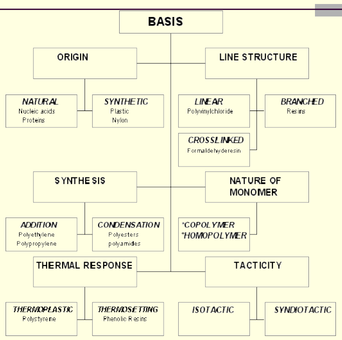
Polymers

- large molecules made up of many smaller and identical repeating units
  - Monomers
- These repeating units joins together by
  - Covalent bonds
- The chemical process that join the monomers together
  - POLYMERISATION

Classification



BASIS

ORIGIN
NATURAL Nucleic acids Proteins
SYNTHETIC Plastic Nylon

LINE STRUCTURE
LINEAR Polyvinylchloride
BRANCHED Resins
CROSSLINKED Formaldehyderesin

SYNTHESIS
ADDITION Polyethylene Polypropylene
CONDENSATION Polyesters polyamides

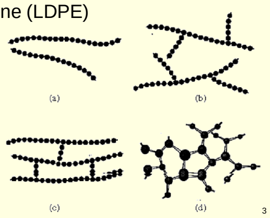
NATURE OF MONOMER
**COPOLYMER*
**HOMOPOLYMER*

THERMAL RESPONSE
THERMOPLASTIC Polystyrene
THERMOSETTING Phenolic Resins

TACTICITY
ISOTACTIC
SYNDIOTACTIC

Line Structure

- **Linear**
  - High Density Polyethylene (HDPE), PVC, Nylon, Cotton
- **Branched**
  - Low Density Polyethylene (LDPE)
- **Cross-linked**
  - Rubber
- **Network**
  - Kevlar, Epoxy



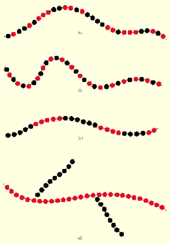
Nature of Monomer

- **Homopolymer**
  - These are polymers containing only one monomer unit.
- **Copolymers**
  - When two or more different monomers unite together to polymerize, their result is called a copolymer and its process is called copolymerization.

Nature of Monomer

Two or more monomers polymerized together

- **Homopolymer**
  - Single monomer
- **Random Copolymer**
  - Monomers randomly positioned along chain
- **Alternating Copolymer**
  - Monomers alternate in polymer chain
- **Block Copolymer**
  - large blocks of one monomer alternate with large blocks of another
- **Graft Copolymer**
  - Chains of one monomer grafted onto backbone of second monomer

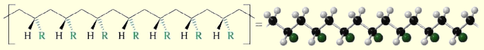


Tacticity (Stereochemistry)

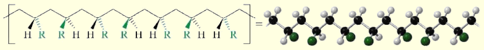
- In the polymerization of the monomer of the type CH_2-CYZ, there are two extreme stereoisomers possible
- All the Y groups lie on one side of the chain and all the Z groups lie on the other side.
  - This type of polymer is known as **Isotactic** polymer.
- When all the Y and Z groups lie alternately on each side of the chain,
  - This is known as **Syndiotactic** polymer.
- Between these two extremes, there are those polymers in which the two groups Y and Z are arranged in random order,
  - This is known as **Atactic** polymers.

Tacticity (Stereochemistry)

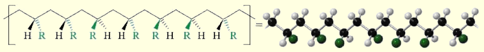
An isotactic polymer (side groups on the same side of the backbone)



A syndiotactic polymer (side groups on alternating sides of the backbone)



An atactic polymer (side groups on random sides of the backbone)



- Isotactic and syndiotactic polymers are stronger and stiffer due to their regular packing arrangement.

Thermal Response

- The response of a polymer to mechanical forces at elevated temperature is related to its dominant molecular structure.
- One classification of polymers is according to its behavior and rising temperature.
  - Thermoplastics
  - Thermosetting (Thermosets)

Thermal Response

- **Thermoplastic**
  - These are polymers that turns to a liquid when heated and freezes to a very glassy state when cooled sufficiently.
  - Most thermoplastics are high-molecular-weight polymers whose chains associate through
    - Weak Van der Waals forces
      - Polyethylene
    - Stronger dipole-dipole interactions and hydrogen bonding
      - Nylon

Thermal Response

- **Thermosetting**
  - These polymers when heated, will chemically decompose, so they can not be recycled. Yet, once a thermoset is cured it tends to be stronger than a thermoplastic.
    - Bakelite
    - Vulcanized rubber
  - Typically, linear polymers with minor branched structures (and flexible chains) are thermoplastics. The networked structures are thermosets.
- Thermoplastic polymers differ from thermosetting polymers since thermoplastics can be remelted and remolded.

Thermal Response

- **Thermoplastics**
  - Little cross linking
  - Ductile
  - Soften with heating
    - Polyethylene
    - Polypropylene
    - Polycarbonate
    - Polystyrene
- **Thermosets**
  - Large cross linking
  - Hard and brittle
  - Do NOT soften with heating
    - Vulcanized rubber,
    - Epoxies,
    - Polyester resin,
    - Phenolic resin

Polymer Synthesis

- There are two major classes of polymer formation mechanisms
  - **Addition polymerization**: The polymer grows by sequential addition of monomers to a reactive site
    - Chain growth is linear
    - Maximum molecular weight is obtained early in the reaction
  - **Step-Growth polymerization**: Monomers react together to make small oligomers. Small oligomers make bigger ones, and big oligomers react to give polymers.
    - Chain growth is exponential
    - Maximum molecular weight is obtained late in the reaction

Polymer Synthesis

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    - Chain growth is exponential
    - Maximum molecular weight is obtained late in the reaction

Addition Polymerization

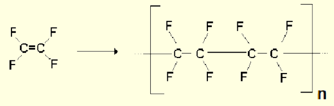
- These polymers are formed by chain reactions.
  - The reactive center may be formed by reaction with a free radical, a cation or an anion.
- Polymerization occurs through the propagation of the active species by the successive additions of a large number of monomer molecules in a chain reaction occurring in a matter of second or so at the most.

Addition Polymerization

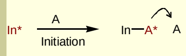
- The reaction generally occurs between molecules containing double or triple bonds.
- There is no liberation of small molecules during addition polymerization.
- The arrangement of monomers could be in the following manners:
  - Head to Tail ï -CH_2-CHY-CH_2-CHY-
  - Head to Head ï -CH_2-CHY-CHY-CH_2-
  - Random ï Combination of above

Addition Polymers

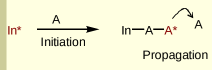
- **Addition polymerization**: a reaction in which unsaturated monomers combine with each other to form a polymer
  - Example: Tetrafluoroethene can be polymerized to form polytetrafluoroethene, commonly known as Teflon



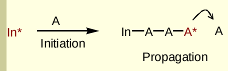
Addition Polymerization



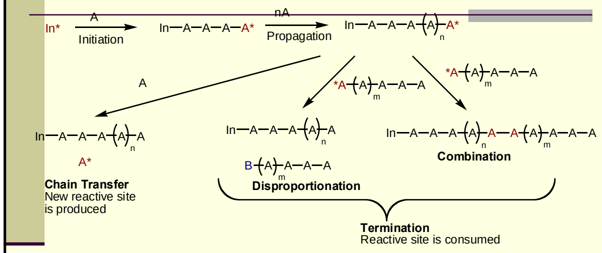
Addition Polymerization



Addition Polymerization


In*
A
Initiation
In—A—A—A*
A
Propagation

Addition Polymerization


In*
A
Initiation
In—A—A—A—A*
nA
Propagation
In—A—A—A—(A)$_n$—A*

A
In—A—A—A—(A)$_n$—A
A*
Chain Transfer
New reactive site
is produced

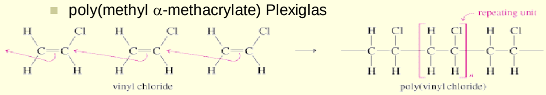
*A—(A)$_m$—A—A—A
In—A—A—A—(A)$_n$—A
B—(A)$_m$—A—A—A
Disproportionation

*A—(A)$_m$—A—A—A
In—A—A—A—(A)$_n$—A—A—(A)$_m$—A—A—A
Combination

Termination
Reactive site is consumed

Addition Polymerization

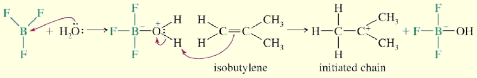
- **Three kinds of intermediates:**
  - Carbocations
  - Carbanions
  - Free radicals
- **Examples of addition polymers:**
  - polypropylene plastics
  - Polystyrene foam insulation
  - poly(acrylonitrile) Orlon® fiber
  - poly(methyl α-methacrylate) Plexiglas



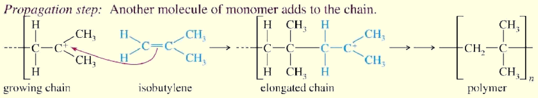
Cationic Polymerization

- Alkene is treated with an acid.
- Intermediate must be a stable carbocation.

Initiation steps: The catalyst protonates the monomer, starting the chain.



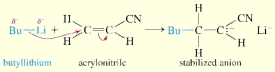
Propagation step: Another molecule of monomer adds to the chain.



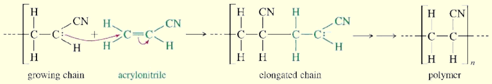
Anionic Polymerization

- Alkene must have an electron-withdrawing group like C=O, C≡N, or NO_2.
  - Initiator: Grignard or organolithium reagent.

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



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



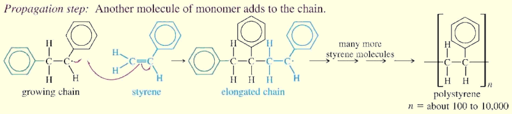
Anionic intermediate usually gives isotactic or syndiotactic polymers.

Free Radical Polymerization

- Free radical polymerization is nearly random, giving branched atactic polymers.

Initiation step: The initiator reacts with the monomer to start the chain.

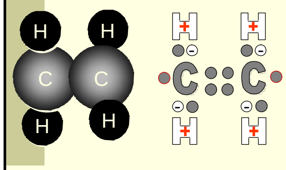
Propagation step: Another molecule of monomer adds to the chain.



Free Radical Polymerization

- Ethylene has two carbons; plus, instead of the two carbons sharing just one electron each, they share two electrons each.
- High temperature or UV light can cause two of these shared (paired) electrons to become unshared (unpaired).

Free Radical Polymerization

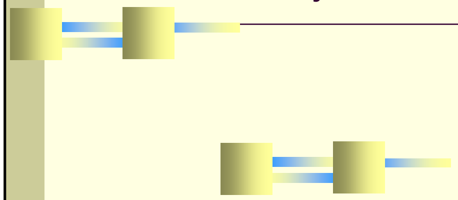


These unpaired electrons are eager to pair up with another electron. If this ethylene molecule bumps another ethylene molecule, the unpaired electrons will cause the one it bumped into to lend one of its inner electrons.

Free Radical Polymerization

- Here's another way to see the chain reaction. These are the carbon atoms with their double-bond (2 shared electrons each). The hydrogen atoms are not shown. A collision breaks the first bond.

Free Radical Polymerization



Once the first double bond is broken, a chain reaction will occur. In about a second an entire chamber of compressed ethylene gas turns into the polymer, polyethylene.

Condensation Polymers

- Condensation polymers form from condensation reactions.
- In a condensation polymer a smaller molecule such as water is eliminated
- In order to form a condensation polymer the monomer must have two functional groups

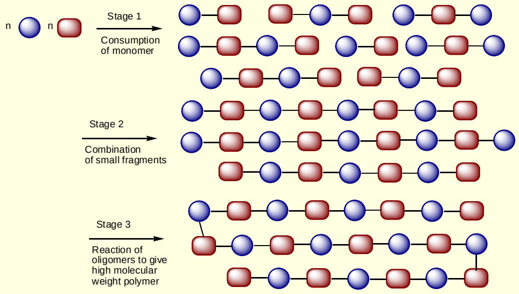
Condensation Polymers

- This is a process of formation of polymers from polyfunctional monomers of organic molecules with the elimination of some small molecule such as water, hydrochloric acid, ammonia etc.
- This type of polymerization is also known as **step-growth polymerization**,
  - The molecular weight of the polymer chain builds up slowly and there is only one reaction mechanism for the formation of the polymer.
- When a bifunctional molecule is used, a linear condensation product is formed.

Condensation Polymers

- Polymer formed by ester or amide linkages between difunctional molecules.
- **Step growth:** Monomers do not have to add one at a time. Small chains may condense into larger chains.
- **Common types:**
    - Polyamides
    - Polyesters
    - Polycarbonates
    - Polyurethanes

Step-Growth Polymerization



Step-Growth Polymerization

$M_1 + M_1 \longrightarrow M_2$

$M_2 + M_1 \longrightarrow M_3$

$M_2 + M_2 \longrightarrow M_4$

$M_3 + M_1 \longrightarrow M_4$

$M_4 + M_1 \longrightarrow M_5$

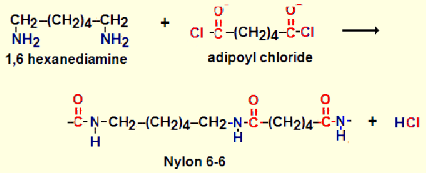
$M_3 + M_2 \longrightarrow M_5$

$M_5 + M_1 \longrightarrow M_6$

Etc.

Example of Condensation Polymer

- Nylon 6-6 is a condensation polymer
- It is also a copolymer since it is made from two different monomers



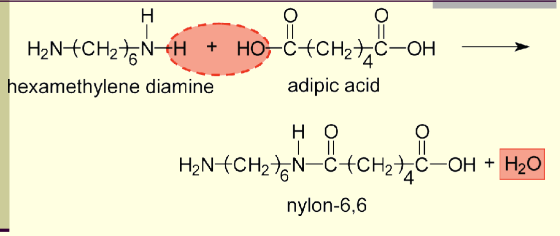
$$\underset{NH_2}{CH_2}-(CH_2)_4-\underset{NH_2}{CH_2} + Cl-\overset{O^-}{\overset{\|}{C}}-(CH_2)_4-\overset{O^-}{\overset{\|}{C}}-Cl \longrightarrow$$

1,6 hexanediamine adipoyl chloride

$$-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-CH_2-(CH_2)_4-CH_2-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\underset{H}{N}- + HCl$$

Nylon 6-6

Condensation (Step) Polymerization



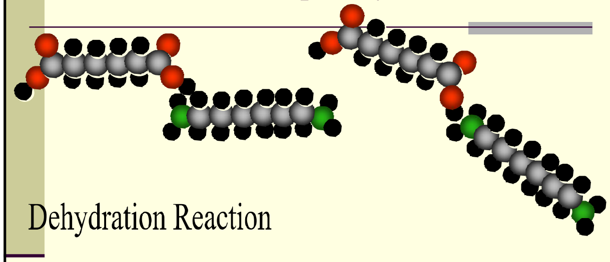
$$H_2N-(CH_2)_6-\overset{H}{\overset{|}{N}}-H + HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \longrightarrow$$

hexamethylene diamine adipic acid

$$H_2N-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + \boxed{H_2O}$$

nylon-6,6

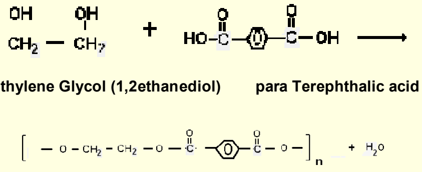
Condensation (Step) Polymerization



Dehydration Reaction

Example of Condensation Polymer

- Dacron is also a condensation polymer



Dacron is an example of a polyester

- It is also a copolymer since it is made from two different monomers

Zieglerï Natta catalyst

- A Zieglerï Natta catalyst, named after Karl Ziegler and Giulio Natta, is a catalyst used in the synthesis of polymers of 1-alkenes (alpha-olefins).

- Both awarded Nobel prize in 1963

Zieglerï Natta catalyst

- A typical Ziegler-Natta catalyst is a combination of $TiCl_4$ and $(CH_3CH_2)_2AlCl$, or $TiCl_3$ and $(CH_3CH_2)_3Al$.
- Many Ziegler-Natta catalyst combinations include a metallocene.

Ziegler Natta Catalyst

- Example: Titanium catalyst

$$AlR_3 + TiCl_4 \longrightarrow AlR_2Cl + TiRCl_3$$

$$AlR_2Cl + TiCl_4 \longrightarrow AlRCl_2 + TiRCl_3$$

$$AlR_3 + TiRCl_3 \longrightarrow AlR_2Cl + TiR_2Cl_2$$

$$TiRCl_3 \longrightarrow TiCl_3 + R\bullet \uparrow$$

$$TiRCl_3 \longrightarrow TiCl_2 + RCl$$

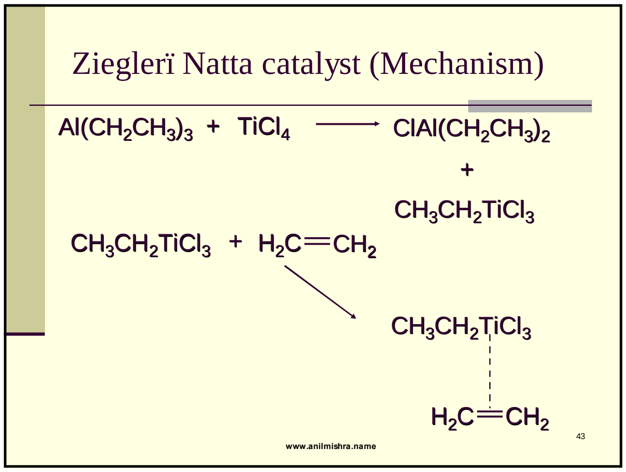
$$TiCl_4 + TiCL_2 \longrightarrow 2\,TiCl_3$$

Zieglerï Natta catalyst

- Two broad classes of Zieglerï Natta catalysts are employed, distinguished by their solubility:
  - **Heterogeneous**
    - Supported catalysts based on titanium compounds are used in polymerization reactions in combination with cocatalysts, organoaluminum compounds such as triethylaluminium, $Al(C_2H_5)_3$.
    - This class of catalyst dominates the industry.
  - **Homogeneous**
    - Catalysts usually based on complexes of Ti, Zr or Hf. They are usually used in combination with a different organoaluminum cocatalyst, methylaluminoxane (or methylalumoxane, MAO).
    - These catalysts traditionally include metallocenes but also feature multidentate oxygen- and nitrogen-based ligands.

Zieglerï Natta catalyst (Mechanism)

$$Al(CH_2CH_3)_3 + TiCl_4 \longrightarrow ClAl(CH_2CH_3)_2 + CH_3CH_2TiCl_3$$



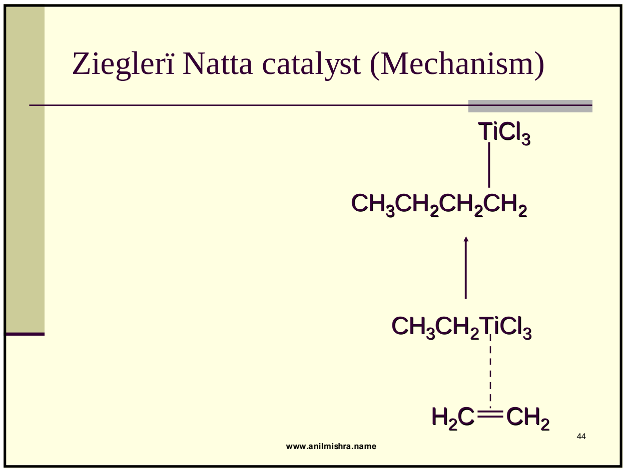
Zieglerï Natta catalyst (Mechanism)

$Al(CH_2CH_3)_3 + TiCl_4 \longrightarrow ClAl(CH_2CH_3)_2 + CH_3CH_2TiCl_3$

$CH_3CH_2TiCl_3 + H_2C{=}CH_2$

$CH_3CH_2TiCl_3$

$H_2C{=}CH_2$



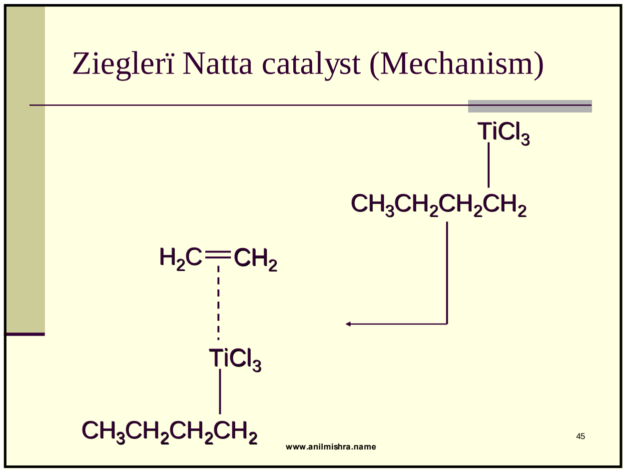
Zieglerï Natta catalyst (Mechanism)

$TiCl_3$

$CH_3CH_2CH_2CH_2$

$CH_3CH_2TiCl_3$

$H_2C{=}CH_2$



Zieglerï Natta catalyst (Mechanism)

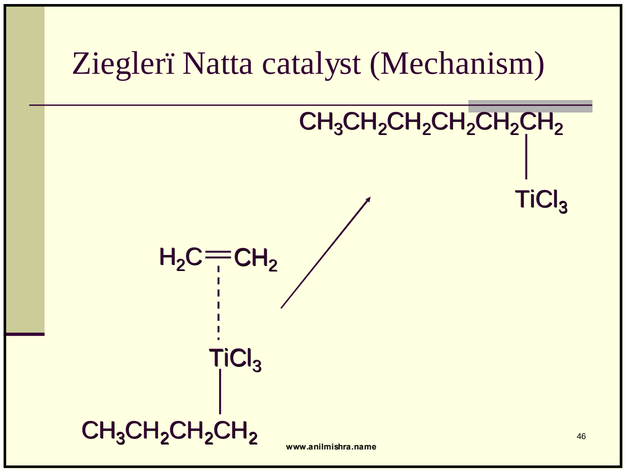
$TiCl_3$

$CH_3CH_2CH_2CH_2$

$H_2C{=}CH_2$

$TiCl_3$

$CH_3CH_2CH_2CH_2$



Zieglerï Natta catalyst (Mechanism)

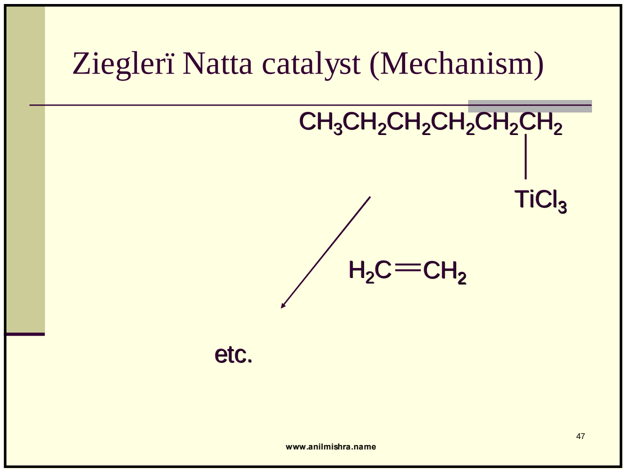
$CH_3CH_2CH_2CH_2CH_2CH_2$

$TiCl_3$

$H_2C{=}CH_2$

$TiCl_3$

$CH_3CH_2CH_2CH_2$



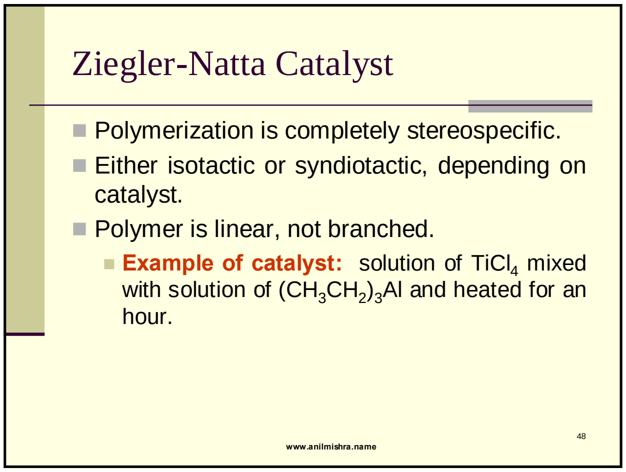
Zieglerï Natta catalyst (Mechanism)

$CH_3CH_2CH_2CH_2CH_2CH_2$

$TiCl_3$

$H_2C{=}CH_2$

etc.

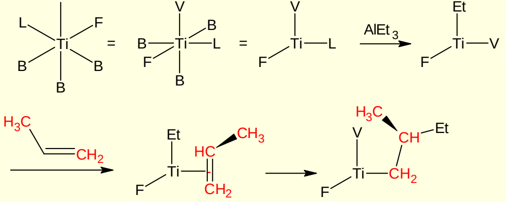


Ziegler-Natta Catalyst

- Polymerization is completely stereospecific.
- Either isotactic or syndiotactic, depending on catalyst.
- Polymer is linear, not branched.
  - **Example of catalyst:** solution of $TiCl_4$ mixed with solution of $(CH_3CH_2)_3Al$ and heated for an hour.

Stereo specificity

Bonding of Propylene

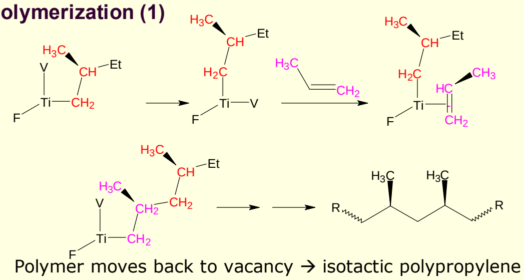


Two possibilities:

1. Alkalyne moves back to vacancy
2. Alkalyne doesn't move back

Stereo specificity

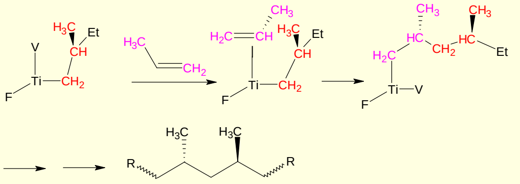
Polymerization (1)



Polymer moves back to vacancy → isotactic polypropylene

Stereo specificity

Polymerization (2)



Polymer doesn't back to vacancy → syndiotactic polypropylene

Experimental: Some syndiotactic PP at -70°

Structure of the catalyst

- Three phases of $TiCl_3$

	Color	*Stucture*	*Activity*
Ŭ-$TiCl_3$	Purple	Hexagonal layered structure	Isotactic
ɓ-$TiCl_3$	Brown	Needle structure	Little stereospecifity
ɔ-$TiCl_3$	Purple	Cubic layered structure	Like Ŭ-$TiCl_3$

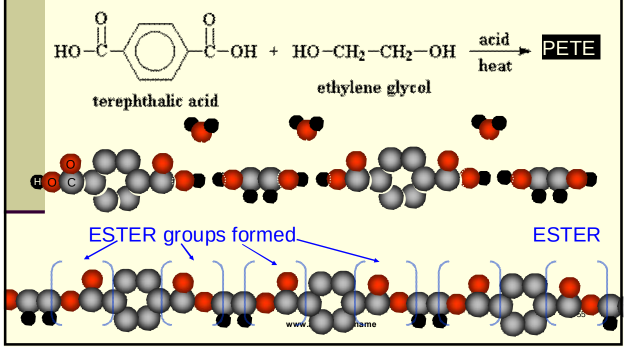
Polyester

- Polyester is a category of polymers that contain the ester functional group in their main chain.
- Depending on the chemical structure, polyester can be a thermoplastic or thermoset.
  - There are also polyester resins cured by hardeners
  - The most common polyesters are thermoplastics

Polyester

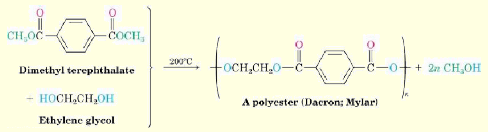
- Polyester is made from the two monomers, terephthalic acid (note: ñphò is silent) and ethylene glycol (car antifreeze).
- This makes a popular plastic called PETE, which is short for Polyethylene Terephthalate.
- The synthesis is also a *dehydration* reaction because water is given off.

Polyester



Polyesters

- The polyester from dimethyl terephthalate and ethylene glycol is called Dacron and Mylar to make fibers.



Characteristics of Polyester

- Polyester fabrics and fibers are extremely strong.
- It is very durable:
  - Resistant to most chemicals, stretching and shrinking, wrinkle resistant, mildew and abrasion resistant.
- It is hydrophobic in nature and quick drying.
  - Can be used for insulation by manufacturing hollow fibers.
- Retains its shape and hence is good for making outdoor clothing for harsh climates.
- It is easily washed and dried.

Uses of Polyester

- The most popular and one of the earliest uses of polyester was to make polyester suits
- Polyester clothes were very popular.
- Due to its strength and tenacity polyester was also used to make ropes in industries.
- PET bottles are today one of the most popular uses of polyester.

Uses of Polyester

- Fabrics woven or knitted from polyester thread or yarn are used extensively in apparel and home furnishings, from shirts and pants to jackets and hats, bed sheets, blankets, upholstered furniture and computer mouse mats.

Uses of Polyester

- Industrial polyester fibers, yarns and ropes are used in tyre reinforcements, fabrics for conveyor belts, safety belts, coated fabrics and plastic reinforcements with high-energy absorption.
- Polyester fiber is used as cushioning and insulating material in pillows, comforters and upholstery padding.
- Polyester fabrics are highly stain-resistantð in fact, the only class of dyes which can be used to alter the color of polyester fabric are what are known is disperse dyes.

Nylons (Poly Amides)

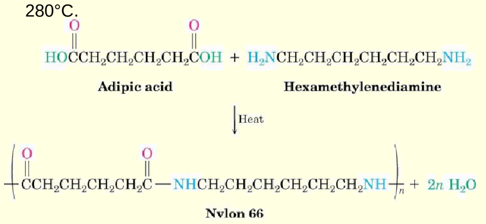
- Nylon is a generic designation for a family of synthetic polymers, more specifically aliphatic or semi-aromatic polyamides.
- Polyamides (nylon) are polymers formed as a condensation product of an acid and amine.
  - They all contain the characteristic amide group: **CO-NH**.
- Nylon is made of repeating units linked by peptide bonds and is a type of polyamide.

Nylons

- Nylons are condensation copolymers, formed by reacting difunctional monomers containing equal parts of amine and carboxylic acid
  - Amides are formed at both ends of each monomer in a process analogous to polypeptide biopolymers.
- Most nylons are made from the reaction of a dicarboxylic acid with a diamine.

Polyamides (Nylons)

- Heating a diamine with a diacid produces a polyamide called Nylon.
  - Nylon 66 is from adipic acid and hexamethylene-diamine at 280°C.



$$HO\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}OH + H_2NCH_2CH_2CH_2CH_2CH_2CH_2NH_2 \xrightarrow{Heat} \left[\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-NHCH_2CH_2CH_2CH_2CH_2CH_2NH\right]_n + 2n\ H_2O$$

Nylons Nomenclature

- The nomenclature used for nylon polymers was devised during the synthesis of the first simple aliphatic nylons and uses numbers to describe the number of carbons between acid and amine functions
  - Including the carbon of the carboxylic acid.
    - Types
      - Most Common
        - Nylon 6
        - Nylon 6/6
      - Nylon 6/10
      - Nylon 6/12
      - Nylon 11
      - Nylon 12

Nylons Nomenclature

- Subsequent use of cyclic and aromatic monomers required the use of letters or sets of letters.
- One number after "PAñ (Poly Amide) for a homopolymer based on one monomer, and two numbers or sets of letters where there are two monomers.
- For copolymers the comonomers or pairs of comonomers are separated by slashes.

Nylons Nomenclature

- Suffixes refer to the number of carbon atoms in each reacting substances involved in condensation process.
  - They are used as an identification factor.
- Nylons with a period between the numbers are homopolymers
  - Nylons with a slash (/) between numbers are a copolymer
    - ex. Nylon 6/12 is a copolymer of nylons 6 and 12

Nylons Nomenclature

- **Homopolymers**
  - **PA 6**
    - [NHī (CH$_2$)$_5$ī CO]$_n$
      - Made from ŮCaprolactam ;
  - **PA 6/6**
    - [NHī (CH$_2$)$_6$ī NHī COī (CH$_2$)$_4$ī CO]$_n$
      - made from hexamethylenediamine and adipic acid
- In common usage, the prefix 'PA' or the name 'Nylon' are used interchangeably and are equivalent in meaning.

Nylons Nomenclature

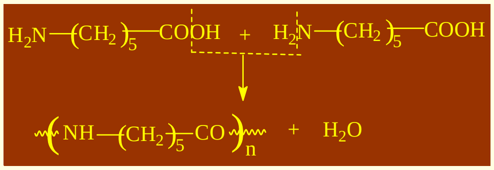
- **Copolymers**
  - **Nylon 6/6 (Nylon 66)**
    - [NH-(CH$_2$)$_6$ī NHī COī (CH$_2$)$_4$ī CO]$_n$ī [NHī (CH$_2$)$_5$ī CO]$_m$
      - Made from caprolactam, hexamethylenediamine and adipic acid ;
  - **Nylon 6/6/6/10**

    [NHī (CH$_2$)$_6$ī NHī COī (CH$_2$)$_4$ī CO]$_n$ī [NHī (CH$_2$)$_6$ī NHī COī (CH$_2$)$_8$ī CO]$_m$
      - Made from hexamethylenediamine, adipic acid and sebacic acid.

Chemical Structure

Nylon 6 or PA-6

Caprolactam ⟶ Amino caproic acid



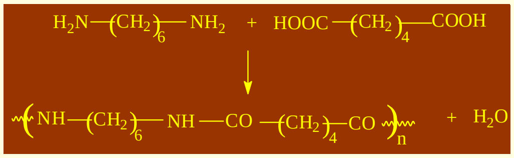
$$\mathrm{H_2N{-}(CH_2)_5{-}COOH} + \mathrm{H_2N{-}(CH_2)_5{-}COOH} \longrightarrow \mathrm{{\sim}\!\left(NH{-}(CH_2)_5{-}CO\right)_n\!{\sim}} + \mathrm{H_2O}$$

Poly(caprolactam)

Chemical Structure

Nylon 6/6 or PA-66

Hexamethylene diamine + Adipic acid



$$\mathrm{H_2N{-}(CH_2)_6{-}NH_2} + \mathrm{HOOC{-}(CH_2)_4{-}COOH} \longrightarrow \mathrm{{\sim}\!\left(NH{-}(CH_2)_6{-}NH{-}CO{-}(CH_2)_4{-}CO\right)_n\!{\sim}} + \mathrm{H_2O}$$

Phenol formaldehyde Resin

(Phenolic Resins)

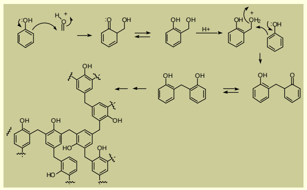
Phenolic Resins

- Phenolic resins are a type of synthetic thermosetting resin invented by Dr. Leo Baekeland in 1907.
  - The material was originally called Bakelite.
- This was effectively the first plastic to be sold commercially, and was typified by the old-style black telephones.

Phenolic Resins

Bakelite

- Phenol-formaldehyde resins which he called **Bakelite**.
  - Thermoset resin.
  - Replaced rubber for insulation in electrics.



Phenol formaldehyde polymer

- Phenol formaldehyde resins (PF) are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde.

Phenol formaldehyde polymer

- Phenol formaldehyde resins are better known, however, for the production of moulded products including billiard balls, laboratory countertops, and as coatings and adhesives.
- In the form of Bakelite, they are the earliest commercial synthetic resin.
- Phenolic resins have been mainly used in the production of circuit boards

Phenol Formaldehyde Formation

- Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed.

Phenol Formaldehyde Formation

- Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers,
  - The concentration of the reactive form of formaldehyde depends on temperature and pH.

Types of Phenol Formaldehyde Resin

- Two major types:
  - Resole
    - Cross-linking thermosetting resin
  - Novolac
    - Resin with some thermoplastic properties
- Both have high temperature stability up to 300° ï 350° C, high water and chemical stability.

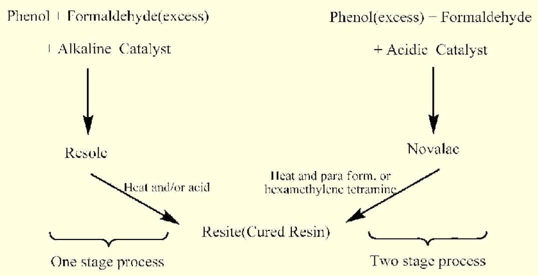
Types of Phenol Formaldehyde Resin

- **Resoles**
  - Base-catalysed phenol-formaldehyde resins are made with a formaldehyde to phenol ratio of greater than one (usually around 1.5).
  - Resoles prepared with excess formaldehyde with base catalysis.
  - The product contain many unreacted methylol groups which upon heating react to produce the net work structure.

Types of Phenol Formaldehyde Resin

- **Novolacs**
  - These are phenol-formaldehyde resins with a formaldehyde to phenol molar ratio of less than one.
  - The polymerization is brought to completion using acid-catalysis such as oxalic acid, hydrochloric acid or sulfonate acids.
  - Novolaks prepared with excess phenol and acid catalysis which promotes condensation reaction of the methylol groups.
  - The prepolymers contain no methylol groups and are unable to crosslink.

Phenolic Resin Processes

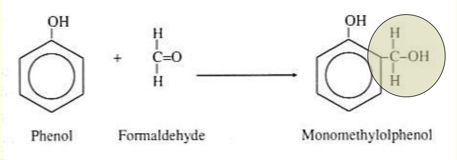


Base-Catalyzed Phenol-Formaldehyde Resins

- Two stages:
  - Methylolation of phenol to produce methylol phenols.
  - First stage, or ñAò stage, is alkaline catalyzed for the synthesis of resoles
    - Alkaline A stage, P/F ratio=1:1 to 1:3
      - i.e., molar EXCESS of formaldehyde

Base-Catalyzed Phenol-Formaldehyde Resins

Resole "A"

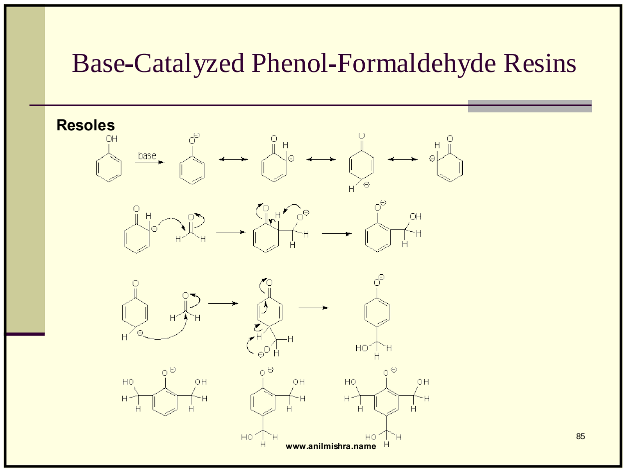


Methylolation may occur at ortho, meta, or para position.

Base-Catalyzed Phenol-Formaldehyde Resins

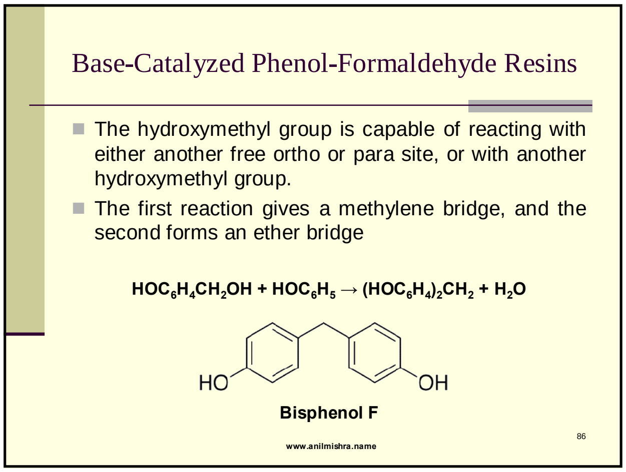
- Phenol reacts with formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring.
- The initial reaction in all cases involves the formation of a hydroxymethyl phenol:

$$HOC_6H_5 + CH_2O \rightarrow HOC_6H_4CH_2OH$$



Base-Catalyzed Phenol-Formaldehyde Resins

Resoles



Base-Catalyzed Phenol-Formaldehyde Resins

- The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group.
- The first reaction gives a methylene bridge, and the second forms an ether bridge

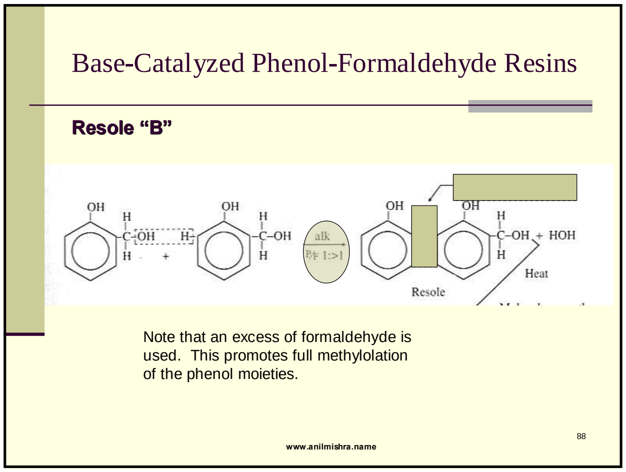
$HOC_6H_4CH_2OH + HOC_6H_5 \rightarrow (HOC_6H_4)_2CH_2 + H_2O$

Bisphenol F

Base-Catalyzed Phenol-Formaldehyde Resins

- The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is an important monomer in the production of epoxy resins.
- Bisphenol-F can further link generating tri- and tetra- and higher phenol oligomers.

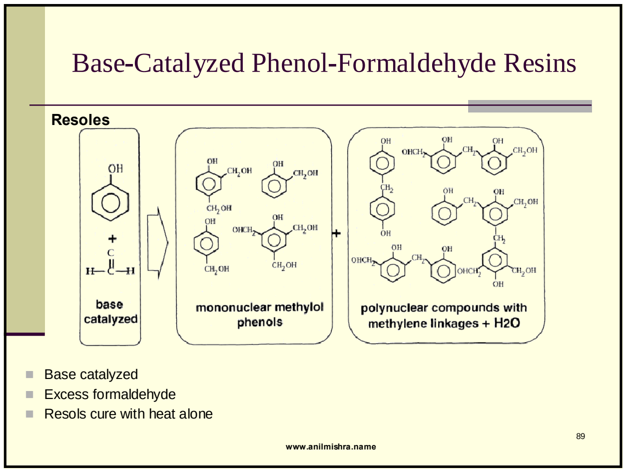
$2\ HOC_6H_4CH_2OH$ Ÿ $(HOC_6H_4CH_2)_2O + H_2O$



Base-Catalyzed Phenol-Formaldehyde Resins

Resole "B"

Note that an excess of formaldehyde is used. This promotes full methylolation of the phenol moieties.



Base-Catalyzed Phenol-Formaldehyde Resins

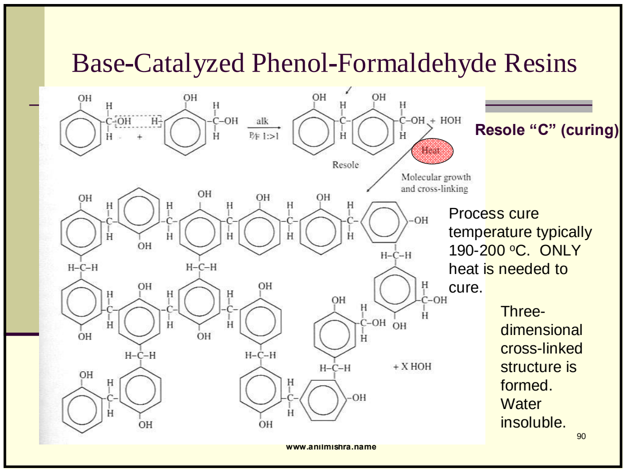
Resoles

base catalyzed

mononuclear methylol phenols

polynuclear compounds with methylene linkages + H2O

- Base catalyzed
- Excess formaldehyde
- Resols cure with heat alone



Base-Catalyzed Phenol-Formaldehyde Resins

Resole "C" (curing)

Process cure temperature typically 190-200 °C. ONLY heat is needed to cure.

Three-dimensional cross-linked structure is formed. Water insoluble.

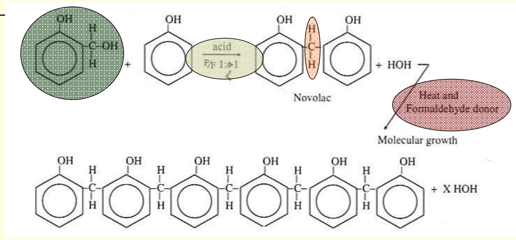
Base-Catalyzed Phenol-Formaldehyde Resins

- **Resoles**
  - Cure of resole prepolymer proceeds under neutral or acidic conditions and at elevated temperature.
  - Crosslinking occurs via the continued formation of methylene links and the formation of dibenzyl ether linkages.
  - Higher temperatures favor the formation of methylene bridges
  - Both are condensation reactions and produce water

Novolac Synthesis

- P/F ratio is > 1.0
- Acid A stage, P/F ratio=1:1 to 1:0.6
- Few methylols are formed;
  - Results in linear, rather than cross-linked structure.
- Has indefinite shelf life.
- Soluble, (partially) thermoplastic.
- Hardener in the form of additional formaldehyde is needed for cure.

Novolac synthesis



Formaldehyde donors for cure:

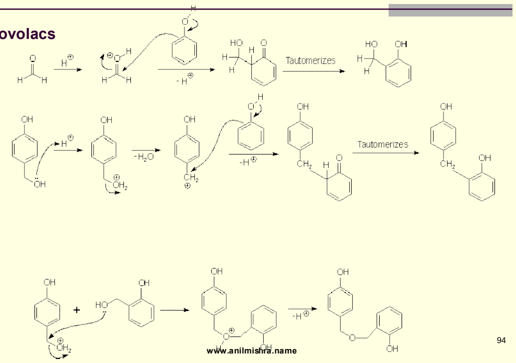
Formalin

Paraformaldehyde

Hexamethylenetetramine (῀hexaὸhardener)

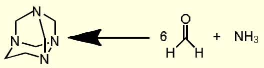
Acid-Catalyzed Phenol-Formaldehyde Resins

Novolacs

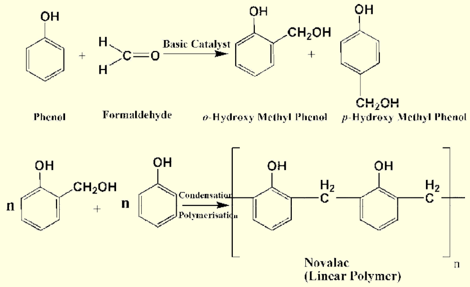


Acid-Catalyzed Phenol-Formaldehyde Resins

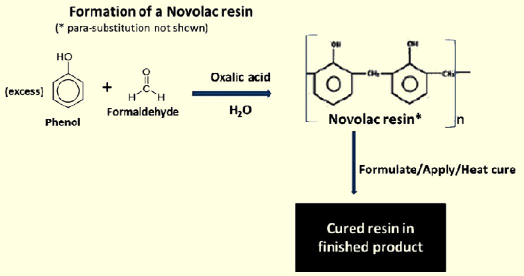
- **Novolacs**
  - Acid Catalyzed
  - Excess phenol
  - No hydroxy methyl groups
  - Tg = 40 C
  - MW = 1 ï 3000 g/mol
  - Require second additive for cure
    - Hexamethylene tetraamine



Acid-Catalyzed Phenol-Formaldehyde Resins



Acid-Catalyzed Phenol-Formaldehyde Resins



Resole vs. Novolac

- **Resole**
  - A-stage is a low molecular weight ñimpregnatingò resin (use for making Impreg, Compreg, and laminating materials)
  - B-stage is a bonding (adhesive) resin
  - Needs ONLY heat to polymerize
  - Continues to polymerize in storage (limited shelf life)
- **Novolac**
  - Fewer methylol groups, thus much less cross-linking (linear structure)
  - Formaldehyde must be supplied to cure, along with heat
  - Resin is soluble and thermoplastic
  - Has an indefinite shelf life
  - May be supplied in sheet or flake form (dry)

Urea-formaldehyde Resin

Urea-formaldehyde Resin

- Urea-formaldehyde, also known as urea-methanal, so named for its common synthesis pathway and overall structure,
- This is a non-transparent thermosetting resin or plastic, made from urea and formaldehyde heated in the presence of a base.
- These resins are used in adhesives, finishes, particle board, MDF, and molded objects.

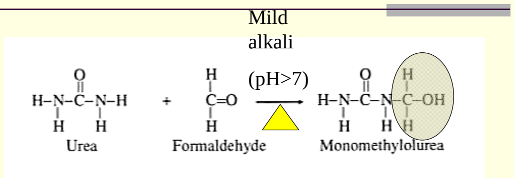
Urea-formaldehyde Resin

- UF is an ñamino resinò or ñamine-formaldehydeò class of adhesive
- UF is synthesized by the reaction of urea and formaldehyde to obtain stable, but reactive intermediates
- Storage stability due to reduced reactivity of intermediates in alkaline conditions (>pH 7)
- Urea formaldehyde (water *resistant* bond), used exclusively for interior applications.

Urea-formaldehyde Resin

- UF and related amino resins are considered a class of thermosetting resins of which urea-formaldehyde resins make up 80% produced globally.
- Examples of amino resins include automobile tires in order to improve the bonding of rubber to tire cord, paper for improving tear strength, molding electrical devices, molding jar caps, etc.

Urea-formaldehyde Synthesis



- pH is used to control reaction rate. Occurs very rapidly under acidic conditions.
- Production of the reactive intermediates is monitored and controlled by viscosity.
- Note methylolation of urea residue.

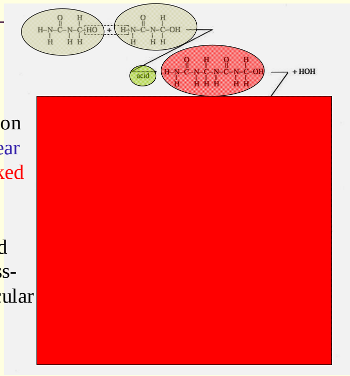
Urea-formaldehyde Synthesis

- Other intermediates, such are dimethylol urea, are also formed
- Again, viscosity is monitored to indicate the stage of the synthesis. Increasing viscosity is correlated to polymer growth; this indicates how ñadvancedò the resin is
- pH is maintained above 7 to slow polymerization and thereby increase storage life

Urea-formaldehyde Curing

- Polymerization of the reaction intermediates
  - Results from chemical reaction to build polymer chain length and molecular weight
  - Polymerization is characterized as a ñcondensation reactionò
  - Resin changes from low to high viscosity liquid and ultimately to solid
  - Resin hardening corresponds to development of mechanical strength of adhesive bond

Urea-formaldehyde Synthesis



UF Condensation Reaction: Favored by acidic conditions

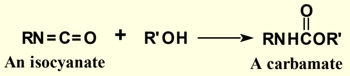
Condensation may be linear or crosslinked

Result: Cured network (cross-linked) molecular structure

Polyurethanes

Polyurethanes

- A urethane, or carbamate, is an ester of carbamic acid, H_2NCH_2COOH.
  - They are most commonly prepared by treatment of an isocyanate with an alcohol.



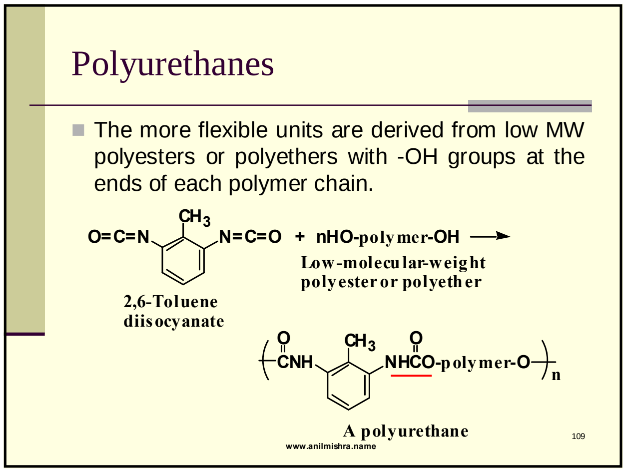
$$RN{=}C{=}O + R'OH \longrightarrow RNH\overset{O}{\overset{\|}{C}}OR'$$

An isocyanate

A carbamate

Addition to the N=C bond

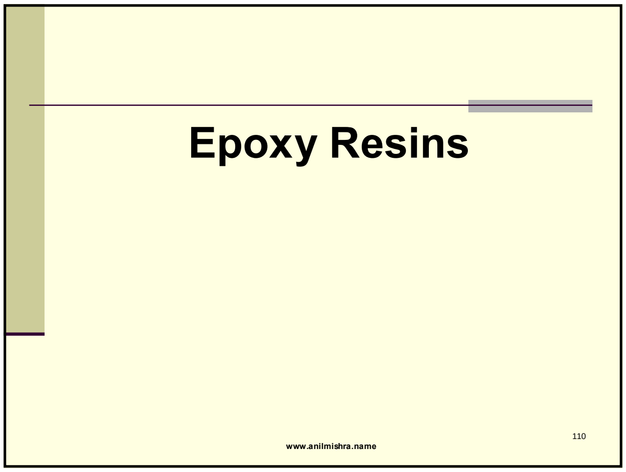
- Polyurethanes consist of flexible polyester or polyether units alternating with rigid urethane units.
  - The rigid urethane units are derived from a diisocyanate.



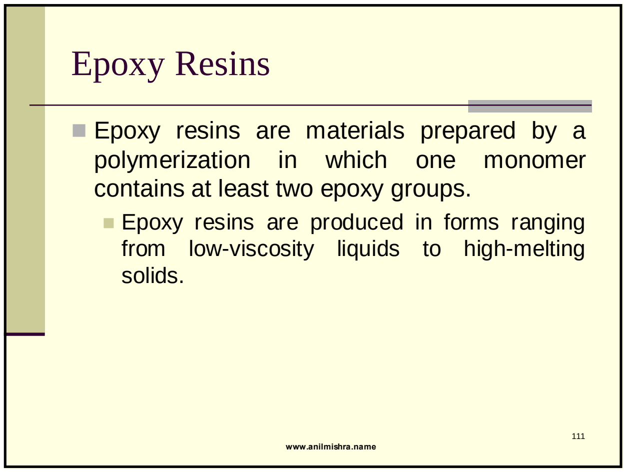
Polyurethanes

- The more flexible units are derived from low MW polyesters or polyethers with -OH groups at the ends of each polymer chain.

A polyurethane

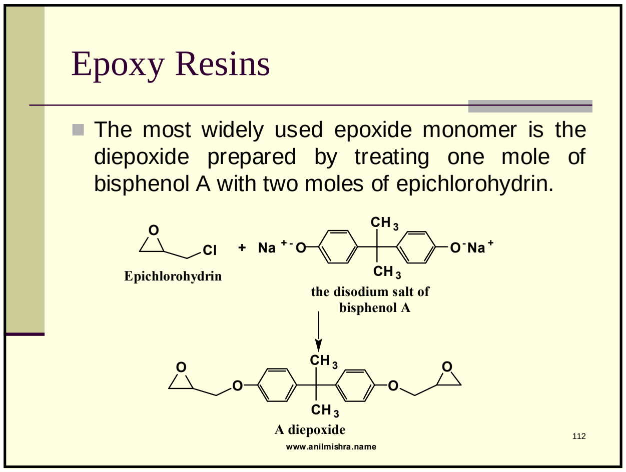


Epoxy Resins



Epoxy Resins

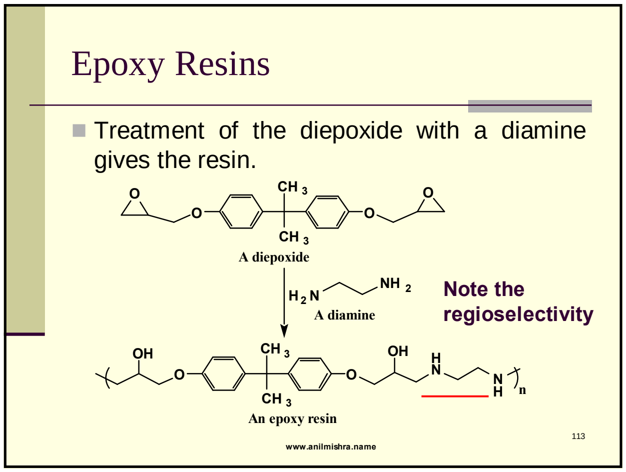
- Epoxy resins are materials prepared by a polymerization in which one monomer contains at least two epoxy groups.
  - Epoxy resins are produced in forms ranging from low-viscosity liquids to high-melting solids.



Epoxy Resins

- The most widely used epoxide monomer is the diepoxide prepared by treating one mole of bisphenol A with two moles of epichlorohydrin.

A diepoxide

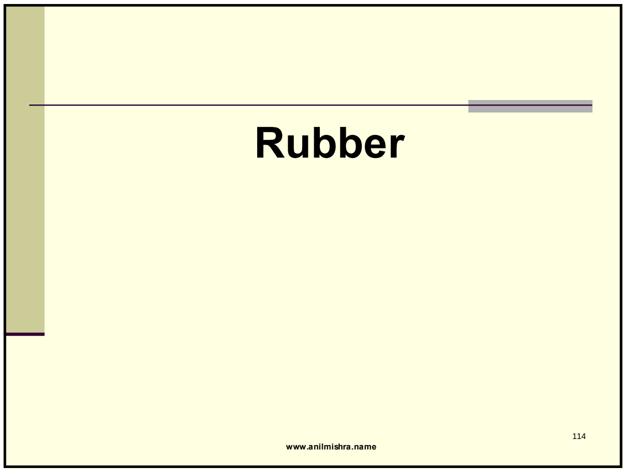


Epoxy Resins

- Treatment of the diepoxide with a diamine gives the resin.

Note the regioselectivity

An epoxy resin



Rubber

Rubber

- Natural rubber, also called India rubber consists of polymers of the organic compound isoprene, with minor impurities of other organic compounds plus water.
- Forms of polyisoprene that are used as natural rubbers are classified as elastomers.
- Natural rubber is used by many manufacturing companies for the production of rubber products.

History of Natural Rubber

- Latex is a mixture of compounds borne in special structures called laticifers.
- The composition differs in different species, but typically contains water, terpenes, sugars, enzymes, etc.
- In many plants latex has a milky appearance, but not in others.

History of Natural Rubber

- In 1770, the famous chemist Priestley discovered that rubber could be used for removing pencil marks.

History of Natural Rubber

- In 1839, Charles Goodyear (whose wife allegedly nagged him) while working in his garage (that's why he worked in the garage) discovered how to vulcanize rubber and make it non-sticky and much more usable.
- In this process, because of added sulfur, the rubber becomes cross linked and also has better elasticity.

History of Natural Rubber

- In 1823, Charles Macintosh discovered that rubber was soluble in hexane.
- Further, when the solution was applied to clothing, a thin layer was left on the clothes.
- He invented the "**Macintosh**"
  - A raincoat -- not a computer.
  - In cold weather, they cracked.
  - In hot weather, two people with Macintoshes often became inseparable. Their coats stuck together.

History of Natural Rubber

- Rubber was extracted mostly from wild trees of *Hevea brasiliensis* until the 1890's.
- The latex was collected (often in leaves) by slashing the trees diagonally.
- The latex is about 30% rubber and the rest is serum.

History of Natural Rubber

- Currently, rubber is harvested mainly in the form of the latex from certain trees.
- The latex is a sticky, milky colloid drawn off by making incisions into the bark and collecting the fluid in vessels in a process called "tapping".
- The latex then is refined into rubber ready for commercial processing.

History of Natural Rubber

- When the latex was collected, it was filtered, mixed with water and slowly poured over a paddle held over a smoky fire.
- A ball of coagulated latex was eventually prepared.
- Today, however, dilute acetic or formic acid is added to coagulate the rubber and the rubber rolled into sheets.

Gutta ï Percha or Balata

- This type of rubber has an all trans structure and has very different physical properties from natural rubber.
- Gutta mostly comes from *Palaquium gutta* (Sapotaceae) or other species from both the Old and New World.
- Gutta is used for golf balls and undersea cables.
- Gutta also is the material of choice for packing teeth in root canals.

Gutta ï Percha or Balata

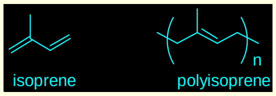
Palaquium gutta
(Sapotaceae) source
of gutta- percha

Gutta ï Percha or Balata

- Balata rubber comes mostly from *Manilkara bidentata* (Sapotaceae) and is particularly good for making machine belts.
- Both gutta-percha and balata have largely been replaced today by synthetic materials.

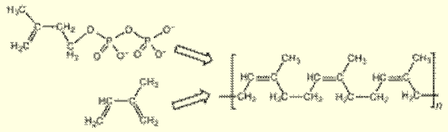
Natural Rubber

- Soft and sticky, obtained from rubber tree.
- Long chains can be stretched, but then return to original structure.
- Chains slide past each other and can be pulled apart easily.
- Structure is *cis*-1,4-polyisoprene.



Structure of Natural Rubber

- Chemical structure of cis-polyisoprene, the main constituent of natural rubber.
- Synthetic cis-polyisoprene and natural cis-polyisoprene are derived from different precursors, isopentenyl pyrophosphate and isoprene.



Vulcanization

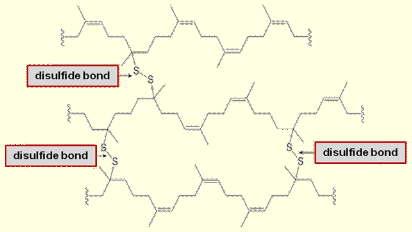
- In 1939, Charles Goodyear discovered that mixing hot rubber with sulfur produced a stronger more elastic material. This process is called vulcanization.
- Process was discovered accidentally by Goodyear when he dropped rubber and sulfur on a hot stove.

Vulcanization

- Vulcanization results in cross-linking of the hydrocarbon chains by disulfide bonds. When the polymer is stretched, the chains no longer can slide past each other, and tearing does not occur.
- Sulfur produces cross-linking that strengthens the rubber.
- Hardness can be controlled by varying the amount of sulfur.

Vulcanization

- ***Vulcanized rubber is an elastomer, a polymer that stretches when stressed but then returns to its original shape when the stress is alleviated.***



Synthetic Rubber

- History
  - Created in 1909 by Fritz Hoffman
  - Similar structure to Natural rubber
  - Cheaper than Natural Rubber
  - 2/3 of todayôs rubber is synthetic

Natural and Synthetic Rubber

- Several types of synthetic rubber were made. For some purposes they are better than natural rubber, but, for others, not as good.
- Despite this, use of natural rubber is greater today than at any time in the past.
- About 2/3 of all rubber goes into tires. Natural rubber is the best for airplane tires and is also important in radial tires.

Types of Synthetic Rubber

- **Styrene Butadiene Rubber** (SBR) and **Butadiene Rubber** (BR) are synthetic rubbers which are most widely used.
- Butadiene rubber is fully substitutable by natural rubber (NR) regarding its use in tyres.
- Emulsion Styrene Butadiene Rubber (ESBR) and BR are both used for tyres, whereas Solution Styrene Butadiene Rubber (SSBR) is used for asphalt applications.

Styrene-butadiene rubber

- Styrene-butadiene or styrene-butadiene rubber (SBR) describe families of synthetic rubbers derived from styrene and butadiene
  - The version developed by Goodyear is called Neolite
- These materials have good abrasion resistance and good aging stability when protected by additives.

Styrene-butadiene rubber

- SBR is derived from two monomers, styrene and butadiene.
- The mixture of these two monomers is polymerized by two processes:
  - From solution (S-SBR)
  - As an emulsion (E-SBR).
    - E-SBR is more widely used.

Styrene-butadiene rubber

- **Emulsion polymerization**
  - E-SBR produced by emulsion polymerization is initiated by free radicals.
  - Reaction vessels are typically charged with the two monomers, a free radical generator, and a chain transfer agent such as an alkyl mercaptan.
  - Radical initiators include potassium persulfate and hydroperoxides in combination with ferrous salts. Emulsifying agents include various soaps.

Styrene-butadiene rubber

- **Emulsion polymerization**
  - By "capping" the growing organic radicals, mercaptans (e.g. dodecylthiol), control the molecular weight, and hence the viscosity, of the product.
  - Typically, polymerizations are allowed to proceed only to ca. 70%, a method called "short stopping".
  - In this way, various additives can be removed from the polymer.

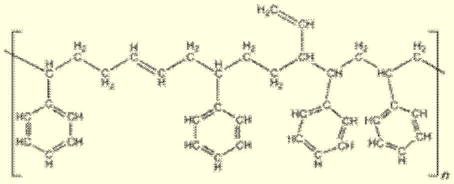
Styrene-butadiene rubber

- **Solution polymerization**
  - Solution-SBR is produced by an anionic polymerization process.
  - Polymerization is initiated by alkyl lithium compounds. Water is strictly excluded.
  - The process is homogeneous (all components are dissolved), which provides greater control over the process, allowing tailoring of the polymer.

Styrene-butadiene rubber

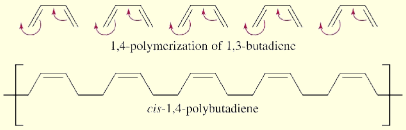
- **Solution polymerization**
  - The organolithium compound adds to one of the monomers , generating a carbanion that then adds to another monomer, and so on.
  - Relative to E-SBR, S-SBR is increasingly favored because it offers improved wet grip and rolling resistance, which translate to greater safety and better fuel economy, respectively.

Styrene-butadiene rubber



Synthetic Rubber

- With a Ziegler-Natta catalyst, a polymer of 1,3-butadiene can be produced, in which all the additions are 1,4 and the remaining double bonds are all cis.
- It may also be vulcanized.



Synthetic Rubber

- Properties
  - Solid, Flexible and Durable
  - It hardens when cool
  - It can be molded when heated
  - Resistant to heat, light and chemicals
  - Heat and electric insulator