CHEM 342

POLYMERS AND PETROCHEMICALS

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE

PRE-REQUISITES COURSE; CHEM 241

CREDIT HOURS; 2 (2+0)

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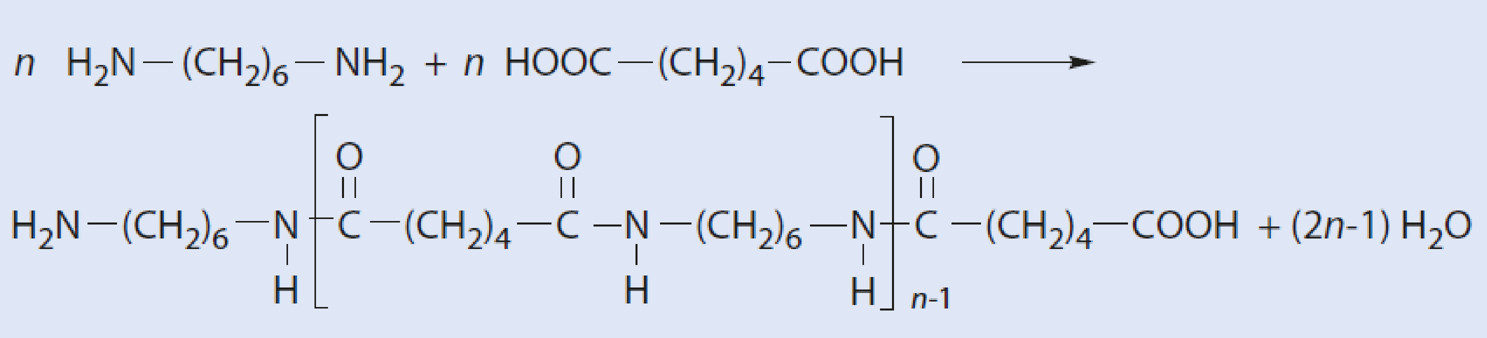
Methods for Synthesis of Polymers

- Synthetic processes of producing polymers from their monomers can be divided into.

  1) ***Step-growth Polymerization*** **(Condensation Polymerization)**

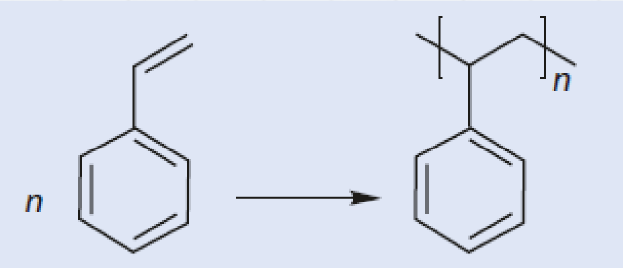


$$n\ H_2N-(CH_2)_6-NH_2 + n\ HOOC-(CH_2)_4-COOH \longrightarrow$$

$$H_2N-(CH_2)_6-\underset{H}{\underset{|}{N}}\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\right]_{n-1}\overset{O}{\overset{\|}{C}}-(CH_2)_4-COOH + (2n-1)\ H_2O$$

Synthesis of a polyamide from 1,6-hexamethylene diamine and adipic acid

  2) ***Chain-growth Polymerization*** **(Addition Polymerization)**



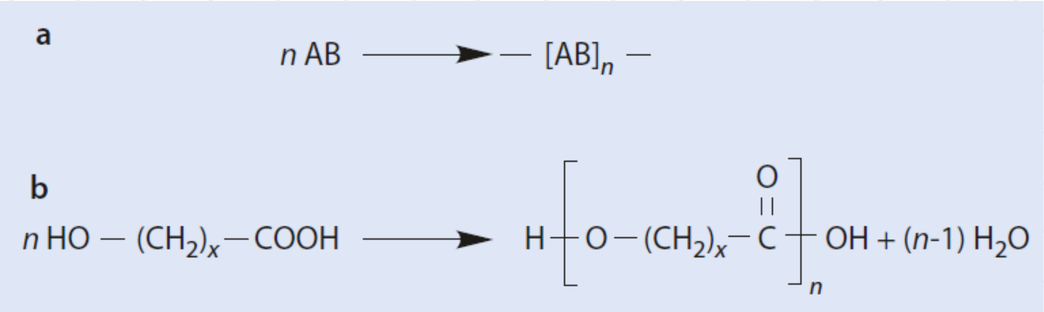
Polymerization of a double bond using styrene (polystyrene)

- These two polymer formation reactions are fundamentally different in their:
  - Mechanisms,
  - Intermediate products,
  - The way the molar mass increases as a function of monomer conversion, and
  - The activation energy of their elementary steps.

Differences Between Step-Growth and Chain-Growth Polymerizations

1) *Step-Growth Polymerization*

- **Step-growth polymerizations** *require that the monomers possess chemical functions that can form covalent bonds with each other.*
  - AB-monomer; these functions can be united in the same molecule



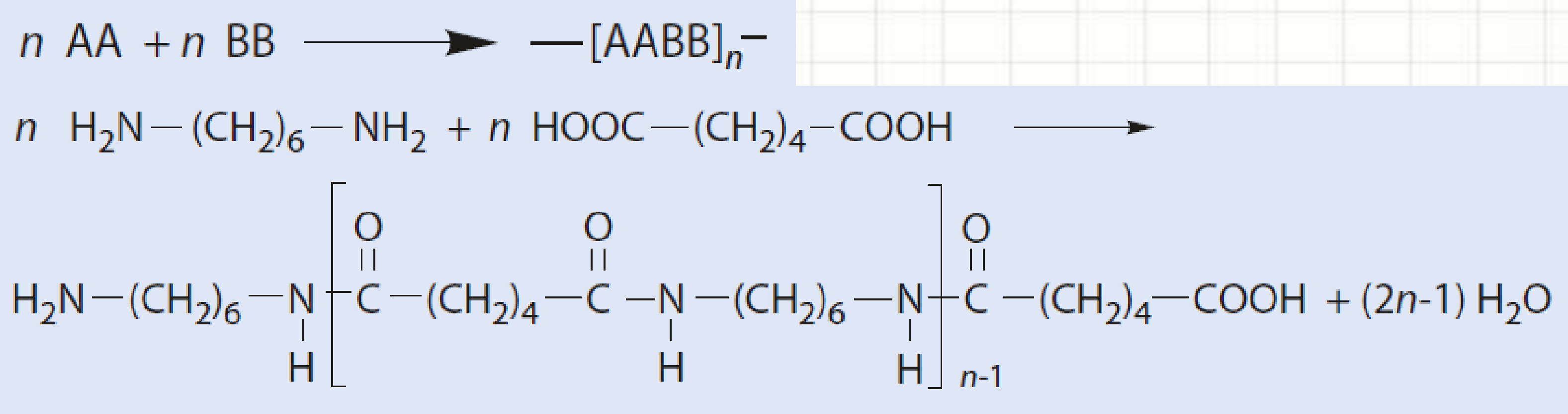
$$n\,AB \longrightarrow -[AB]_n-$$

$$n\,HO-(CH_2)_x-COOH \longrightarrow H\left[O-(CH_2)_x-\overset{O}{\overset{\|}{C}}\right]_n OH + (n-1)\,H_2O$$

(a) a general scheme and

(b) polymerization of a ω-hydroxyl carboxylic acid to a polyester

  - AA and BB-monomer; wo di- or multi-functional molecules can react with each other to form the polymer



$$n\ AA + n\ BB \longrightarrow -[AABB]_n-$$

$$n\ H_2N-(CH_2)_6-NH_2 + n\ HOOC-(CH_2)_4-COOH \longrightarrow$$

$$H_2N-(CH_2)_6-\underset{H}{\underset{|}{N}}\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}\right]_{n-1}\overset{O}{\overset{\|}{C}}-(CH_2)_4-COOH + (2n-1)\,H_2O$$

Differences Between Step-Growth and Chain-Growth Polymerizations

1) ***Step-Growth Polymerization***

- At least bifunctional monomers, AA and BB, are needed in stoichiometry of the reacting molecules if high molar masses are required.

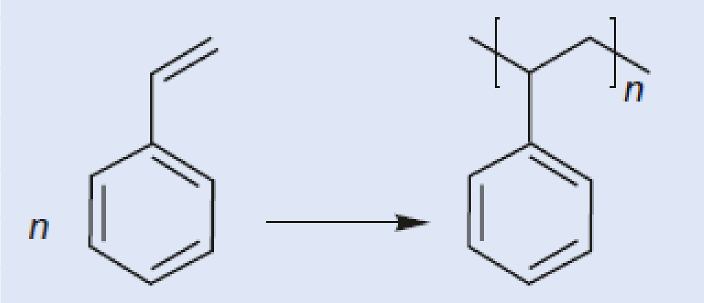
  If there is an excess of BB monomer, all the A-functionalities react and the oligomers are terminated with B groups, which cannot react with each other.

- This polymerization is activated by heat, and no chemical initiator.
- A new monomer results from each individual reaction step and has the same reactivity as the original monomers.
- All intermediate products are stable and can be isolated.
- In contrast to chain-growth polymerization;
  - it is impossible to differentiate between active and passive particles.
  - it takes considerable time for polymers with a high molar mass to form.

Differences Between Step-Growth and Chain-Growth Polymerizations

2) *Chain-Growth Polymerization*

- Polymerization of unsaturated compounds can be caused by radicals, ions, or transition metal catalysts.
- Example: Radical polymerization of styrene



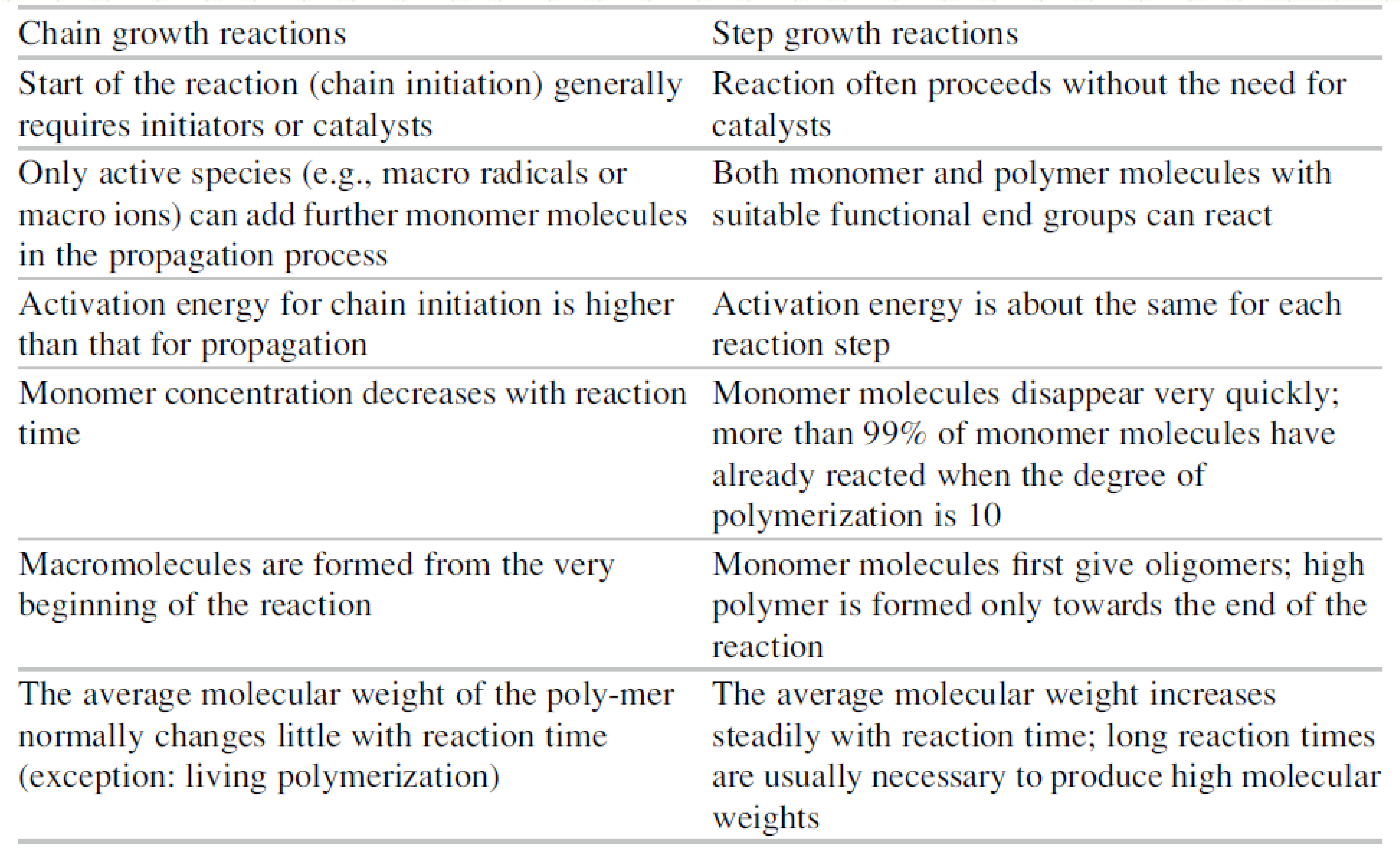
- An initiating radical adds to the double bond of monomeric styrene and creates a styryl radical.
- Styryl radical, can attack another styrene molecule.
- Because the reaction can occur several thousand times before it ends, and always leads to a chain terminating with a styryl radical.
- *Because of its chain reaction character, such a process is referred to as a chain-growth polymerization.*

Differences Between Step-Growth and Chain-Growth Polymerizations

2) ***Chain-Growth Polymerization***

- Chain-growth polymerization have various distinguishing characteristics:
  - It is initiated by a highly reactive particle.
  - Only a small portion of the molecules in the process are actively involved in the polymerization process (in this case, the growing styryl terminated radicals).
  - The remaining molecules are unreactive (they can only react with radicals but not with themselves).
  - The chain grows quickly (generally within a matter of seconds) to a high molar mass.

Differences Between Step-Growth and Chain-Growth Polymerizations



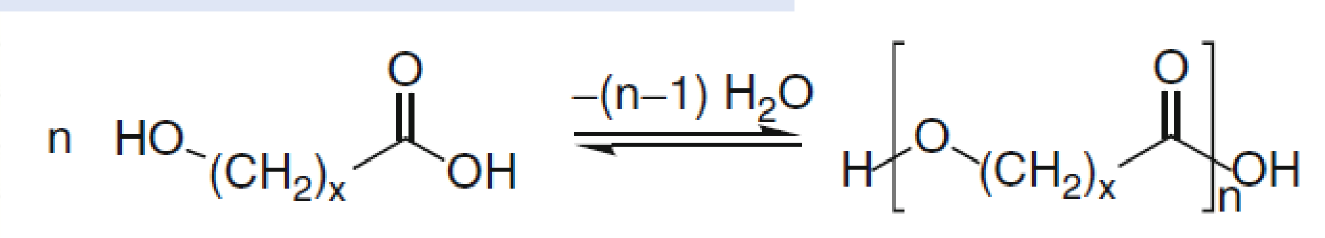
Chain growth reactions	Step growth reactions
Start of the reaction (chain initiation) generally requires initiators or catalysts	Reaction often proceeds without the need for catalysts
Only active species (e.g., macro radicals or macro ions) can add further monomer molecules in the propagation process	Both monomer and polymer molecules with suitable functional end groups can react
Activation energy for chain initiation is higher than that for propagation	Activation energy is about the same for each reaction step
Monomer concentration decreases with reaction time	Monomer molecules disappear very quickly; more than 99% of monomer molecules have already reacted when the degree of polymerization is 10
Macromolecules are formed from the very beginning of the reaction	Monomer molecules first give oligomers; high polymer is formed only towards the end of the reaction
The average molecular weight of the poly-mer normally changes little with reaction time (exception: living polymerization)	The average molecular weight increases steadily with reaction time; long reaction times are usually necessary to produce high molecular weights

STEP-GROWTH POLYMERIZATION

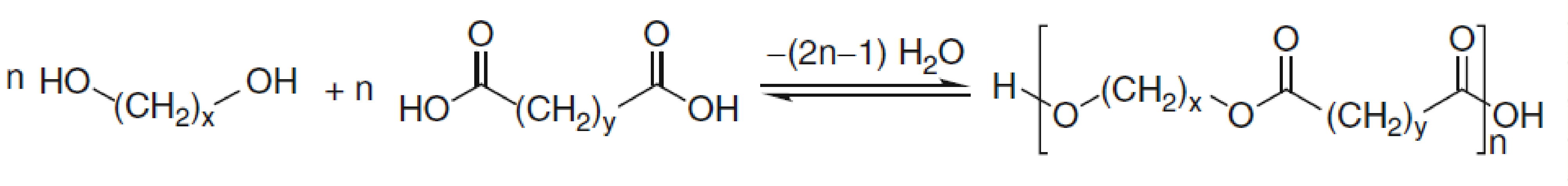
Step-Growth Polymerization

- **Step-Growth Polymerization** is also known as *Condensation polymerizations* (*polycondensations*).
- **Step-growth polymerization** are stepwise reactions between *bifunctional* or *polyfunctional* components (*AB-monomer or of a stoichiometric AA/BB-system*), with elimination of small molecules such as water, alcohol, or hydrogen halide and the formation of macromolecular substances.

$$n\ \mathrm{AB} \longrightarrow -[\mathrm{AB}]_n-$$



$$n\ \mathrm{AA} + n\ \mathrm{BB} \longrightarrow -[\mathrm{AABB}]_n-$$



Step-Growth Polymerization

- *Bifunctional compounds* lead to Linear condensation polymers.
- *Polyfunctional compounds* lead to branched, hyperbranched, or crosslinked condensation polymers

$$n\ \mathrm{AB} \longrightarrow -[\mathrm{AB}]_n-$$

$$n\ \mathrm{AA} + n\ \mathrm{BB} \longrightarrow -[\mathrm{AABB}]_n-$$

- The molar mass is calculated by multiplying the molar mass of the components AB, AA and BB, respectively, by the number *n* of repetitions in the polymer molecule:

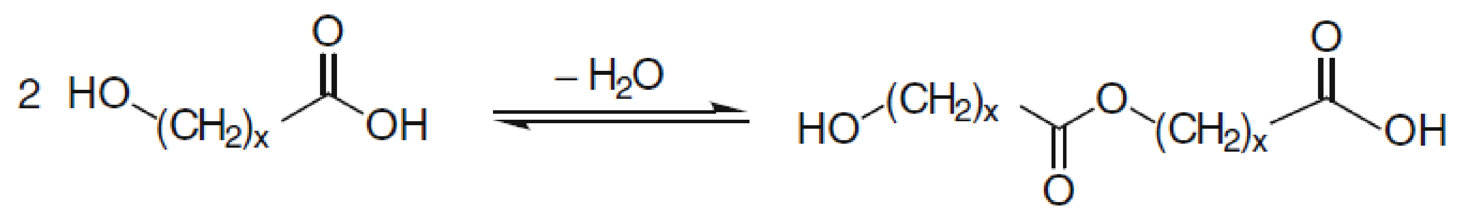
$$\mathrm{M}_{\mathrm{Polymer}} = n\left(\mathrm{M}_{\mathrm{AB}}\right)$$

$$\mathrm{M}_{\mathrm{Polymer}} = n\left(\mathrm{M}_{\mathrm{AA}} + \mathrm{M}_{\mathrm{BB}}\right)$$

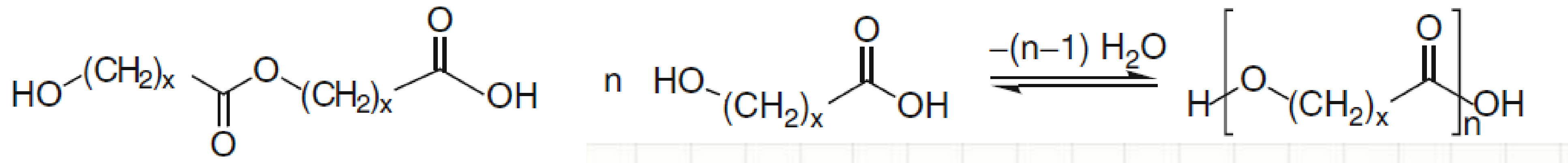
$M_{Polymer}$ represents the molar mass of the polymer,
M_{AB} the molar mass of the monomer AB,
M_{AA} the molar masses of the monomer AA,
M_{BB} the molar masses of the monomer BB.

Step-Growth Polymerization

- **The formation of a condensation polymer is a stepwise process.**
  - **The first step;** the *formation of a dimer* that possesses the same end groups as the initial monomer:



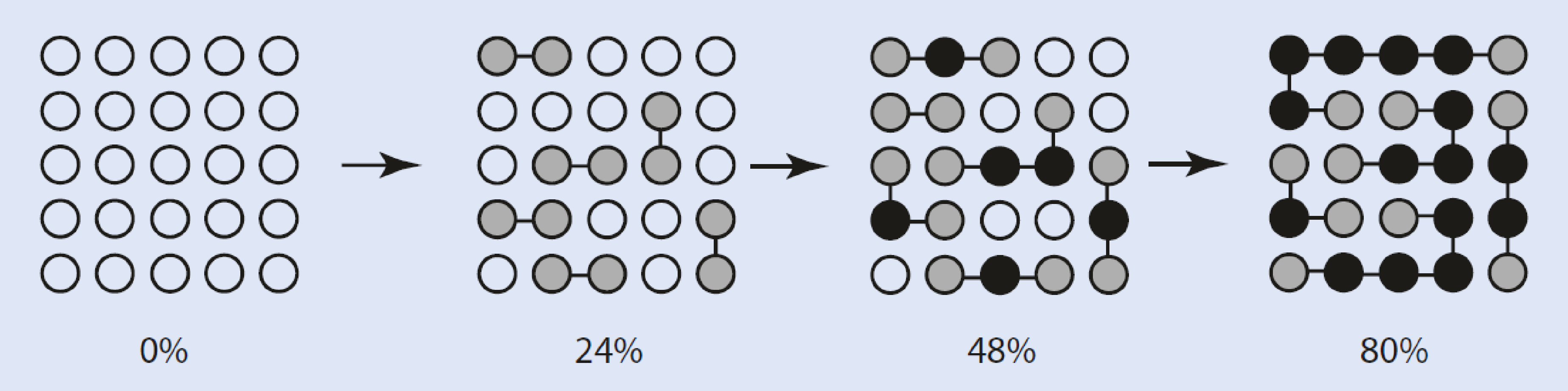
  - **The next step;** the end groups of this dimer can react either with the monomeric compound or with another dimer molecule, and so on.



  - The molecular weight of the resulting macromolecules increases continuously with reaction time, unlike addition polymerizations.
  - The intermediates are oligomeric and polymeric molecules with the same functional end groups as the monomeric starting compound.

Step-Growth Polymerization

- A visualization of a polycondensation at 0 %, 24 %, 48 %, and 80 % functional group conversion.

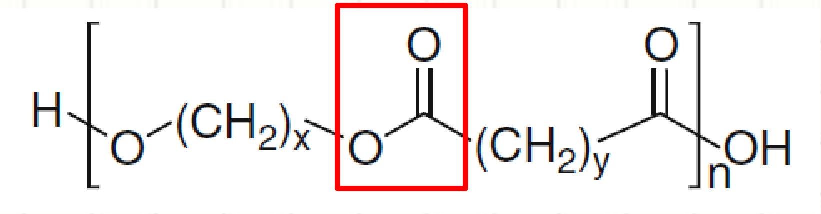


White balls represent monomers, which have not reacted yet,
Gray balls those monomers, which have reacted at one of their two active groups,
Black balls are those molecules which have reacted at both ends

- With a conversion of 80 % of the functional groups, there are five “polymer chains” with “degrees of polymerization” of 3, 4, 5, 6, and 7.
- Not until very high conversions do the oligomers formed condense to chains with a high molar mass.

Step-Growth Polymerization; Polyesters

- **Polyesters** *are macromolecules whose monomeric units are linked with an ester group.*



- **Their properties depend markedly on their chemical composition.**
  - **Pure aliphatic polyesters** are generally
    - *Crystalline* and have *melting points below 100°C*.
    - At room temperature they are soluble in formic acid, and methylene chloride.
    - They are easily hydrolyzed.
  - **Polyesters made from aromatic or cycloaliphatic dicarboxylic acids and diols,**
    - Like; from terephthalic acid and ethylene glycol, or terephthalic acid and 1,4-cyclohexylenedimethanol.
    - They also crystallize but have significantly higher melting points.
    - At room temperature, they are insoluble.
    - They are hard to hydrolyze.
    - They have good mechanical properties, which make them suitable for the preparation of fibers, films, and moldable plastics.

Step-Growth Polymerization; Polyesters

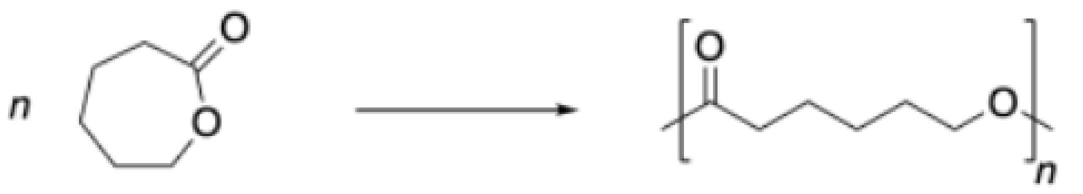
- **Polyesters can be produced by direct esterification of**
  - **Polycondensation of hydroxycarboxylic acids,**

$$n\mathrm{HO{-}R{-}CO_2H} \longrightarrow \mathrm{H}\!\left(\mathrm{O{-}R{-}CO}\right)_n\!\mathrm{OH} + (n-1)\mathrm{H_2O}$$

  - **Polycondensation of diols with dicarboxylic acids,**

$$n\mathrm{HO{-}R{-}OH} + n\mathrm{HO_2C{-}R'{-}CO_2H} \longrightarrow \mathrm{HO}\!\left(\mathrm{R{-}OCO{-}R'{-}COO}\right)_n\!\mathrm{H} + (2n-1)\mathrm{H_2O}$$

  - **Ring-opening polymerization (ROP) of lactones.**
    - Cyclic esters (lactones) are opened up to make extended chain structures.
    - The reaction is typically driven by the release of ring strain.
    - For example, caprolactone is ring-opened to produce polycaprolactone.



Step-Growth Polymerization; Polyesters

Polycondensation of diols with dicarboxylic acids,

- Control of the reaction temperature is important to minimize side reactions such as dehydration of the diol to form diethylene glycol

$$HOCH_2CH_2OH \longrightarrow HOCH_2CH_2OCH_2CH_2OH + H_2O$$

The T_m is decreased by the introduction of diethylene glycol units in place of ethylene glycol units in the polymer chain.

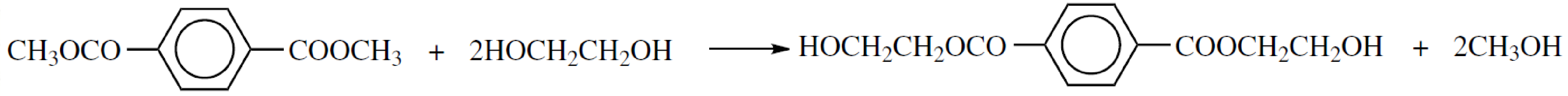
- Direct reactions of diacids or anhydrides with diols are often avoided because of the high temperatures required to completely eliminate water.

  However, these reactions are used to produce low-molecular-weight and crosslinked polyesters based on phthalic and maleic anhydrides

- Ester interchange, typically using a dimethyl ester, has often been used because the reaction is fast and the *dimethyl ester is often more easily purified and has better solubility characteristics*.

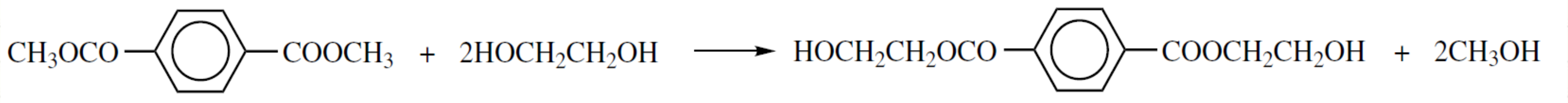
Step-Growth Polymerization; Polyesters

The most important commercial polyester is poly(ethylene terephthalate) (PET).

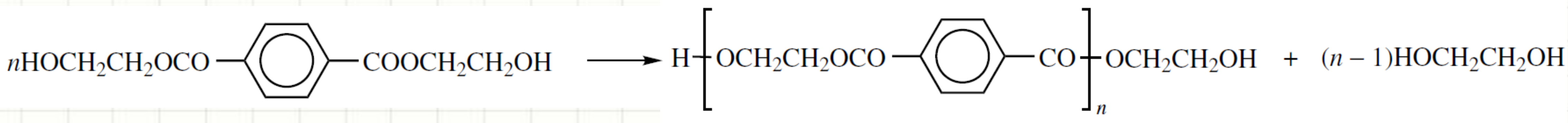


Two processes are used for the synthesis of PET, based on *dimethyl terephthalate (DMT)* or *terephthalic acid (TA)*

- **Two-stage ester interchange process between DMT and ethylene glycol.**
  - **Stage 1: ester interchange to produce bis(2-hydroxyethyl)terephthalate.**
    The reactants are heated at temperatures increasing from 150 to 210C and methanol is distilled off.



  - **Stage 2;** polymerization proceeds
    the temperature is raised to 270–280C with the removal of ethylene glycol.



Step-Growth Polymerization; Polyesters

- **Two-stage ester interchange process between DMT and ethylene glycol.**
  - The **first stage;** solution polymerization.
  - The **second stage;** is a melt polymerization since the reaction temperature is above the crystalline melting temperature of the polymer.

- **High-molecular-weight polymer** requires the complete removal of ethylene glycol.

  If ethylene glycol were not removed, equilibrium would be established at too low an extent of reaction and the product would be of very low molecular weight

- **At the start of the polymerization**, no need for stoichiometric balance of the two functional groups

  an excess of ethylene glycol is initially used to increase the rate of formation of bis(2-hydroxyethyl)terephthalate)

- **At the end of the second stage of the process**, stoichiometric balance is inherently achieved.

Step-Growth Polymerization; Polyesters

- **General properties of PET**
  - Trade names of PET; Mylar, Dacron, and Terylene.
  - PET was not introduced as a commercial product until 1953.
  - **Properties of PET**
    - High crystalline melting temperature (270C)
    - Stiff polymer chains,
    - Good mechanical strength, toughness, and fatigue resistance up to 150–175C.
    - Good chemical, hydrolytic, and solvent resistance.

Step-Growth Polymerization; Polyesters

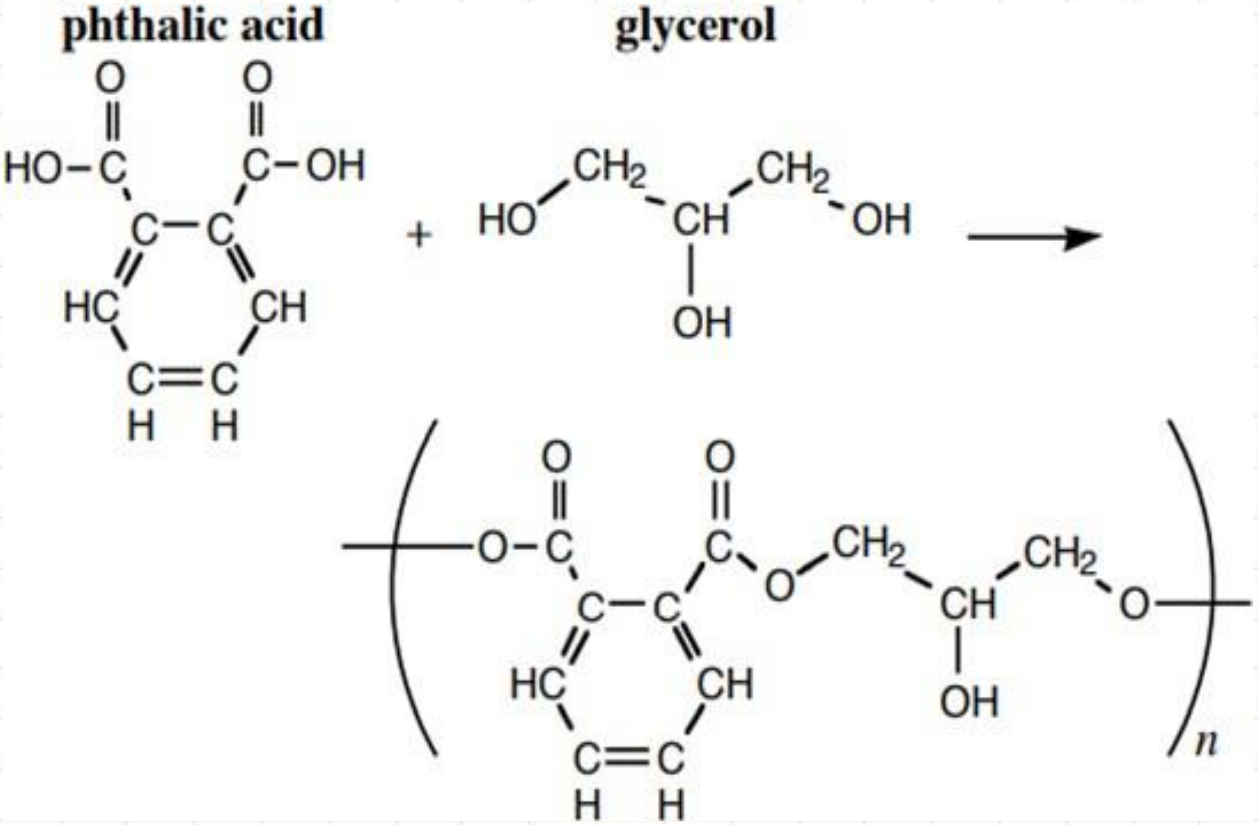
- Applications of PET
  - **Fiber applications**
    - About 45% of the total PET production
    - PET fiber as textile
      - has crease resistance,
      - has good abrasion resistance,
      - can be blended with cotton and other cellulosic fibers to give better feel and moisture permeation.
  - **Plastics applications**
    - For blow-molded bottles for soft drinks, beers, spirits, and other food products
  - **Film applications**
    - photographic, magnetic, and X-ray films or tapes, and electrical insulation
  - **Engineering plastic**
    - it replaces steel, aluminum, and other metals in the manufacture of precision moldings for electrical and electronic devices, domestic and office appliances, and automobile parts.
    - PET is often reinforced with glass fiber or compounded with silicones, graphite, or Teflon to improve strength and rigidity.
    - Glass reinforced grades of PET are rated for continuous use at temperatures up to 140–155C.

Step-Growth Polymerization; Polyesters

- **Poly(butylene terephthalate) (PBT),**
  - produced by substituting 1,4-butanediol for ethylene glycol,
  - crystallizes much faster than PET,
  - competes with PET in engineering plastics applications.
  - Its maximum use temperature is 120–140C, slightly lower than that of PET.
- **Completely aliphatic polyesters**
  - They are made from aliphatic diacid and aliphatic diol components
  - They are not of major industrial importance because of their low melting temperatures and poor hydrolytic stability.
  - Low-molecular-weight aliphatic polyesters are used as plasticizers and prepolymer reactants in the synthesis of polyurethanes.

Step-Growth Polymerization; Crosslinked Polyesters

- Crosslinked polyester can be obtained by reacting phthalic anhydride and glycerol in the presence of metal acetate.

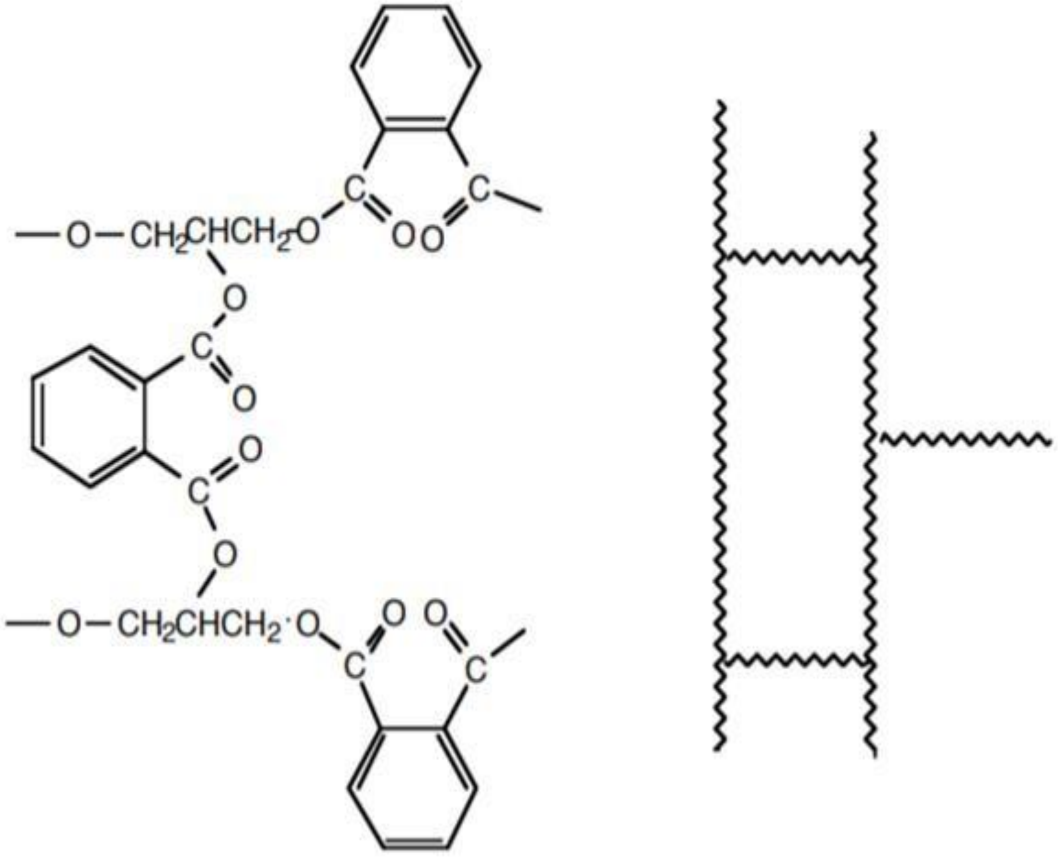


Glyptal resin

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

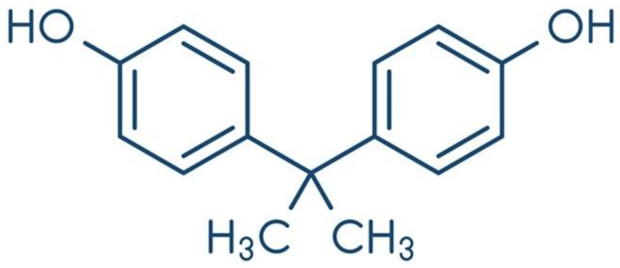
Step-Growth Polymerization; Crosslinked Polyesters

- 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

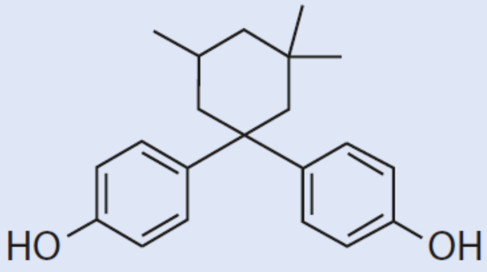


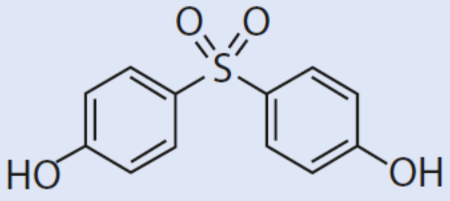
Step-Growth Polymerization; Polycarbonates (PC)

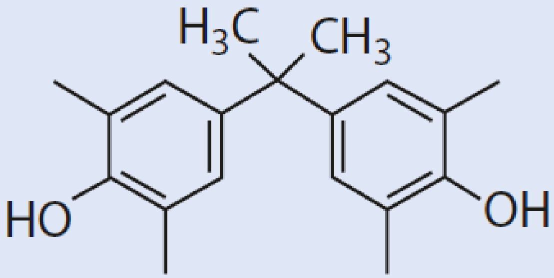
- **Polycarbonates** *are linear polyesters of carbonic acid.*
- The most important commercial polycarbonate is based on 2,2’-bis(4-hydroxyphenyl)propane (bisphenol A)


bisphenol A

- Some alternative bisphenols for the preparation of polycarbonates

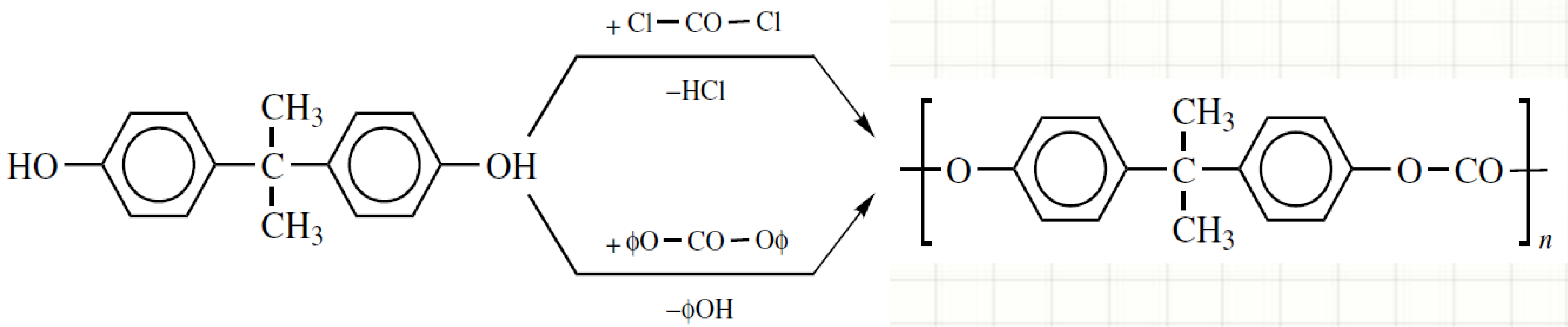

1,1-Bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (BPTMC)


Bisphenol S


Tetramethyl-bisphenol A

Step-Growth Polymerization; Polycarbonates (PC)

- **The polymerization is usually a two-stage reaction at 0-50C;**
  - Oligomers are formed in the first stage.
    - Bisphenol A is dissolved in aqueous alkali to form the phenolate salt and then the organic solvent added followed by phosgene.
    - The organic solvent prevents the loss of phosgene by hydrolysis and precipitation of the polymer before it has reached the desired molecular weight.
  - Tertiary amines are added in the second stage to
    - enhance the transfer of the phenolate salt across the interfacial boundary into the organic phase.
    - catalyze the further reaction to high-molecular-weight polymer.



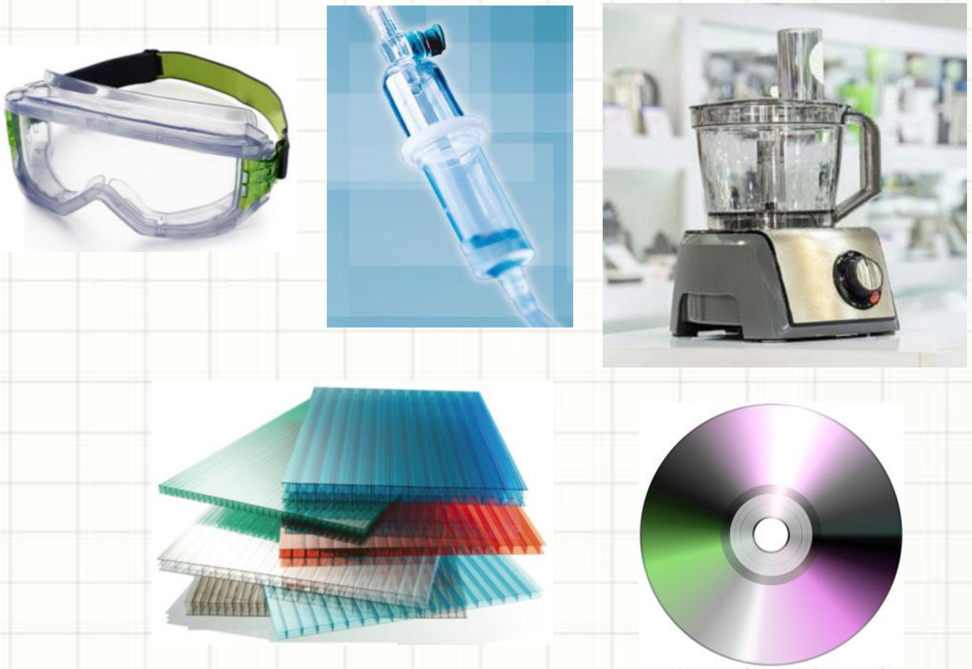
Step-Growth Polymerization; Polycarbonates (PC)

- **General properties of PC**
  - PC has excellent resistance to acids and oxidants, better than PET.
  - PC is less resistant to bases compared to PET.
  - PC is comparable to PET in resistance to organic solvents at ambient temperature.
  - At higher temperatures, PC is more resistant to aliphatic and aromatic solvents but less resistant to polar organic solvents.
  - PC finds are transparency and impact resistance (toughness).
  - They have higher glass transition temperatures and lower melt viscosities and hence are easier to process.

Step-Growth Polymerization; Polycarbonates (PC)

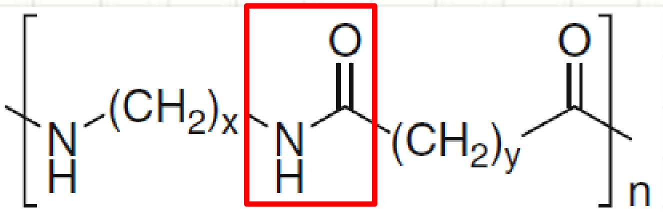
Applications of PC

- Trade names of polycarbonates are Makrolon (Bayer Material Science), Lexan (SABIC), and Xantar (Mitsubishi).
- **Applications include**
  - compact disks,
  - glazing (windows, doors, face shields, sunglasses, aircraft interiors),
  - automotive (instrument panels and components, exterior panels)
  - medical (components for dialysis, blood collection, and surgical devices),
  - other uses (power tool and appliance housings, refrigerator interiors, safety helmets, electrical connectors).

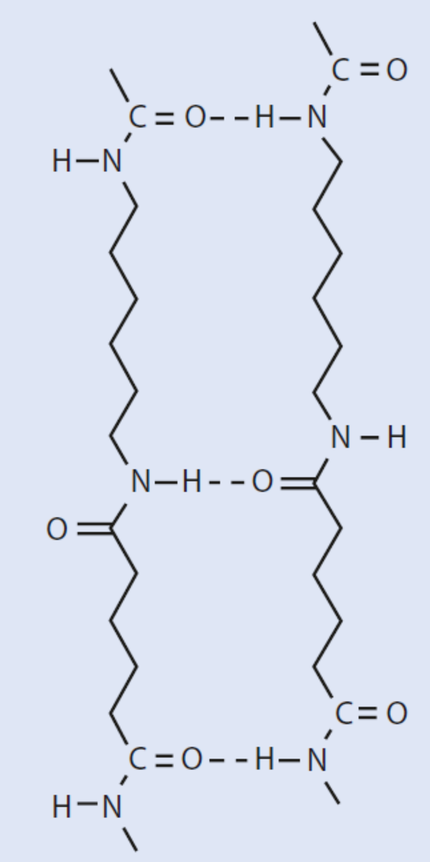


Step-Growth Polymerization; **Polyamides**

- **Polyamides** *are macromolecules whose constitutional repeating units are joined by amide groups*.



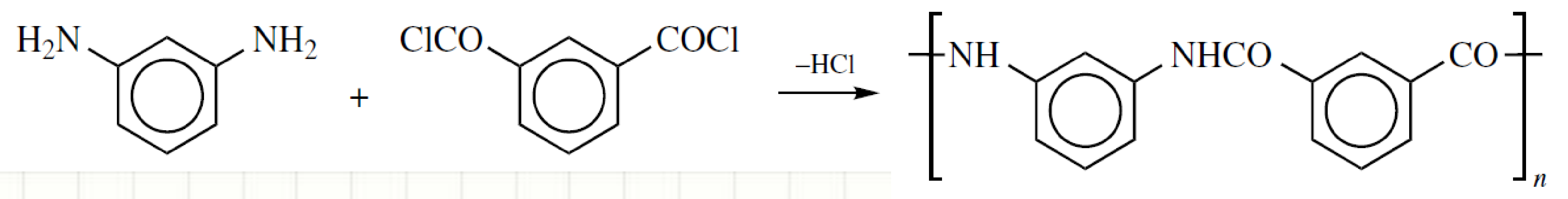
- **Aliphatic Polyamides**
  - Polyamide-6,6 (Nylon-6,6); from hexamethylenediamine and adipic acid.
  - Polyamide-6,10 (Nylon-6,10); from hexamethylenediamine and sebacic acid.
  - Polyamide-6 (Nylon-6); from an aminocarboxylic acid (ε-aminocaproic acid) or from ring-opening polymerization of lactams (ε-caprolactam).
  - Many properties of polyamides are attributted to the formation of hydrogen bonds between NH and CO groups of neighboring macromolecules.
  - **This is evidenced by**
    - Their solubility in special solvents (sulfuric acid, formic acid, m-cresol),
    - Their high melting points (even when made from aliphatic components),
    - Polyamides with a regular chain structure crystallize very readily.
  - Aliphatic polyamides are used as fibers.



Step-Growth Polymerization; Polyamides

Aromatic Polyamides (Aramid Polymers)

- Synthesis of aromatic polyamides is difficult to carry out using diacid and diamine reactants because of lower reactivity of aromatic amines compared to aliphatic amines
- Aromatic polyamides are produced by using the faster reaction of a diamine with a diacid chloride.
- **Example;** poly(*m*-phenylene isophthalamide) (trade name: Nomex).



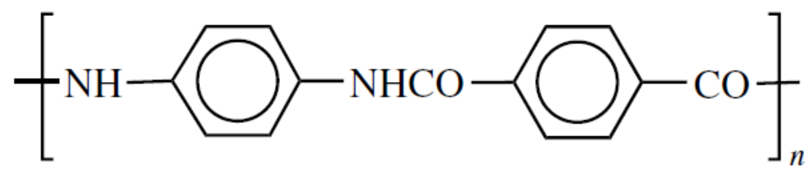
- The polymerization is carried out in solution at 100C with a tertiary base.
- Highly polar aprotic solvents such as dimethylacetamide, have been used to prevent the precipitation of the growing polyamide chains.
- The resulting polymer solutions from these polymerizations are often used directly to spin fibers.

Step-Growth Polymerization; Polyamides

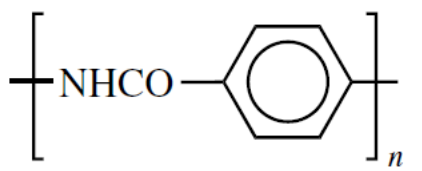
- **Aromatic Polyamides (Aramid Polymers)**

Examples:

- Poly(imino-1,4-phenyleneiminoterephthaloyl) is synthesized from *para*-substituted diamine and diacid chloride.
- Poly(iminocarbonyl-1,4-phenylene) is based on *p*-aminobenzoic acid.



Poly(imino-1,4-phenyleneiminoterephthaloyl)
(trade names: Kevlar, Twaron)



Poly(iminocarbonyl-1,4-phenylene)
(trade name; Kevlar)

- **Aramid polymers** are much more expensive than the aliphatic polyamides.
- The use of aramid polymers is limited to those applications that justify the high cost.
- **The applications;**
  - very high flame resistance (clothing for firefighters and welders, protective shield and drapes),
  - heat resistance (ironing board covers, insulation film for electrical motors),
  - strength and modulus (circuit boards and automobile tire cord).

Step-Growth Polymerization; Polyamides

The following are the main reactions employed for the preparation of polyamides:

1) ***Direct Amidation;*** **Polycondensation of diamines with dicarboxylic acids.**

   Polycondensation of diamines with derivatives of dicarboxylic acids (e.g., acid chlorides).

2) ***Self-Amidation;*** **Polycondensation of ω-Aminocarboxylic acids.**

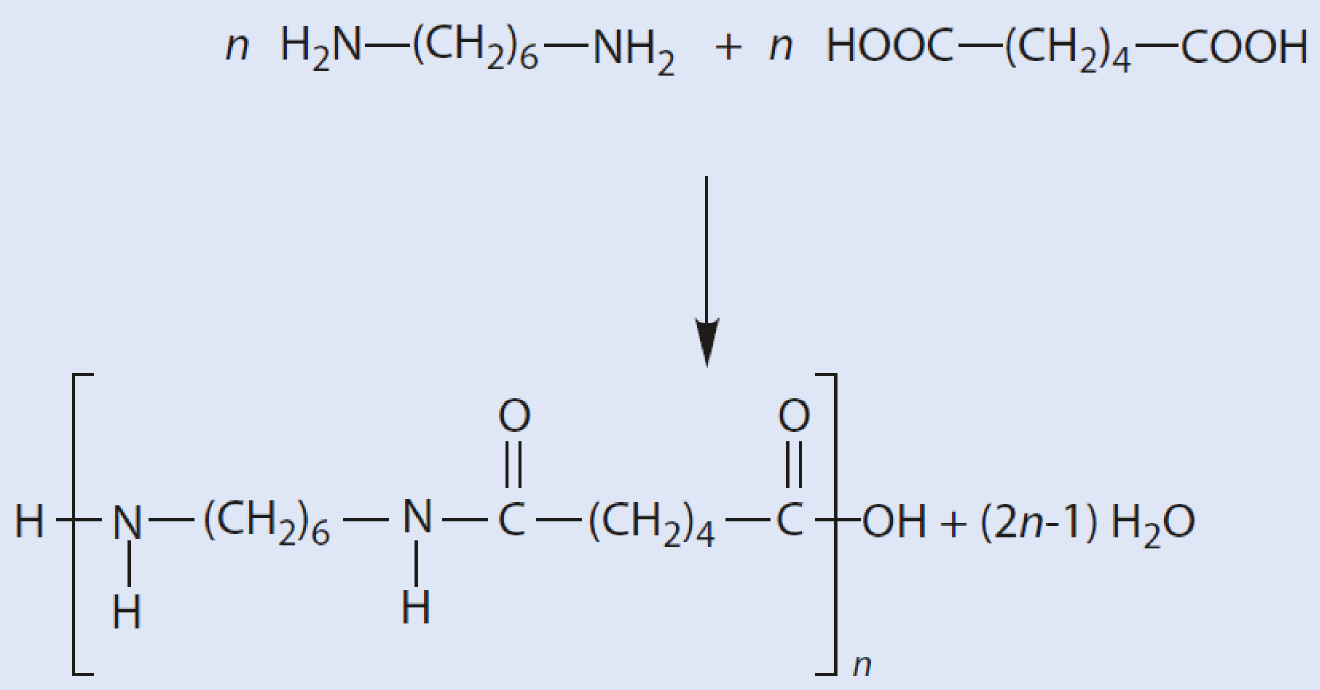
3) ***Ring-Opening*** **polymerization of lactams**

- Polycondensation of diamines with dicarboxylic acid and self-amidation are carried out in the melt; solution polycondensations at higher temperature, are of significance only in a few cases on account of the poor solubility of polyamides.
- Polycondensation of diamines with dicarboxylic acid chlorides can be carried out either in solution at low temperature or as interfacial condensation

Step-Growth Polymerization; Polyamides

1) Direct Amidation; Polycondensation of diamines with dicarboxylic acids

- Poly(hexamethylene adipamide) (nylon-6,6) is synthesized from hexamethylene diamine and adipic acid.

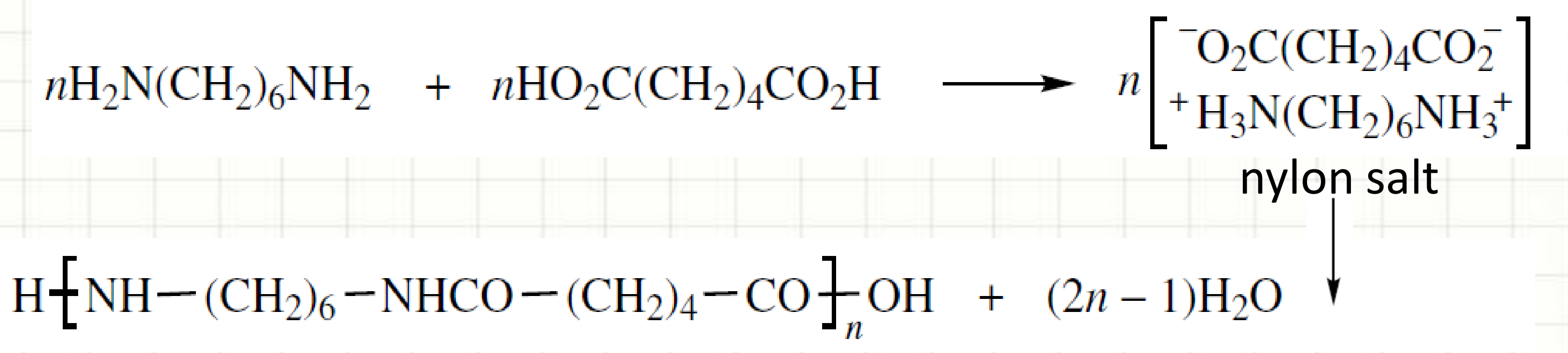


$$n\ H_2N{-}(CH_2)_6{-}NH_2 + n\ HOOC{-}(CH_2)_4{-}COOH \longrightarrow H{-}\left[N(H){-}(CH_2)_6{-}N(H){-}C({=}O){-}(CH_2)_4{-}C({=}O)\right]_n{-}OH + (2n\text{-}1)\ H_2O$$

Step-Growth Polymerization; Polyamides

1) Direct Amidation; Polycondensation of diamines with dicarboxylic acids

- Stoichiometric balance of amine and carboxyl groups is obtained by preliminary formation of 1:1 ammonium salt (nylon salt) in aqueous solution at a concentration of 50%.



$$nH_2N(CH_2)_6NH_2 + nHO_2C(CH_2)_4CO_2H \longrightarrow n\left[\begin{matrix}{}^{-}O_2C(CH_2)_4CO_2^{-} \\ {}^{+}H_3N(CH_2)_6NH_3^{+}\end{matrix}\right]$$

nylon salt

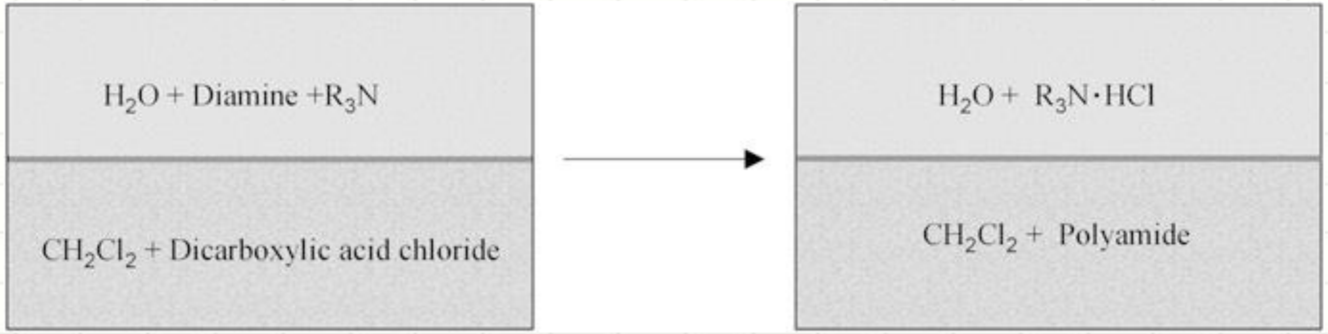
$$H\left[NH-(CH_2)_6-NHCO-(CH_2)_4-CO\right]_nOH + (2n-1)H_2O$$

- The aqueous salt solution is concentrated to a slurry of approximately 60% or higher salt content by heating above 100C.
- Polymerization is carried out by raising the temperature to about 210C.
- Polyamidation is carried out without an external strong acid.
- Molecular weight can be controlled by addition of a calculated amount of a monofunctional acid such as acetic acid.

Step-Growth Polymerization; Polyamides

1) Direct Amidation; Polycondensation of diamines with dicarboxylic acids Chloride

- Polycondensation of dicarboxylic acid chlorides and diamines can be carried out in solution or interfacial polycondensation.
- **Advantages:**
  - It is carried out at low temperature (0–40C);
  - it is very fast, *the reaction usually being over in a few minutes*.
  - At low temperatures practically no side reactions occur.
  - It yields a high-molecular weight polymer in a short time with simple equipment.
- **Disadvantages;**
  - Large amounts of solvent must be purified and handled;
  - Large amounts of salts are formed as by-products.

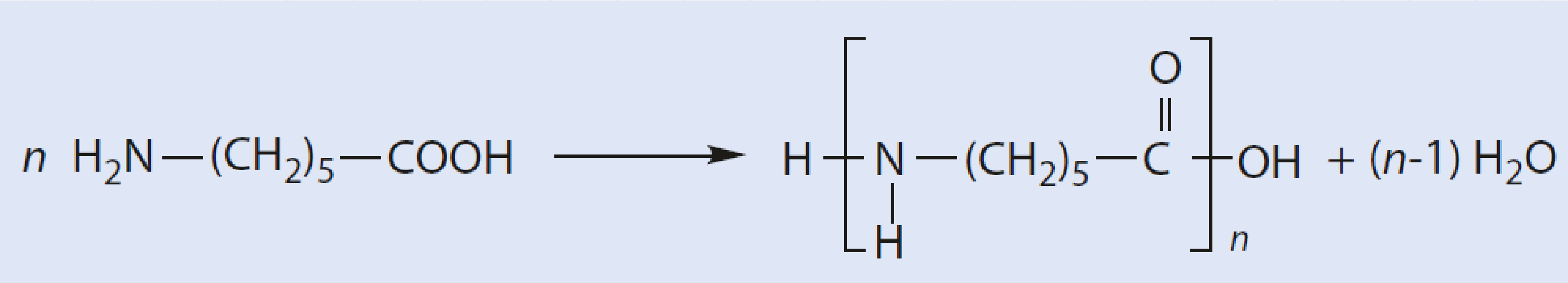


Interfacial polycondensation of dicarboxylic acid and diamine

Step-Growth Polymerization; Polyamides

2) Self-Amidation; Polycondensation of ⍰-Aminocarboxylic acids

- The formation of polyamides by elimination of water from aminocarboxylic acids at high temperature is generally only possible with acids having more than four methylene groups between the amino and carboxyl groups.
  - **Example;** Synthesis of polyamide 6 (Nylon-6)



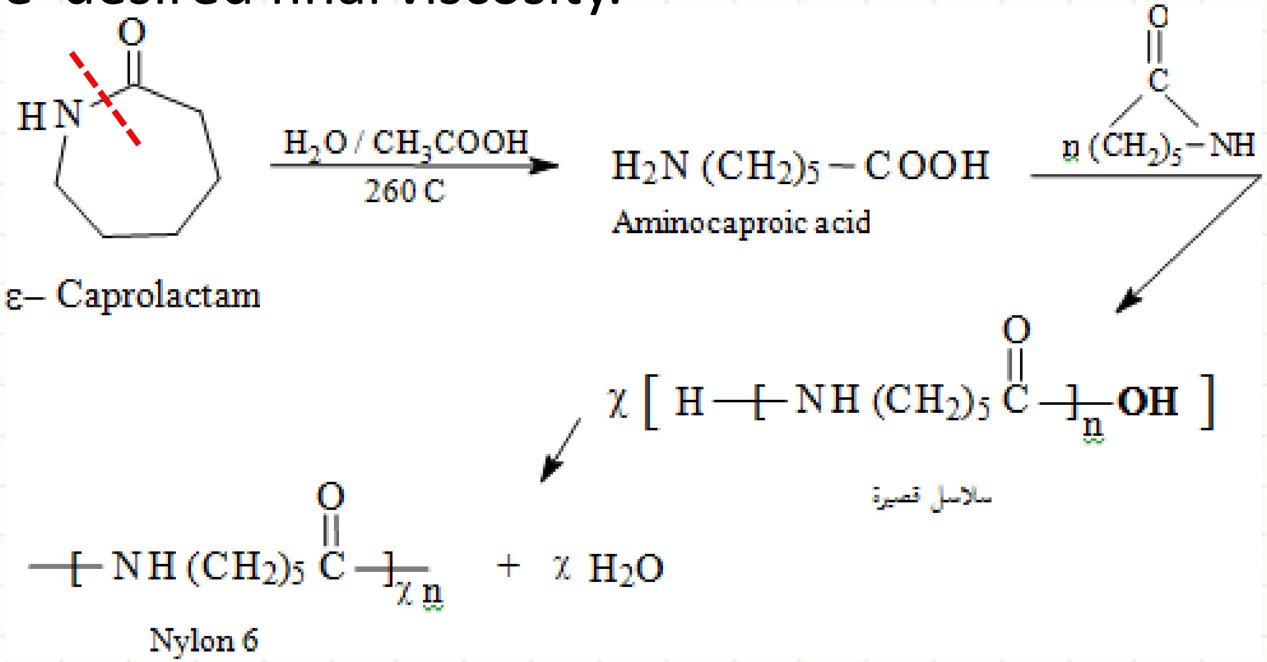
$$n\ H_2N-(CH_2)_5-COOH \longrightarrow H\!\left[\underset{H}{\underset{|}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n\!OH + (n\text{-}1)\ H_2O$$

  - **Example;** Synthesis of polyamide 11 (Nylon-11)

Step-Growth Polymerization; Polyamides

3) Ring-Opening polymerization of lactams

- 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.



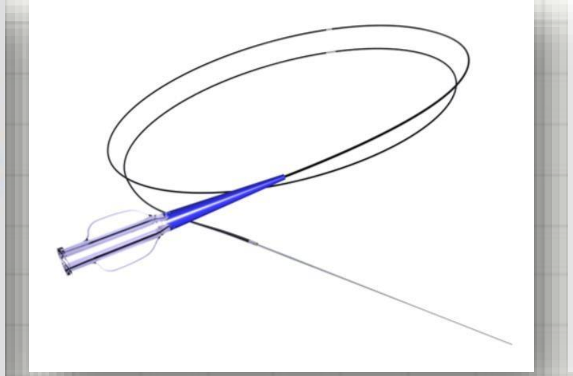
Step-Growth Polymerization; Polyamides

- 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

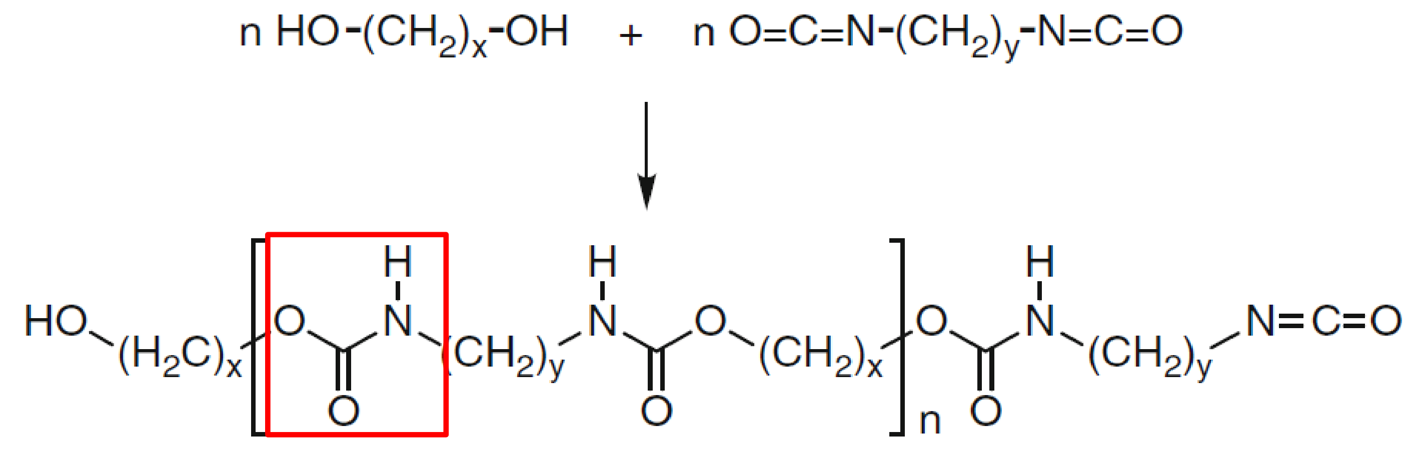
Openable double shell

Step-Addition Polymerization (Polyaddition)

- **Stepwise Addition Polymerization** involve a stepwise reaction of at least two bifunctional compounds, leading to the formation of macromolecules.
  - ***In contrast to* condensation polymerization**,
    - *No low-molecular-weight compounds are eliminated; coupling of the monomer units.*
  - ***Like* condensation polymerization,**
    - *It is also a stepwise reaction.*
    - *The average molecular weight of the resulting polymer steadily increases during the course of the reaction.*
    - *The oligomeric and polymeric products formed in the individual steps possess the same functional end groups and the same reactivity as the starting materials.*
    - *They are governed by kinetic laws similar to those for condensation polymerization.*

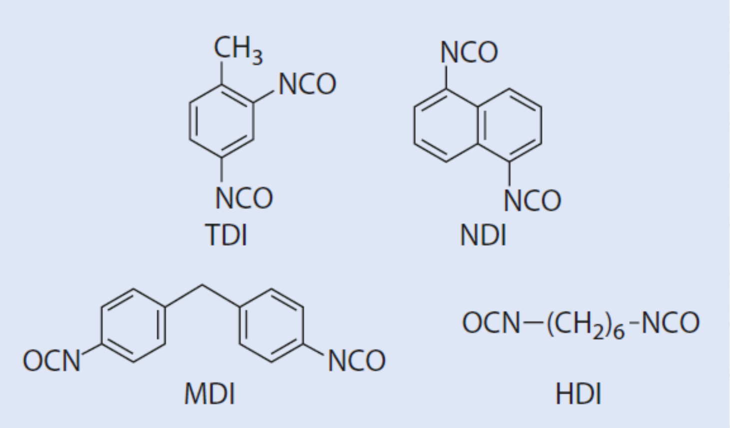
Step-Addition Polymerization (Polyaddition); Polyurethanes

- **Polyurethanes** *are macromolecules in which the constitutional repeating units (CRUs) are coupled with one another through urethane (oxycarbonylamino) groups*.
- They are prepared by **stepwise addition polymerization** reactions of di- or polyfunctional hydroxy compounds with di- or polyfunctional isocyanates:



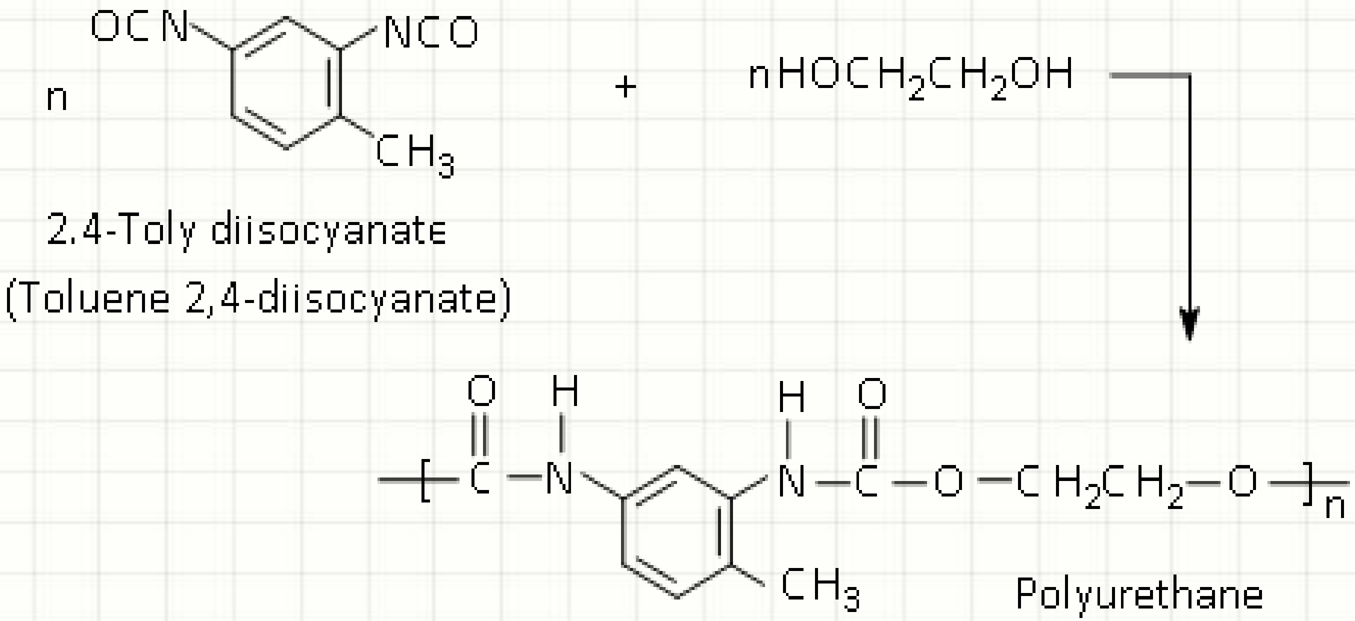
$$n\ HO{-}(CH_2)_x{-}OH + n\ O{=}C{=}N{-}(CH_2)_y{-}N{=}C{=}O \longrightarrow HO{-}(H_2C)_x\left[O{-}C(=O){-}NH{-}(CH_2)_y{-}NH{-}C(=O){-}O{-}(CH_2)_x\right]_n O{-}C(=O){-}NH{-}(CH_2)_y{-}N{=}C{=}O$$

- **Commonly used diisocyanates;**
  TDI: 2,4-tolyl diisocyanate
  NDI: 1.5-naphthyl diisocyanate,
  MDI: 4,4'-methylene diphenyl isocyanate,
  HDI: 1,6 hexamethylene diisocyanate)



Step-Addition Polymerization (Polyaddition); Polyurethanes

- **Primary aromatic diisocyanates**: toluene diisocyanate (TDI) used in the production of Aromatic polyurethanes



Step-Addition Polymerization (Polyaddition); Polyurethanes

Linear Polyurethanes

- They made from short-chain diols and diisocyanates.

  They are high melting, crystalline, thermoplastic substances whose properties are comparable with those of the polyamides because of the similarity in chain structure.

- The addition of isocyanates to hydroxy compounds is inhibited by acid compounds and can be accelerated by basic compounds and metal salts or organometallic compounds.
- Linear polyurethanes with a high molecular weight can be prepared in solution (inert solvents; toluene, xylene);
  - *The diisocyanate is normally dripped into the solution of the dihydroxy compound at the desired temperature (boiling point of the solvent).*
  - *The resulting polyurethane often separates from the reaction mixture.*
- Linear polyurethanes with molecular weights up to about 15,000 can be obtained.

Step-Addition Polymerization (Polyaddition); Crosslinked Polyurethanes

Branched and Crosslinked Polyurethanes

- They can be prepared by two methods;

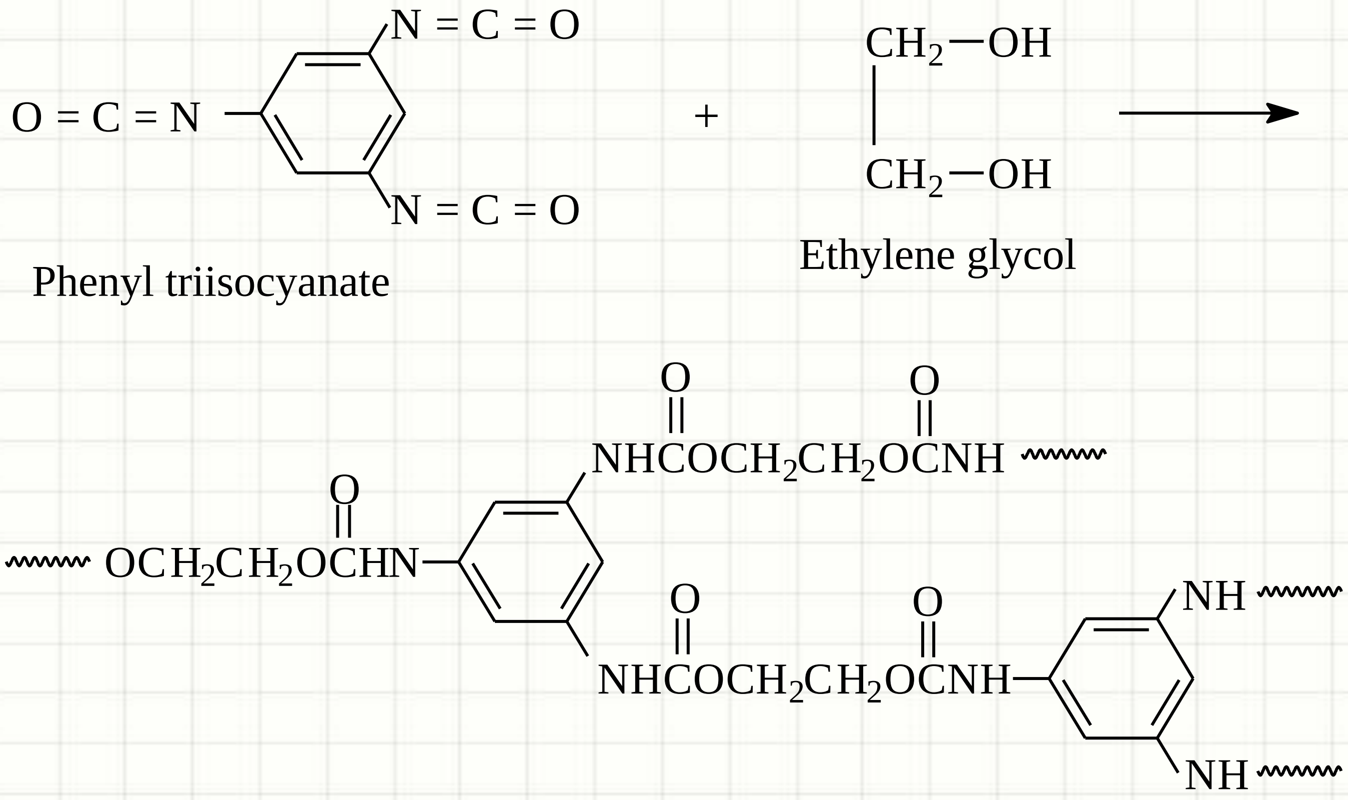
(a) Reaction of diisocyanates with compounds that possess more than two hydroxy groups per molecule.

(b) Reaction of linear oligourethanes, which possess either hydroxy or isocyanate end groups, with suitable reactive compounds.

Low-molecular-weight, aliphatic polyester or polyether with hydroxy end groups (poly(ethylene oxide), poly(propylene oxide) or poly(oxytetramethylene) with molecular weights around 2,000) is reacted with an excess of diisocyanate.

Step-Addition Polymerization (Polyaddition); Crosslinked Polyurethanes

- 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 .

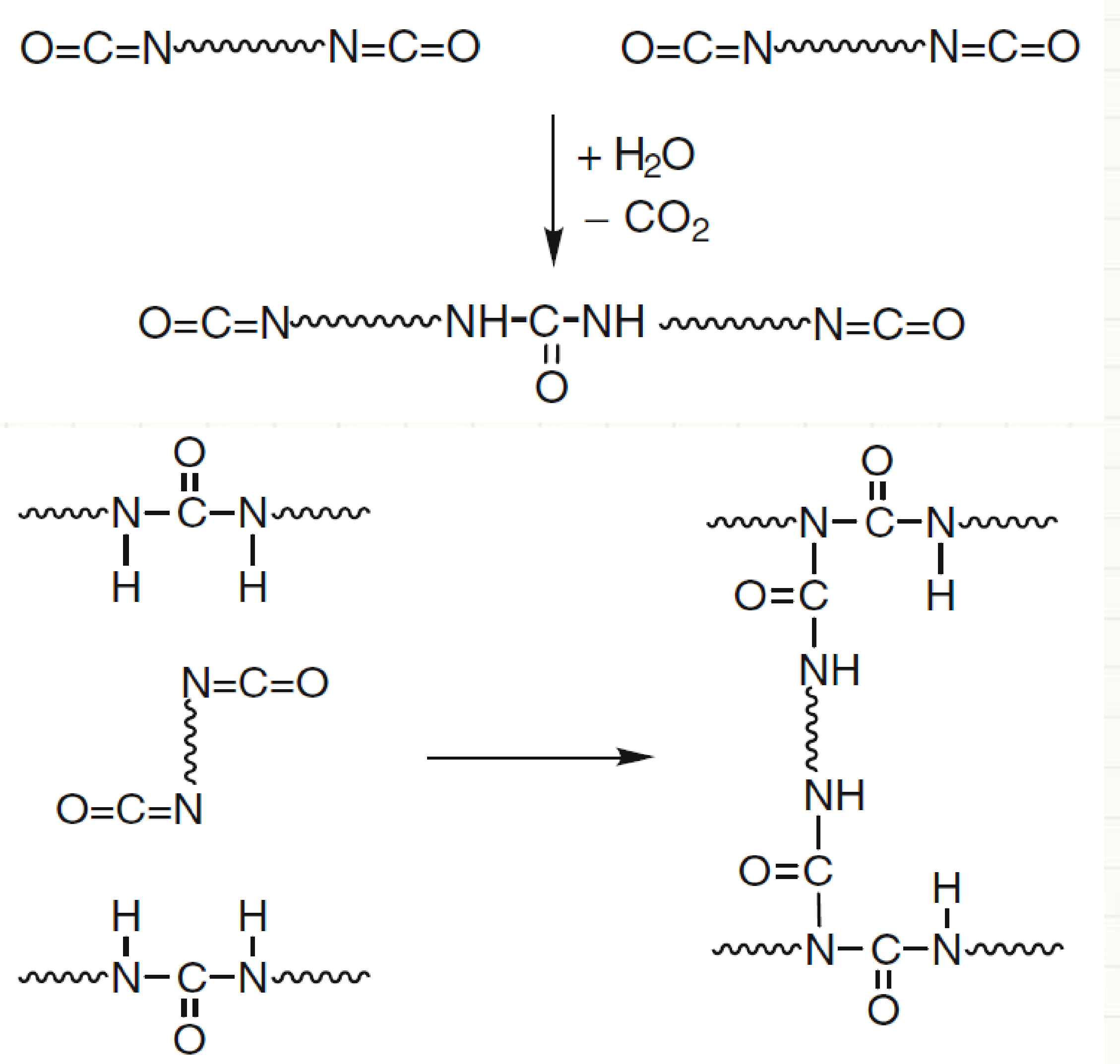
Step-Addition Polymerization (Polyaddition); Crosslinked Polyurethanes

- The chain-extended, linear poly(ester urethanes) so obtained can now be crosslinked in a second stage, involving reaction with – water – or glycols – or diamines.

Polyurethane Foams

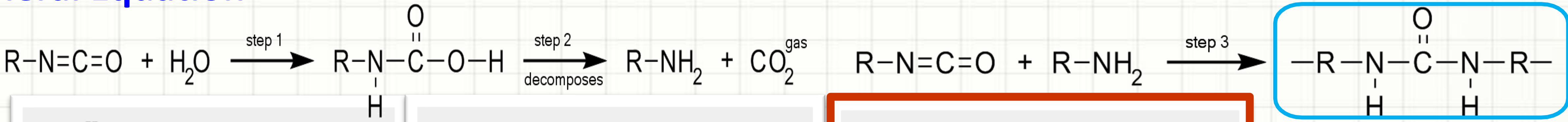
- **In crosslinking with water**, pairs of isocyanate end groups in the chain-extended polymer OCN–X–NCO first react with a molecule of water; this results in a linear coupling through urea groupings, with simultaneous elimination of CO_2

- Crosslinking occurs by reaction of the hydrogen atoms of the resulting urea groups with isocyanate groups still present in the starting polymer

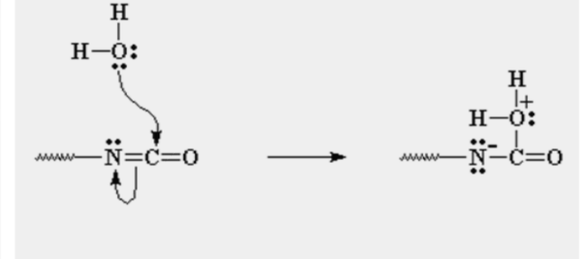


Step-Addition Polymerization (Polyaddition); Polyurethanes

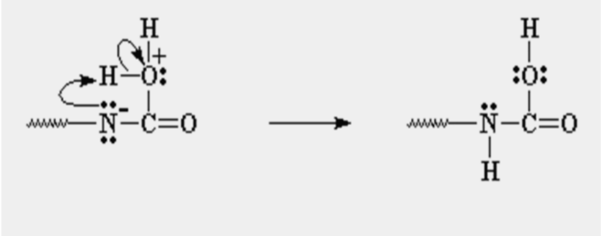
General Equation



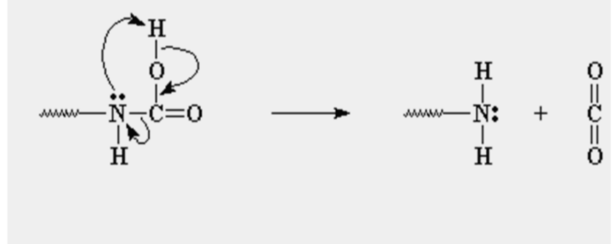
$$R-N=C=O + H_2O \xrightarrow{\text{step 1}} R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[\text{decomposes}]{\text{step 2}} R-NH_2 + CO_2^{\text{gas}} \qquad R-N=C=O + R-NH_2 \xrightarrow{\text{step 3}} -R-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-R-$$



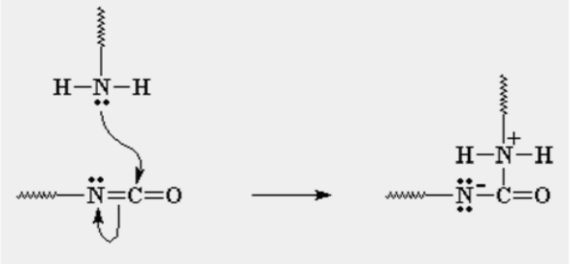
Step 1: A water molecule attacks the isocyanate carbon, giving us an ionic species.



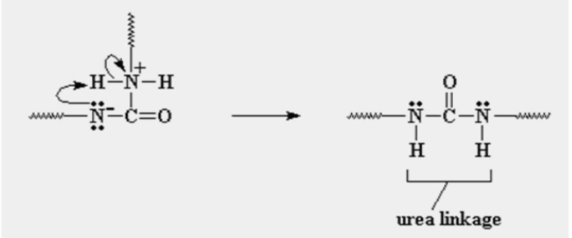
Step 2: The isocyanate nitrogen swipes a hydrogen from the water.



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.

Step-Addition Polymerization (Polyaddition); Polyurethanes

- Crosslinking with glycols or diamines proceeds according to a similar scheme (but without elimination of CO_2).
  - **With glycols,** this occurs with the formation of urethane groups, which can then react with residual isocyanate end groups to give crosslinking with formation.
  - **With diamines.** the linear coupling occurs through urea groups and the crosslinking reaction then proceeds as formulated in structure.

- Crosslinking with glycols and diamines plays a major role in the preparation of polyurethane elastomers.
- The properties of the resulting products can be widely varied by choice of starting components and the number of crosslinks (“mesh width”).

Step-Addition Polymerization (Polyaddition); Polyurethanes

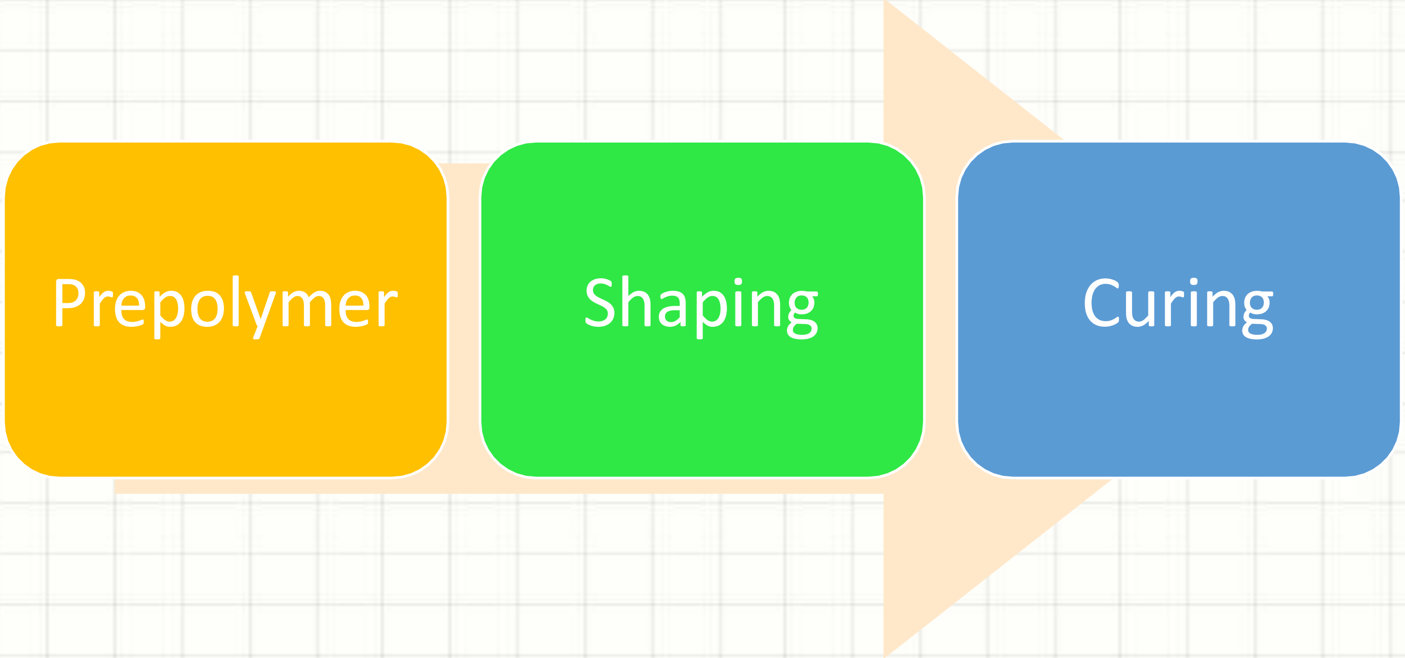
Polyurethane Foam Application

- **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

Step-Growth Polymerization; NETWORK POLYMERS

Three steps are needed to prepare a network polymer;



Prepolymer

Shaping

Curing

- In these type of polymers, monomeric units are linked together to constitute 3D network.
- The links involved are called crosslinks. And they are **hard**, **rigid** and **brittle** due to their network structure.

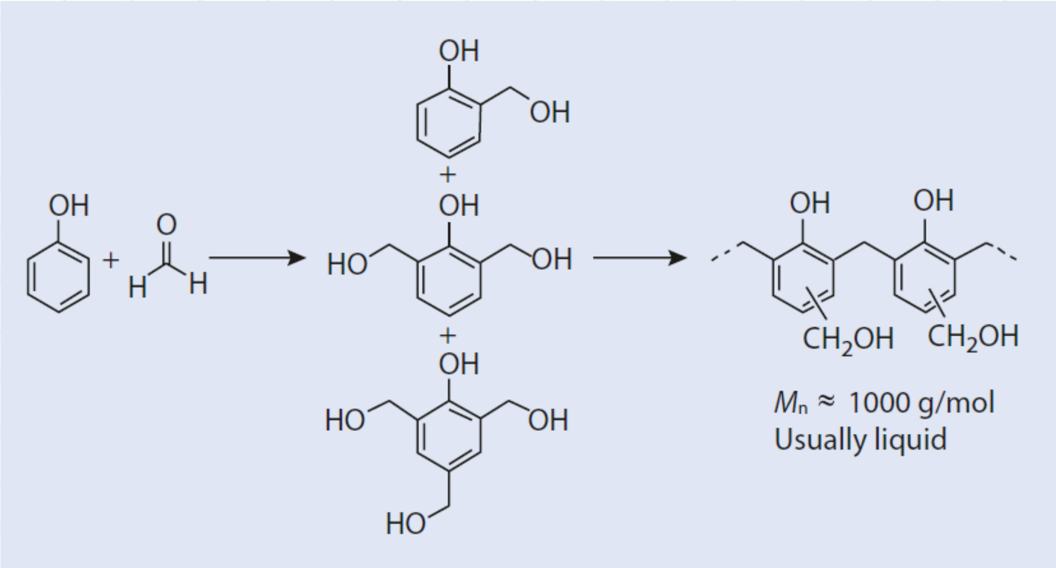
Phenolic Resins (*Phenol-Formaldehyde Resin*)

- Condensation of phenol with formaldehyde can yield low molar mass, soluble, often still liquid intermediate materials (prepolymers).
- By further reactions (e.g., by heating), prepolymers can be converted into networks that are insoluble and do not melt.
- The condensation of phenol with formaldehyde in aqueous solution is pH-dependent.
  - **Resole;** prepolymers obtained in an alkaline medium
  - **Novolac;** prepolymers prepared in acidic solution.
- Phenolic resins are used mainly as molding compounds with fillers.
- The hardened (cross-linked) resins are tough construction materials with good resistance to stress cracking.
- Webs of paper or tissues impregnated with phenolic resins can be processed into laminates.

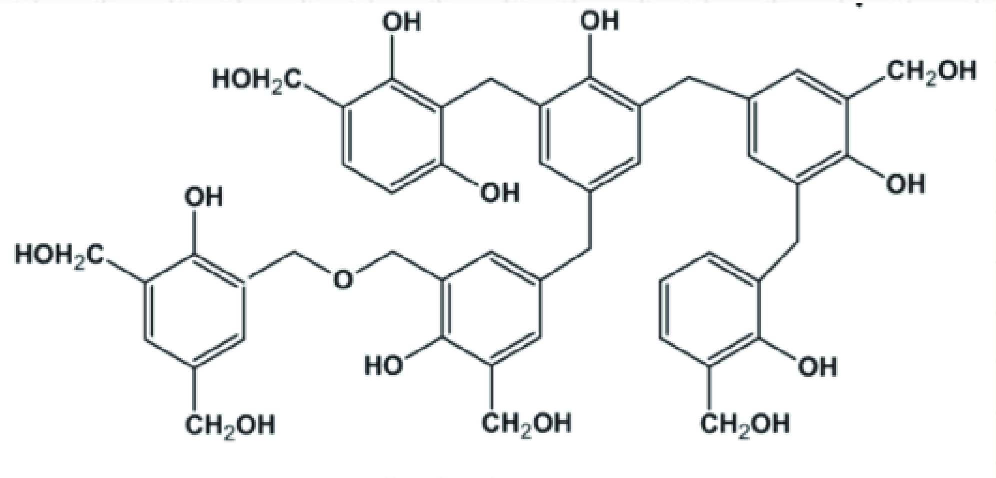
Phenolic Resins (*Phenol-Formaldehyde Resin*)

Resole;

- Synthesis of resol (in a basic medium, ratio of phenol : formaldehyde = 1:1.5)

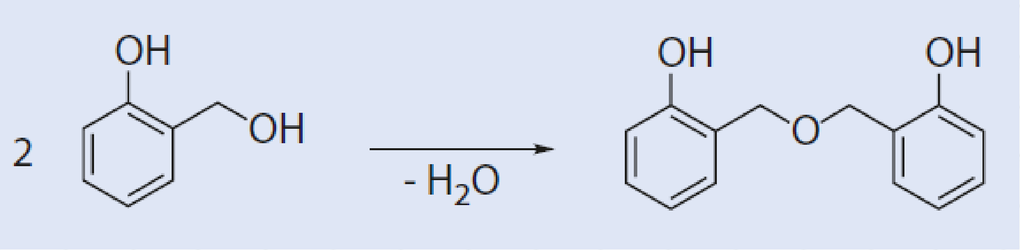


$M_n \approx$ 1000 g/mol
Usually liquid



Resol resin

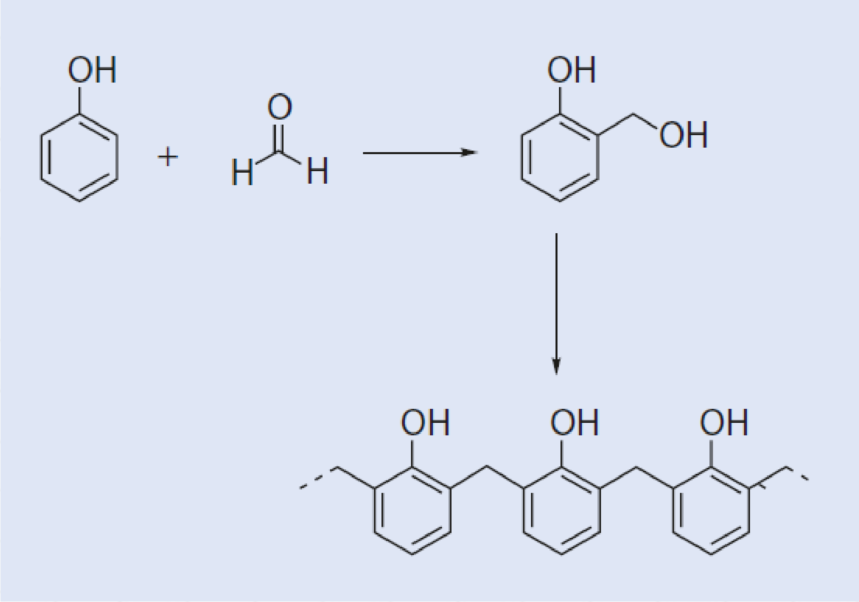
- Cross-linking of resols is accomplished by heating.
- At 130 C, methylol phenols simply dehydrate.



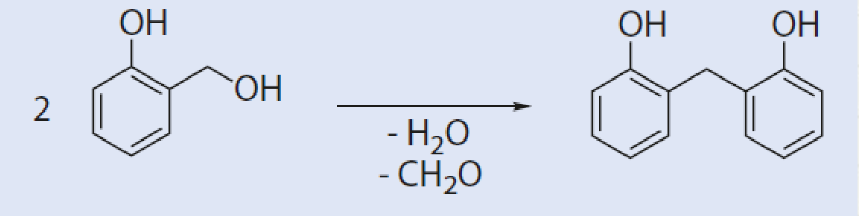
Phenolic Resins (*Phenol-Formaldehyde Resin*)

Novolac

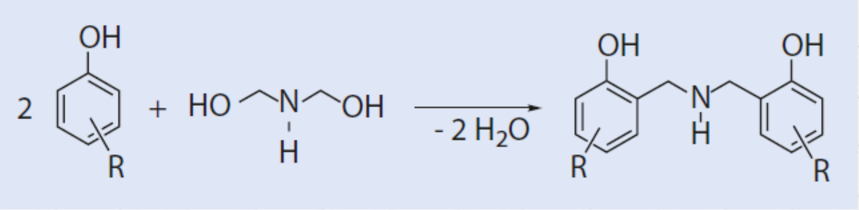
- Synthesis of Novolac (at pH ≤ 3, ratio of phenol:formaldehyde = 1:0.8)



- At 150C, methyl groups are predominantly formed as formaldehyde and water are eliminated.



- The crosslinking of Novolac is achieved by adding crosslinking agents, such as hexamethylene tetramine.
- The cross-linking of Novolac with dimethylol amine

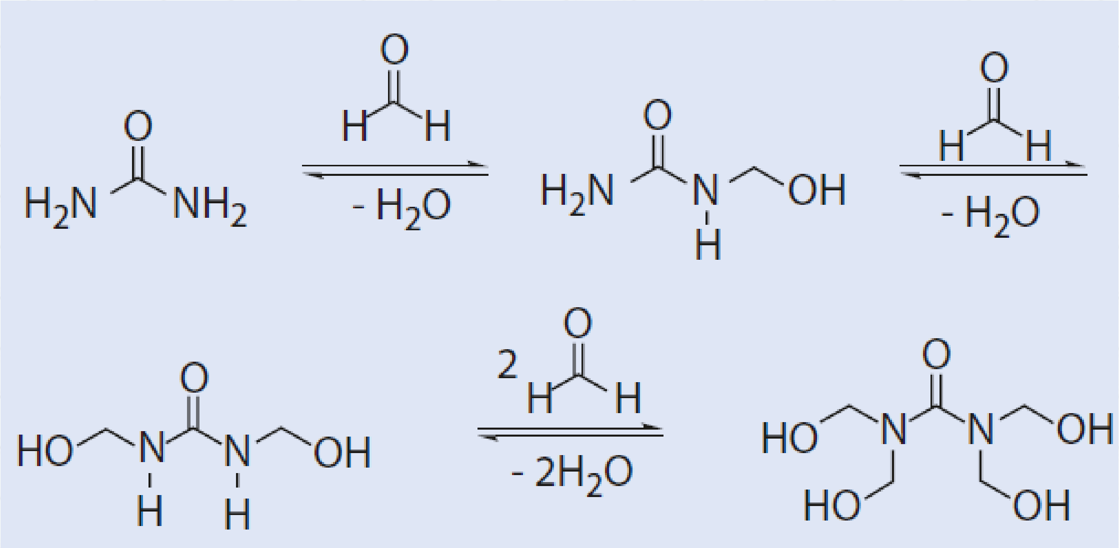


Phenolic Resins (*Phenol-Formaldehyde Resin*)

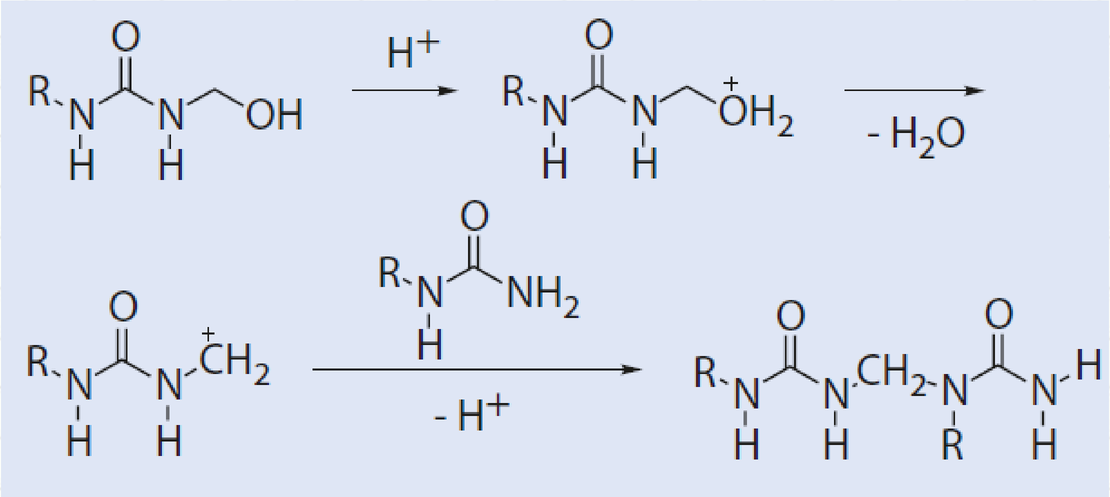
Resole	**Novolac**
Reaction is carried out in basic medium.	Usually obtain in acidic medium.
Phenol functionality is ortho, meta & para	Phenol functionality is ortho and para.
Phenol: formaldehyde is **1**:**1.2**	Phenol: formaldehyde is **1**:**0.8**
Already cross-linked	Can be cross-linked
Not soluble 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

Urea Resins (*Urea-Formaldehyde Resin*)

- The reaction products of formaldehyde with urea (carbamide) are called urea resins.
- This reaction is pH-dependent.
  - In a neutral to slightly alkaline environment; conversion of urea with formaldehyde to urea resin precursors

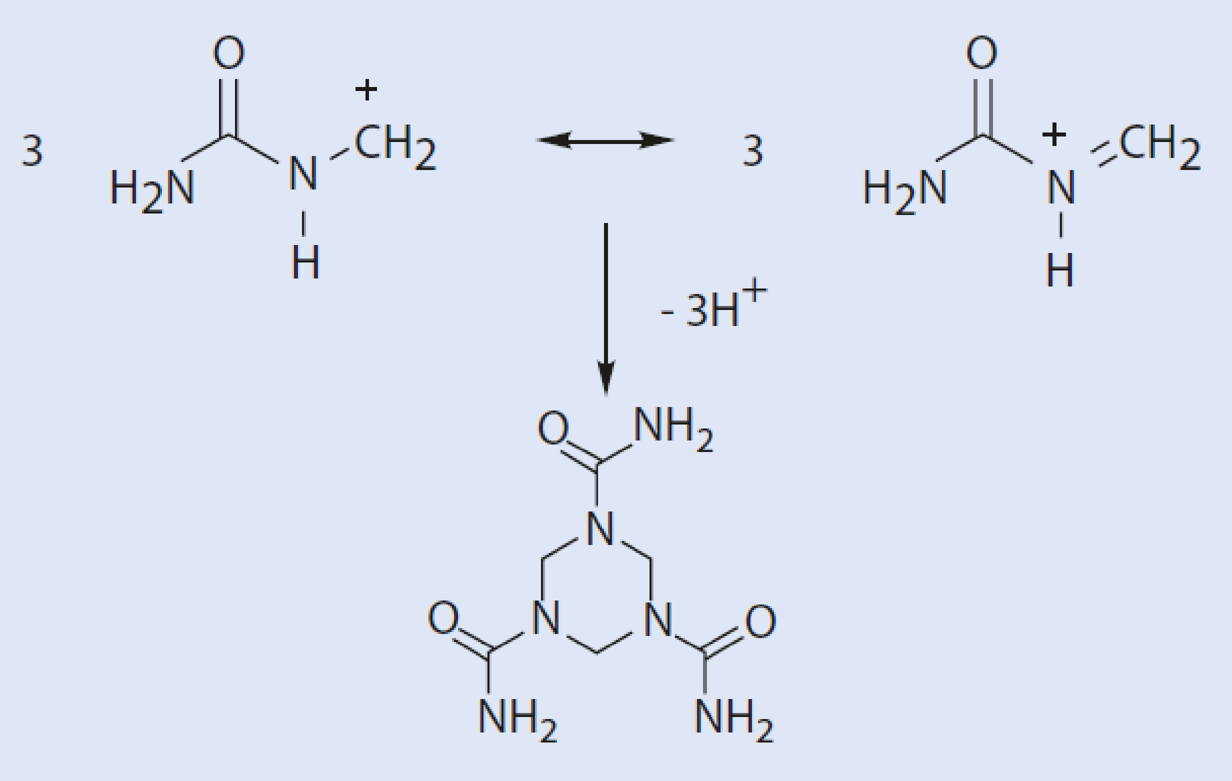


  - In an acidic environment; individual steps of the acid-catalyzed cross-linking of urea resin precursors.
  - The cross-linking can be continued to incorporate all the $-NH_2$ groups.



Urea Resins (*Urea-Formaldehyde Resin*)

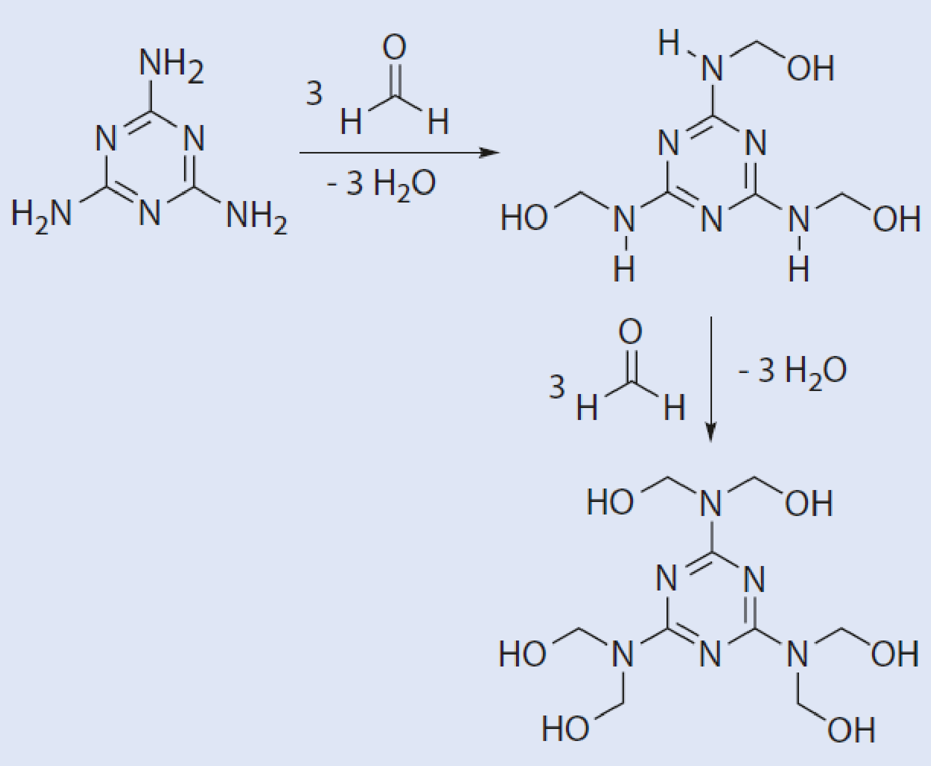
- In a neutral to slightly alkaline environment; Trimerization of urea in an acidic environment



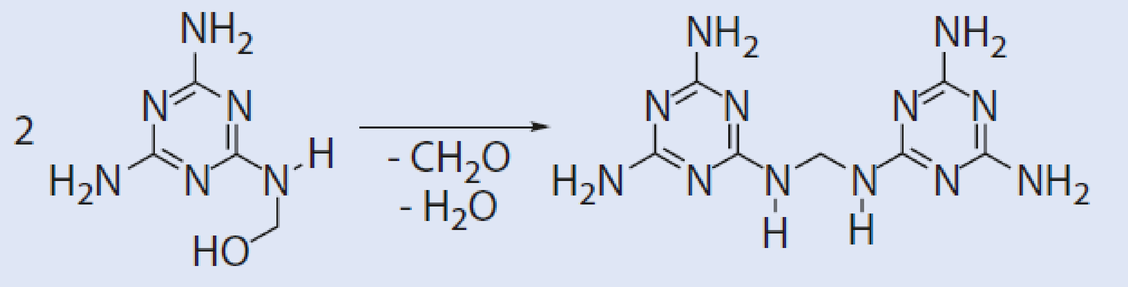
- Thereafter, the NH_2 groups can react further and cross-link.
- The urea resins are similar in their properties and their applications to phenolic resins.

Melamine Resins (*Melamine-Formaldehyde Resins*)

- Melamine (1,3,5-triaminotriazine) and formaldehyde react stepwise to yield intermediates, which have similar structures to those of urea resins.



Formation of melamine resin precursors
from melamine and formaldehyde

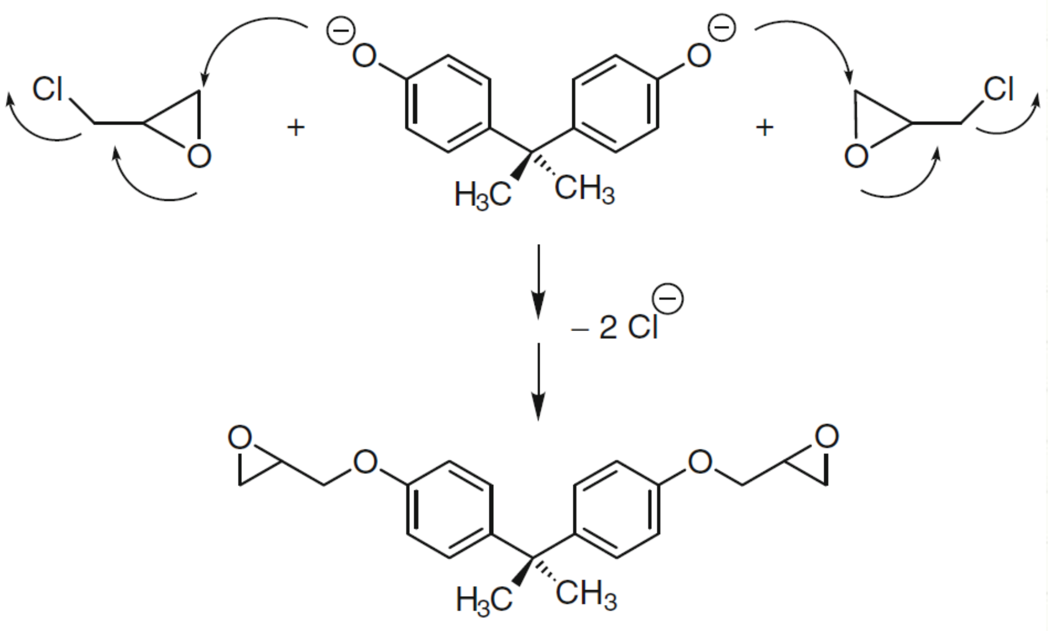


Principle step in the cross-linking of melamine resins with elimination of water and formaldehyde

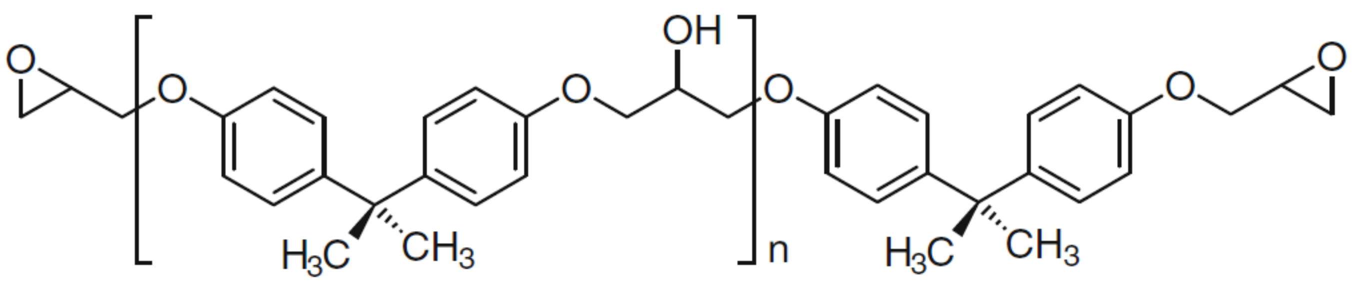
- At elevated temperatures (140–160C), the molecules bridge and form a network.
- Cross-linked melamine resins have slightly better mechanical and thermal properties than both phenolic and urea resins.
- They are used especially for the production of light-colored or white components, instead of phenolic and urea resins which have a dark, natural color.

Epoxy Resins

- **Epoxy resins** are usually understood to be products of reaction of polyfunctional hydroxy compounds with 1-chloro-2,3-epoxypropane (epichlorohydrin) in basic medium.



- In the simplest case two mol of epichlorohydrin react, with one mol of bisphenol A:
- They have molecular weights between 450 and 4,000
- Higher-molecular-weight result from coupling of epoxide with further bisphenol:



Epoxy Resins

- The structure and molecular weight of the resulting epoxy resin are strongly influenced by the reaction conditions:
  - A large excess of epichlorohydrin favors the formation of terminal epoxy groups; however, the molecular weight (and hence the softening point) of the product decreases with increasing amount of epichlorohydrin.
  - The reaction temperature is also important: high temperatures promote secondary reactions such as hydrolytic cleavage of epoxy groups, leading to the formation of additional hydroxy groups.
- Crosslinking (curing) can be brought about with any di- or polyfunctional compound that adds to epoxy groups (e.g., amines, aminoamides, thiols).
- Self-crosslinking can also be achieved by addition of catalytic amounts of a tertiary amine or acid compound, such as a sulfonic acid.
- The crosslinking is generally carried out in bulk (casting resin), but sometimes in solution (lacquers, adhesives).
- Most crosslinking reactions set in at higher temperatures, so the epoxy resin and crosslinker (polybasic carboxylic acids, acid anhydrides, and amines) can be mixed and stored at room temperature.

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CHAIN-GROWTH POLYMERIZATION