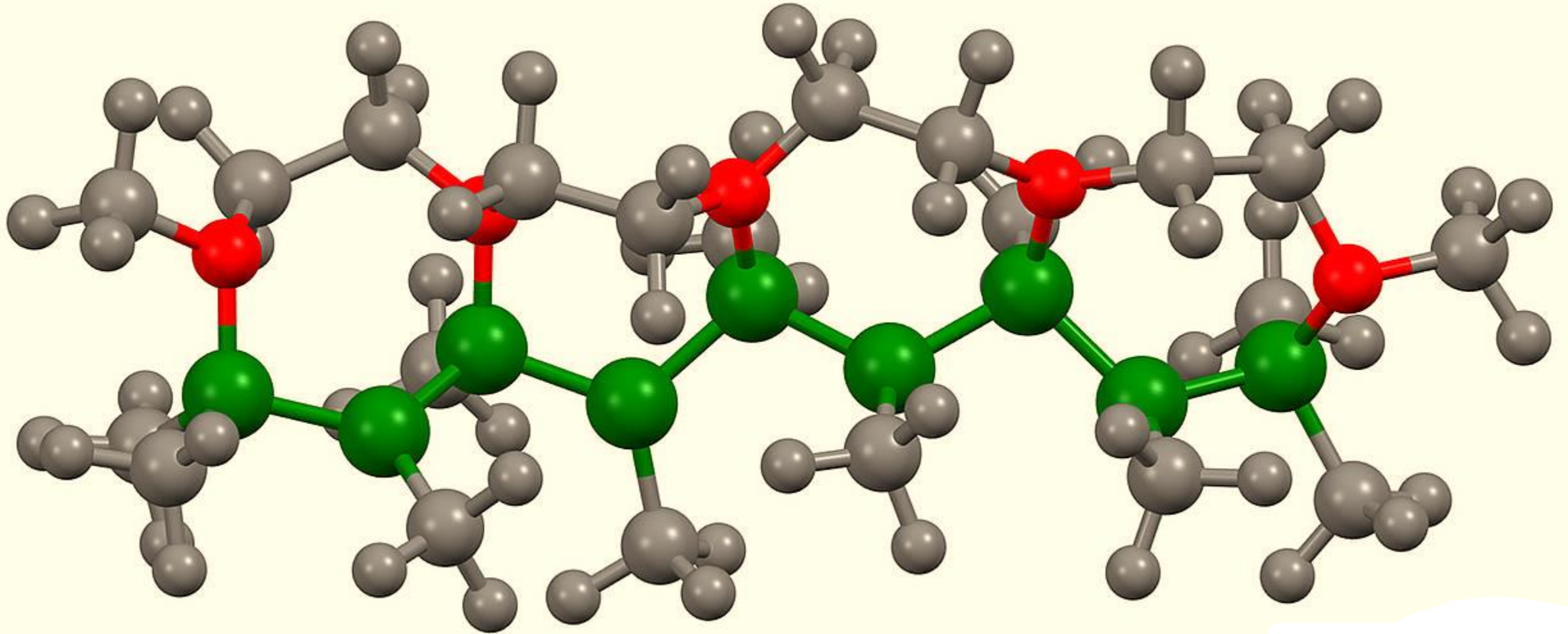


# Chapter 2:

## General Methods for preparing Polymers



# 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

```
graph TD; A[Synthetic Methods] --> B[Step-Growth Polymerization]; A --> C[Chain-Growth Polymerization]; B --> D[Condensation Polymerization]; D --> E[Examples: Polyamides & Polyesters]; C --> F[Addition Polymerization]; F --> G[Examples: Polystyrenes];
```

The diagram is a flowchart starting with a central box labeled 'Synthetic Methods'. Two arrows branch out from this box to 'Step-Growth Polymerization' on the left and 'Chain-Growth Polymerization' on the right. From 'Step-Growth Polymerization', an arrow points down to 'Condensation Polymerization', which then points down to 'Examples: Polyamides & Polyesters'. From 'Chain-Growth Polymerization', an arrow points down to 'Addition Polymerization', which then points down to 'Examples: Polystyrenes'. Each box is color-coded: 'Synthetic Methods' is red, 'Step-Growth Polymerization' is purple, 'Chain-Growth Polymerization' is green, 'Condensation Polymerization' is pink, 'Addition Polymerization' is green, and the example boxes are pink and green respectively.

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.

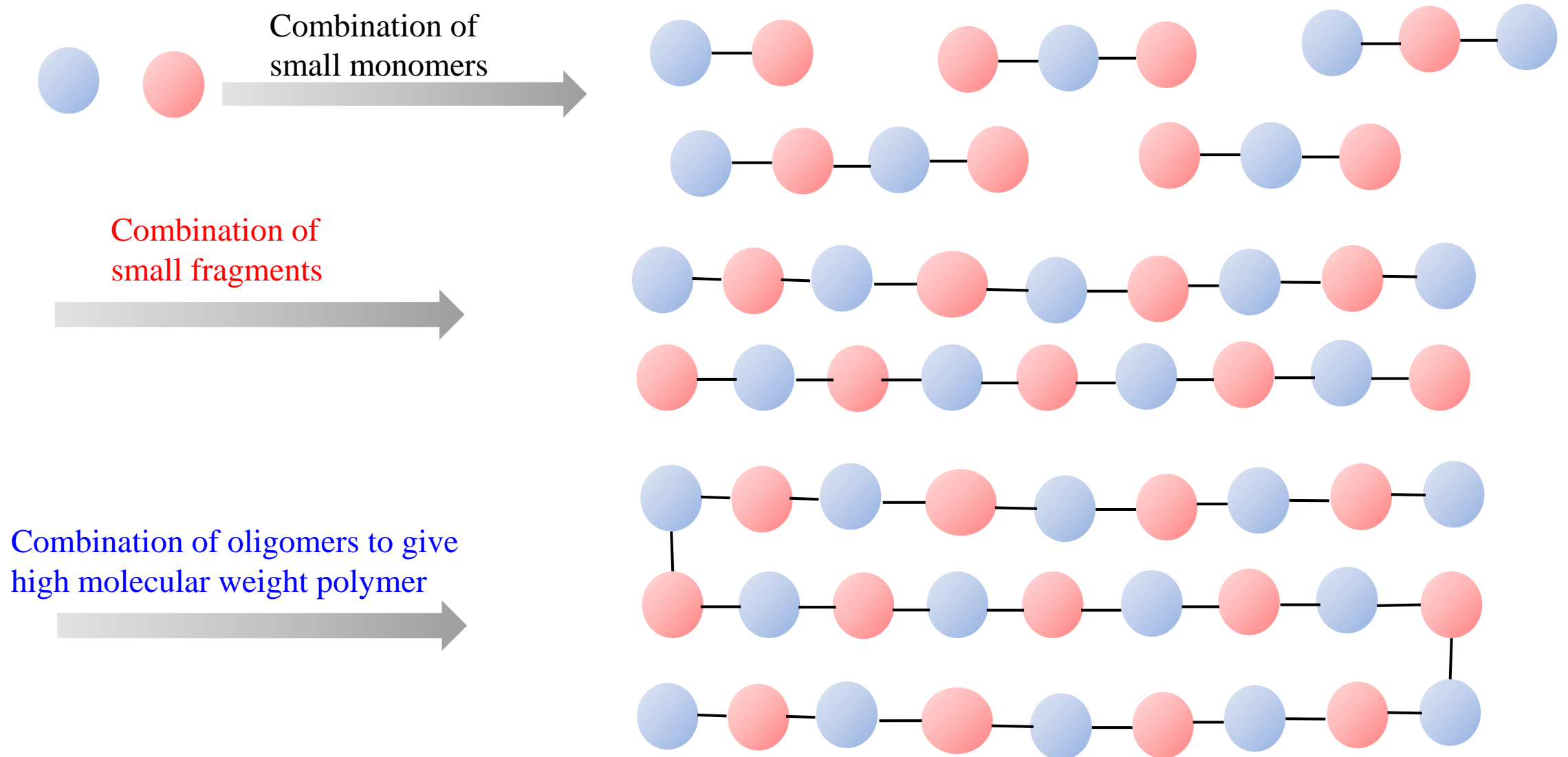
## Characteristics of Condensation Polymers

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 give:  
*Linear Polymer* Or *Cross linked polymer*.

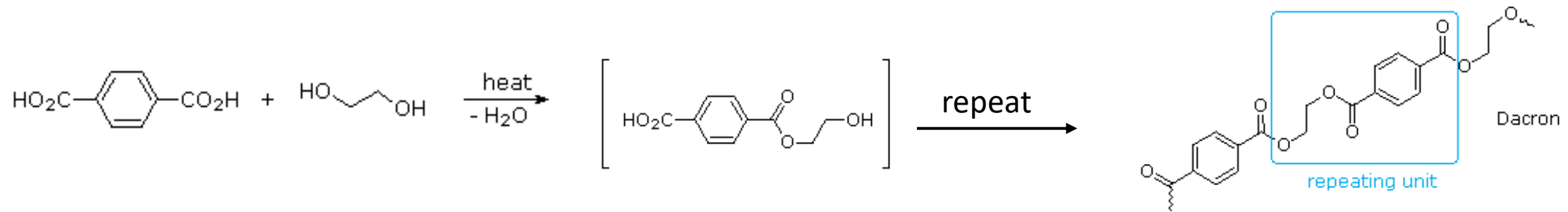
### A representation of step-growth polymerization



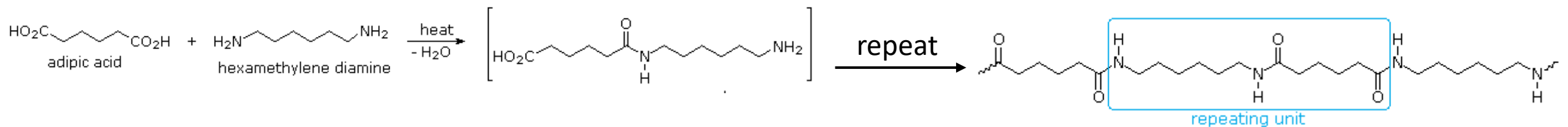
# Examples of **Condensation polymerization** “step-growth polymerization”

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 transference 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  $\text{-NHCO-}$

2. Preparation methods:

A. Direct amidation between diacid & diamine

B. Self amidation for amino acids

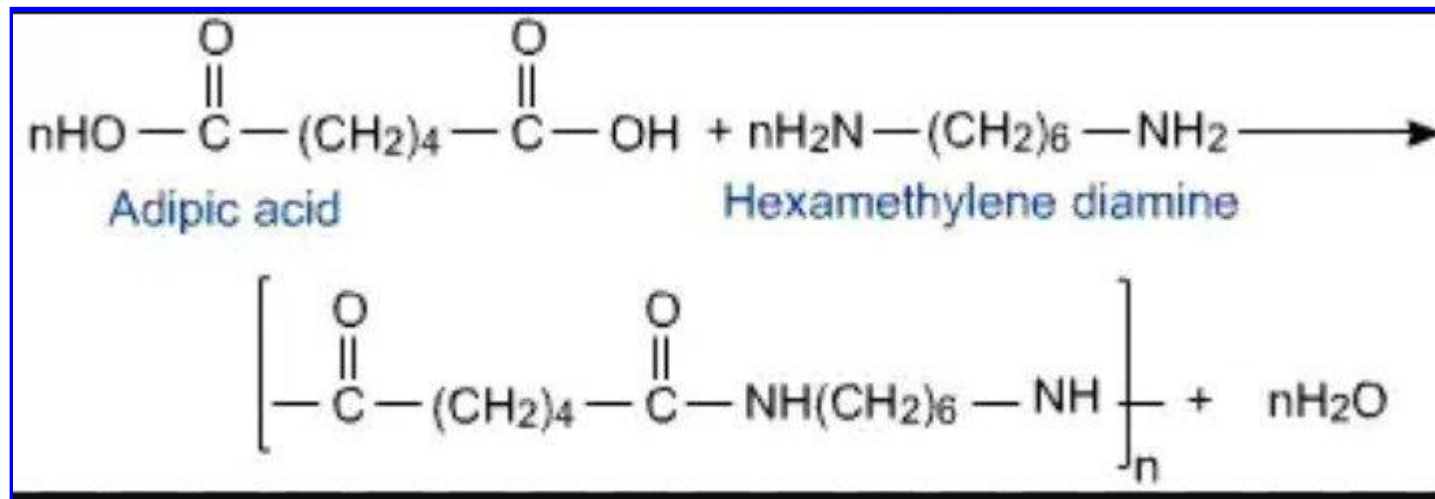
C. Ring-opening polymerization reactions for cyclic amides



## 1. Linear Condensation Polymers

### ■ Polyamides

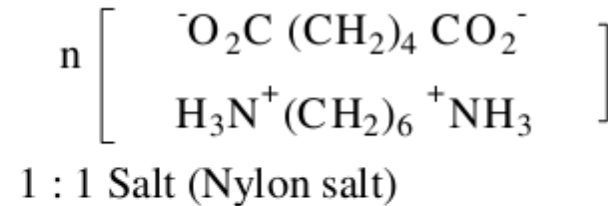
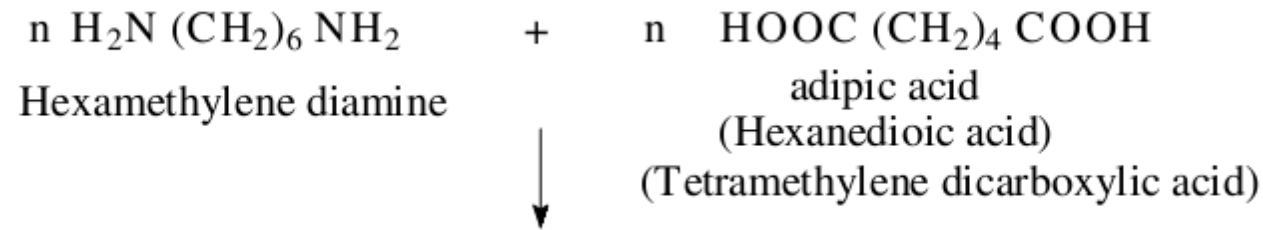
#### Synthesis of Nylon 6,6



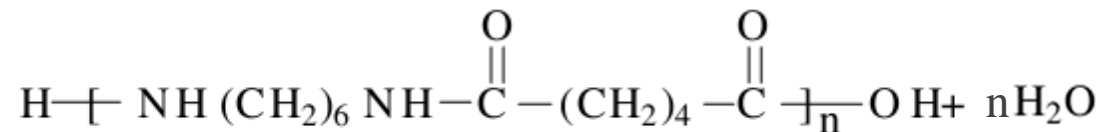
Ammonium salt is formed in the beginning which is called **Nylon salt**,  
By heating the salt water is lost and a polymer with 10,000 Mwt is formed.

## 1. Linear Condensation Polymers

### ■ Polyamides Direct Amidation **Synthesis of Nylon 6,6**



270 C  
2600 lb/sq.ft.



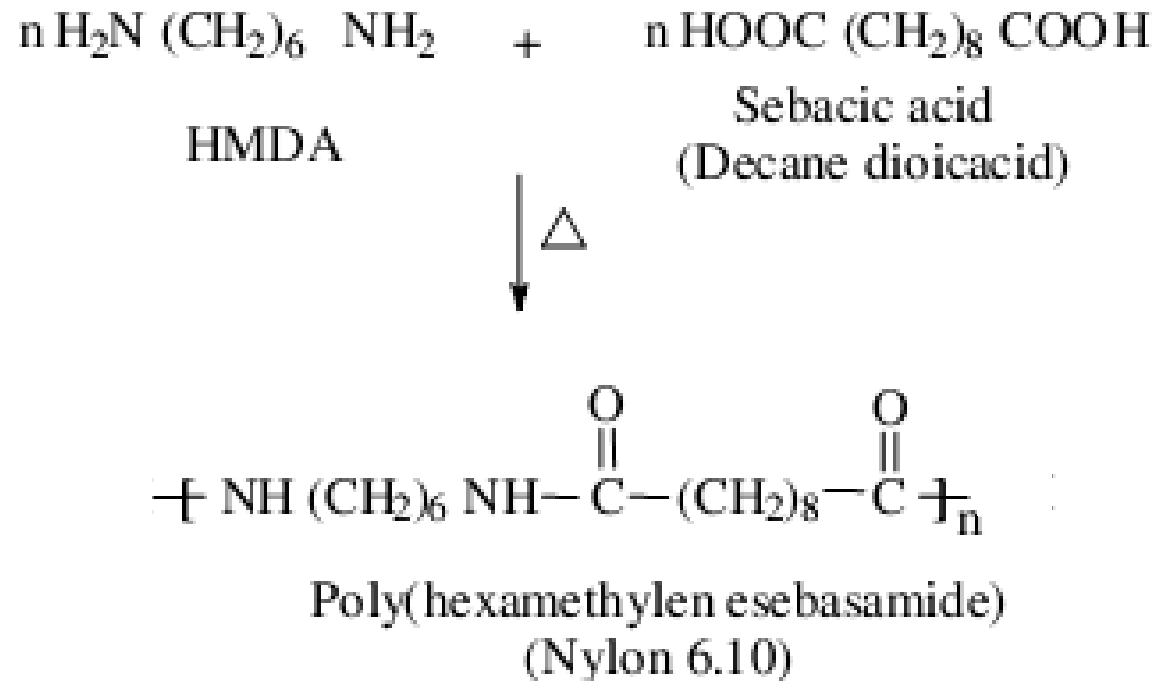
Poly ( hexamethylene adipamide)

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



## 1. Linear Condensation Polymers

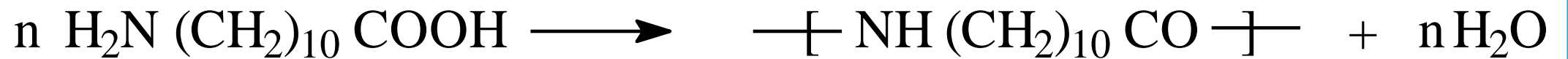
### ■ Polyamides

#### B. Self amidation for amino acids

## Synthesis of Nylon 11

Amino acid polymerization with different function groups

**As the reaction of Amino undecanoic acid:**



$\omega$ -Amino undecanoic acid

Nylon 11

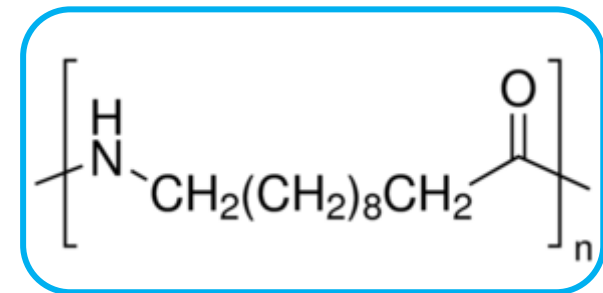
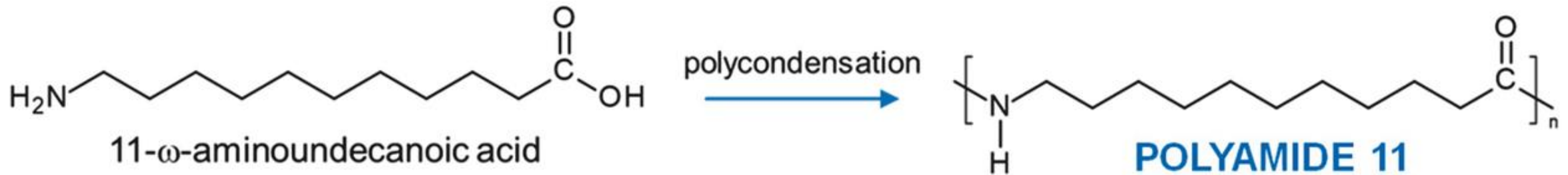
# Condensation Polymerization

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

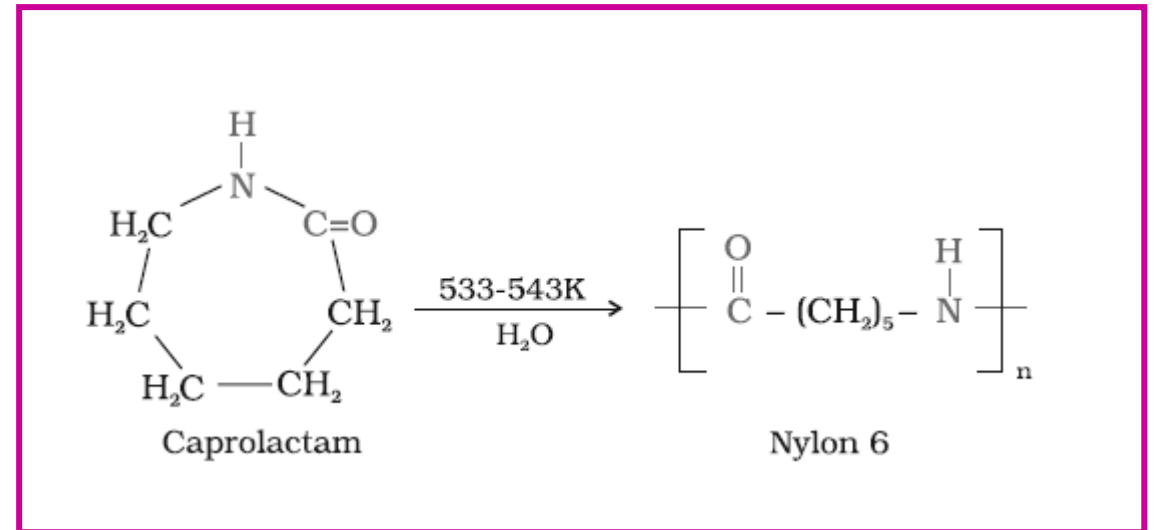
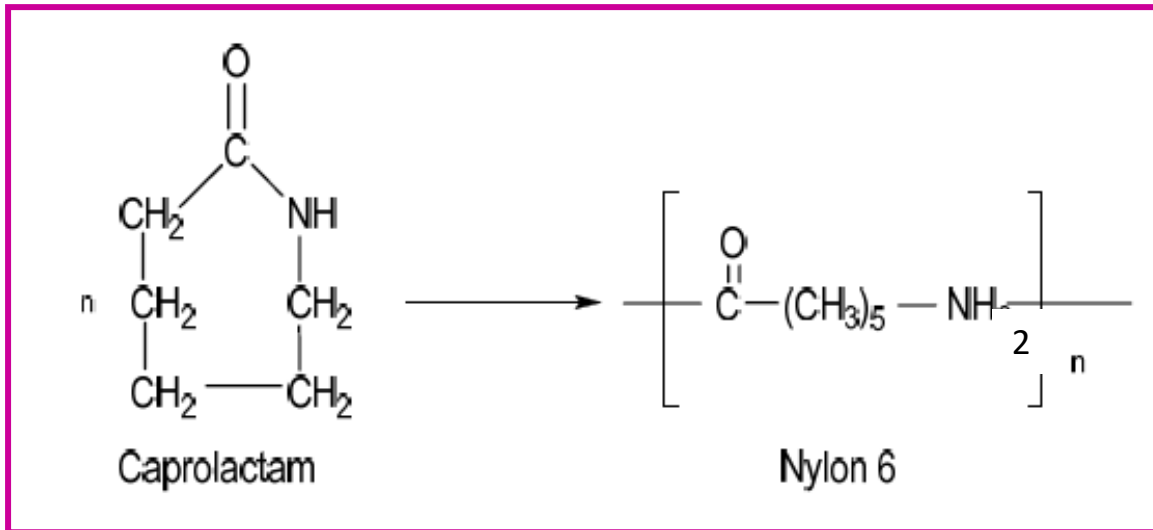
## C. Ring-opening polymerization reactions for cyclic amides

Example

Nylon 6

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

or

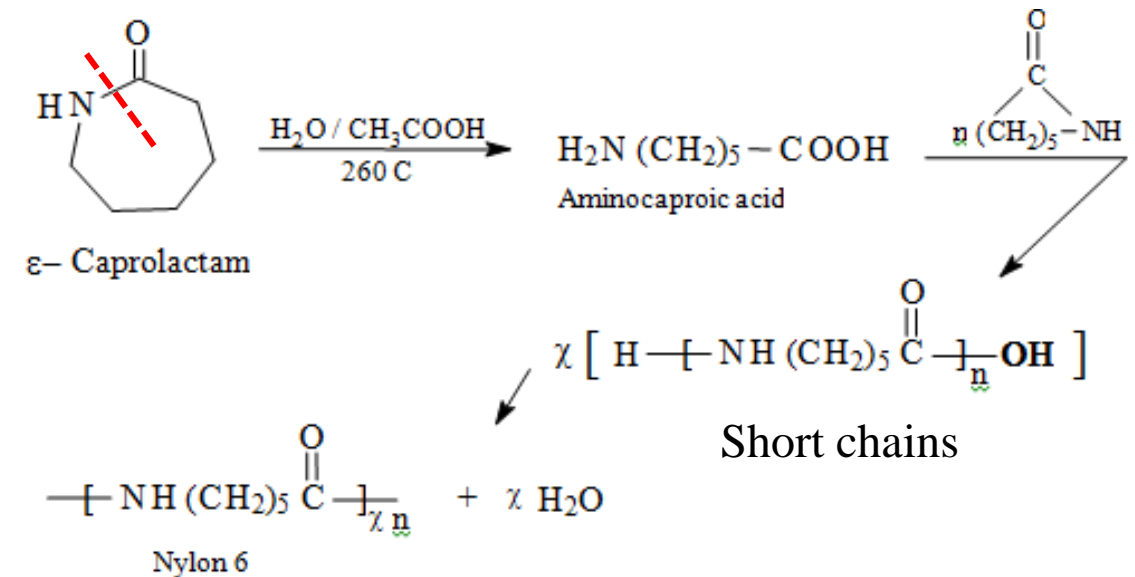


## C. Ring-opening polymerization reactions for cyclic amides

### 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.



## C. Ring-opening polymerization reactions for cyclic amides

Growth  
Polymerization

### ✓ Advantages of Polyamide Polymers

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



## 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.



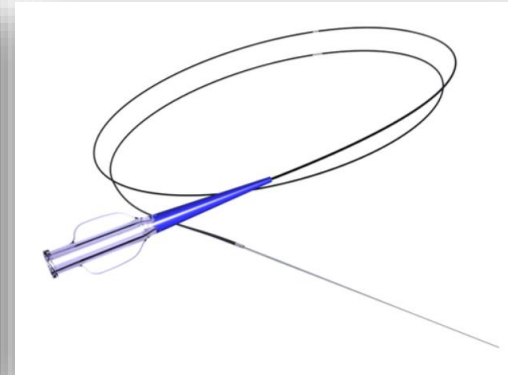
Carpets



Furniture fabrics



Women's socks



Medical instruments  
*Ex: hypotube*



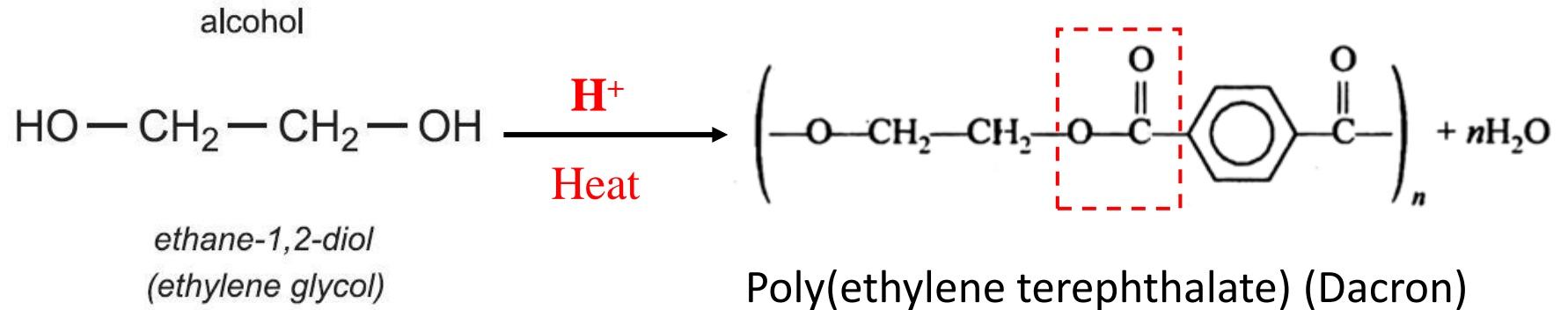
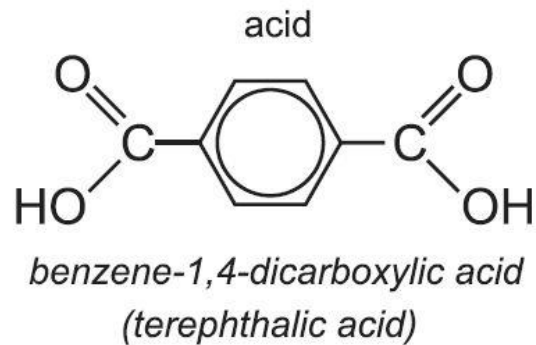
Openable double shell

# 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.



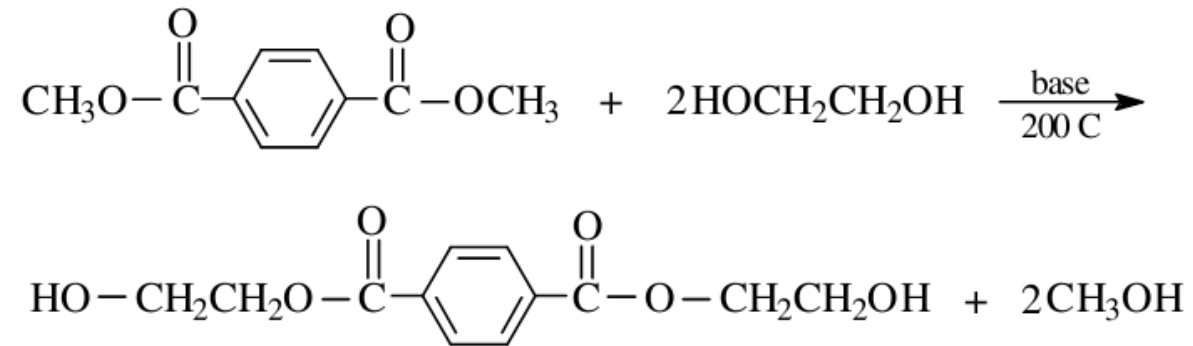
# Condensation Polymerization

Growth  
Polymerization

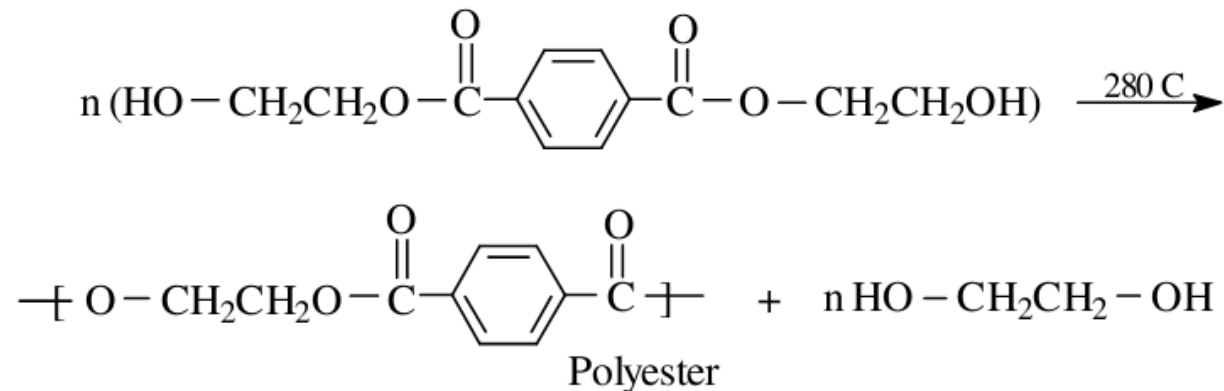
## ■ Polyesteres

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

Step 1



Step 2



## ▪ 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.



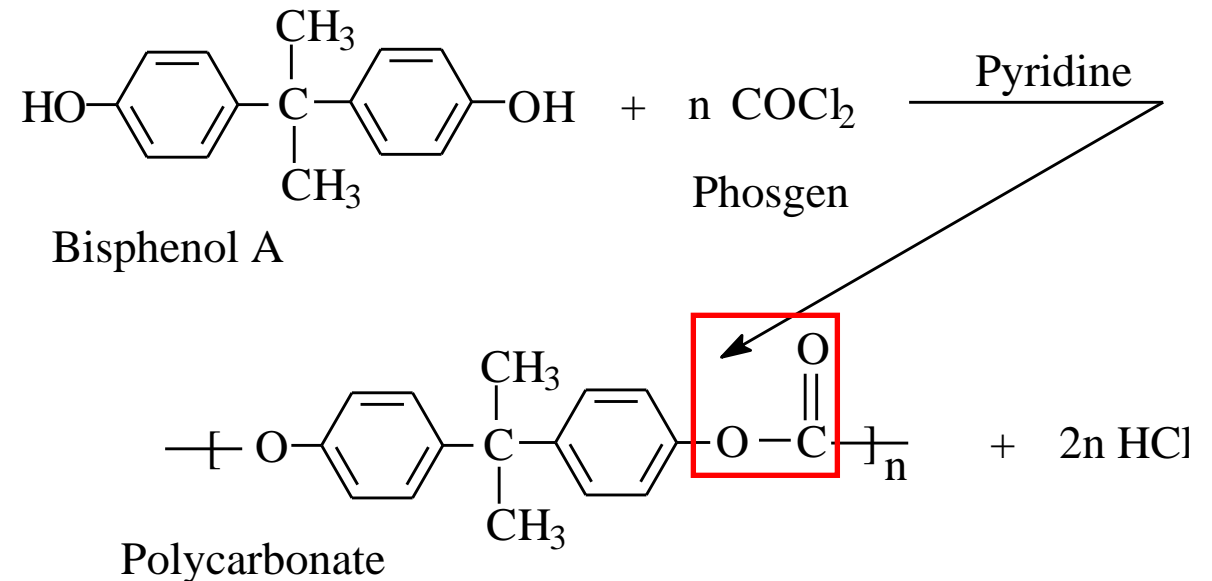
# Condensation Polymerization

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)

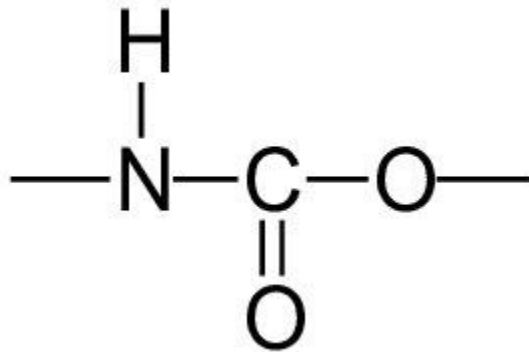
- ❑ Some of the **common applications** are compact disc, safety helmets, bullet-proof glass, car headlamp lenses, baby feeding bottles, domes, roofing and glazing etc.
- ❑ Polycarbonate has been used safely in tubes and connectors for medical usage.



## ▪ Polyurethane

- Urethanes are also called **carbamate esters**.
- Carbamate are organic compounds derived from carbamic acid ( $\text{NH}_2\text{COOH}$ )

Chemical structure of the **urethane** group.

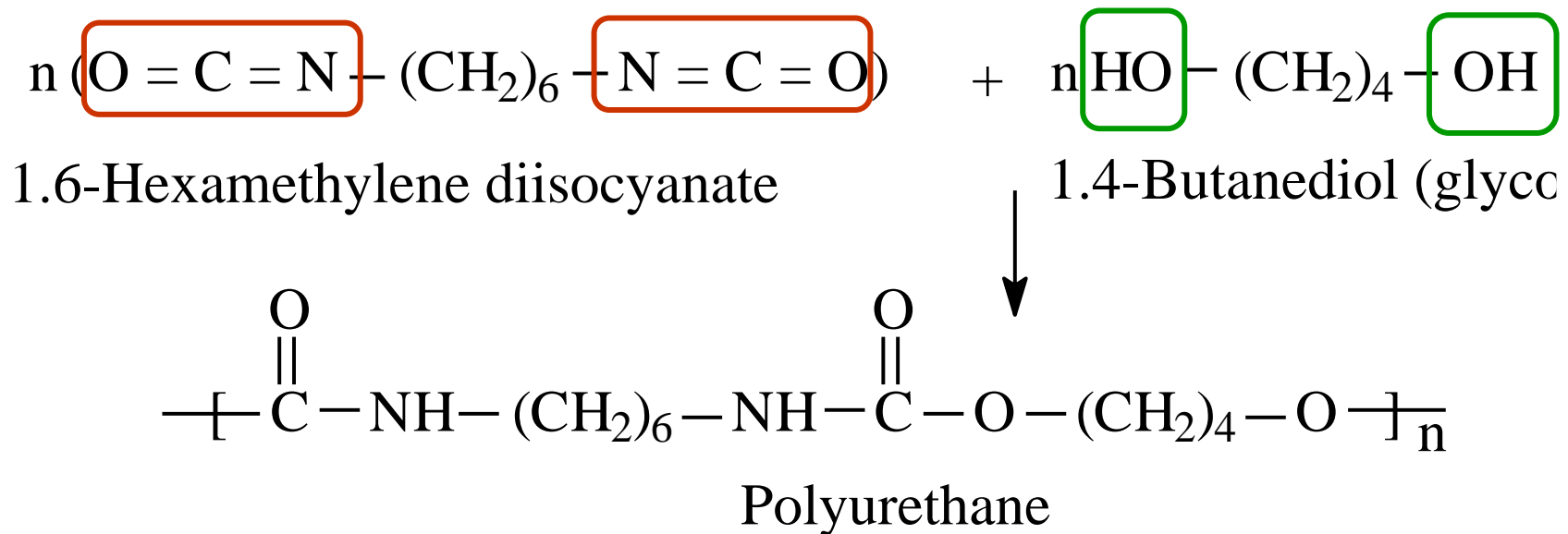


# Condensation Polymerization

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.





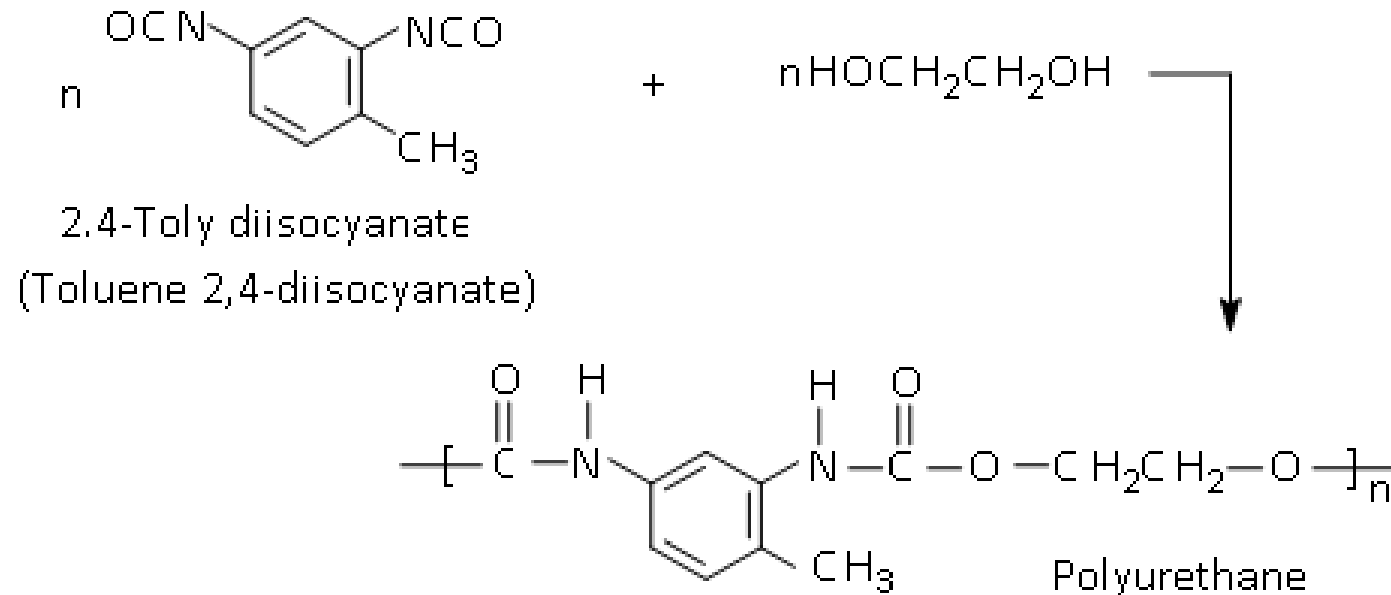
# Condensation Polymerization

Growth  
Polymerization

## ■ Polyurethane

### Synthesis of Aromatic Polyurethane

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



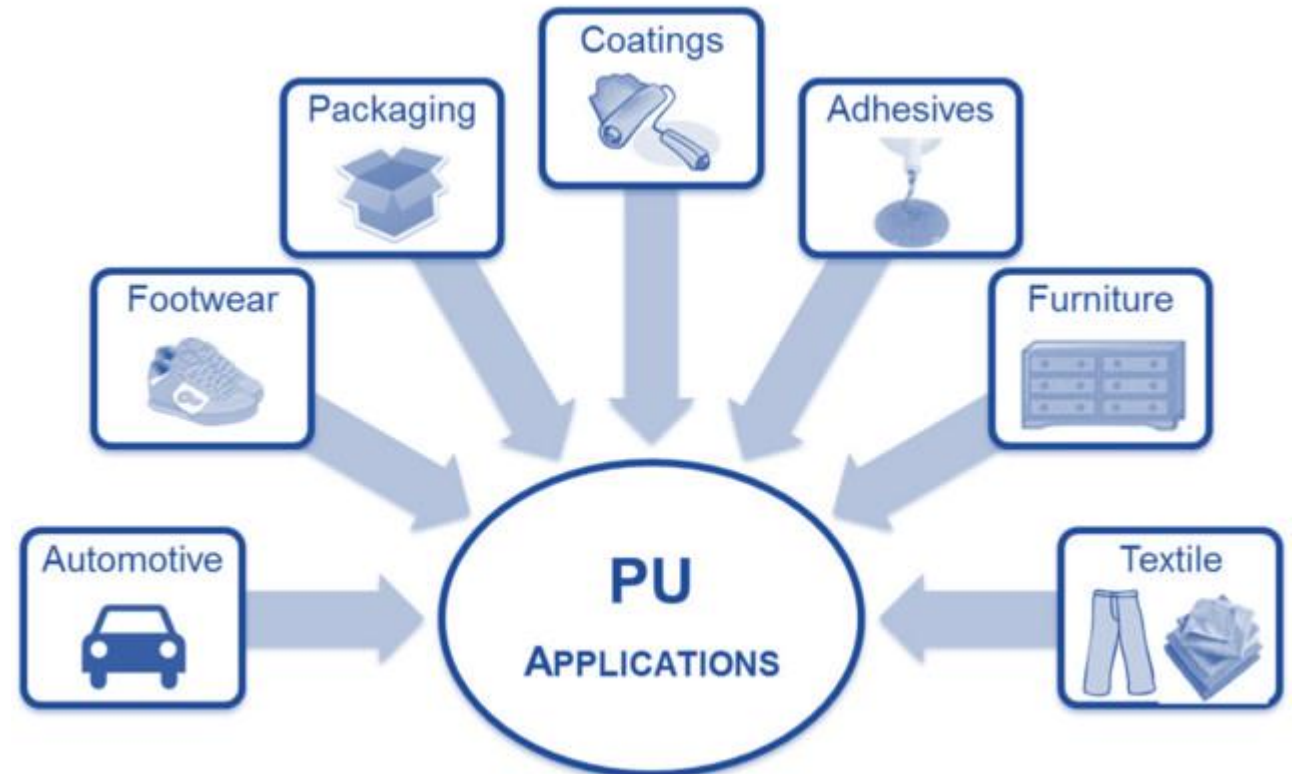
- This is a **step-growth polymerization**, but unlike other many polymerization such as; polyamides & polyesters ***no small molecule is eliminated***.

# Condensation Polymerization

Growth  
Polymerization

## ▪ 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.



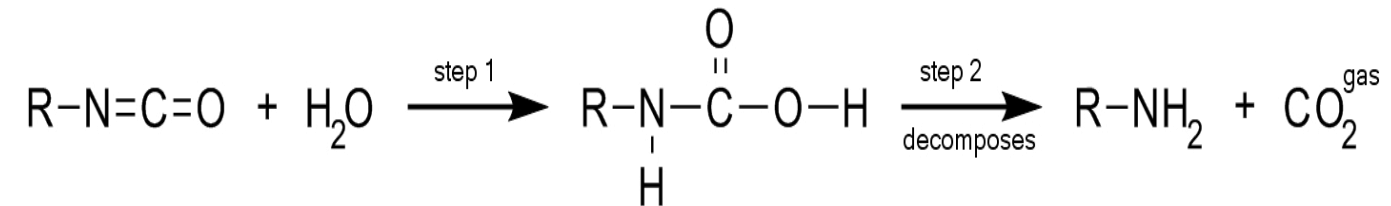
# Condensation Polymerization

Growth  
Polymerization

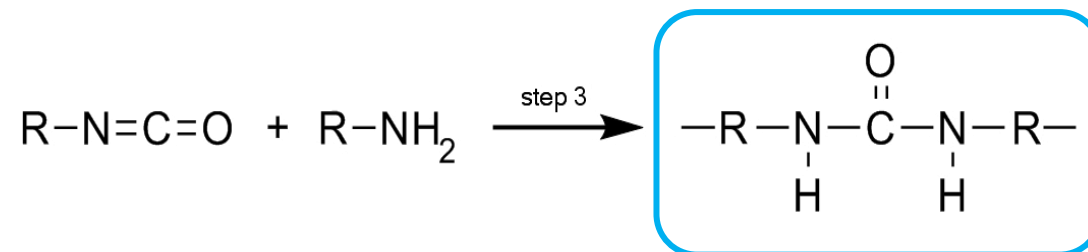
## ▪ Polyurethane Foam

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.



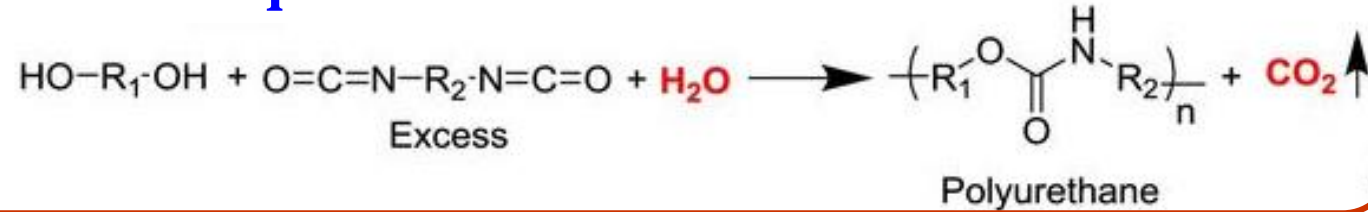
The amine reacts with more isocyanate to give a substituted urea which tends to form separate (Hard segment) phases consisting mostly of polyurethane.



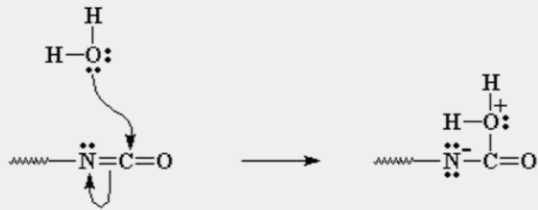
# Condensation Polymerization

## ■ Polyurethane Foam

### General Equation



Growth  
Polymerization



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<sub>2</sub> 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.



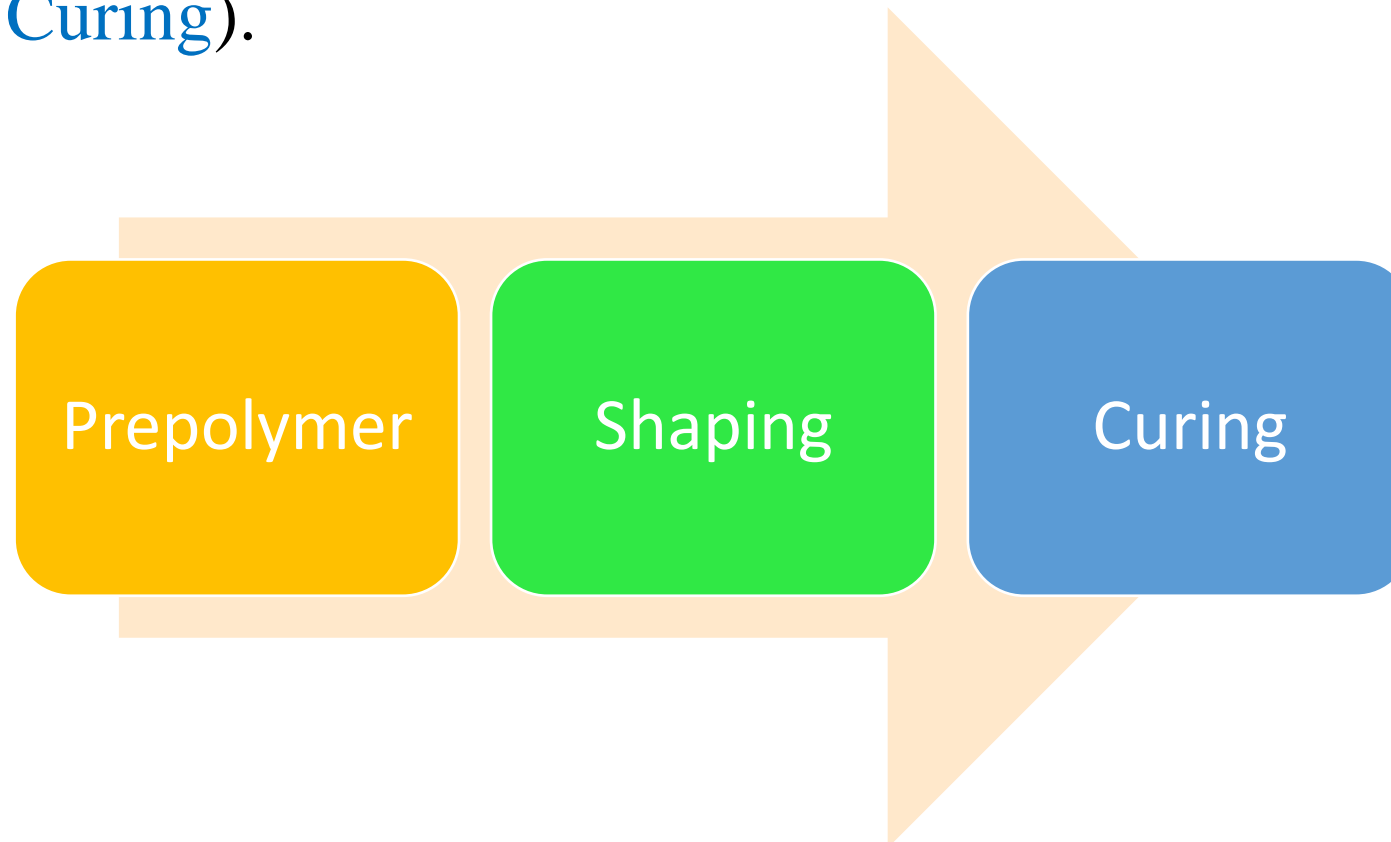
### □ Polyurethane Foam in Shoes & Clothing

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



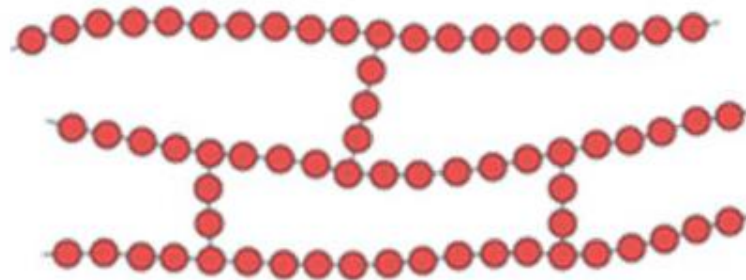
## NETWORK POLYMERS

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



## 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.





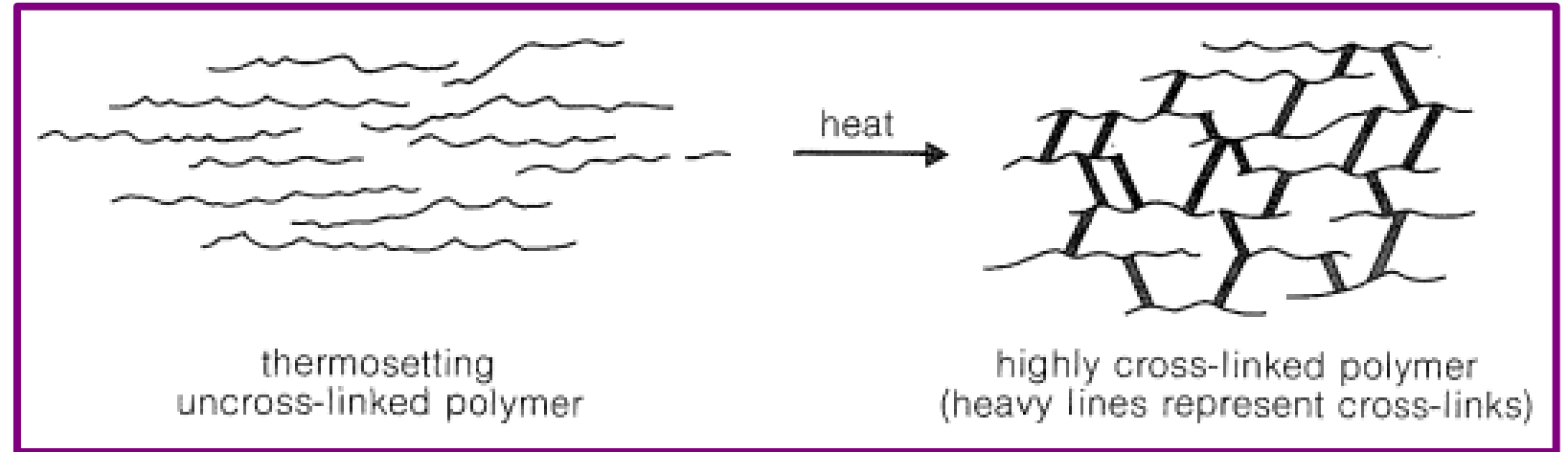
# Condensation Polymerization

## II. Crosslinked Polymers

Cross-linked  
Polymerization

### *Examples*

- 1- Polyesters
- 2- Polyurethanes
- 3- Urea formaldehyde resins
- 4- phenol formaldehyde resins
- 5- Epoxy resins



# Condensation Polymerization

Cross-linked  
Polymerization

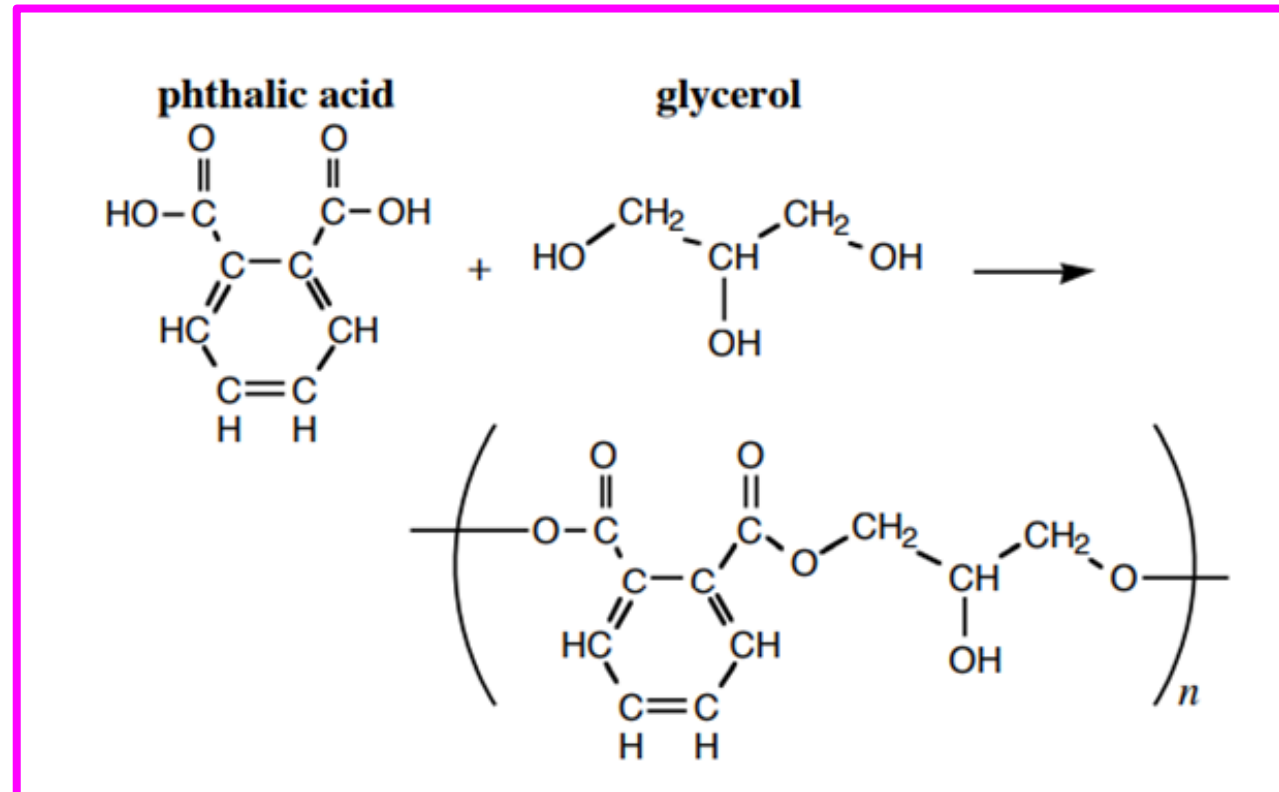
## II. Crosslinked Polymers

### 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

**Glyptals** are used in **paints**,  
**lacquers** and surface coatings.



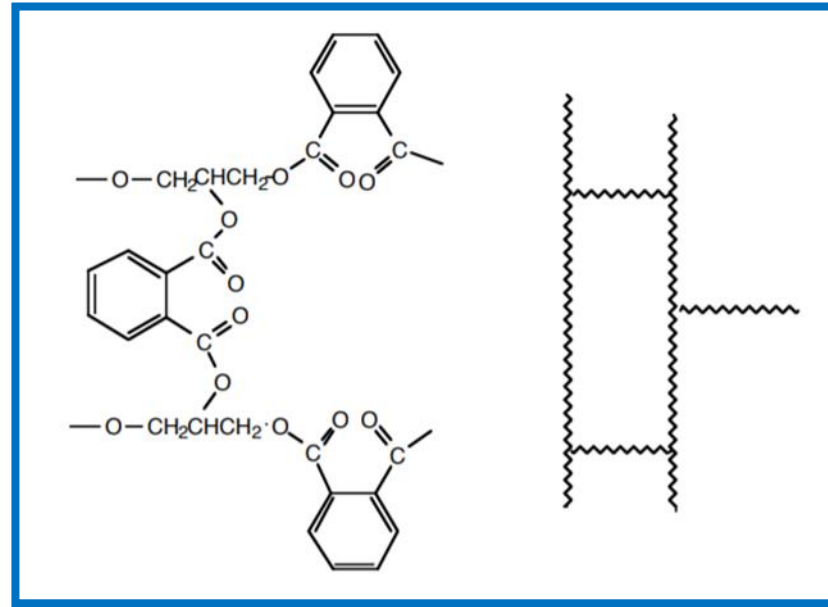
Glyptal resin

## 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.

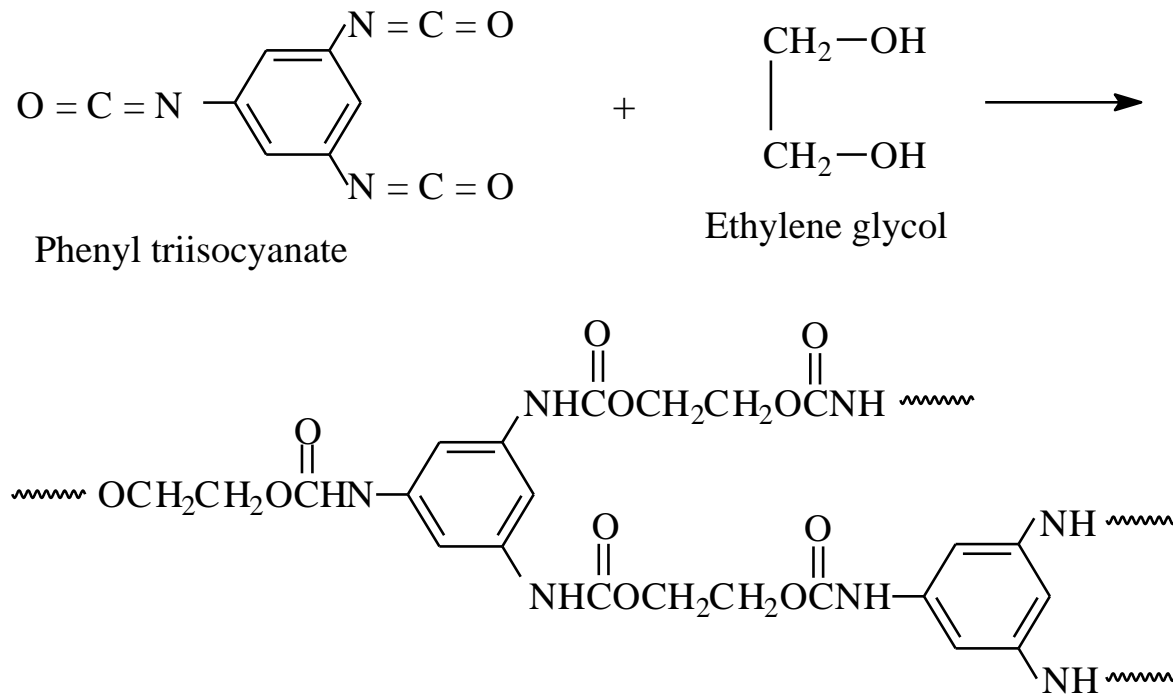
# Condensation Polymerization

Cross-linked  
Polymerization

## 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

# NETWORK POLYMERS

Formaldehyde prepared by polymerization in two stages.

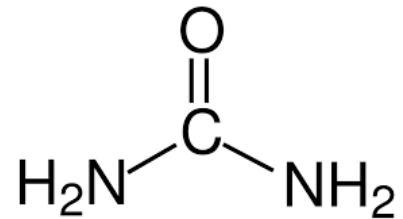
1. Formation of a prepolymer of low molar mass.
2. Prepolymer is forced to flow under pressure to fill a heated mold in which cross linking takes place.  $\implies$  highly crosslinked rigid polymer in the shape at the mold.

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

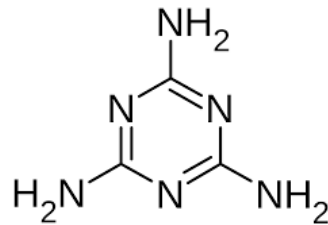
## NETWORK POLYMERS

- The most commonly employed to form Network polymers are:

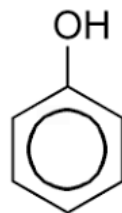
□ Urea ( $f = 4$ )



□ Melamine ( $f = 6$ )



□ Phenol ( $f = 3$ )



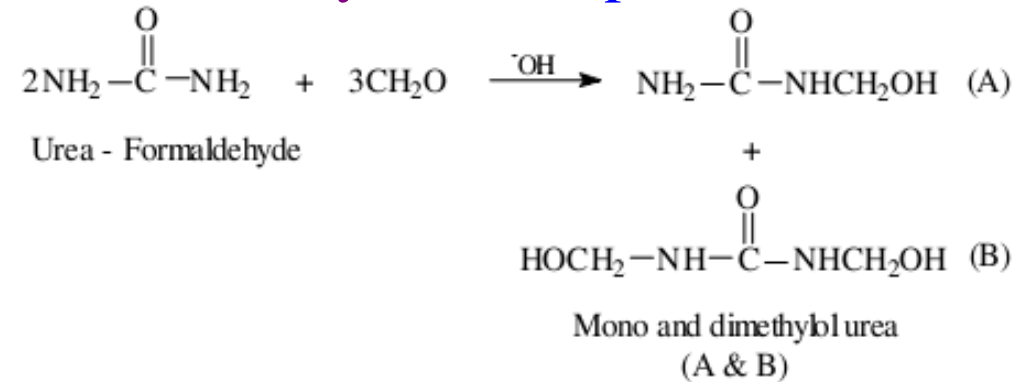
# Condensation Polymerization

Cross-linked  
Polymerization

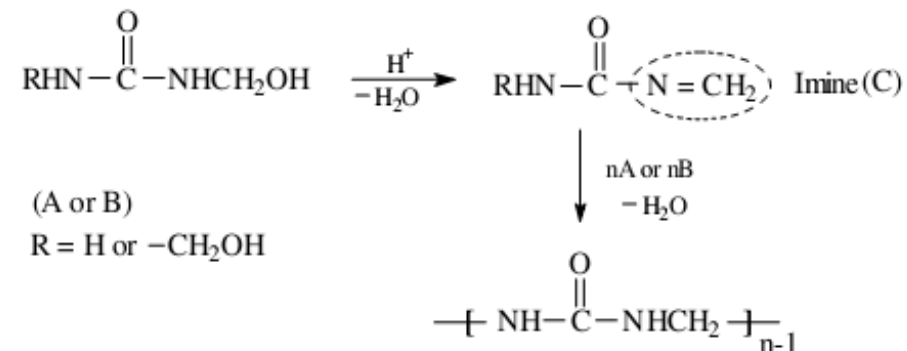
## II. Crosslinked Polymers

### 3- Urea Formaldehyde Resins

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



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





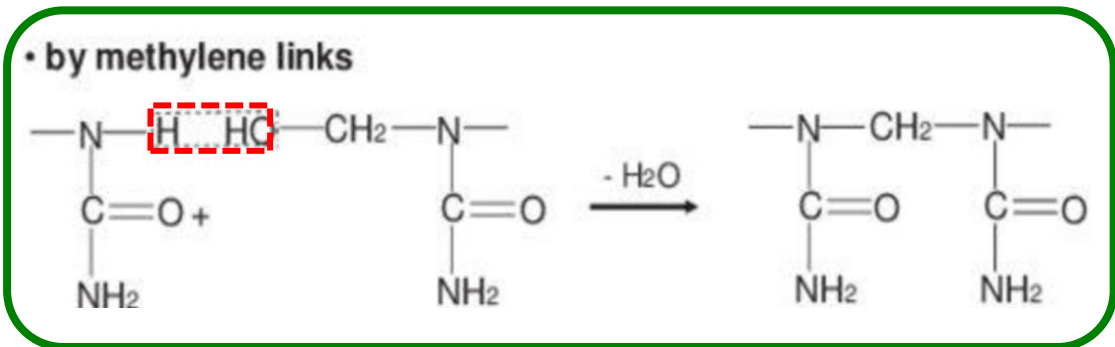
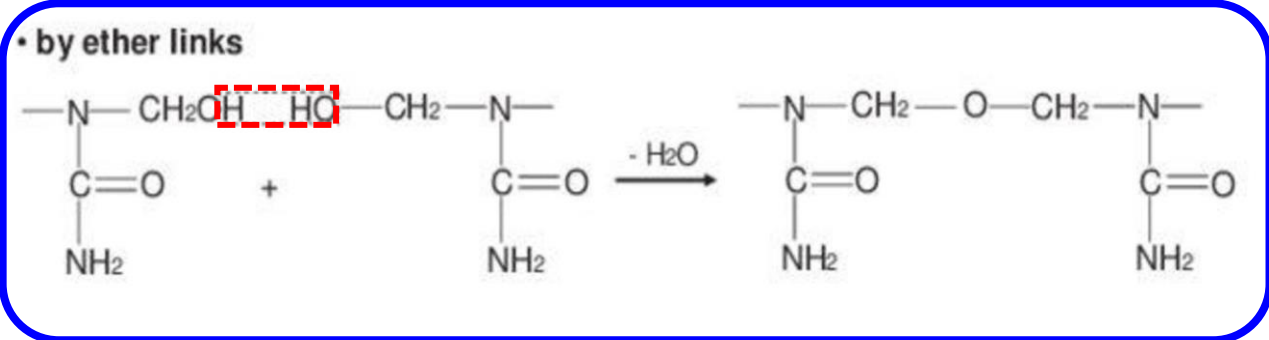
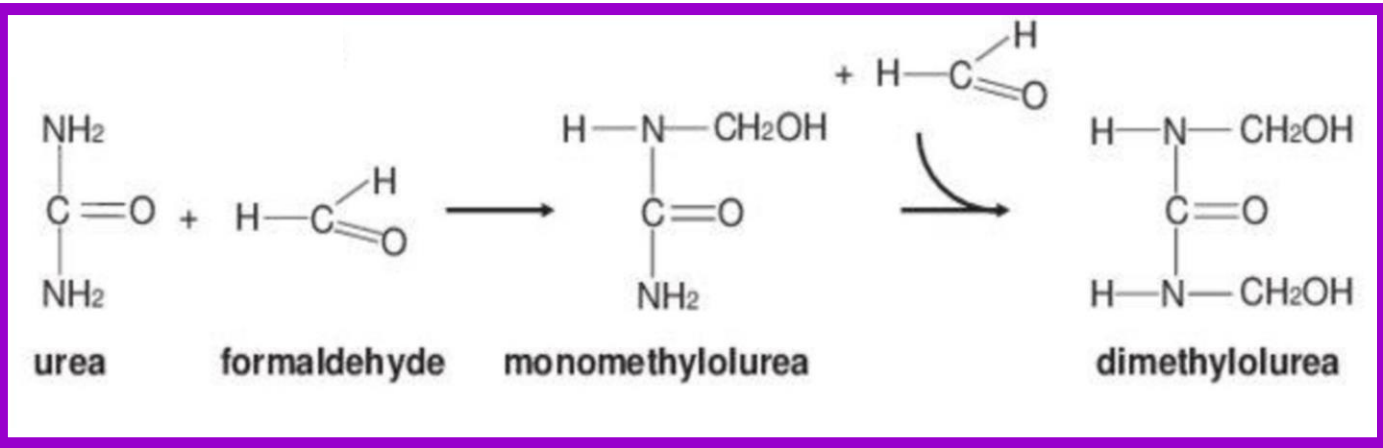
# Condensation Polymerization

## II. Crosslinked Polymers

### 3- Urea Formaldehyde Resins

Cross-linked Polymerization

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



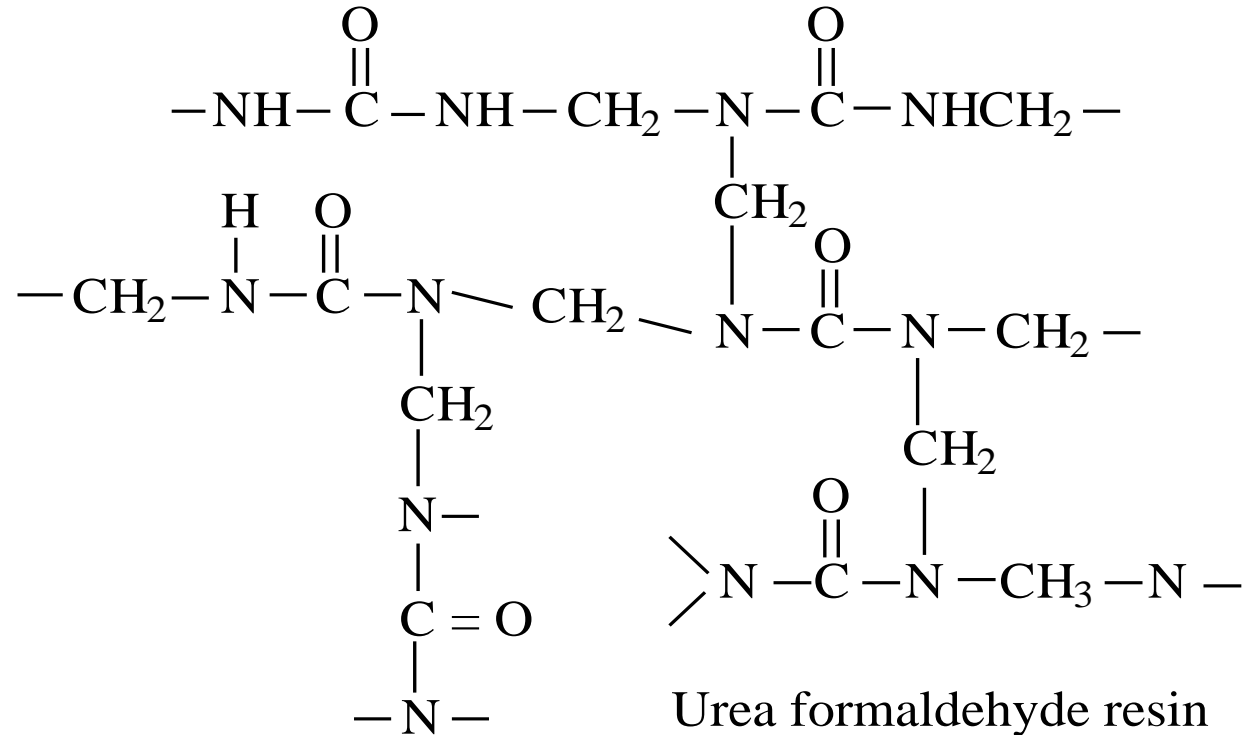
# Condensation Polymerization

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.



## 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.



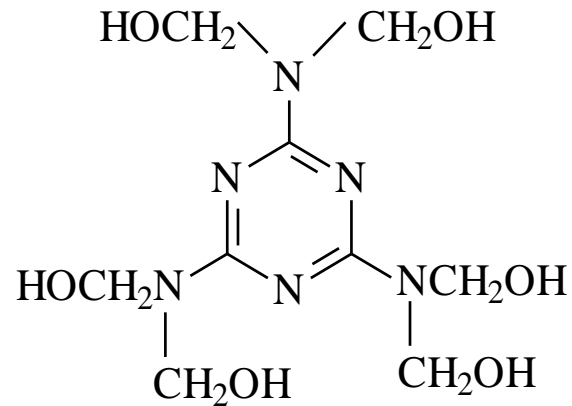
# Condensation Polymerization

## II. Crosslinked Polymers

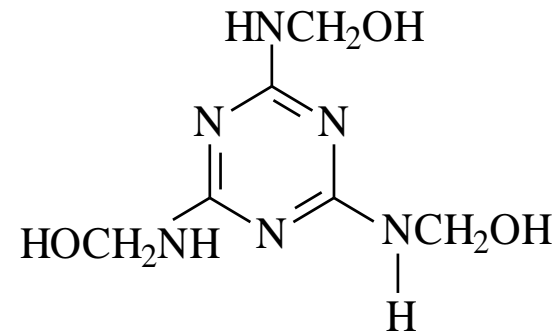
Cross-linked  
Polymerization

### 4-Melamine-Formaldehyde Resins

By using trimethylol & hexamethylol



Hexamethylol



Trimethylol

# Condensation Polymerization

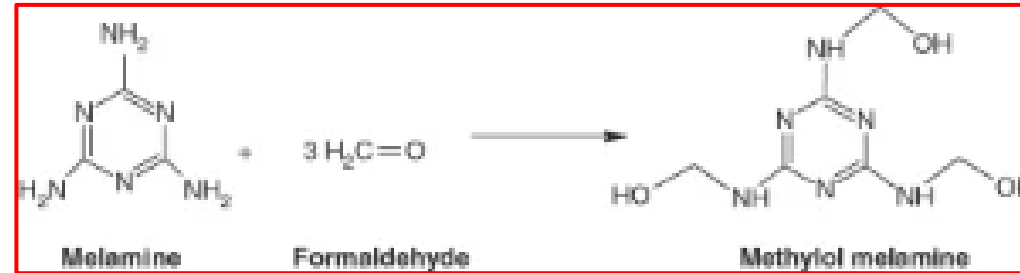
## II. Crosslinked Polymers

Cross-linked  
Polymerization

### 4-Melamine-Formaldehyde Resins

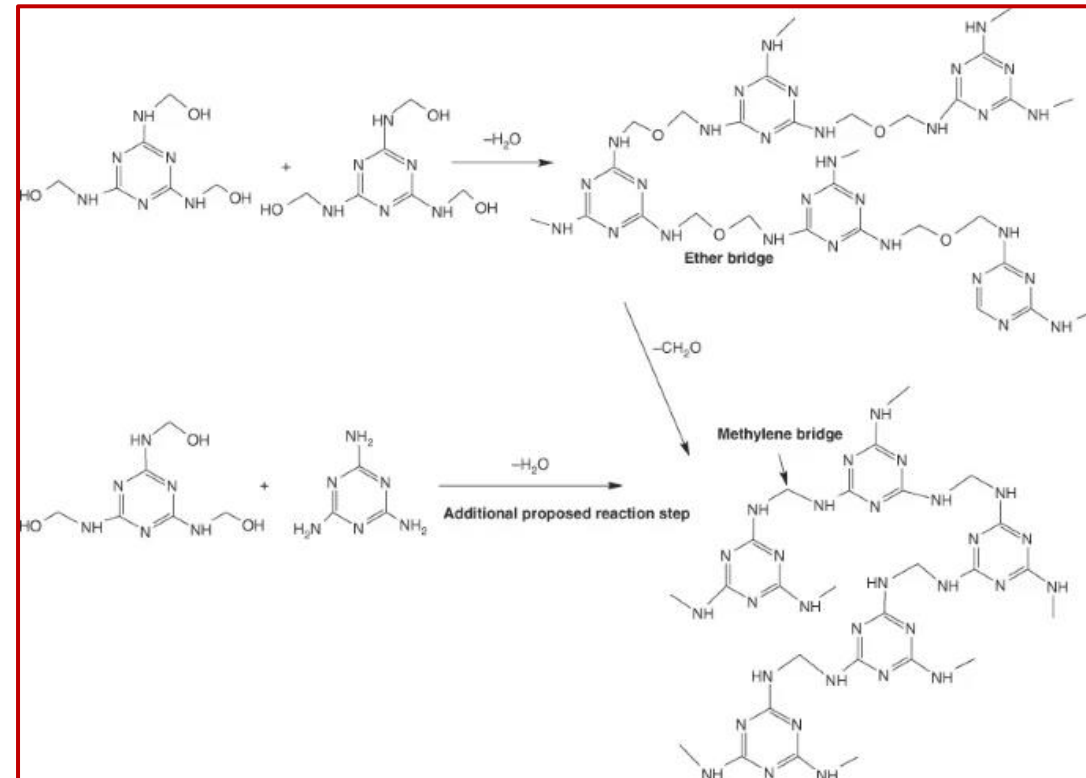
#### Methylation step

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

Cross-linked  
Polymerization

### 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

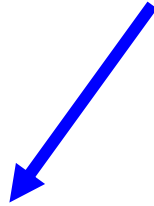
the resin is treated to form network polymer

## II. Crosslinked Polymers

Cross-linked  
Polymerization

### 5-Phenol-Formaldehyde Resins

There are two types of low molecular weight resin:



**Resole phenols**

Alkaline medium



**Novolak phenols**

Acidic medium

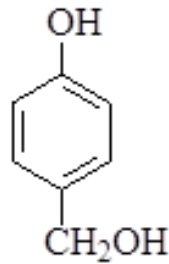


# Condensation Polymerization

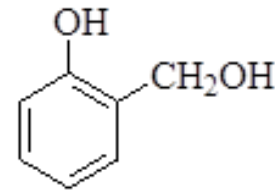
## II. Crosslinked Polymers

### 5-Phenol-Formaldehyde Resins

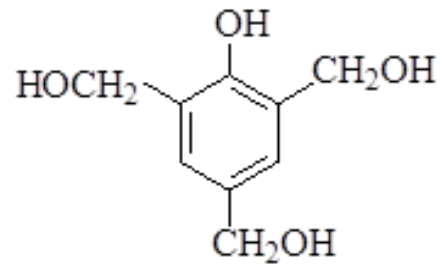
#### Type 1 Resole phenols



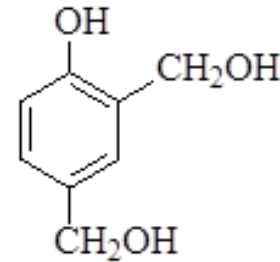
p-Methylol-Phenol



o-Methylol-Phenol



2,4,6- Tri-methylol-Phenol



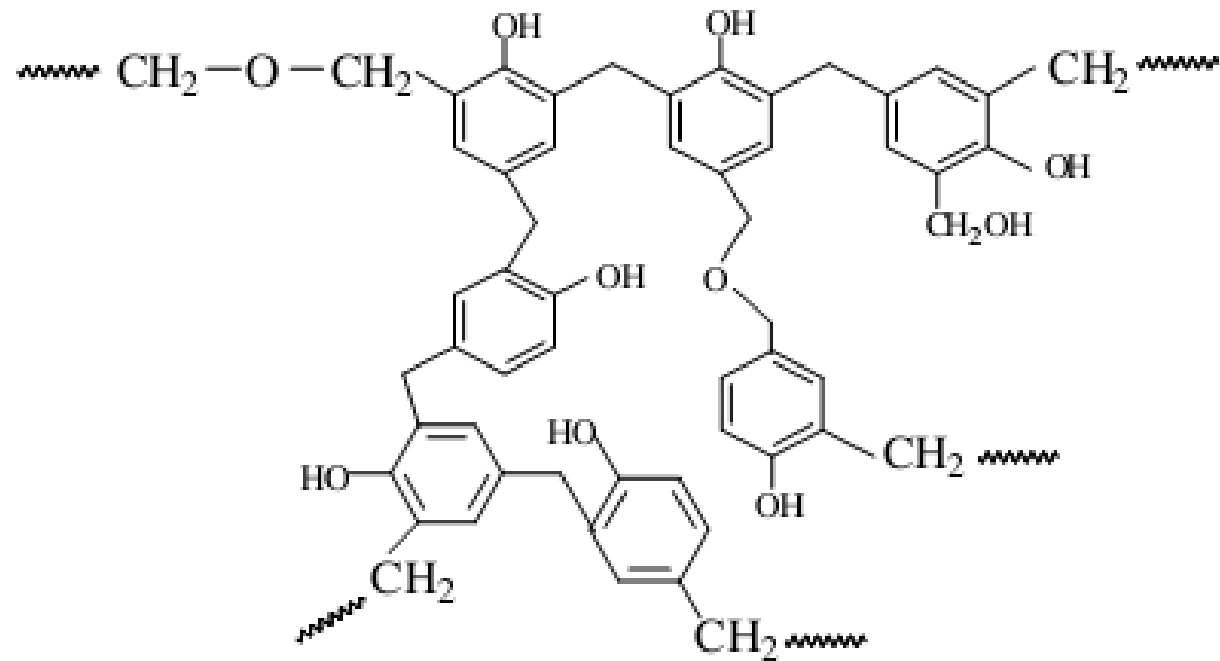
2,4-Di-methylol-Phenol

Cross-linked  
Polymerization

## II. Crosslinked Polymers

### 5-Phenol-Formaldehyde Resins

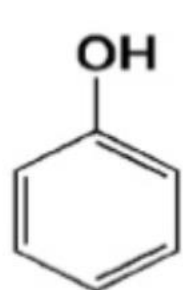
- Alkaline catalyst and excess formaldehyde methylene(-CH<sub>2</sub>) bridge formation as well as (Oxygen) bridge formation may result in the release of **water**:



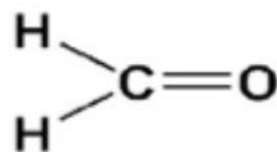
Chemical Structure of Resole Phenol-Formaldehyde Resin

## II. Crosslinked Polymers

Cross-linked  
Polymerization

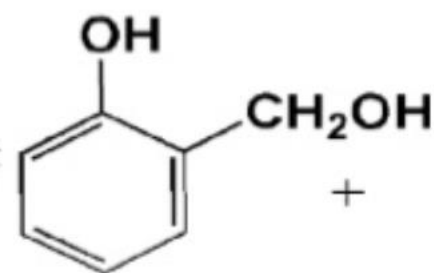


Phenol

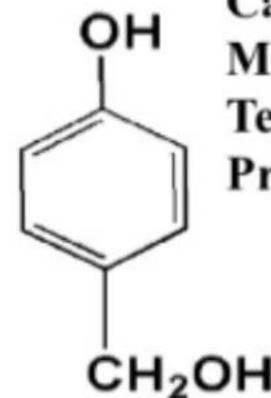


Formaldehyde

Basic Catalyst



*o*-Hydroxy Methyl Phenol



*p*-Hydroxy Methyl Phenol

Catalyst: **Sodium hydroxide** (powdered)

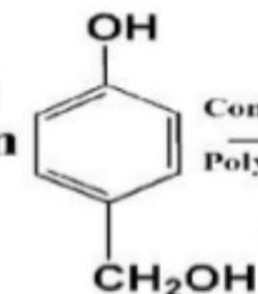
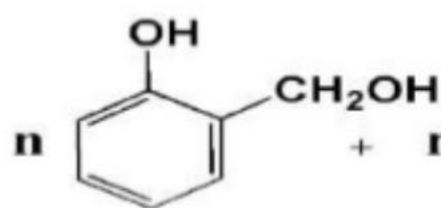
Medium: **Distilled Water**

Temp: **At around 70°C**

Pressure: **1 atm**

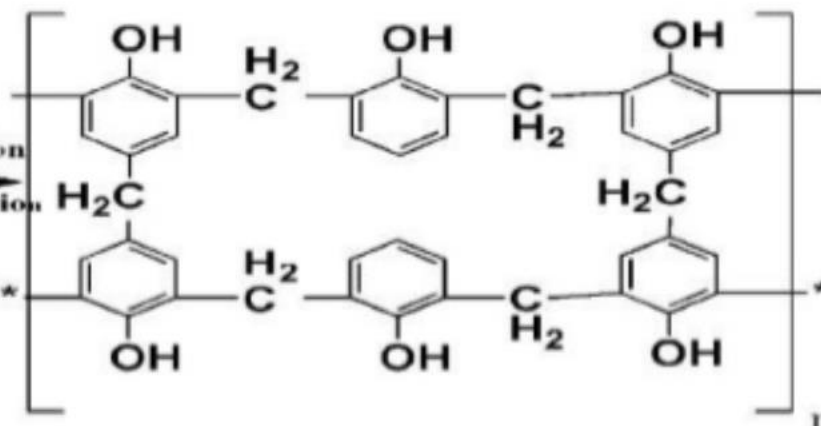
Heat of reaction: **180 cal/g**

### Resole:



Condensation  
Polymerisation

$-H_2O$



**Bakelite**  
(Cross-linked Polymer)

Temperature:

**Hydroxymethyl phenols** will crosslink on heating to around **120 °C**

By product: **Water**

## 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 therefore incapable of condensing with other novolak molecules in heating without 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**.

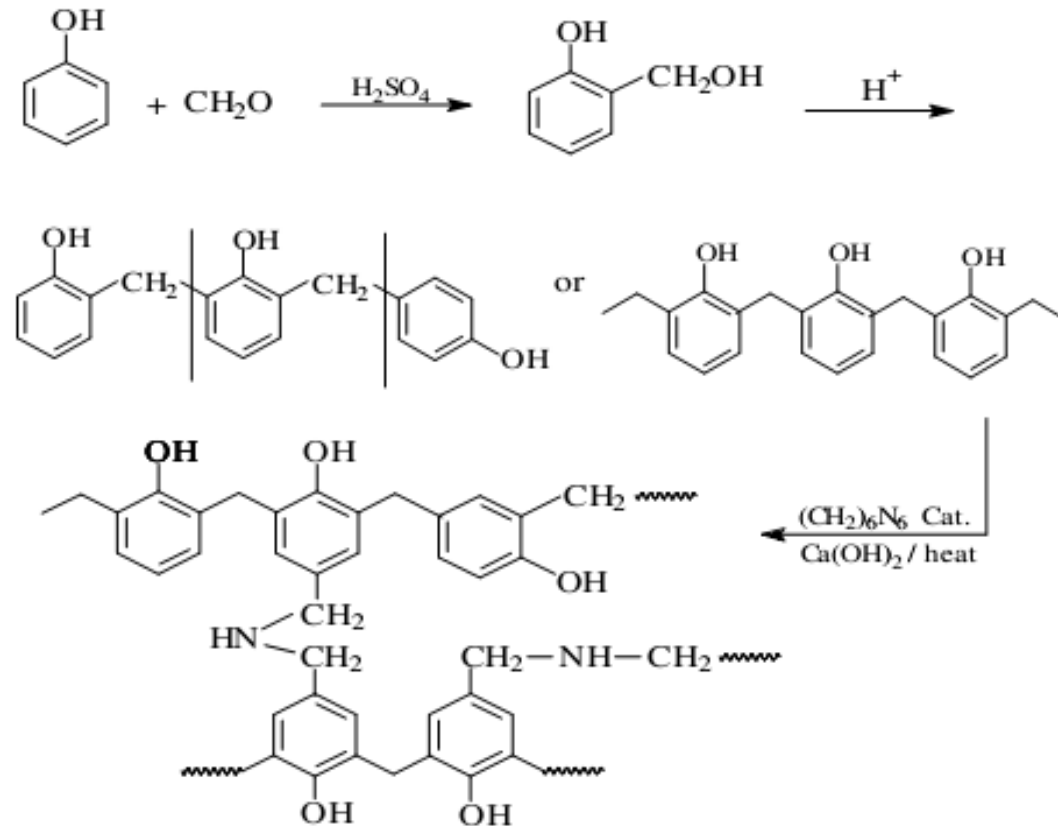
# Condensation Polymerization

## II. Crosslinked Polymers

### 5-Phenol-Formaldehyde Resins

#### Type 2: Novolak phenols

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



Cross-linked  
Polymerization

- 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, or HMTA.

## II. Crosslinked Polymers

### 4-Phenol-Formaldehyde Resins

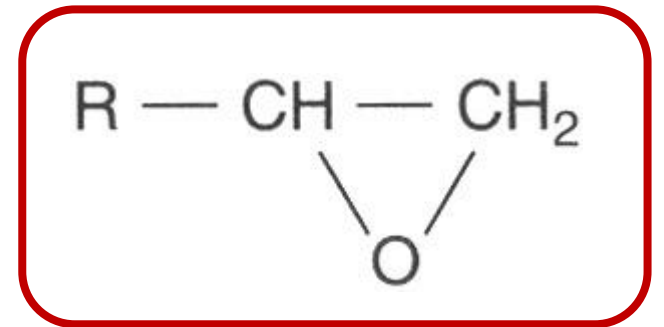
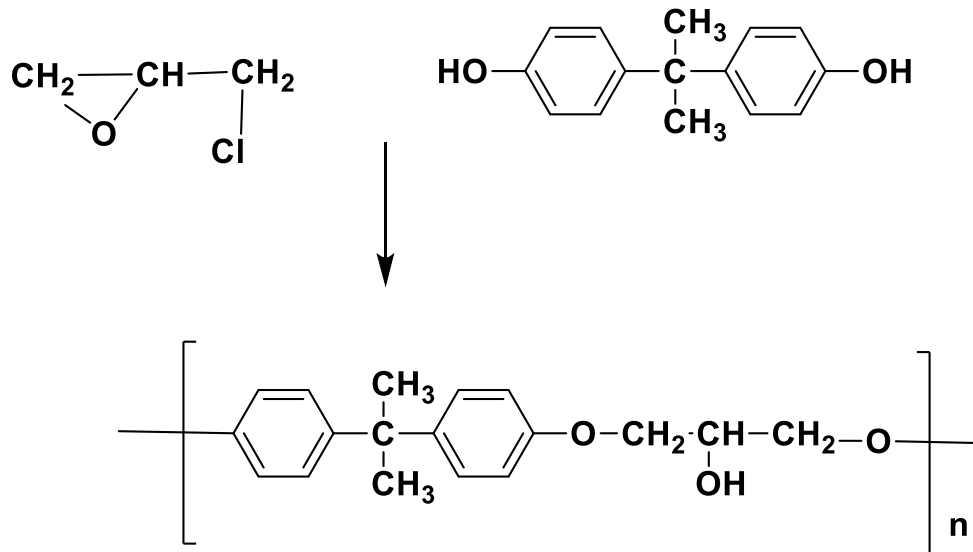
Resole	Novolak
Reaction is carried out in <b>basic</b> medium.	Usually obtain in <b>acidic</b> medium.
Phenol functionality is <b>ortho, meta &amp; para</b>	Phenol functionality is <b>ortho and para</b> .
Phenol: <b>formaldehyde</b> is <b>1:1.2</b>	Phenol: <b>formaldehyde</b> is <b>1:0.8</b>
<b>Already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

## II. Crosslinked Polymers

Cross-linked  
Polymerization

### 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

# Condensation Polymerization

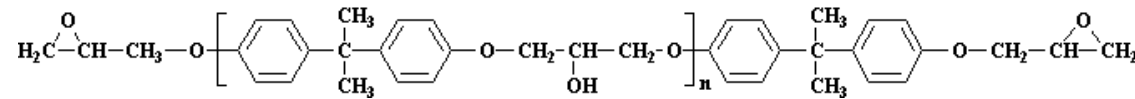
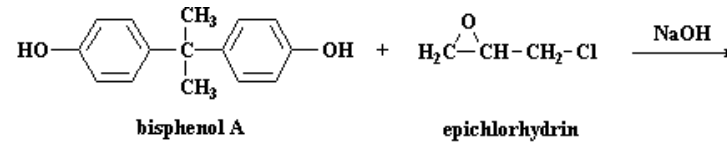
## II. Crosslinked Polymers

### Reaction Mechanism of forming Epoxy Resins

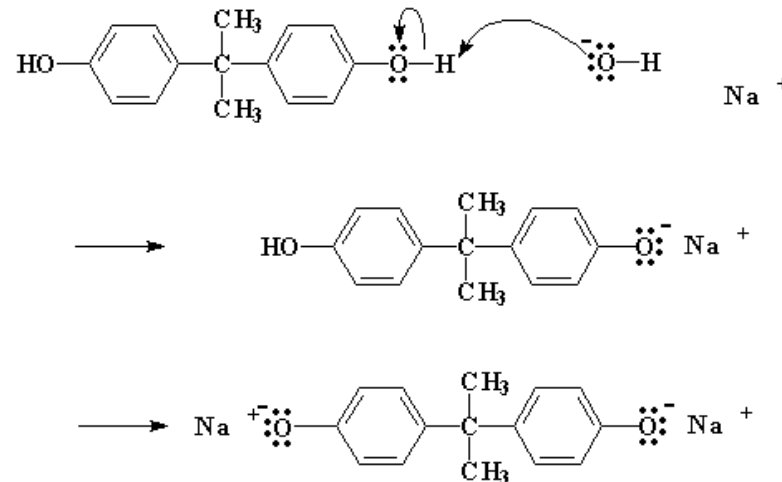
#### Stage 1. Making the Diepoxy

Cross-linked  
Polymerization

- 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**.

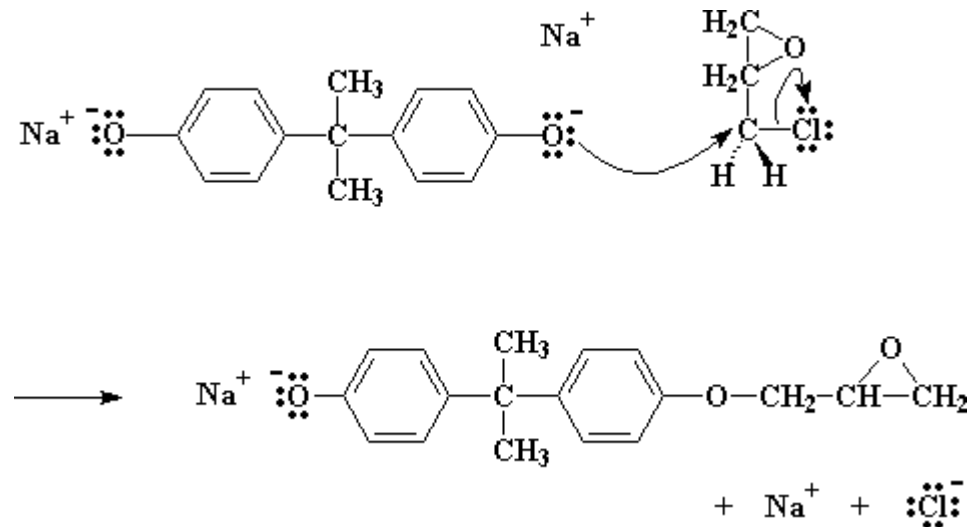




## II. Crosslinked Polymers

### Reaction Mechanism of forming Epoxy Resins

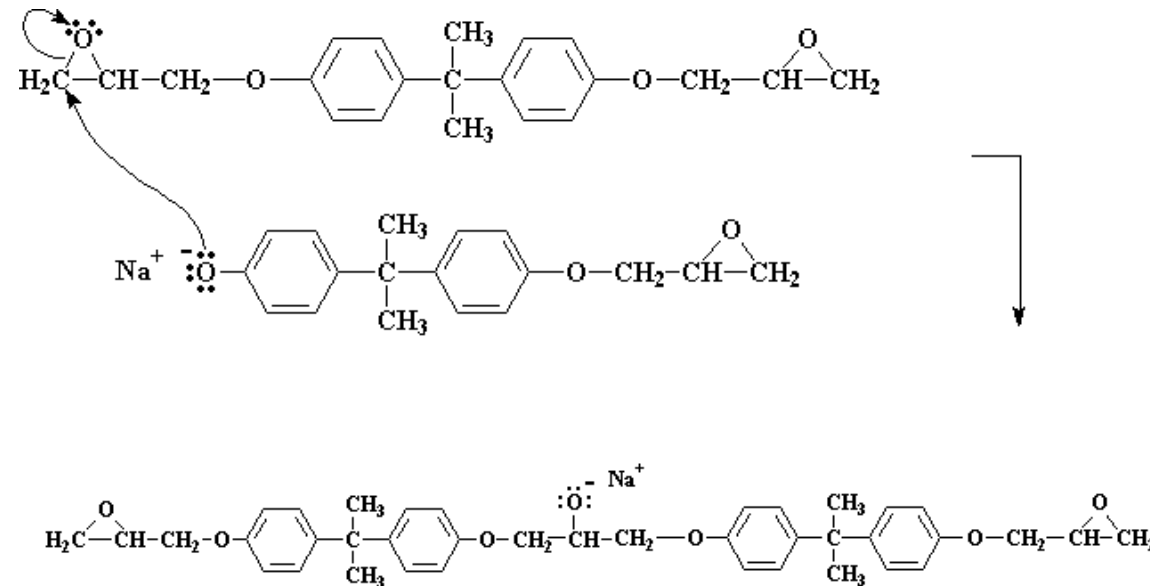
- The oxygen with three pairs of electrons will share its electrons with carbon atom on a nearby epichlorohydrin. The chlorine atom next to supposed to be sharing a pair of electrons with that carbon, but being electronegative as it is, tends to leave the molecule with electron pair.



## 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.

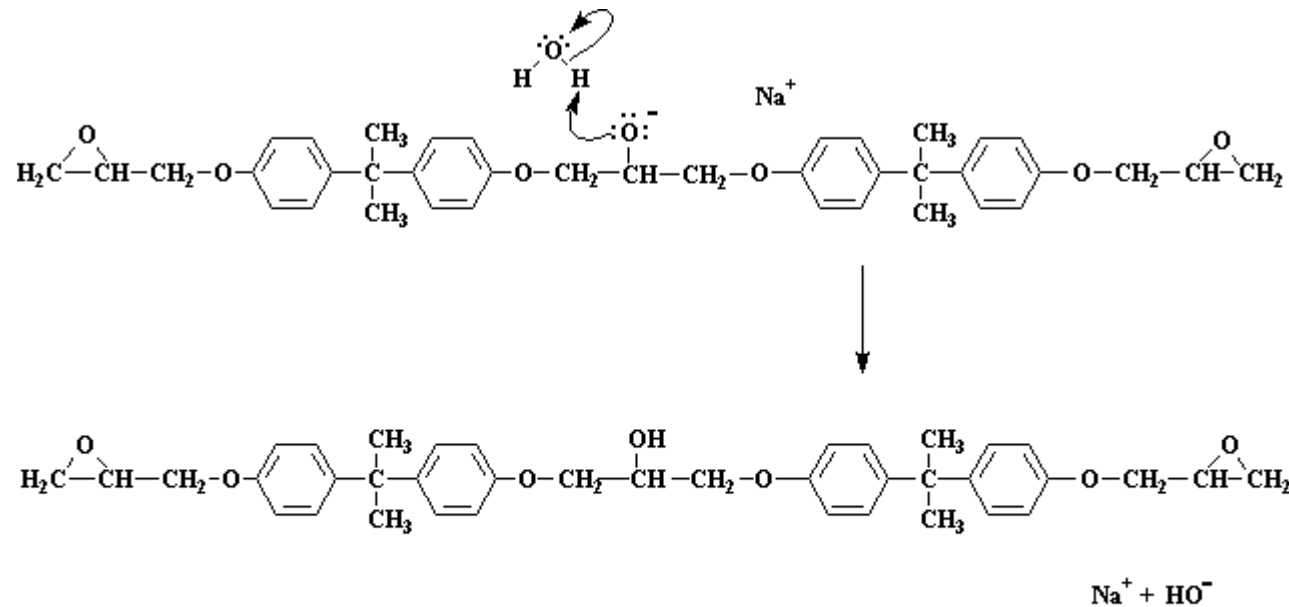


The sodium salt attacks the epoxide, giving a dimer. That dimer is a sodium salt.

## 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.



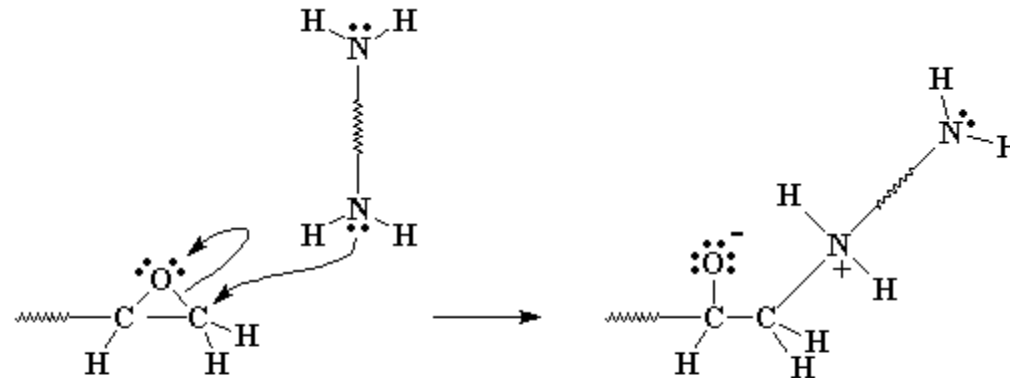
A water molecule comes along and the negative oxygen swipes a proton from it. This way we get an alcohol group, and we get our NaOH back.

## 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.

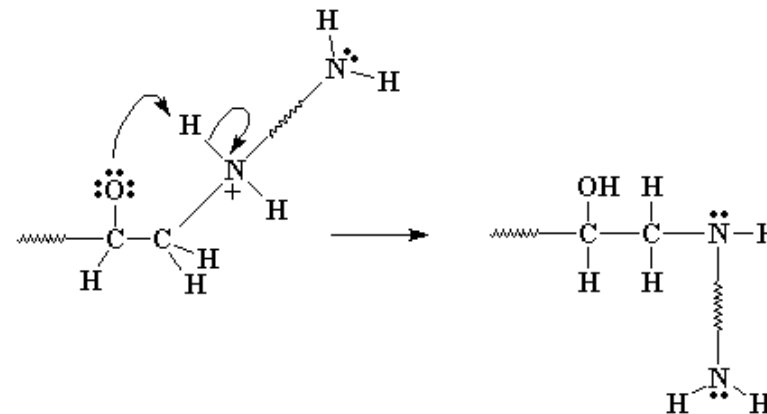


The diamine's electrons attack the carbon atom next to the epoxide oxygen, giving us a negative charge on the oxygen, and a positive charge on the nitrogen.

## 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.

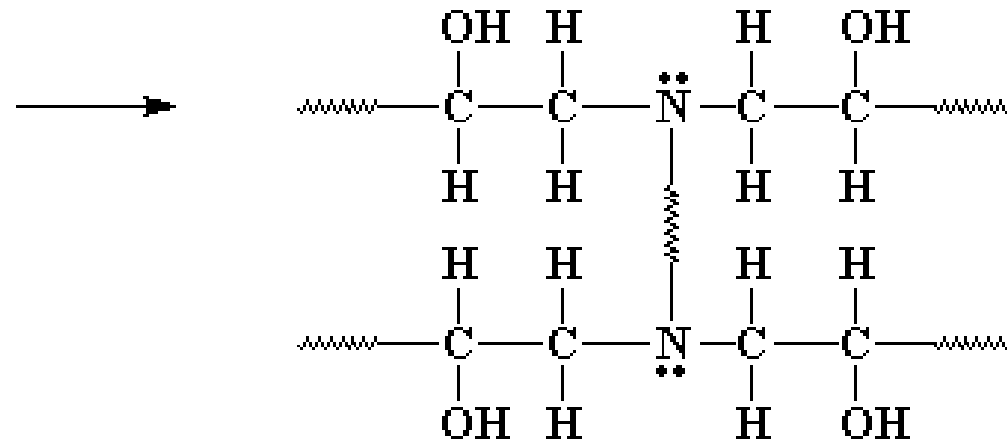


The oxygen's extra pair of electrons swipes a hydrogen from the ammonium nitrogen, making an alcohol group and an amine group.

## 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.

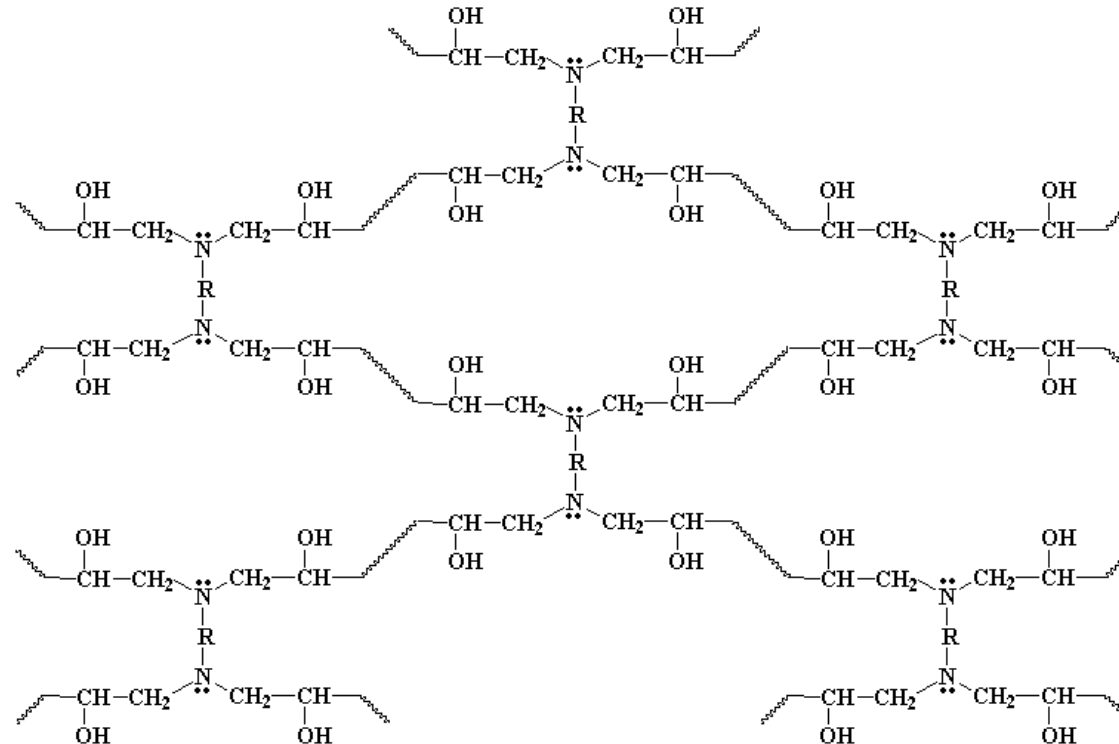


Then two more epoxide groups add to the amine at the other end of the diamine, eventually tying all the diepoxy oligomers into one big molecular network.

## II. Crosslinked Polymers

### Reaction Mechanism of forming Epoxy Resins

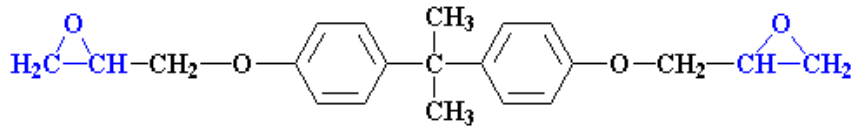
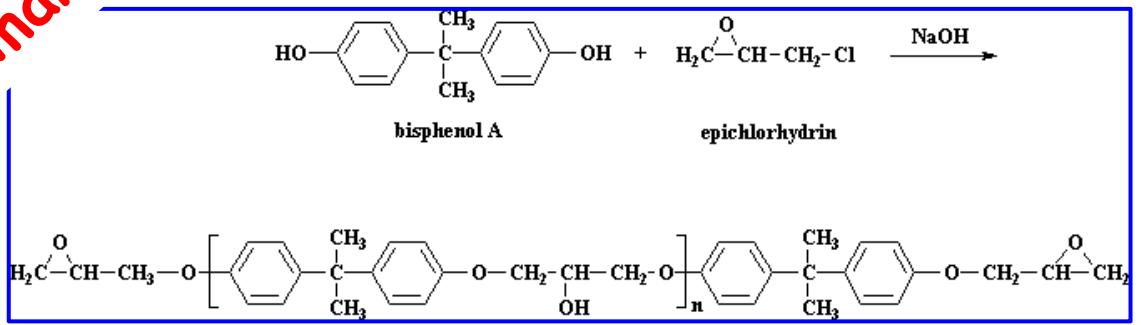
- When all the diamine molecules and all the diepoxy molecules become tied together (in the same manner) giving finally the cross-linked resins.



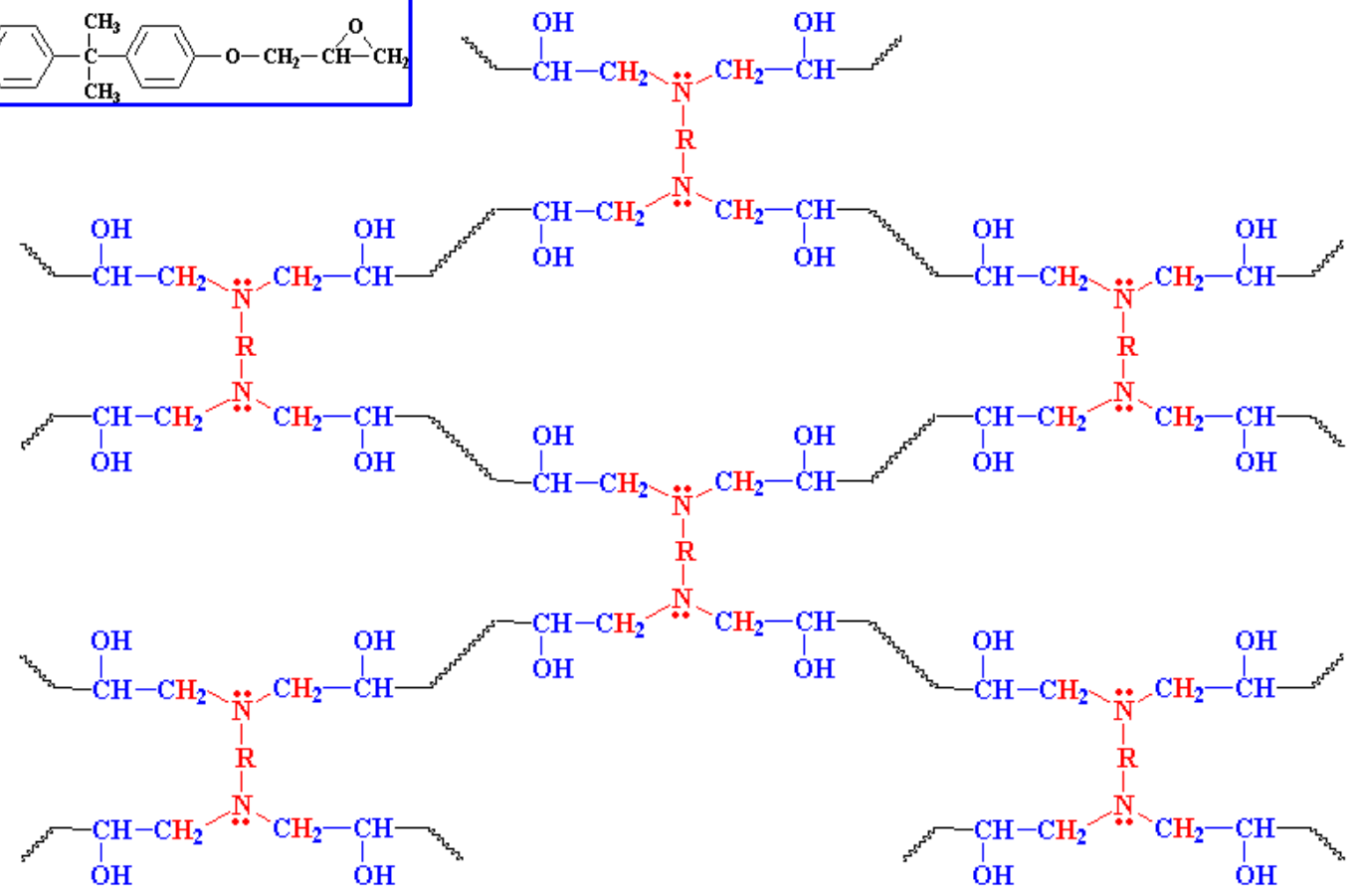
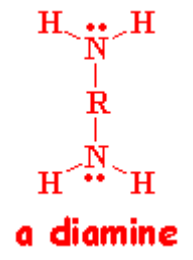
Cross-linked  
Polymerization

## Reaction Mechanism of forming Epoxy Resins

Reaction Summary



Diepoxy unit; n=1





## III. Synthetic fibers Polymers

Cross-linked  
Polymerization

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

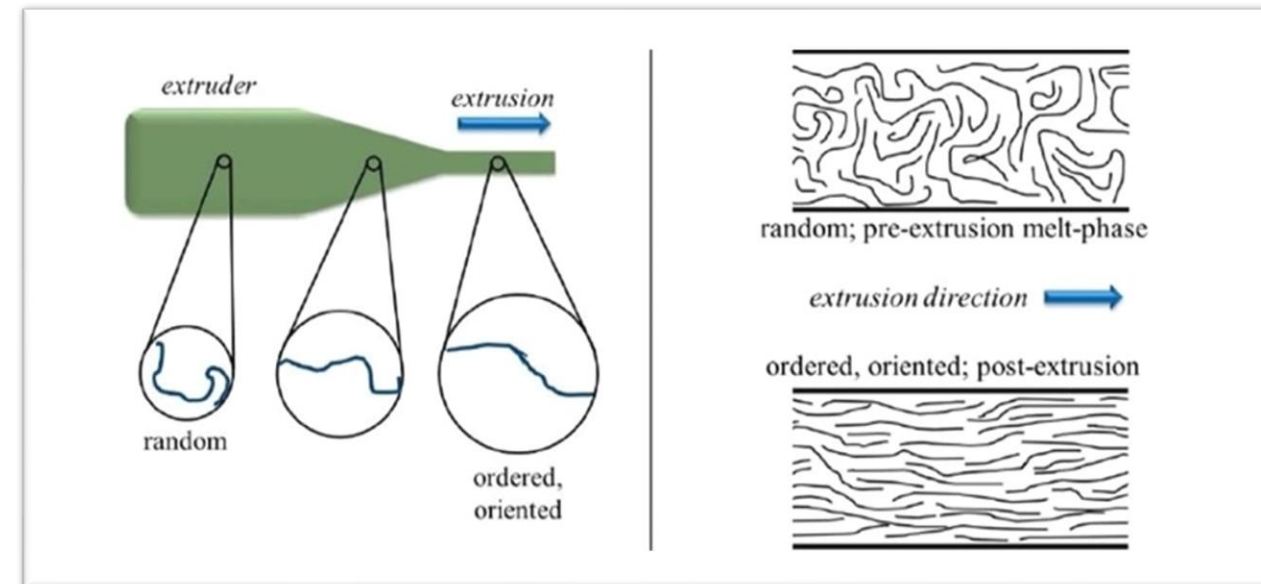
### General Properties of Synthetic Fibers

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

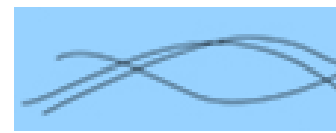
- ❑ One parameter reflecting the length of a polymer chain is the degree of polymerization (DP).

(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



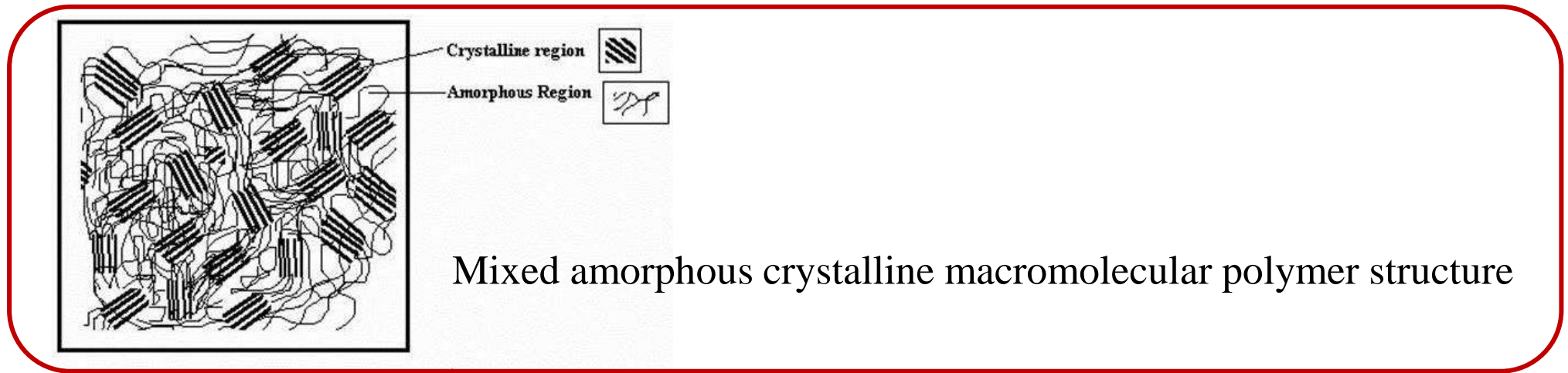
Filament fibers ( $7.6$  cm  $<$  long  $< 91.4$ )  
e.g. silk, polyester

## 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.



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

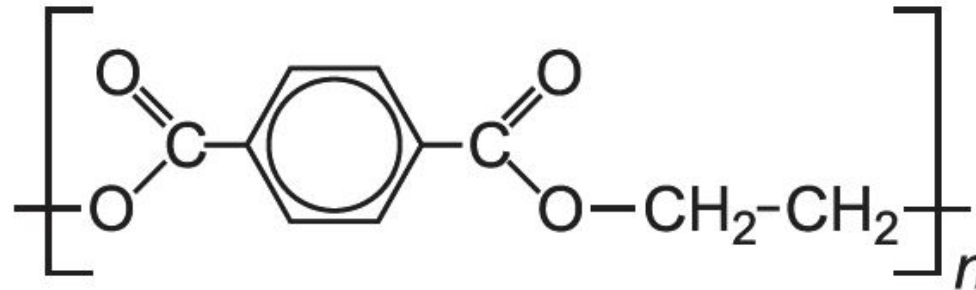
## III. Synthetic fibers Polymers

### General Properties of Synthetic Fibers

Cross-linked  
Polymerization

#### 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**.