Module – 37.1 & 37.2

Polymers - I

Introduction:

The word polymer has been derived from Greek **(Poly = many; mer = part)**.
Polymers are macro – sized molecules of relatively high molecular masses, some of which find extensive use in our daily life.

Polymers are large but single chained molecules. In these molecules the repeating unit is derived from small molecules called monomers and these are covalently linked.

Structurally, they are characterized by linear chains or a cross – linked network.

Common examples of materials made of polymers are plastic dishes, cups, non – stick pans, automobile tyres, plastic bags, rain coats, television and computer cabinets, flooring materials and materials for biomedical and surgical operations.

Some Important Terms:

Polymer:

Polymer is a compound of high molecular mass formed by a repeated combination of small molecules called monomers.

Monomers:

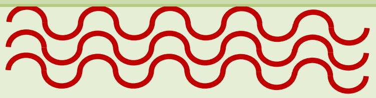
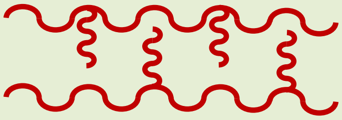
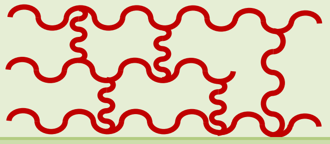
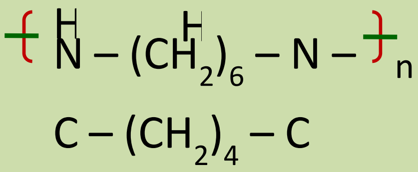
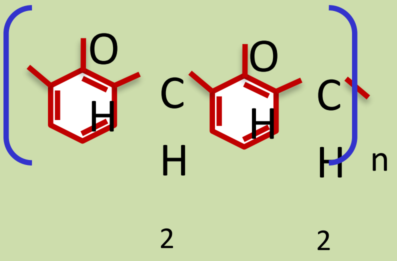
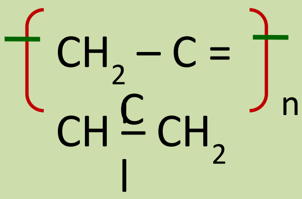
Monomers are small units, which constitute the repeating units in polymers.

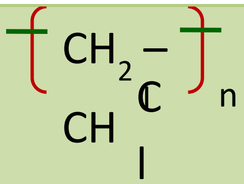
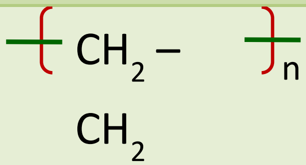
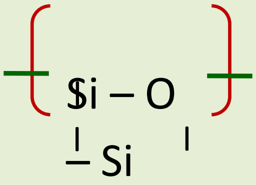
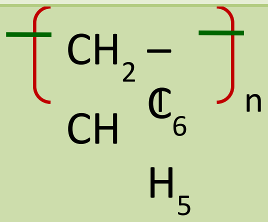
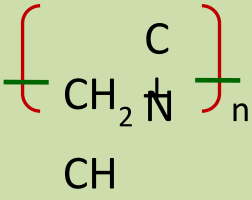
Polymerization:

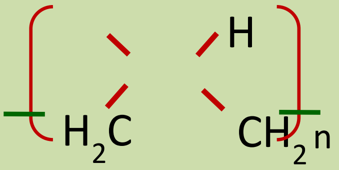
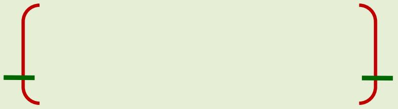
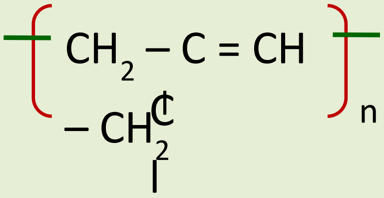
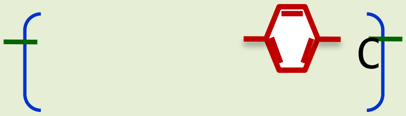
The repeated addition of similar or dissimilar simple units to form a giant molecule is known as polymerization. In the process monomers are transformed into polymers.

Classification of polymers:

S.NO (1)	Basis of classification (2)	Nature of polymers (3)	Common examples (if any) (4)	Some simple structures (5)
1.	Source of polymer	a. Natural polymers b. Semisynthetic polymers	Cotton, silk, wool and rubber etc Cellulose rayon; cellulose nitrate	

		c. Synthetic polymers	Polyethylene, PVC, nylon, terylene	
2.	Structure of polymers	a. Linear polymer	Polythene, PVC	
		b. Branched polymer	Low density polythene	
		c. Cross linked or network polymers	Bakelite; melamine	
3.	Mechanism of polymerization	a. Condensation polymers	Terylene; Nylon – 6, 6 Bakelite	 $\left[\overset{H}{N}-(CH_2)_6-\overset{H}{N}-\right]_n$ $C-(CH_2)_4-C$ 
		b. Addition polymers	Neoprene; polyvinyl pyrrolidone (PVP), PVC	 $\left[CH_2-C=\right]_n$ $CH\overset{C}{-}CH_2$

				 $\left[CH_2 - \underset{Cl}{CH} \right]_n$
4.	Heat treatment	a. Thermoplastic polymers b. Thermosetting polymers	Polyethylene, PVC, Nylon and sealing wax Bakelite, polysiloxanes	 $\left[CH_2 - CH_2 \right]_n$  $\left[Si - O \right]$
5.	Polarity	a. Cationic polymerization polymers b. Anionic polymerization polymers	Polystyrene; Polyvinyl ethers, poly isobutene Buna type synthetic rubbers Polyacrylonitrile Poly isoprene	 $\left[CH_2 - \underset{C_6H_5}{CH} \right]_n$  $\left[CH_2 - \underset{CN}{CH} \right]_n$

				
6.	Molecular forces	a. Elastomers	Buna – N	
			Buna – S	
			Neoprene	 $\left[CH_2 - \underset{Cl}{C} = CH - CH_2 \right]_n$
		b. Fibres	Polyamides; Nylon 6, 6; Polyesters Terylene (or) dacron	
		c. Thermoplastic polymers	Polythene; Polystyrene; Polyvinyl	
		d. Thermosetting polymers	Bakelite Urea – HCHO resins	They soften on heating and harden on cooling They undergo extensive cross – linking in moulds and become infusible afterwards
7.	Organic and inorganic substances	a. Organic polymers	Leather; cellulose; rayon	$(C_6H_{10}O_5)_n$
		b. Inorganic polymers	Glass, silicone rubbers etc	

General Methods of Polymerization:

A few major methods that are generally used for preparing polymers are:

a. Condensation polymerization.
b. Addition polymerization.
c. Co-polymerization

a. Condensation polymerization method:

Condensation polymers are formed when the monomers containing active functional groups (generally two), react together with the elimination of a small molecule like water, ammonia, alcohol etc.

Examples: Nylon-66, polyester, bakelite etc.

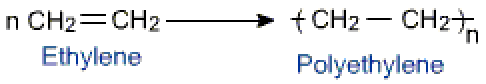
Nylon – 66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:

Hexamethylene diamine **Adipic acid** → **Nylon - 66**

b. Addition polymerization method:

Addition polymers are formed when monomer units are separately added to form long chains without elimination of any molecules. These polymers are formed by reactions between monomer molecules having multiple bonds.

Example: Ethylene undergoes polymerization to form polythene.



The empirical formula of the monomer and polymer are the same.

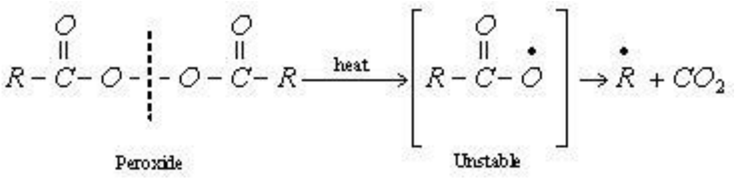
Addition polymerization reactions take place. The mechanisms of these processes are of two types. They are:

a. Free Radical mechanism and
b. Ionic Addition Polymerization.

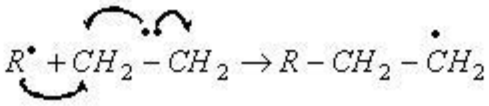
a. Free-radical mechanism of polymerization:

Free-radical polymerisation is initiated by organic peroxide or other reagents. These reagents decompose to give free radicals. Following steps are involved.

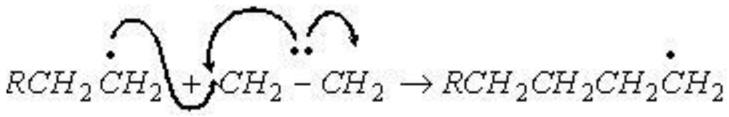
i. **Chain initiation:** Organic peroxides undergo homolytic fission to form free radicals.



ii. **Chain propagation:** Free radical adds to the monomer (i.e. an alkene) molecule to form a new free radical.



The free radical formed attacks another alkene molecule and the process continues in building a long chain.



iii. **Chain termination:** The chain reaction comes to halt when two free radicals (either chains or monomer units) combine.

$$2[R(CH_2CH_2)_n\ CH_2CH_2] \longrightarrow R\ (CH_2CH_2)_n\ CH_2CH_2 : CH_2CH_2\ (CH_2CH_2)_n\ R$$

Benzoyl or t – Butyl peroxide is common initiators, used.

Free radical polymerisation can also be initiated by a mixture of ferrous sulphate and hydrogen peroxide ($FeSO_4 + H_2O_2$).

b. Ionic Addition Polymerization:

Vinylic monomers can undergo addition polymerization through the formation of ionic intermediates instead of free radicals. Here the initiator is an ion, and not a free radical. Ionic polymerization may be:

a. Cationic addition polymerization
b. Anionic addition polymerization

a. Cationic mechanism:

Cationic polymerisation is initiated by use of acids such as H_2SO_4, *HF* or BF_3 in H_2O .

The following steps are involved:

i. **Chain initiation:** The acid furnishes proton.

$$H_2SO_4 \rightleftharpoons H^+ \; HSO_4^-$$

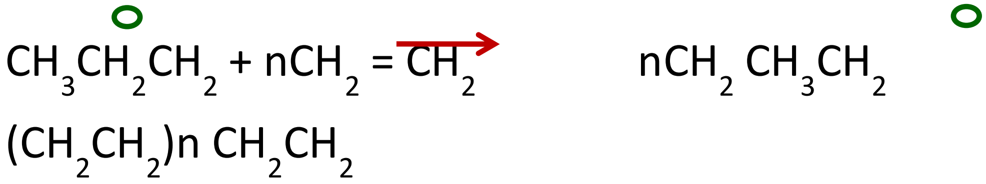
$$HF \rightleftharpoons H^+ + F^-$$

$$BF_3 + H_2O \rightleftharpoons H^+ + BF_3\,(OH)^-$$

The proton adds to the carbon of the double bond of the monomer (alkene) to form a carbonium ion.

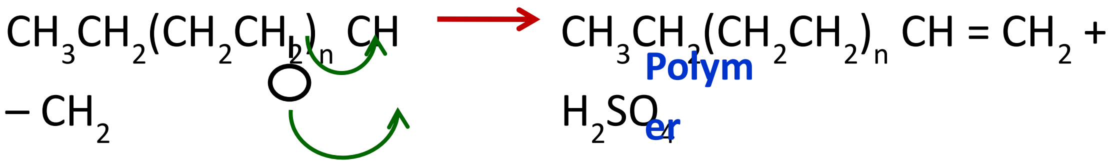
$$H^{+} + CH_2 \overset{\curvearrowleft}{=} CH_2 \rightarrow CH_3\overset{+}{C}H_2$$

ii. **Chain propagation:** The carbonium ion combines with another molecule of alkene to form a new carbonium ion and the process continues to form a long chain.



$$CH_3CH_2\overset{\ominus}{C}H_2 + nCH_2=CH_2 \rightarrow nCH_2\ CH_3CH_2\ (CH_2CH_2)n\ CH_2\overset{\ominus}{C}H_2$$

iii. **Chain termination:** The chain may be halted by combination with negative ion or loss of a proton.

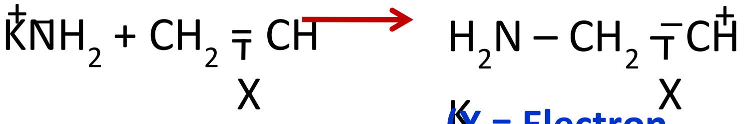


$$CH_3CH_2(CH_2CH_2)_n\ \overset{\ominus}{C}H - CH_2 \rightarrow CH_3CH_2(CH_2CH_2)_n\ CH = CH_2 + H_2SO_4$$

b. Anionic Addition Polymerization:

An anionic initiator will generate a carbanion as an intermediate and thus the polymerization is of anionic addition type. Here the active centre of the propagating species is negatively charged. Hence it occurs easily with monomers containing electron withdrawing groups such as phenyl, nitrile etc., which are able to stabilize the propagating species.

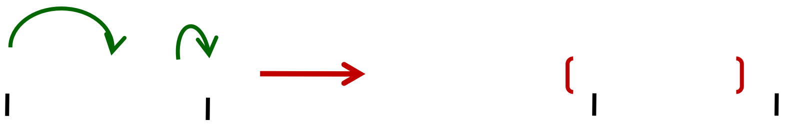
i. **Chain initiation:** Initiation can be brought about by reagents such as n-butyl lithium or potassium amide. In the initiation step, the base adds to a double bond to form a carbanion.



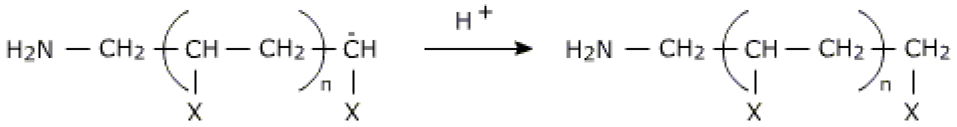
$$\overset{+}{K}\overset{-}{N}H_2 + CH_2 = \underset{X}{CH} \rightarrow H_2N - CH_2 - \underset{X}{\overset{-}{C}H}\ \overset{+}{K}$$

(X = Electron withdrawing group)

ii. **Chain propagation:** In the chain propagation, this carbanion adds to the double bond and the process repeats to form a long chain.



iii. Chain termination: The chain reaction can be terminated by addition of an acid.



$$H_2N-CH_2\left(\underset{X}{CH}-CH_2\right)_n\underset{X}{\overset{-}{C}H}\xrightarrow{H^+}H_2N-CH_2\left(\underset{X}{CH}-CH_2\right)_n\underset{X}{CH_2}$$

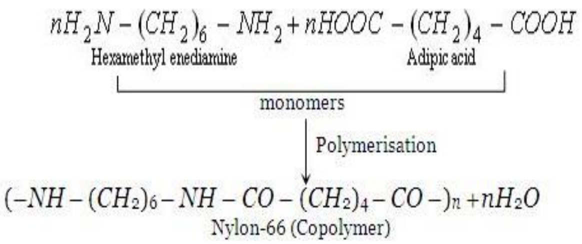
The formation of polystyrene from styrene in the presence of potassium amide is another example of this type of polymerization.

Difference between Addition and Condensation polymers:

Addition polymers	Condensation polymers
Formed by addition reaction. No elimination takes place.	Formed by condensation process with elimination of small molecules like H_2O.
Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
Generally involves identical monomer unit.	Generally involves more than one different monomer unit.
Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
Generally chain growth polymers.	Generally step growth polymers.

c. Co-polymerization:

A polymer formed from two or more different monomers is called **copolymer** or **mixed polymer**. For example, nylon-66 is a polymer of two types of monomers : hexamethylenediamine and adipic acid.

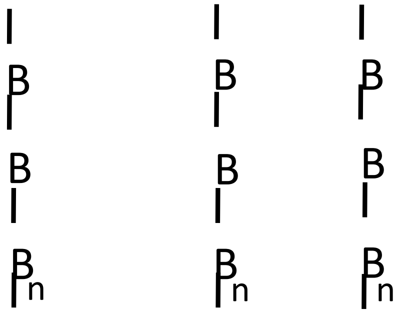


$$nH_2N-(CH_2)_6-NH_2+nHOOC-(CH_2)_4-COOH \xrightarrow{\text{Polymerisation}} (-NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-)_n+nH_2O$$

It may be noted that many types of copolymers can be obtained depending upon the distribution of monomer units in the chain. Two monomers can combine in either regular fashion (although this is rare) or random fashion. For example, if monomer A is copolymerised with monomer B, the resultant product may have a random distribution of the two units throughout the chain or it might have alternating distribution.

(– A – B – A – B – A – B – A – B –) **Alternating copolymer**

(– A – A – A – B – A – B – B – A – B –) **Random copolymer**



Assignment questions:

1. How are polymers classified? Give one example to each type
2. What is polymerisation? Give examples for different kinds of polymerization

Review questions:

Example set:

1. A high molecular weight molecule built form a large number of simple molecules is called a
    a. Mesomer
    b. Isomer
    c. Polymer
    d. Tautomer

Solution: c)

2. Terylene; nylon – 6, 6 and Bakelite are all examples of
    a. Addition polymers
    b. Condensation polymers
    c. Thermoplastic polymers
    d. Inorganic polymers

Solution: d)

3. Catonic polymerization is initiated by
    a. BF_3
    b. $NaNH_2$
    c. Base
    d. Both b) and c)

Solution: a)

4. In the propogation step of radical polymerization the reaction intermediate is
    a. Carbocation
    b. Carbanion
    c. Free radical
    d. Both a) and b)

Solution: c)

5. Write a note on
    a. Anionic polymerisation
    b. Cationic polymerization

Solution:

a. Cationic mechanism:

Cationic polymerisation is initiated by use of acids such as H_2SO_4, *HF* or BF_3 in H_2O

The following steps are involved:

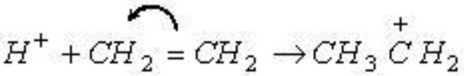
i. **Chain initiation:** The acid furnishes proton.

$$H_2SO_4 \rightleftharpoons H^+ HSO_4^-$$

$$HF \rightleftharpoons H^+ + F^-$$

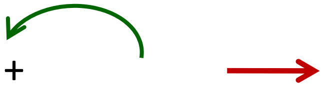
$$BF_3 + H_2O \rightleftharpoons H^+ + BF_3(OH)^-$$

The proton adds to the carbon of the double bond of the monomer (alkene) to form a carbonium ion.



$$H^+ + CH_2 = CH_2 \rightarrow CH_3\overset{+}{C}H_2$$

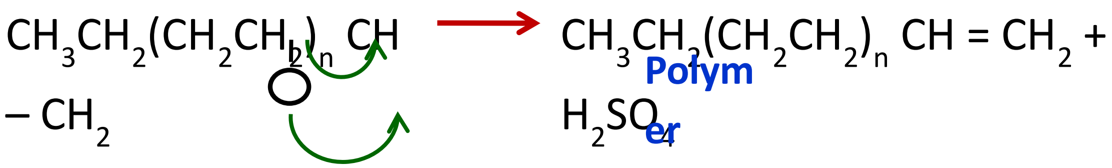
ii. **Chain propagation:** The carbonium ion combines with another molecule of alkene to form a new carbonium ion and the process continues to form a long chain.



$$CH_3\overset{\circ}{CH_2}CH_2 + nCH_2 = CH_2 \rightarrow nCH_2\,CH_3CH_2^{\circ}$$

$$(CH_2CH_2)n\;CH_2CH_2$$

iii. **Chain termination:** The chain may be halted by combination with negative ion or loss of a proton.

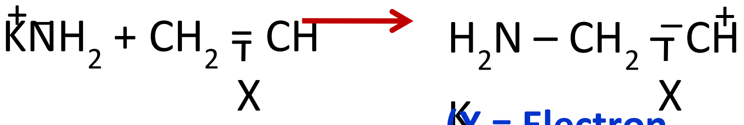


$CH_3CH_2(CH_2CH_2)_n\ CH - CH_2 \longrightarrow CH_3CH_2(CH_2CH_2)_n\ CH = CH_2 + H_2SO_4$

b. Anionic Addition Polymerization:

An anionic initiator will generate a carbanion as an intermediate and thus the polymerization is of anionic addition type. Here the active centre of the propagating species is negatively charged. Hence it occurs easily with monomers containing electron withdrawing groups such as phenyl, nitrile etc., which are able to stabilize the propagating species.

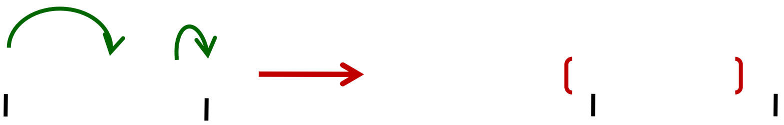
i. **Chain initiation:** Initiation can be brought about by reagents such as n-butyl lithium or potassium amide. In the initiation step, the base adds to a double bond to form a carbanion.



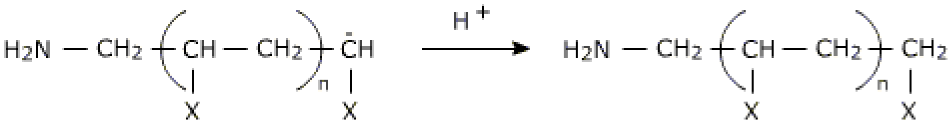
$$\overset{+}{K}\overset{-}{N}H_2 + CH_2 = \underset{X}{CH} \longrightarrow H_2N - CH_2 - \underset{X}{\overset{-}{C}H}\ \overset{+}{K}$$

(X = Electron withdrawing group)

ii. **Chain propagation:** In the chain propagation, this carbanion adds to the double bond and the process repeats to form a long chain.



iii. **Chain termination:** The chain reaction can be terminated by addition of an acid.



$$H_2N - CH_2 \left(\underset{X}{CH} - CH_2 \right)_n \underset{X}{\overset{-}{C}H} \xrightarrow{H^+} H_2N - CH_2 \left(\underset{X}{CH} - CH_2 \right)_n \underset{X}{CH_2}$$

The formation of polystyrene from styrene in the presence of potassium amide is another example of this type of polymerization.

6. Distinguish between condensation polymerization and addition polymerization

Solution: Difference between Addition and Condensation polymers:

Addition polymers	**Condensation polymers**
Formed by addition reaction. No elimination takes place.	Formed by condensation process with elimination of small molecules like H_2O.
Molecular mass is a whole number multiple of the monomer.	Molecular mass is not whole number multiple of the monomer units.
Generally involves identical monomer unit.	Generally involves more than one different monomer unit.
Monomers are unsaturated molecules.	Monomer units must have two active functional groups.
Generally chain growth polymers.	Generally step growth polymers.

Problem set:

1. The structure $-\!\!\left[CH_2 - CH_2 \right]\!\!-_n$ represents the polymer
   a. PVC
   b. Polyethene
   c. Nylon – 6, 6
   d. Bakelite

Solution: b)

2. Which of the following monomers undergoes cationic polymerization

a $CH_2 = CH$

b $CH_2 - CH$ – Cl

c – CN

d $(CH_3)_2C = CH_2$

.

Solution: d)

3. Which of the following monomers gives the polymer neoprene on polymerization
   a. $CH_2 = CHCl$
   b. $CCl_2 = CCl_2$
   c. $CH_2 = CHCl - CH = CH_2$
   d. $CF_2 = CF_2$

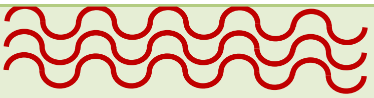
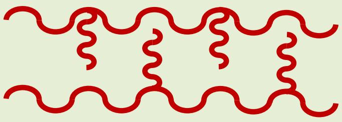
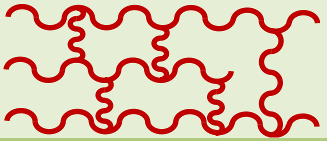
Solution: c)

4. Which of the following is a synthetic polymer
   a. Starch
   b. Silk
   c. Protein
   d. Polystyrene

Solution: d)

5. How are polymers classified on the basis of their structures

Solution:

1.	**Structure of polymers**	**a. Linear polymer** **b. Branched polymer** **c. Cross linked or network polymers**	**Polythene, PVC** **Low density polythene** **Bakelite; melamine**	  

6. Give a monomer in a condensation polymerization reaction

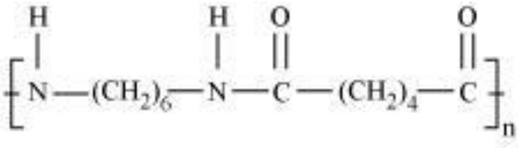
Solution: Nylon – 66 is formed by condensation between hexamethylene diamine and adipic acid as shown below:

→ — —

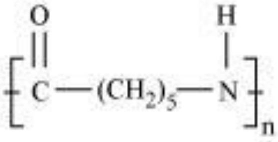
Hexamethylene diamine **Adipic acid** **Nylon - 66**

Exercise questions:

1. Write the names of monomers of the following polymers:

(i)


$$\left[\overset{H}{\overset{|}{N}} - (CH_2)_6 - \overset{H}{\overset{|}{N}} - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} \right]_n$$

(ii)


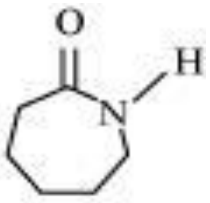
$$\left[\overset{O}{\overset{\|}{C}} - (CH_2)_5 - \overset{H}{\overset{|}{N}} \right]_n$$

(ii) $\left[CF_2 - CF_2 \right]_n$

2. Classify the following as addition and condensation polymers: Terylene, Bakelite, Polyvinyl chloride, Polythene.
3. Write the free radical mechanism for the polymerisation of ethene.
4. Write the name and structure of one of the common initiators used in free radical addition polymerisation.
5. Explain the term copolymerisation and give any two examples.

Solutions to exercise questions:

1. (i) Hexamethylenediamine [$H_2N - (CH_2)_6 - NH_2$] and adipic acid [$HOOC - (CH_2)_4 - COOH$]
   (ii)



Caprolactam

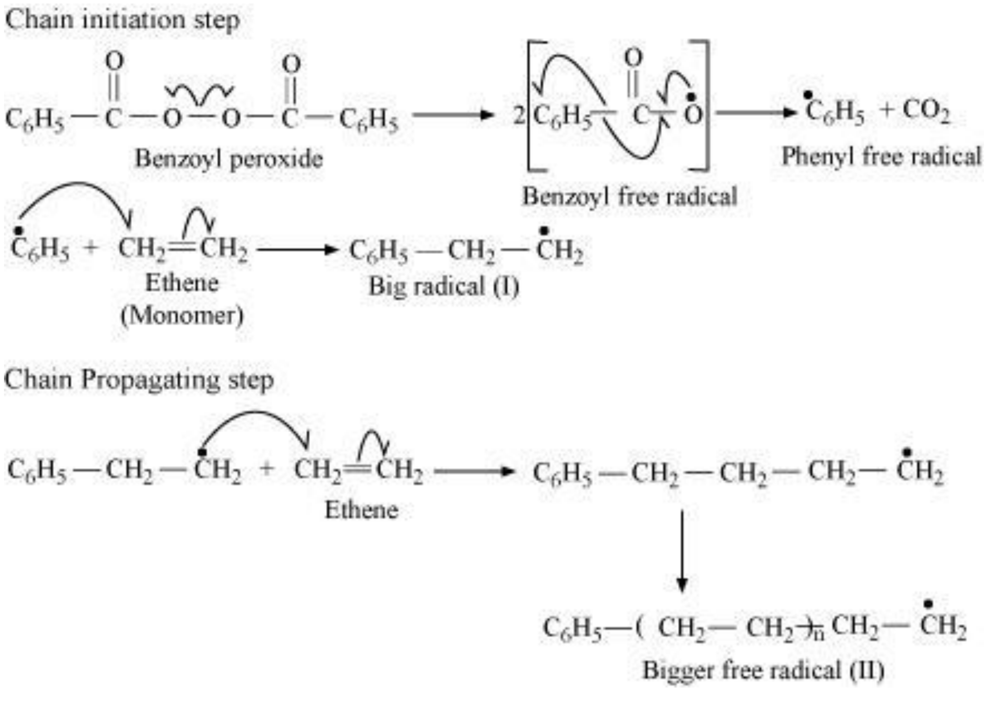
(iii) Tetrafluoroethene ($CF_2 = CF_2$)

2. Addition polymers: Polyvinyl chloride, polythene

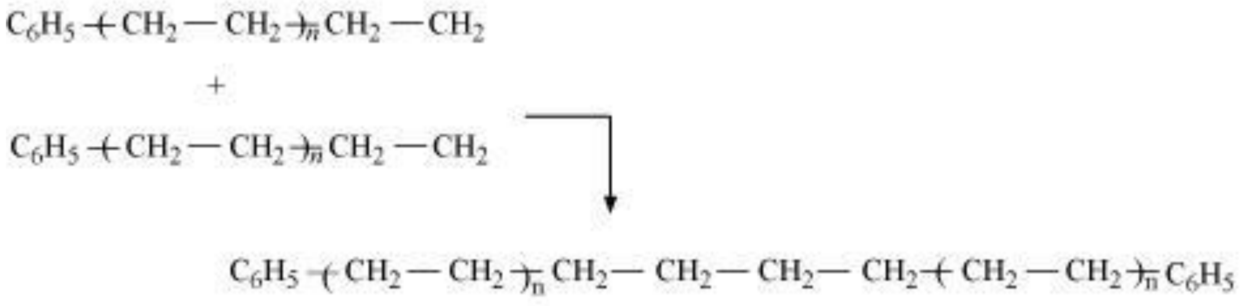
   Condensation polymers: Terylene, bakelite

3. Polymerization of ethene to polythene consists of heating or exposing to light a mixture of ethene with a small amount of benzoyl peroxide as the initiator.

   The reaction involved in this process is given below:



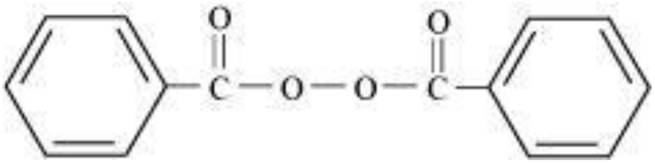
Chain Terminating step



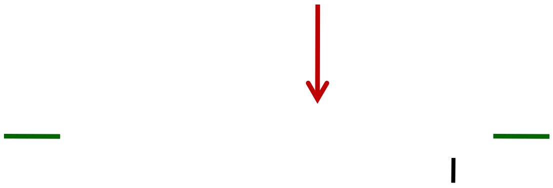
$$C_6H_5(CH_2-CH_2)_nCH_2-CH_2^{\cdot} + C_6H_5(CH_2-CH_2)_nCH_2-CH_2^{\cdot} \rightarrow C_6H_5(CH_2-CH_2)_nCH_2-CH_2-CH_2-CH_2(CH_2-CH_2)_nC_6H_5$$

Polythene

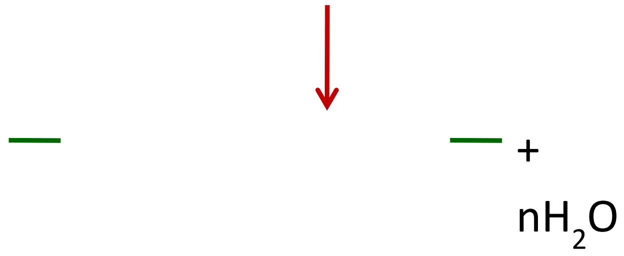
4. One common initiator used in free radical addition polymerization is benzoyl peroxide. Its structure is given below.



5. The process of forming polymers from two or more different monomeric units is called copolymerization. Multiple units of each monomer are present in a copolymer. The process of forming polymer Buna−S from 1, 3-butadiene and styrene is an example of copolymerization



Nylon 6, 6 is also a copolymer formed by the interaction of hexamethylenediamine and adipic acid.


+
nH_2O

Module – 37.3 and 37.4

Polymers – II

Rubber:

It is a polymer which is capable of returning to its original length, shape or size after being stretched or deformed. It is the example of an elastomer. Rubber is of two types.

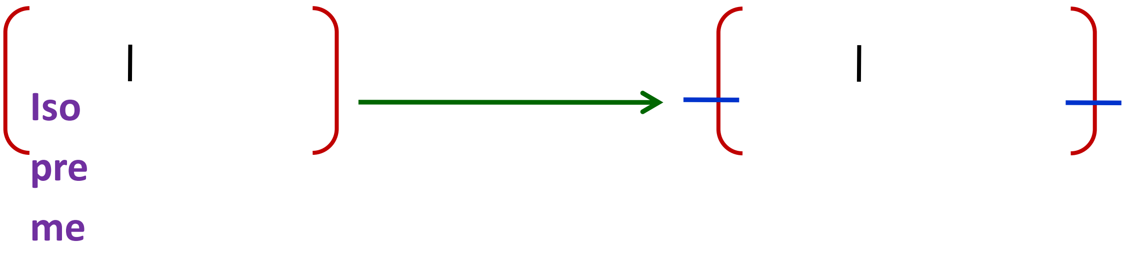
a. Natural rubber
b. Synthetic rubber

a. **Natural rubber:** It is obtained as latex from rubber trees. The latex is coagulated with acetic acid or formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dil. Acids and alkalies but soluble in benzene, chloroform, ether, petrol and carbon disulphide. It absorbs a large amount of water. It has low elasticity and tensile strength.

Destructive distillation of natural rubber gives mainly isoprene (2-methyl butadiene).

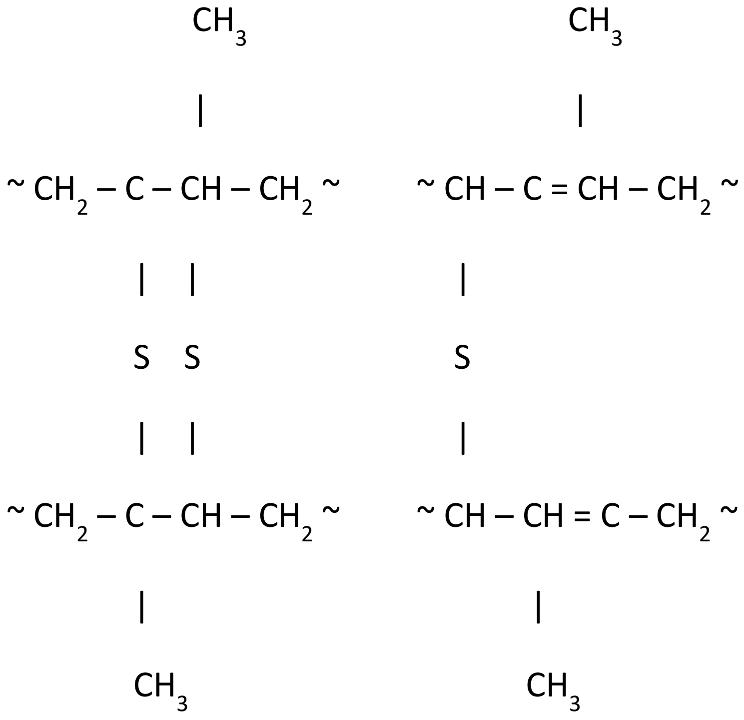
So it can be concluded that isoprene is a monomer of natural rubber. The number of isoprene units varies from 11,000 to 20,000, in rubber which are linked together in a chain.



Vulcanization of rubber:

The process of heating natural rubber with sulphur to improve its properties is called vulcanization. Vulcanization was introduced by Charles Goodyear.

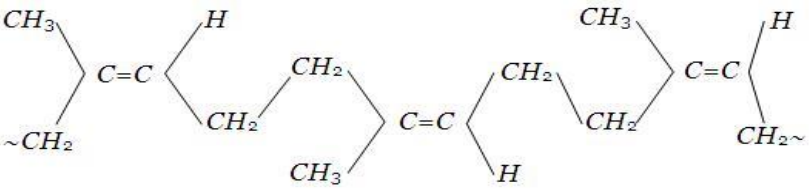
Although natural rubber is a thermoplastic substance in which there are no cross links between the polymer chain and it, on vulcanization, sets into a given shape which is retained.



$$\begin{array}{ll}
\begin{array}{c} \mathrm{CH_3} \\ | \\ \sim \mathrm{CH_2 - C - CH - CH_2} \sim \\ |\quad | \\ \mathrm{S}\quad \mathrm{S} \\ |\quad | \\ \sim \mathrm{CH_2 - C - CH - CH_2} \sim \\ | \\ \mathrm{CH_3} \end{array} &
\begin{array}{c} \mathrm{CH_3} \\ | \\ \sim \mathrm{CH - C = CH - CH_2} \sim \\ | \\ \mathrm{S} \\ | \\ \sim \mathrm{CH - CH = C - CH_2} \sim \\ | \\ \mathrm{CH_3} \end{array}
\end{array}$$

The vulcanization process was found to be slow. Now a days, some additives such as zinc oxide etc. are used to accelerate the rate of vulcanization. During vulcanization, sulphur cross links are formed (given above figure) the double bonds in the rubber molecule acts as reactive sites. The allylic – CH_2, present in alpha position to double bond is also very reactive. During vulcanization, sulphur forms cross links at these reactive sites. As a result, rubber gets stiffened and intermolecular movement of rubber springs is prevented resulting in physical character of rubber. The extent of stiffness of vulcanized rubber depends upon the amount of sulphur added. For example about 5% sulphur is used for making tyre rubber, while 30% of the sulphur is used for making battery case rubber.

In a polymer, the chains are normally tangled up with each other. When the rubber is stretched, the chains straighten out to some extent. The chains cannot slip past each other because of the polysulphide bridges. Thus, rubber can be stretched only to a limited extent. When the tension is removed, the chains try to coil up again and the rubber resumes its original shape.



Natural rubber
All *cis* configuration

The differences between the natural rubber and valcunised rubber are briefly listed in the table that forms.

Differences between Natural Rubber And Vulcanized Rubber:

Natural rubber	Vulcanized rubber
a. Natural rubber is soft and sticky	Vulcanized rubber is hard and non-sticky.
b. It has low tensile strength.	It has high tensile strength.
c. It has low elasticity.	It has high elasticity.
d. It can be used over a narrow range of temperature (from 10° to 60°C).	It can be used over a wide range of temperature (– 40° to 100°C).
e. It has low resistance to wear and tear.	It has high resistance to wear and tear.
f. It is soluble in solvents like ether, carbon, tetrachloride, petrol, etc.	It is insoluble in all the common solvents.

b. **Synthetic rubber:** The synthetic rubber is obtained by polymerising certain organic compounds which may have properties similar to rubber and some desirable properties. Most of these contain carbon-carbon double bonds and are derived from butadiene. The synthetic rubbers are either homopolymers of 1, 3 - butadiene or copolymer in which one of the monomers is 1, 3 - butadiene or its derivatives so that the polymer has the availability of double bonds for its vulcanization. Some important examples are Neoprene, styrene, butadiene rubber (SBR) Thiokol, silicones, polyurethane, rubber etc.

Molecular masses of polymers:

A polymer sample contains chain of varying lengths and therefore its molecular mass is always expressed as an average. On the other hand, natural polymer such as proteins contain chain of identical length and therefore they have definite molecular mass.

The molecular mass of a polymer can be expressed in two ways.

1. Number average molecular mass (M_N)
2. Weight average molecular mass (M_W).

1. **Number average molecular mass (M_N) :** If N_1, N_2, N_3 ….. are the number of molecules with molecular masses M_1, M_2, M_3 …… respectively, then the number average molecular mass is

$$M_N = [N_1M_1 + N_2M_2 + N_3M_3 + ...]/[N_1 + N_2 + N_3 ...]$$

This may be expressed as: $M_N = \Sigma N_iM_i/\Sigma N_i$

Where N_i is the number of molecules of the ith type with molecular mass M_i.

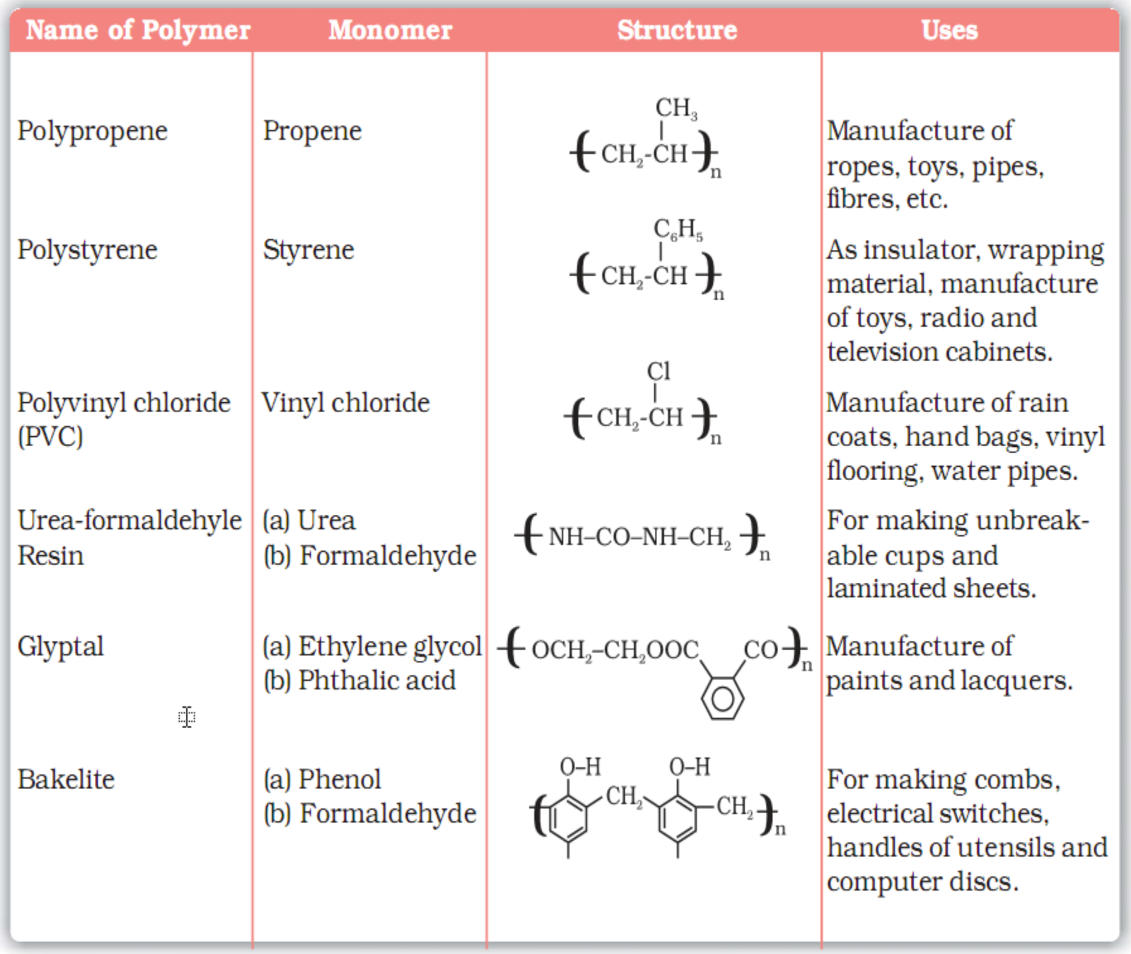
2. **Weight average molecular mass (M_W):** If m_1, m_2, m_3 …. are the masses of the species with molecular masses M_1, M_2, M_3… respectively, then the weight average molecular mass is

$$M_W = [m_1M_1 + m_2M_2 + m_3M_3 \ldots]/[m_1 + m_2 + m_3 + \ldots] \text{ or } = \Sigma m_iM_i/\Sigma m_i$$

$$\text{But } m_i = N_iM_i \text{, so that } M_W = \Sigma N_iM_i^2/\Sigma N_iM_i$$

Where N_i is the number of molecules of mass M_i.

Polymers of Commercial Importance: commercially important polymers along with their structures and uses are given below in the table.



Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left(CH_2-\underset{}{\overset{CH_3}{\overset{\vert}{CH}}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
Polystyrene	Styrene	$\left(CH_2-\overset{C_6H_5}{\overset{\vert}{CH}} \right)_n$	As insulator, wrapping material, manufacture of toys, radio and television cabinets.
Polyvinyl chloride (PVC)	Vinyl chloride	$\left(CH_2-\overset{Cl}{\overset{\vert}{CH}} \right)_n$	Manufacture of rain coats, hand bags, vinyl flooring, water pipes.
Urea-formaldehyde Resin	(a) Urea (b) Formaldehyde	$\left(NH-CO-NH-CH_2 \right)_n$	For making unbreak-able cups and laminated sheets.
Glyptal	(a) Ethylene glycol (b) Phthalic acid		Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde		For making combs, electrical switches, handles of utensils and computer discs.

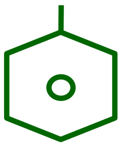
Assignment questions:

1. Discuss the structure of natural rubber
2. What is vulcanization? Write the consequences of the valcunization of rubber
3. Explain
    a. Number of average molecular mass
    b. Weight average of molecular mass

Review questions:

Example set:

1. Natural rubber is a polymer of
    a. $CH_2 = CH - CH = CH_2$
    b. $CH_2 = CH_2$



Solution: d)

2. The commonly used vulcanizing agent is
    a. Sulphur
    b. Graphite
    c. Carbon black
    d. CO_2

Solution: a)

3. The formula for calculating weight average molecular mass of a polymer is given by
    a. $\frac{\varepsilon NiMi}{\varepsilon Ni}$
    b. $\frac{\varepsilon NiMi}{\varepsilon Mi}$
    c. $\frac{\varepsilon Mi^2}{\varepsilon Ni}$

d. $\frac{\varepsilon NiMi^2}{\varepsilon Ni}$

Solution: d)

4. The natural rubber on vulcanization becomes
    a. Less elastic
    b. More elastic
    c. Plastic
    d. Soft

Solution: a)

5. What is the cross linking agent used in vulcanization

Solution: sulphur

6. Distinguish between natural rubber and vulcanized rubber

Solution: Differences between Natural Rubber And Vulcanized Rubber:

Natural rubber	**Vulcanized rubber**
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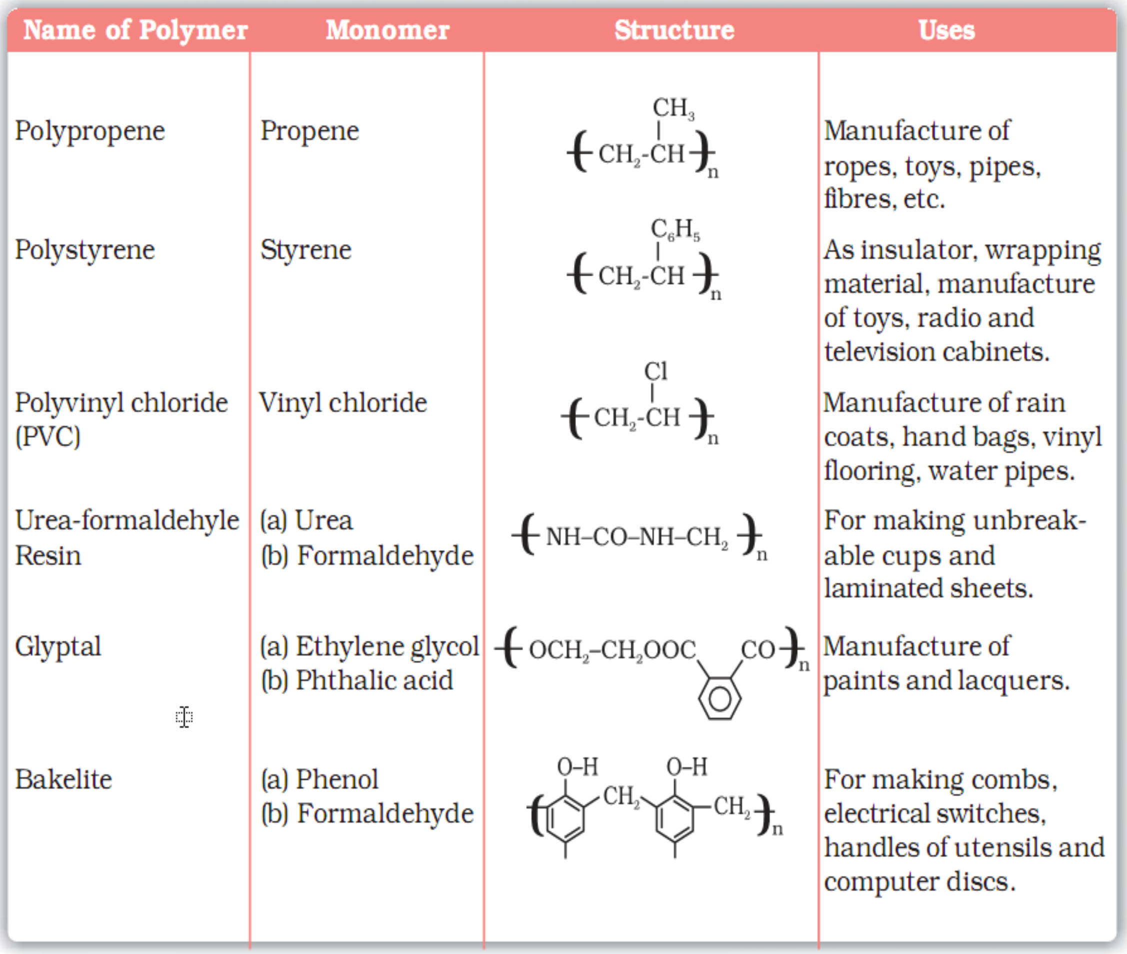
7. Give the importance of polymers in commercial life

Solution:



Name of Polymer	Monomer	Structure	Uses
Polypropene	Propene	$\left(CH_2-\underset{\vert}{\overset{CH_3}{CH}} \right)_n$	Manufacture of ropes, toys, pipes, fibres, etc.
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Glyptal	(a) Ethylene glycol (b) Phthalic acid	$\left(OCH_2-CH_2OOC \quad CO \right)_n$	Manufacture of paints and lacquers.
Bakelite	(a) Phenol (b) Formaldehyde	O-H CH$_2$ O-H CH$_2$ $)_n$	For making combs, electrical switches, handles of utensils and computer discs.

Problem set:

1. In valcunization of rubber
    a. Rubber reacts to form new compound

b. Sulphur cross – links are introduced
c. Sulphur forms very thin protective layer over rubber
d. All statements are correct

Solution: b)

2. The formula for calculating number average molecular mass of a polymer is given by
   a. $\frac{\varepsilon NiMi}{\varepsilon Ni}$
   b. $\frac{\varepsilon NiMi^2}{\varepsilon NiMi}$
   c. $\frac{\varepsilon NiMi}{\varepsilon Mi}$
   d. $\frac{\varepsilon Mi^2}{\varepsilon Ni}$

Solution: a)

3. In order to give strength and elasticity, natural rubber is heated with
   a. Sulphur
   b. Oxygen
   c. Nitrogen
   d. Chlorine

Solution: a)

4. Which of the following relations is true for macro molecues?
   a. $\overline{M}_n < \overline{M}_w$
   b. $\overline{M}_n > \overline{M}_w$
   c. $\overline{M}_n = \overline{M}_w$
   d. $\overline{M}_n > \sqrt{\overline{M}_w}$

Solution: a)

5. Equal numbers of polymer molecules with M_1 = 10,000 and M_2 = 40, 000 are mixed to give a polymer mixture. Calculate the number average and mass average molar masses.

Solution:

$$\bar{M}_n = \frac{n_1M_1+n_2M_2}{n_1+n_2}$$

$$\bar{M}_m = \frac{n_1M_1^2+n_2M_2^2}{n_1M_1+n_2M_2}$$

Here $n_1 = n_2$; $M_1 = 10,000$ and $M_2 = 40,000$

Hence, $\bar{M}_n = \frac{1 \times 10,000+1\times 40,000}{(1+1)}$

$= 25,000$

$$\bar{M}_m = \frac{1\times(10,000)^2+1\times(40,000)^2}{1\times 10,000+1\times 40,000}$$

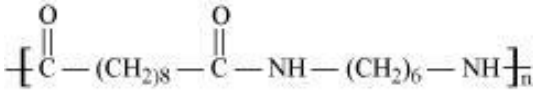
$$= \frac{(1+16)\times 10^8}{(1+4)\times 10^4} = \frac{17}{5}\times 10^4$$

$= 34,000$

Exercise questions:

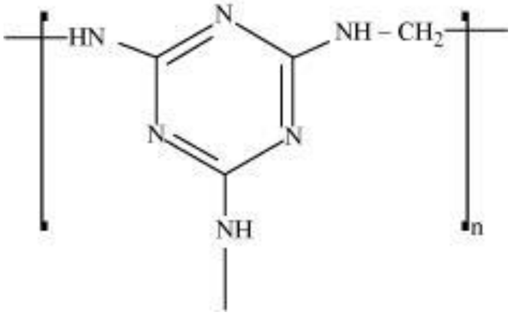
1. How does the presence of double bonds in rubber molecules influence their structure and reactivity?
2. Discuss the main purpose of vulcanisation of rubber.
3. Identify the monomer in the following polymeric structures.

(i)



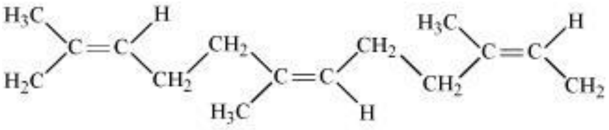
$$\left[\overset{\overset{O}{\|}}{C} - (CH_2)_8 - \overset{\overset{O}{\|}}{C} - NH - (CH_2)_6 - NH \right]_n$$

(ii)



Solutions to exercise questions:

1. Natural rubber is a linear cis-polyisoprene in which the double bonds are present between C_2 and C_3 of the isoprene units.



Natural rubber

Cis – polyisopreme

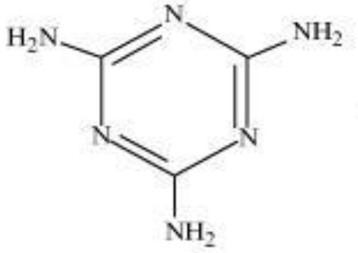
Because of this cis-configuration, intermolecular interactions between the various strands of isoprene are quite weak. As a result, various strands in natural rubber are arranged randomly. Hence, it shows elasticity.

2. Natural rubber, though useful, has some problems associated with its use. These limitations are discussed below:
    a. Natural rubber is quite soft and sticky at room temperature. At elevated temperatures (> 335 K), it becomes even softer. At low temperatures (< 283 K), it becomes brittle. Thus, to maintain its elasticity, natural rubber is generally used in the temperature range of 283 K-335 K.
    b. It has the capacity to absorb large amounts of water.
    c. It has low tensile strength and low resistance to abrasion.
    d. It is soluble in non-polar solvents.
    e. It is easily attacked by oxidizing agents.

Vulcanization of natural rubber is done to improve upon all these properties. In this process, a mixture of raw rubber, with sulphur and appropriate additive like ZnO, is heated to a temperature range between 373 K and 415 K.

3. **(i)** The monomers of the given polymeric structure are decanoic acid [$HOOC - (CH_2)_8 - COOH$] and hexamethylene diamine [$H_2N(CH_2)_6NH_2$].

   (ii) The monomers of the given polymeric structure are



and HCHO