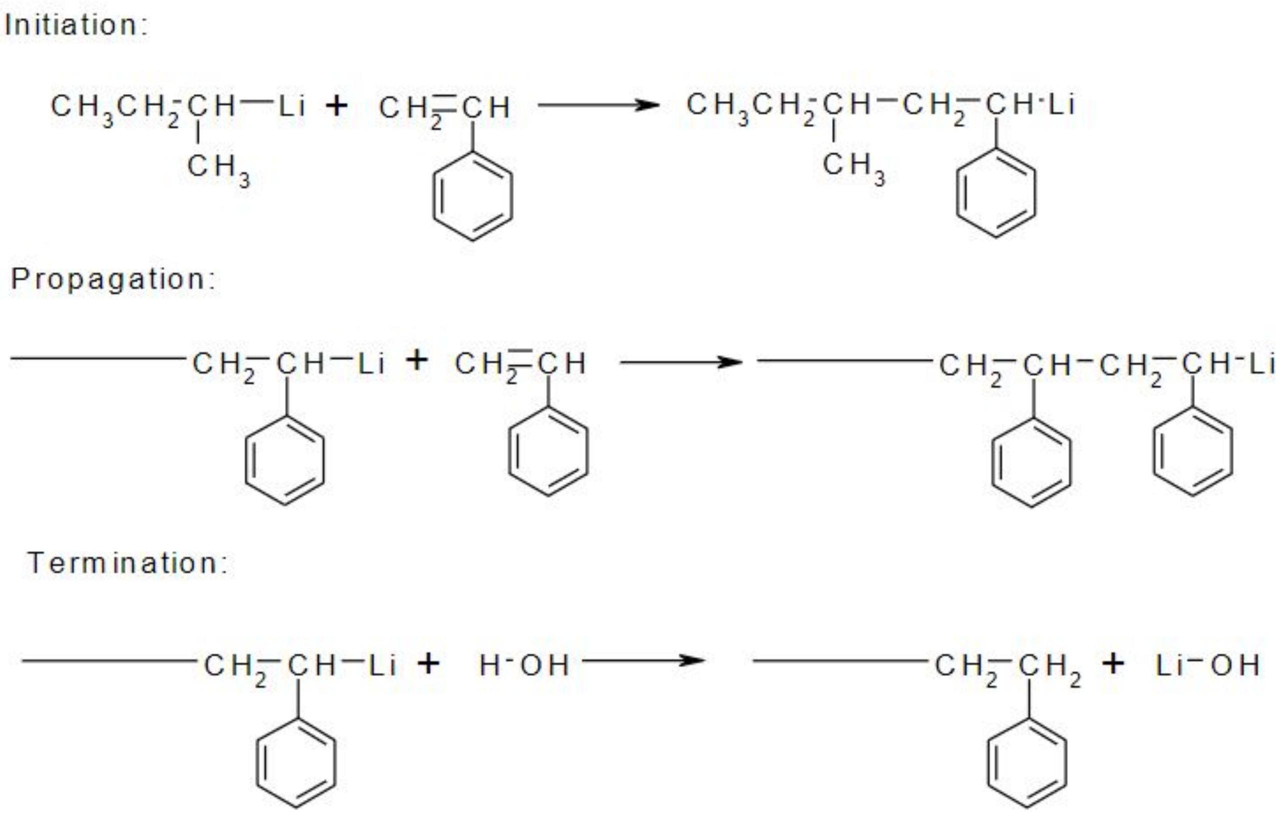


Addition Polymerization

(Polymerization through Double Bond)

2-1.*Anionic polymerization*

Example 2: Styrene Polymerization



Addition Polymerization
(Polymerization through Double Bond)

Addition
Polymerization

❑ Living Polymerization

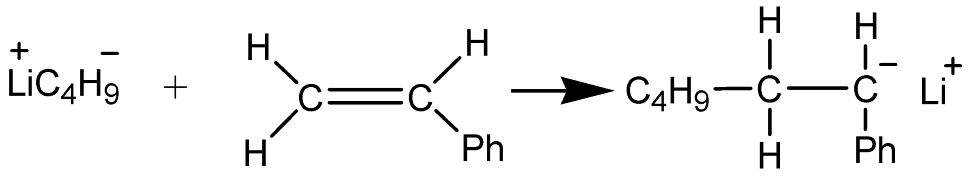
Living polymerizations are chain growth polymerizations which proceed in the absence of irreversible chain transfer and termination steps.

❑ Living Polymer

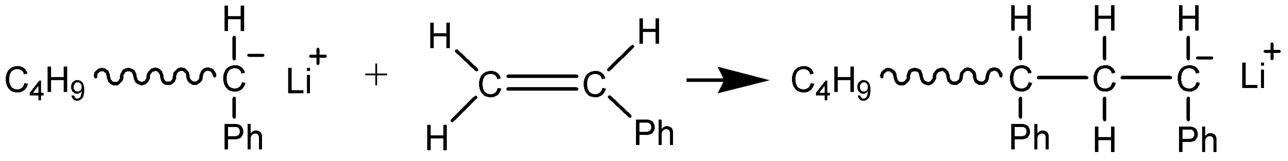
Polymer with stable, polymerization-active sites formed by a chain polymerization in which irreversible chain transfer and chain termination are absent.

Example; Anionic Polymerization of styrene using THF in the presence of n-Butyl lithium

1) Initiation Step



2) Propagation Step



Addition Polymerization

(Polymerization through Double Bond)

❑ Living Polymerization

***Living polymerization** will lead to well-defined polymers only if the following additional prerequisites are fulfilled:*

- ✔ The reaction proceeds until all monomer is consumed. If more monomer is introduced then the polymerization will continue.
- ✔ All terminal groups remain active and can participate in the polymerization process.
- ✔ The final product will be a block copolymer if a new monomer, different from the previous one, is added.
- ✔ Initiation is fast in comparison with propagation.
- ✔ Exchange between species of different reactivities is fast in comparison with propagation.
- ✔ Rate of de-propagation is low in comparison with propagation.
- ✔ System is sufficiently homogenous, in sense of the availability of active centers and mixing.

The termination reaction in anionic polymerization most probably takes place by the chain

Addition Polymerization

(Polymerization through Double Bond)

2-2.Cationic polymerization

is a type of chain growth polymerization in which a cationic initiator transfers charge to a monomer which then becomes **reactive**. This reactive monomer goes on to react similarly with other monomers to form a polymer.

There are a variety of initiators available for cationic polymerization:

- **Protic acids**
- **Lewis acids/Friedel crafts catalysis**
- **Carbenium ion salt**

Addition Polymerization

(Polymerization through Double Bond)

Addition
Polymerization

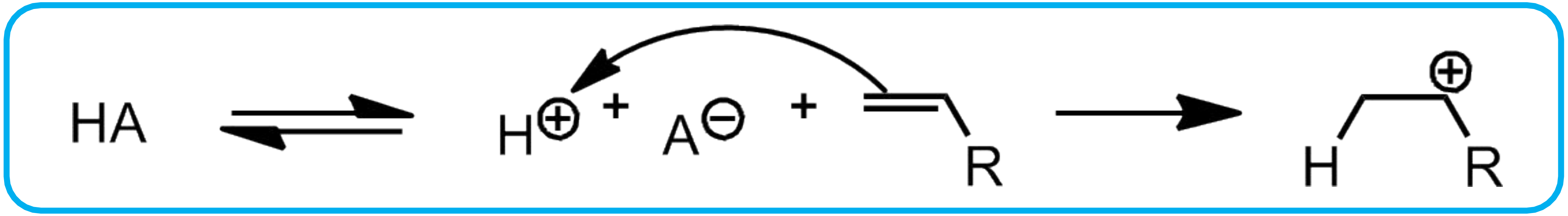
Cationic polymerization

1- Protic Acids Initiator for cationic polymerization

Strong protic acids can be used to form a cationic initiating species. High concentrations of the acid are needed in order to produce sufficient quantities of the cationic species.

Common acids used are:

$HOSO_2CF_3$ - Trifluoromethanesulfonic
Acid H_2SO_4 - Sulfuric Acid
$HClO_4$ -Perchloric acid



Initiation by protic acids

Addition Polymerization

(Polymerization through Double Bond)

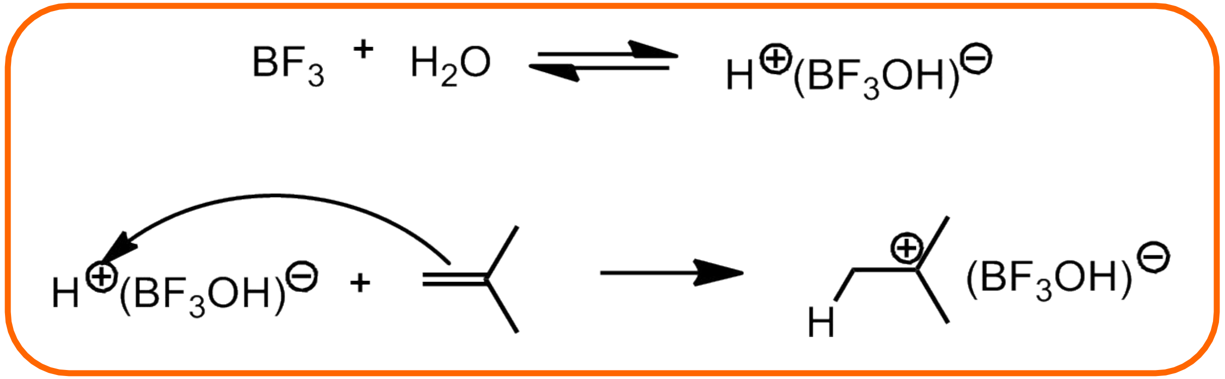
The counterion (C^-)

Is the ion that accompanies an ionic species in order to maintain electric neutrality. The counterion (C^-) produced must be weakly nucleophilic so as to prevent early termination due to combination with the protonated alkene.

i.e. the counterion to an anion will be a cation, and vice-versa

Lewis acids/Friedel-Crafts catalysts

Lewis acids are the most common compounds used for initiation of cationic polymerization. The more popular Lewis acids are $SnCl_4$, $AlCl_3$, BF_3, and $TiCl_4$. Although these Lewis acids alone are able to induce polymerization, the reaction occurs much faster with a suitable **cation source**. The cation source can be water or alcohols.



Note that: Only low molecular weight polymers are formed with these initiators

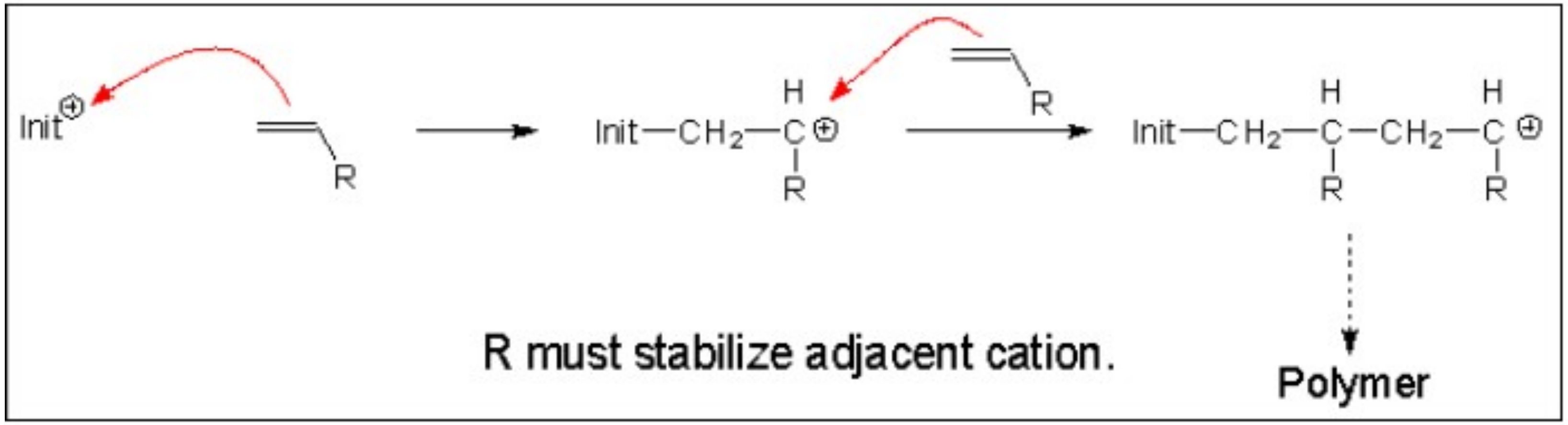
Addition Polymerization

(Polymerization through Double Bond)

Cationic Polymerization Mechanism

The proton donner or cation donner is referred to as the initiator while the Lewis acid is the co-initiator, since the proton donner or cation donner ultimately supplies the proton or cation which adds to monomer that initiates polymerization.

Cationic Polymerization -the growing chain end bears a *positive* charge

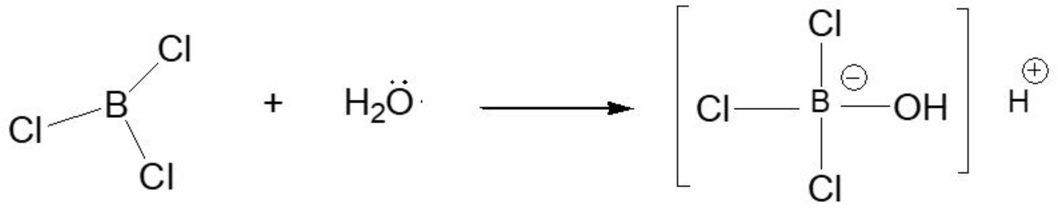


The mechanism of cationic polymerization is a kind of repetitive alkylation reaction.

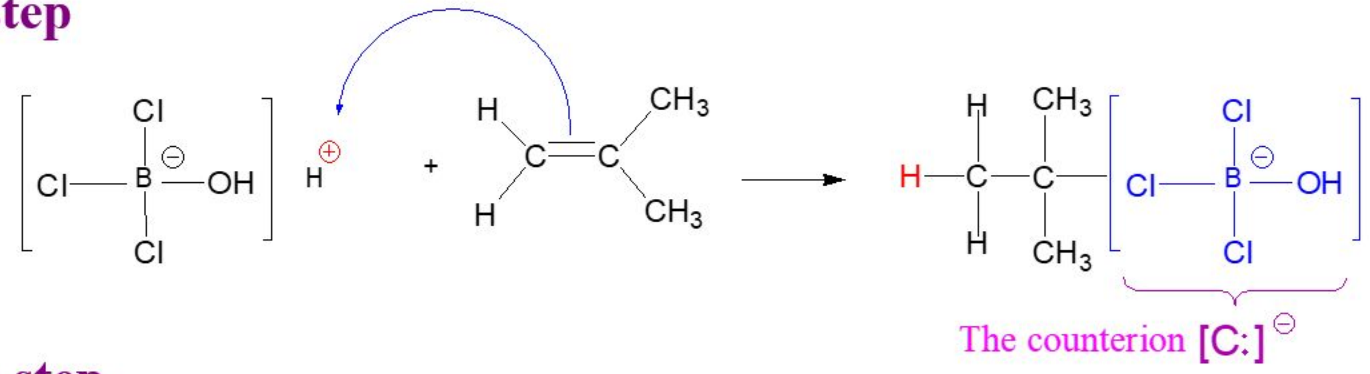
Addition Polymerization
(Polymerization through Double Bond)

Cationic Polymerization Mechanism

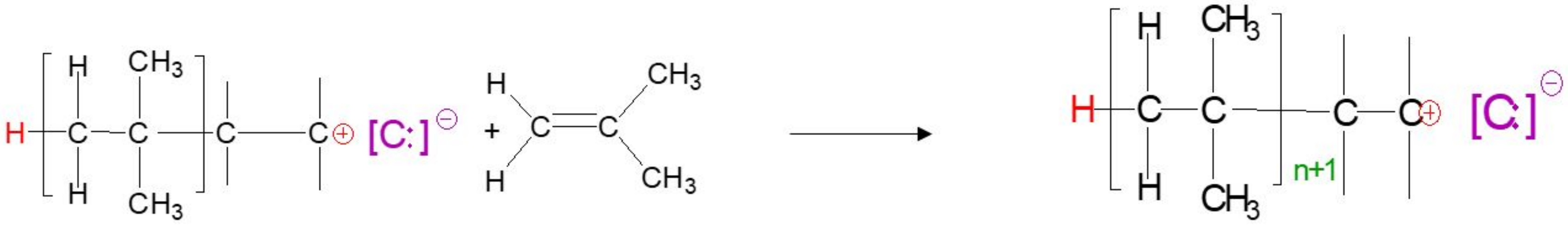
Initiator catalyst



Initiation step



Propagation step



Addition Polymerization
(Polymerization through Double Bond)

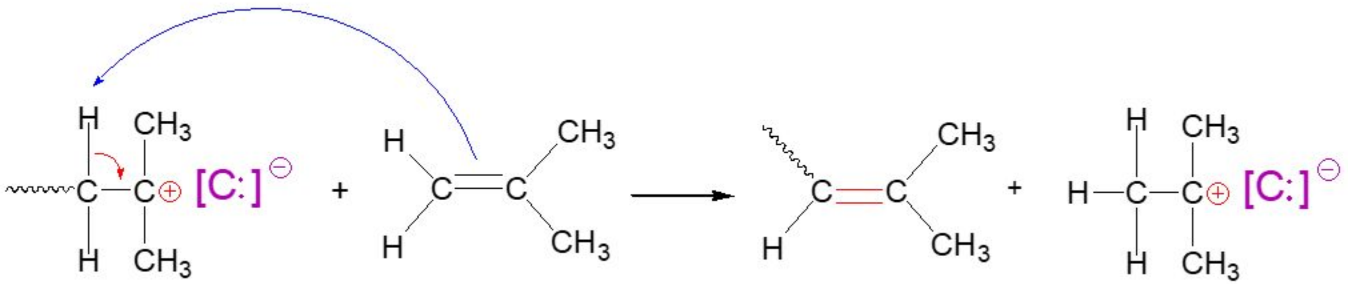
Addition Polymerization

Cationic Polymerization Mechanism

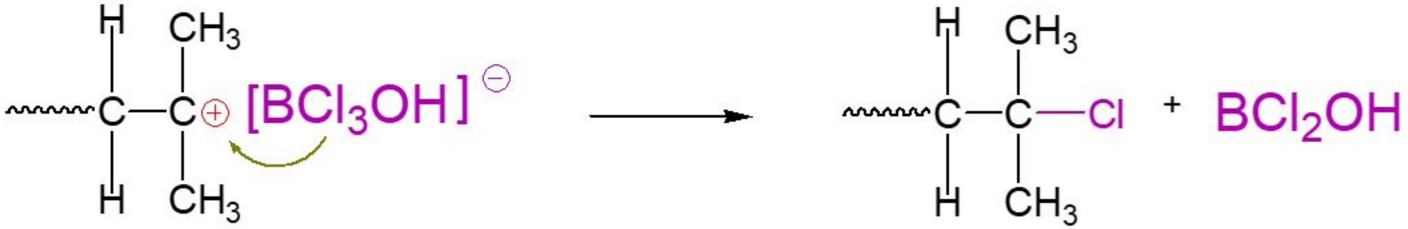
Termination step

Termination step may occur by either

1. Chain transfer

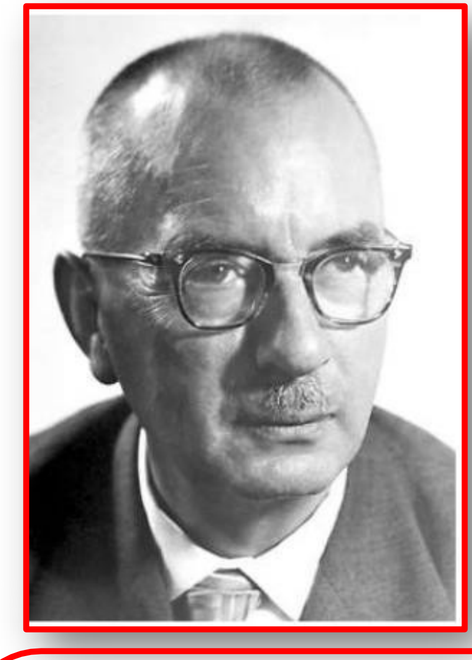


2. Termination step



Addition Polymerization

(Polymerization through Double Bond)



Karl Ziegler **(1898-1973)**;
The German Chemist has discovered in 1953 that $TiCl_3$ and Al Et_3 are combined together they produced an extremely active *heterogeneous* catalyst for the polymerization of ethylene at atmospheric pressure.

Giulio Natta (1903-1979),
An Italian chemist, extended the method to other olefins like propylene and developed variations of Ziegler catalyst based on his findings on the mechanism of polymerization reaction.

Addition Polymerization

(Polymerization through Double Bond)

The Ziegler-Natta catalyst family includes halides of titanium(Ti), chromium(Cr), vanadium (V) and zirconium(Zr), typically activated by alkyl aluminum compounds.

Karl-Ziegler and Giulio Natta won the **Nobel Prize** in Chemistry in 1963 for their work.

Addition Polymerization
(Polymerization through Double Bond)

Coordination Polymerization

The Ziegler- Natta catalyst consists of:

Co-Catalyst

- Group III metallic compounds, such as;

$AlEt_3$, $AlEt_2Cl$, $Al(OEt)Et_2$

Catalyst

- Group IV transition metal halide, such as;

$TiCl_4$, $TiCl_3$, VCl_4, $ZrCl_4$, $NiCl_2$, $MnCl_2$

Addition Polymerization

(Polymerization through Double Bond)

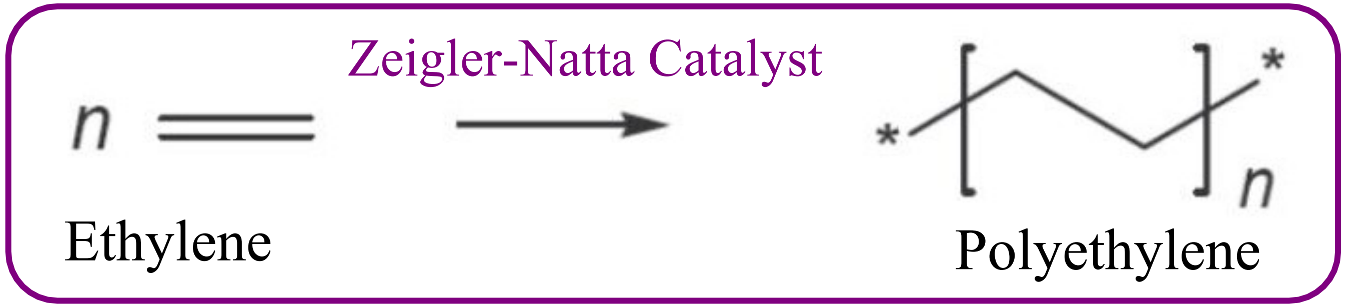
Coordination Polymerization

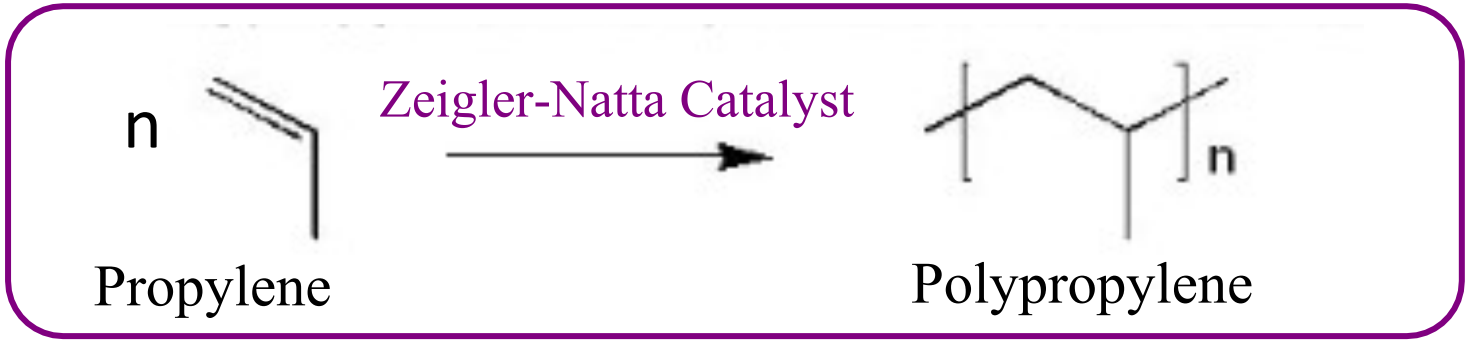
General Reaction

- Most of the time catalyst /co-catalyst pair are **$TiCl_3$** and **$Al(C_2H_5)_2Cl$**

Or **$TiCl_4$** with **$Al(C_2H_5)_3$**

- This catalytic system able to polymerize olefins (such as; ethylene and Propylene) into **linear**, **high molecular weight** polyethylene which conventional polymerization techniques.





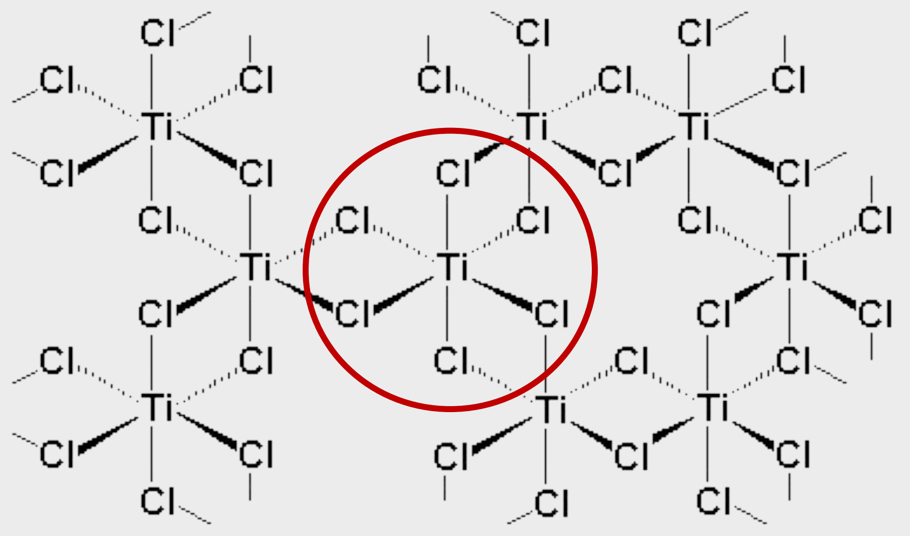
Addition Polymerization
(Polymerization through Double Bond)

Addition
Polymerization

Coordination Polymerization

Mechanism of Zeigler-Natta catalyst Polymerization

- $TiCl_3$ can arrange itself into a number of crystal structures, such as α-$TiCl_3$.



a crystal of α-$TiCl_3$

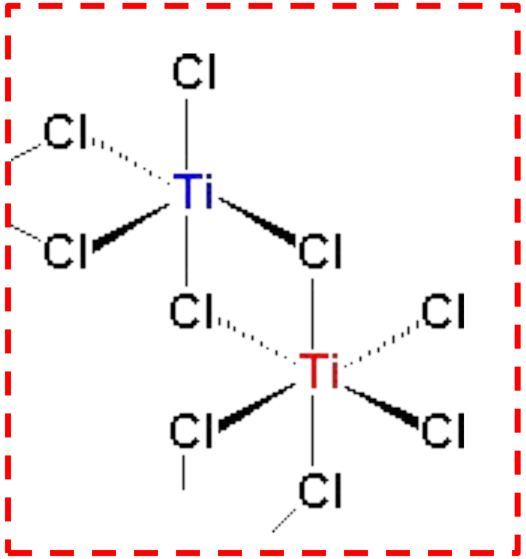
- Each titanium atom is coordinated to six chlorine atoms, with octahedral geometry.

Addition Polymerization

(Polymerization through Double Bond)

Mechanism of Zeigler-Natta catalyst Polymerization

- ❑ In the interior of the crystal, each titanium is surrounded by six chlorines, but on the surface, a titanium atom is surrounded on one side by five chlorine atoms.



Titanium is from transition metals, that have six empty orbitals (resulting from one 4*s* and five 3*d*-orbitals).

The titanium on the interior (in red) has six chlorine neighbors,
The surface titanium (blue) only has five.

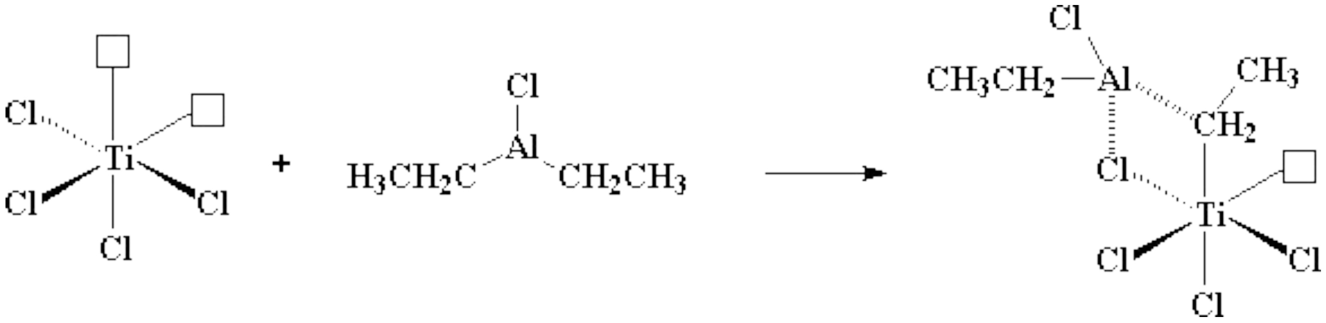
Addition Polymerization

(Polymerization through Double Bond)

Mechanism of Zeigler-Natta catalyst Polymerization

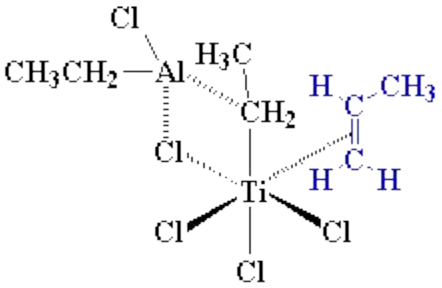
1. Initiator catalyst

First, $Al(C_2H_5)_2Cl$ donates one of its ethyl groups to titanium, and one of the chlorines leaves the molecules. And new empty orbital is obtained.



2. Initiation Step

When a vinyl monomer such as propylene which has two electrons in the π-system of a carbon-carbon double bond. Those electrons are able to fill the empty orbital of the titanium. i.e; propylene and the titanium form a *complex*



The π-electrons from propylene end up filling titanium's empty orbital.

Addition Polymerization

(Polymerization through Double Bond)

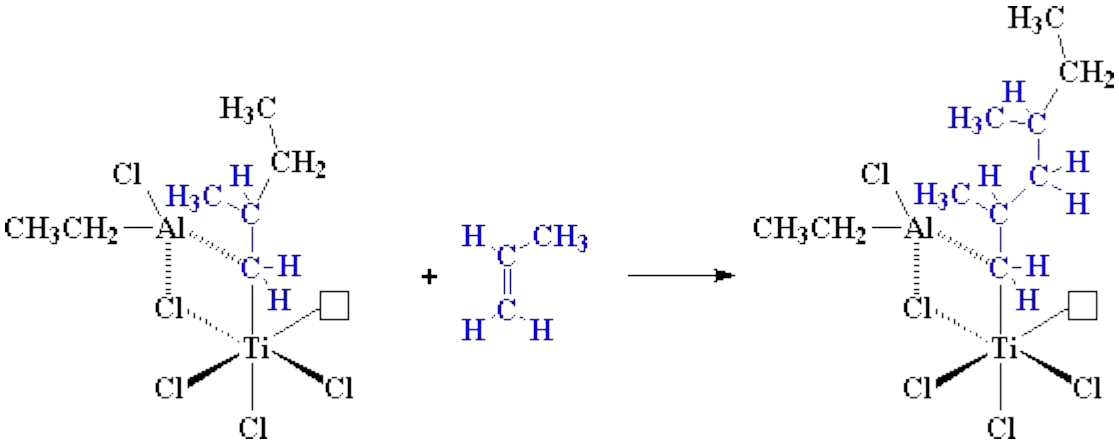
Addition Polymerization

Mechanism of Zeigler-Natta catalyst Polymerization

3. Propagation Step

When other Propylene molecules are come in, Propagation is continues over and over again, repeatedly adding links to the polymer chain.

The more monomer is added the more polymer chain grows



Addition Polymerization

(Polymerization through Double Bond)

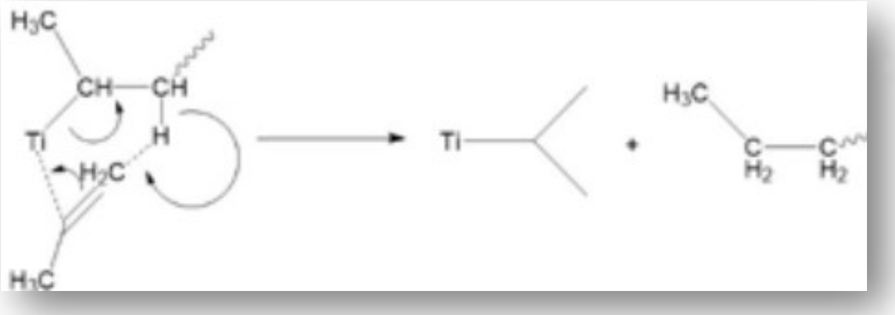
Mechanism of Zeigler-Natta catalyst Polymerization

1. Termination step

There are three termination approaches from the use of $AlEt_3$ as co-catalyst:

A. β-elimination from the polymer chain-forming metal hydride

B. β-elimination with hydrogen transfer to the monomer



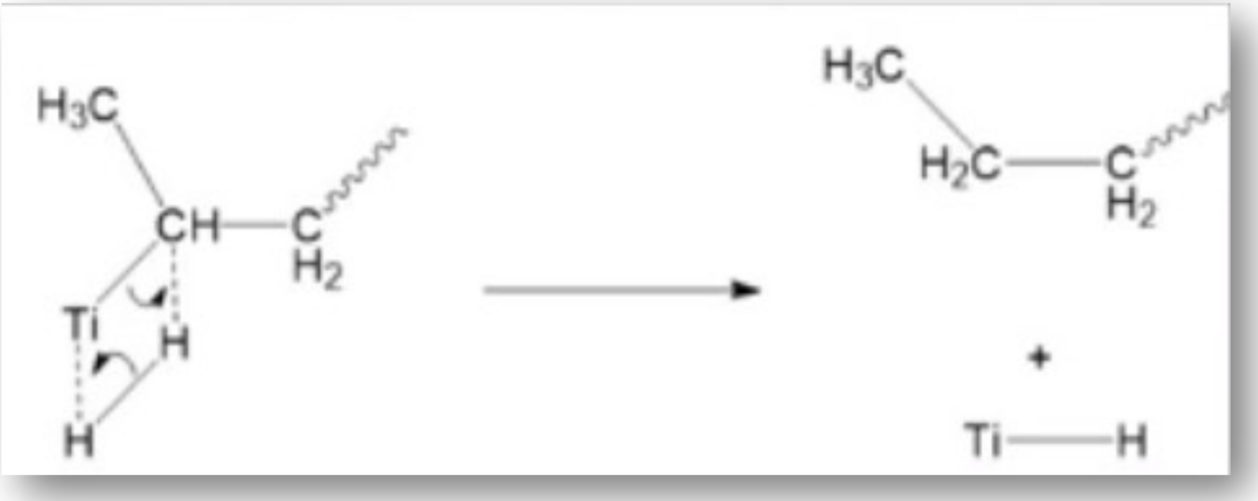
Addition Polymerization

(Polymerization through Double Bond)

Mechanism of Zeigler-Natta catalyst Polymerization

1. Termination step

C. Hydrogenation



Addition Polymerization
(Polymerization through Double Bond)

What means by Tacticity?

- The term tacticity is derived from the Greek word “tacitikos”, means arrangement or order.
- Is the relative stereochemistry of adjacent chiral centers within macromolecule. a
- The practical significance of tacticity rests on the effects on the physical properties of the polymer .

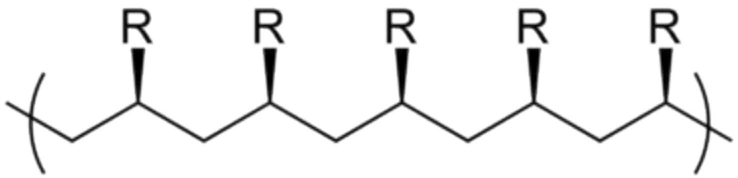
A **tactic macromolecule** in the IUPAC definition is a macromolecule in which essentially all the configurational (repeating) units are identical.

Addition Polymerization

(Polymerization through Double Bond)

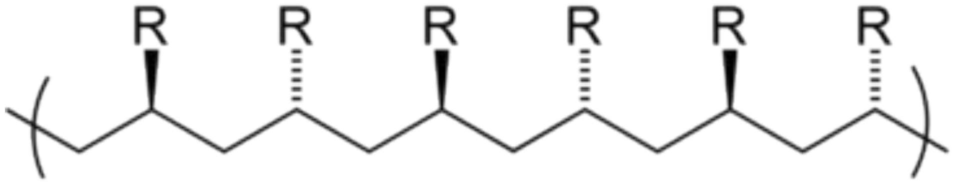
Stereospecific Polymers or Tacticity

Isotactic polymers



In isotactic macromolecules all the substituents are located on the same side of the macromolecular backbone. An isotactic macromolecule consists of 100% meso diads. Polypropylene formed by Ziegler-Natta catalysis is an isotactic polymer

Syndiotactic polymers



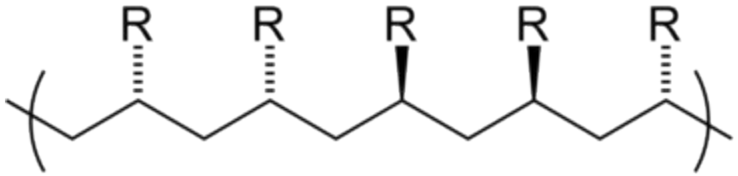
In syndiotactic or **syntactic** macromolecules the substituents have alternate positions along the chain.

Addition Polymerization
(Polymerization through Double Bond)

Stereospecific Polymers or Tacticity

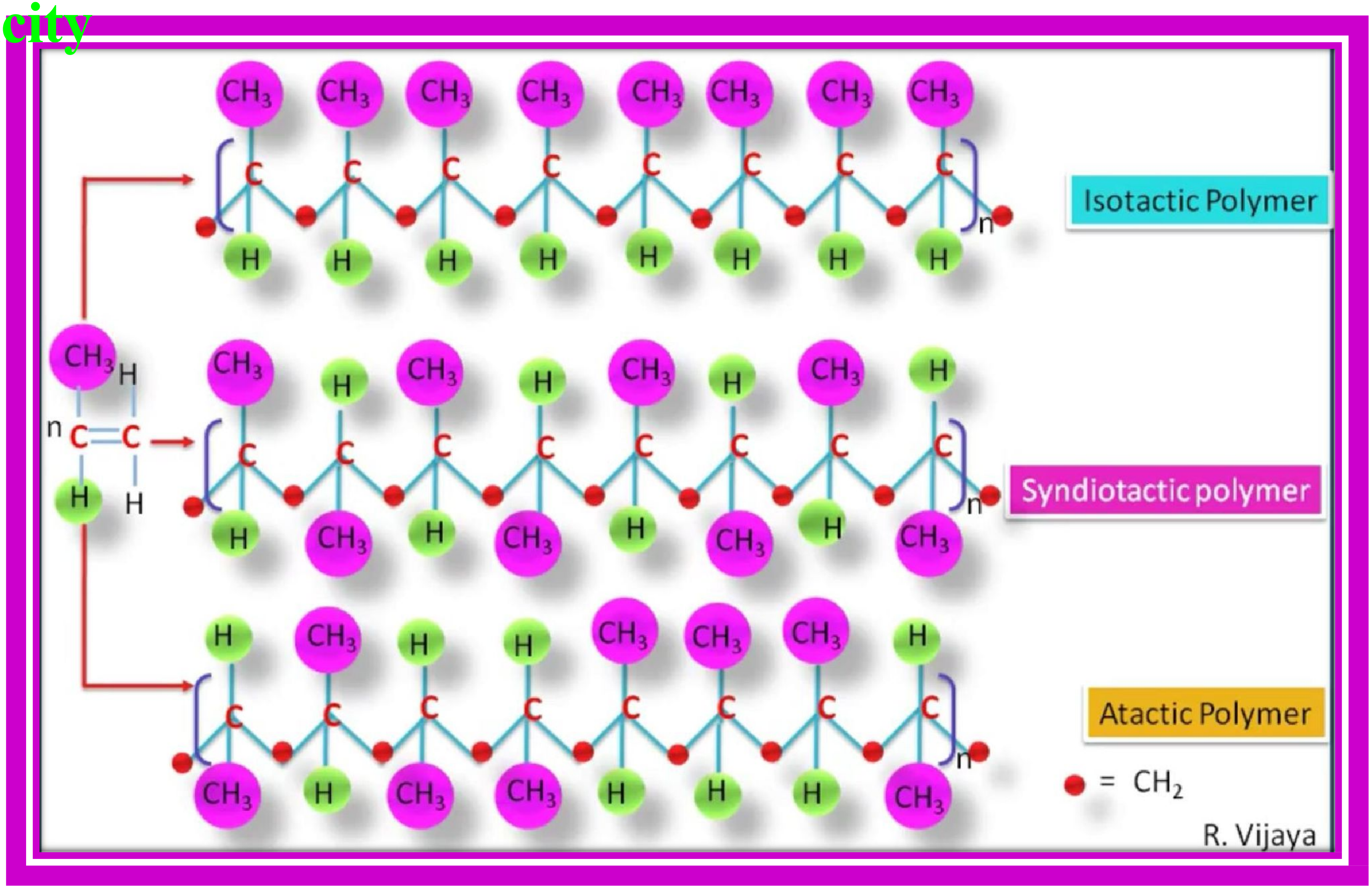
Atactic polymers

In atactic macromolecules the substituents are placed randomly along the chain.



atactic polymers

Stereospecific Polymers or Tacticity



Addition Polymerization

(Polymerization through Double Bond)

Ring-opening polymerization

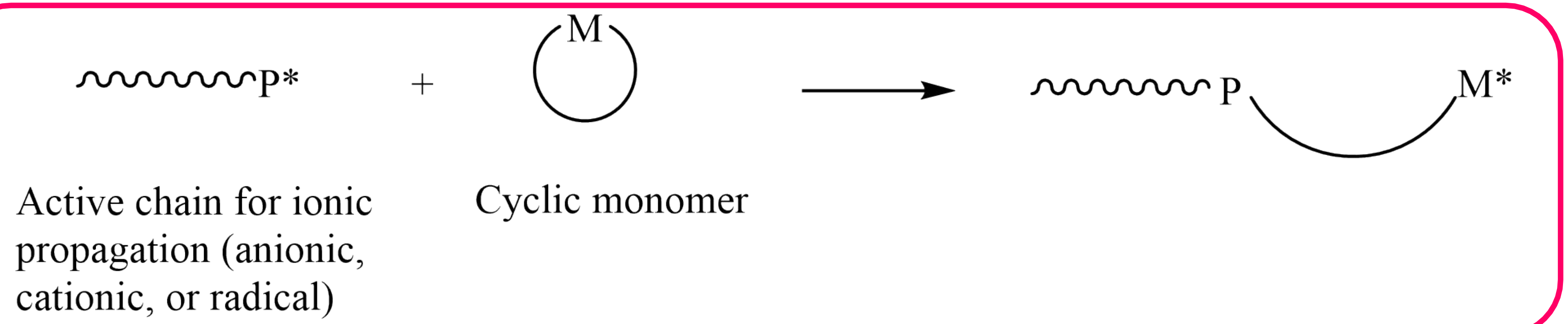
Definition

A polymerization in which a cyclic monomer yields a monomeric unit which is acyclic or contains fewer cycles than the monomer.

Note:

If the monomer is polycyclic, the opening of a single ring is sufficient to classify the reaction as ring opening polymerization.

Ring-opening polymerization (ROP) is a form of chain-growth polymerization , in which the terminus of a polymer chain attacks cyclic polymer to form a longer polymer (see figure).



Addition Polymerization

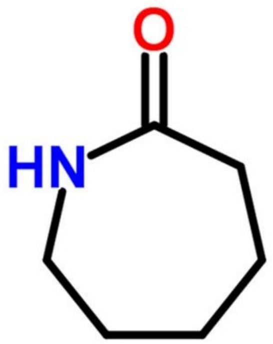
(Polymerization through Double Bond)

Ring-opening polymerization

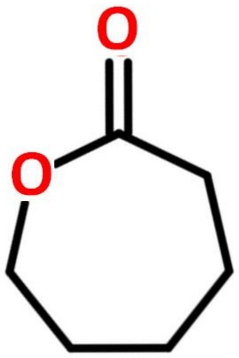
A ring-opening polymerization (ROP) is another form of chain-growth polymerization

- in which the terminal end group of a polymer chain acts as a reactive center where further cyclic monomers can be added by ring-opening and addition of the broken bond.
- Typical monomers that can be polymerized via ROP are di-functional monomers that carry two different reactive groups like one amine or alcohol and one carboxylic acid that have undergone a cyclization reaction.

Examples :



caprolactam



caprolactone

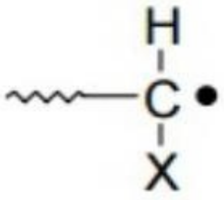
Addition Polymerization

(Polymerization through Double Bond)

Ring-opening polymerization

Ring-Opening Polymerization can be proceed via:

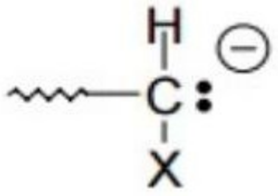
1. Radical Polymerization



"Free" radical

7 valence electrons, electron deficient
Charge = 0 (usually, radical ions are possible)
sp^2, planar, odd electron in "p" orbital
Stabilized by X = electron donating

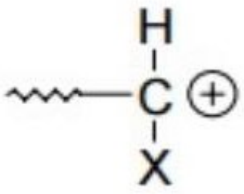
2. Anionic Polymerization



Carbanion

8 valence electrons, lone pair, Lewis **base**
Charge = -1
sp^3, tetrahedral, lone pair in "sp^3" orbital
Stabilized by X = electron withdrawing

3. Cationic polymerization



Carbocation

6 valence electrons, electron deficient, Lewis **acid**
Charge = +1
sp^2, planar, vacant "p" orbital
Stabilized by X = electron donating

Addition Polymerization

(Polymerization through Double Bond)

Ring-opening polymerization

1. Free Radical Ring Opening Polymerization (RROP):

- ❑ Free radical ring-opening polymerizations are rare.
- ❑ For example **cyclic disulfide** with equal to or >8 ring size, the ring can follow *free radical ring opening polymerization*.

Cyclic Disulfide

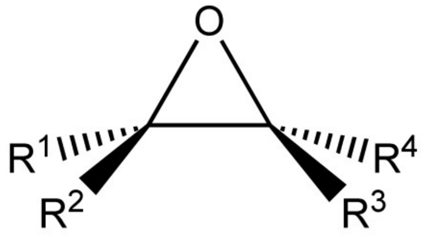
Addition Polymerization

(Polymerization through Double Bond)

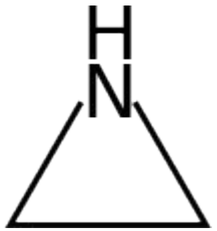
Ring-opening polymerization

2. Anionic Ring Opening Polymerization (AROP):

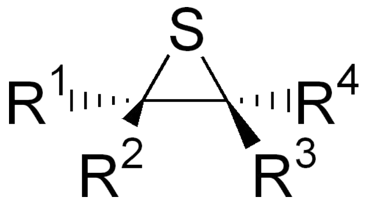
- Monomers with a three-membered structure- such as epoxide, aziridine and episulfide- are able to undergo anionic ROP due to the ring-distortion, despite having a less electrophilic functional group (e.g. ether, amine, and thioether).



epoxide



aziridine



episulfide

- These cyclic monomers are important for many practical applications. The polarized functional group in cyclic monomers is characterized by one atom (usually a carbon) that is electron- due to deficient adjacent atom that is highly electron-withdrawing (e.g. oxygen, nitrogen, sulfur etc).

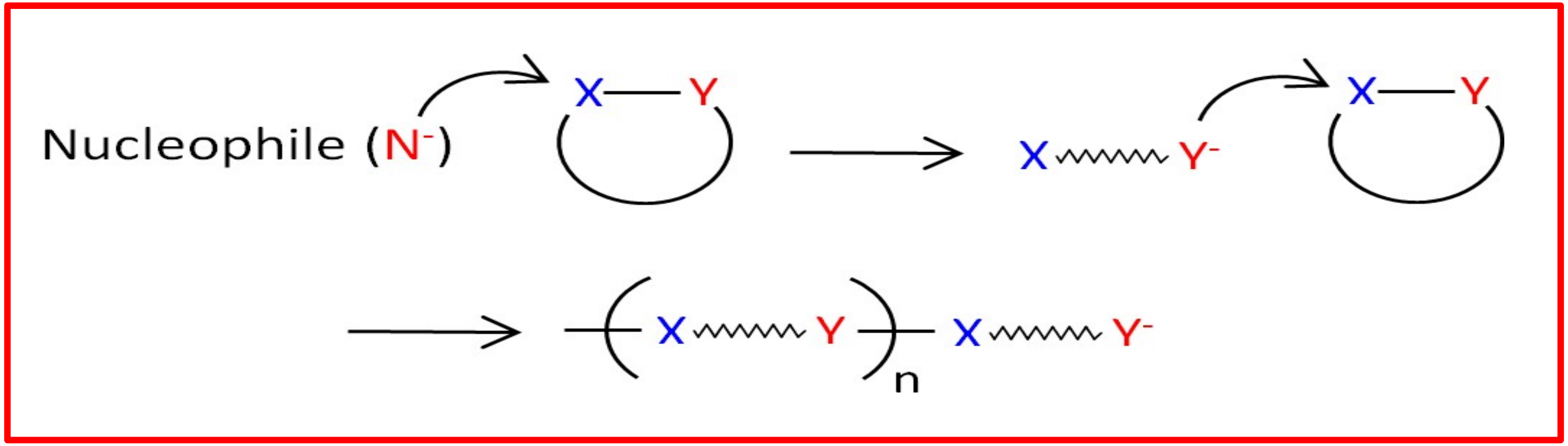
Addition Polymerization

(Polymerization through Double Bond)

Ring-opening polymerization

2. Anionic Ring Opening Polymerization (AROP):

To polymerize these moieties, one of the rings has to open prior polymerization. This can be achieved, for example, by adding a small amount of a nucleophilic reagent (Lewis base) as an initiator. This reaction is called *anionic ring-opening polymerization* (AROP).



Addition Polymerization
(Polymerization through Double Bond)

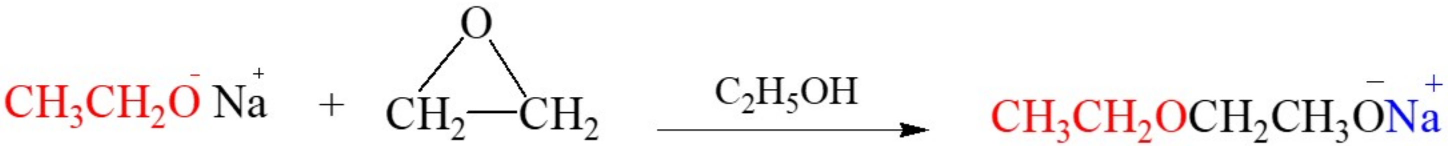
Addition Polymerization

Example: Anionic Ring-opening polymerization

1. Epoxide Polymerization (Anionic ROP)

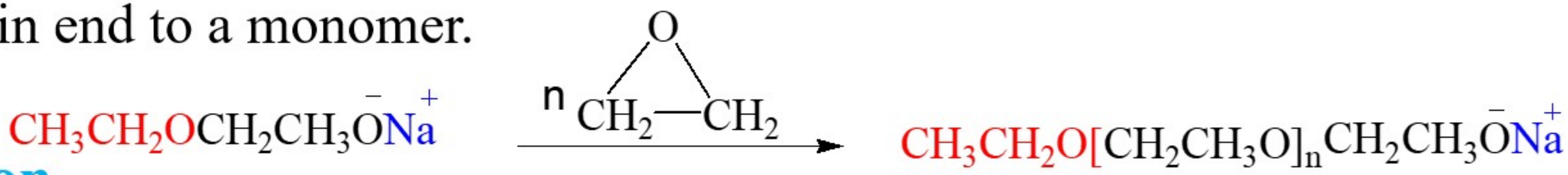
A) Initiation

The nucleophilic reagent used for the initiation of AROP such as; sodium alkoxide reacts with the monomer rings will open with nucleophilic attack on the least substituted carbon atom.



B) Propagation

The general mechanism of propagation for anionic ROP relies on the nucleophilic attack of a propagation chain end to a monomer.



C) Termination

The active centers of AROP monomers are nucleophilic and also act as bases to abstract protons from the monomer.

$$CH_3CH_2O[CH_2CH_3O]_nCH_2CH_3\overset{-}{O}\overset{+}{Na} \xrightarrow{C_2H_5OH} CH_3CH_2O—[CH_2CH_3O]_n—CH_2CH_3OH$$

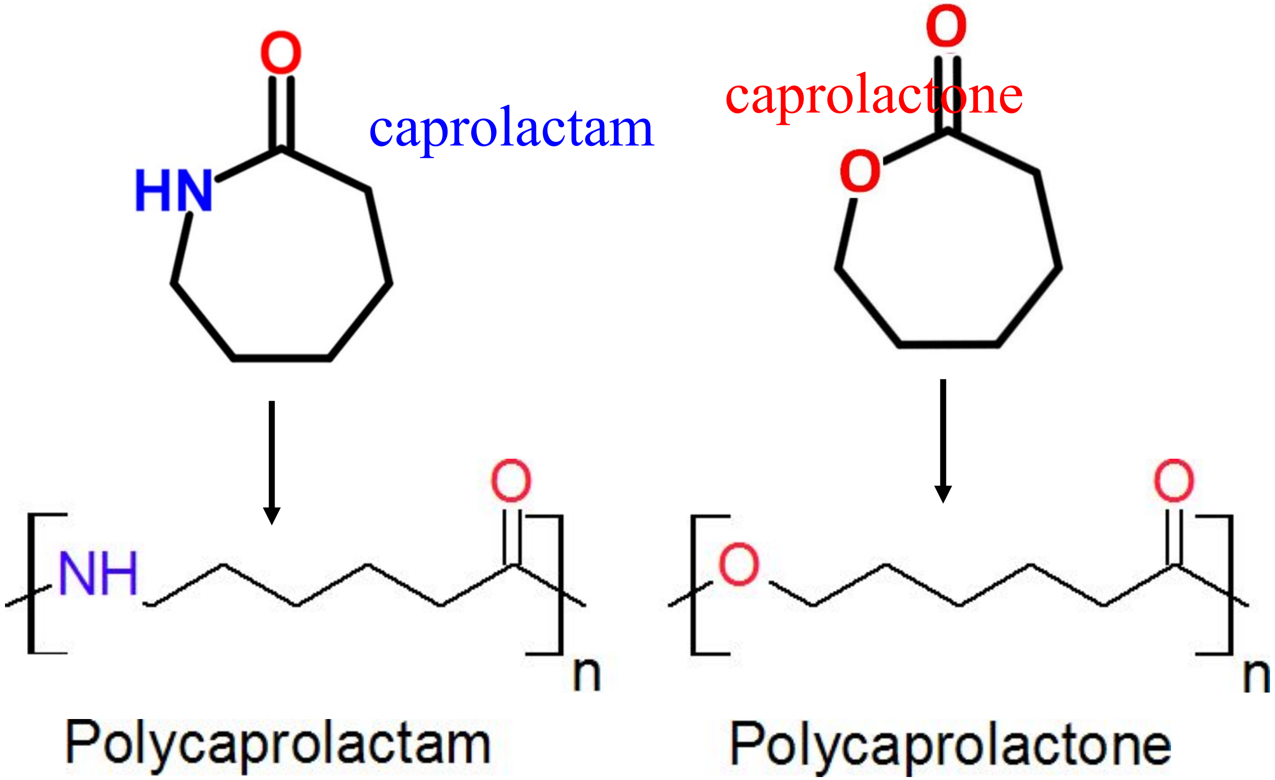
Addition Polymerization

(Polymerization through Double Bond)

Cationic Ring-opening polymerization

❑ Cationic ring-opening polymerization (CROP) is characterized by having a cationic initiator and intermediate.

❑ Examples of cyclic polymers that polymerize through this mechanism include lactones, lactams, amines and ethers.



Polycaprolactam Polycaprolactone

Addition
Polymerization

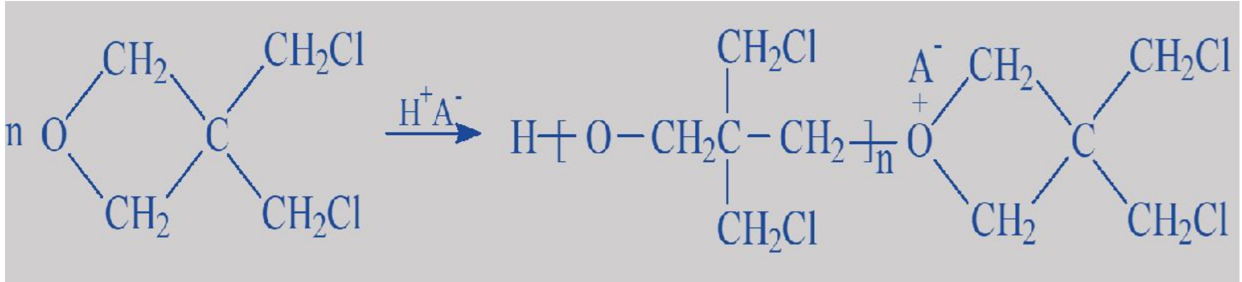
Addition Polymerization

(Polymerization through Double Bond)

Ring-opening polymerization

1. 3.3-bis (chloromethylene) oxa cyclobutene Polymerization (Cationic ROP):

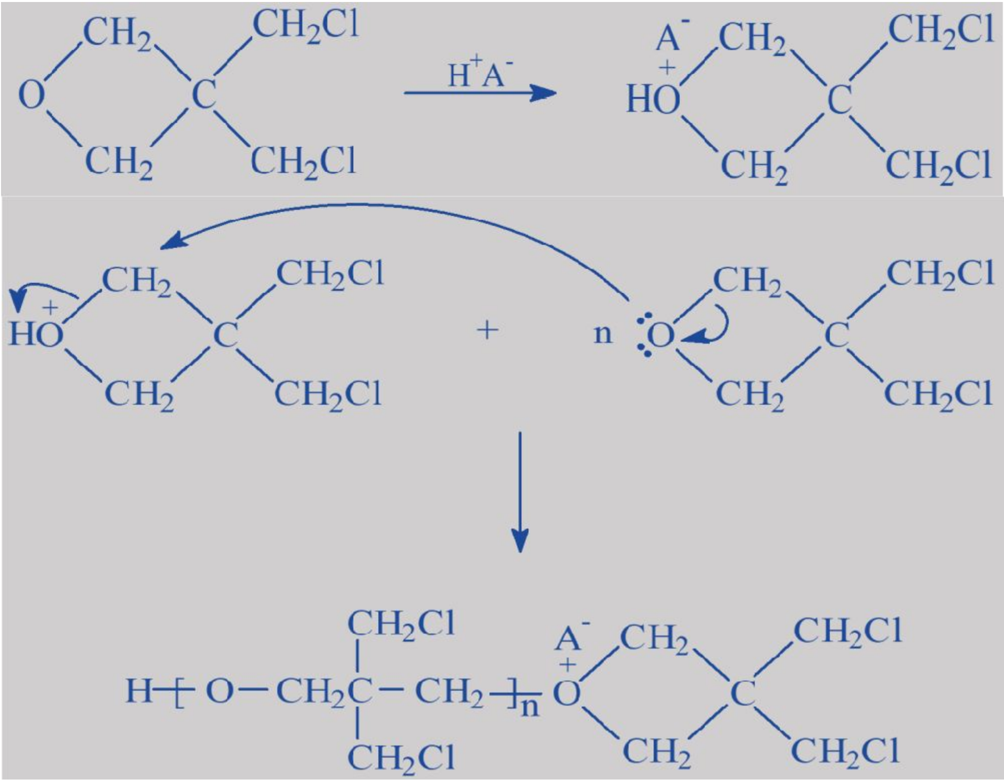
General Equation



3,3 Bis (chloromethyl) Oxa cyclobutane

$[BF_3OH]^- H^+ \equiv H^+A^-$

Reaction Mechanism

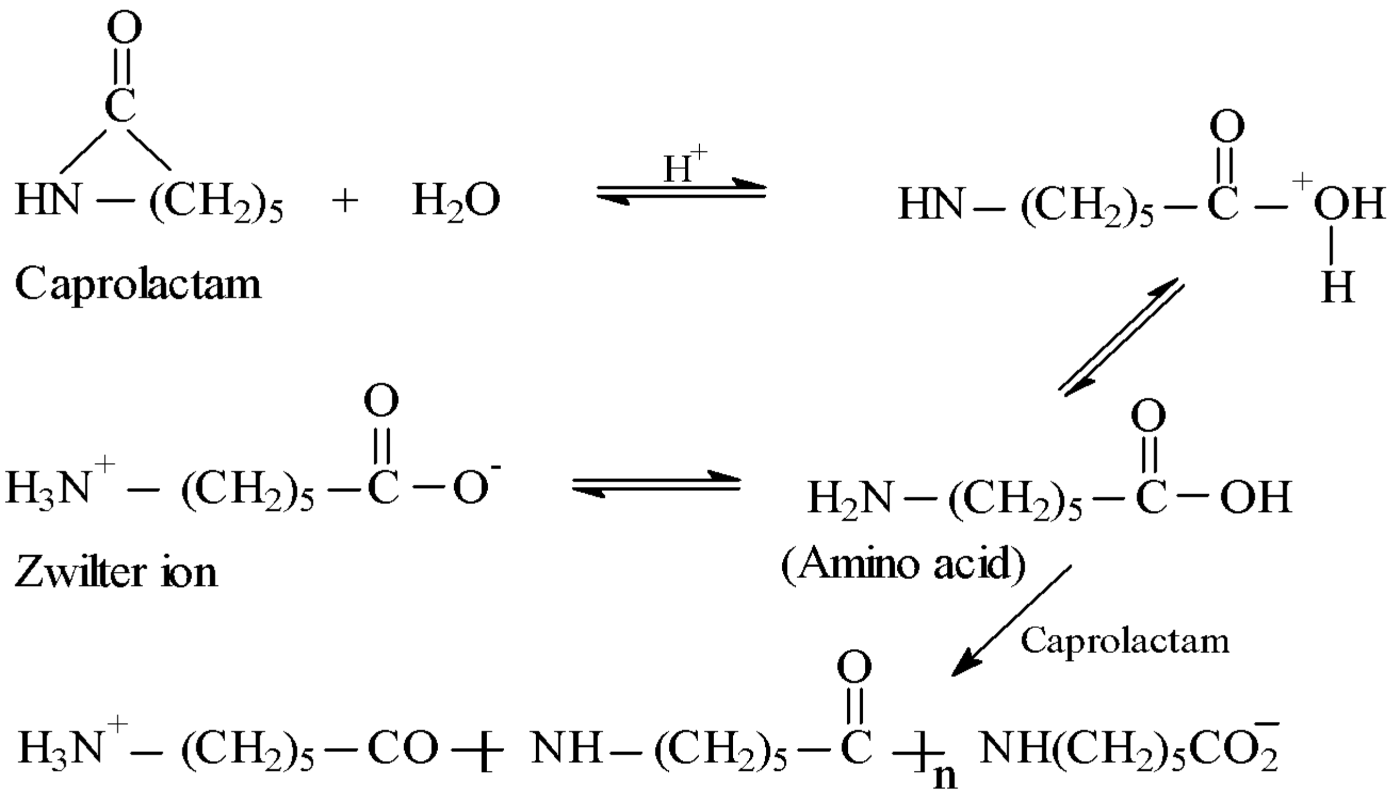


Addition Polymerization
(Polymerization through Double Bond)

Ring-opening polymerization

2. Cyclic Amide Polymerization (Cationic ROP):

By using cationic catalyst with water

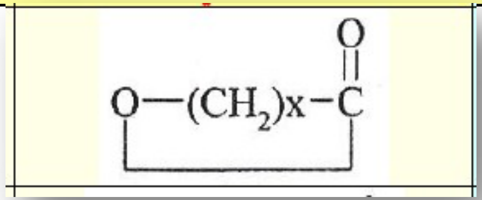
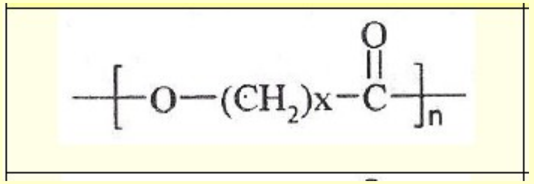
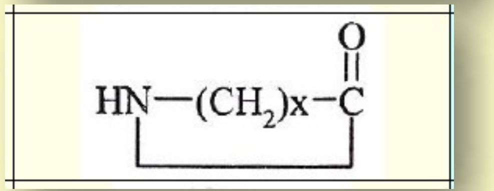
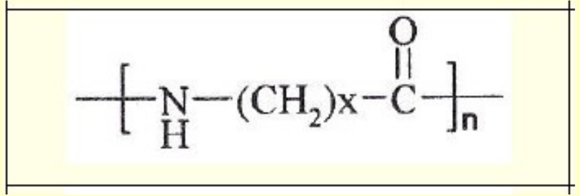
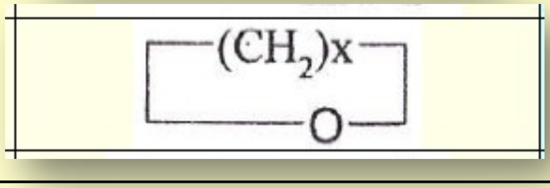
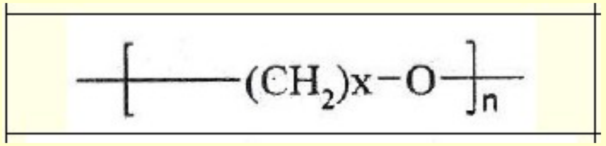
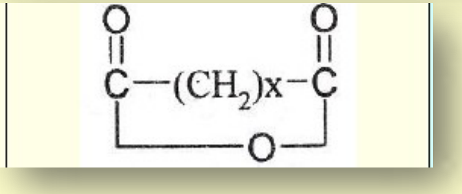
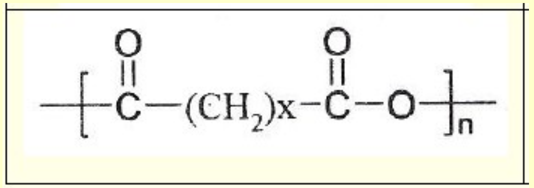


Addition Polymerization

(Polymerization through Double Bond)

Ring-opening polymerization

Addition
Polymerization

Cyclic Monomer	Monomer structure	Polymer Structure
Lactone		 $\left[O-(CH_2)_x-\overset{O}{\overset{\|}{C}} \right]_n$
Lactam		 $\left[\underset{H}{N}-(CH_2)_x-\overset{O}{\overset{\|}{C}} \right]_n$
Cyclic Ether		 $\left[(CH_2)_x-O \right]_n$
Cyclic Anhydrous Acids		 $\left[\overset{O}{\overset{\|}{C}}-(CH_2)_x-\overset{O}{\overset{\|}{C}}-O \right]_n$

Addition Polymerization

(Polymerization through Double Bond)

Modification of Polymerization

Natural and synthetic polymers are converted to other polymers if they undergo chemical reactions

Examples:

✔ Hydrolysis of Poly vinyl acetate

✔ Halogenation of Polyethylene and Rubber

✔ Esterification and Etherification of Cellulose

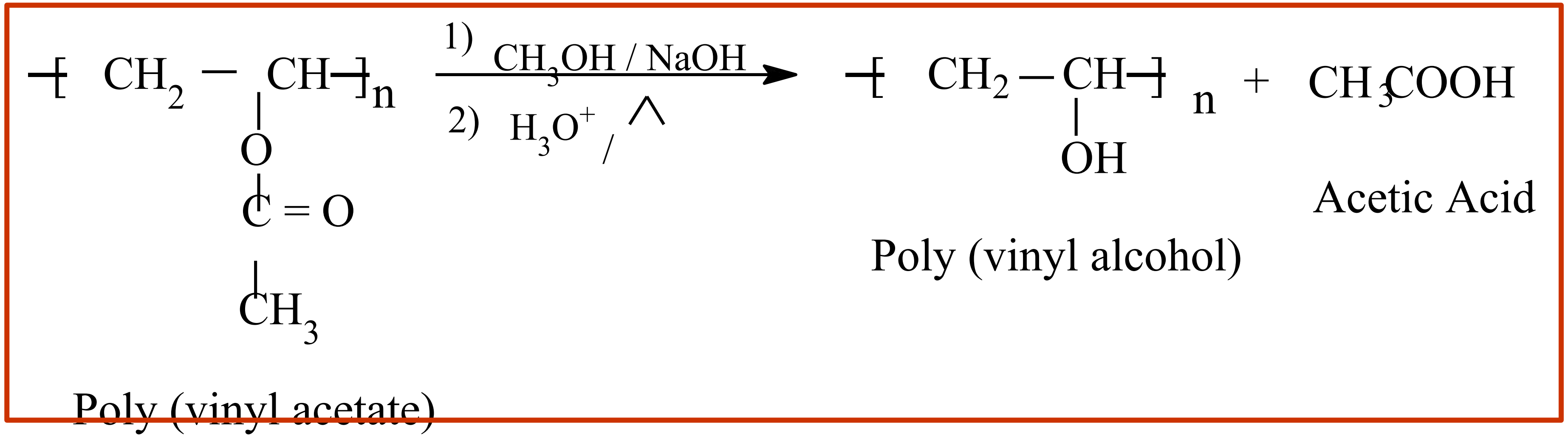
✔ Crosslinking of unsaturated polyesters

Addition Polymerization

(Polymerization through Double Bond)

Modification of Polymerization

PVA is manufactured commercially by several methods; alkaline hydrolysis is usually used as an industrial scale. Sodium hydroxide and sodium methoxide are the most important catalyst for alcoholysis with present of alcohol such as methanol or ethanol.



$$\left[CH_2-\underset{\underset{CH_3}{\underset{|}{\underset{C=O}{\underset{|}{O}}}}}{\underset{|}{CH}} \right]_n \xrightarrow[2)\ H_3O^+/\Delta]{1)\ CH_3OH\,/\,NaOH} \left[CH_2-\underset{OH}{\underset{|}{CH}} \right]_n + CH_3COOH$$

Poly (vinyl acetate)

Poly (vinyl alcohol)

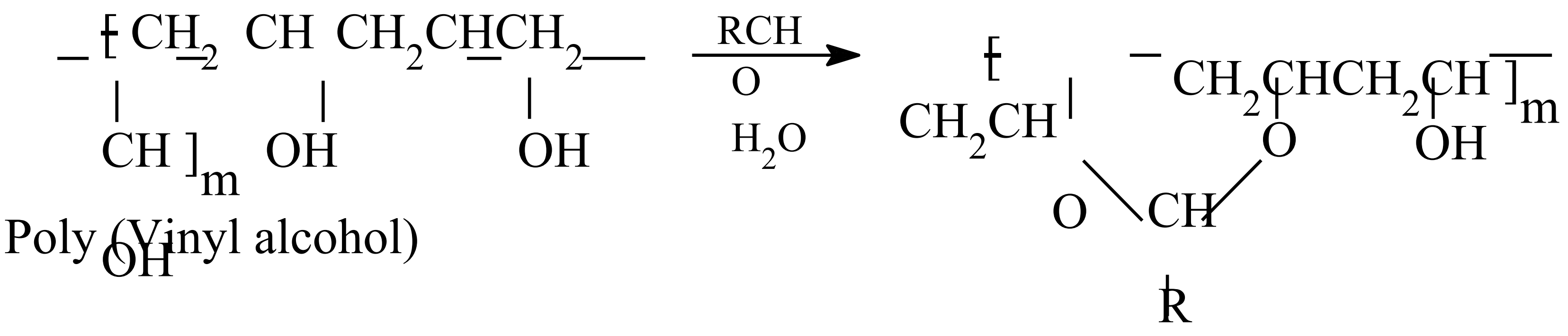
Acetic Acid

Addition Polymerization
(Polymerization through Double Bond)

Addition
Polymerization

Modification of Polymerization

Poly (vinyl acetal) is formed when poly (vinyl acetal) interacts with aldehydes in aqueous medium and in the presence of acid as a catalyst as follows:



Poly (Vinyl alcohol)

R = H or $-CH_2CH_2CH_3$

Polyvinyl acetal


Thank you!