US05CCHE21

UNIT III

DIENES & MACROMOLECULES

[Compiled by Dr M M Moreker, V P Science College, 2020]

INTRODUCTION :

Monomer:

The molecule, group (or compound) from which a dimer, trimer or polymer is formed is known as monomer.

OR

Any compound from which polymers are made is known as monomer.

e.g. $CH_2 = CH_2$ Ethene forms polyethene $—\left(CH_2 – CH_2 — \right)_n$

Dimer:

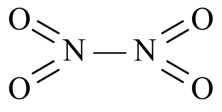
A compound (or molecule) formed by combination (or association) of two molecules of a monomer is known as dimmer.

e.g. Aluminum chloride is a dimer (Al_2Cl_6) in the vapour

OR

A molecule which is made up of two identical molecules (monomers) which are bonded together is known as dimer.

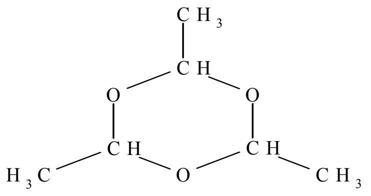
e.g.



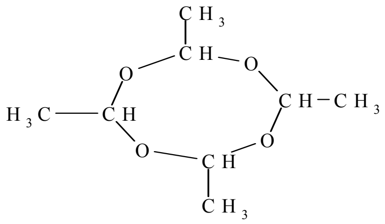
Dimer N_2O_4 as a dimer of NO_2

Trimer:

A molecule (or compound) formed by addition of three identical molecules are known as trimer.



Trimer of Ethanal



Tetramer of Ethanal

Polymer:

A large molecule in which one or more group of atoms (or monomers) is repeated is known as polymer.

e.g. – X – X – X – X – X – X – X – X OR – X – Y – X – Y – X – Y – X – Y

Polymerization:

The process in which one or more compounds react to form a polymer is known as polymerization.

DIENES : STRUCTURE AND PROPERTIES:

Dienes:

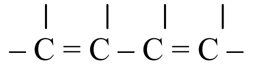
Alkenes which contain two carbons – carbon double bonds are known as Dienes.

The double bond in a diene has same properties as a double bond in alkene.

But in certain dienes, these properties are modified by the presence of second double bond.

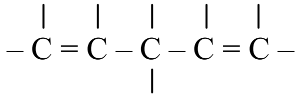
Classification of Dienes:

Dienes are divided into three classes according to the arrangement of the double bonds.



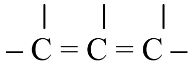
$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-$

Conjugated Double Bonds



$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-$

Isolated Double Bonds



$-\overset{|}{C}=\overset{|}{C}=\overset{|}{C}-$

Cumulated Double Bonds

$CH_2 = CH - CH = CH_2$
1, 4 – butadiene
A conjugated diene

$CH_2 = CH - CH_2 - CH = CH_2$
1,4 – pentadiene

$CH_3 - CH = C = CH_2$
1,2 – butadiene
An allene

- *Double bonds that alternate with single bonds are called conjugated diene*
- *Double bonds that are separated by more than one single bond are known as isolated diene.*
- *Double bonds that share a carbon are cumulated diene, and compounds are called allenes.*

The chemical properties of a diene depend upon this arrangement of its double bonds.

Conjugated dienes differ from simple alkene in four ways:

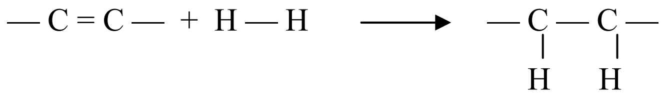
(a) They are more stable
(b) They are the preferred products of elimination
(c) They undergo 1,4 – addition, both electrophilic and free radical
(d) Towards free radical addition, they are more reactive.

Isolated double bonds exert little effect on each other, and hence each reacts as though it were the only double bond in the molecule.

Isolated and cumulated dienes consume large amounts of reagents.

Heat of hydrogenation:

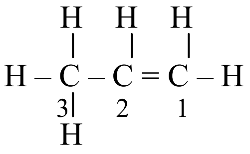
The quantity of heat evolved when one mole of an unsaturated compound is hydrogenated is called the heat of hydrogenation.

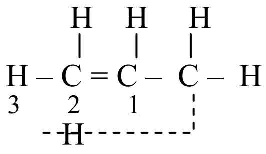


$$-C=C- \;+\; H-H \longrightarrow -\underset{\underset{H}{|}}{C}-\underset{\underset{H}{|}}{C}-$$

ΔH = heat of hydrogenation.

Hyper conjugation in propylene is represented by contribution from structures like II as shown below.





II

And two more equivalent structures

Due to hyper conjugation C_2–C_3 bond has some double bond character and C_1–C_2 bond has some single bond character in propylene.

Due to partial double bond character the carbon – carbon single bond in propylene is 1.50 A° for a pure single bond.

The greater number of alkyl groups attached to the doubly bonded carbon atoms, the greater the number of contributing structure likes II, the greater the delocalization of electrons and the more stable the alkene.

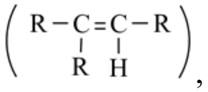
STABILITY OF CONJUGATED DIENES :

The values for heat of hydrogenation of alkenes as given below.

For Mono substituted alkenes ($R-CH=CH_2$) ,
heat of hydrogenation (ΔH) is Very close to 30 K Cal /mole

For Disubstituted alkenes ($R_2C=CH_2$) or ($R-CH=CH-R$) ,
heat of hydrogenation (ΔH) is 28 K Cal /mole

For Trisubstituted alkenes

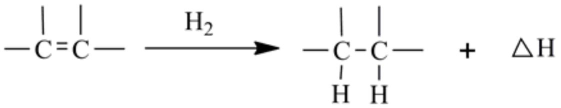


$$\left(R-\underset{\underset{R}{|}}{C}=\underset{\underset{H}{|}}{C}-R \right),$$

heat of hydrogenation (ΔH) is 27 K Cal /mole

Heat of hydrogenation (ΔH) :

The quantity of heat evolved when one mole of an unsaturated compound is hydrogenated is called the **heat of hydrogenation**, it is simply (ΔH) of the reaction.



Now, for compound which containing more than one double bond, we might expect a heat of hydrogenation that is the sum of the heats of hydrogenation of individual of individual double bonds.

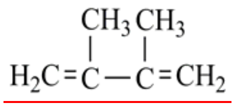
The values for heat of hydrogenation of conjugated diene are lower than expected.

Heat of hydrogenation of Dienes

Diene	**Heat of hydrogenation (ΔH)** **K Cal / mole**
1, 4 - Pentadiene	60.8
1, 5 - Hexadiene	60.5
1, 3 - Butadiene	57.1
1, 3 - Pentadiene	54.1
2 - Methyl - 1, 3 - Butadiene (Isoprene)	53.1
2 , 3 - Methyl - 1, 3 - Butadiene	53.9
1, 2 - Propanediene (Allene)	71.3

$CH_2 = CH - CH = CH - CH_3$
1, 3 - Pentadiene
ΔH Expected : 30 + 28 = 58 K Cal
Observed : 54.1

$CH_2 = CH - CH = CH_2$
1, 3 - Butadiene
ΔH Expected : 30 + 30 = 60 K Cal
Observed : 57.1



$$H_2C=\overset{\overset{\textstyle CH_3}{|}}{C}-\overset{\overset{\textstyle CH_3}{|}}{C}=CH_2$$

2 , 3 - Methyl - 1, 3 - Butadiene
ΔH Expected : 28 + 28 = 56 K Cal
Observed : 53.9

Heat of hydrogenation of 1, 4 - Pentadiene and 1, 5 - Hexadiene very close to
2 × 30 K Cal / mole or 60 K Cal / mole.

Non - Conjugated Dienes

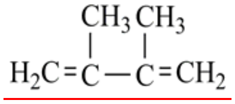
$CH_2 = CH - CH_2 - CH = CH_2$
1, 4 - Pentadiene
ΔH : 60.8 K Cal / mole

$CH_2 = CH - CH_2 - CH_2 - CH = CH_2$
1, 5 - Hexadiene
ΔH : 60.5 K Cal / mole

Conjugated Dienes

$CH_2 = CH - CH = CH_2$
1, 3 - Butadiene
ΔH Expected : 30 + 30 = 60 K Cal
Observed : 57.1
(3 K Cal lower)

$CH_2 = CH - CH = CH - CH_3$
1, 3 - Pentadiene
ΔH Expected : 30 + 28 = 58 K Cal
Observed : 54.1
(3.9 K Cal lower)



$H_2C = \overset{CH_3}{\overset{|}{C}} - \overset{CH_3}{\overset{|}{C}} = CH_2$

2 , 3 - Methyl - 1, 3 - Butadiene
ΔH Expected : 28 + 28 = 56 K Cal
Observed : 53.9
(2.1 K Cal lower)

Q. : 1, 3 - Pentadiene is more stable than the 1, 4 - Pentadiene. Explain it.

Upon hydrogenation 1, 3 - Pentadiene and 1, 4 - Pentadiene both consume two moles of hydrogen and yield the same product (n- Pentane) as given below.

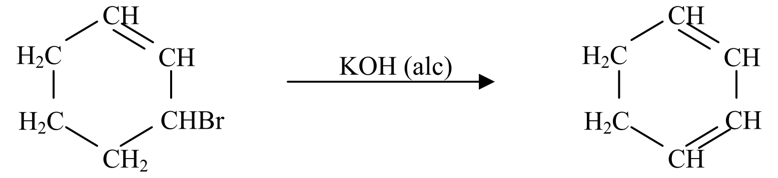
$CH_2 = CH - CH = CH - CH_3 \xrightarrow{2H_2} CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
1, 3 – Pentadiene → 1, 3 - Pentane
ΔH : 54.1 K Cal / mole

$CH_2 = CH - CH_2 - CH = CH_2 \xrightarrow{2H_2} CH_3 - CH_2 - CH_2 - CH_2 - CH_3$
1, 4 - Pentadiene → 1, 3 - Pentane
ΔH : 60.8 K Cal / mole

1, 3 - Pentadiene is conjugated diene and because of conjugation it evolves less energy than non-conjugated 1, 4 - Pentadiene , it can only means taht 1, 3 - Pentadienet contains less energy. Therefore, conjugated 1, 3 - Pentadiene is more stable than the nonconjugated 1, 4 - Pentadiene.

EASE OF FORMATION OF CONJUGATED DIENES:

The greater stability of conjugated dienes is reflected in their greater ease of formation. Where possible, they are the preferred diene products of elimination reactions. For example,

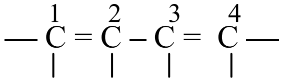


3 – Bromocyclohexene 1,3 – Cyclohexadiene

The most important diene, 1, 3 – butadiene (used to make rubber substitutes) is obtained industrially in very large amounts by the cracking of hydrocarbons.

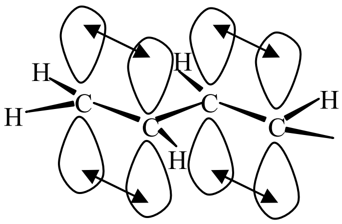
RESONANCE IN CONJUGATED DIENES:

In conjugated diene, carbon – carbon bonds are double in between C_1–C_2 and C_3–C_4 as given below.

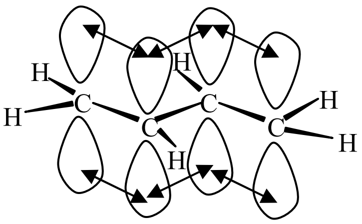


$$—\overset{1}{\underset{|}{C}} = \overset{2}{\underset{|}{C}} – \overset{3}{\underset{|}{C}} = \overset{4}{\underset{|}{C}}—$$

In above structure carbon – carbon double bonds (π bonds) are formed by overlap of the p – orbital of C–1 and C–2 and overlap of the p – orbital of C–3 and C–4. This p – orbital consists of two equal lobes, one lying above and the other lying below the plane of the other three orbital of each carbon as shown below in structure (a). this 4 π electrons delocalized and delocalization form a conjugated system as shown in structure (b) which makes the molecule more stable.

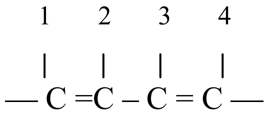


Overlap of p – orbitals to form two double bond



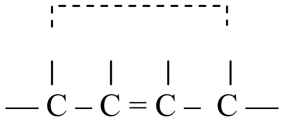
Overlap of p – orbitals to form conjugated system: delocalization of π electron

Due to delocalization of 4π electrons in conjugated diene resulted into resonance. Thus conjugated diene is a resonance hybrid of two structures I and II as shown below.



$$—\overset{1}{\overset{|}{C}} = \overset{2}{\overset{|}{C}} – \overset{3}{\overset{|}{C}} = \overset{4}{\overset{|}{C}}—$$

I



$$—\overset{|}{C} – \overset{|}{C} = \overset{|}{C} – \overset{|}{C}—$$

II

The dotted line is structure II represents a formal bond. It gives a certain double bond character to the $C_2 - C_3$ bond i.e. 1.48 A° as compared with 1.53 A° for a pure single bond in 1, 3 – butadiene formation of a double bond release energy and stabilized a system.

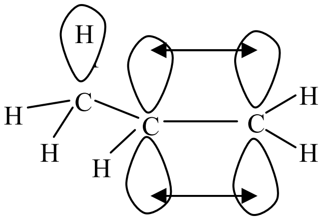
Resonance: *A molecule consists of two or more hybrid structures which differ only in arrangement of electrons than such structures are known as resonance.*

Resonance energy: *In a molecule an increase in stability due to resonance hybrid is known as resonance energy.*

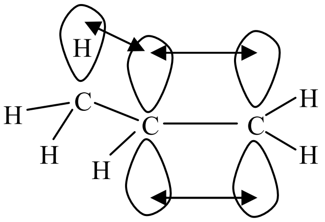
RESONANCE IN ALKENES: HYPER CONJUGATION:

Hyper conjugation:

In an allyl radical delocalization of electron through overlap between p – orbital occupied by the odd electron and 1 σ orbital of the alkyl group. Through this overlap individual electrons can bind together three nuclei, two carbons and one hydrogen. This kind of delocalization which involve σ bond orbital is known as hyper conjugation.



Propylene



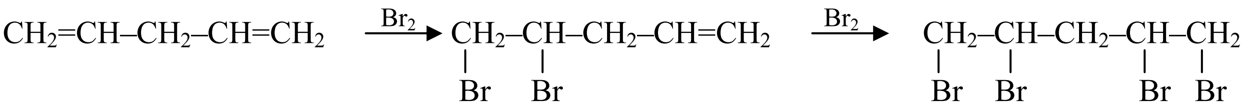
Hyper conjugation in propylene:
overlap between σ and π orbitals

Heats of hydrogenation showed that alkenes are stabilized by conjugation and also by the presence of alkyl group through hyper conjugation. The greater the number of alkyl groups attached to the doubly bonded carbon atoms, the more stable the alkene.

Heats of hydrogenation of propylene (30.1 kcal / mole) is 2.7 kcal lower than ethylene (32.8 kcal / mole) indicating that propylene is 2.7 kcal more stable than ethylene.

ELECTROPHILIC ADDITION TO CONJUGATED DIENES (1, 4 – ADDITION) :

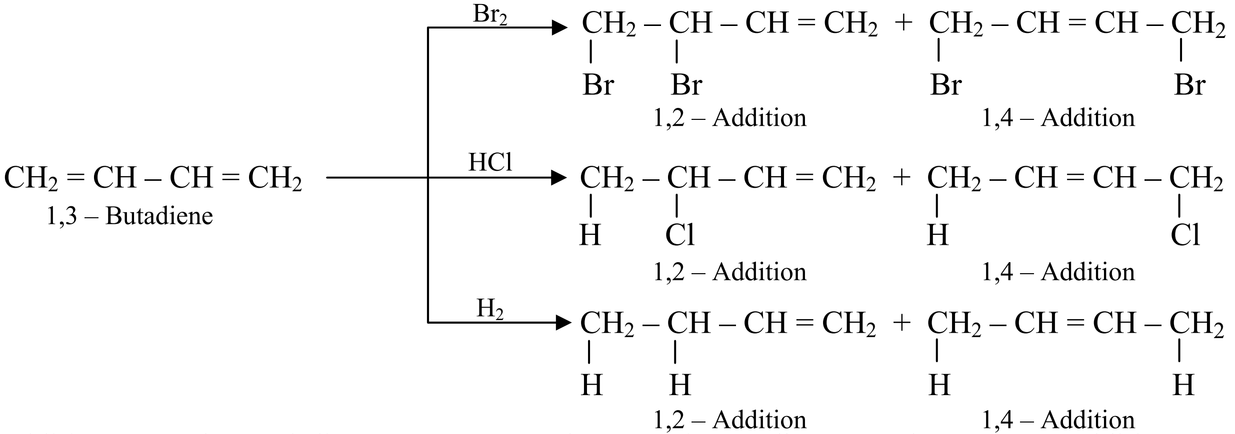
When 1, 4 – pendadiene is treated with Br_2 under condition gives dihalide, 4, 5 – dibromo – 1 – pentene and addition of more Br_2 gives 1,2,4,5 – tetrabromopentane.



$$CH_2{=}CH{-}CH_2{-}CH{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH_2{-}CH{=}CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH_2{-}\underset{Br}{CH}{-}\underset{Br}{CH_2}$$

When, 1,3 – butadiene is treated with Br_2 under similar conditions gives mixture of isomeric product 3,4 – dibromo – 1 – butane and 1,4 – dibromo – 2 –butene

Addition of HCl and H_2 gives similar results.

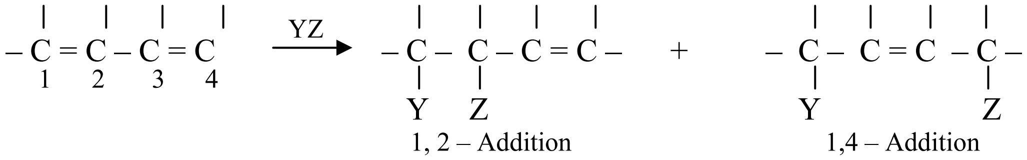


$$CH_2=CH-CH=CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}-\underset{Br}{CH}-CH=CH_2 + \underset{Br}{CH_2}-CH=CH-\underset{Br}{CH_2}$$

$$CH_2=CH-CH=CH_2 \xrightarrow{HCl} \underset{H}{CH_2}-\underset{Cl}{CH}-CH=CH_2 + \underset{H}{CH_2}-CH=CH-\underset{Cl}{CH_2}$$

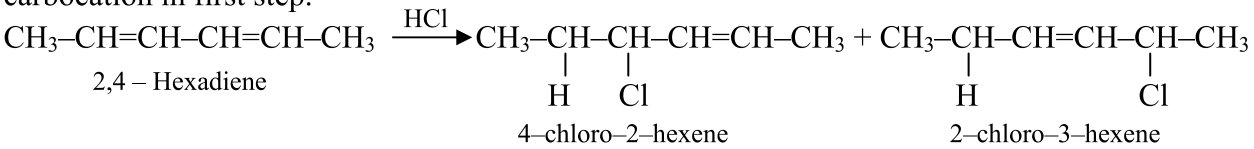
$$CH_2=CH-CH=CH_2 \xrightarrow{H_2} \underset{H}{CH_2}-\underset{H}{CH}-CH=CH_2 + \underset{H}{CH_2}-CH=CH-\underset{H}{CH_2}$$

Addition to conjugated dienes reagent attach to a pair of adjacent carbons (1,2 – addition) and also to the carbons at the two ends of the conjugated system (1,4 – addition), and where 1,4 – addition product is major product.



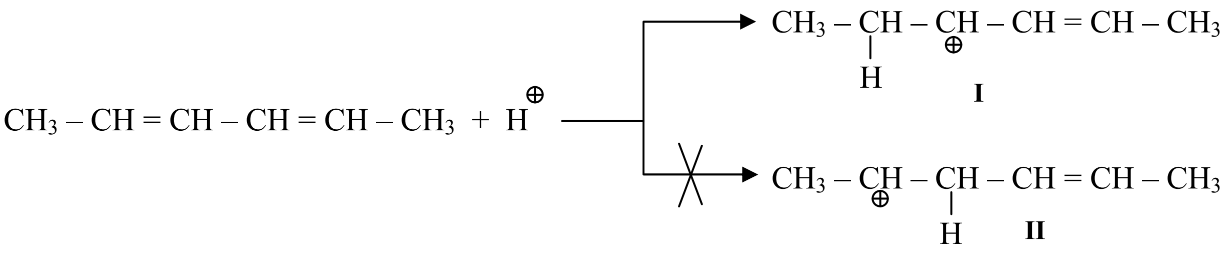
$$-\underset{1}{C}=\underset{2}{C}-\underset{3}{C}=\underset{4}{C} \xrightarrow{YZ} -\underset{Y}{C}-\underset{Z}{C}-C=C- \;+\; -\underset{Y}{C}-C=C-\underset{Z}{C}-$$

Mechanism of electrophilic addition reaction involves two steps with the formation of carbocation in first step.



$$CH_3-CH=CH-CH=CH-CH_3 \xrightarrow{HCl} CH_3-\underset{H}{CH}-\underset{Cl}{CH}-CH=CH-CH_3 + CH_3-\underset{H}{CH}-CH=CH-\underset{Cl}{CH}-CH_3$$

In first step of above reaction hydrogen adds to C–2 to give carbocation I, rather than to C–3 to yield carbocation II.



$$CH_3-CH=CH-CH=CH-CH_3 + \overset{\oplus}{H} \longrightarrow CH_3-\underset{H}{CH}-\underset{\oplus}{CH}-CH=CH-CH_3 \;(\mathbf{I})$$

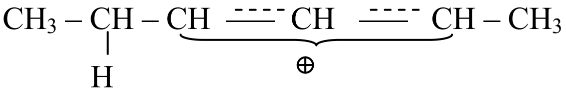
$$CH_3-CH=CH-CH=CH-CH_3 + \overset{\oplus}{H} \not\longrightarrow CH_3-\underset{\oplus}{CH}-\underset{H}{CH}-CH=CH-CH_3 \;(\mathbf{II})$$

Thus hydrogen adds to C–2 and gives more stable carbocation which leads to the formation of allylic carbocation due to conjugation as shown below.

$$\left(\mathrm{CH_3-\underset{\underset{H}{|}}{C}H-\underset{\oplus}{C}H-CH=CH-CH_3}\qquad\mathrm{CH_3-\underset{\underset{H}{|}}{C}H-CH=CH-\underset{\oplus}{C}H-CH_3}\right)$$

I **III**

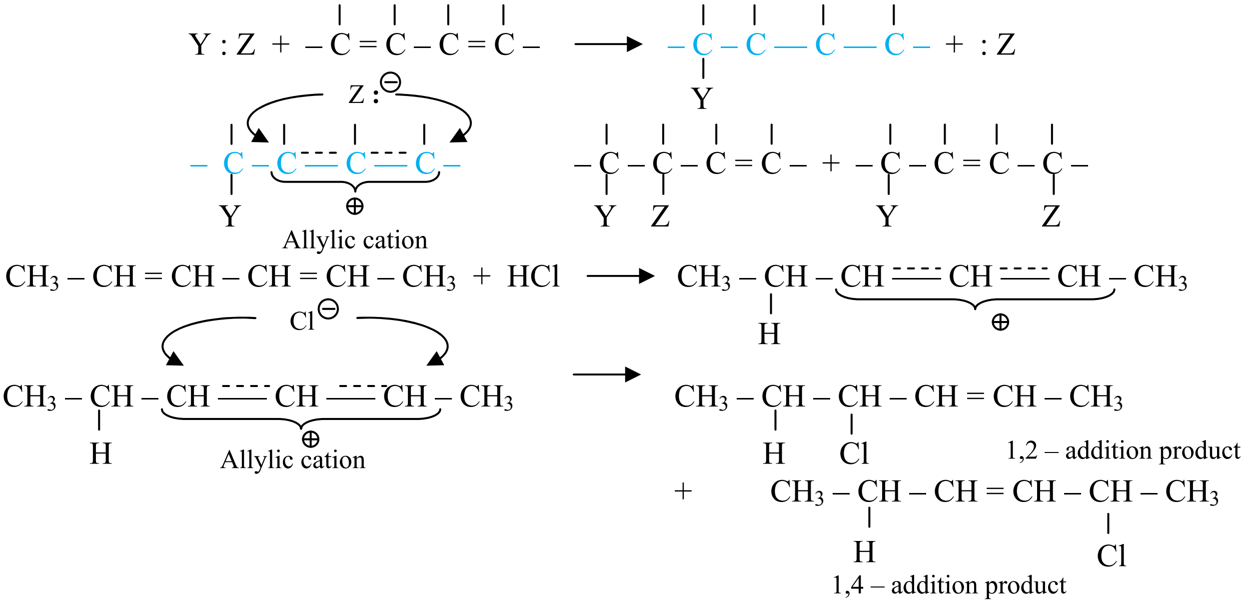
Equivalent to



$$\mathrm{CH_3-\underset{\underset{H}{|}}{C}H-\underbrace{CH\overset{----}{=}CH\overset{----}{=}CH}_{\oplus}-CH_3}$$

IV

As a cation that is both secondary and allylic, I is more stable than II, and is the preferred cationic intermediate.



$$\mathrm{CH_3-CH=CH-CH=CH-CH_3\ +\ HCl\ \longrightarrow\ CH_3-\underset{\underset{H}{|}}{C}H-\underbrace{CH\overset{----}{=}CH\overset{----}{=}CH}_{\oplus}-CH_3}$$

$$\mathrm{CH_3-\underset{\underset{H}{|}}{C}H-\underbrace{CH\overset{----}{=}CH\overset{----}{=}CH}_{\oplus}-CH_3\ \xrightarrow{Cl^{\ominus}}\ CH_3-\underset{\underset{H}{|}}{C}H-\underset{\underset{Cl}{|}}{C}H-CH=CH-CH_3\ +\ CH_3-\underset{\underset{H}{|}}{C}H-CH=CH-\underset{\underset{Cl}{|}}{C}H-CH_3}$$

Thus the hybrid nature of the allylic cation governs both steps electrophilic addition to conjugated dienes through stabilization of cation and then by permitting attachment to either of two carbon atom.

FREE RADICAL POLYMERIZATION OF DIENE: RUBBER AND RUBBER SUBSTITUTES:

Polymerization which proceeds with free radicals as the chain carrying particles is known as free radical polymerization.

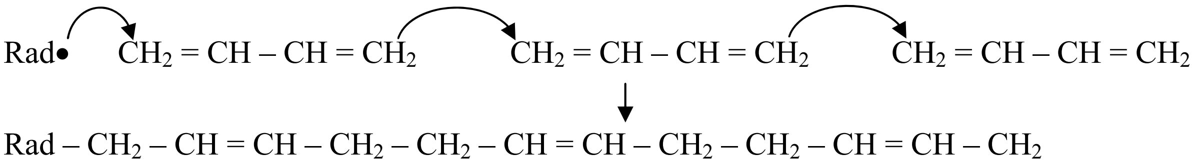
Ethylenes undergo free radical polymerization

$$\underset{\text{Ethylene}}{CH_2 = CH_2} \longrightarrow \underset{\text{Polyethylene}}{-\!\!\left[CH_2 - CH_2 \right]\!\!-_n}$$

Similarly, conjugated dienes undergo free radical polymerization.

$$\text{e.g. } \underset{\text{1, 3 – butadiene}}{CH_2 = CH - CH = CH_2} \longrightarrow \underset{\text{Polybutadiene}}{-\!\!\left[CH_2 - CH = CH - CH_2 \right]\!\!-_n}$$

Polymerization of 1,3 – butadiene indicates 1,4 – addition occurs predominantly.



$$Rad\bullet \quad CH_2 = CH - CH = CH_2 \quad CH_2 = CH - CH = CH_2 \quad CH_2 = CH - CH = CH_2$$

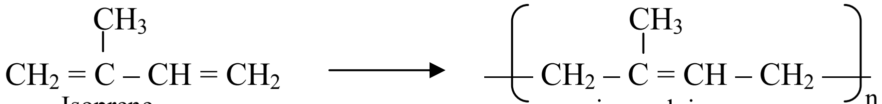
$$\downarrow$$

$$Rad - CH_2 - CH = CH - CH_2 - CH_2 - CH = CH - CH_2 - CH_2 - CH = CH - CH_2$$

Such polymer differs from the polymers of simple alkenes in one very important way: each unit still contain one double bond.

Structure of natural rubber strongly resembles to contain one double bond in each unit like synthetic polydienes.

e.g. polymer of conjugated diene, 2 – methyl – 1,3 – butadiene (isoprene)

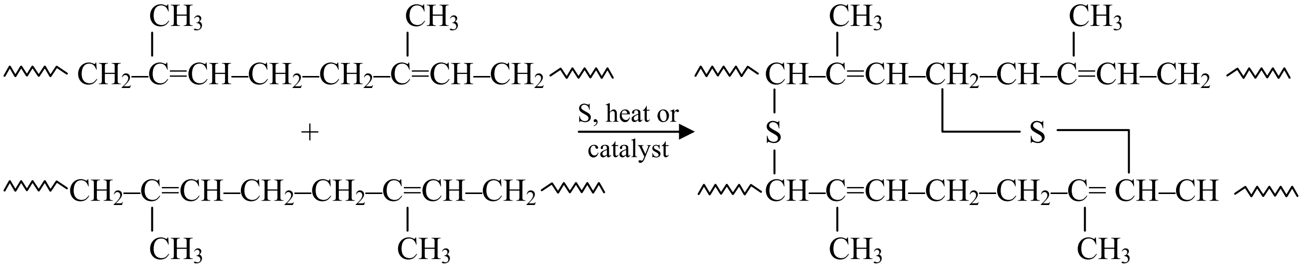


$$\underset{\substack{\text{Isoprene}\\ \text{2–methyl–1,3-butadiene}}}{CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2} \longrightarrow \underset{\substack{\text{cis – polyisoprene}\\ \text{Natural Rubber}}}{-\!\!\left[CH_2 - \overset{\overset{CH_3}{|}}{C} = CH - CH_2 \right]\!\!-_n}$$

The double bonds in the rubber molecule are highly important because they provide reactive allylic hydrogens which are permitting vulcanization.

Vulcanization:

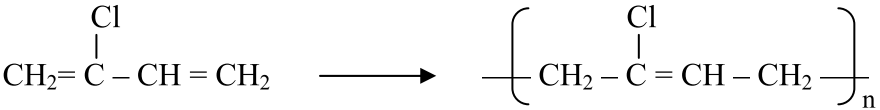
The formation of sulfur bridges between different chains of polymer is known as vulcanization. Such type of link is also known as cross – link. These cross – links makes the rubber harder and stronger.



NATURAL RUBBER **VULCANIZED RUBBER**

Polymerization of dienes to form substitutes for rubber was the forerunner of the enormous present day plastic industry.

Polychloroprene (neoprene, duprene) was the first commercially successful rubber substitute in the United States.



$$CH_2=\overset{Cl}{\overset{|}{C}}-CH=CH_2 \longrightarrow \left[CH_2-\overset{Cl}{\overset{|}{C}}=CH-CH_2 \right]_n$$

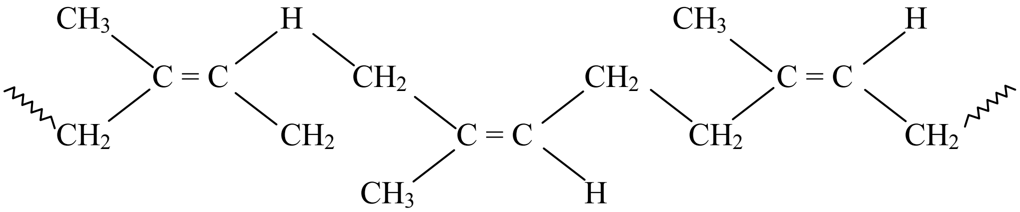
Chloroprene Polychloroprene

Some properties of polychloroprene are inferior to natural rubber but superior in its resistance to oil, gasoline and other organic solvents.

Synthetic rubber made by free radical polymerization of isoprene is different than natural rubber by its stereochemistry.

In natural rubber has the cis configuration at every double bond where as synthetic rubber was a mixture of cis and Trans configuration.

After 1955 synthetic rubber was made by new catalyst and new mechanism of polymerization from stereo selective polymerization of isoprene with cis configuration.



Natural rubber
All – cis configuration

MACROMOLECULES:

Small molecules:

Containing as many as 50 to 75 atoms.

Macromolecules:

Contain hundreds of thousands of atoms.

Macromolecules are giant molecule which contains hundreds of thousands of atoms. They are known as polymer

Macromolecules are of two types:

1. **Natural macromolecules:** Starch, cellulose, protein, rubber, silk, nucleic acid.
2. **Synthetic macromolecules:** Elastomers, fibres, plastics.

Polysaccharides starch and cellulose: Provide us food, clothing and shelter.

Protein: Which constitute much of animal body, hold it together and run it.

Nucleic acid : Which control heredity on the molecular level.

Elastomers: Which have particular kind of elasticity characteristic of rubber.

Fibers: Long, thin and threadlike with the great strength.

Along the fibre that characterizes cotton, wool and silk.

Plastics: Which can be extruded as sheets or pipes painted on surfaces or moulded to form countless objects.

(If a polymer is shaped into a hard and tough utility article by the application of heat and pressure than it is called plastic.

e.g. PVC, polyethylene, polymethylmethacrylate, polystyrene etc.

POLYMERS AND POLYMERIZATION:

Macromolecules, natural or man – made (synthetic) are known as polymers because they have great size.

The process by which polymer are formed is known as polymerization (The joining together of many small molecules to form very large molecules).

The compounds from which polymers are made are called monomers.

Polymers are formed in two general ways.

(a) Chain – reaction polymerization
(b) Step – reaction polymerization

Chain reaction polymerization:

Polymerization which involves a series of reaction each of which consumes a reactive particle and produces another similar reactive particle is known as chain reaction polymerization.

(The process is also known as addition polymerization).

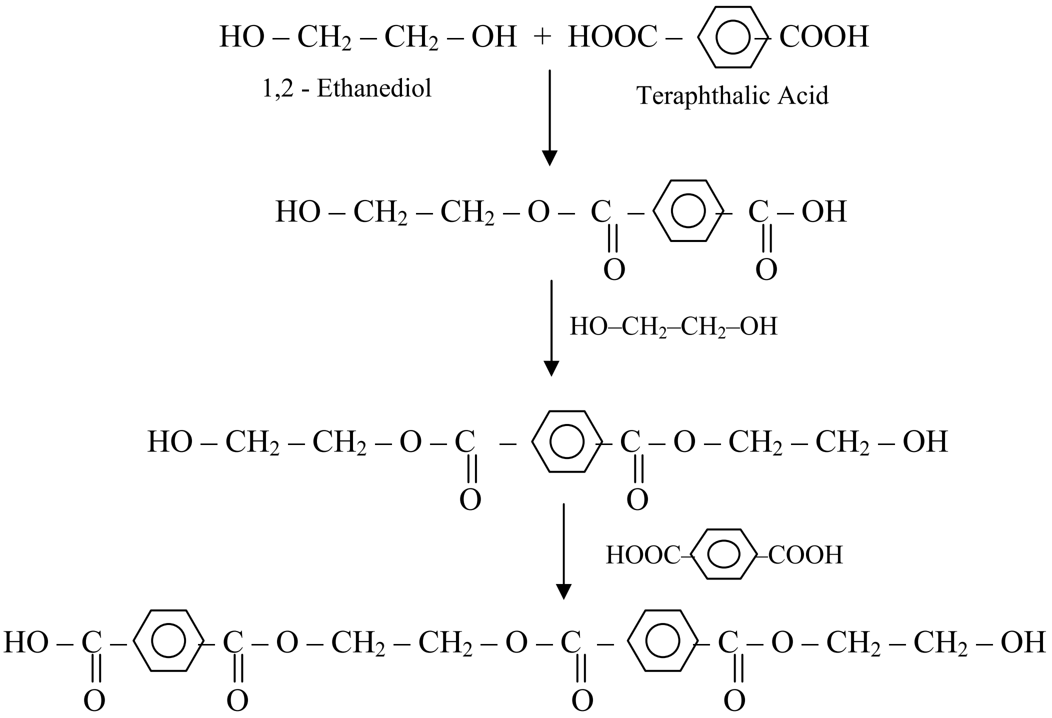
Thus each individual reaction depends upon the previous reaction.
The reactive particle may be free radicals, cations or anions.
e.g. polymerization of ethylene.

$$\text{Rad}\bullet + CH_2 = CH_2 \longrightarrow \text{Rad } CH_2CH_2\bullet \xrightarrow{CH_2=CH_2} \text{Rad } CH_2CH_2CH_2CH_2\bullet \longrightarrow \ldots\ldots \text{ etc.}$$

Here the chain carrying free radicals as reactive particle, each of which adds to a monomer molecule to form a new bigger free radical.
e.g. polyethylene, polypropylene, polystyrene, polybutadiene, poly vinyl chloride

Step reaction polymerization:

Polymerization which involves a series of intermolecular reactions between bifunctional or polyfunctional monomer molecules are known as step reaction polymerization (The process is also known as condensation polymerization).
The reactive functional group may be –OH, –COOH, $-NH_2$, –NCO etc.
In step reaction polymerization the functional group react with each other by stepwise and producing condensed structural linkages with the elimination of a small molecule in each step of reaction.
e.g. polyamides, polyesters, polyethers, polyurethanes, phenolics, epoxy resins
e.g. a diol reacts with dicarboxylic acid to form as ester.
Each moiety of ester contains a group which react to generate another ester linkage giving a large molecule, which itself can react further and so on.



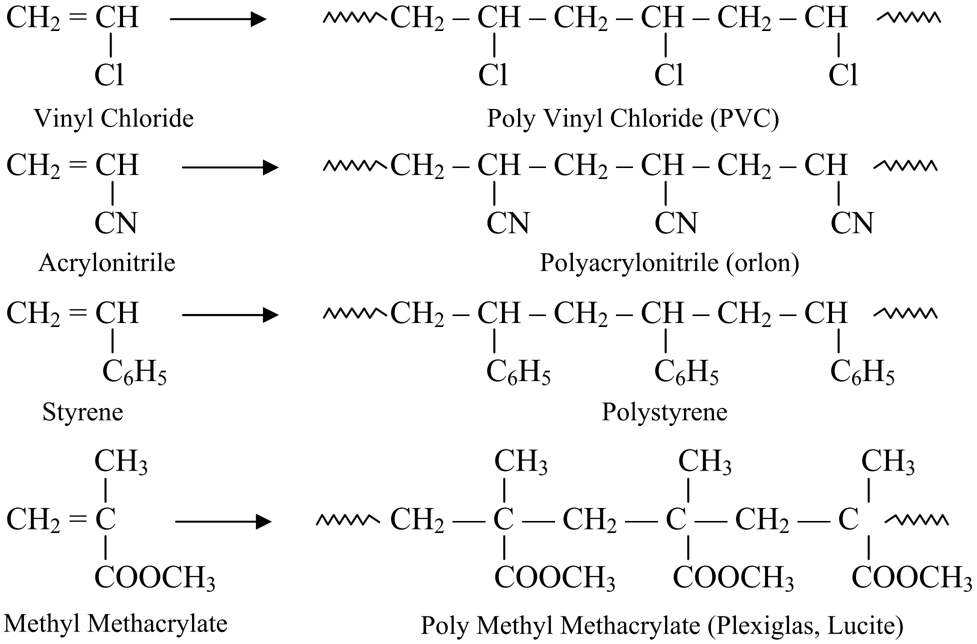
Addition Polymerization	**Condensation Polymerization**
1. In addition polymerization molecules of monomer are simply added together 2. Chain reaction polymerization involve addition polymerization	1. In condensation polymerization monomer molecules combine with loss of some simple molecule like water. 2. Step reaction polymerization involves condensation polymerization.

FREE RADICAL VINYL POLYMERIZATION:

Free radical Polymerization of substituted ethylene in presence of small amounts of an initiator (peroxide) in which reaction occurs at the doubly bonded carbons (vinyl groups) is called free radical vinyl polymerization.

A wide variety of unsaturated monomers may be used to yield polymers with different pendant group (G) attached to the polymer backbone.

e.g.



$$CH_2=\underset{Cl}{\underset{|}{CH}} \longrightarrow \sim\!\sim CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}-CH_2-\underset{Cl}{\underset{|}{CH}}\sim\!\sim$$

Vinyl Chloride — Poly Vinyl Chloride (PVC)

$$CH_2=\underset{CN}{\underset{|}{CH}} \longrightarrow \sim\!\sim CH_2-\underset{CN}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}\sim\!\sim$$

Acrylonitrile — Polyacrylonitrile (orlon)

$$CH_2=\underset{C_6H_5}{\underset{|}{CH}} \longrightarrow \sim\!\sim CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-\underset{C_6H_5}{\underset{|}{CH}}\sim\!\sim$$

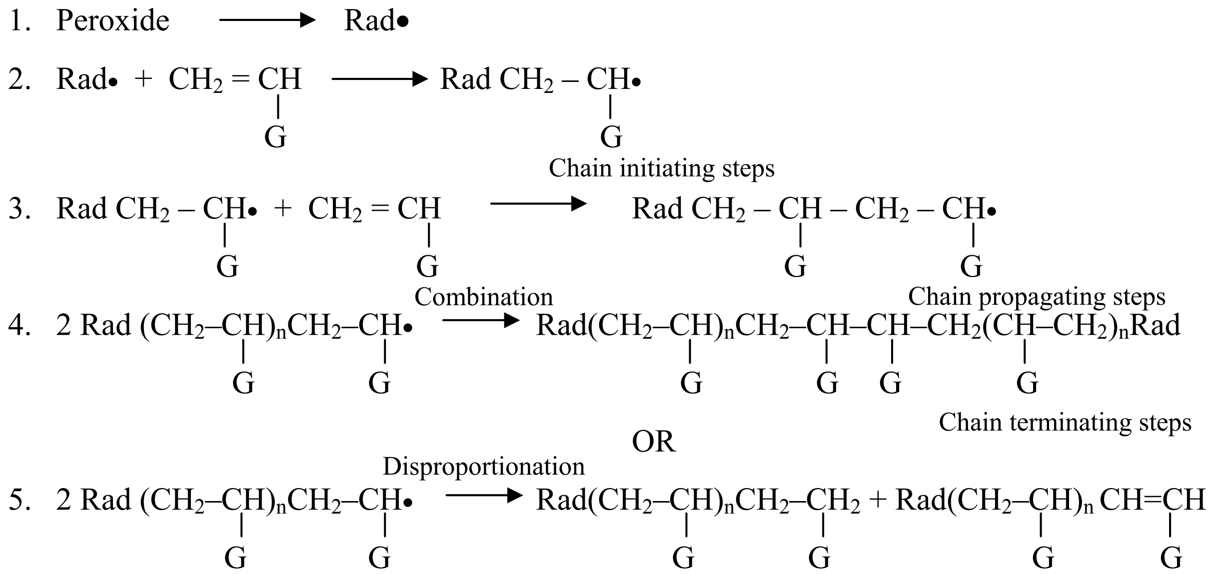
Styrene — Polystyrene

$$CH_2=\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}} \longrightarrow \sim\!\sim CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}-CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}}\sim\!\sim$$

Methyl Methacrylate — Poly Methyl Methacrylate (Plexiglas, Lucite)

Free radical vinyl polymerization is an example of chain reaction polymerization.
Polymerization involves addition of free radical to the double bond of the monomer.
Firstly free radical generated from the initiator and then of the growing polymer molecule.

Mechanism:



1. $$\text{Peroxide} \longrightarrow \text{Rad}\bullet$$

2. $$\text{Rad}\bullet + CH_2=\underset{G}{CH} \longrightarrow \text{Rad}\,CH_2-\underset{G}{CH}\bullet$$

Chain initiating steps

3. $$\text{Rad}\,CH_2-\underset{G}{CH}\bullet + CH_2=\underset{G}{CH} \longrightarrow \text{Rad}\,CH_2-\underset{G}{CH}-CH_2-\underset{G}{CH}\bullet$$

Chain propagating steps

4. $$2\,\text{Rad}\,(CH_2-\underset{G}{CH})_nCH_2-\underset{G}{CH}\bullet \xrightarrow{\text{Combination}} \text{Rad}(CH_2-\underset{G}{CH})_nCH_2-\underset{G}{CH}-\underset{G}{CH}-CH_2(\underset{G}{CH}-CH_2)_n\text{Rad}$$

Chain terminating steps

OR

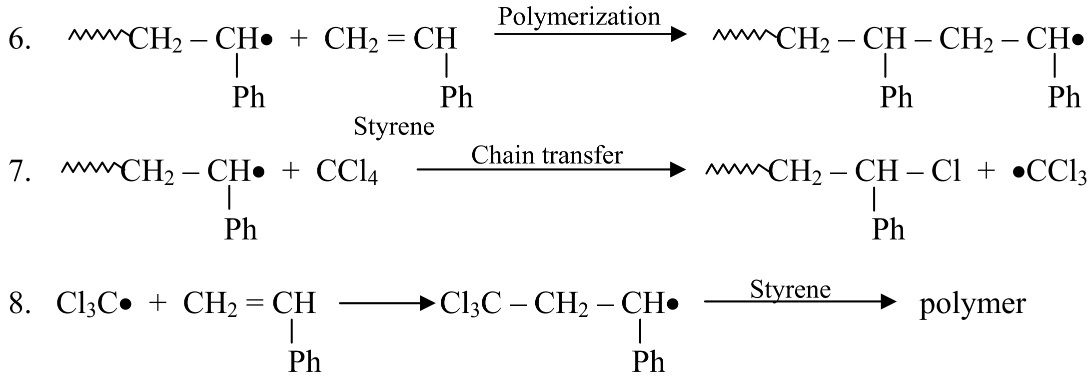
5. $$2\,\text{Rad}\,(CH_2-\underset{G}{CH})_nCH_2-\underset{G}{CH}\bullet \xrightarrow{\text{Disproportionation}} \text{Rad}(CH_2-\underset{G}{CH})_nCH_2-\underset{G}{CH_2} + \text{Rad}(CH_2-\underset{G}{CH})_n\,\underset{G}{CH}=\underset{G}{CH}$$

In chain initiating and chain propagating each step consumes a free radical and generate a new bigger free radical chain terminating step consume free radical but not generated free radical.

Added compound can modify polymerization process drastically.

e.g. in presence of CCl_4, styrene undergoes polymerization at the same rate as in its absence, but the polystyrene obtained has a lower average molecular weight. Polystyrene also contain small amount of chlorine.

This is an example of chain transfer, the termination of one polymerization chain (7) with the simultaneous initiation of another (8).



6. $$\sim\!\sim CH_2-\underset{Ph}{CH}\bullet + \underset{\text{Styrene}}{CH_2=\underset{Ph}{CH}} \xrightarrow{\text{Polymerization}} \sim\!\sim CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{CH}\bullet$$

7. $$\sim\!\sim CH_2-\underset{Ph}{CH}\bullet + CCl_4 \xrightarrow{\text{Chain transfer}} \sim\!\sim CH_2-\underset{Ph}{CH}-Cl + \bullet CCl_3$$

8. $$Cl_3C\bullet + CH_2=\underset{Ph}{CH} \longrightarrow Cl_3C-CH_2-\underset{Ph}{CH}\bullet \xrightarrow{\text{Styrene}} \text{polymer}$$

In step 6 growing polystyrene radical adds to styrene monomer to continue the reaction chain.

In step 7 growing polystyrene radical abstract an atom from the chain transfer agent (CCl_4) to end the original polymerization chain and generate a new particle CCl_3.

In step 8 CCl_3 initiate a new polymerization chain.

Since the reaction chain is replaced by another, the rate of polymerization is unaffected.

Since the average number of chain propagating steps in each reaction chain is reduced, the average molecular weight of polymer is lowered.

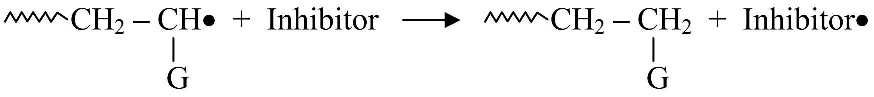
A transfer agent competes with the monomer for the growing radicals.

The ratio of rate constant of step 7 and step 6 $K_{transfer} / K_{polymerization}$ is called transfer constant.

It is a measure of how effective the transfer agent is lowering the molecular weight of polymer.

A compound which combines with growing polymer chain and stops the polymerization is known as inhibitor.

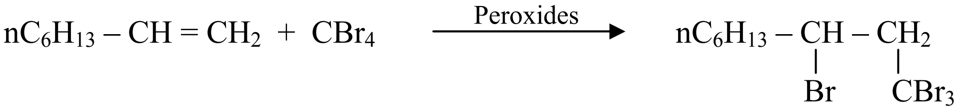
e.g. amines, phenols, quinines act as inhibitor.



$$\sim\!\sim CH_2-\underset{G}{\underset{|}{CH}}\bullet + \text{Inhibitor} \longrightarrow \sim\!\sim CH_2-\underset{G}{\underset{|}{CH_2}} + \text{Inhibitor}\bullet$$

Low reactive alkene + High reactive chain transfer agent ⟶ no polymerization but undergo addition reaction.

e.g.



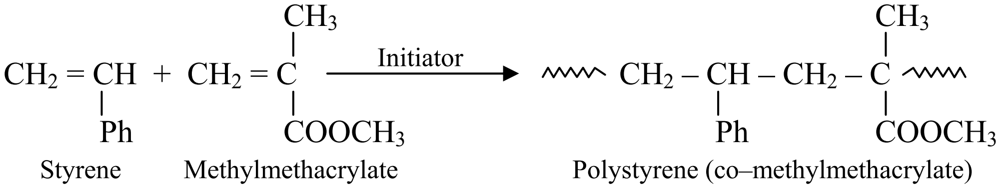
$$nC_6H_{13}-CH=CH_2 + CBr_4 \xrightarrow{\text{Peroxides}} nC_6H_{13}-\underset{Br}{\underset{|}{CH}}-\underset{CBr_3}{\underset{|}{CH_2}}$$

COPOLYMERIZATION:

Polymer prepared from single (one) monomer in known as homopolymer and process in known as homopolymerization.

e.g. $M ---- M ---- M ---- M$ ———— $[M]_n$

Polymer prepared from two or more different monomers are known as copolymer and process is known as copolymerization.



$$\underset{Ph}{\underset{|}{CH_2=CH}} + CH_2=\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}} \xrightarrow{\text{Initiator}} \sim\!\sim CH_2-\underset{Ph}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{\underset{COOCH_3}{\underset{|}{C}}}} \sim\!\sim$$

Co – polymer can be prepared from two, three, four or even more different monomer.

Co – polymer can be prepared by free radical chain reaction, ionic, coordination or step reaction polymerization.

There are two types of copolymers

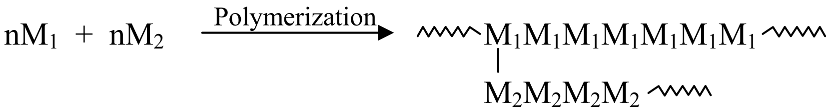
Block Copolymer:

Copolymer in which two monomers get united in a section made up of one monomer alternate with section of another monomer is called block copolymer.

$$nM_1 + nM_2 \xrightarrow{\text{Polymerization}} \sim\!\sim M_1M_1M_1M_1M_1 - M_2M_2M_2M_2M_2 \sim\!\sim$$

Graft Copolymer:

Copolymer in which a branch of one monomer unit grafted (added) on to the linear chain of another monomer unit is known as graft copolymer



$$nM_1 + nM_2 \xrightarrow{\text{Polymerization}} \sim\!\sim M_1M_1M_1M_1M_1M_1M_1 \sim\!\sim \quad (\text{branch: } M_2M_2M_2M_2 \sim\!\sim)$$

Through copolymerization of homopolymer, properties can be modified or upgraded.

Polystyrene (homopolymer):

Good electric insulator molded into parts for radios television sets and automobiles.

Copolymerization of polystyrene

1. With butadiene (30%) : Adds toughness
2. With acrylonitrile (20 – 30%) : Increases resistance to impact and to hydrocarbon.
3. With maleic anhydride : Yield a material on hydrolysis is water soluble and used as dispersant and sizing agent
4. With butadiene (75%) : Is elastomers. This elastomer is a principle rubber substitute manufactured in USA since world war II

IONIC POLYMERIZATION : LIVING POLYMERS

Polymerization which proceeds with free radicals as the chain carrying particles is known as free radical polymerization.

Polymerization which proceeds with ions (cations / anions) as the chain carrying particle is known as ionic(cationic / anionic) polymerization.

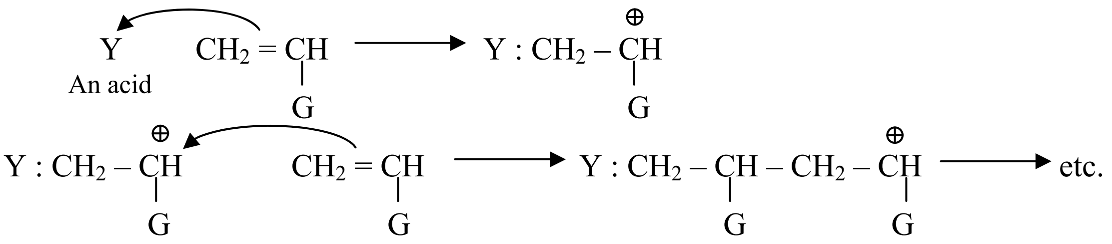
Ionic polymerization is of two types:

1. Cationic polymerization and
2. Anionic polymerization.

Cationic polymerization:

Polymerization which proceeds with cations as the chain carrying particle is known cationic polymerization.

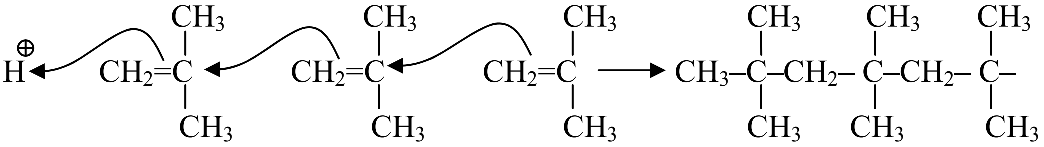
Cationic polymerization is initiated by acids. H_2SO_4, $AlCl_3$, or BF_3 plus a trace of water can be used as initiator



$$\underset{\text{An acid}}{Y} \quad CH_2=\underset{\substack{|\\G}}{CH} \longrightarrow Y:CH_2-\overset{\oplus}{\underset{\substack{|\\G}}{CH}}$$

$$Y:CH_2-\overset{\oplus}{\underset{\substack{|\\G}}{CH}} \quad CH_2=\underset{\substack{|\\G}}{CH} \longrightarrow Y:CH_2-\underset{\substack{|\\G}}{CH}-CH_2-\overset{\oplus}{\underset{\substack{|\\G}}{CH}} \longrightarrow \text{etc.}$$

e.g. isobutylene undergo cationic polymerization as given below.



$$\overset{\oplus}{H} \leftarrow CH_2=\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}} \leftarrow CH_2=\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}} \leftarrow CH_2=\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}} \longrightarrow CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-$$

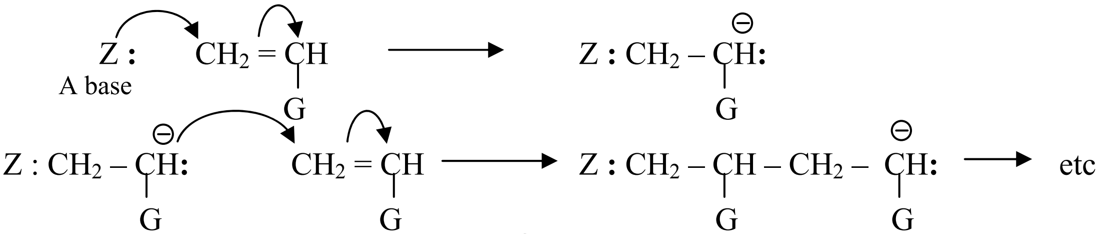
Polyisobutylene

Polyisobutylene is a tacky material which is used in adhesives. Copolymerization of isobutylene with isoprene gives butyl rubber which is used to make automobile inner tubes and tire liners.

Anionic polymerization:

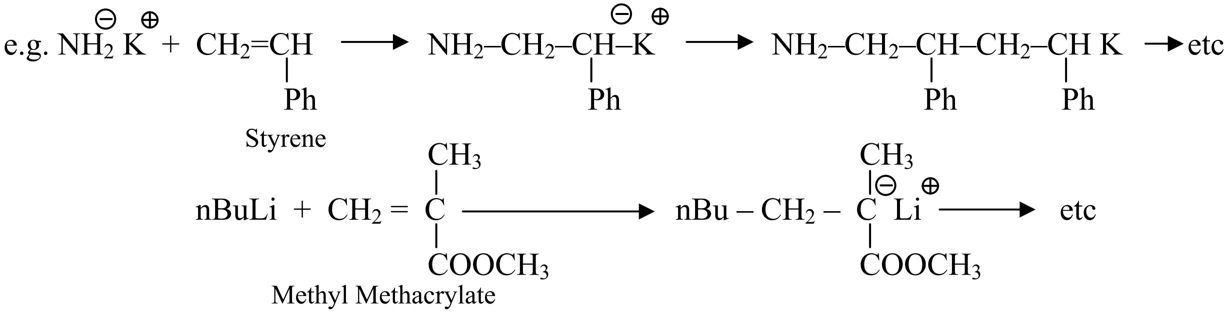
Polymerization which proceeds with anions as the chain carrying particle is known as anionic polymerization.

Anionic polymerization is initiated by bases like $Li^+NH_2^-$ or organometallic compound like n – butyllithium.



$$\underset{\text{A base}}{Z:} \quad CH_2=\underset{\substack{|\\G}}{CH} \longrightarrow Z:CH_2-\overset{\ominus}{\underset{\substack{|\\G}}{CH}}:$$

$$Z:CH_2-\overset{\ominus}{\underset{\substack{|\\G}}{CH}}: \quad CH_2=\underset{\substack{|\\G}}{CH} \longrightarrow Z:CH_2-\underset{\substack{|\\G}}{CH}-CH_2-\overset{\ominus}{\underset{\substack{|\\G}}{CH}}: \longrightarrow \text{etc}$$



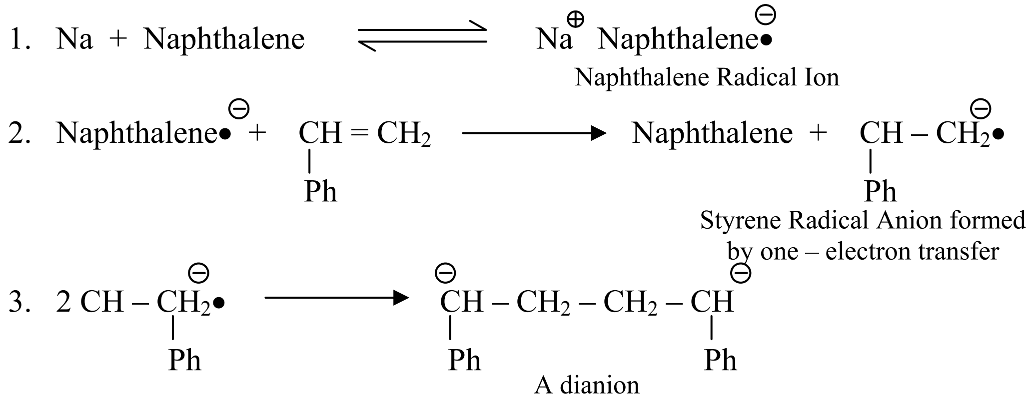
$$\text{e.g. } \overset{\ominus}{NH_2}\overset{\oplus}{K} + CH_2=\underset{\substack{|\\Ph}}{CH} \longrightarrow NH_2-CH_2-\underset{\substack{|\\Ph}}{\overset{\ominus}{CH}}-\overset{\oplus}{K} \longrightarrow NH_2-CH_2-\underset{\substack{|\\Ph}}{CH}-CH_2-\underset{\substack{|\\Ph}}{CH}\,K \longrightarrow \text{etc}$$

Styrene

$$nBuLi + CH_2=\overset{\substack{CH_3\\|}}{\underset{\substack{|\\COOCH_3}}{C}} \longrightarrow nBu-CH_2-\overset{\substack{CH_3\\|\ominus}}{\underset{\substack{|\\COOCH_3}}{C}}\overset{\oplus}{Li} \longrightarrow \text{etc}$$

Methyl Methacrylate

In anionic polymerization active metals like Na or Li can be used as initiators. Initiation is carried by the action of sodium metal and naphthalene. A sodium atom transfers an electron to naphthalene to form a radical anion.

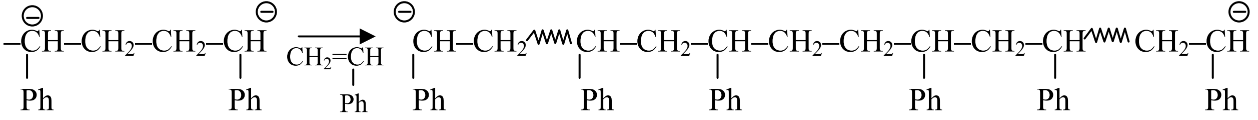


1. $\mathrm{Na} + \text{Naphthalene} \rightleftharpoons \overset{\oplus}{\mathrm{Na}}\ \text{Naphthalene}\overset{\ominus}{\bullet}$
2. $\text{Naphthalene}\overset{\ominus}{\bullet} + \underset{\mathrm{Ph}}{\mathrm{CH}}=\mathrm{CH_2} \longrightarrow \text{Naphthalene} + \underset{\mathrm{Ph}}{\mathrm{CH}}-\mathrm{CH_2}\overset{\ominus}{\bullet}$
3. $2\,\mathrm{CH}-\underset{\mathrm{Ph}}{\mathrm{CH_2}}\overset{\ominus}{\bullet} \longrightarrow \underset{\mathrm{Ph}}{\overset{\ominus}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\ominus}{\mathrm{CH}}}$

In step 1 sodium atom transfers an electron to naphthalene to form a radical anion.

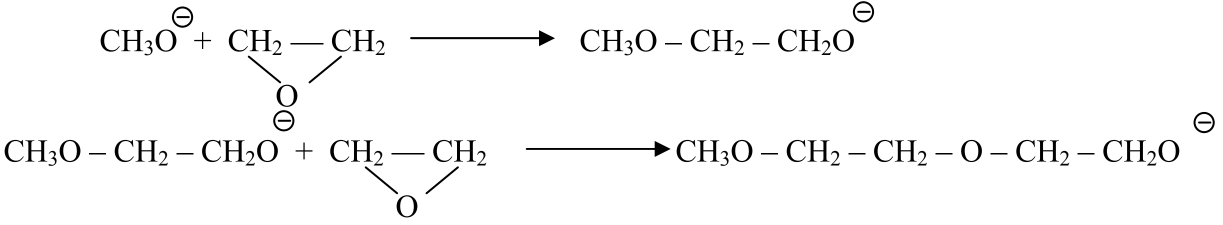
In step 2 radical anion donates electron to styrene to form styrene radical anion.

In step 3 styrene radical anion dimerize to form dianion. This dianion is the true initiator and begins to grow at both ends as given below.



$$-\underset{\mathrm{Ph}}{\overset{\ominus}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\ominus}{\mathrm{CH}}} \xrightarrow[\underset{\mathrm{Ph}}{\mathrm{CH_2=CH}}]{} \underset{\mathrm{Ph}}{\overset{\ominus}{\mathrm{CH}}}-\mathrm{CH_2}\sim\underset{\mathrm{Ph}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}\sim\mathrm{CH_2}-\underset{\mathrm{Ph}}{\overset{\ominus}{\mathrm{CH}}}$$

Ethylene oxide is converted into a high molecular weight polyether by a small amount of base.



$$\mathrm{CH_3}\overset{\ominus}{\mathrm{O}} + \underset{\mathrm{O}}{\mathrm{CH_2}-\mathrm{CH_2}} \longrightarrow \mathrm{CH_3O}-\mathrm{CH_2}-\mathrm{CH_2}\overset{\ominus}{\mathrm{O}}$$

$$\mathrm{CH_3O}-\mathrm{CH_2}-\mathrm{CH_2}\overset{\ominus}{\mathrm{O}} + \underset{\mathrm{O}}{\mathrm{CH_2}-\mathrm{CH_2}} \longrightarrow \mathrm{CH_3O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}\overset{\ominus}{\mathrm{O}}$$

In anionic polymerization no termination step took place under controlled conditions and a carbanion or dianion remain active such polymer is known as living polymers.

Living polymers can form block polymers by introduction of a variety of monomer. (e.g. butadiene) (e.g. addition of butadiene to polystyrene).

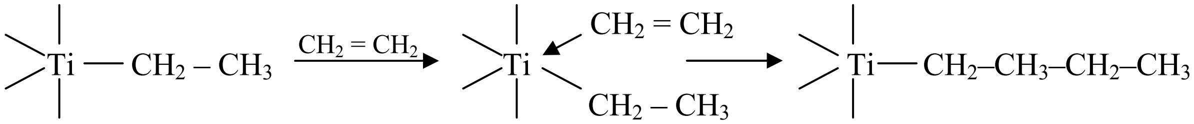
In cationic polymerization termination took place in two different ways:

1. Growing carbocation undergo ejection of a proton to form an alkene or
2. Growing carbocation combine with an anion.

In anionic polymerization termination often involves reaction with an impurity or some other molecule not a necessary part of the polymerization system.

COORDINATION POLYMERIZATION:

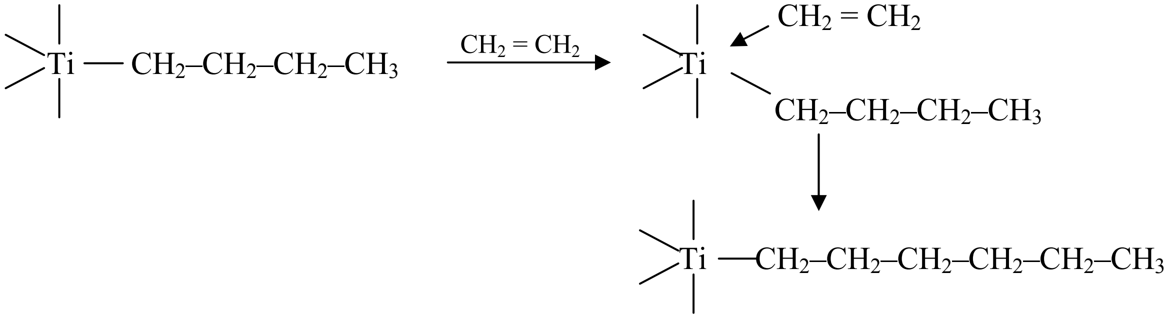
Coordination polymerization discovered by Karl Ziegler (Max Plank Institute for Coal Research) and by Giulio Natta (Polytechnic Institute of Milan) and jointly received Nobel prize in 1963.
[Ziegler – Natta develop a catalyst which permit control of polymerization process, this catalyst is known as Zigler – Natta Catalyst].
Ziegler Natta catalyst is made from titanium chloride (transition metal salt) and triethylaluminium (alkyl metal). These react to form active catalyst: A titanium complex holding an ethyl group.



(I) (II) (III)

1. In Ziegler Natta catalyst alkene attach with titanium by a π bond. (π cloud of alkene overlaps with an empty orbital of metal titanium).
2. Ethyl and alkene both held by the titanium metal
3. The ethylene unit insert between metal and ethyl group. (In place of ethyl group there is now n – butyl group is attached to titanium).

The bonding site where ethylene was held is vacant again and catalyst is ready to work again.
Another ethylene becomes π bonded to the metal and then insert between metal and alkyl group as given below.



The process continues over and over again with the alkyl group growing by two carbons in each cycle.
Finally, insertion of hydrogen the long chain separated from the metal and molecule of polyethylene has been formed.
(In place of titanium, cobalt or rhodium metal used as catalyst).

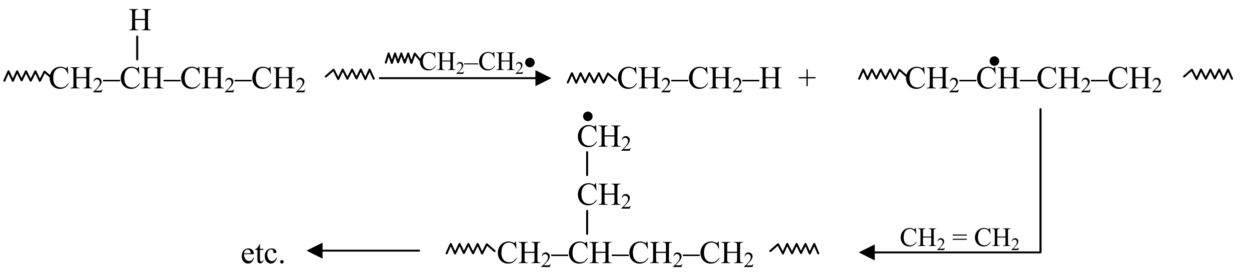
(Ti $\underset{\uparrow}{-}$ CH$_2$ – CH$_3$ Co $\underset{\uparrow}{-}$ H Rh $\underset{\uparrow}{-}$ H)

Polymerization with Ziegler Natta catalysts has two important advantages over free radical polymerization.

1. It gives linear polymer molecules and
2. It permits stereo chemical control.

Polyethylene made by free radical polymerization is highly branched chain due to chain transfer, where chain transfer agent is a polymer molecule. High temperature is required for this polymerization. The growing free radical added to a double bond of a monomer and also abstract hydrogen from a chain already formed. This abstraction of hydrogen generates a free radical centre from which a branch can grow.

This highly branched polyethylene molecules fit together poorly and in a random way and compound have low crystallinity. It has a low melting point and is mechanically weak. It has low density.



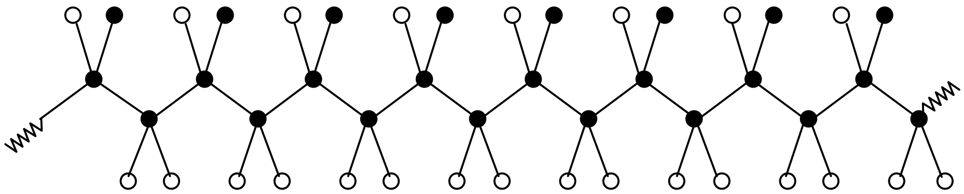
In contrast, polyethylene made by coordination polymerization is unbranched. This unbranched molecule fit together well and polymer has a high degree of crystallinity. It has a higher melting point and higher density and is mechanically much stronger.
In coordination polymerization due to stereochemical control polymer may polymerize in three different arrangements.

1. Isotactic
2. Syndiotactic
3. Atactic

e.g. polymerization of propylene.

Isotactic:

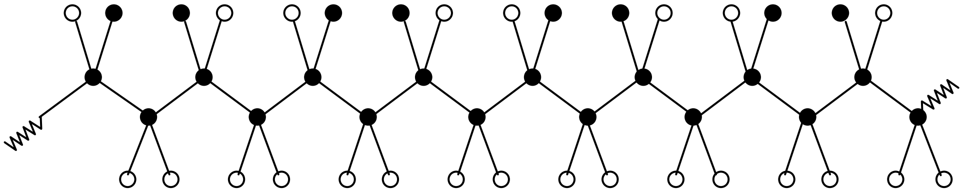
All methyl groups arrange on one side of an extended chain



Isotactic polypropylene is highly crystalline, regularity of structure permits their molecules to fit together well. Over three billion pound of isotactic polypropylene is produced every year and used to molded or extruded as sheets pipes and filaments. It is one of the principal synthetic fibres.

Syndiotactic:

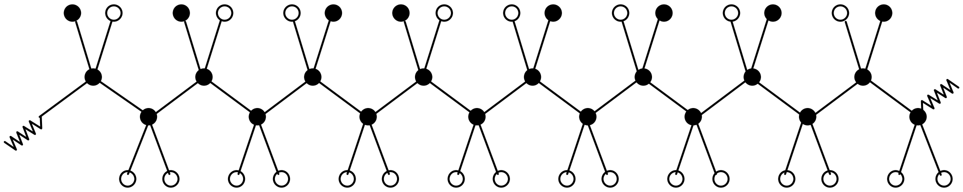
Methyl groups arrange alternating regularly from side to side.



Syndiotactic polypropylene is highly crystalline regularity of structure permits their molecule to fit together well.

Atactic:

All methyl groups distributed at random.



Attaching polypropylene is a soft, elastic, rubbery material.

By proper choice of experimental condition – catalyst, temperature, solvent – isotactic, syndiotactic or atactic polymers has been made.

Coordination catalyst also permits stereochemical control about carbon – carbon double bond.

Isoprene polymerized to give cis – 1,4 – polyisoprene which is virtually identical with natural rubber has arrangement like formation of isotactic polypropylene and like hydrogenation with Wilkinson's catalyst.

The Zeigler – Natta polymerization of ethylene can be adopted to make molecules of only modest size (C_6–C_{20}) and containing certain functional groups.

e.g. $$M–(CH_2–CH_2)_n–CH_2–CH_3 \xrightarrow[\text{heat}]{CH_2=CH_2Ni} CH_2=CH–(CH_2–CH_2)_{n-1}–CH_2–CH_3$$

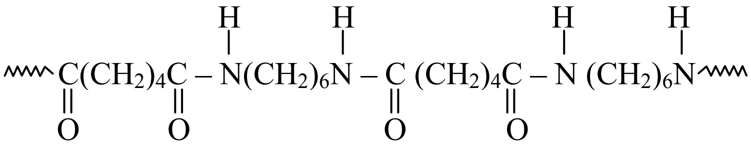
Metal alkyls are heated with ethylene i.p.o. nickel catalyst the hydrocarbon groups are displaced as straight chain 1 – alkene of even carbon number. Large quantities of such alkenes in the C_{12}–C_{20} range are consumed in the manufacture of detergents. Methyl alkyl can be oxidized by air to give straight chain primary alcohols.

$$M–(CH_2–CH_2)_n–CH_2–CH_3 \xrightarrow[30–95°C]{\text{Air}} M–O(CH_2CH)_3–CH_2–CH_3 \xrightarrow[4°C]{H_2O,\ H_2SO_4,} HO(CH_2–CH_2)_n–CH_2–CH_3$$

STEP REACTION POLYMERIZATION :

Carboxylic acids react with amines to yield amides. Carboxylic acids which contains more than one –COOH group when reacts with an amide which contains more than one $-NH_2$ group gives polyamides.

e.g. $\underset{\text{Adipic Acid}}{HOOC-(CH_2)_4-COOH} + \underset{\text{Hexamethylenediamine}}{H_2N-(CH_2)_6-NH_2} \longrightarrow \text{Salt} \xrightarrow[-H_2O]{\text{Heat}}$

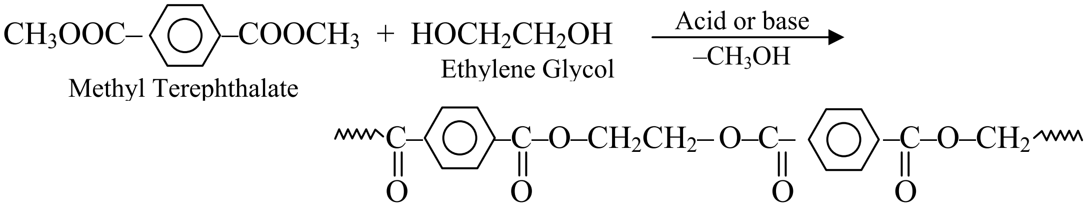


$$\sim\underset{O}{\underset{\|}{C}}(CH_2)_4\underset{O}{\underset{\|}{C}}-\overset{H}{\overset{|}{N}}(CH_2)_6\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}(CH_2)_4\underset{O}{\underset{\|}{C}}-\overset{H}{\overset{|}{N}}(CH_2)_6\overset{H}{\overset{|}{N}}\sim$$

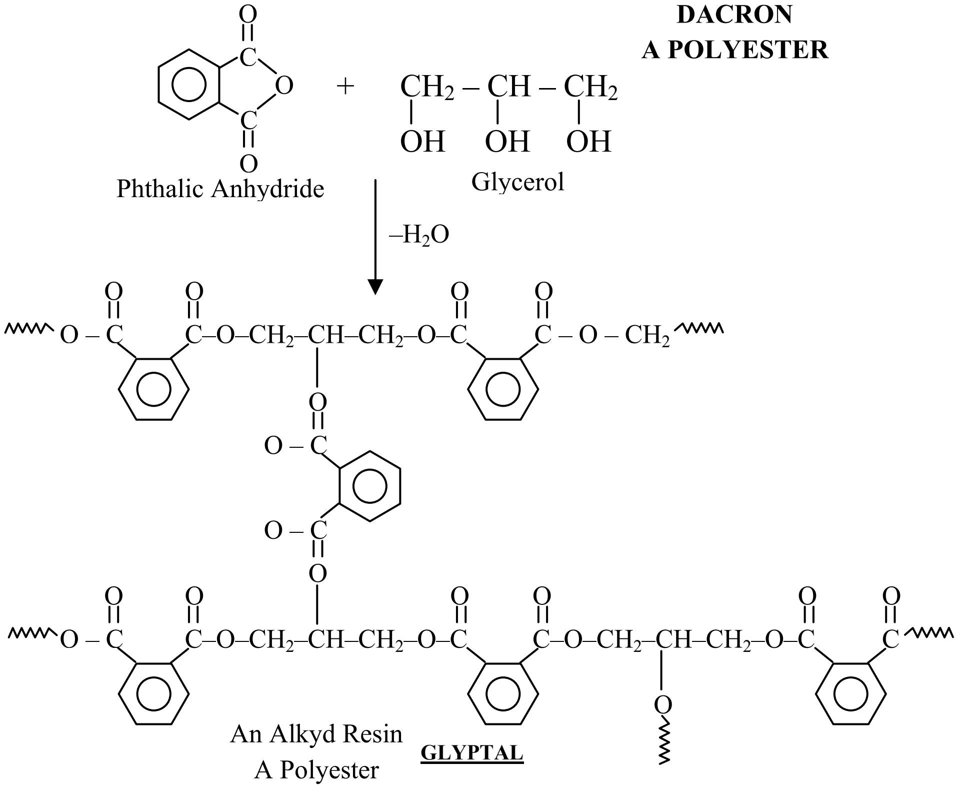
Nylon – 6, 6 (a Polyamide)

Carboxylic acids react with alcohol to give esters. Carboxylic acids which contains more than one –COOH group when reacts with an alcohol which contains more than one –OH group gives polyesters.

e.g.



DACRON
A POLYESTER



An Alkyd Resin
A Polyester

GLYPTAL

In chain reaction polymerization reaction depends on chain carrying free radical or ions where as step reaction polymerization involves more than one functional group in a monomer molecule.

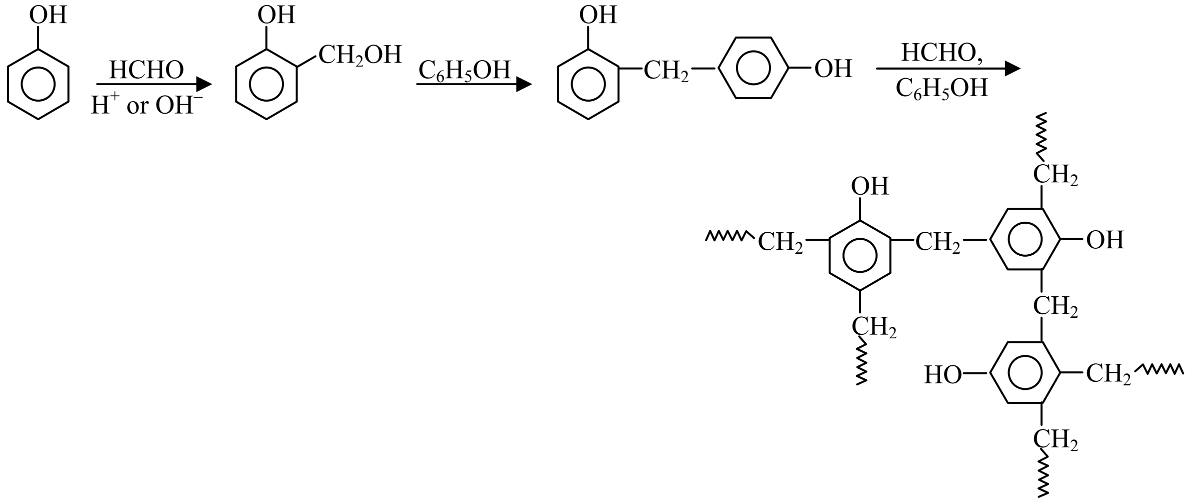
If each monomer molecule contains two functional groups, growth can occur in only two directions and a linear polymer is obtained, as in Dacron.

If each monomer molecule contains more than two functional groups reaction can occur at more than two positions in a monomer and a highly cross – linked space network polymer is formed, as in glyptal, an alkyd resin.

Dacron and glyptal both are polyesters but their structures are different. (Their properties are also different).

PHENOL – FORMALDEHYDE RESINS (BAKELITE AND RELATED POLYMERS) :

When phenol is treated with formaldehyde in presence of alkali or acid gives a high molecular weight phenol – formaldehyde resin in which many phenol rings are held together by $-CH_2-$ groups.



In phenol – formaldehyde polymerization, phenol reacts with formaldehyde to form o – or p – hydroxymethylphenol. Hydroxymethyl phenol then react with another molecule of phenol and gives a compound in which two rings are joined by a $-CH_2-$ link with loss of water. This process is continues and gives a high molecular weight product.

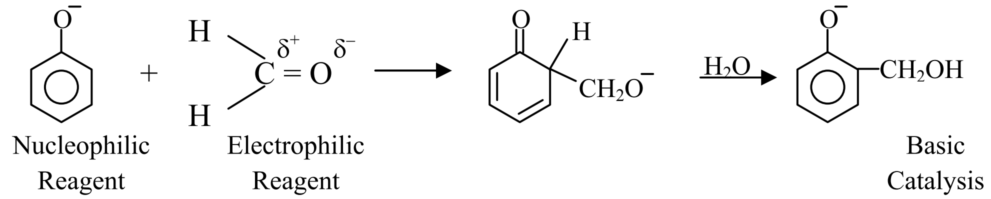
In each phenol molecule three positions are susceptible to attack and gives a final product which contains many cross links and has a rigid three dimentional structure.

Thus phenol – formaldehyde polymer is a space network polymer.

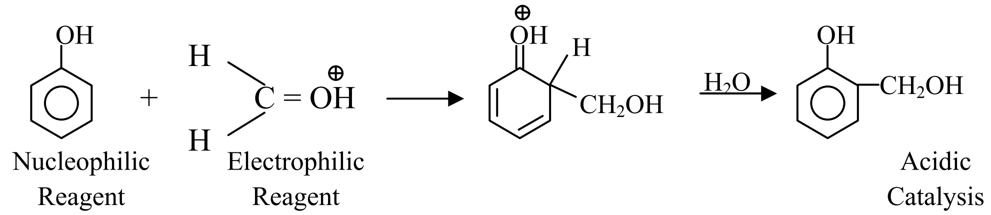
Mechanism:

1. **Basic catalysis:**

   In first stage both electrophilic substitution on the ring by electron – deficient carbon of formaldehyde and nucleophilic addition of aromatic ring to the carbonyl group takes place in presence of base catalyst by converting phenol into more reactive (more nucleophilic) phenoxide ion.

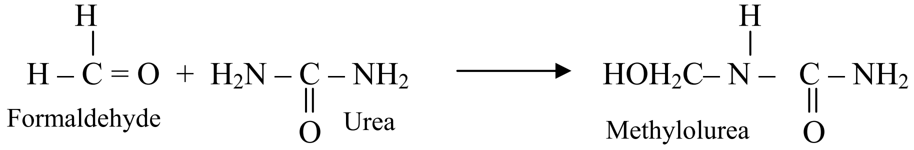


2. **Acidic catalysis:**
   In first stage both electrophilic substitution on the ring by electron – deficient carbon of formaldehyde and nucleophilic addition of aromatic ring to the carbonyl group takes place in presence of acidic catalyst by protonating formaldehyde and increasing electron deficiency of the carbonyl carbon.



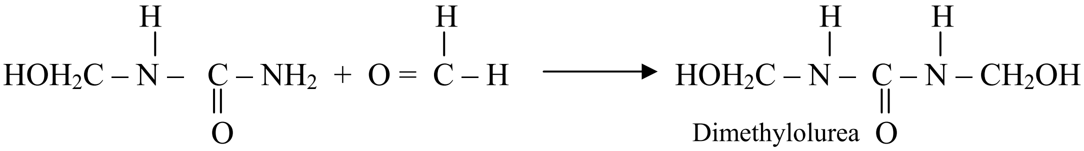
UREA – FORMALDEHYDE RESINS :

Urea is a diamine and is capable to form polymers. Urea on reaction with formaldehyde gives a space network polymer, urea – formaldehyde resins which use in molded plastics.



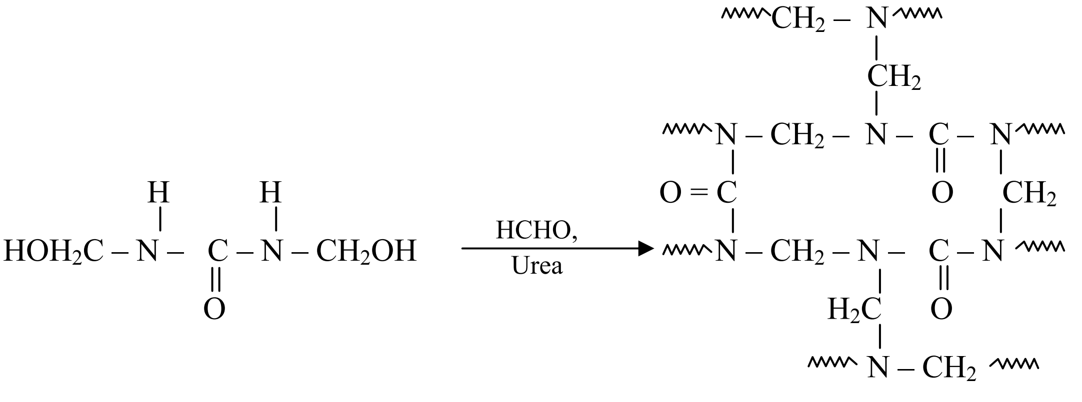
$$H-\overset{H}{\overset{|}{C}}=O + H_2N-\underset{O}{\underset{\|}{C}}-NH_2 \longrightarrow HOH_2C-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-NH_2$$

Formaldehyde Urea Methylolurea

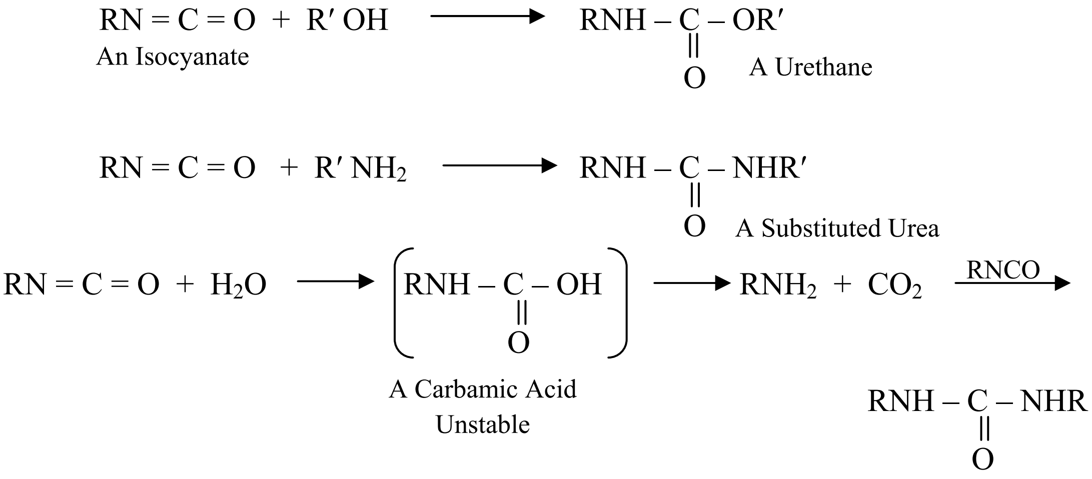


$$HOH_2C-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-NH_2 + O=\overset{H}{\overset{|}{C}}-H \longrightarrow HOH_2C-\overset{H}{\overset{|}{N}}-\underset{O}{\underset{\|}{C}}-\overset{H}{\overset{|}{N}}-CH_2OH$$

Dimethylolurea



Organic isocyanates, RNCO undergo the following synthesis of polymers.



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

An Isocyanate

A Urethane

$$RN=C=O + R'NH_2 \longrightarrow RNH-\underset{\underset{O}{\|}}{C}-NHR'$$

A Substituted Urea

$$RN=C=O + H_2O \longrightarrow \left(RNH-\underset{\underset{O}{\|}}{C}-OH \right) \longrightarrow RNH_2 + CO_2 \xrightarrow{RNCO} RNH-\underset{\underset{O}{\|}}{C}-NHR$$

A Carbamic Acid
Unstable

Reaction of diisocyanate with dihydroxy alcohols gives polyurethanes.

STRUCTURE AND PROPERTIES OF MACROMOLECULES:

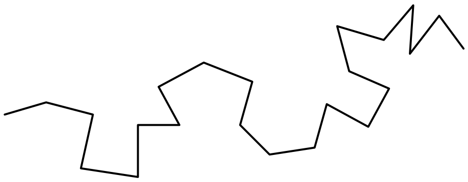
Macromolecules have a great size which has little effect on their chemical properties.

Physical properties of macromolecules differ from any ordinary molecule.

In a crystalline solid (in case of non-ionic compound), the structural unit –molecules are arranged in a very regular, symmetrical way , with a geometric pattern repeated over and over and extended in a regular zigzag. This regularity and close fitting of the molecule in crystal permits formation of strong intermolecular forces- Hydrogen bonding, dipole-dipole attractions, Van der Waals forces which results in a crystalline formation.

Long Chain Extended Conformation

If in a solid compound, the structural unit- molecules are arranged in a looped and coiled into a random conformation which permits formation of a weak intermolecular force – Hydrogen bonding, dipole-dipole attractions, Van der Waals forces which does not result in a crystalline formation.



Long Chain Random Conformation

A high polymer does not exist entirely in a crystalline form because of their big size of the molecule. When solidification begins, the viscosity of the polymer rises and polymer molecule find difficult to move about to arrange their long chain in the regular pattern needed for crystal formation.

Chains become entangled- a change in shape of a chain must involve rotation about single bonds but this become difficult because of hindrance to the swinging about of pendant groups. As a result polymer embedded in amorphous material.

Polymer can be used in various forms depending upon their structure- molecule and intermolecular as fibres, elastomers and plastics.

Fibres are long, thin, threadlike bits of materials having great tensile (pulling) strength in the direction of the fibre. Fibres are twisted into threads which can be woven into clothes or embedded in plastic material to impart strength.

The natural fibres are cotton, wool and silk. The tensile strength of synthetic fibres is enormous and as good as steel on a weight basis.

Fibre molecules are long, thin and threadlike which lie stretched out alongside each other and lined up in the direction of fibre. The strength of the fibre depends upon the strength of chemical bonds of the polymer chains. The lining up in fibre brought about by drawing-stretching- the polymeric material. This lining up have tendency to return to random looping and coiling which is overcome by strong intermolecular attraction in fibres.

The linear molecular shape of fibre permits side by side alignment and strong intermolecular forces which prevent slipping of one molecule past another by hydrogen bonding as shown in Nylon-6,6 resulted powerful dipole –dipole attractions and strong wander waals forces to maintain alignment.

The principal synthetic fibres are polyamides (nylon), polyesters (Dacron, terylene, vycron), polyacrylonitriles (acrylic fibres , orlon, acrilan), Polyurethanes (Spandex, vycra) and isotactic polypropylene.

In nylon, polyurethanes and polyacrylonitriles, molecular chains are held with each other by hydrogen bonds.

In polyesters and polyacrylonitriles, the polar carbonyl and cyano groups lead to powerful dipole-dipole attractions.

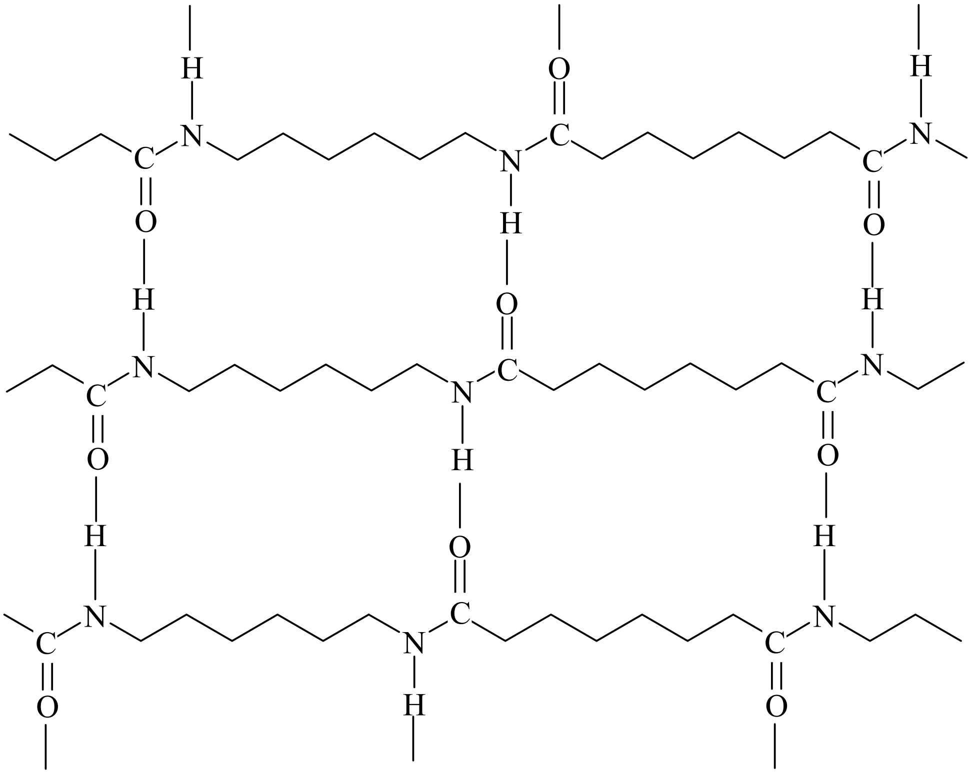
The stereoregular chains of isotactic polypropylene fit together so well that wander waals forces are strong enough to maintain alignment.

An elastomer possess high degree of elasticity which the characteristic of rubber.

An elastomer is the polymers which stretched (deformed) under tension to eight times its original length with little loss of energy as heat. When stretching force is removed, molecular chains of an elastomer do not remain extended and aligned but return to their original random conformations because of weak intermolecular forces.

lastomer do not contain highly polar groups or sites for hydrogen bonding and the extended chains do not fit together very well as a result wander waals forces are weak.

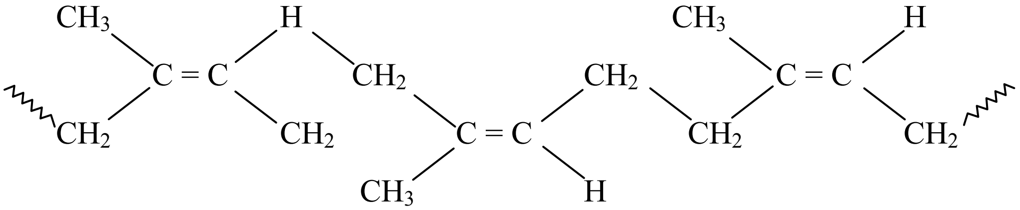
In elastomer, long chain is connected to each other by occasional cross linking which prevents slipping of the molecule past one another which deprived the chains of the flexibility which is needed for ready extension and return to randomness.



Hydrogen Bonding In Crystallites of nylon-6,6

Natural rubber is an elastomer which contains long, flexible chain with weak intermolecular forces and occasional cross linking.

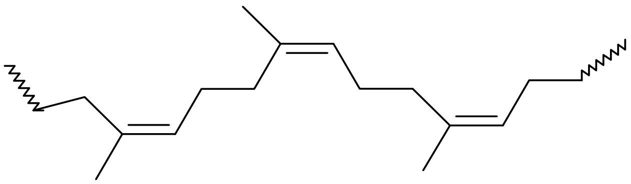
Natural Rubber (cis-1,4-polyisoprene) does not contains any highly polar substitutions and also because of all cis configuration about the double bond they will not fit together well, as a result intermolecular force of attractions is weak and wander waals forces is also weak. Therefore melting point of natural rubber is lower compare to its trans stereoisomer (synthetic rubber).



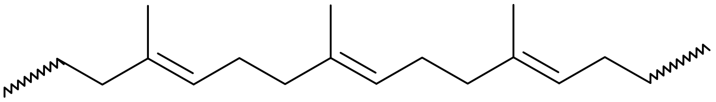
Natural rubber
All – cis configuration

In synthetic rubber, trans configuration permits a highly regular zigzag configuration which fit together well as a result intermolecular force of attractions is higher and wander waals forces is also higher. Therefore melting point of synthetic rubber is higher compare to its cis stereoisomers (natural rubber).

The all Trans stereoisomer occurs naturally as gutta percha which is highly crystalline and non elastic.



Extended chains of natural rubber, cis-1,4-polyisoprene



Extended chains of gutta precha, its trans stereoisomer

Synthetic elastomer SBr is a copolymer of butadiene (75%) and styrene (25%) used for the making of automobile tyres.

Plastics materials used in the form of sheets, pipes, films and molded objects like toys, bottles, knobs, handles, switches, dishes, fountain pens, tooth brushes, valves, gears, bearings, cases for radios & television sets, boats, automobile bodies and for houses.

The molecular structure of plastics is of two types, linear and branched.

Plastics which on heating become soften are known as thermoplastic can be molded or extruded. Space network polymers like urea formaldehyde, phenol formaldehyde are highly cross linked, rigid three dimensional –gigantic molecules, heating does not soften it. Since softening would require breaking of covalent bonds but heating may cause formation of additional cross linking and make them harder. Such polymers are called thermo setting polymers.

DISTINGUISHING FEATURES OF ADDITION AND CONDENSATION POLYMERIZATIONS:

ADDITION POLYMERIZATION	CONDENSATION POLYMERIZATION
1. Only growth reaction adds repeating units at a time to the chain	1. Any two molecular species can undergo reaction.
2. Monomer concentration has been found to decrease steadily continuously throughout reaction.	2. Monomer disappears early in reaction.
3. As high polymer is formed at once, its molecular weight changes little throughout the reaction.	3. The molecular weight of high polymer increases steadily throughout reaction.
4. Long reaction times give high yields but molecular weight changes little	4. Long reaction times are essential for getting high molecular weights.
5. At the end of reaction, the reaction mixture will have monomer, high polymer and about 10 – 8 part of growing chains.	5. At any stage of the reaction all molecular species have been found to be present in a calculatable distribution ranging from pure monomer to the highest polymer present.

COPOLYMERS:

There are the polymers which contain two or more monomeric units. The properties of a copolymer are entirely different from a physical mixture of the two individual polymers. Thus, it is often possible in a copolymer to combine the good qualities of each polymer, whereas a physical mixture often merely emphasizes the bad ones. For example, the copolymer of vinyl acetate and vinyl chloride combines the higher softening point of polyvinyl chloride with the greater thermal stability of polyvinyl acetate.

When two monomers are polymerized together, the composition of the copolymer will not be the same as that of the monomer mixture. If the copolymerization of two monomers A and B is considered, the polymerization occurs by a combination of the following four reactions:

(a) Alternating Copolymer	– ABABABAB –
(b) Random Copolymer	– ABBBAABAAAABBABABBAB –
(c) Block Copolymer	– AAAAAAAAAAAABBBBBBBBBBBBB–
(d) Graft Copolymer	– AAAAAAAAAAAAAAAAAAAAAAAAA –

```
        |          |      |
        B          B      B
        B          B      B
        B          B      B
```

A block copolymer consists of one in which blocks of repeating units of one type alternate with blocks of another type. Block copolymers are produced by the introduction of end groups which can be made to react under different conditions.

Block copolymers may be produced by the following four techniques:

(a) Utilize reactive end groups.
(b) Activate end groups
(c) Fragment a chain to produce active end groups or
(d) Transport reactive end groups into a different media.

A graft copolymer consists of linear polymer chains of one type to which has been grafted side – chains of different types of polymer. The formation of a graft copolymer can be brought about by either of two general methods:

1. Initiation of chain growth of monomer B on an existing polymer molecule formed from monomer A or
2. Termination of chain growth of polymer B by an existing polymer molecule formed from monomer A.

The importance of the block and graft copolymers is that the resultant material tends to exhibit the properties of each homopolymer. For example, pure polystyrene is quite brittle, whereas polymerization in the presence of about 5 percent of rubber produces a material which is strong and tough.

Polyacrylonitrile is an excellent textile fibre but is difficult to dye. However, by its copolymerization or by grafting on a second polymer, it is possible to maintain the desirable properties of the fibre, yet produce a textile which can be processed in the usual way.

CLASSIFICATION OF POLYMERS:

Polymers are classified into the following three classes as given below.

1. Classification based on method of preparation:

   The synthetic polymers may be classified into two groups depending upon the process involved during their preparation.

   These groups are **CONDENSATION** and **ADDITION POLYMERS** which involve condensation and addition polymerization processes respectively during their syntheses.
2. Classification based on the behavior of heating:

   On the basis of behavior of heating the synthetic polymers may be classified into the following two types.

   (a) **Thermoplastics:** These are the polymers which soften on heating and regain their original properties on cooling.
   (b) **Thermosettings:** These are the polymers which are changed irreversibly into hard and rigid materials on heating.

Linear polymers are generally thermoplastics whereas cross linked polymers are always thermosetting.

3. Classification based on physical properties:

   On the basis of physical properties the synthetic polymers may be classified into the following three groups:

   (a) **Fibres:** These are linear polymers which have relatively high tensile strength but low elasticity in the direction of the fibre axis. Normally for a material to be classed as a fibre, its length must be at least 100 times its diameter.

   (b) **Plastics:** According to the American Society For Testing Materials, a plastic is defined as a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and at some stage in its manufacture or in it's processing into finished articles, can be shaped by flow.

   The above definition is quite broad and includes essentially all the synthetic polymers. In practice, a plastic is usually considered to be an amorphous or crystalline polymer which is hard and brittle at ordinary temperatures.

   (c) **Elastomers:** There are the polymers which must stretch rapidly under tension to several times its original length with little loss of energy as heat. Elastomers are amorphous polymers with considerable cross – linkage to prevent gross mobility of linear chains.

   A good elastomer should not undergo plastic flow in either the stretched or relaxed state and when stretched should have a "memory" of its relaxed state.

   These conditions are best achieved in a natural rubber by vulcanization. This process introduces sulphur cross links into the chains, these cross links prevent slipping and serve a sort of a frame work for the stretched polymer to return to, when allowed to relax.

PLASTICS AND RESINS:

As no sharp line of demarcation exists between plastics and resins, these terms are sometime employed interchangeably. However both these terms are defined as follows:

1. **Plastics:** These are relatively tough substances of high molecular weights and soften on heating. Unlike resins, plastics are readily attacked by chemicals.
2. **Resins:** These are generally of low molecular weights and withstand high temperatures. Unlike plastics, these are resistant to chemicals.

Due to their similarities, plastics and resins are studied together under two broad categories which are differentiated by the action of heat.

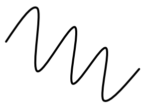
1. **Thermoplastics:** These are the substances which can be softened and molded on heating.

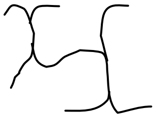
2. **Thermosetting resins:** These are substances which involve cross – linking so that the finished substances cannot be made to flow or melt.

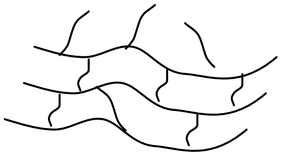
We shall discuss these as given below.

1. **Thermoplastics:** These are obtained either from cellulose, natural rubber, etc. or by the addition polymerization of compounds having a terminal double bond, > C = C <. Certain substances like high – boiling liquids are added to the plastic polymers during their manufacture to impart toughness, and flexibility at ordinary temperatures. These substances are called plasticizers. The common plasticizers are esters of phthalic acid, tricresyl phosphates (TCP) and stearic acid esters.

   Thermoplastics have been studied under two categories:
    1. Derivatives of natural polymers or cellulose.
    2. Addition polymers derived from substituted ethylenes.
2. **Thermosetting Resins:** Network polymers are also called thermosetting polymers. Simulated linear, branched and network polymer structure are shown in figure.


Linear


Branched


Network

Thermosetting resins are obtained by introducing cross linkages between the polymer chains. These are usually introduced by heat. The amount of heat required to introduce cross linkages depends upon the manner and the number of cross – linkages in the product. Thermosetting resins are infusible, insoluble products.

The necessary condition for the formation of thermosetting resins is that one of the monomers must possess more than two functional groups because if both the monomers possess two functional groups each, only a linear polymer is obtained which will be thermoplastic in nature.

PHASE SYSTEM FOR POLYMERIZATION :

Polymerization is an exothermic reaction. Therefore, it is carried out under conditions which control temperature and catalyst.

This process may be carried out in homogeneous system (e.g. Bulk and Solution Polymerization) or heterogeneous system (e.g. Suspension and Emulsion Polymerization).

(a) Bulk Polymerization :

The bulk Polymerization of liquid or gaseous monomer is carried out without adding any solvent.

This polymerization is preferred when the reaction is not too strongly exothermic and the mixture does not become too viscous before the polymerization reaches an advanced stage.

The advantages associated with bulk Polymerization are the employment of a simple apparatus, minimum contamination and straight forward recovery of the polymer.

Bulk Polymerization is mainly employed in condensation polymerization.

(b) Solution Polymerization :

This type of polymerization involves the control of temperature in an easy manner because in this process the monomers are dissolved in suitable solvent and the upper temperature limit of the system depends upon the boiling point of the solvent.

The main disadvantages of Solution Polymerization are as follows.

(i) The polymer produced is of low average molecular weight.

(ii) The polymer produced is contaminated with traces of the solvent.

(iii) Another difficulty arises when the solvent also acts as a chain transfer agent.

(c) Emulsion Polymerization :

The drawbacks of the both Bulk Polymerization and Solution Polymerization are overcome by emulsion Polymerization.

In emulsion Polymerization, the aqueous monomer is polymerized in the presence of an emulsifier (e.g., a fatty acid) and an initiator (e.g., an organic persulphate or hydrogen peroxide in the presence of Fe^{3+} ion).

Emulsion Polymerization proceeds rapidly and yields products whose molecular weights are higher than that of the products obtained in both Bulk and Solution Polymerizations.

Emulsion Polymerization is preferred when the product is required in emulsion form.

Emulsion Polymerization is mainly used for the manufacture of most of the commercial polymers.

(c) Suspension Polymerization :

In this type of polymerization, the aqueous monomer is agitated in the presence of a stabilizer which keeps the monomer disappeared in small globules (0.1 to 5 mm in diameter).

The initiator added to the monomer is generally oil soluble organic peroxide which is soluble in monomer droplets. Thus, the reaction system may be considered to be made up of a large number of small bulk polymerization in a form which controls the evolved heat effectively.

By suspension Polymerization, the polymer obtained is in the form of spheres or pearls. This polymer may be easily recovered on a drum filter, washed and dried.

Suspension Polymerization is mainly used in the manufacture of various vinyl polymers like polystyrene, polyvinyl chloride, polyacrylonitrile and polymethylmethacrylate.

QUESTIONS

Q – I : Choose the correct option from the following.(Multiple choice question) **(" C " is correct option)**								
(1)	Which of the following stop the polymerization ?							
	(a)	Initiator	(b)	Monomer	(c)	**Inhibitors**	(d)	Catalyst
(2)	Polymer prepared from single monomer is known as -----------.							
	(a)	Copolymer	(b)	Cross- linked polymer	(c)	**homopolymer**	(d)	None of these
(3)	Polymer prepared from two or more different monomer is known as -----------.							
	(a)	homopolymer	(b)	Cross- linked polymer	(c)	**Copolymer**	(d)	None of these
(4)	Which of the following is used as adhesives?							
	(a)		(b)		(c)	**polyisobutylene**	(d)	None of these
(5)	Which of the following polymerization permit stereochemical control?							
	(a)	Anionic	(b)	Cationic	(c)	**Coordination**	(d)	None of these
(6)	Which of the following extruded as sheets or pipes?							
	(a)	Elastomers	(b)	Fibres	(c)	**Plastics**	(d)	None of these
(7)	Which of the following soften on heating and regain original properties on cooling?							
	(a)	Fibres	(b)	Thermosetting resins	(c)	**Thermoplastics**	(d)	None of these
(8)	Which of the following is cross-linked and harden on heating?							
	(a)	Fibres	(b)	Thermoplastics	(c)	**Thermosetting resins**	(d)	None of these
(9)	Anionic polymerization is also known as --------------- polymerization?							
	(a)	Dying	(b)	Coordination	(c)	**Living**	(d)	None of these
(10)	What is the configuration at every double bond in Natural rubber?							
	(a)	Aii cis	(b)	Cis and trans	(c)	**All cis**	(d)	None of these
(11)	Which of the following is used as electric insulator?							
	(a)	Bakelite	(b)	Teflon	(c)	**Polystyrene**	(d)	None of these

(12)	Which of the following have very high tensile strength?							
	(a)	Plastics	(b)	Elastomers	(c)	**Fibres**	(d)	None of these
(13)	Which of the following molecular formula will correspond to an alkene with two double bonds?							
	(a)	C_4H_{12}	(b)	C_5H_{12}	(c)	**C_8H_{16}**	(d)	C_6H_{12}
(14)	How many sigma bonds are there in $CH_2=CH-CH=CH_2$?							
	(a)	3	(b)	6	(c)	**9**	(d)	12
(15)	Which of the following is obtained as major product when 1,3-butadiene reacts with Br2?							
	(a)	3,4-dibromo-1-butene	(b)	4-bromo-1-butene	(c)	**1,4-dibromo-2-butene**	(d)	1-bromo-2-butene
(16)	Propadiene ($CH_2=C=CH_2$) is -----------							
	(a)	Planar compound	(b)	Isolated diene	(c)	**Cumulated diene**	(d)	Conjugated diene
(17)	Bakelite is obtained from -------------							
	(a)	Adipic acid and hexamethylene diamine	(b)	neoprene	(c)	**Phenol and formaldehyde**	(d)	Dimethylterephthalate and ethylene glycol
(18)	Which of the following is obtained when Adipic acid reacts with hexamethylene diamine?							
	(a)	Bakelite	(b)	Nylon-6	(c)	**Nylon-6,6**	(d)	Terylene
(19)	Which of the following is thermosetting polymer?							
	(a)	Bakelite	(b)	Nylon-6,6	(c)	**Teflon**	(d)	Polyethyelene
(20)	Which of the following is obtained when ethylene glycol reacts with dimethylterephthalate?							
	(a)	Nylon-6,6	(b)	Teflon	(c)	**Dacron**	(d)	Orlon
(21)	Natural rubber is a polymer of _______							
	(a)	Propene	(b)	formaldehyde	(c)	**isoprene**	(d)	Phenol
(22)	Neoprene is a polymer of __________ monomer.							
	(a)	isoprene	(b)	isobutane	(c)	**Chloroprene**	(d)	isopentane
(23)	Which of the following is more stable ?							
	(a)	1, 4 - Pentadiene	(b)	1, 5 - Hexadiene	(c)	**2 , 3 - Methyl - 1, 3 - Butadiene**	(d)	1, 3 - Butadiene

(24)	Which of the following is least stable ?							
	(a)	1, 3 - Pentadiene	(b)	1, 3 - Butadiene	(c)	**1, 4 - Pentadiene**	(d)	2 - Methyl - 1, 3 - Butadiene
(25)	Which of the following is known as Isoprene ?							
	(a)	2 , 3 - Dimethyl - 1, 3 - Butadiene	(b)	1, 5 - Hexadiene	(c)	**2 - Methyl - 1, 3 - Butadiene**	(d)	1, 4 - Pentadiene
(26)	Which of the following is known as Allene ?							
	(a)	2 - Methyl - 1, 3 - Butadiene	(b)	2 ,3 -Dimethyl - 1, 3 - Butadiene	(c)	**1, 2 - Propanediene**	(d)	1, 3 - Butadiene
(27)	The values for heat of hydrogenation of 1, 3 - Pentadiene is _______ K Cal / mole .							
	(a)	60.8	(b)	60.5	(c)	**54.1**	(d)	53.1
(28)	The values for heat of hydrogenation of 1, 3 - Butadiene is _______ K Cal / mole .							
	(a)	54.1	(b)	53.1	(c)	**57.1**	(d)	53.9
(29)	Which of the following is conjugated diene ?							
	(a)	1, 4 - Pentadiene	(b)	1, 5 - Hexadiene	(c)	**1, 3 - Pentadiene**	(d)	1, 2 - Propanediene
(30)	Which of the following is non - conjugated diene ?							
	(a)	1, 3 - Pentadiene	(b)	1, 3 - Butadiene	(c)	**1, 4 - Pentadiene**	(d)	2 - Methyl - 1, 3 - Butadiene
Q – II: Define the following terms.								
	(1)	Vulcanization	(2)	Resonance	(3)	Hyper conjugation	(4)	Plastics
	(5)	Elastomers	(6)	Inhibitors	(7)	Living polymer	(8)	Copolymerization
	(9)	Conjugation	(10)	Heat of hydrogenation	(11)	Polymerization	(12)	Polymer
	(13)	Resonance	(14)	Resonance Energy	(15)	Free radical Polymerization	(16)	Chain reaction radical Polymerization
	(17)	Step raection Polymerization	(18)	Free radical vinyl Polymerization	(19)	Copolymerization	(20)	Block copolymer
	(21)	Graft copolymer	(22)	Ionic polymerization	(23)	Cationic polymerization	(24)	Anionic polymerization
Q – III: Answer the followings. (Short questions)								

(1)	Give the classification of diene.
(2)	1, 3 - Pentadiene is more stable than 1, 4 - Pentadiene. Explain it.
(3)	Discuss resonance in conjugated diene.
(4)	What is hyperconjutation ?
(5)	Differentiate between Addition Polymerization and Condensation Polymerization.
(6)	Give the synthesis of vulcanized rubber.
(7)	Differentiate chain reaction polymerization from step reaction polymerization.
(8)	Write the reaction mechanism of cationic polymerization.
(9)	Explain isotacticity and syndiotacticity in polymers.
(10)	Melting point of natural rubber is lower than synthetic rubber. Explain it.
(11)	What is Bulk Polymerization ?
(12)	What is Solution Polymerization ?
(13)	What is Emulsion Polymerization ?
(14)	What is Suspension Polymerization ?
Q – III: Answer the followings. (Long questions)	
(1)	Give the classification of polymers.
(2)	Give the reaction mechanism for electrophilic addition reaction of 2,4- hexadiene with HCl.
(3)	What is step reaction polymerization? Write the synthesis of Dacron.
(4)	Define free radical polymerization. Give reaction mechanism of free radical polymerization of vinyl chloride.
(5)	Define copolymerization and give its classification in detail.
(6)	Give an account of coordination polymerization.
(7)	Give an account of ionic polymerization.
(8)	Discuss Coordination polymerization.
(9)	Discuss step reaction polymerization.
(10)	Discuss structure and properties of macromolecules.
(11)	Discuss phase system for polymerization.

SARDAR PATEL UNIVERSITY
Programme: B.Sc (Chemistry)
Semester: V
Syllabus with effect from June 2020
(30 +70 Marks, 4 hrs per week)

Subject Code: US05CCHE21		**Total Credit: 4**
Title of Subject: Organic Chemistry		
Learning outcomes of the paper: From the study of this paper, student will learnt about basic concept of heterocyclic chemistry, reaction mechanism, Dienes And Macromolecules and Terpenoids. This study will helpful them in further studies and in industries.		
Unit	**Description in detail**	**Weightage (%)**
I	**Heterocyclic Compounds** Heterocyclic systems, Structure of Pyrole, furan and thiophene, Source of Pyrole, furan and thiophene, Electriphilic substitution in Pyrrole, furan and thiophene Reactivity and orientation, Saturated five – membered heterocycle, Structure of pyridine, Sources of pyridine compounds, Reactions of pyridine, Electrophilic substitution in pyridine, Nucleophilic substitution in pyridine, Basicity of pyridine, Reduction of pyridine, Quinoline. The skraup synthesis, Isoquinoline. The Bischler–Napieralski synthesis. Knorr pyrrole synthesis.	25%
II	**Reaction Mechanism** Baeyer Villiger oxidation, Hofmann rearrangement, Mannich reaction, Curtius–Schmidt rearrangement, Benzilic acid rearrangement, Sommlet rearrangement, Birch reduction, Favorskii rearrangement, Benzoin condensation, Beckmann rearrangement, Wittig reaction, Perkin reaction.	25%
III	**Dienes And Macromolecules** Dienes: Structure and properties, Stability of conjugated dienes, Resonance in conjugated dienes, Hyperconjugation, Ease of formation of conjugated dienes, Electrophilic addition to conjugated diene : 1,4- addition,1,2 Vs 1,4-addition, Rate Vs equilibrium, Free-radical polymerization of diene, Polymer and polymerization, Free radical vinyl polymerization, Co-polymerization, Ionic polymerization, Coordination, polymerization, Step reaction, polymerization, Structure and properties of macromolecules. Distinguishing features of addition and condensation polymerization Copolymer, classification of polymers, plastics and resins, Phase system for polymerization (like bulk, solution, emulsion and suspension polymerization).	25%
IV	**Terpenoids** General introduction including nomenclature, General properties of terpenoids, Isolation, Isoprene rule, Classification of terpenoids, General methods for the determination of structure of terpenoids. Introduction, isolation and constitution of Citral, α- terpineol, Camphor, B-carotene.	25%

Reference Books :-

1. Organic chemistry of natural products by Gurdeep Chatwal, Vol. II.

2. Organic Chemistry by Morrison and Boyd, 6th ed.
3. Synthetic organic chemistry by Gurdeep R. Chatwal
4. Reaction mechanism in Organic Chemistry by S. M. Mukherji.
5. Organic reaction mechanism by R.K. Bansal, 3rd ed.
6. Org. Chem., Vol II, by I.L. Finar.