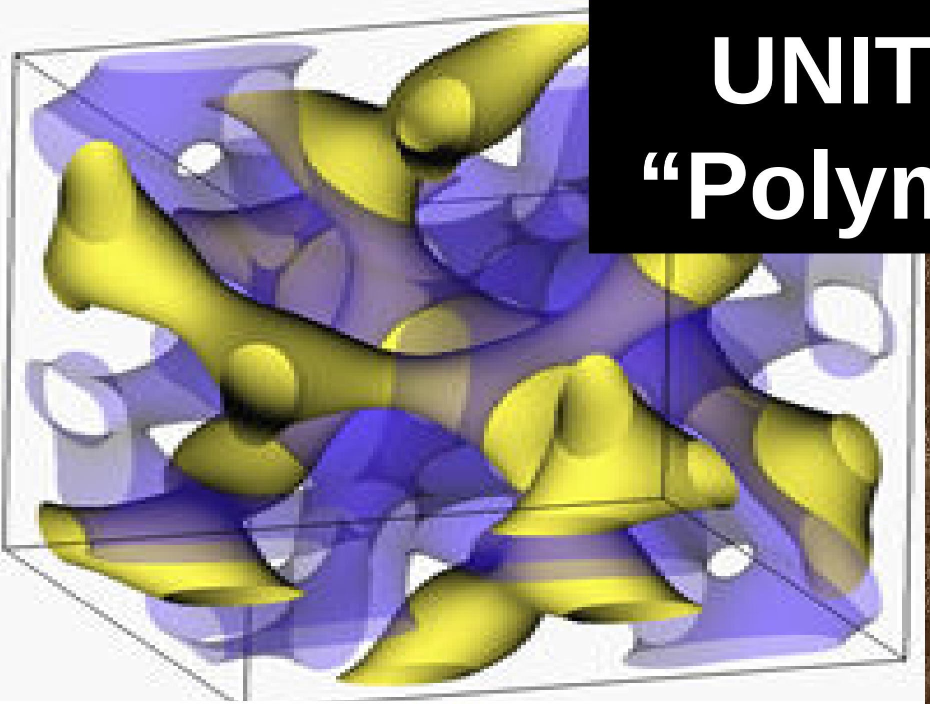
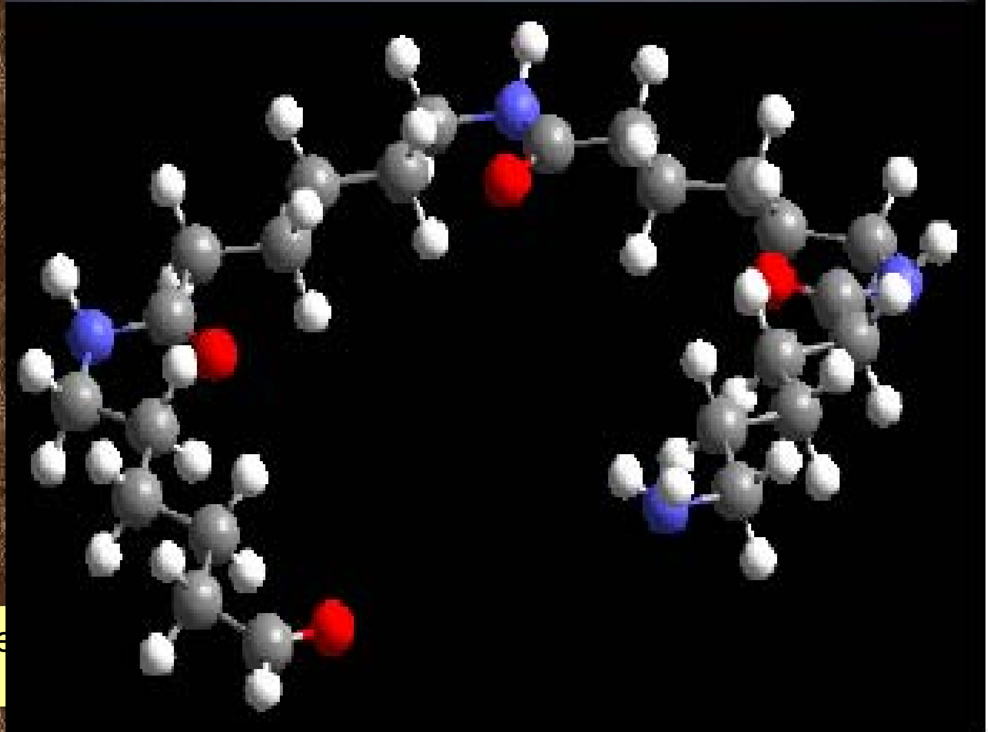
UNIT – 4
“Polymers”





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Syllabus

- Industrial applications of thermoplastics. Thermosetting polymers, properties and applications of the major polymers viz.

- polyethylene, Teflon, PVC, Nylon,
- Phenol formaldehyde, Elastomers,
- natural rubbers.

A *polymer* is a high molar mass molecular compound made up of many repeating chemical units (monomers).

Naturally occurring polymers:

- Proteins
- Nucleic acids
- Cellulose
- Rubber

Synthetic polymers:

- Nylon
- Dacron
- Polythene

Teflon (low friction synthetic polymer)

protein (naturally-occuring or *bio*polymer)

POLYMERISATION

TYPES
THERMOPLASTICS
THERMOSETTING RESINS

L-37 Thermosetting & Thermoplastic Polymers

Introduction

POLYMERS

- The word "Polymer" is derived from two Greek words. **Poly= many**,
  Units or parts Polymers = many parts or units.
- "A polymer is a long molecule formed by joining together of **thousands of small molecular units by chemical bonds**.
  Due to their large size they can be called **macromolecules".**

L-37 Thermosetting & Thermoplastic Polymers

Introduction

“Polymer” two Greek words.

Poly= many,

- Due to their large size they can be called **macromolecules.**

- The molecule, which is a unit of a polymer is called a **monomer.**

- The process is called **polymerization.**

What are polymers? (p. 1039-40)

-large molecules made from repeated bonding of smaller organic molecule units (***monomers***)

-cf. -**proteins**, polymers of repeating ***amino acid*** monomers

-**starch**, a polymer of repeating ***glucose*** monomers

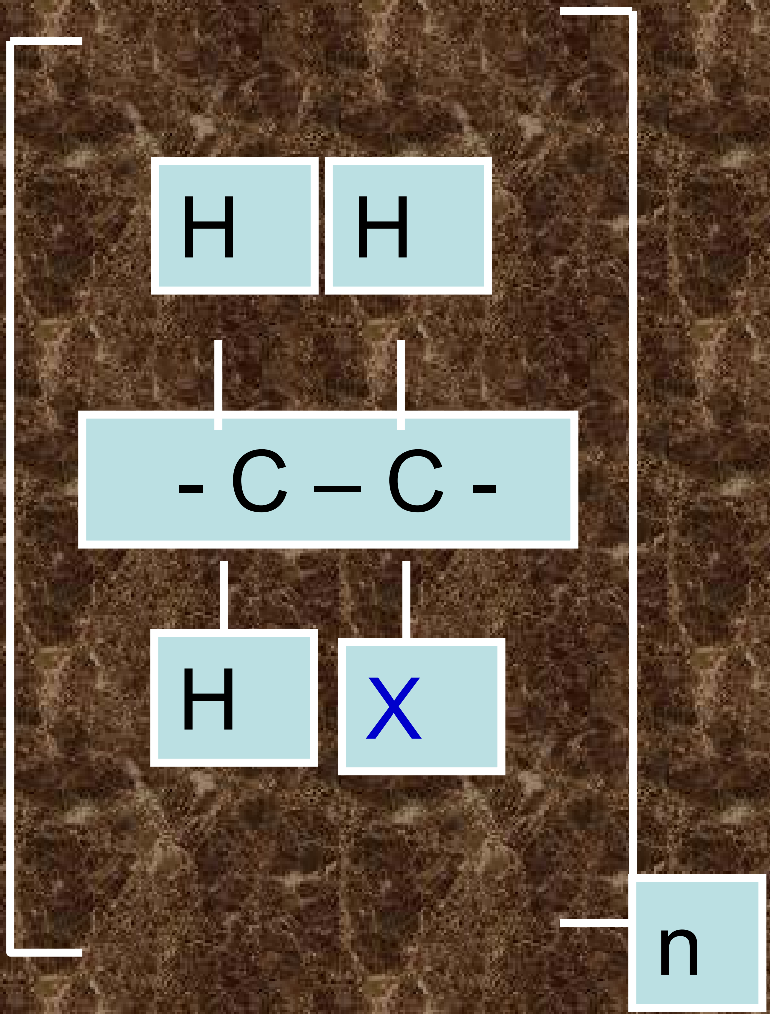
-many artificial polymers are solids with very useful physical properties:

- **-inert** (resistant to corrosion and biodegradation)
- **-flexible** (elastic)
- **-low melting point** (can be moulded)

Other Carbon Chain Polymers

Homopolymers

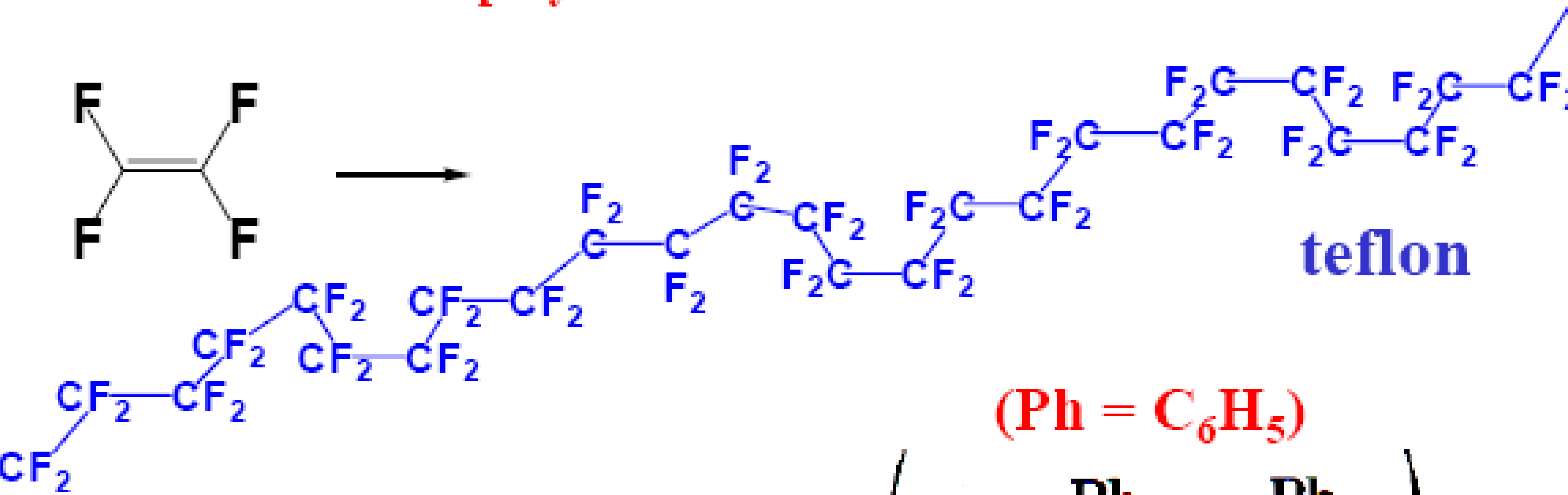
- **If X=H** then
  polyethylene
- **If X = CH_3** then
  polypropylene
- **X = Cl** then
  polyvinylchloride
- If **X = Benzene** ring then
  polystyrene



$$\left[\begin{array}{cc} H & H \\ | & | \\ -C & -\,C- \\ | & | \\ H & X \end{array}\right]_n$$

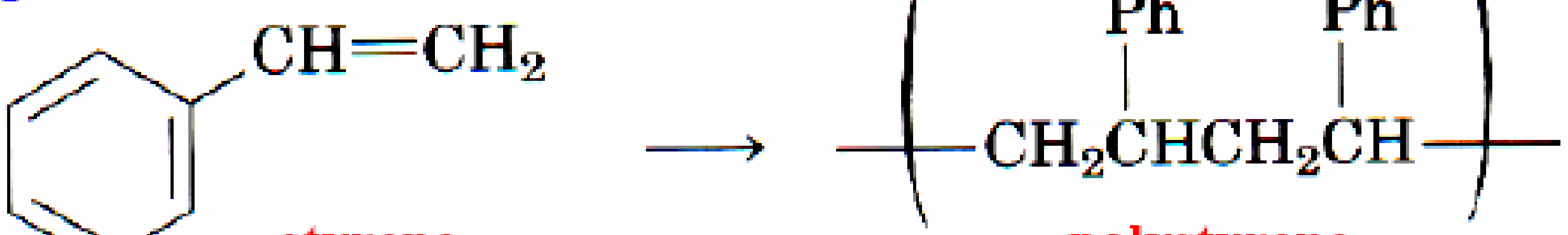
Homopolymers (p. 1041)

- polymers made from just one type of monomer building block are known as **homopolymers**



teflon

(Ph = C_6H_5)

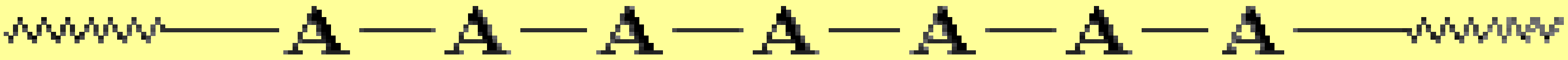


$$\mathrm{C_6H_5CH{=}CH_2} \longrightarrow -\!\!\left(\mathrm{CH_2\overset{\overset{\displaystyle Ph}{|}}{C}HCH_2\overset{\overset{\displaystyle Ph}{|}}{C}H}\right)\!\!-$$

styrene **polystyrene**

-when air blown through mixture - ‘light’ polystyrene for packaging

Molecular Arrangement of Polymers

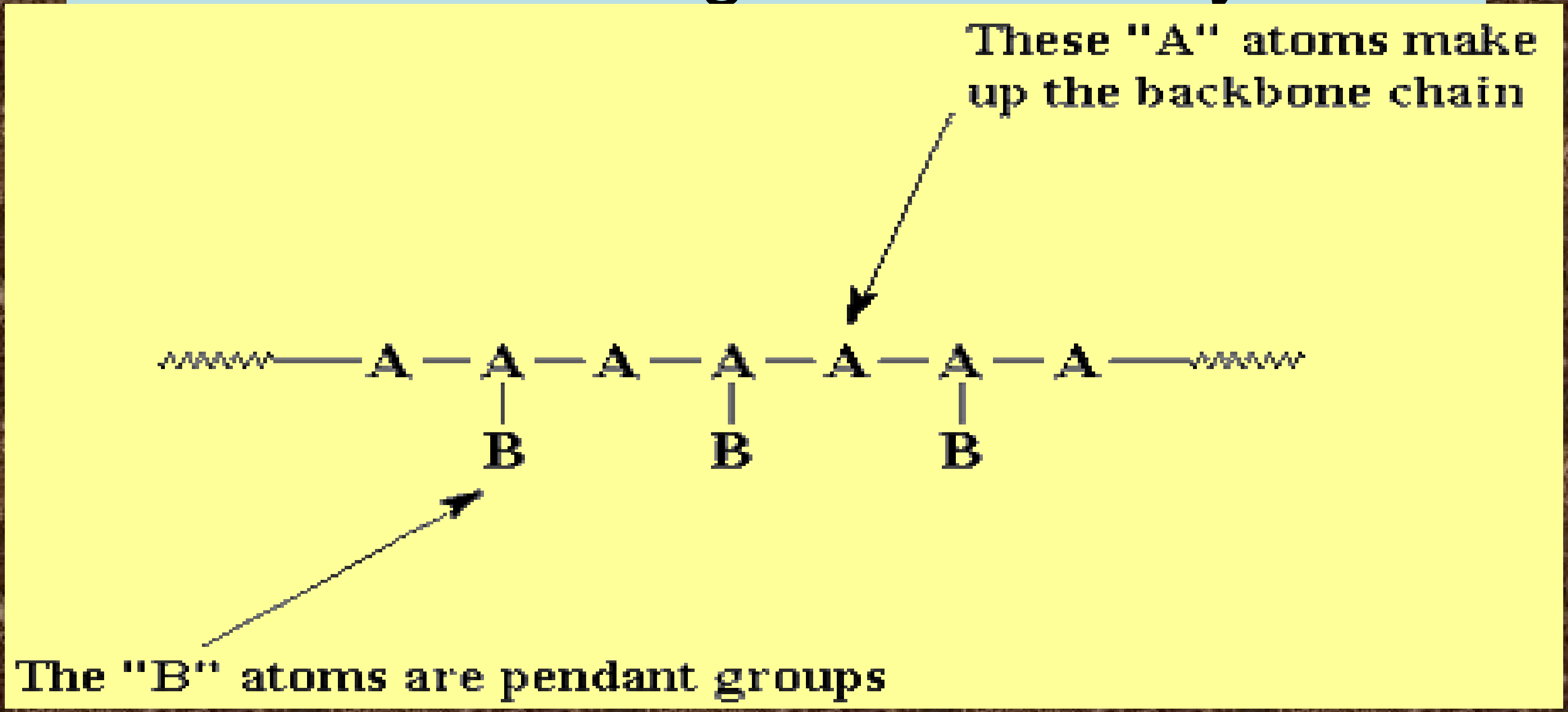


a linear polymer made of "A" atoms

- Most polymers are large linear macro-molecules.
- This chain is called the ***backbone,*** which may have hundreds of thousands of atoms.

- Some of these atoms in the chain may have small chains of atoms attached to them.
- These are called ***pendant groups.***

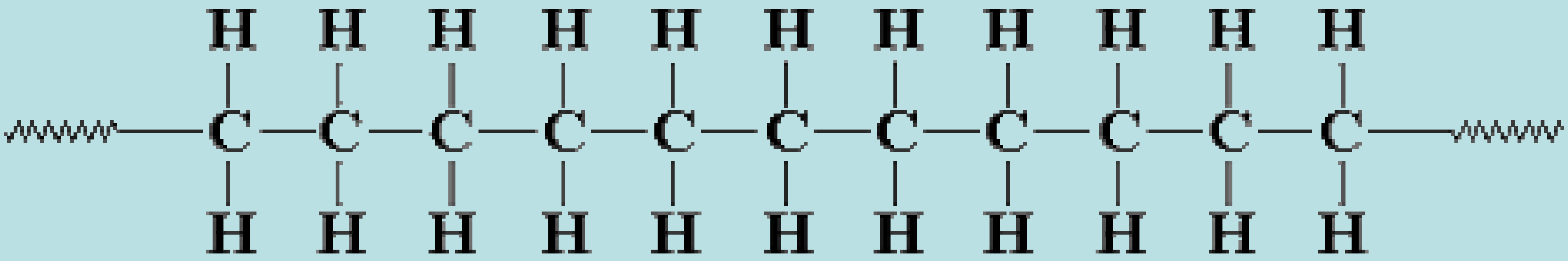
Molecular Arrangement of Polymers



- Most polymers are large linear macro-molecules. This chain is called the ***backbone*.**
- The small chains attached to the backbone are called ***pendant groups*.**

The Structure of Polymers

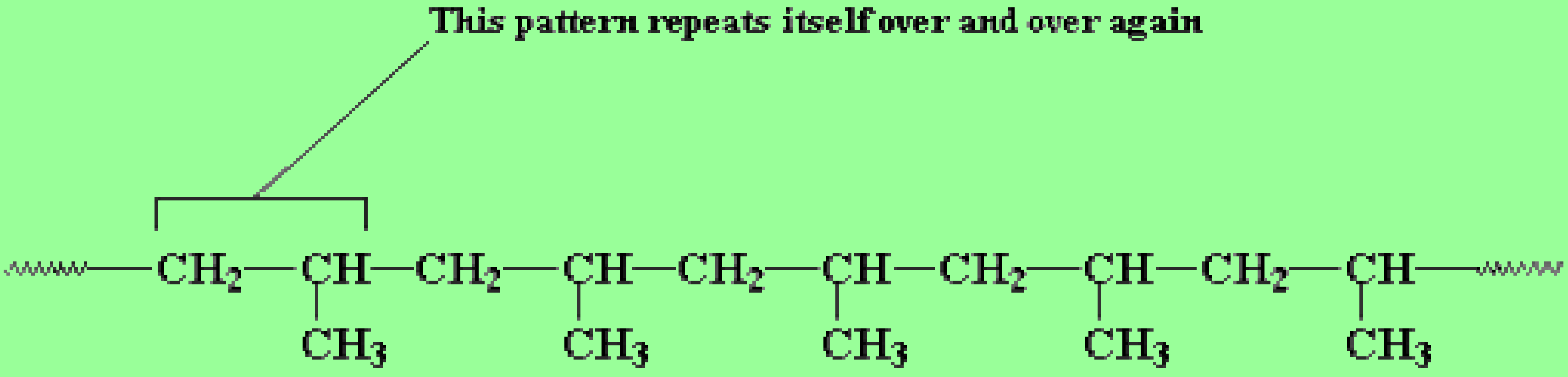
- Below is a diagram of **polyethylene,** the simplest polymer structure



- There are polymers that contain only **carbon and hydrogen.**

- These are referred to as hydrocarbon-polymer. **Polypropylene, polybutylene, polystyrene, and polymethylpentene.**

Polymers have a Repeating Structure

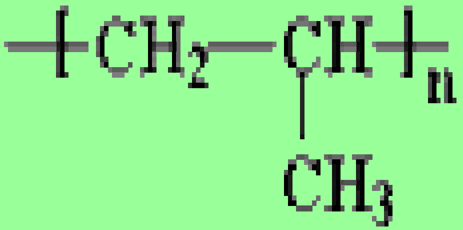


$$\sim\!\sim CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-\sim\!\sim$$

This pattern repeats itself over and over again

Polypropylene

The atoms of the backbone of a polymer chain in a **regular order**, and this order is **repeated**.



$$\left[CH_2-\underset{CH_3}{CH} \right]_n$$

e.g. in **polypropylene**, , the backbone chain is made **up of just two carbon atoms** repeated over and over again.

L-37 Thermosetting & Thermoplastic Polymers
Introduction

Degree of Polymerization (DP):-

- The number of monomers involving to form a polymer in polymerization reaction is know as Degree of polymerization.

- Polymers with a **high DP** are called

“high polymers”

- and those with low degree of polymerization are called

oligopolymers.

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Introduction

- High polymers have very high molecular weights (104 to 106) and are called macromolecules

FUNCTIONALITY:

- Functionality means the **number of bonding or reactive sites** in a molecule.
- If a molecule is having TWO reactive sites then it is called a Bifunctional monomer.
- it will give linear straight chain polymer

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Introduction

FUNCTIONALITY:

- When a functionality of a monomer is two (bifunctional), it will give linear straight chain polymer
- e.g. polyethylene
- When a functionality of a monomer is three (trifunctional), it will give 3 D
- three dimensional structure.
- e.g. Bakelite

L-37 Thermosetting & Thermoplastic Polymers

Introduction

Polymer classification

According to the origin

(i) Natural (ii) Synthetic

Natural:

Polymers which are extracted from natural materials are natural Polymer. **e.g. :- Cellulose**

Synthetic:-

Polymers which are made by man are synthetic.

e.g.:- Polyethylene

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Introduction

- According to the structure

(1) Linear (2) Branched (3) Cross-link

(1) Linear :- Linear in shape

(2) Branched:- branched- containing side chain.

Eg.:- **Low density polyethylene**

(3) Cross-link :- main chains will give rise to cross-link, 3D structure. e.g. **Bakelite**

- a strong polymer
- have network structure.
- Do not break up easily.

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Introduction

(1) Linear :- Linear in shape

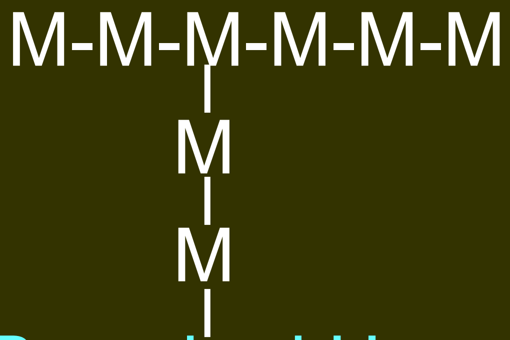
M-M-M-M-M-M-M-

Linear homopolymer

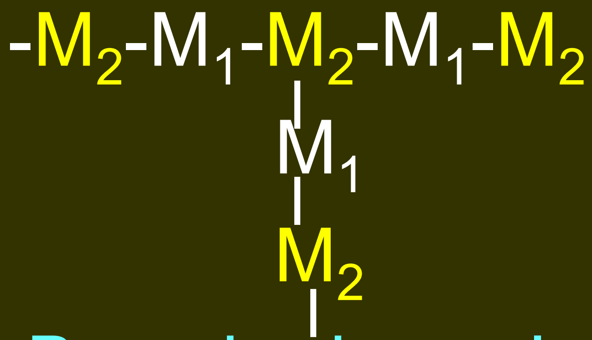
$M_1-M_2-M_1-M_2-M_1$

linear copolymer

(2) Branched :-containing side chain.


M-M-M-M-M-M
|
M
|
M
|

Branched Homopolymer


$-M_2-M_1-M_2-M_1-M_2$
|
M_1
|
M_2
|

Branched copolymer

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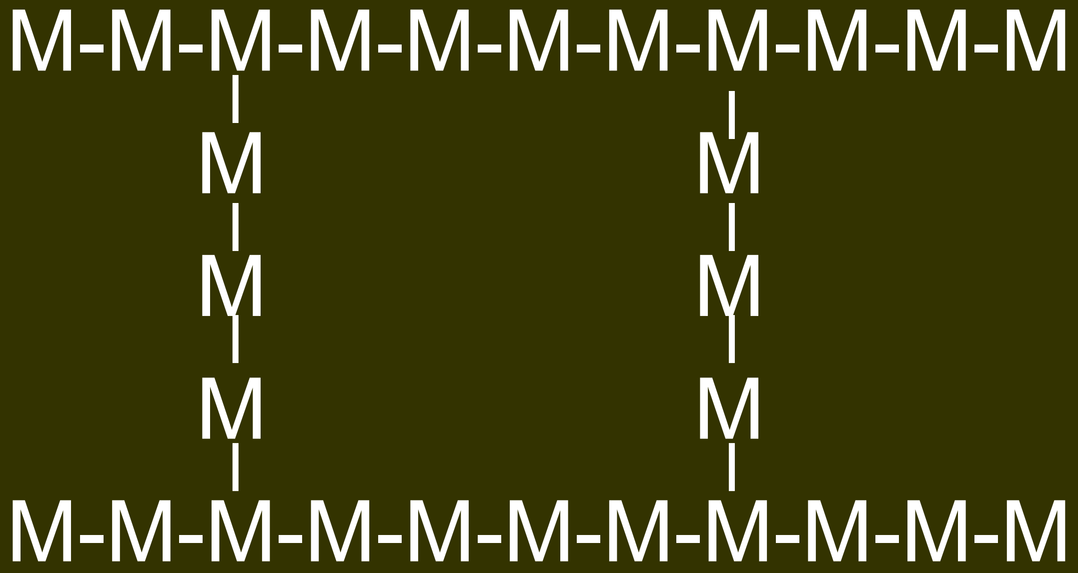
Introduction

(3) Cross-link :- main chains will give rise to cross-link, 3D structure.



```
M-M-M-M-M-M-M-M-M-M-M
    |         |
    M         M
    |         |
    M         M
    |         |
    M         M
    |         |
M-M-M-M-M-M-M-M-M-M-M
```

Introduction

Based on structure / no. of monomers:-

(1) **Homopolymer:** contain single type of monomers (same type).

e.g. polyethylene,

all the monomers are ethylene only.

(2) **Co-polymers:**

Introduction

Based on structure / no. of monomers:-

(1) **Homopolymer:** **e.g. polyethylene**,

(2) **Co-polymers:** contain different types of (or different no. of) monomers.

The process is called Co-polymerization.

These are of 4 types:-

(1) Random **(2) Alternate**

(3) Graft **(4) Block**

L-37 Thermosetting & Thermoplastic Polymers

Introduction

- **(1) Random :** A polymer contains 2 or more no. of monomers in chain by random arrangement.

  A & B_ are two monomers

- **(2) Alternate:**_polymer containing 2 or more no. of monomers in chain by alternate arrangement.

- A & B are two monomers

L-37 Thermosetting & Thermoplastic Polymers

Introduction

- A & B are two monomers
- **(3) Graft:** polymer will contain 2 or more no. of monomers. Here homopolymer will be linked with the other homopolymer.

- This link or branch we will have 2nd type or other type of polymer. This arrangement is graft arrangement.
- **Block:** Long sequence of monomers in linear.

L-37 Thermosetting & Thermoplastic Polymers

Introduction

Graft Coplymer

$-M-M-M_1-M_1-M_1-M_{1-}M_1-M_1M_1M_1$

M_2 M_2

M_2 M_2

M_2 M_2

M_2 M_2

$M-M-M_1-M_1-M_1-M_{1-}M_1-M_1M_1M_1$

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Introduction

Tacticity: the difference in configuration (tacticity) affect the physical properties

- the orientation of monomeric units in a polymer molecule can take place in
- an orderly or disorderly fashion which repeat to main chain.

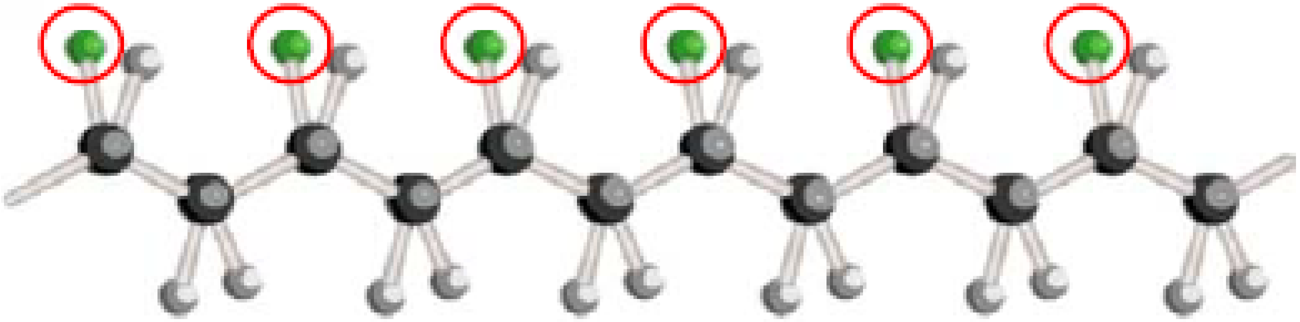
i) Isotactic ii) atactic iii) Syndiotactic

Stereochemistry of Polymers (p. 1042)

Isotactic

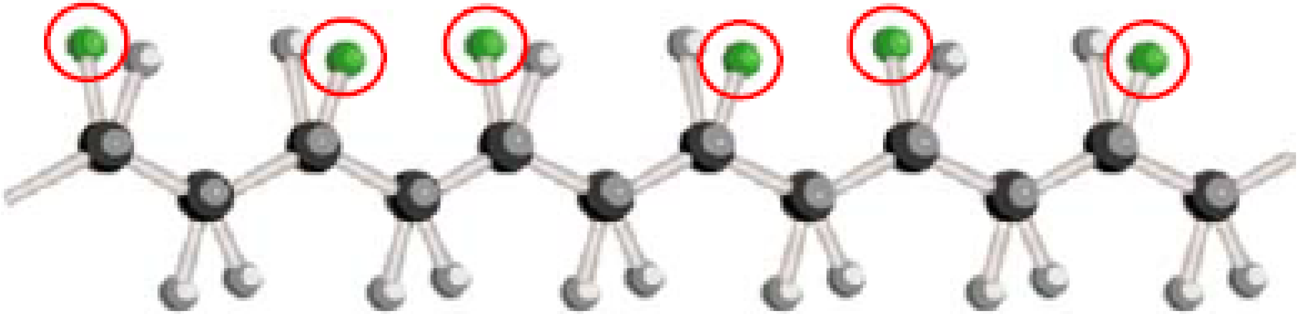
R groups on same side of chain

(strong, crystalline high m.p.)



Syndiotactic

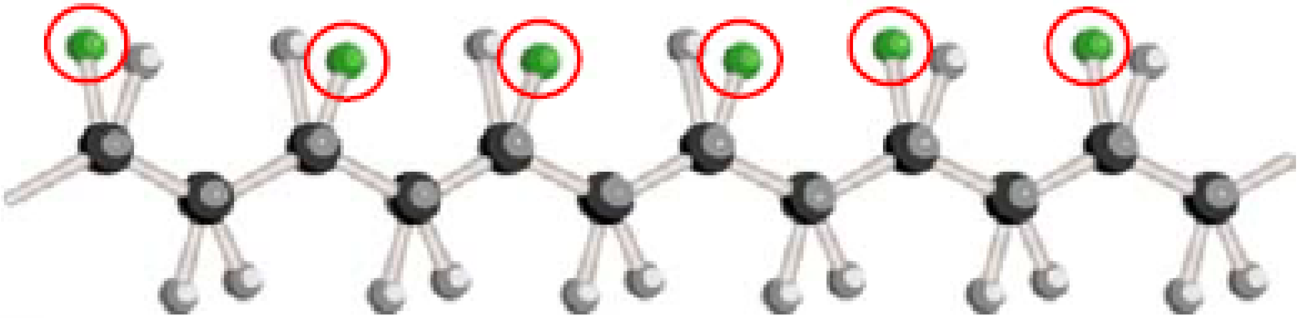
R groups alternate from side to side



Atactic

R groups disposed at random

(rubbery, weak melts easily)



L-37 Thermosetting & Thermoplastic Polymers
Introduction

i) Isotactic : the head to tail configuration, in which the groups are all in the same side of the chain.

ii) Atactic if the functional groups are at random around the main chain, it is called atactic polymer.

iii) Syndiotactic

L-37 Thermosetting & Thermoplastic Polymers

Introduction

i) Isotactic : head to tail …..same side..

ii) Atactic ……at random…..

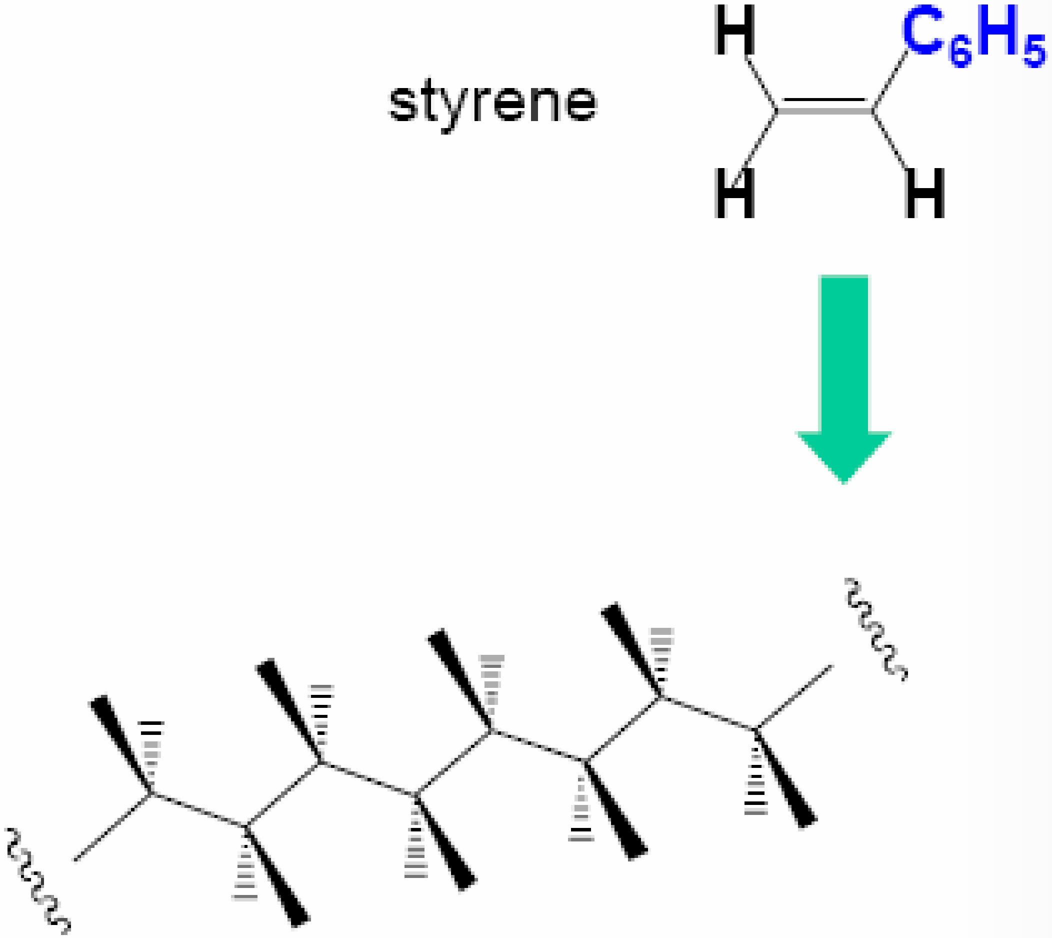
iii) Syndiotactic if the arrangement of the side groups is in alternating fashion,

it is called syndiotactic polymer.

e.g. gutta percha

Stereochemistry of Polymers (p. 1042)

Q: Draw four repeating units of *isotactic* polystyrene, using wedged bonds to show the stereochemistry.



2. Draw wedged bonds to show tetrahedrally aranged bonds of each sp^3 carbon

L-37 Thermosetting & Thermoplastic Polymers

Introduction

Plastics are high molecular weight organic compounds which can be moulded by the application of heat or pressure.

These are mainly of 2 types:

(1) Thermoplastic resins.

(2) Thermosetting resins

L-37 Thermosetting & Thermoplastic Polymers

(1) Thermoplastic resins: Thermoplastic resins **on heating and become plastic** so that

- it can be converted to any shape by moudling.
- **On cooling, they become hard or rigid.**
- On heating , they soften again & the **material can be remoulded to any desired shape.**
- e.g. **Polyvinyls, Polyethylene**

L-37 Thermosetting & Thermoplastic Polymers

- **(2) Thermosetting resins:-**

Thermosetting resins are those

- **which set upon heating & can't be reformed**

.

Generally these resins are formed by **condensation.**

- These have **3 dimensional structure &**
- **high molecular weight.**

e.g. **Bakelite, Dacron.**

Introduction

polymerization :-It is of two types based synthesis.

(1) Addition Polymerization

(2) Condensation Polymerization

Addition Polymerization thermoplastics	Condensation Polymerization thermosets.
1) Polymer is synthesized by addition Polymerization same type of monomers .Eg. Polyethylene	**(1) Polymer is formed or synthesized by condensation of two different monomers Eg. Nylon 6,6**

L-37 Thermosetting & Thermoplastic Polymers

• Thermoplastic resins.	Thermosetting resins
2) Molecular weight will not change on Heating.	2) In this molecular weight will increase with the formation of cross-link structure.
3) Elimination of small molecules will not be Seen.	3) Elimination of small molecules is seen like H_2O, CH_3OH, HCl etc.

L-37 Thermosetting & Thermoplastic Polymers

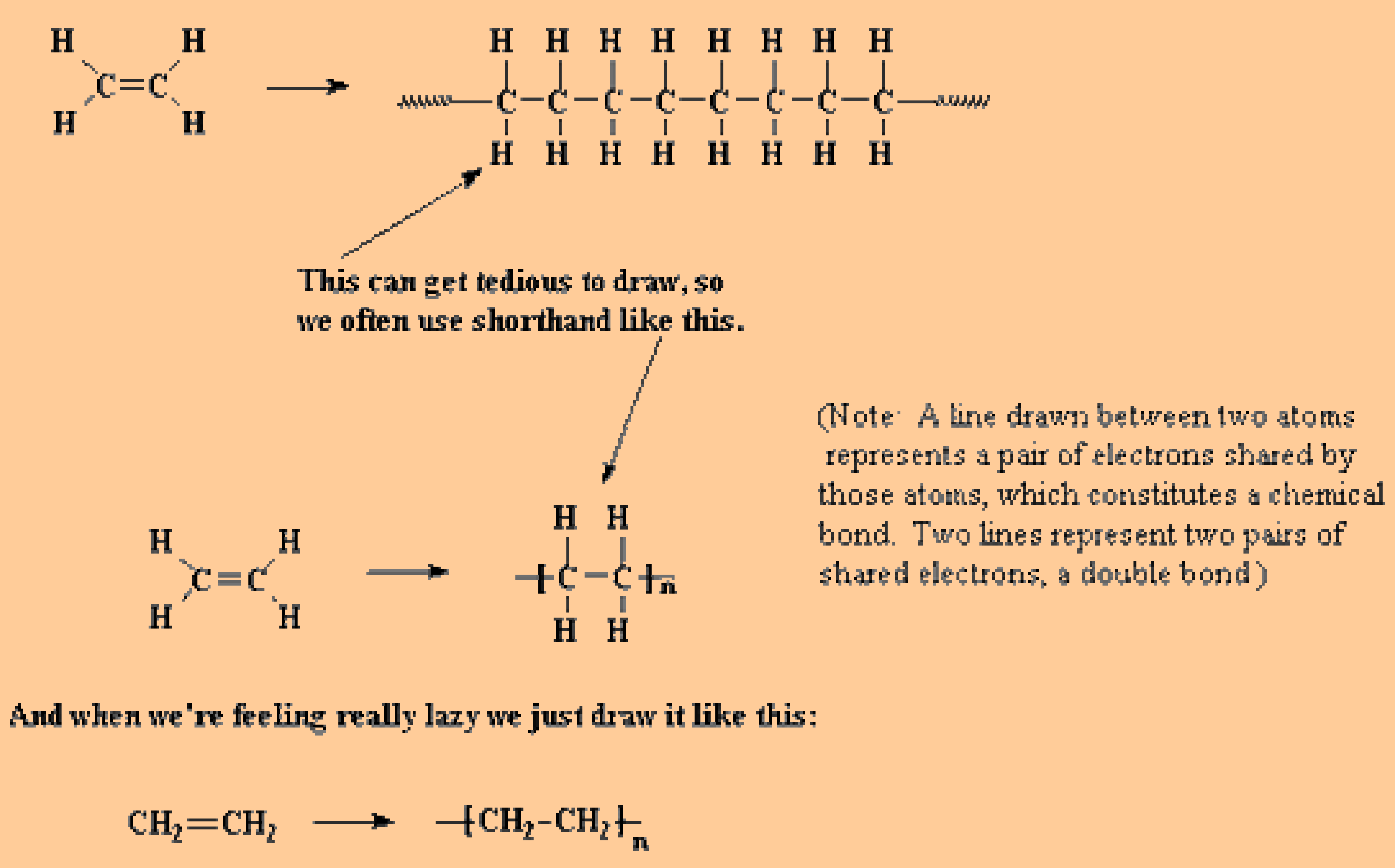
Thermoplastic resins.	**Thermosetting resins**
4) These soften on heating readily & can be reshaped.	4) These do not soften on heating and can't be reshaped or remoulded.
5) These are usually Soft, weak and less brittle.	5) These are usually hard, Strong and more brittle.

L-37 Thermosetting & Thermoplastic Polymers

Thermoplastic resins.	Thermosetting resins
6) These can be regenerated from wastes.	6) These can't be reclaimed from wastes.
7) They are usually soluble in some organic solvents.	7) Due to strong bonds & cross-links these are insoluble in almost all organic solvents.
8) In this vander waal's forces are present H-bonding is also seen.	8)In this covalent bonds are seen.

Polyethylene

Thermoplastic [Addition polymerization]



This can get tedious to draw, so we often use shorthand like this.

(Note: A line drawn between two atoms represents a pair of electrons shared by those atoms, which constitutes a chemical bond. Two lines represent two pairs of shared electrons, a double bond)

And when we're feeling really lazy we just draw it like this:

$$CH_2{=}CH_2 \longrightarrow -\!\!\left[CH_2-CH_2\right]\!\!-_n$$

Nylon -6,6

Thermoset [Condensation polymerization]

- **Preparation**

- Nylon 6,6 is obtained by the polymerisation of **adipic acid** with **hexamethylene diamine.**

$$n\ H_2N\text{-}(CH_2)_6\text{-}NH_2 + n\ COOH\text{-}(CH_2)_4\text{-}COOH$$

$$\downarrow$$

$$-\left[HN\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}\right]_n + 2nH_2O$$

Introduction

Addition Polymerization thermoplastics	Condensation Polymerization thermosets.
9) Polymer is the exact multiple of monomer	9) Polymer is not the exact multiple of monomer because elimination of small molecules takes place.
10) In general, homo chain polymer gives thermoplastics	10) In general, Hetero -chain polymer give thermosets.

Introduction

Addition Polymerization thermoplastics	Condensation Polymerization thermosets.
Homo chain polymer • (same type monomer) 11) In general addition, polymerization will proceed in 3 types. (1) free radical (2) Cationic(3) Anionic	Hetero chain (different (monomers will be there) 11) In condensation polymerization (1) free Radical (2) Anionic (3) cationic reactive centres are not observed.

FREE RADICAL POLYMERISATION

CATIONIC POLYMERISATION

ANIONIC POLYMERIZATION

Free radical polymerisation

- Monomer is activated by its transformation into radical by the action of light, heat or any radiation
- Polymerisation involves three steps

  Initiation

  Propagation

  Termination

Free radical……

INITIATION

To start the reaction a few free radicals which act as initiator should be generated with the help of initiators.

Initiation involves 2 steps

1. Formation of free radical
2. Action of free radical with a monomer to form a free radical monomer

Free radical polymerisation

- **Propagation**
- In this type free radical monomer will add to the free monomer present.
- This will go on adding as many as possible.
- This is independent of the chain length.

Free radical polymerisation

Termination

i) **Disproportionation :-** Two free radicals combine together &

a hydrogen atom is transferred from one radical to another forming

a saturated & an unsaturated molecule.

ii) **Coupling:-**

Free radical polymerisation

Termination

i) Disproportination :- ………………forming a saturated & an unsaturated molecule.

ii) Coupling:- Two free radicals will combine by

making a single bond into double bond

Polymerisation: Chain Growth by Addition Reaction (p. 1040)

-**chain growth** involves heating monomer under pressure with small amount of radical initiator:

radicals are molecules with an unpaired electron (R•)

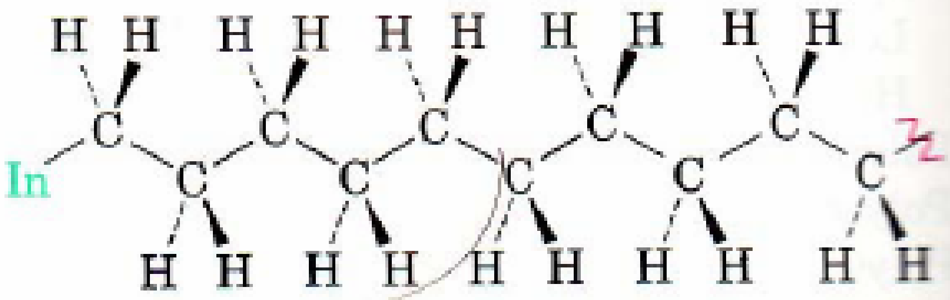
initiation

propagation

$$In\cdot + CH_2{=}CH_2 \longrightarrow [In{-}CH_2CH_2\cdot] \xrightarrow[\text{1000 atm, 250 °C}]{CH_2{=}CH_2} [In{-}CH_2CH_2CH_2CH_2\cdot]$$

A radical initiator

chain addition reaction ↓ Repeat many times



A section of a polyethylene chain

-polyethylene is also called '**polythene**'

CATIONIC POLYMERISATION

- It proceeds by a polar or heterolytic cleavage of double bond.
- Reaction starts with cation formation
- Three step process
  - Initiation
  - Propagation
  - Termination

CATIONIC POLYMERISATION

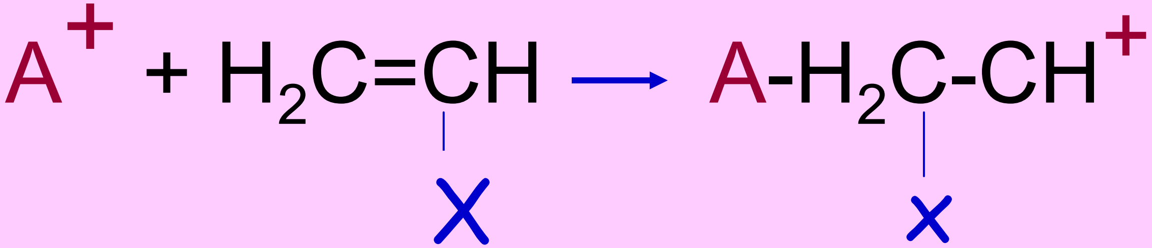
Mechanism

- Initiation : Lewis acid act as initiator.
- It will take an electron from the monomer and the monomer becomes a cation.
- Propagation: Cation monomer reacts with a free monomer to form a bigger cation.
- Termination:

Cationic Polymerisation

Mechanism

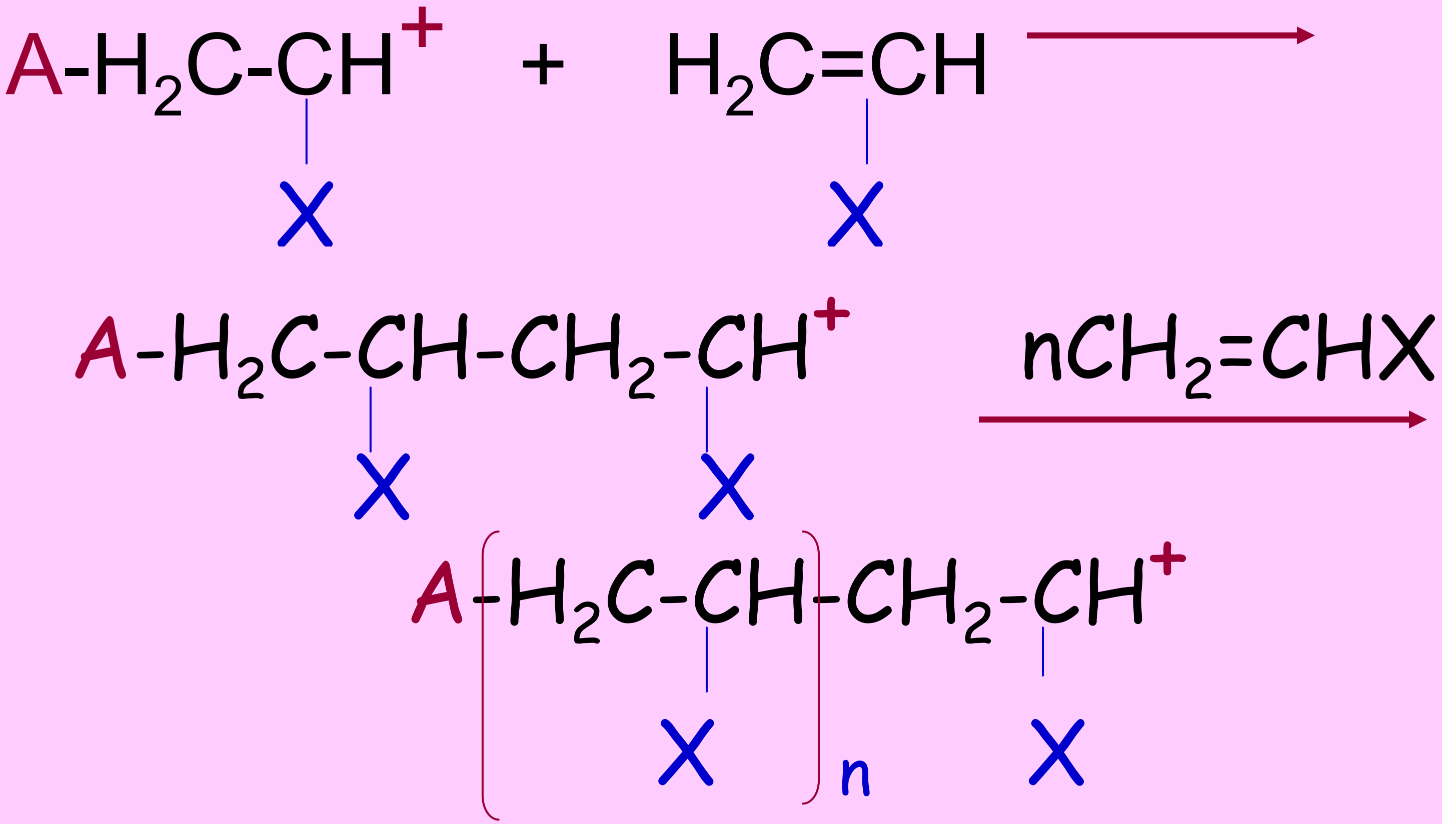
- **Initiation**
- This step will start when a lewis acid takes an **electron from a monomer** to form a cation.



$$A^{+} + H_2C=\underset{X}{\underset{|}{CH}} \longrightarrow A-H_2C-\underset{x}{\underset{|}{CH}}^{+}$$

Anionic Polymerisation

Propagation



$$\mathrm{A{-}H_2C{-}\underset{X}{CH}^{+}} + \mathrm{H_2C{=}\underset{X}{CH}} \longrightarrow$$

$$\mathrm{A{-}H_2C{-}\underset{X}{CH}{-}CH_2{-}\underset{X}{CH}^{+}} \xrightarrow{\mathrm{nCH_2{=}CHX}}$$

$$\mathrm{A}\left(\mathrm{{-}H_2C{-}\underset{X}{CH}}\right)_n\mathrm{{-}CH_2{-}\underset{X}{CH}^{+}}$$

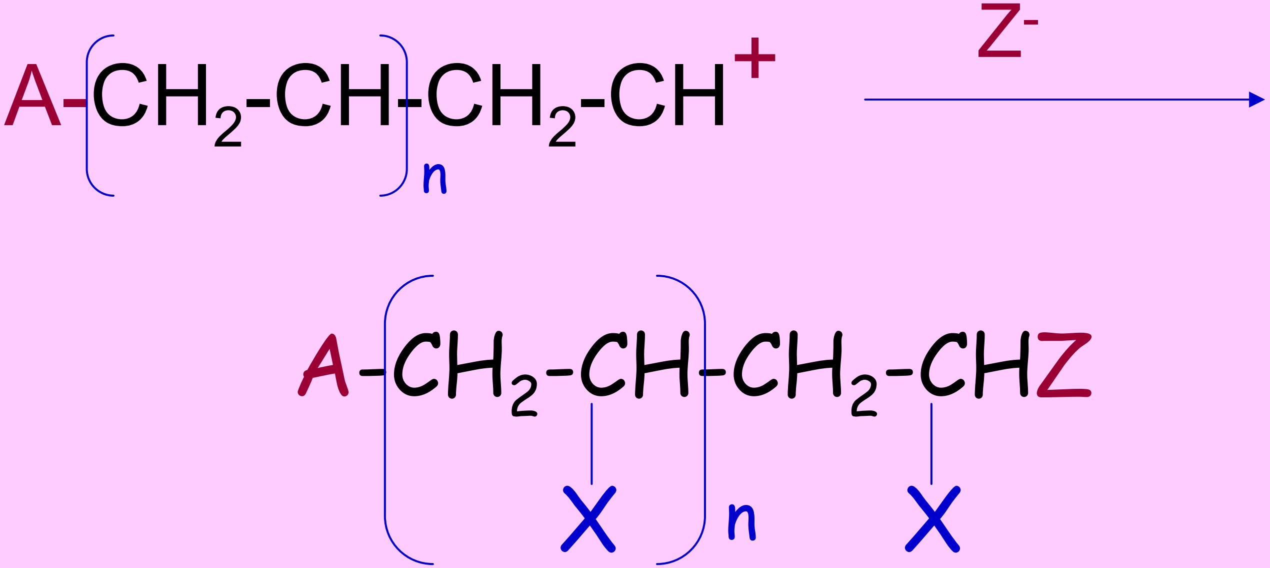
CATIONIC POLYMERISATION

Mechanism

- Initiation : Lewis acid act as initiator….. monomer becomes a cation
- Propagation: …..form a bigger cation.
- Termination: Termination takes place either by
- combination with a base or
- by disproportionation

cationic Polymerisation

Termination



$$\mathrm{A}-\left(\mathrm{CH_2}-\mathrm{CH}\right)_n-\mathrm{CH_2}-\mathrm{CH}^{+} \xrightarrow{Z^-}$$

$$\mathrm{A}-\left(\mathrm{CH_2}-\underset{\mathrm{X}}{\mathrm{CH}}\right)_n-\mathrm{CH_2}-\underset{\mathrm{X}}{\mathrm{CH}}\mathrm{Z}$$

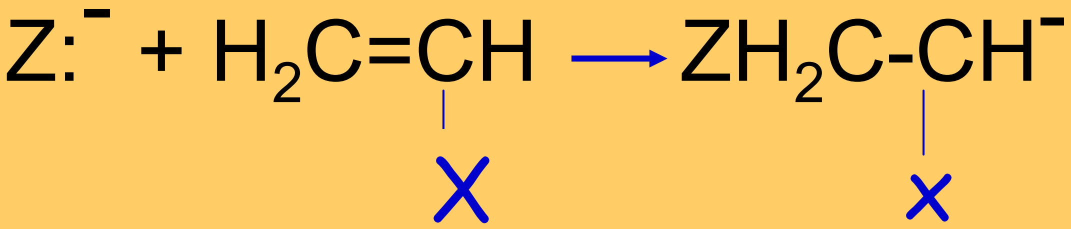
Anionic Polymerisation

- Anionic polymerisation proceeds by
- a polar or heterocyclic cleavage of
- the double bond
- by the action of electron donor or a base.
- Steps involved are
  - Initiation
  - Propagation
  - Termination

Anionic Polymerisation

Mechanism

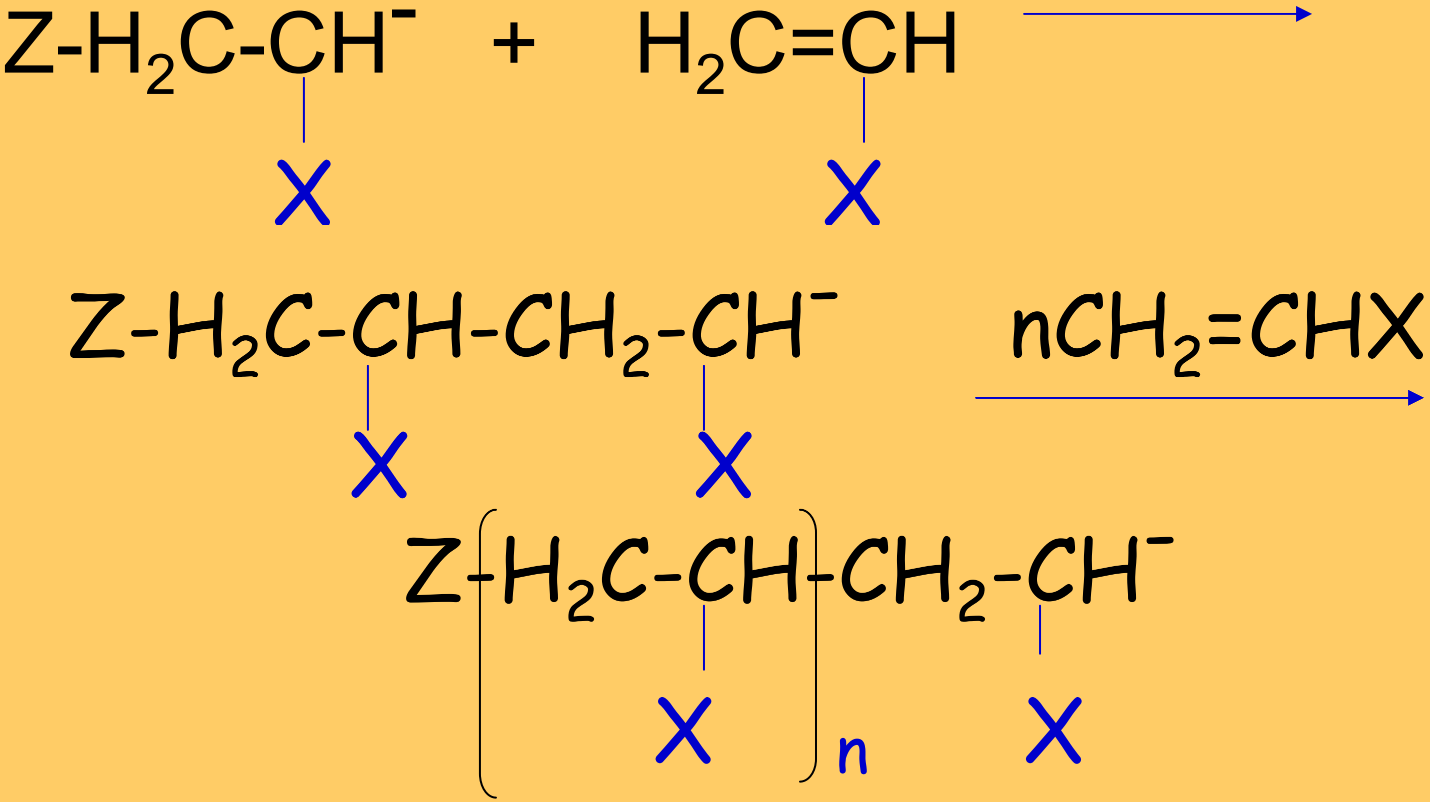
- **Initiation**
- This step will start when a **monomer accepts electrons** from a base and form anion.



$$Z:^- + H_2C{=}\underset{|\atop X}{CH} \longrightarrow ZH_2C{-}\underset{|\atop X}{CH}^-$$

Anionic Polymerisation

Propagation



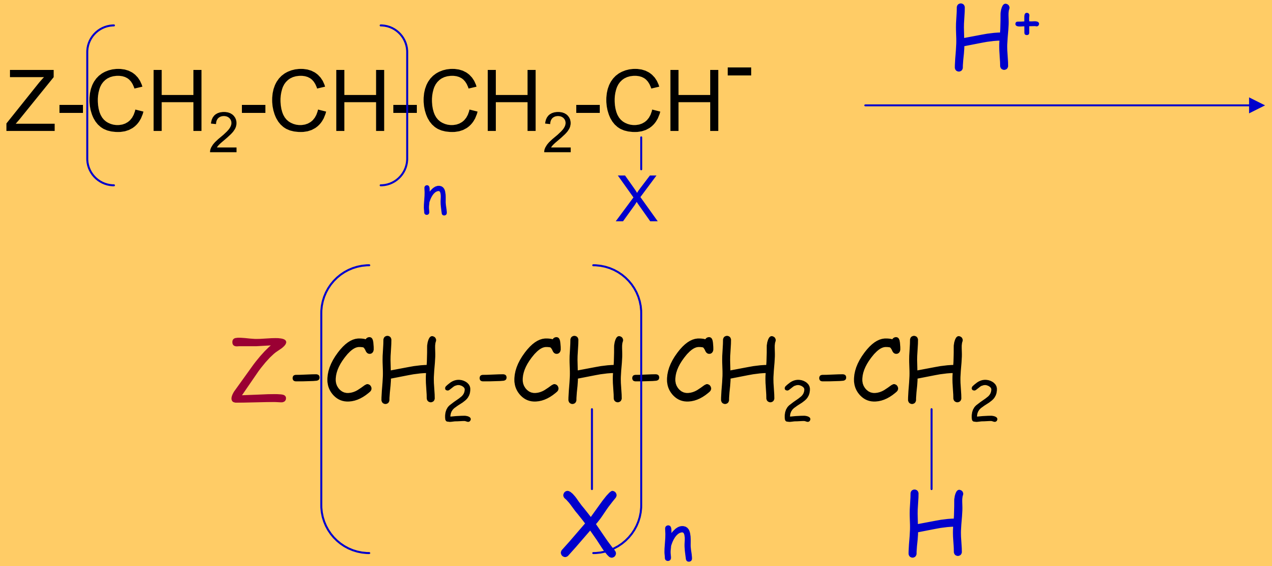
$$\text{Z-H}_2\text{C-}\underset{X}{\text{CH}^-} \quad + \quad \text{H}_2\text{C=}\underset{X}{\text{CH}} \longrightarrow$$

$$\text{Z-H}_2\text{C-}\underset{X}{\text{CH}}\text{-CH}_2\text{-}\underset{X}{\text{CH}^-} \xrightarrow{n\text{CH}_2\text{=CHX}}$$

$$\text{Z-}\left(\text{H}_2\text{C-}\underset{X}{\text{CH}}\right)_n\text{-CH}_2\text{-}\underset{X}{\text{CH}^-}$$

Anionic Polymerisation

Termination



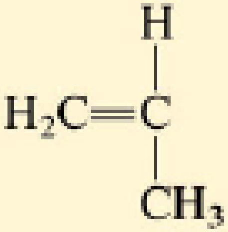
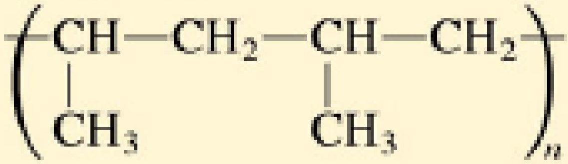
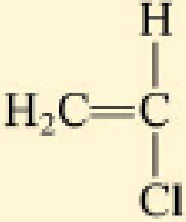
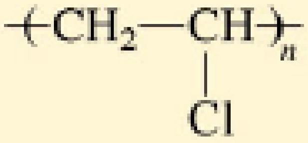
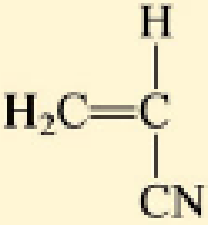
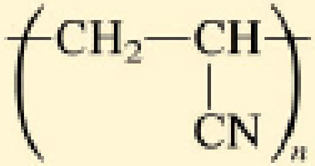
$$Z-\left(CH_2-CH\right)_n-CH_2-\underset{X}{\underset{|}{CH^-}} \xrightarrow{H^+} Z-\left(CH_2-\underset{X}{\underset{|}{CH}}\right)_n-CH_2-\underset{H}{\underset{|}{CH_2}}$$

Syllabus: polyethylene, Teflon, PVC, Nylon, Phenol formaldehyde, Elastomers, natural polymers.

L-38 Preparation & Properties of

PE, Teflon, PVC, Nylon

Some Monomers and Their Common Synthetic Polymers

Monomer		Polymer	
Formula	**Name**	**Name and Formula**	**Uses**
$H_2C{=}CH_2$	Ethylene	Polyethylene $\left(CH_2-CH_2\right)_n$	Plastic piping, bottles, electrical insulation, toys
 $H_2C{=}\overset{H}{\underset{CH_3}{C}}$	Propylene	Polypropylene  $\left(\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-CH_2\right)_n$	Packaging film, carpets, crates for soft-drink bottles, lab wares, toys
 $H_2C{=}\overset{H}{\underset{Cl}{C}}$	Vinyl chloride	Poly(vinyl chloride) (PVC)  $\left(CH_2-\underset{Cl}{CH}\right)_n$	Piping, siding, gutters, floor tile, clothing, toys
 $H_2C{=}\overset{H}{\underset{CN}{C}}$	Acrylonitrile	Polyacrylonitrile (PAN)  $\left(CH_2-\underset{CN}{CH}\right)_n$	Carpets, knitwear

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Vinyl Polymers

- **Vinyl polymers are polymers made from *vinyl monomers*; that is, small molecules containing carbon-carbon double bonds.**

They make up largest family of polymers.

- **Let's see how we get from**

a vinyl monomer to a vinyl polymer using for an example the simplest vinyl polymer, polyethylene.

Polyethylene (PE) [Thermoplastic]

There are three types.

1. **Type I** or Low density polyethylene (LDPE) [0.91 to 0.925 g/cm^3]
2. **Type-II** or Medium density polyethylene [0.925 to 0.940 g/cm^3]
3. **Type-II** or High density polyethylene (HDPE) [0.941 to 0.965 g/cm^3]

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Polyethylene (PE) [Thermoplastic]

1. **Low density polyethylene (LDPE):-**

Preparation: It is prepared by polymerizing ethylene at high pressure of 1000-5000 atm. & at 250^0 C in the free initiator CO_2.

Polymerisation: Chain Growth by Addition Reaction (p. 1040)

-**chain growth** involves heating monomer under pressure with small amount of radical initiator:

radicals are molecules with an unpaired electron (R•)

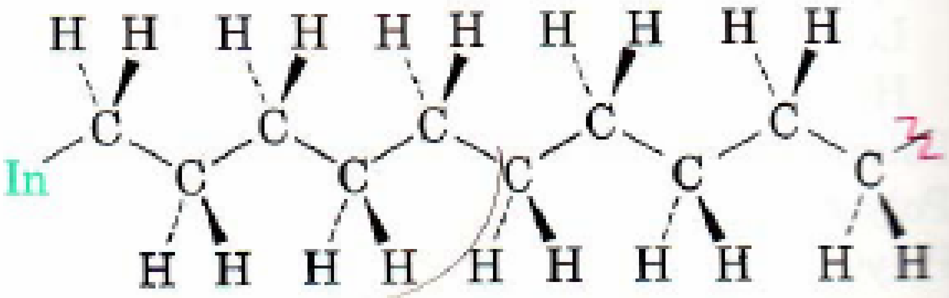
initiation

propagation

$$In\cdot + CH_2{=}CH_2 \longrightarrow [In{-}CH_2CH_2\cdot] \xrightarrow[\text{1000 atm, 250 °C}]{CH_2=CH_2} [In{-}CH_2CH_2CH_2CH_2\cdot]$$

A radical initiator

chain addition reaction ↓ Repeat many times



A section of a polyethylene chain

-polyethylene is also called **‘polythene’**

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Polyethylene (PE) [Thermoplastic]

- Properties **(LDPE):-**
  - Low density.
  - Low crystallinity.
  - Chemically inert & has good chemical resistance.
  - Excellent electrical insulation property.
  - Tough & flexible even at low temp. But it has a low impact strength and is relatively brittle.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Polyethylene (PE) [Thermoplastic]

Uses: (LDPE):-

LDPE is used in following application

1. **Films for general packaging and carrier bags.**
2. **Squeeze bottles particularly for detergents**
3. **Moulded toys, bottle caps ,flexible bottles,**
4. **kitchen and domestic applications.**
5. **Ink tubes for pens & mugs.**

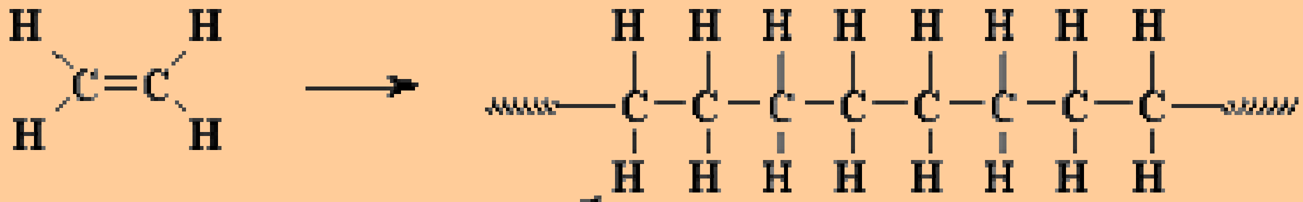
L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Low density polyethylene (LDPE):-

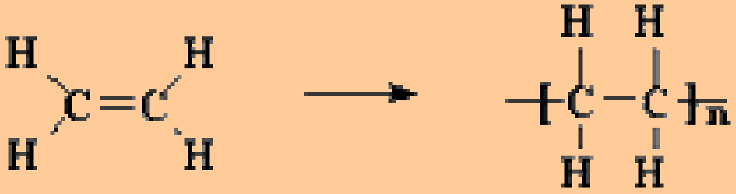
- **Liminations:**

- **LDPE is permeable to gases.**
- **Because of low density & crystallinity.**
- **LDPE has low rigidity & is not suitable for load bearing application.**

Polyethylene



This can get tedious to draw, so we often use shorthand like this.



(Note: A line drawn between two atoms represents a pair of electrons shared by those atoms, which constitutes a chemical bond. Two lines represent two pairs of shared electrons, a double bond.)

And when we're feeling really lazy we just draw it like this:

$$CH_2{=}CH_2 \longrightarrow -\!\left[CH_2-CH_2 \right]\!-_n$$

High density polyethylene (HDPE):

- it is prepared by using ionic catalyst. It is completely linear, higher softening point (125^0C to 135^0C)
- **Properties:**

1. Molecules are linear so HDPE has high density & more % crystallinity.

2….

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

High density polyethylene (HDPE):

- **Properties:**

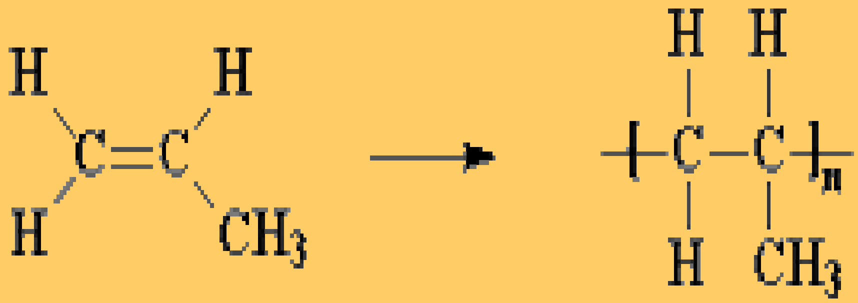
2. Softening temperature is higher.
3. Excellent chemical resistance.
4. Good electrical insulation property.
5. Low water & gas permeability.
6. Free from odour & toxicity.
7. More stiff, heard & possesses greater tensile strength.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

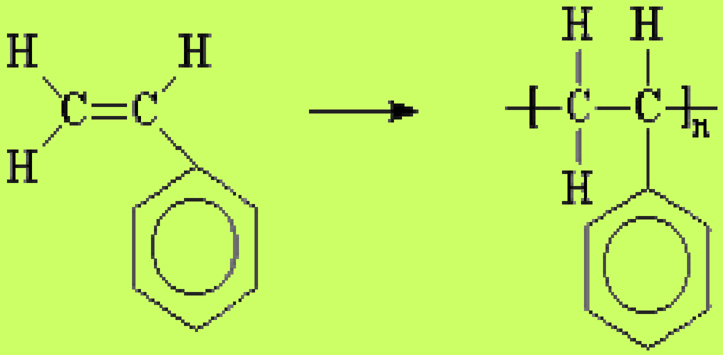
High density polyethylene (HDPE):

- **Uses:**
- Used as wrapping material
- Bottles of milk, household chemicals & drug packaging are also made from it.
- Used for domestic water & gas piping.

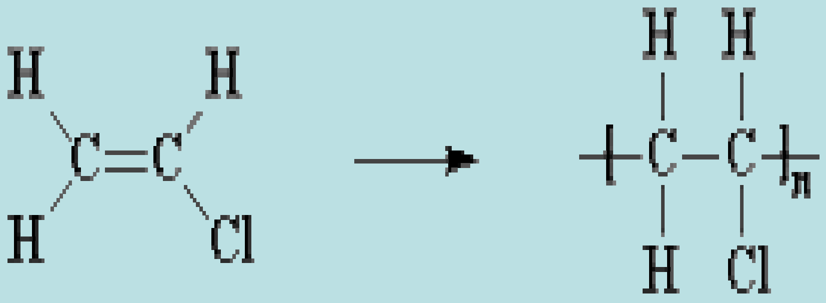
Vinyl Polymers



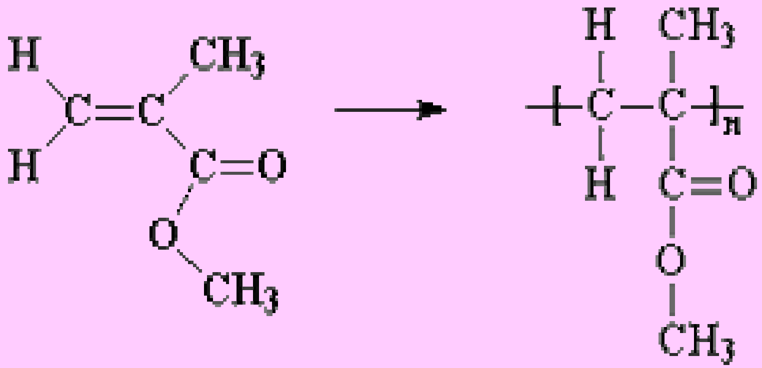
polypropylene



polystyrene



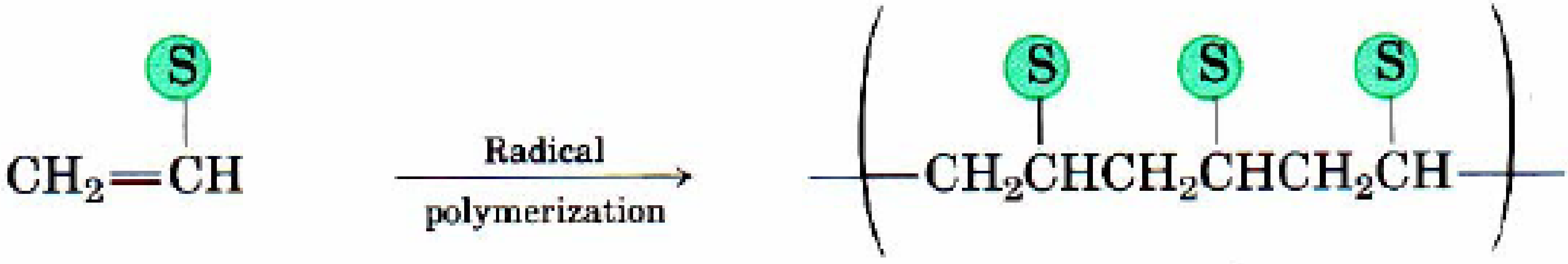
polyvinylchloride



polymethylmethacrylate

Polymerisation processes: Chain Growth

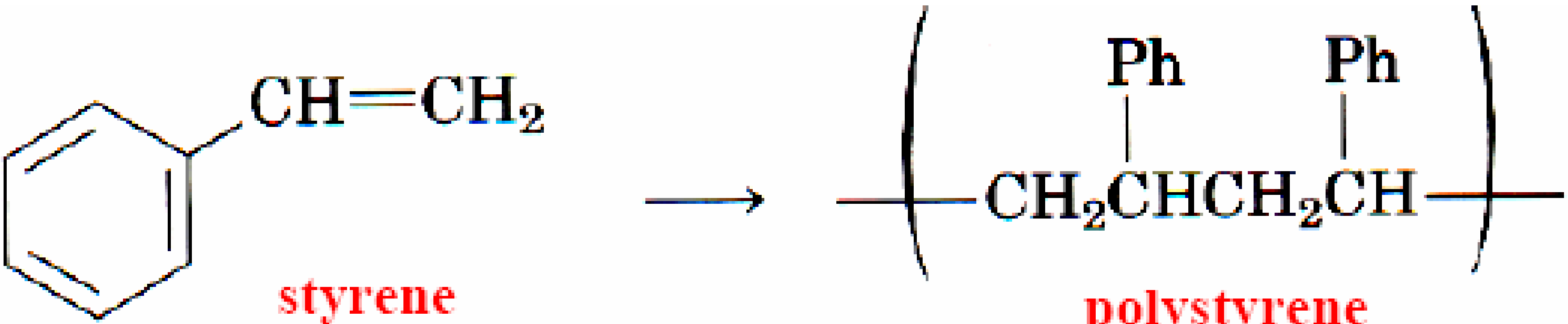
- non-symmetrical alkene monomers produce polymers with side-chain:



$$\mathrm{CH_2{=}\overset{\overset{S}{|}}{C}H} \xrightarrow[\text{polymerization}]{\text{Radical}} \left(\mathrm{CH_2\overset{\overset{S}{|}}{C}HCH_2\overset{\overset{S}{|}}{C}HCH_2\overset{\overset{S}{|}}{C}H}\right)$$

Monomer **Polymer**

- substituent groups are on alternating carbon atoms of chain e.g.



styrene **polystyrene**

-every other carbon of the backbone bears a phenyl (C_6H_5) group

L-37 Thermosetting & Thermoplastic Polymers

Examples for Thermoplastic resins

Polyvinyl Chloride (PVC):

- Vinyl chloride undergo polymerization to give PVC.

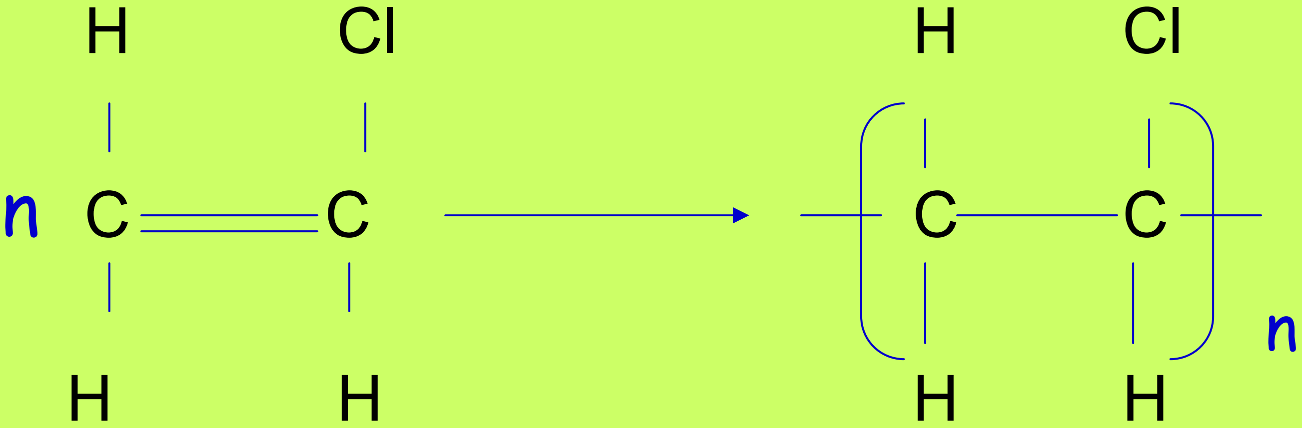
PVC is obtained by

- heating a water – **emulsion of vinyl chloride**
- in presence of a small amount of
- **benzyl peroxide or hydrogen peroxide**
- in an autoclave under pressure.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Polyvinyl chloride (PVC)

- **Preparation :**PVC is obtained by a heating a water emulsion of vinyl chloride in presence of a small amount of benzyl peroxide or hydrogen peroxide.



$$n\,\mathrm{CH_2{=}CHCl} \longrightarrow \left(\mathrm{CH_2{-}CHCl}\right)_n$$

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Properties

It is colourless, odourless & non inflammable

It is resistant to light, flame, & chemicals.

It is rigid, stiff but brittle.

It is insoluble in common solvents.

Uses

It is used for making pipes for drainage, making bottles, raincoats, ladies handbags, refrigerator components.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **PVC is of two types:**
- Plasticized PVC
- Un Plasticized PVC or Rigid PVC
- **Properties:**
  - PVC is colourless, odourless & non inflammable.
  - PVC is resistant to light, to flame & to chemicals.
  - Highly rigid, stiff but also brittle.
  - It is insoluble in common solvents.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **Applications: Rigid or unplasticized PVC:**

Superior chemical resistance, high rigidity but brittle

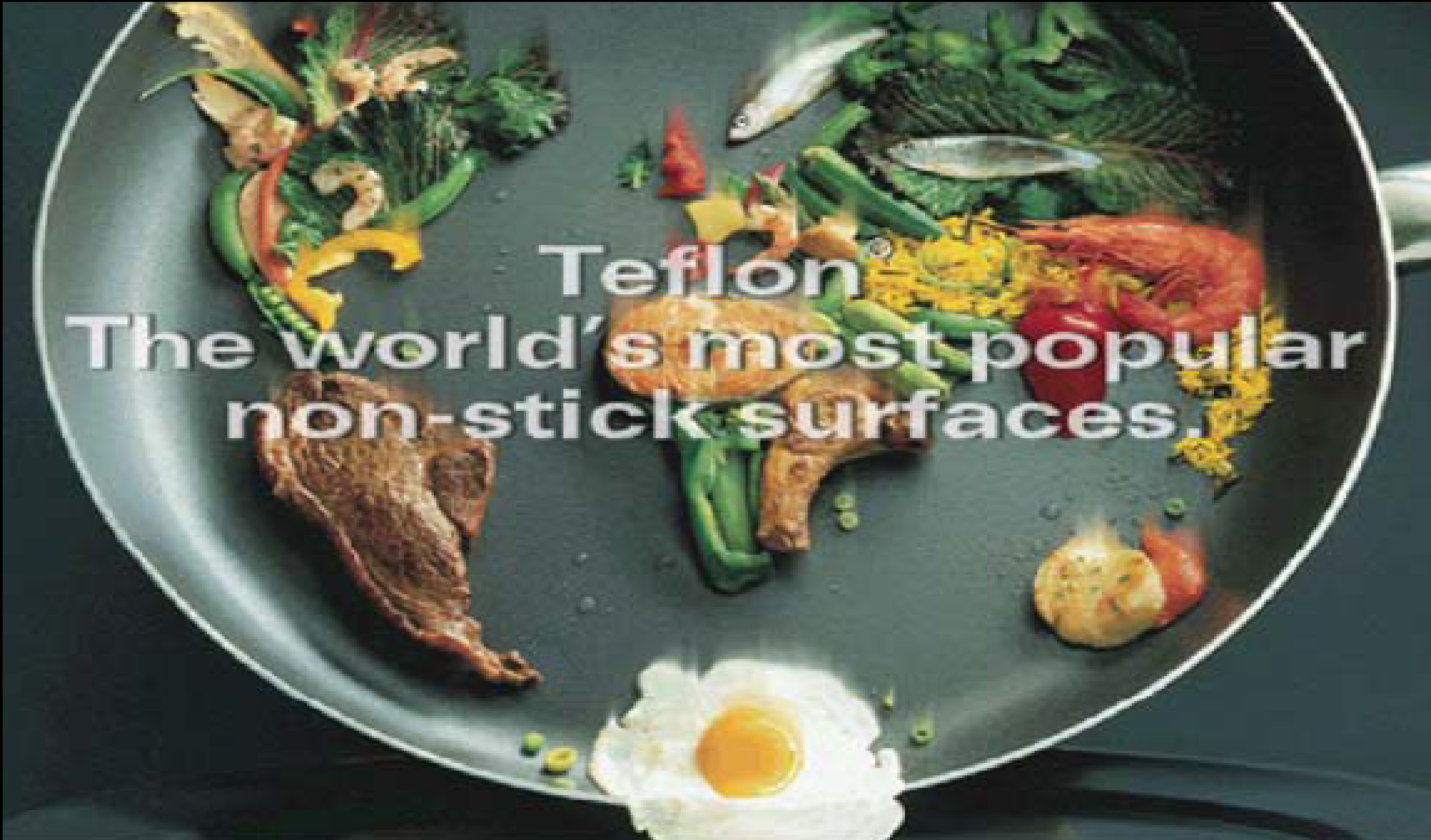
1. It is used for making pipes for drainage & guttering.
2. It is used for making sheets used for light fittings, safety helmets, refrigerator components.
3. Tyres, cycle and motorcycle mudguards.
4. Used to prepare bottles, ladies hand bags.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **plasticized PVC:**
- It is obtained by adding plasticizers such as di-butyl phthalate, tri-oxylphosphate di-octyl phthalate etc.
  - It is used for covering electric cables.
  - plastic rain wear, table cloths & curtains.
  - Toys, tool handles. PVC pipes,
  - PVC, thermal insulating foam
  - Conveyor belts used in coal mines.

Polymerisation processes: Chain Growth

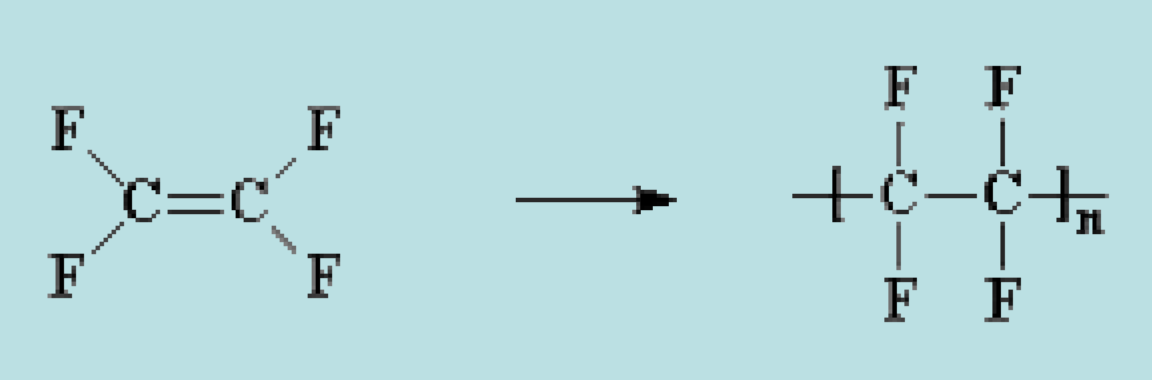
- PTFE is used to coat 'non-stick' frying pans:



L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Polytetra fluoro ethylene (PTFE):- (Teflon)

- **Preparation:** Teflon is prepared by the polymerisation of tetra fuoroethylene under pressure in the presence of benzoyl peroxide as catalyst



polytetraflouroethylene

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **Properties:**
- Due to highly_electronegative F atoms very strong attractive forces exist between the chains .
- giving extreme toughness, high softening points(350^{0}C)
- high chemical resistance to all chemicals except hot alkali and hot fluorine.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **Properties:**
- High density(2.1 to 2.3 g/cm^{-3}) waxy touch & non adhesive.
- High density & low co-efficient friction.
- Excellent toughness & heat resistance.
- Disadvantage: it cannot exist in a true molten state.

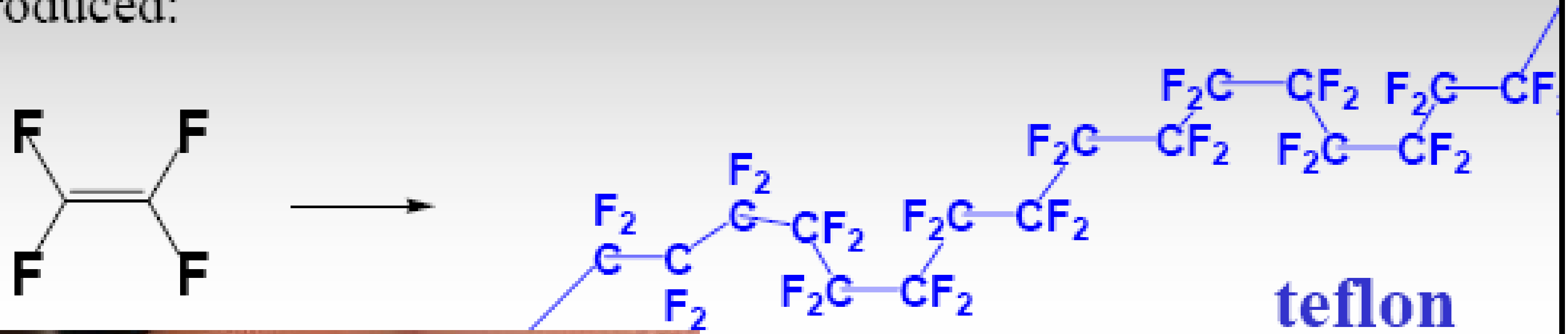
L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **Applications:**
- For insulating motors, cables, transformers wires etc.
- For non-stick utensils like frying pans.

- For coating glass fibres asbestos fibres and cloths
- Non-lubricating bearings, making gaskets, pump parts, pipes, tubing etc.
- Insulators for motors, generators.

Polymerisation: Chain Growth by Addition Reaction (p. 1040)

- when tetrafluoroethylene is used as monomer PTFE or *teflon* is produced:



teflon

-very chemically inert

(strong C-F bond)

-very smooth

(low friction surface)

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon 6:6

- **Nylon:- Preparation:**

  Synthetic fibre forming **polyamide** are termed as nylons. Nylons are of different type.

- **Nylon 6:6**
- Nylon 6:6 is obtained by the polymerization of **adipic acid with hexamethylene diamine.**

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon 6:6

Nylon 6:6

- Nylon 6:6 is obtained by the polymerization of **adipic acid with hexamethylene diamine.**
- The chain length depends on the time & temp. at which the condensation proceeds.
- The number 6 & 6 refers to **no. of carbons contributed by the diamine & the dicarboxylie acid respectively.**

Nylon -6,6

- **Preparation**
- Nylon 6,6 is obtained by the polymerisation of adipic acid with **hexamethylene diamine**.

$$n\ H_2N\text{-}(CH_2)_6\text{-}NH_2 + n\ COOH\text{-}(CH_2)_4\text{-}COOH$$

$$\downarrow$$

$$-\left(HN\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-} \right)_n + 2nH_2O$$

- **Properties**
- It is a linear polymer having strength, elasticity, toughness & abrassion resistance.
- It is highly resistant to moisture

Uses

- It is used to make ropes, elastic hosiery & carpets.
- It is used in textile industry
- It is used to prepare brushes, films, bearings etc.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **Properties:**

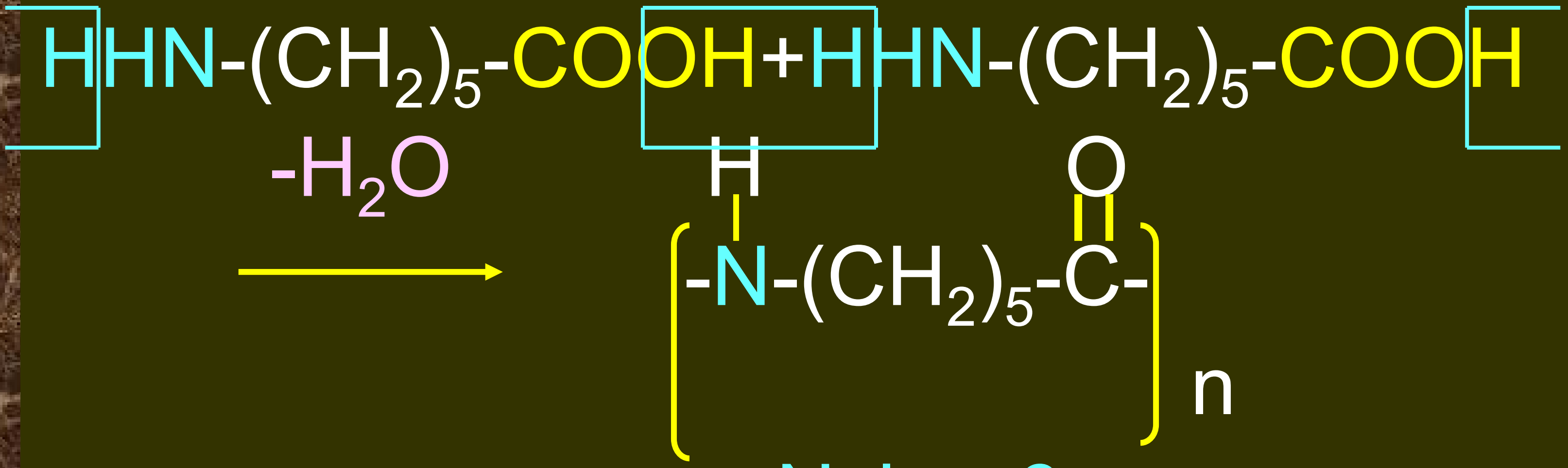
- it is a linear polymer having high strength elasticity, toughness & abrasion resistance.
- Melting point is 264^0 C.
- Moisture resistance

Uses: In making ropes

- It is used to make elastic hosiery & carpets.
- It is also used for jacketing electric wires.
- It is used in textile industry.
- Used to prepare brushes, films & gears.

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

- **Nylon 6:** It can be made either by self condensation of
- є-amino caproic acid or by
- ring opening polymerization of caprolactm.



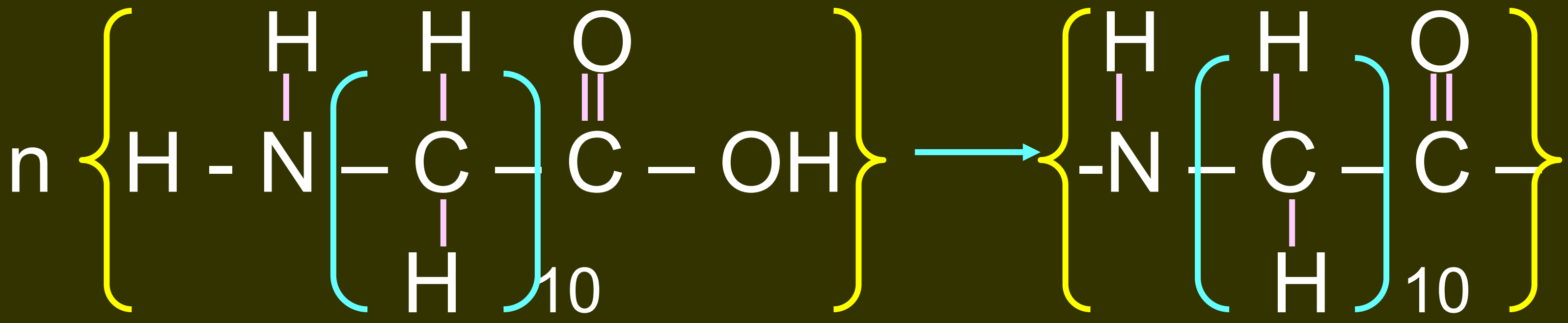
$$\boxed{H}HN\text{-}(CH_2)_5\text{-}CO\boxed{OH+H}HN\text{-}(CH_2)_5\text{-}COO\boxed{H}$$

$$\xrightarrow{-H_2O} \left[-\overset{H}{\overset{|}{N}}\text{-}(CH_2)_5\text{-}\overset{O}{\overset{\|}{C}}- \right]_n$$

Nylon-6

L-38 Preparation & Properties of PE, Teflon, PVC, Nylon

Nylon 11: It is made by self condensation reaction of ω-amino undecanoic acid.



$$n\left\{ H-\overset{H}{\overset{|}{N}}-\left(\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}\right)_{10}-\overset{O}{\overset{\|}{C}}-OH \right\} \longrightarrow \left\{ -\overset{H}{\overset{|}{N}}-\left(\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}\right)_{10}-\overset{O}{\overset{\|}{C}}- \right\}$$

ω-amino undecanoic acid.

Nylon-11

L-38 Preparation & Properties of PE,Teflon, PVC, Nylon

- **Application of Nylon:**
- Nylon 11 is used for making flexible tubing.
- Nylon 6,6 is used in mechanical engineering.
- Nylon 6, is suitable for monofilament which are used for bristles, brushes etc.
- Nylon 6 is also used for making tyre cords.

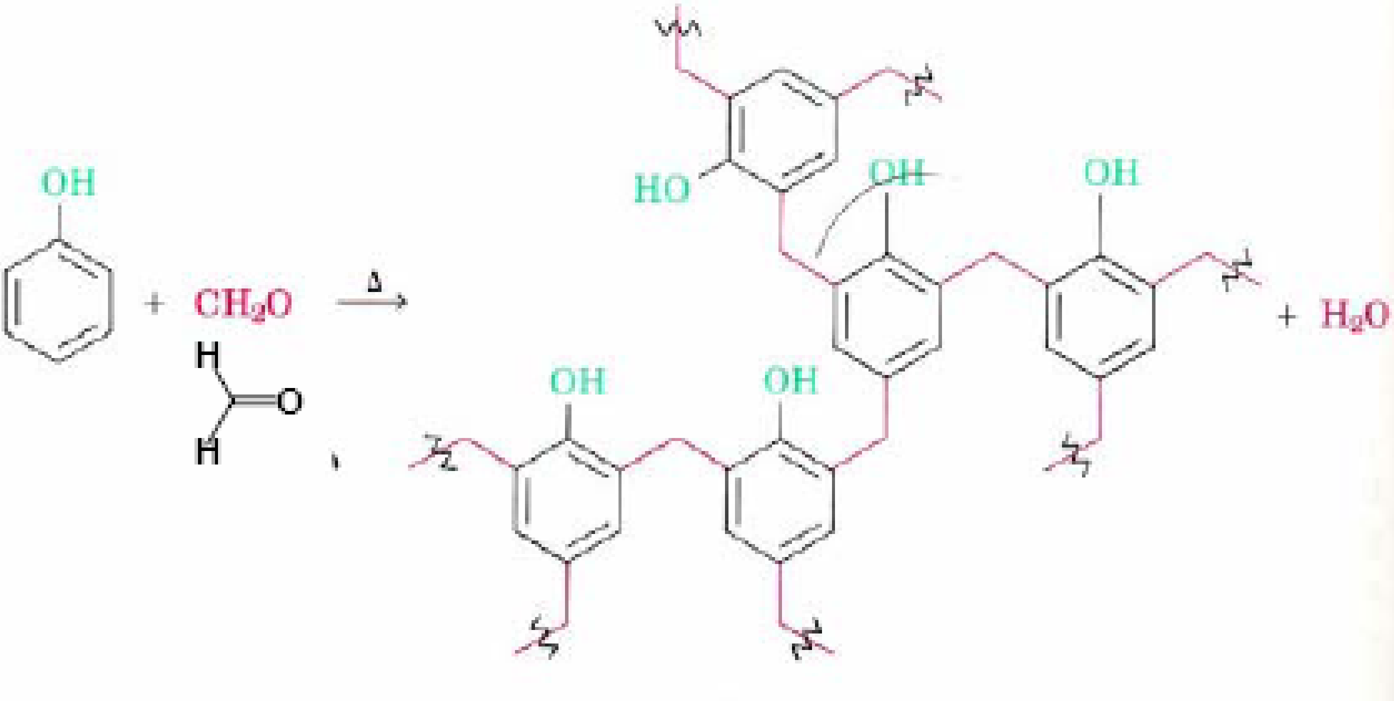
The first synthetic polymer?

-in 1907 Leo Baekeland heated formaldehyde and phenol

⇒ rapid solid residue formed - WHY?

-two compounds polymerised

-long chains of alternating PhOH and CH_2 units formed in three dimensions



Bakelite

⇒ Bakelite - brittle resin, poor physical properties

(5) Bakelite :(Thermosetting resin) Phenolic resin

This is formed by **condensation t of phenol & formaldehyde** also known as

phenol formaldehyde resins (PF resins)

Phenol, formaldehyde may not be in same proportions in these phenolic resins.

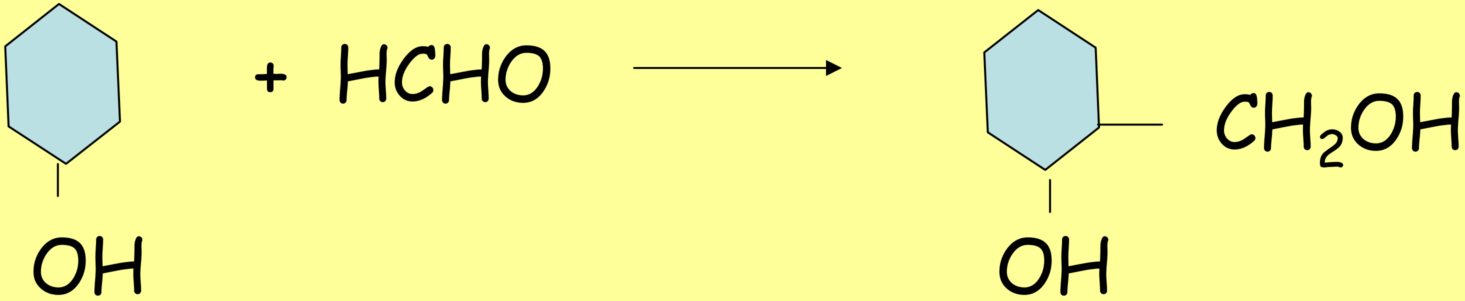
The ratio can more than one or less than one.

- **Phenol formaldehyde ratio will effect the product.**

Bakelite

- **Preparation**

This is formed by the condensation of phenol and formaldehyde



(5) Bakelite :(Thermosetting resin)
NOVOLAC & RESOLE

1. Novalac

If phenol formaldehyde **ratio is greater than 1** it will result in

- **Novalac** formation in the **presence of acid.**
- This is a linear low polymer called **Novolac.**

2. Resole.

If phenol formaldehyde **is less than 1 in alkaline media** will result into linear called **Resole.**

(5) Bakelite :(Thermosetting resin) Phenolic resin

If phenol formaldehyde is **less than 1 in alkaline media** will result into linear called **Resole.**

Here formaldehyde will be in excess.

- This **Novolac Resole** under some process fuse to form Bakelite independently.
- **Bakelite is a thermosetting resin** which is a cross link ?(net) structure--> which is a very hard polymer.

Properties

It is resistant to electricity moisture & chemicals

It is very hard, rigid, scratch resistant & strong material.

They are usually dark coloured

Uses

Used in electric field used as **T.V parts,ion exchage resins**, used in decorative & varnishes' preparation

Properties

- It is resistant to electricity, moisture & chemicals.
- It is very hard, rigid & strong materials.
- It is scratch resistor.
- They are usually **dark coloured (pinkish brown)**
- Low molecular weight grades have good bonding strength
- Good adhesive

Uses:-

- These are used in electric field, in automobiles, radio T.V. parts.
- Production of ion exchange resins.
- Electric insulator production.
- Decorative & varnishes preparation.

Rubber

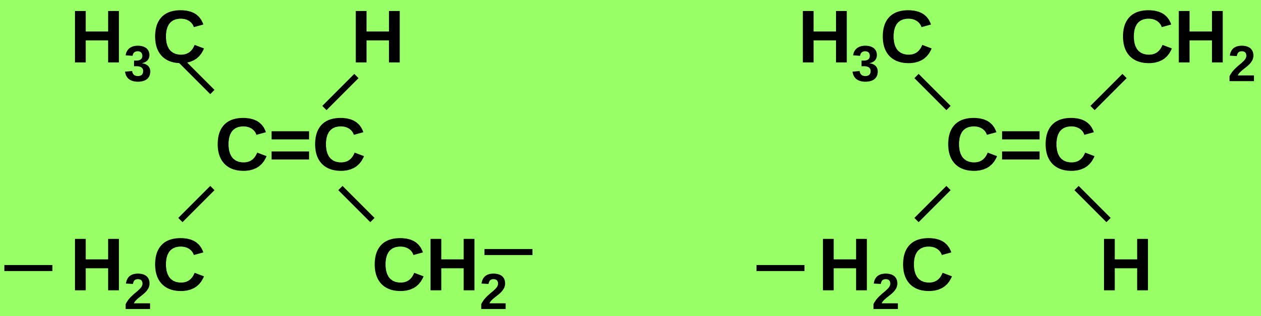
- Natural rubber –cis & trans form
- Structure
- Isolation
- Vulcanization

RUBBER:-

- It is one of naturally occurring polymer which has elastic properties in excess of 300%.
- That is why rubber band can be stretched to nearly 4 times of their original strength.
- Rubber is of two types-
- **(1) Natural (2) Synthetic**

Rubber

- It consist of basic material latex, which is a **dispersion of isoprene.**
- **Natural rubber** is cis-configuration & trans – form is **Guttapercha.**



- Cis [natural rubber] Trans (**Guttapercha).**

Natural rubber:

- The main source of Natural rubber is the sap of tree called ***havea brasiliians*** and ***gauyule.***
- Found in countries like India, Malaysia , Indonesia, Ceylon etc.
- It consists of **basic material latex**, which is a dispersion.

Natural rubber:

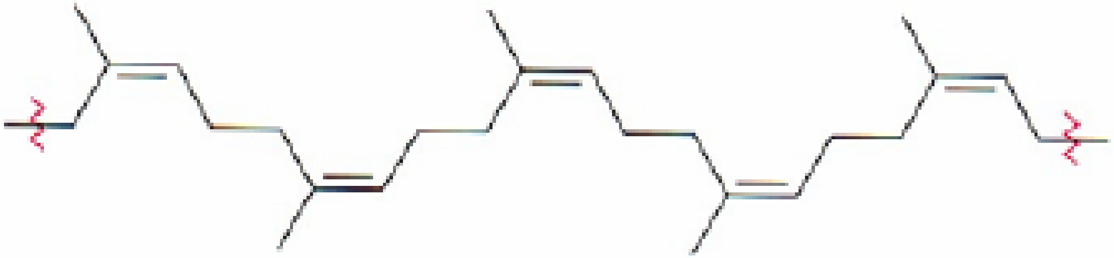
- Natural rubber is a cis-configuration.
- Due to this cis-configuration about the double bonds, the chains do not fit together well.
- Hence there are **only weak Vander waal’s forces**

Natural rubber:

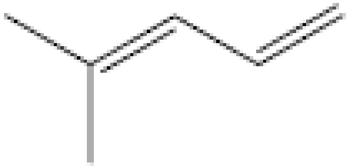
- **Isolation or extraction from latex:-**
- To extract rubber from latex at first a groove is cut around the tree & collect latex in a pot.
- Latex is a milky suspension containing
- 2-40% rubber, while the remainder is made up of
- mainly water & small quantities of protein & resinous material.

Rubber: a natural hydrocarbon homopolymer (p. 1042)

-natural rubber is an elastomer - *cis* double bonds lead to poor packing ⇒ non crystalline



natural rubber (cis)



(isoprene building block)

-latex is a suspension of rubber particles in water

collecting latex in Ko Kradan

-equivalent *trans* polymer is crystalline, hard, non-elastic solid

Gutta Percha (trans)

Natural rubber:

- **Isolation or extraction from latex:-**
- When we cut the bark (tree), some **gummy liquid called latex** . This process is called **tapping**.
- This can be done once in every six months. Latex contains
- **60% water, 35% hydrocarbons, proteins,**
- **enzymes & numeric acid,**
- **3% fatty acids,**
- **0.5% inorganic salts & 1% esters.**

Natural rubber:

- **Isolation or extraction from latex:-**
- To obtain rubber from latex following steps are used.
- (1) Seiving (2) Dilution (3) Coagulation

(1) Seiving:- It is the first step, in this step latex is pass through a sieve, due to the bigger impurities like leaves, bark, dirt etc., can be easily be removed.

Natural rubber:

- **Isolation or extraction from latex:-**
- **(2) Dilution:-** latex is diluted to about 15-20% rubber then stained (filtered) again.
- **(3) Coagulation:-**For this, a small amount of NH_3 is added as a preservative to the latex,
- then it is co-agulated by the addition of
- 5% solution of acetic acid or formic acid of 90% strength. The co-agulum is washed & dried.

Isolation of rubber

Diluted latex

↓ Acetic acid

Mixture

↓

Coagulation

↓ Passed through rollers

Sheet of rubber

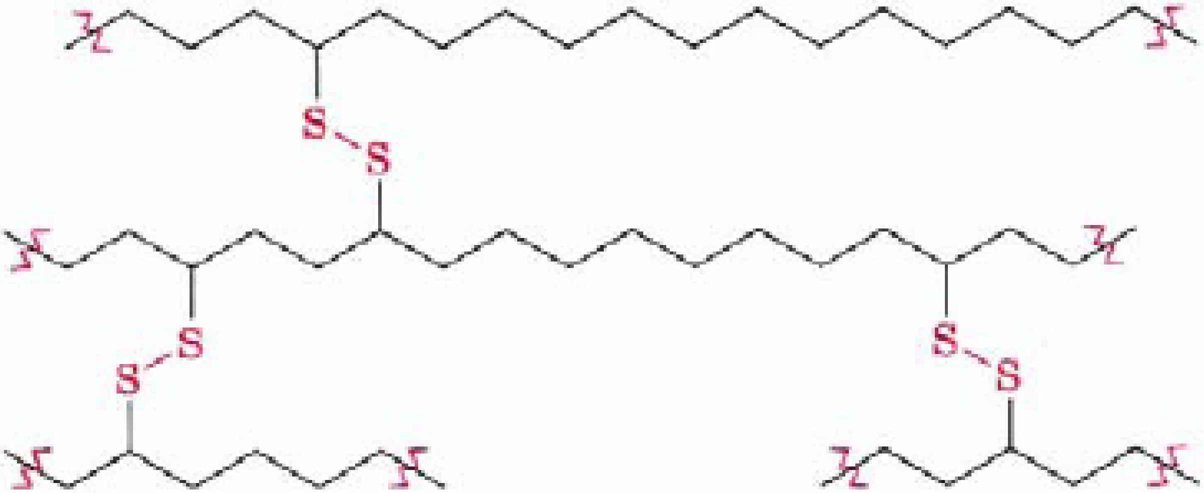
↓ Hanged in smoke house

Smoked rubber

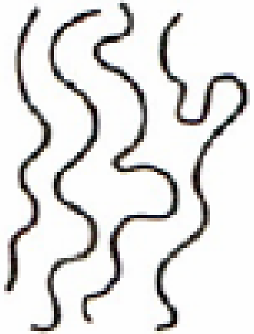
Rubber and Vulcanisation

-if natural rubber is treated with hot sulphur, becomes vulcanised: many extra disulphide cross links form between chains

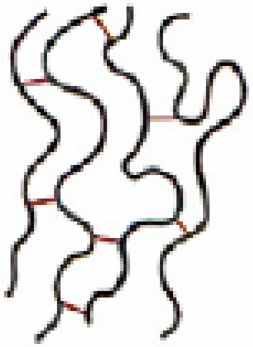
⇒ rubber still elastic but becomes much harder, resistant to wear and abrasion ⇒ car tyres



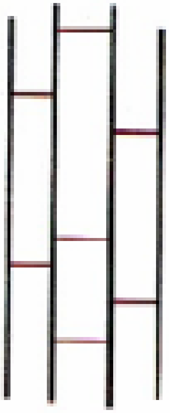
Sulfur cross-linked chains resulting from vulcanization of rubber.



no crosslinks



elastomer



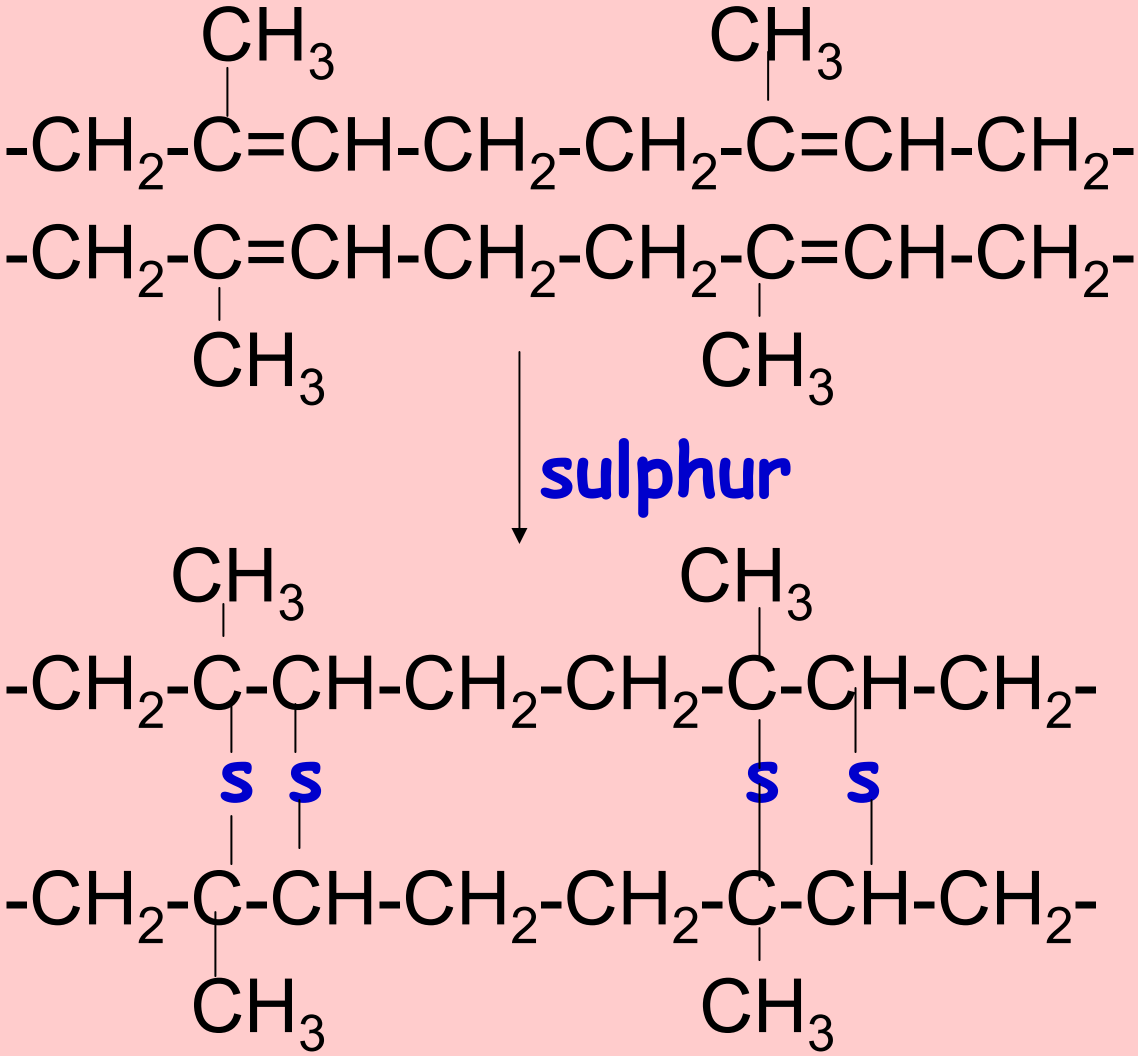
vulcanised elastomer

Vulcanization

- **Introduction of sulphur to the natural rubber is called vulcanization**

- Stiffness of rubber depends on the quantity of sulphur.

- Vulcanization results in the crosslinking.



$$\begin{array}{l}
-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH-CH_2- \\
-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-
\end{array}$$

$$\Big\downarrow \textbf{sulphur}$$

$$\begin{array}{l}
-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}-CH-CH_2-CH_2-\overset{\displaystyle CH_3}{\overset{|}{C}}-CH-CH_2- \\
\quad\quad\quad\;\; | \quad\;\; | \quad\quad\quad\quad\quad\quad\quad\quad\quad\;\; | \quad\;\; | \\
\quad\quad\quad\;\; S \quad\; S \quad\quad\quad\quad\quad\quad\quad\quad\quad\; S \quad\; S \\
\quad\quad\quad\;\; | \quad\;\; | \quad\quad\quad\quad\quad\quad\quad\quad\quad\;\; | \quad\;\; | \\
-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}-CH-CH_2-
\end{array}$$

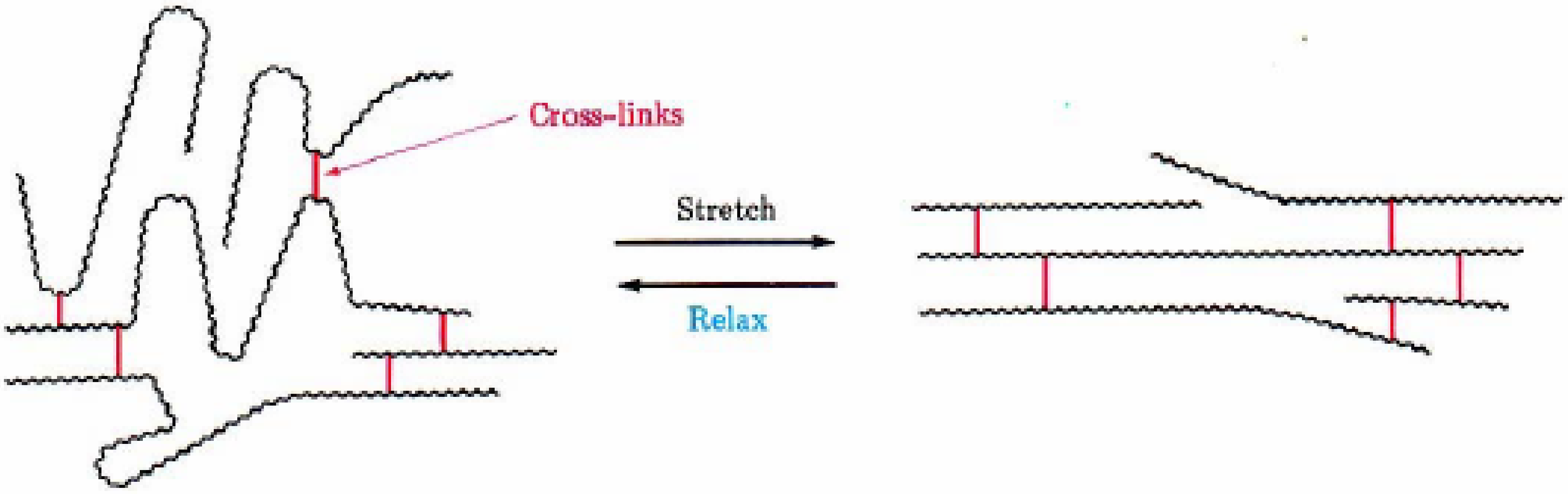
Elastomers: Synthetic rubber:

- **Elastomers:**
- An elastomer is **vulcanizable man made rubber like polymer,** which can be streched to at least twice its length, but it returns to its original shape.
- **Synthetic rubber:**
- styrene rubber or **Buna – S or (GR-S)** (styrene buta rubber)
- nitrile rubber **(GR-A) (Buna – N)**
- neoprene or polychloroprene or (GR-M)

Elastomers

-sometimes, there are bridges between polymer chains: *crosslinks*

-when force is applied (e.g. stretching) to an amorphous (i.e. no crystallites) polymer containing occasional cross-links layers can slide past each other

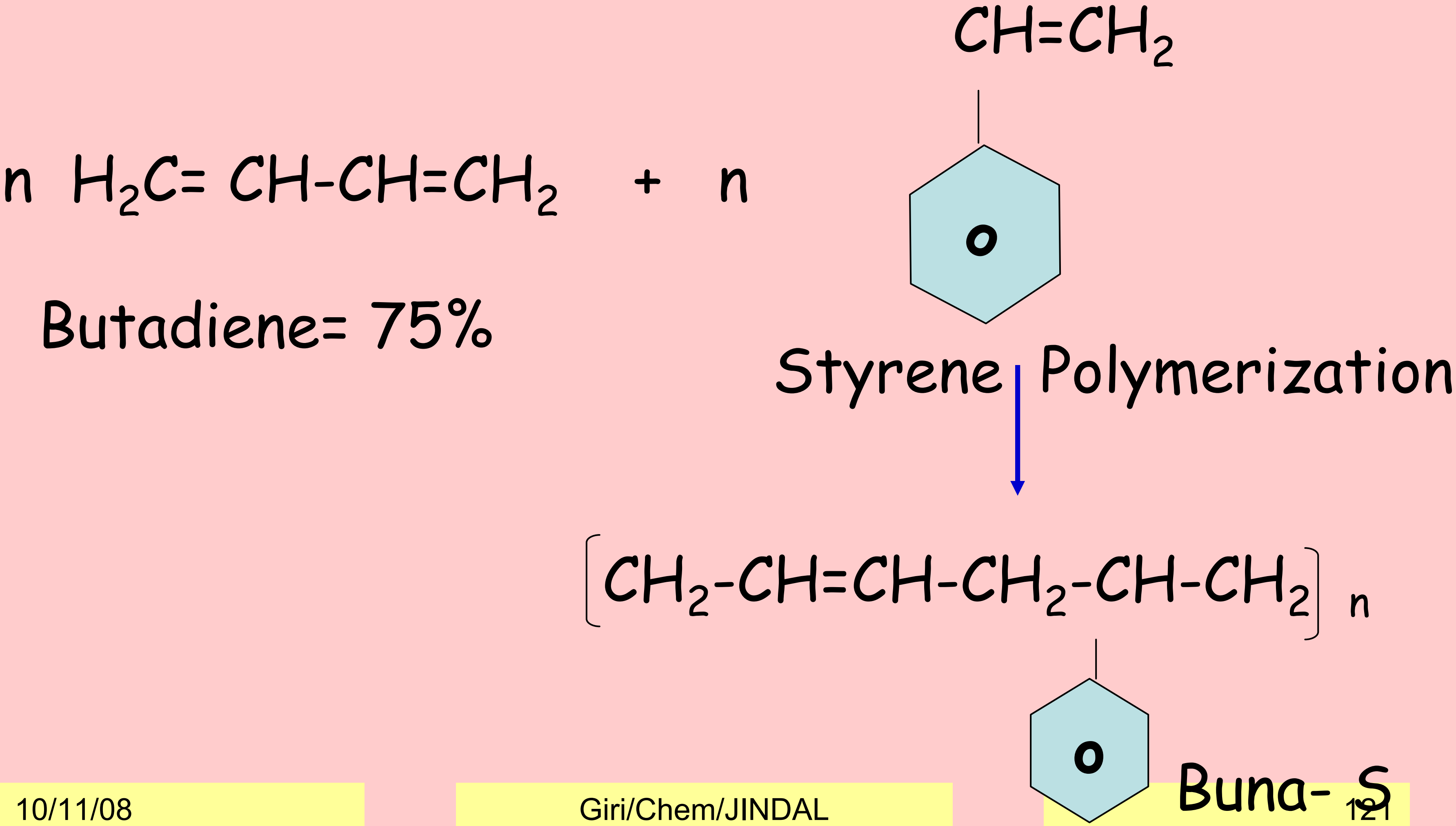


-BUT crosslinks ensure solid springs back to original form - the solid is an *elastomer*

styrene rubber or Buna – S or (GR-S) (styrene buta rubber):-

- Buna – S is a co-polymer of about 75% butadiene & 25% styrene.
- The two components above are allowed to react in a mixing vessel containing an emulsifying agent.
- Initiators like H_2O_2 are used in the presence of anti – freeze, to produce cold SBR or “Cold rubber”

STYRENE RUBBER (GR-S)OR BUNA-S Or AMERIPOL:



$n\ H_2C{=}\ CH{-}CH{=}CH_2 \quad + \quad n$

Butadiene= 75%

Styrene

Polymerization

$$\left[CH_2{-}CH{=}CH{-}CH_2{-}CH{-}CH_2 \right]_n$$

Buna- S

styrene rubber or Buna – S or (GR-S) (styrene buta rubber):-

- **Properties:**
- Buna-s resembles natural rubber.
  - it gets oxidized readily in oils & solvents.
  - It can be vulcanized same as natural rubber; but it requires less amount of sulphur.
- **Uses:-**
- Useful for lighter tyres, molded goods.
- Unvulcanized sheet, rubber, flooring & for electrical insulations

Properties:

Buna- S resembles natural rubber.

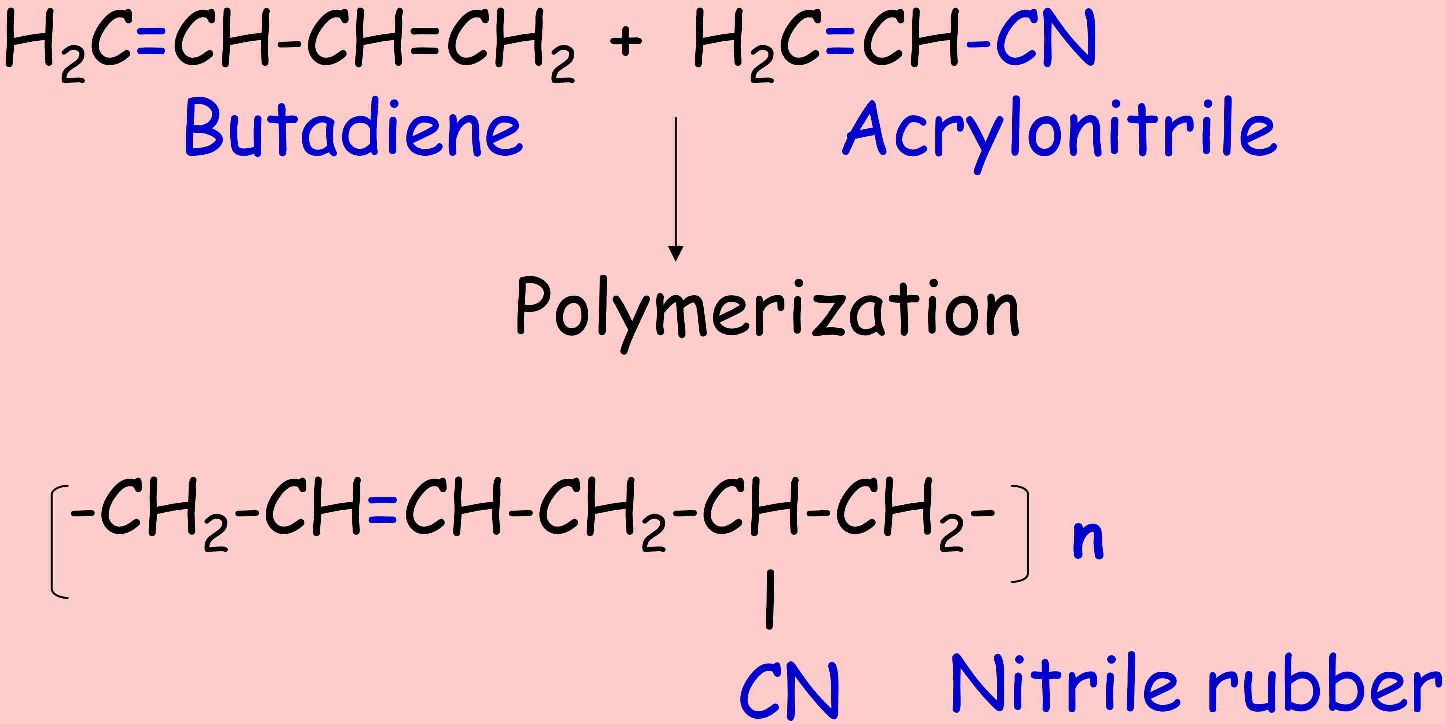
- It gets oxidized readily on oils and solvent.
- It can be vulcanized.

Uses:

- This is useful for lighter duty tires, hoses, molded goods.
- Useful for unvulcanized sheet, gum, flooring, rubber shoe soles and for electric insulations.

NITRILE RUBBER (GR-A) OR BUNA-N:

It is a copolymer of butadiene and acrylonitrile. The technique of emulsion polymerization is used for the synthesis.



$H_2C{=}CH{-}CH{=}CH_2 + H_2C{=}CH{-}CN$

Butadiene Acrylonitrile

$\downarrow$

Polymerization

$$\left[-CH_2-CH=CH-CH_2-\underset{\displaystyle CN}{\underset{|}{CH}}-CH_2- \right]_n$$

Nitrile rubber

Properties:

- These rubbers have good heat resistance.
- These rubbers have low swelling, low solubility, good tensile strength even after immersion in gasoline or oils.

Uses :

- They are used in the form of latex.
- They are used to make printing rollers and automobile parts.
- They are used as adhesives for fuel tanks.

- **Schematic representation of coiled elastomers chain of natural rubber (poly isoprene)**

- **Gutta percha & Balata rubber**
- This is obtained from the mature leaves of the trees knows as Dichopsis gutta & Palaguim gutta. These leaves are treated with water at 700 C ½ an hour & then dropped into cold water. Then this Gutta purcha rubber will float on the water & can be collected.
- It is very tough, it burns at 1000C.
- Gutta purcha rubber is a trans form of rubber.

- Trans- polymer of isoprene
- (Gutta – percha rubber)
- **Cis rubberTrans rubber** Obtained from Havea brasilensis Obtained from Gutta tree It is prepared from cutting the tree It is prepared from mature leaves of plants Mostly formed in North America Mostly formed in Sumatra & MalayaIt is cis form of isoprene It is the trans form of isoprene

- **(Buna -N) Nitrile rubber (GR-A), General rubber Acrylonitraile:**
- It is co-polymer of butadiene & acrylonitrile.
- The technique of emulsion polymerization is used for the synthesis.
- **Properties:**
- These rubber have swelling, low solubility, good tensile strength & abrasion even after immersion in gasoline or oils.
- Rubbers have good heat resistance.

- **Uses:-**
- Used as adhesives for fuel tanks gasoline hoses.
- They are used to make printing rollers, oil resistant & automobileparts.
- **Butyl rubber (GR-I):-** It is a co-polymer having 98% isobutylene & nearly 2% butadiene
- **Catalyst:** $AlCl_3$ anhydrous + CH_3Cl

- **Properties:** Low permeability to air & other gases.
- Under normal conditions butyl rubber is amorphous.
- Resistant to heat, chemicals & poler solvents & also to ozone layer.
- Good elutrical insulator.
- **Uses:** It is used as inner tubes.
- Used in the preparation of automobile parts, belts & tyres.
- Cable insulator

- (4) **Neoprene:** It is a co-polymer of chloroprene.
- Chloroprene is obtained by dimerisation of acetylene to vinyl acetylene followed by HCl.
- **Properties:** It possess high tensile strength
- Resistant to peroleum oils & gaso line
- **Uses:** Linings of oil tasks
- Wire insulations & gaskets are prepared.

- **Vulcanization:** To improve the properties of rubber charles Good year (1839) discovered a process called vulcanization.
- This is the process where some compound especially ”sulphur” is heated along with rubber, it will be added to the rubber the product will become more & more stiff
- When charles scientist heated sulphur along with rubber, the tensile strength, elasticity & resistance to swelling are increased very much. This introduction of sulphur to the natural rubber is called vulcanization.

- In vulcanization sulphur is introduced to make the rubber more stiff at 1100 -1400C.
- Linear polymer (natural rubber) will result in cross – link polymer which is very rigid (vulcanized rubber)
- This stiffness depends on the sulphur quantity.
- Tyre rubber contains 3-5% sulphur.
- Battery case contains 30% sulphur.

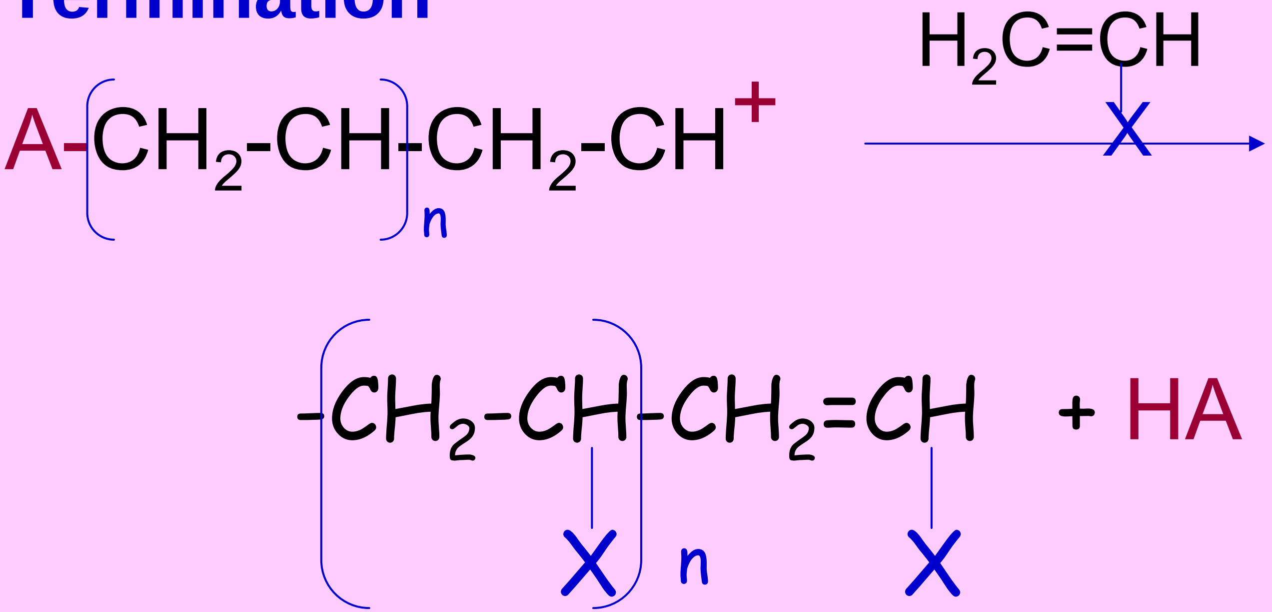
- Vulcanization can be carried out in several ways-
  - The article is immersed in hot water under pressure.
  - The article to be Vulcanized are heated with steam under in fire house.
  - By heating in fire house.
  - By heating in air or CO2.
    - Ordinary soft vulcanized rubber is 1-5% sulpher, heard rubber 40-46% of sulpher

- **Properties:** It has good tensile strength & can bear a load of 2000 kg/cm2 before it breaks.
- Water resistance is improved.
- Has higher resistance to oxidation & to abrasion.
- It is very easy to shape.
- It has useful working temperature range - 400 C to 1000 C

- **Uses:-** Manufacture of tyres, gaskwets.
- Rubber threads are used to shock absorber cords heat bands for spects , helmets, golf balls etc.
- **Smoked rubber:** when latex is mixed with acetie acid in along task. It should be kept constant for 15-16 hrs.
- The product is passed through rollers by continuous water spray.
- These shuts are subjected to smoke treatment for 4 days at 600 C
- The coloured rubber is obtained called smoked rubber.

Anionic Polymerisation

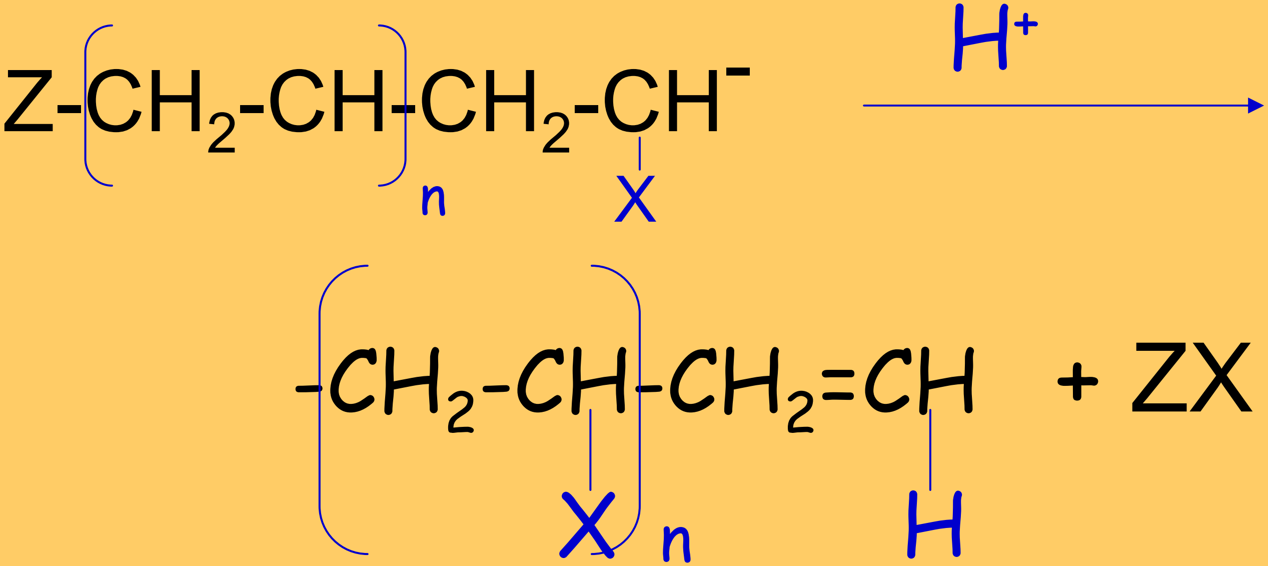
Termination



$$A-\left(CH_2-CH\right)_n-CH_2-CH^{+} \xrightarrow{H_2C=\underset{X}{CH}} -\left(CH_2-\underset{X}{CH}\right)_n-CH_2=\underset{X}{CH} + HA$$

Anionic Polymerisation

Termination



$$Z\text{-}\left[CH_2\text{-}CH\right]_n\text{-}CH_2\text{-}\underset{X}{CH^-} \xrightarrow{H^+} \text{-}\left[CH_2\text{-}\underset{X}{CH}\right]_n\text{-}CH_2=\underset{H}{CH} + ZX$$