POLYMER & PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS & POC-II

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ymers : Properties a	nd uses of some important polymers : Natura	
PVC.		
	Organic Compounds : Practical organic che	mistry : Chemical method
	onal organic compounds from binary mixtures.	
ection of extra elemer	ts (N,S, halogens) in organic compounds ; Dete	ction of the following functi
	ic and phenolic carbonyl (aldehyde and ketone)	•

JEE(MAIN) SYLLABUS

Polymers– General introduction and classification of polymers, general methods of polymerization – addition and condensation, copolymerization; Natural and synthetic rubber and vulcanization; some important polymers with emphasis on their monomers and uses – polythene, nylon, polyester and bakelite.

POLYMER

Introduction

The term polymer is used to describe a very large molecule that is made up of many small repeating molecular units. These small molecular units from which the polymer is formed are called monomers.

The chemical reaction that joins the monomers together is called polymerisation.

Starting from n molecules of a compound M, linking in a linear manner will form polymer $x-M-(M)_{n-2}-M-y$. The nature of linkages at the terminal units i.e. M - x and M - y depends upon the mode of reaction used in making the polymers.

Polymers can be classified in following ways :

(A) Homopolymers and Copolymers

(Monomer)

(i) Homopolymers : Polymers in which repeating structural units are derived from only one type of monomer units are called homopolymers.

Ethylene (Monomer)	Polyethylene (Polymer)
Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fructose
Polyethylene	Ethylene
Polyvinyl chloride (PVC)	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon–6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan) (PAN)	Acrylonitrile
Plexiglas (Lucite)	Methyl methaacrylate
Polyvinyl acetate	Vinyl acetate

n-CH₂ = CH₂ Polymerization $(-CH_2 - CH_2)$

(ii) **Copolymers :** Polymers in which repeating structural units are derived from two or more types of monomer units are called copolymers.

n
$$H_2N - (CH_2)_6 - NH_2$$

Hexamethylenediamine
(Monomer) +
n HOOC - (CH_2)_4 - COOH -
Adipic acid

Copolymer Monomers Saran Vinyl chloride and vinylidene chloride SAN Styrene and acrylonitrile ABS Acrylonitrile, butadiene and styrene Butyl rubber Isobutylene and Isoprene Buna-S. SBR Styrene and Butadiene Buna-N, NBR Acrylonitrile and Butadiene Nylon-66 Hexamethylenediamine and Adipic acid Terylene Terephthalic acid and ethylene glycol

(1) Random Copolymer

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is

 $nA + nB \longrightarrow -A-A-B-A-B-B-A-B-A-A-A-B-$

segment of random copolymer

(2) Alternating Copolymer

If the two monomer units present alternatively throughout the polymer chain, it is said to be alternating copolymer. For example,

 $nA + nB \longrightarrow -A-B-A-B-A-B-$

segment of alternating copolymer

The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

(3) Block copolymer

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers.

For example,

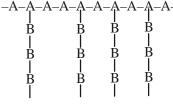
-B-B-A-A-A-A-A-A-B-B-B-B-B-B-A-A-

segment of a block polymer

Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

(4) Graft copolymer

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co-polymers. For example:



(Segment of a graft copolymer)

Graft copolymers are prepared by γ -irradiation of a homopolymer chain in the presence of a second monomer. the high energy radiation knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerisation of the second monomer.

(B) Classification based on source of origin :

(1) Natural polymers

Polymers which are obtained from animals and plants are known as natural polymers. Examples of natural polymers are given below.

Natural polymer	Monomers
1. Polysaccharide	Monosaccharide
2. Proteins	α -L-Amino acids
3. Nucleic acid	Nucleotide
4. Silk	Amino acids
5. Natural Rubber (cis polyisoprene)	Isoprene (2-Methyl-1,3-butadiene)
Gutta purcha (trans polyisoprene)	Isoprene
Natural polymers which take part in metabolic p	rocesses are known as biopolymers.

Examples are polysaccharides, proteins, RNA and DNA.

Polymer

JEE (Adv.)-Chemistry

(2) Semisynthetic polymers

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

(3) Synthetic polymers

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

(C) Classification based on shape :

(1) Linear polymers

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

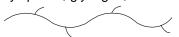
Note :

- (i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.
- (ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

(2) Branched chain polymers

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers.

Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene.

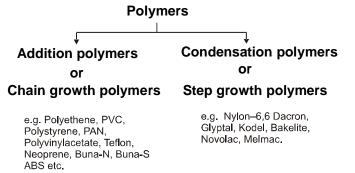


(3) Cross-linked or Three Dimensional network polymers

In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers, Urea-formaldehyde resin, phenol-formaldehyde resin.



(D) Classification based on mode of Polymerisation :



(1) Condensation polymerisation

They are formed due to condensation reactions. Condensation polymerisation is also known as step growth polymerisation. For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different. Monomers having only two functional group always give linear polymer.

For example,

$$nNH_{2}-R-NH_{2} + nHOOC-R'-COOH \xrightarrow{Condensation}_{reaction} \left| \begin{array}{c} O & O \\ -NH-R-NH-C-R'-C- \\ \end{array} \right|_{n}^{+} (n-1)H_{2}O$$

$$Polyamide$$

$$nHO-R-OH + nHO-C-R'-C-OH \xrightarrow{Condensation}_{reaction} \left[\begin{array}{c} O & O \\ -O-R-O-C-R'-C- \\ \end{array} \right]_{n}^{+} (n-1)H_{2}O$$

$$Polyester$$

$$nNH_{2}-R-COOH \xrightarrow{Condensation}_{reaction} \left[\begin{array}{c} O \\ -NH-R-C- \\ \end{array} \right]_{n}^{+} \left(\frac{n}{2} - 1 \right)H_{2}O$$

$$Polyamide$$

Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules. Monomer having three functional groups always gives cross-linked polymer. **Examples are :** Urea-formaldehyde resin, phenol-formaldehyde resin.

(2) Addition polymerisation

Polymers which are formed by addition reaction are known as addition polymers. If monomer is ethylene or its derivative, then addition polymer is either linear polymer of branch- chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc. If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene $(CH_2 = C - CH = CH_2)$, then polymer is always branched chain polymer.

(Monomer)

(i) G = H : 1,3 - Butadiene

(ii) $G = CH_3$; 2 - Methyl-1,3-butadiene or isoprene

(iii) G = Cl ; 2 -Chloro-1,3-butadiene or chloroprene

(Polymer)

(i) Polybutadiene

(ii) Polyisoprene

(iii) Polychloroprene (Neoprene)

Addition polymers retain all the atoms of the monomer units in the polymer. Addition polymerisation takes place in three steps. Initiation, chain propagation and chain termination. Addition polymers are called as chain growth polymers.

Types of Addition Polymerisation

(a) Radical Polymerisation :

Radical polymerisation takes place in the presence of radical initiators. The radical initiator may be any of the following :

Reaction intermediate of radical polymerization is a free radical. Radical polymerization has more chance for those monomers whose free radicals are more stable.

Examples are :

		CH ₂ =CH–O–C–CH ₃
$C_6H_5-CH=CH_2$,	$CH_2 = CH - CI$,	en ₂ -en o e en ₃
Styrene	Vinyl chloride	Vinyl acetate
	CH ₂ =C-CH ₃	G
CH ₂ =CH–CN	C–O–CH ₃	$CH_2 = C - CH = CH_2(G = H, CH_3 \text{ and } Cl)$
Acrylonitrile	II O	
(vinyl cyanide)	Methyl methacrylate	2-substituted-1,3-butadiene

Radical polymer has linear as well as branched chain structure.

Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives $CH_2=CH[G \text{ is } H, C_6H_5, R \text{ etc.}]$. This type of polymerisation is preformed by heating the monomer with only a G

very small amount of the initiator or by exposing the monomer to light. the general mode of radical polymerisation of vinyl monomers is depicted below :

Chain initiation step :

Initiator
$$\rightarrow$$
 In
In•+ CH₂=CH \rightarrow In-CH₂-CH
G

Chain propagating step :

$$\begin{array}{c} \mathrm{CH}_2=\mathrm{CH}+\mathrm{In-CH}_2-\mathrm{CH}\to\mathrm{In-CH}_2-\mathrm{CH-CH}_2-\mathrm{CH}\to\mathrm{In-(CH}_2-\mathrm{CH})-\mathrm{CH}_2-\mathrm{CH}\\ \mathrm{G}&\mathrm{G}&\mathrm{G}&\mathrm{G}\\ \end{array}$$

Chain terminating step :

$$2\mathrm{In}(\mathrm{CH}_{2}=\mathrm{CH})_{\mathrm{CH}_{2}}-\mathrm{CH}_{2}-\mathrm{CH}_{3} \rightarrow \mathrm{In}(\mathrm{CH}_{2}-\mathrm{CH})_{\mathrm{CH}_{2}}-\mathrm{CH}-\mathrm{CH}-\mathrm{CH}_{2}(\mathrm{CH}-\mathrm{CH}_{2})_{\mathrm{In}}$$

$$\overset{\bullet}{G} \qquad \overset{\bullet}{G} \qquad \overset{$$

Polymer

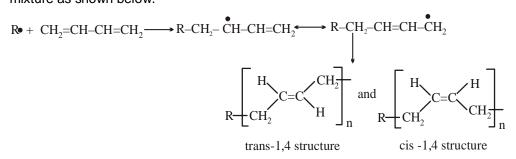
In vinylic polymerisation, various other reaction of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called as chain transfer agents and include CCl₄, CBr₄ etc.

For example, in the presence of CCl₄, styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerisation chain and thereby forms a new polymer as depicted below.

If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerisation chain reaction. Hence, the monomers could be free from such inhibitors. In case the alkene is a (diene), the following kinds of polymerisation is possible :

1,4 - polymerisaiton

When the polymerisation takes place at C_1 and C_4 of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene having a double bond, which at each of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below.



1,2-Polymerisation

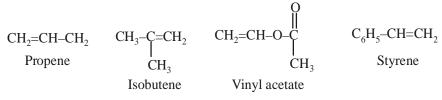
Alternatively, 1,3 -butadiene can undergo polymerisaiton at C_1 and C_2 to yield the polymeric product, polyvinly polythene.

$$\begin{array}{c} \overset{4}{} CH_{2} & \overset{4}{} CH_{2} \\ 3 \overset{1}{||}_{CH} & 3 \overset{1}{||}_{CH} \\ 2n CH_{2} = CH - CH = CH_{2} \xrightarrow{\mathbb{R}} \mathbb{R} \left(\begin{array}{c} 1 & 2l & 1 & 2l \\ 2n & CH_{2} - CH - CH_{2} - CH_{2} \end{array} \right)$$

The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubber.

(b) Cationic Polymerisation :

Polymerisation which is initiated by an electrophile is known as cationic polymerisation. Reaction intermediate of cationic polymerisation is a carbocation. Carbocations can undergo rearrangement leading to the formation of a more stable carbocation. The electrophile commonly used for initiation is BF₃.OEt₂. Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron - donating substituents that can stabilise the carboncation. Some examples are:



It is terminated by a base.

Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below.

Chain initiation step :

$$\overset{\leftarrow}{H} + \overset{\leftarrow}{C} \overset{\leftarrow}{H}_2 = \overset{\leftarrow}{C} \overset{\leftarrow}{H} \xrightarrow{} C \overset{\leftarrow}{H}_2 - \overset{\oplus}{C} \overset{\leftarrow}{H}_3 \xrightarrow{} \overset{\leftarrow}{H}_2 \xrightarrow{\phantom}$$

Chain propagating step :

$$CH_3$$
- CH_4 + CH_2 = CH_3 - CH_3 - CH_2 - CH_2 - CH_3 - CH_2 - CH_3 - CH_2 - CH_3 - CH_2 - CH_3 - $CH_$

Chain terminating step:

$$CH_{3}-CH(CH_{2}-CH)-CH_{2}-CH_{2}-CH_{3}-CH_{3}-CH(CH_{2}-CH)-CH=CH+HA$$

Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing $-CH_3$ groups that will stabilize the intermediate carbocation.

$$\begin{array}{c} \overbrace{H}^{CH_{3}} \\ \overbrace{H}^{CH_{3}} \\ \hline \\ CH_{3} \\ - \\ \overbrace{CH_{3}}^{CH_{3}} \\ \hline \\ CH_{3} \\ CH_{3$$

(Butyl Rubber)

(c) Anionic Polymerisation :

Anionic polymerisation takes place in the presence of base or nucleopile, which is initiator in this polymerization. Reaction intermediate in propagation steps are carboanion. The suitable initiator can be NaNH₂ or RLi. Those monomers undergo anionic polymerisation reaction whose anion is stable. Example of monomers are :

$$\begin{array}{ccc} CH_2=CH-Cl & CH_2=CH-CN & CH_3=C-CH_3 & C_6H_5-CH=CH_2 \\ Vinyl chloride & Acrylonitrile & C-OCH_3 & Styrene \\ 0 & 0 & 0 \end{array}$$

Methyl methacrylate

Anionic polymerisation always gives linear polymer. Anionic polymerisation termnated by an acid. The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below: **Chain initiation step :**

$$K^{+} \overset{\bullet}{NH}_{2} + \overset{\bullet}{CH}_{2} \overset{\bullet}{=} \overset{\bullet}{CH} \overset{\bullet}{\longrightarrow} NH_{2} - CH_{2} - \overset{\bullet}{C}HK^{+}$$

Chain propagating step :

$$NH_2 - CH_2 - \overrightarrow{CH} + \overrightarrow{nCH}_2 = \overrightarrow{CH} \longrightarrow NH_2 - CH_2 + (CH - CH_2) \overrightarrow{n} \overrightarrow{CH} K^+$$

Chain terminating step :

$$NH_2 - CH_2 - CH_2 - CH_2 \xrightarrow{n_1} CH \xrightarrow{H^+} H_2N - CH_2 + CH_2 - CH_2 \xrightarrow{n_1} CH_2$$

(d) Ziegler- Natta polymerisation :

Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst $[(C_2H_5)_3Al \text{ and TiCl}_4]$ is known as Ziegler- Natta polymerisation or coordination olymerisation. Ziegler- Natta polymerisation always gives linear, stereo-regular polymers. Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat.

High density polyethylene is prepared using a Ziegler- Natta catalyst.

(E) Classification based on intermolecular forces (secondary forces)

Intermolecular forces present between polymeric chains are (a) Van der waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions. Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains. Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains. Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following categories.

(1) Elastomers

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Vander Waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Vander Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length. Important examples are vulcanized rubbers.

Note : Addition polymers obtained from butadiene and its derivatives are elastomers.

(2) Fibres

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another. Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. they have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

Note :

(i) Condensation polymers formed from bifunctional monomers are fibres in character.

(ii) Addition polymers of alkene derivatives having strong- I group are fibres in character.

(3) Thermoplastic Polymers

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non crystalline regions (the regions of the polymer in which the chains are randomly oriented. The intermolecular forces of attraction are in between elastomers and fibres. There are no cross links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscous. this soft and viscous material become rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are : polyethene, polypropylene, polystyrene, polyvinyl chloride, teflon etc.

Note : Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

(4) Thermosetting Polymers

Polymers which become hard on heating are called thermosetting polymers. thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating.

Thermosetting polymers are cross- linked polymers . Greater the degree of cross - linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. the hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin ,melamine - formaldehyde resin.

S.No.	Thermoplastic polymers	Thermosetting polymers
1.	Soften and melt on heating and become hard on cooling	Become hard on heating and
	i.e. process is reversible	process is irreversible.
2.	Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped.
3.	They are addition polymers	They are condensation polymers.
4.	Structure is generally linear	Structure is cross - linked.

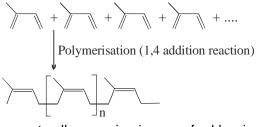
Difference between thermoplastic and thermosetting polymers

RUBBER

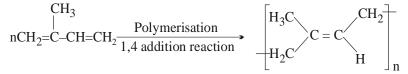
1. Natural Rubber

Natural rubber is obtained from nearly five hundred different plants but the main source is a braziliensis tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1,3-butadiene (isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is cis polyisoprene.



Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds trans. Thus, guttapercha is trans-polyisoprene.



It is harder and more brittle than rubber. It is the filling material that dentists use in root canal treatment. In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at 150° C for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives

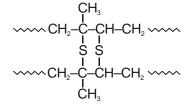
mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerators. The common accelerators are:

$$\begin{array}{ccc} C_{6}H_{5}-NH-C-NH-C_{6}H_{5}\\ NH\\ Diphenyl guanidine\\ \end{array} \qquad \begin{array}{cccc} CH_{3}\\ H_{3}\\ CH_{3}\\ CH_$$

In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

Vulcanization : .Raw rubber does not posses the characteristic of the rubber with which we are familar. In order to give it strength & elasticity it is vulcanised. **In the vulcanization process, raw rubber is mixed with small amount of sulphur and heated**. Use of external sulpher increases the cross-linking and toughness.1-3 % S is used in rubber bands and 5% S is used in tyre rubber.



(2) SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

Polymers of 1,3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic. Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

(a) Homopolymers

Monomer of this class is 2 - substituted - 1,3- butadienes.

$$CH_2=C-CH=CH_2$$
 where G=H, CH₃ or CL

Polymerisation is always carried out in the presence of Zieglar-Natta catalyst which gives stereo regular polymers.

Neoprene was the first synthetic rubber manufactured on large scale. It is also called dieprene. Its monomer, chloroprene(2-chlorobutadiene) is prepared from acetylene.

$$2HC \equiv CH \xrightarrow{Cu_2Cl_2} CH_2 = CH - C \equiv CH \xrightarrow{HCl} CH_2 = CH - C = CH_2$$

$$Acetylene \xrightarrow{Cu_2Cl_2} CH_2 = CH - C \equiv CH \xrightarrow{HCl} CH_2 = CH - C \equiv CH_2$$

$$CH_2 = CH - C \equiv CH_2$$

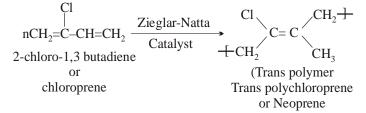
$$CH_2 = CH - C \equiv CH_2$$

$$CH_2 = CH - C \equiv CH$$

$$CH_2 = CH - C \equiv CH$$

$$CH_2 = CH - C \equiv CH$$

Cloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).



Polymer

Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non-inflammable. It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

(b) Copolymers

The following synthetic rubbers are example of copolymers.

Synthetic rubber	Monomers
1. Buna-S, SBR (Styrene-butadiene rubber)	C_6H_5 -CH=CH ₂ + CH ₂ =CH-CH=CH ₂
	(25%) (75%)
2. Buna-N, NBR (Nitrile-butadiene rubber)	$CH_2=CH-CN + CH_2=CH-CH=CH_2$
	(25%) (75%)
3. Butyl rubber	CH_3 – $C=CH_2$ + Butadiene
	CH ₃ 2%
	98%
4. ABS; Acrylonitrile, Butadiene, Styrene	$CH_2=CH-CN + CH_2=CH-CH=CH_2 + C_6H_5CH=CH_2$

(i) **Thiokol** : Thiokol is made by polymerising ethylene chloride and sodium polysulphide.

$$2\text{Cl}-\text{CH}_2-\text{CH}_2-\text{Cl} + \text{Na}-\text{S}-\text{S}-\text{Na} \xrightarrow{\text{Polymerisation}} -\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-\text{CH}$$

Thiokol rubber

The repeating unit is $-CH_2-S-S-CH_2-$. Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(ii) Buna -S (SBR : Styrene-butadiene rubber) : Buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In Buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is a polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).

nCH₂=CH-CH=CH₂ + n
$$($$
 $CH=CH_2$ $($ $CH_2-CH=CH-CH_2-CH-CH_2$ $)$ $($ $CH_2-CH=CH-CH_2-CH-CH_2$ $)$ $($ n $)$ $($ n

Buna-S

ONT

Buna-S is generally compounded with carbon black and vulcanised with sulpur. It is extremely resistant to wear and tear and therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

(iii) **Buna-N**: It is obtained by copolymerisation of butadiene and acrylonitirile (General Purpose Rubber acrylonitirle or GRA).

It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.

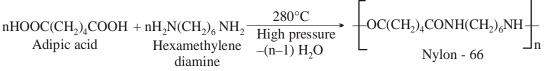
(iv) Cold Rubber : Cold rubber is obtained by polymerisation of butadiene and styrene at -18° to 5°C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e., having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

(1) NYLON - 66 (Nylon six, six)

It is obtained by the condensation polymerisation of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).



(2) NYLON-610 (Nylon six, ten)

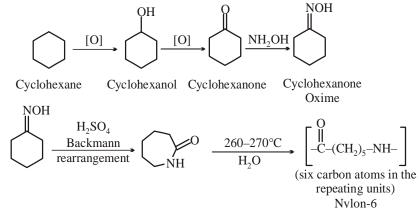
It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms.)

Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes, etc.

(3) NYLON-6 (Perlon L)

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon - 6 (USA). It is prepared by prolonged heating of caprolactum at 260–270°C. It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactum is more easily available, it is used for polymerization, with is carried out in the presence of H_2O that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and onto form the polyamide polymer.

Carpolactam is obtained by Backmann rearrangement of cyclohexanone oxime.



(4) NYLON-2–NYLON-6

It is in alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

POLYETHYLENE

Polyethylene is of two types :

(1) Low Density Poly Ethylene (LDPE) : It is manufactured by heating ethylene at 200°C under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.

 $nCH_2=CH_2 \xrightarrow{200^{\circ}C} (CH_2-CH_2)_n$

Polymer

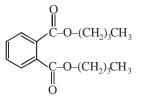
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110°C). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

(2) High Density Poly Ethylene (HDPE) : It is prepared by the use of Zieglar - Natta catalyst at 160°C under pressure of 6 to 7 atmosphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point (130°C). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

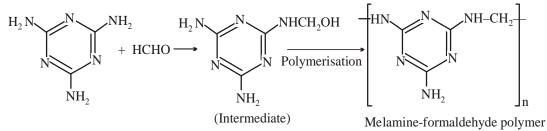
PLASTICISER

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly used plasticiser.



MELAMINE - FORMALDEHYDE RESIN

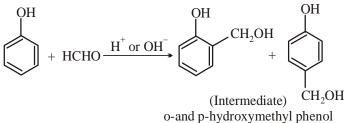
This resin is formed by condensation polymerisation of melamine and formaldehyde.

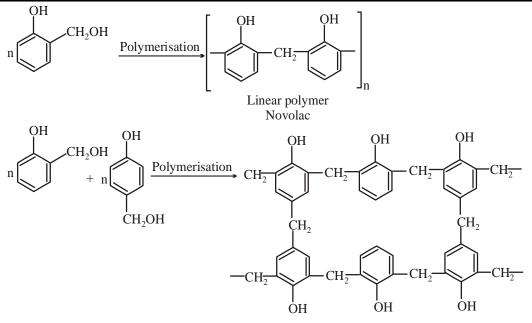


It is a quite hard polymer and is used widely for making plastic crockery under the name melamine. The articles made from this polymer do not break even when dropped from considerable height.

BAKELITE

Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and parahydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $-CH_2$ groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross - linked materials are obtained depending on the conditions of the reaction.

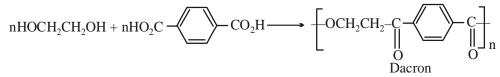




Cross - linked polymer (Bakelite)

POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140° to 180° C in the presence of zinc acetate and Sb₂O₃ as catalyst.



The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile

strength. It is mainly used in making wash and wear garments, in blending with wood to provide better crease and wrinkle resistance.

MOLECULAR MASS OF POLYMER

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contains chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

(a) Number average molecular mass (M_n)

$$\overline{M}_{n} = \frac{\sum N_{i}M_{i}}{\sum N_{i}}$$

where N_i is the number of molecules of molecular mass M_i

(b) Weight average molecular mass (M_w)

$$\overline{M}_{w} = \frac{\sum N_{i}M_{i}^{2}}{\sum_{i}N_{i}M_{i}}$$

where N_i is the number of molecules of molecular mass M_i . Methods such as light scattering and ultracentrifuge depend on the mass of the individual molecules and yield weight average molecular masses. \overline{M}_n is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. colligative properties like osmotic pressure.

The ratio of the weight and number average molecular masses (M_w / M_n) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodisperesed, the PDI is unity (i.e. $\overline{M}_w = \overline{M}_n$).

In synthetic polymers, which are always polydispersed, PDI > 1 because \overline{M}_w is always higher than \overline{M}_n .

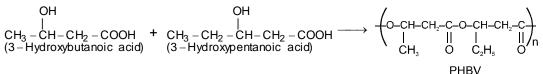
Biodegradable Polymers :

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric soild waste materials. These soild wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric soild wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable poylmers. Some examples are given below :

(A) Poly β -hydroxybutyrate – co– β -hydroxy valerate (PHBV) :

It is obtained by the copolymerisatin of 3-hydroxybutanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.



(B) Nylon–2–nylon–6 :

It is an alternating polyamide copolymer of glycine (H_2N-CH_2-COOH) and amino caproic acid [H_2N (CH_2)₅ COOH] and it is also biodegradable polymer.

Polymer	Monomer A	Monomer B
Poly β-hydroxybutyrate – co–β-hydroxy valerate (PHBV)	OH CH ₃ – CH– CH ₂ – COOH (3 – Hydroxybutanoic acid)	OH I CH ₃ – CH ₂ – CH– CH ₂ – COOH (3 – Hydroxypentanoic acid)
Nylon–2–nylon–6	(H ₂ N–CH ₂ –COOH)	$[H_2N (CH_2)_5 COOH]$

Polymer

Some Common Addition Polymers/ Chain Growth Polymer (Homopolymers)				
S.No.	Name(s)	Formula	Monomer	Uses
1.	Polyethylene (low density (LDPE))	-(CH ₂ -CH ₂) _n -	CH ₂ =CH ₂ (ethylene)	film wrap, plastic bags
2.	Polyethylene (high density (HDPE))	-(CH ₂ -CH ₂) _n -	CH ₂ =CH ₂ (ethylene)	electrical insulation bottles, toys
3.	Polypropylene (PP) different grades	$\begin{array}{c} CH_3\\ +\\ CH-CH_2\\ \mathbf{-}\\ n \end{array}$	CH ₂ =CHCH ₃ (propylene)	similar to LDPE carpet, upholstery
4.	Poly vinyl chloride (PVC)	$ \begin{array}{c} CI \\ - \\ CH - CH_2 \end{array} \right]_{n} $	CH ₂ =CHCI (vinyl chloride)	pipes, siding, flooring
5.	Poly(vinylidene chloride) (Saran A)	CI {C CI CI CI	CH ₂ =CCl ₂ (vinylidene chloride)	seat covers, films
6.	Polystyrene (PS) (Styron)		CH₂=CHC ₆ H₅ (styrene)	toys, cabinets packaging (foamed)
7.	Polyacrylonitrile (PAN, Orlon, Acrilan)		CH₂=CHCN (acrylonitrile)	rugs, blankets clothing
8.	Polytetrafluoroethylene (PTFE, Teflon)	-(CF ₂ -CF ₂) _n -	CF ₂ =CF ₂ (tetrafluoroethylene)	non-stick surfaces electrical insulation
9.	Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas, perspex)	–[CH ₂ C(CH ₃)CO ₂ CH ₃] _n –	CH ₂ =C(CH ₃)CO ₂ CH ₃ (methyl methacrylate)	lighting covers, signs skylights
10.	Poly(vinyl acetate) (PVAc)	–(CH ₂ -CHOCOCH ₃) _n –	CH ₂ =CHOCOCH ₃ (vinyl acetate)	latex paints, adhesives
11.	Polyisoprene Ziegler-Natta Cis form Trans form (Natural rubber) (Gatta-Purcha) (1, 4-addition) (H_2C, CH_2) $(H_2C=CH_2)$ H (H_2C, CH_2) $(H_2C=CH_2)$	–[CH ₂ -CH=C(CH ₃)-CH ₂] _n –	CH ₂ =CH-C(CH ₃)=CH ₂ (isoprene)	requires vulcanization for practical use
12.	Polychloroprene (cis + trans) (Neoprene)	-[CH ₂ -CH=CCI-CH ₂] _n -	CH ₂ =CH-CCI=CH ₂ (chloroprene)	synthetic rubber oil resistant

Polymer

	Some Condensation POLYMERS (Step Growth Polymers)				
S. No.	Name(s)	Formula	Monomer	Classification	Uses
1.	Polyester/Dacron/ Terylene/Mylar		HO ₂ C C ₆ H ₄ CO ₂ H (Terephthalic acid) HO–CH ₂ CH ₂ –OH Ethylene glycol	Copolymer Step growth, Linear Polymer	Fabric, Tyrecord
2.	Glyptal or Alkyds resin	$ - CH_2 - CH_2 - O - C + C + C + C + C + C + C + C + C + C$	$HO_2C-C_6H_4-CO_2H$ (Phthalic acid) $HO-CH_2CH_2-OH$	Copolymer Step growth, Linear Polymer	Paints and Lacquers
3.	Polycarbonate Lexan		$\begin{array}{l} (HO-C_6H_4-)_2C(CH_3)_2\\ (Bisphenol A)\\ X_2C=O \; (X=OCH_3 \; or \; CI) \end{array}$	Copolymer Step growth, Linear Polymer	Bike helmet, goggles, bullet proof glass
4.	Polyamide (Nylon 6,6)	~[CO(CH ₂) ₄ CO–NH(CH ₂) ₆ NH] _n ~	$HO_2C-(CH_2)_4-CO_2H$ $H_2N-(CH_2)_6-NH_2$	Copolymer Step growth, Linear Polymer	Parachutes & Clothing
5.	Nylon 6,10	O O II II - (C–(CH ₂) ₆)–C–NH–(CH ₂) ₆ –NH)_n	HOOC–(CH ₂) ₈ –COOH H ₂ N–(CH ₂) ₆ –NH ₂	Copolymer Step growth, Linear Polymer	
6.	Polyamide Nylon 6, Perlon-L	~[CO(CH ₂) ₅ NH] _n ~	()_=0 NH	Homopolymer, Step growth, Linear Polymer	Rope & Tyrecord
7.	Polyamide Kevlar		Para HO₂C–C ₆ H₄–CO₂H	Copolymer Step growth Linear polymer	Tyre
8.	Polyamide Nomex		Meta HO ₂ C–C ₆ H ₄ –CO ₂ H Meta H ₂ N–C ₆ H ₄ –NH ₂	Copolymer step growth Linear polymer	
9.	Polyurethane Spandex	$ \begin{bmatrix} & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$	HOCH ₂ CH ₂ OH H ₃ C N C O	Copolymer step growth Linear polymer	Foams, Shoes, Automobile seats and components
10.	Bakelite	$(-H) \xrightarrow{O-H} \xrightarrow{O-H} \xrightarrow{O-H} \xrightarrow{CH_2} \xrightarrow{O-H} \xrightarrow{CH_2} \xrightarrow{D-H} \xrightarrow{D-H} \xrightarrow{CH_2} \xrightarrow{D-H} $	PhOH + HCHO in (excess)	Copolymer Cross-linked polymer Step growth	Electrical switch and Bowling Balls
11.	Urea- formaldehyle resin	(-NH-CO-NH-CH ₂ -)n	H ₂ N–CO–NH ₂ (Urea) HCHO (Formaldehyde)	Copolymer Step growth Cross-linked polymer	
12.	Melamine formaldehyde resin	HN-CH ₂ N N NH I	H ₂ N N N NH ₂ HCHO (formaldehyde)	Cross-linked polymer	Unbreakable crockery

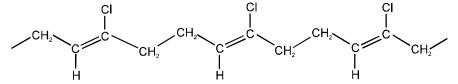
Exercise #1

A Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Polymers

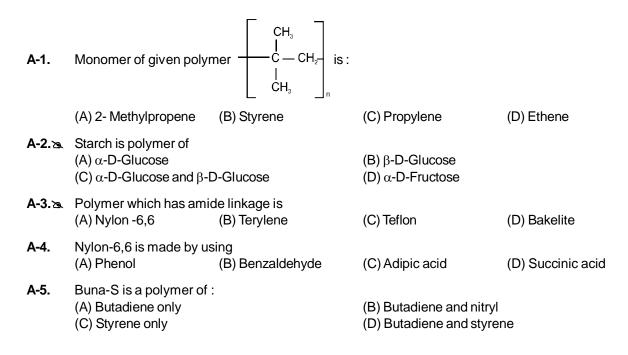
- A-1. Differentiate between a homopolymer and a copolymer. Give one example of each type.
- A-2. What is meant by vulcanisation of rubber ? Why is rubber vulcanised? Give an important application of vulcanised rubber.
- A-3. The partial structure of neoprene, a polymer is given below. Identify the monomer unit.



- A-4. Classify the following as addition or condensation polymer **polymers :** Terylene, Bakelite, polyvinyl chloride, polythene, glyptal, Buna-N
- A-5. What is the difference between Buna-N and Buna-S?
- A-6. Arrange the following in the increasing order of their intermolecular forces Nylon-6, Neoprene, Polyvinyl chloride (1) (11) (11)
- A-7. Write down the heterogenous catalyst involved in the polymerisation of ethylene.

PART - II : OBJECTIVE TYPE QUESTIONS

Section (A) : Polymers



A-6.	Condensation product of (A) nylon-6	of caprolactum is : (B) nylon-6,6	(C) nylon-60	(D) nylon-6, 10
A-7.	Ziegler-Natta catalyst i (A) K[PtCl ₃ (C ₂ H ₄)]		(C) $Al_2(C_2H_5)_6 + TiCl_4$	(D) $Fe(C_5H_5)_2$
A-8.	Which of the following is (A) Starch	s a chain growth polymer' (B) Nucleic acid	? (C) Polystyrene	(D) Proteins
A-9.	Cellulose acetate (Rayon) is a (A) Natural polymer (C) Synthetic polymer		(B) Semi synthetic Polymer (D) None of these	
A-10.	Which of the following set contains addition home (A) Polythene, natural rubber, cellulose (C) Teflon, bakelite, orlon		o polymer? (B) Starch, nylon, polyester. (D) Neoprene, PVC, polythene	
A-11.	Which is true for elastomers? (A) They possess elasticity (B) They possess weak intermolecular force of attraction between polymer chain. (C) vulcanized rubber is an example of elastomer. (D) All of these			r chain.
A-12.	Which of the following is (A) Polythene (C) Polyester	s a thermosetting polyme	r? (B) Melamine formaldeł (D) Buna-S	nyde resin
A 40	Which of the following or	ali waa ana ta bia da awa da bia	n alver at a final vanst da al	2000

A-13.Which of the following polymers is biodegradable polymer of polyamide class?(A) Dextran(B) Nylon-2-nylon-6(C) Nylon-66(D) PHBV

PART - III : MATCH THE COLUMN

- 1. Match Column-I with Column-II. Column-I (polymer) (A) Bakelite (B) Polypropylene (C) Glyptal
 - (D) Nylon-6

Column-II

- (monomer)
- (p) ω caprolactum
- (q) Ethylene glycol + phthalic anhydride
- (r) propene
- (s) Phenol + formaldehyde

Exercise #2

> Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

1.24	Which of the following co (A) Natural rubber	ontains isoprene unit ? (B) Polyethylene	(C) Nylon – 6,6	(D) Dacron
2.2	Which of the following is (A) Polystyrene	condensation polymer ? (B) PVC	(C) Polyester	(D) Teflon
3.	Which of the following period (A) $CH_3CH_2C \equiv CH$ (C) $CH_3CH_2-CH = CH_2$	olymerises most easily ?	(B) $CH_2 = CH - CH = CH$ (D) $CH = C - C = CH$	H ₂

Polymer

 H_2C N - C - N CH_2OH CH_2OH 4.2 HOH,C The polymer obtained by the above compound is : (A) Bakelite (B) Urea formaldehyde resin (C) Melamine formaldehyde resin (D) Tefflon 5. Which of the following is radical initiator (A) R - N = N - R(B) (C) $CH_3 CH_3 H_3$ $I CH_3 CH_3 - C - O - O - C - CH_3$ $CH_3 CH_3 CH_3$ (D) All 6. The polymerisation reaction shown below $2 \text{ CH} \equiv \text{CH} \xrightarrow{\text{CuCl}} \text{CH} \equiv \text{C} - \text{CH} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_2 \xrightarrow{\text{CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \xrightarrow{\text{CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \xrightarrow{\text{CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \xrightarrow{\text{CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \xrightarrow{\text{CH}_2 \text{ CH}_2 \text{ CH}_2 \text{ CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{\text{CH}_2 \text{ CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{\text{CH}_2 \text{ CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{\text{CH}_2 \xrightarrow{CH}_2 \xrightarrow{CH}_2 \xrightarrow$ $-CH_2 - C = CH - CH_2$ CH_3 would produce : (D) Rubber (A) PVC (C) chloroprene (B) neoprene PART - II : NUMERICAL TYPE QUESTIONS Among the following no. of condensation polymers are 1. Nylon-6, Buna-N, Buna-S, Nylon-6,6, Nylon-6,10, PVC, Polystyrene, Teflon.

2. Molecular mass of monomer used in the following polymer is :

$$\begin{bmatrix} O-CH-CH_2-C-\\I\\CH_3 \end{bmatrix}_n^n$$

- 3. Number of Nitrogen atoms in the one monomer limit of melamine is :
- 4. Percentage Nitrogen in the monomer unit of nylon-2,6 is

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1.	Which of the following are polyamide polymers?						
	(A) Protein	(B) Nylon–6,6	(C) Nylon–6	(D) Polystyrene			
2.	Preparation of nylon from hexamethylene diamine (A) addition polymerisation (C) condensation polymerisation		ne and adipic acid is an example of : (B) homopolymerisation (D) copolymerisation				
3.	Which of the following is (A) Starch	/are natural polymers? (B) Polyisoprene	(C) Buna-S	(D) Cellulose Nitrate			
4.	Which of the following is (A) Polythene	/are synthetic polymers? (B) Buna-S	(C) Nylon 66	(C) Rayon			

Polymer

[JEE-2007, 6/162]

[JEE(Advanced)-2013, 4/120]

- 5. The man made polymers is/are (A) Cellulose (B) Cellulose acetate
- (C) Neoprene

(D) Nylon 66

6. Which of the following are linear polymers? (A) HDPE (C) PVC

(B) Bakelite

(D) Melamine-Formaldehyde resin

Exercise # 3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

* Marked Questions may have more than one correct option.

1. Match the chemical substances in Column-I with type of polymers/type of bonds in Column-II.

(s)

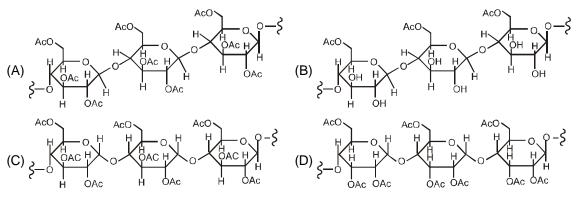
Column-I

sucrose

- (A) cellulose
- (B) nylon-6,6
- (C) protein

(D)

- Column-II natural polymer (p)
- (q) synthetic polymer
- amide linkage (r)
 - glycoside linkage
- 2. Cellulose upon acetylation with excess acetic anhydride/H₂SO₄ (catalytic) gives cellulose triacetate whose structure is [JEE-2008, 4/163]



3. Among celluose, poly vinyl chloride, nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is : [JEE 2009, 3/160] (B) Poly vinyl chloride (D) Natural Rubber

(A) Nylon

(C) Cellulose

4.* The correct functional group X and the reagent/reaction conditions Y in the following scheme are

$$X - (CH_{2})_{4} - X \xrightarrow{(i) Y} condensation polymer : [JEE 2011, 4/180]$$

$$(i) \xrightarrow{(i)}_{OH} - (CH_{2})_{4} - (CH$$

- 5. The total number of lone-pairs of electrons in melamine is
- 6. On complete hydrogenation, natural rubber produces [JEE(Advanced)-2016, 3/124] (A) ethylene-propylene copolymer (B) vulcanised rubber (C) polypropylene (D) polybutylene

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1.	Complete hydrolysis of (1) D-fructose	cellulose gives (2) D-ribose	(3) D-glucose	(4) L-glucose	[AIEEE-2003]
2.	Nylon threads are made (1) Polyvinyl polymer	e up of (2) Polyester polymer	(3) Polyamide polymer	(4) Polyethylen	[AIEEE-2003] e polymer
3.	Which of the following i (1) Bakelite	s a polyamide ? (2) Terylene	(3) Nylon-6,6	(4) Teflon	[AIEEE-2005]
4.	Which of the following is (1) PVC	s fully fluorinated polymer (2) Thiokol	? (3) Teflon	(4) Neoprene	[AIEEE-2005]
5.	Bakelite is obtained from (1) CH ₃ CHO	m phenol by reacting with (2) CH_3COCH_3	(3) HCHO	[AIEEE (4) (CH ₂ OH) ₂	E-2008, 3/105]
6.	Buna-N synthetic rubbe	er is a copolymer of :		[AIEEE	E-2009, 4/144]
	(1) H ₂ C=CH–CH=CH ₂ a	nd $H_{5}C_{6}$ -CH=C H_{2}	(2) $H_2C=CH-CN$ and H_2C	C=CH-CH=CH ₂	
			CI		
	(3) $H_2C=CH-CN$ and H_2	$C=CH-C = CH_2$ $ CH_3$	(4) $H_2C=CH-C = CH_2$ ar	nd H ₂ C=CH–CH=	CH ₂
7.	The polymer containing (1) teflon	g strong intermolecular for (2) nylon 6,6	ces e.g. hydrogen bondin (3) polystyrene	g is [AIEE (4) natural rubb	E-2010, 4/144] er
8.	Which one is classified as a condensation polymer ?(1) Dacron(2) Neoprene(3) Teflon			[JEE Main-201 (4) Acrylonitrile	• •
9.	Which polymer is used (1) Bakelite	in the manufacture of pa (2) Glyptal	ints and lacquers ? (3) Polypropene	[JEE M (4) Poly vinyl cł	lain 2015, 4/120] hloride
10.	Match the polymers in	column-A with their main			
	Column - A	Column-B	[JEE Main 201	5 Online(10-04-	2016), 4/120]

Column - AColumn-B(A) Polystyrene(i) Paints and lacquers(B) Glyptal(ii) Rain coats(C) Polyvinyl chloride(iii) Manufacture of toys(D) Bakelite(iv) Computer discs(1) (A) - (iii), (B) - (iv), (C) - (ii), (D) - (i)(2) (A) - (iii), (B) - (i), (C) - (iii), (D) - (iv)(3) (A) - (iii), (B) - (iv), (C) - (iii), (D) - (iv)(4) (A) - (ii), (B) - (iv), (C) - (iii), (D) - (i)

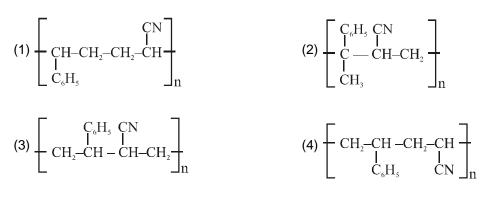
11. Which one of the following structures represents the neoprene polymer?

[JEE Main 2015 Online(11-04-2015), 4/120]

(1) $-(CH_2-CH_2)_n$ (2) $-(CH_2-CH_2)_n$ (3) $-(CH_2-C=CH-CH_2)_n$ (4) $-(CH_2-CH_2)_n$ (5) $-(CH_2-CH_2)_n$ (4) $-(CH_2-CH_2)_n$

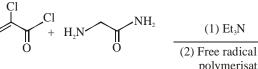
JEE(Adv.)-Chemistry Polymer 12. Which of the following statements about low density polythene is FALSE? [JEE Main 2016, 4/120] (1) It is a poor conductor of electricity. (2) Its synthesis required dioxygen or a peroxide initiator as a catalyst. (3) It is used in the manufacture of buckets, dust-bins etc. (4) Its synthesis requires high pressure. 13. Assertion: Rayon is a semisynthetic polymer whose properties are better than natural cotton. **Reason :** Mechanical and aesthetic properties of cellulose can be improved by acetylation. (1) Both assertion and reason are incorrect [JEE Main 2016 Online(9-04-2016), 4/120] (2) Assertion is incorrect statement, but the reason is correct (3) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion (4) Both assertion and reason are correct, and the reason is the correct explanation for the assertion 14. Which of the following polymers is synthesized using a free radical polymerization technique ? [JEE Main 2016 Online(10-04-2016), 4/120] (1) Terylene (2) Teflon (3) Nylon 6,6 (4) Melamine polymer 15. The formation of which of the following polymers involves hydrolysis reaction? [JEE Main)-2017] (1) Nylon 6 (2) Bakelite (3) Nylon 6, 6 (4) Tervlene 16. Which of the following is a biodegradable polymer? [JEE Main 2017 Online(09-04-2017), 4/120] (1) $\begin{bmatrix} 0 \\ HN-(CH_2)_5 - C \end{bmatrix}$ (2) f_{C} COO-(CH₂)₂-O f_{n} (3) $+HN-(CH_2)_6NHCO-(CH_2)_4-C$

17. The copolymer formed by addition polymerization of styrene and acrylonitrile in the presence of peroxide is : [JEE Main 2018 Online(15-04-2018), 4/120]



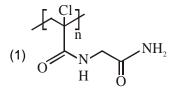
- **18.** Which of the following statement is not true :-
- [JEE Main 2018 Online(15-04-2018), 4/120]
- (1) Step growth polymerisation requires a bifunctional monomer
- (2) Nylon 6 is an example of step-growth polymerisation
- (3) Chain growth polymerisation includes both homopolymerisation and copolymerisation
- (4) Chain growth polymerisation involves homopolymerisation only.

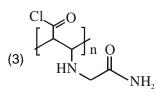
19. Major product of the following reaction is :



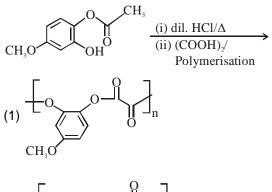
(1) Et₃N

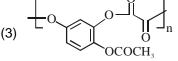
polymerisation

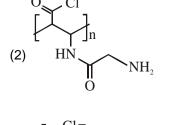


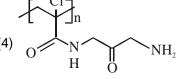


20. The major product of the following reaction is:

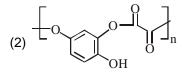


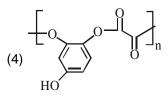




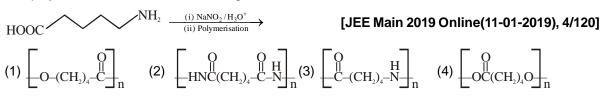


[JEE Main 2019 Online(10-01-2019), 4/120]





21. The polymer obtained from the following reactions is :



22. The homopolymer formed from 4-hydroxy-butanoic acid is :-

[JEE Main 2019 Online(11-01-2019), 4/120]

(1)
$$\begin{bmatrix} 0 & 0 \\ -C(CH_2)_2C \end{bmatrix}_n$$
 (2) $\begin{bmatrix} 0 & 0 \\ -C(CH_2)_2C - 0 \end{bmatrix}_n$ (3) $\begin{bmatrix} 0 \\ -OC(CH_2)_3 - 0 \end{bmatrix}_n$ (4) $\begin{bmatrix} 0 \\ -C(CH_2)_3 - 0 \end{bmatrix}_n$

Polymer

[JEE Main 2019 Online(09-01-2019), 4/120]

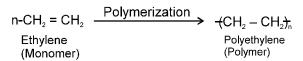
23.	Poly- β -hydroxybutyrate-co- β -hydroxyvalerate(PHBV) is a copolymer of					
	[JEE Main 2019 Online(12-01-2019), 4/120]					
	(1) 3-hydroxybutanoic acid and	4-hydrox	kypentanoic aci	d		
	(2) 2-hydroxybutanoic acid and	3-hydrox	kypentanoic aci	d		
	(3) 3-hydroxybutanoic acid and	2-hydro	kypentanoic aci	d		
	(4) 3-hydroxybutanoic acid and	3-hydro>	kypentanoic aci	d		
24.	The two monomers for the synt	hesis of	Nylone-6, 6 are	э:		
				[JEE Main 20 ⁻	19 Online(12-01-2019), 4/120]	
	(1) HOOC(CH ₂) ₆ COOH, H ₂ N(CH	$I_2)_6 NH_2$	(2) HC	OC(CH ₂) ₄ COOF	$H, H_2N(CH_2)_4NH_2$	
	(3) HOOC(CH ₂) ₆ COOH, H ₂ N(CH	l ₂) ₄ NH ₂	(4) HC	OC(CH ₂) ₄ COOH	$H_2 H_2 N(CH_2)_6 NH_2$	
25.	Which one of the following poly	mers is	not obtained by	condensation po	olymerisation?	
				[JEE Main 202	20 Online(05-09-2020), 4/100]	
	(1) Buna - N (2) Bał	kelite	(3) Ny	rlon 6	(4) Nylon 6, 6	
26.	Consider the Assertion and Re	ason giv	en below.			
	Assertion (A) : Ethene polymeriz	zed in the	presence of Zie	gler Natta Cataly	st at high temperature and pressure	
	is used to make buckets and c	lustbins.				
	Reason (R): High density polym	ners are o	closely packed a	ind are chemicall	y inert. Choose the correct answer	
	from the following :			[JEE Main 202	20 Online(06-09-2020), 4/100]	
	(1) (A) is correct but (R) is wro	ng.				
	(2) (A) and (R) both are wrong.					
	(3) Both (A) and (R) are correct	t and (R)	is the correct e	explanation of (A).	
	(4) Both (A) and (R) are correc	t but (R)	is not the corre	ct explanation o	f (A).	
27.	The correct match between Iten	n-I and It	em-II :	[JEE Main 202	20 Online(06-09-2020), 4/100]	
	ltem-l		Item-II			
	(a) Natural rubber	(I)	1, 3-butadiene	e + styrene		
	(b) Neoprene	(II)	1, 3-butadiene	e + acrylonitrile		
	(c) Buna-N	(III)	Chloroprene			
	(d) Buna-S	(IV)	Isoprene			
	(1) (a) - (III), (b) - (IV), (c) - (I),	(d) - (II)				
	(2) (a) - (IV), (b) - (III), (c) - (II),	(d) - (l)				
	(3) (a) - (IV), (b) - (III), (c) - (I),	(d) - (II)				
	(4) (a) - (III), (b) - (IV), (c) - (II),	(d) - (l)				

ANSWER KEY

EXERCISE # 1

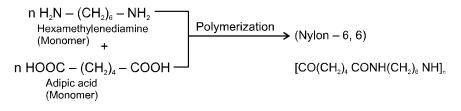
PART - I

A-1. (i) Homopolymers : Polymers in which repeating structural units are derived from only one type of monomer units are called homopolymers.



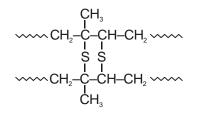
Other examples polypropylene, polyvinyl chloride (PVC), polyisoprene, neoprene (polychloroprene) polyacrylonitrile (PAN), nylon-6, polybutadiene, teflon (polytetrafluoroethylene), cellulose, starch, glycogen etc.

(ii) Copolymers : Polymers in which repeating structural units are derived from two or more types of monomer units are called copolymers.



A-2. Raw rubber does not posses the characteristic of the rubber with which we are familar in order to give it strength & elasticity it is vulcanised. In the vulcanization process, raw rubber is mixed with small amount of sulphur and heated.

1-3 % S is used for rubber bands & 5% S is used for tyre rubber.



A-3.
$$CH_2 = C - CH = CH_2$$

CI

- A-4. Addition polymer : Polyvinyl chloride, polythene, Buna-N Condensation polymer : Bakelite, terylene, glyptal
- A-5. Buna-N \rightarrow Copolymer of 1, 3-butadiene and acrylonitrile Buna-S \rightarrow Copolymer of 1, 3-butadiene and styrene
- **A-6.** || < ||| < |
- **A-7.** Ziegler Natta catalyst. $(R_3AI + TiCl_4)$

JEE(/	JEE(Adv.)-Chemistry					P (olymer		
				PAR	RT - II				
A-1.	(A)	A-2.	(A)	A-3.	(A)	A-4.	(C)	A-5.	(D)
A-6.	(A)	A-7.	(C)	A-8.	(C)	A-9.	(B)	A-10.	(D)
A-11.	(D)	A-12.	(B)	A-13.	(B)				

PART - III

1. $A \rightarrow s, B \rightarrow r, C \rightarrow q D \rightarrow p$

				EXER	CISE # 2				
	PART - I								
1.	(A)	2.	(C)	3.	(B)	4.	(B)	5.	(D)
6.	(D)								
				PA	RT - II				
1.	3	2.	104	3.	6	4.	16.47		
	PART - III								
1.	(ABC)	2.	(CD)	3.	(AB)	4.	(ABC)	5.	(CD)
6.	(AC)								
				EXER	CISE # 3				
				PA	RT - I				
1.	(A) – (p, s)	; (B) – (q, I	r) ; (C) – (p	o, r) ; (D) – (s)	2.	(A)	3.	(D)	
4.	(CD)		5.	6	6.	(A)			
				PA	RT - II				
1.	(3)	2.	(3)	3.	(3)	4.	(3)	5.	(3)
6.	(2)	7.	(2)	8.	(1)	9.	(2)	10.	(3)
11.	(3)	12.	(3)	13.	(4)	14.	(2)	15.	(1)
16.	(4)	17.	(4)	18.	(4)	19.	(1)	20.	(1)
21.	(1)	22.	(4)	23.	(4)	24.	(4)	25.	(1)
26.	(3)	27.	(2)						

IEE/Adv _Chamidav

SELF ASSESSMENT PAPER

PART-1: PAPER JEE (MAIN) PATTERN

	SECTION-I : (M	aximum Marks : 80)					
•	This section contains TWENTY questions.						
•	Each question has FOUR options (A), (B), (C) and (D). ONLY ONE of these four options is correct.						
•	For each question, darken the bubble correspo	onding to the correct option in the ORS.					
•	For each question, marks will be awarded in g	ne of the following categories :					
	-	rresponding to the correct option is darkened.					
	Zero Marks : 0 If none of the bubble	es is darkened.					
	Negative Marks : -1 In all other cases						
1.	Among the following the branched chain polym	eris					
	(A) PVC	(B) Polyester					
	(C) Low density polythene	(D) Nylon 66					
2.	Which of the following is cross linked polymer?						
	(A) low density polythene	(B) High density Polythene					
	(C) PVC	(D) Bakelite					
3.	An example of condensation homo polymer is						
	(A) Bakelite	(B) Melamine formaldehyde resin					
	(C) Glyptal	(D) Nylon-6					
4.	Among the following weakest intermolecular for	ce of attraction are present in					
	(A) Thermosetting polymer	(B) Thermoplastic					
	(C) Fibers	(D) Elastomer					
5.	Thermosetting polymer is :						
	(A) cross linked polymer.	(B) does not melt or soften on heating.					
	(C) irreversible.	(D) all above are correct.					
6.	The widely used plastic, PVC is a polymerization	on product of					
	(A) $CH_2 = CH_2$	$(B) CH_2 = CCI_2$					
	(C) CI-CH=CH-CI	(D) $CH_2 = CH-CI$					
7.	Rubber is heated with sulphur for its modification	on. The process is known as					
	(A) Sulphonation	(B) Vulcanization					
	(C) Sensitization	(D) Addition					
8.	Melmac a thermosetting plastic often used to n	nake plastic dishes is prepared by copolymerization of					
	(A) Urea and formaldehyde						
	(C) Phenol and formaldehyde	(D) Terephthalic acid and ethylene glycol					
9.	The catalyst used for olefin polymerisation to s	op branching is :					
	(A) Ziegler Natta catalyst	(B) Wilkinson catalyst					
	(C) Raney Nickel catalyst	(D) None of these					
10.	Monomers are converted to polymers by						
	(A) Hydrolysis of monomer	(B) Condensation between monomers					
	(C) Protonation of monomers	(D) none					
11.	Glyptal polymer is obtained from glycol by read	tion with-					
	(A) Malonic acid (B) Phthalic acid	(C) Maleic acid (D) Acetic acid					

Polymer

12.	What percentage of su (A) 10%	lphur is used in vulcanised (B) 5%	d rubber generally ? (C) 25%	(D) 50%
13.	Which of the following (A) PVC	is used to make nonstick (B) Teflon	cook wares? (C) Polystyrene	(D) Nylon-6
14.	Strong intermolecular f (A) vander waal force (C) dipole-dipole interac	orce present in Nylon-66 i ction	is : (B) hydrogen bond (D) disulphide linkage	
15.	A synthetic rubber whic (A) Isoprène	ch resemble natural rubbe (B) Buna-S	er is : (C) Neoprene	(D) Buna-N
16.	Which of the following (A) Polystyrene	is not an addition polymer (B) Orlon	? (C) Polypropylene	(D) Dacron
17.	What is the order of dec (I) CH_3 - $CH=CH_2$ (A) III > II > I	creasing reactivity of the f (II) Ph-CH=CH ₂ (B) I > II > III		ds anionic polymerization? (D) II > III > I
18.	IUPAC name of isoprer (A) 2-Chloro-1,3-butadio (C) Isobutene		(B) 2-Methyl-1,3-butadie (D) 2-Methylpropene	ene
19.	Which of the following i (A) Polythene	s a biodegradable polyme (B) Bakelite	er? (C) PLA	(D) PVC
20.	Formation of terylene is (A) Esterfication (C) Addition polymersa	·	(B) Saponification (D) Condensation polyn	nerization

PART- 2 : NUMERICAL TYPE QUESTIONS

SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, -0.33, -.30, 30.27, -127.30, if answer is 11.36777.... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.
 - For Example : If answer is -77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:
 Full Marks : +4 If ONLY the correct numerical value is entered as answer.
- 1. Difference between the molecular mass of the monomers used in the biodegradable polymer PHBV is :
- 2. How many oxygen atoms are present per mononer unit of natural polymer starch?
- 3. How many among the following polymers give bromine water test for unsaturation?

	(a) polyisoprene (e) Teflon	(b) polypropylene (f) Buna-S	(c) Nylon-6 (g) PAN	(d) Glyptal (h) Gutta Percha
4.	NC	H₂, Pt →[L] Adipic ac Polymeri		
	Molecular mass of an	o monomor unit of poly	mor Mio :	

Molecular mass of one monomer unit of polymer M is :

5. A co-polymer of ethylene chloride and propylene contains alternate monomers of each type. What is the mass percentage of ethylene chloride in this polymer ?

	Answers								
PART - 1									
1.	(C)	2.	(D)	3.	(D)	4.	(D)	5.	(D)
6.	(D)	7.	(B)	8.	(B)	9.	(A)	10.	(B)
11.	(B)	12.	(B)	13.	(B)	14.	(B)	15.	(C)
16.	(D)	17.	(A)	18.	(B)	19.	(C)	20.	(D)
PART - 2									
1.	14	2.	5	3.	3	4.	212	5.	59.80

SAP Solutions

PART - 1

10. Polymerization takes place either by condensation or addition reactions.

PART - 2

 Monomers used in PHBV are β-hydroxybutyric acid and β-hydroxyvaleric acid. Difference between the molecular mass of the monomers used in the biodegradable polymer PHBV is 14 because both are homologues.

Molecular formula of 1-unit is $C_{11}H_{20}O_2N_2$ Molecular mass = 212

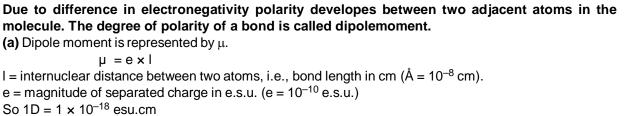
5. Structure of co-polymer is $\begin{bmatrix} -CH-CH_2-CH-CH_2 \\ I \\ CI \\ CH_3 \end{bmatrix}^n$

Molecular mass of ethylene chloride is 62.5 Molecular mass of propylene is 42

Mass percentage of ethylene chloride = $\frac{62.5 \times 100}{104.5} = 59.80$

PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS & POC-II

A. Dipole moment



The Debye (D) is the unit of dipole moment.

(b) The dipole moment is represented by arrow head pointing towards the positive to the negative end.



(c) Charge and distance oppose each other, with the larger halogens having longer bond but weaker electronegativity. The overall result is that the bond dipole moment increase in the order as follows.

$$H_3C - I < H_3C - Br < H_3C - F < H_3C - CI$$

 μ : 1.29 D 1.48 D 1.51 D 1.56 D

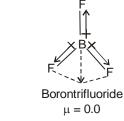
Ex.
$$\mu$$
: $CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl_3$

(d) Dipole moment of the compound also depends on the shape of the molecule.

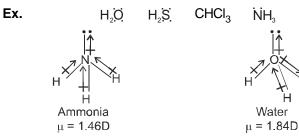
(e) Dipole moment of symmetrical compound is always zero. ($\mu = 0$)

Ex. $\mathbf{\overset{\leftarrow}{O}}_{\mathsf{Result}}$





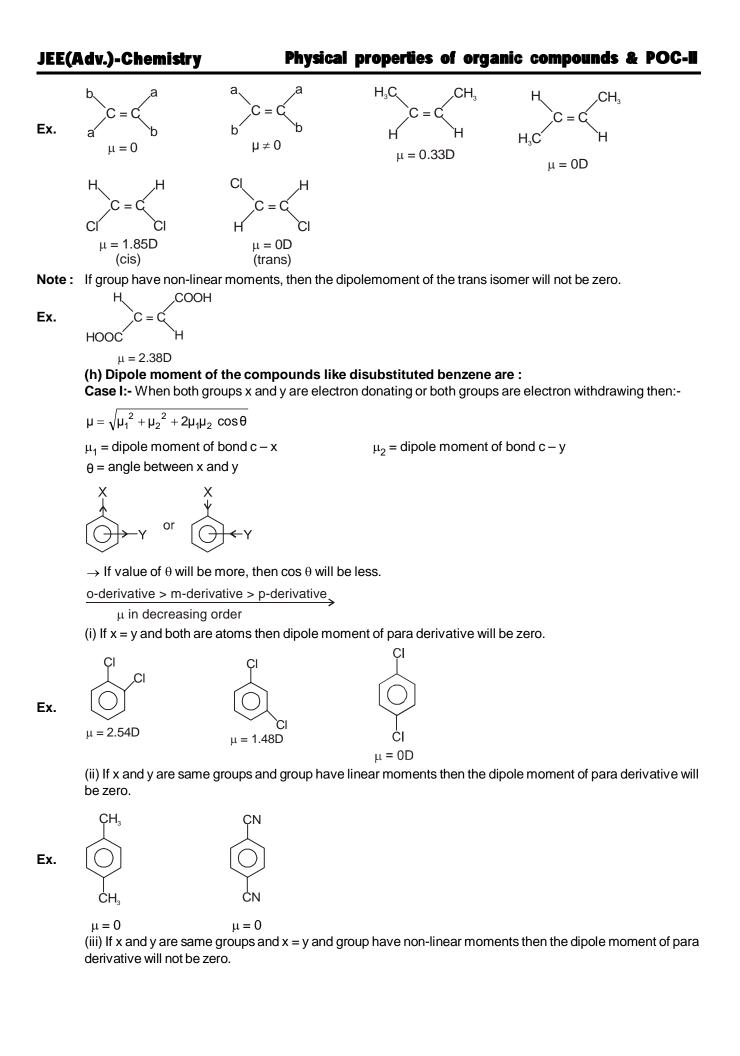
(f) Dipole moment of **unsymmetrical** compound is always greater than zero ($\mu > 0$).

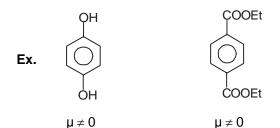


(g) $\mu \propto$ electronegativity of central atom or surrounding atoms present on the central atom of the molecule.

 μ : CHF₃ > CHCl₃ > CHBr₃ > CHI₃

Net dipole moment of the trans derivative of the compound will only be zero if both the atoms attached to carbons are in the form a and b with linear dipole moment.





Case-II:- When one group is electron withdrawing and the other group is electrondonating then:-

$$\mu = \sqrt{{\mu_1}^2 + {\mu_2}^2 - 2\mu_1\mu_2 \,\cos\theta}$$

Ex.

CH_3 CN CN_2 CN_3 CN_3 CN_3 (Para-derivative > meta-derivative > ortho-derivative)

Intermolecular forces:

 Attractions between molecules are particularly important in solids and liquids. In these "Condensed" phases, the molecules are continously in contact with each other. The melting points, boiling points, and solubilities of organic compounds show the effects of these forces. Two major kinds of attractive forces cause molecules to associate into solids and liquids;

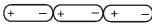
(A) Dipole-dipole interactions (B) VanderWaals forces

(a) Dipole-Dipole interaction :

Dipole-dipole interactions result from the approach of two polar molecules.

- If their positive and negative ends approach, the interaction is an attractive one.
- If two negative ends or two positive ends approach, the interaction is repulsive one.
- In a liquid or a solid the molecules are mostly oriented with the positive and negative ends together and the net forces is attractive.

Symbolized by :



An especially strong kind of dipole- dipole attraction is hydrogen bonding

Hydrogen Bonding :

(1). Definition :

The hydrogen bond is an electrostatic attractive force between covalently bonded hydrogen atom of one molecule and an electronegative atom (such as F, O, N) of another molecule.

eg:- Consider the hydrogen fluorine bond in hydrogen fluoride, HF. This bond is a polar covalent bond in which hydrogen is attached to a strongly electronegative element.

 $\begin{array}{cc} \delta + & \delta - \\ H & - - F \end{array}$

The positive charge on hydrogen will be attracted electrostatically by the negative charge on F atom by another molecule of HF.

H – F ----- H – F ----- H – F Covalent – bydrogen bond bond

Hydrogen bond is a very weak bond (strength about 2–10 kcal/mol) as compared to normal covalent bond. But stronger than vander Waal's force of attraction.

Physical properties of organic compounds & POC-II

(2). Conditions for hydrogen bonding :

(a) The molecule must contain a highly electronegative atom linked to hydrogen atom.

(b) The size of electronegative atom should be small.

Only F, O and N atoms form effective hydrogen bonding.

Example :

Greater the electronegativity and smaller the size of the atom (F, O, N), the stronger is the hydrogen bond.

H – F ----- H > H – O ----- H > H – N ----- H

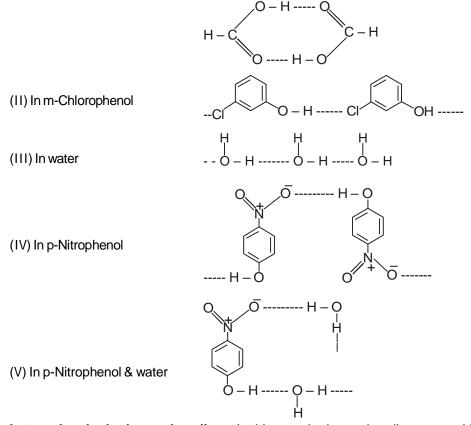
(3). Types of Hydrogen Bonding :

(a) Intermolecular hydrogen bonding : In such type of linkages the two or more than two molecules of the same compound combine together to give a polymeric aggregate.

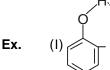
This phenomena is also known as association.

Example :

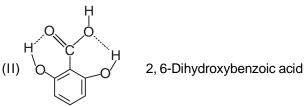
(I) Hydrogen bonding in carboxylic acids e.g. formic acid (Dimerisation)



(b) Intramolecular hydrogen bonding:- In this type, hydrogen bonding occur within two atoms of the same molecule. This type of hydrogen bonding is commonly known as chelation.



o-Nitrophenol



Conclusion :

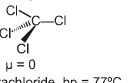
(a) The chelation between the ortho substituted groups restricts the possibility of intermolecular hydrogen bonding.

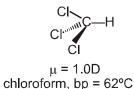
(b) Chelation does not take place in m - & p - isomers because the two groups far away from each other.

Physical properties of organic compounds & POC-II

(b) Vander-Waal forces :

- Vander Waals forces or London dispersion force can be observed in nonpolar molecules such as carbon tetrachloride.
- A small temporary dipole moment is induced when one molecule approaches another molecule in which the electrons are slightly displaced from a symmetrical arrangement.
- The electron in the approaching molecule are displaced slightly so that an attractive dipole-dipole interaction results.
- These temporary dipoles last only a fraction of a second, and they change continuously; yet they are correlated so their net force is attractive.
- This attractive force depends on close surface contact of two molecules, so it is roughly proportional to the molecular surface area.
- Carbon tetrachloride (CCl₄) has zero dipole moment, yet its boiling point is higher than of chloroform ($\mu = 1.0D$).





Carbon tetrachloride, bp = 77°C

• Carbon tetrachloride has a larger surface area than chloroform (a chlorine atom is much larger than a hydrogen atom), so the intermolecular van der Waals attractions between carbon tetrachloride molecules are stronger than they are between chloroform molecules.

B. Boiling Point

- The boiling point (bp) of a compound is the temperature at which the compound's vapor pressure equals the atmospheric pressure. In order for a compound to vaporize, the force that hold the molecules close to each other in the liquid must overcome. This means that the boiling point of a compound depends on the strength of the attractive forces between the individual molecules.
- If the molecules are held together by strong forces, it will take a lot of energy to pull the molecules away from each other and the compound will have a high boiling point.
- If however, the molecule are held together by weak forces, only a small amount of energy will be needed to pull the molecules away from each other and the compound will have a low boiling point.

Factors affecting boiling point :

(1) Hydrogen Bonding :

Alcohols :

Alcohols have much higher boiling points than alkanes or ethers of comparable molecular weight because, in addition to van der Waals forces and the dipole–dipole interactions of the carbon–oxygen bond alcohols can form hydrogen bonds.

The successive replacement of hydrogen atom of the –OH group of alcohol by alkyl group to form ether blocks the probability of hydrogen bonding reduces and thus B.P. of alcohols are higher than ether.

Ex.

	$CH_2 - OH$	$CH_2 - OCH_3$	$CH_2 - OCH_3$
	$\dot{C}H_2 - OH$	$\dot{C}H_2 - OH$	$\dot{C}H_2 - OCH_3$
B.P.	197⁰C	125ºC	84ºC

Water :

Water has the lowest molecular weight among hydrides of the VI group of periodic table, it has the highest boiling point. Water molecules associate through intermolecular hydrogen bonding and thus require more energy to separate the molecules for vaporization.

Ex.

Η	H	H	Η
н–о	н–о	H–Ó	-Н-О-

Compound	H ₂ O	H_2S	H_2Se
B.P.	100°C	-59.6	–42°C

Amines :

Ex.

- Primary and secondary amines also form hydrogen bonds, so these amines have higher boiling points than alkanes with similar molecular weights.
- Nitrogen is not as electronegative as oxygen, however, which means that the hydrogen bonds between amine molecules are weaker than the hydrogen bonds between alcohol molecules.
- Amines, therefore, have lower boiling points than alcohols with similar molecular weights.
- Because primary amines have two N–H bonds, hydrogen bonding is more significant for primary amines than
 for secondary amines. Tertiary amines cannot form hydrogen bonds with each other because they do not
 have a hydrogen attached to the nitrogen. Consequently if you compare amines with the same molecular
 weight and similar structures, primary amines have higher boiling point than secondary amines and secondary
 amines have higher boiling points than tertiary amines.

$$\begin{array}{cccc} \mathsf{CH}_3 & \mathsf{CH}_3 & \mathsf{CH}_3 \\ \mathsf{I} & \mathsf{I} & \mathsf{I} \\ \mathsf{CH}_3 \mathsf{CH}_2 \mathsf{CH} \mathsf{CH}_2 \mathsf{NH}_2 & \mathsf{CH}_3 \mathsf{CH}_2 \mathsf{CH} \mathsf{NH} \mathsf{CH}_3 & \mathsf{CH}_3 \mathsf{CH}_2 \mathsf{CH}_2 \mathsf{CH}_3 \\ \texttt{a primary amine} & \texttt{a secondary amine} & \texttt{a tertiary amine} \\ \texttt{bp} = 97 \ ^\circ \mathsf{C} & \texttt{bp} = 84 \ ^\circ \mathsf{C} & \texttt{bp} = 65 \ ^\circ \mathsf{C} \end{array}$$

(2) Dipole - Dipole interactions :

Dipole–dipole interactions, are stronger than van der Waals forces but not as strong as ionic or covalent bonds. Ethers generally have higher boiling points than alkanes of comparable molecular weight because both van der Waals forces and dipole–dipole interactions must be overcome for an ether to boil.



EX. B.P:
$$CI = C = CH$$
 > $H = C = CH$

(3) Molecular weight :

The boiling points for any homologous series of compounds increase as their molecular weights increase because of the increase in van der Waals forces. So the boiling points of a homlogous series of ethers, alkyl halides, alcohols, and amines increase with increasing molecular weight.

Ex. B. P :
$$CH_3 I > CH_3 Br > CH_3 - CI > CH_3 - F$$

Ex. B. P:
$$CH_3OH < C_2H_5OH < H_3C - CH_2 - CH_2 - OH < H_3C - CH_2 - CH_2 - CH_2 - OH < (Methanol) (Ethanol) (Propan - 1-ol) (Butan - 1-ol)$$

$$<$$
 H₃C - CH₂ - CH₂ - CH₂ - CH₂ - OH
(Pen tan - 1 - ol)

Ex. B.P:
$$CH_3 CH_2 CH_2 CHO < CH_3 - C - CH_2 - CH_3 < Ph - CHO < Ph - CH_2CHO < Ph - C - CH_3$$

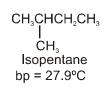
(ketone is more polar than aldehyde).

(4) Vander Waals forces

- The molecules of an alkane are held together by these induced dipole-induced dipole interactions known as van der Waals forces or London forces. In order for an alkane to boil, these van der Waals forces must be overcome.
- The homologous series of alkanes boiling points increase as their size increases. This occurs becuase each additional methylene group increases the area of contact between the molecules.

Physical properties of organic compounds & POC-II

- Because the strength of van der Waals force depends on the area of contact between molecules, branching in a compound lowers its boiling point because it reduces the area of contact.
- If two alkanes have the same molecular weight, the more highly branched alkane will have a lower boiling point.
- **Ex.** $CH_3 CH_2 CH_2 CH_2 CH_3$ pentane $bp = 36.1^{\circ}C$

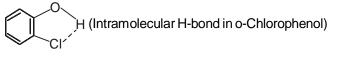


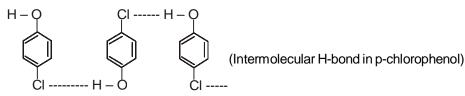
CH₃ | CH₃CCH₃ | CH₃ neopentane bp = 9.5°C

General order of boiling point of various F.G.

 $\begin{array}{ccc} & O & O \\ \parallel & \parallel \\ B.P: R-CONH_2 > R-COOH > R-OH > R - C - R > R - C - H > R - X > R-OR \\ > R-C=CH > R-H > R-CH=CH_2 (Terminal) \end{array}$

Ex. o-Chlorophenol has lower boiling point in comparison to its p-isomer.





C. Melting Point

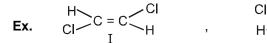
The temperature at which the thermal energy of the particles is great enough to overcome the intracrystalline forces that hold them in position is known as melting point.

• Melting is the change from the highly orderd arrangment of particles in the crystalline lattice to the more random arrangment that characterizes a liquid.

Factors affecting melting point :

(1) Molecular weight :

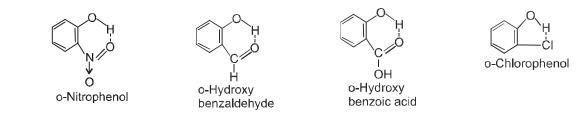
- Melting points of alkanes increase in a homologous series as the molecular weight increases.
- **Ex. M.P.** : $CH_3 CH_2 CH_3 < CH_3 CH_2 CH_3 CH_3 CH_2 CH_2 CH_2 CH_2 CH_3$
- (2) Packing :
- Packing is a property that determines how well the individual molecules in a solid fit together in the crystal lattice. The tighter they fit, the more energy required to break the lattice and melt the compound.
- Alkanes with an odd number of carbon atoms pack less tightly than alkanes with an even number of carbon atoms. This decreases the intermolecular forces between alkanes with odd number of carbon atoms, which decreases their melting points.
- In geometrical isomers the trans isomers are more symmetrical than cis isomers (C_{ab}=C_{ab} type alkenes) so trans form have higher M.P. than cis isomers.
 - * The heavier the molecule and stronger the intermolecular forces, higher will be the M.P. of the compound.
 - * Ortho isomers of hydroxy, nitro, carbonyl compounds have low M.P. than their corresponding m & p isomers.



$$c = c < H$$

M.P. | > II

Ex. Ortho - hydroxy, nitro-, carbonyl, carboxylic or chloro compounds have lower melting and boiling points than the respective meta or para isomer due to interamolecular H-bonding in ortho substituted compound.



D. Solubility

(1) Solvation of ionic salts by ion dipole interaction :

Intermolecular forces are of primary importance in explaining the solubilities of substances. Dissolution of a solid in a liquid is, in many respect, like the melting of a solid. The orderly crystal structure of the solid is destroyed, and result in the formation of the more disorderly arrangement of the molecules (or ions) in solution. In the process of dissolving, too, the molecules or ions must be separated from each other, and energy must be supplied for both changes. The energy required to overcome lattice energies and intermolecular or interionic attractions comes from the formation of new attractive forces between solute and solvent.

Consider the dissolution of an ionic substance as an example. Hence both the lattice energy and interionic attractions are large. We find that water and only a few other very polar solvents are capable of dissolving ionic compound. These solvents dissolve ionic compounds by hydrating or solvating the ions.

Water molecules, by virtue of their great polarity as well as their very small, compact shape, can very effectively surround the individual ions as they are free from the crystal surface. Positive ions are surrounded by water molecules with the negative end of the water dipole pointed toward the positive ion; negative ions are solvated in exactly the opposite way. Because water is highly polar, and because water is capable of forming strong hydrogen bond, the dipole-ion attractive forces are also large. The energy supplied by the formation of these forces is great enough to overcome both the lattice energy and interionic attractions of the crystal.

(2) Solvation of compounds by dipole-dipole interaction :

A thumb rule for predicting solubilities is that "like dissolves like." Polar and ionic compound tend to dissolve in polar solvents. Polar liquids are generally miscible with each other. Nonpolar solids are usually soluble in nonpolar solvents. On the other hand nonpolar solids are insoluble in polar solvents. Nonpolar liquids are usually mutually miscible, but nonpolar liquids and polar liquids "like oil and water" do not mix.

(3) Solvation of compounds by hydrogen bonding :

Methanol and water are miscible in all proportions; so too are mixtures of ethanol and water and mixtures of both propyl alcohols and water. In these cases the alkyl groups of the alcohols are relative small, and the molecules therefore resemble water more than they do an alkane. Another factor in understanding their solubility is that the molecules are capable of forming strong hydrogen bonds to each other.

$$CH_{3}CH_{2}H^{\delta^{+}}Hydrogen bond$$

Physical properties of organic compounds & POC-II

If the carbon chain of an alcohol is long, however, we find that the alcohol is much less soluble in water. Decyl alcohol (see following structures) with a chain of 10 carbon atoms is only very slightly soluble in water. Decyl alcohol resembles an alkane more than it does water. The long carbon chain of decyl alcohol is said to be hydrophobic (hydro, water ; phobic, fearing or avoiding – "water avoiding"). Only the OH group, a rather small part of the molecule, is hydrophilic (philic, loving or seeking - "water seeking"). (On the other hand, decyl alcohol is guite soluble in less polar solvents, such as chloroform.) Hydrophilic

Hydrophobic portion

An explanation for why nonpolar groups such as long alkane chains avoid an aqueous environment, that is, for the so-called hydrophobic effect, is complex. The most important factor seems to involve an unfavorable entropy change in the water. Entropy changes have to do with changes from a relatively ordered state to a more disordered one or the reverse. Changes from order to disorder are favorable, whereas changes from disorder to order are unfavorable. For a nonpolar hydrocarbon chain to be accommodated by water, the water molecules have to form a more ordered structure around the chain, and for this, the entropy change is unfavorable.

(4) Solubility in water :

As molecular weight increases solubility in water decreases. The lower alcohols are miscible with water. This is due to intermolecular hydrogen bonding between alcohol and water molecules.

Intermolecular H bond between water & alcohol molecules

But this is true only for the lower alcohols, where the – OH group constitutes a large part of the molecule. As the alkane like alkyl group becomes larger, water solubility decreases. For practical purpose we consider that the borderline between solubility and insolubility in water occurs at about four to five carbon atoms for normal primary alcohols.

Polyhydroxy alcohols provide more than one site per molecule for hydrogen bonding and their solubility is appreciable till seven carbon atoms. Amongst isomers, as branching increases, the surface area of hydrocarbon part (hydrophobic part) decreases so solubility increases.

3° alcohol > 2° alcohol > 1° alcohol. It follows the order :

POC - II (CHEMICAL SEPARATION OF ORGANIC COMPOUNDS)

Purification of organic compounds :

- The organic compounds derived from natural sources or prepared in the laboratory are seldom pure. They are usually contaminated with other substances.
- Purification means the removal of undesirable impurities associated with a particular organic compound, i.e to obtain the organic compound in pure state.
- Various methods have been developed to purify organic compound

(1) **Physical methods:**

(i) Crystallisation	(ii) Sublimation	(iii) Distillation
(iv) solvent extraction	(v) chromatography	

(2) Chemical methods :

Chemical methods of separation depend upon the nature of the functional group present in the component. Hence these can be applied to solid as well as liquid compounds.

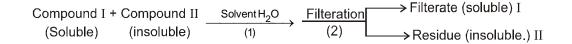
- **Physical properties of organic compounds & POC-II**
- A chemical method can be applied only when one of the components of the mixture is soluble in a particular solvent while the other is insoluble in the same solvent.
- Separation is the first step during the actual analysis of organic mixture. It is the most important step in the sense that if separation is incomplete the result will not be correct because the impure compound will give tests of different functional group and its melting point will also be very much different from that of the pure compound obtained from complete separation.

Separation of Binary mixtures of organic compounds :

The usual systematic scheme for separating a solid binary mixture is discussed below.

- (i) Separation with water (ii) Separation with sodium bicarbonate
- (iii) Separation with sodium hydroxide (iv) Separation with hydrochloric acid Solubility of two components.

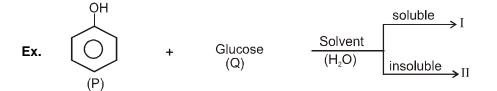
Separation Scheme for organic compounds :



- The mixture of organic compounds can be separated by using appropriate solvent.
- Most of the aromatic compounds are water insoluble due to large hydrophobic group of six carbon atom
- Aromatic acids are insoluble in water but soluble in aqueous NaHCO₃ solution or NaOH solution, due to salt formation.
- Aromatic hydroxy compounds are water insoluble but are soluble in aqueous NaOH solution due to salt formation.
- Aromatic amine (Aniline 1[°], 2[°], 3[°]) are organic base and water insoluble but are soluble in aqueous HCI solution due to salt formation.
- Aliphatic compoud with atleast two functional group (which can form H-bonding) are water soluble.
- **Ex.** Diacids, diols. diamines, hydroxy acids (OH,COOH), Amino acids (– NH₂, –COOH).
- **Ex.** oxalic acid , malonic, maleic, fumaric acid, glycol, glycerol, sucrose, glucose etc.

Table : Solubility of Organic Compounds

Compound	H ₂ O(cold)	aq.NaHCO ₃	aq. NaOH	aq. HCI
(I) Small aliphatic compound with F.G.(Hydrogen bonding) C_1 to C_2 (a) R – COOH (b) R – OH (c) R – NH ₂ (d) R – C – NH ₂ $\prod_{i=1}^{i}$	soluble	soluble	soluble	soluble
 (11) Small aliphatic compound containing two F.G (Hydrogen bonding) C₁ to C₅ (a) 2(COOH) - diacids (b) 2(-OH) - diols/glycol/ sugar (c) 2(NH₂) (d) - COOH + (-OH) (e) (-COOH) + (NH₂) (f) -CONH₂ some common compounds are urea, glucose, oxalic acid, succinic acid 	soluble	soluble	soluble	soluble
 (III) Aromatic acids (H₂O insoluble) Benzoic acid & dervative (a) Ar - COOH (b) Ar - SO₃H (c) picric acid (d) Ar - C - CI I O 	Insoluble Insoluble Insoluble Insoluble	soluble ArCOONa soluble soluble —	soluble ArCOONa soluble soluble —	Insoluble Insoluble Insoluble Insoluble
(IV) Phenols	Insoluble	Insoluble	soluble Ph – ONa	Insoluble
(V) Aromatic Amines, Anilines (weaker bases) Ar – NH _z	Insoluble	Insoluble	Insoluble	Soluble Ar NH₃CI [−]



Identify P, Q

 $\label{eq:sol} \textbf{Sol.} \quad \ \ I \to Q \;, \qquad \quad II \to P$

JEE(Adv.)-	Chemistry	Phy	sical properties	of organic compounds & POC-II
Ex.	Binary	mixtures - (Two com A	ponents)	В	Appropriate Solvent
	(1)	CH₂– NH₂ COOH	+		H ₂ O
	(2)	$H_2N - C - NH_2$ $\parallel O$	+	OH C_2H_5	H2O
	(3)	Fructose	+	NMe ₂	H ₂ O
	(4)	COOH O CH ₃	+	$\bigcirc \bigcirc \bigcirc$	aq. NaHCO ₃
	(5)		+		aq. NaOH
	(6)	NMe ₂	+	CI	aq. HCl

Exercise #1

> Marked Questions may have for Revision Questions.

PART - I : OBJECTIVE TYPE QUESTIONS

(C) ||| > | > ||

(C) CH₃–Br

 $H_{3}C = C CH_{3} H_{3}C = C CI CI CI CI CI CI CH_{3}$

Section (A) : Dipole Moment

A-1. Arrange the following in decreasing order of dipole moments.

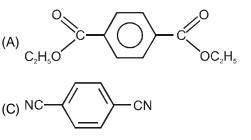
 $H_{3}C = C$

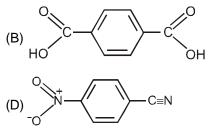
(A) | > || > |||

A-2.

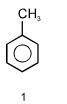


- (A) CH₃-F (B) CH₃-Cl
- A-3. False statement about dipole moment is : (A) Dipole moment is a vector quantity. (C) Geometrical isomers have same dipole moment.
- A-4. Which compound has zero dipole moment?

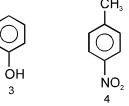




A-5. The increasing order of dipole moment of following compounds is :

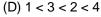








(A) 3 < 1 < 4 < 2 (B) 1 < 4 < 3 < 2 (C) 1 < 3 < 4 < 2



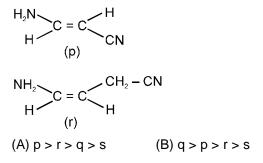
(D) || > | > ||

(D) CH₃-I

(D) Enantiomers have same dipole moment.

(B) Dipole moment depends on charge.

A-6. The correct order of dipole moment is :

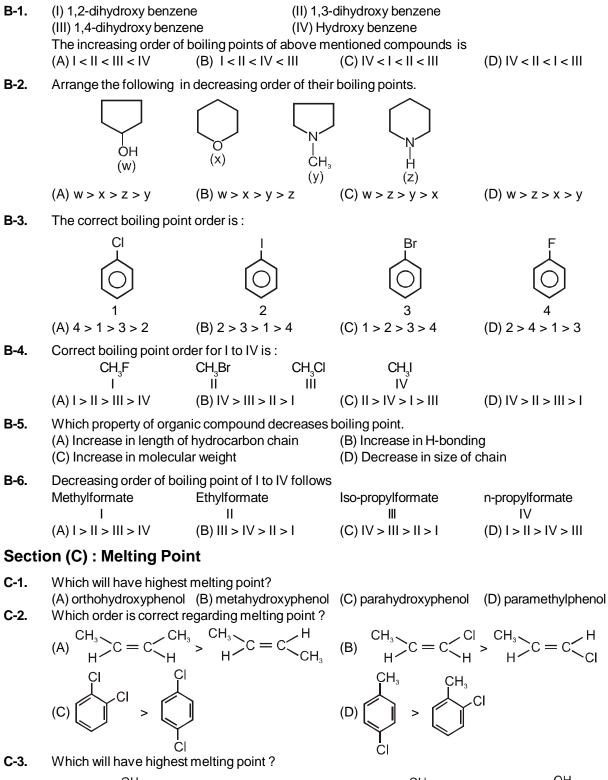


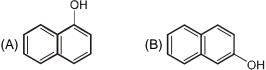
 $H_{2}N = C = C H_{(q)}$ NC = C = C CN(s)



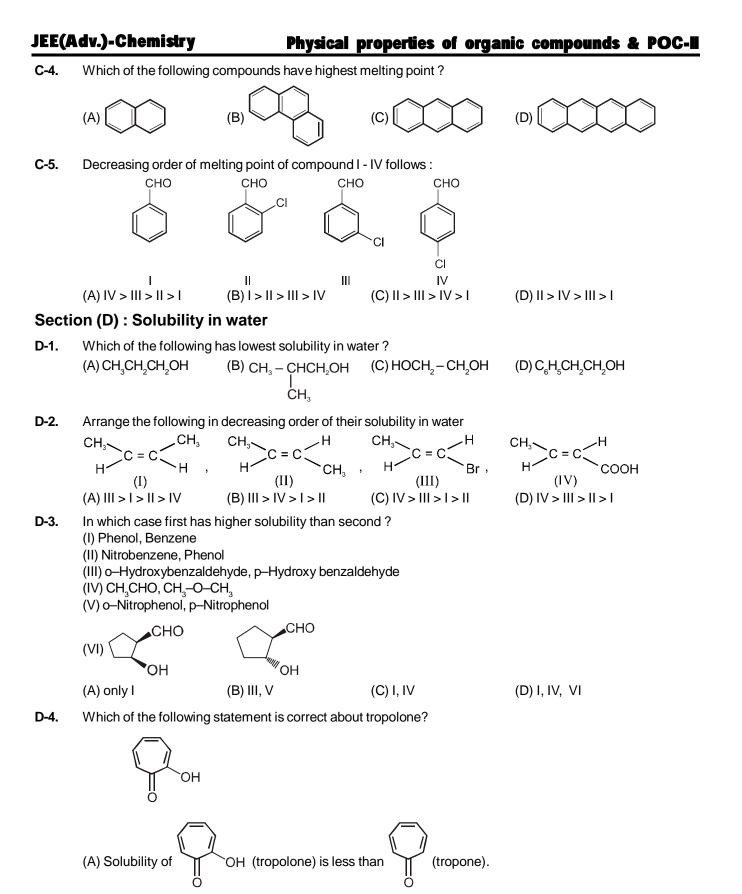
Physical properties of organic compounds & POC-II

Section (B) : Boiling point





(C) OH (D) OH OH OH OH OH



- (B) Tropolone has more stability and aromatic character than tropone.
- (C) Tropolone has higher dipole moment than tropone.
- (D) Tropolone has lower boiling point than tropone.

Physical properties of organic compounds & POC-II

D-5. Which carboxylic acid has maximum solubility in water ? (A) Malonic acid (B) Succinic acid (C) Salicylic acid

(D) Phthalic acid

Section (E) : POC-II

E-1. Which of the following compounds form salt with HCl?



E-2. Which of the following compounds form salt with NaHCO₃?



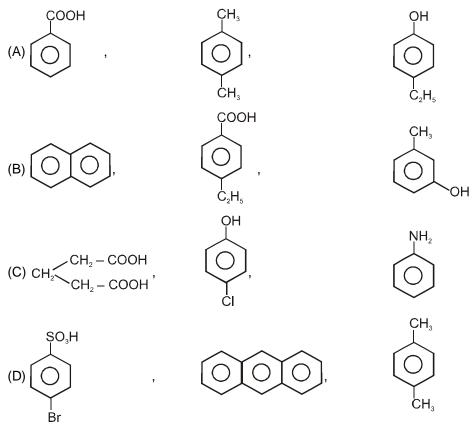




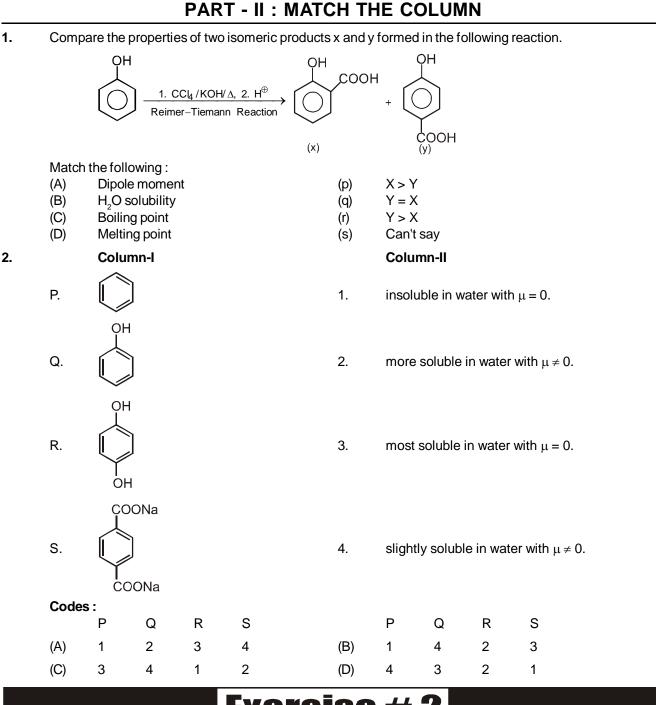
E-3. Which of the following compounds does not form salt with NaOH?



E-4. When the mixture of [A + B + C] is dissolved in NaHCO₃, A dissolves in NaHCO₃, B & C remain as a residue after that residue dissolves in aq. NaOH, C dissolves in it and B remains as residue. A, B and C will be respectively.



(D) Fittialica



Exercise #2

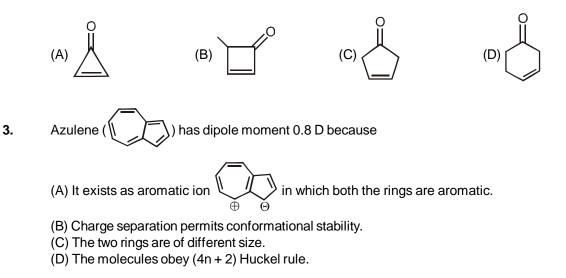
> Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

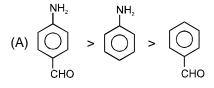
- 1. Which statement is incorrrect ?
 - (A) Aspirin is an antibiotic.
 - (B) Methyl orange is an azo dye.
 - (C) Phenyl butazone is considered as a unsafe drug.
 - (D) The chemical name of aspirin is acetyl salicyclic acid

Physical properties of organic compounds & POC-II

2. Which compound have maximum dipole moment?

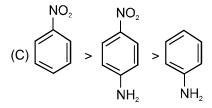


- 4. Which of the following compounds posses highest dipole moment. (A) Naphthalene (B) Phenanthrene (C) Anthracene (D) Azulene
- 5. Which of the following is listed for correct order of polarities :



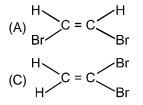
(B)
$$CH_3 - CH = CH - NO_2 > CH_3CH = CH - NO_2$$

(trans) (cis)

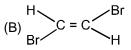


(D) $CH_3 - CH_3 > CH_3 - CH_2 - CI$

6. Which of the following isomers having molecular formula C₂H₂Br₂ has highest dipole moment and boiling point but lowest melting point.



Glycerol is purified by :
 (A) steam distillation
 (C) fractional distillation



(D) Not applicable to any single isomer

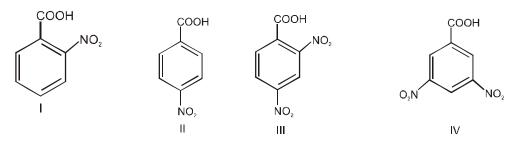
(B) vacuum distillation(D) simple distillation

Physical properties of organic compounds & POC-II

Two immiscible liquids are separated by :
 (A) separating funnel
 (C) chromatrography

(B) fractional distillation (D) sublimation

9. Decreasing order of melting point of compound I to IV follows.



(A) | > || > || > |V

(B) |V > ||| > || > |

(C) ||| > |V > || > |

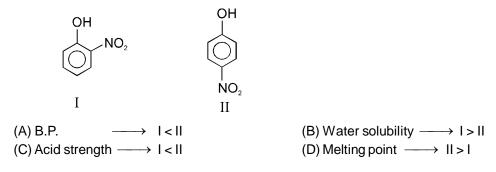
(D) ||| > |V > | > ||

- **10.** A is a lighter phenol and B is an aromatic carboxylic acid. Separation of a mixture of A and B can be carried out easily by using a solution of
 - (A) Sodium hydroxide

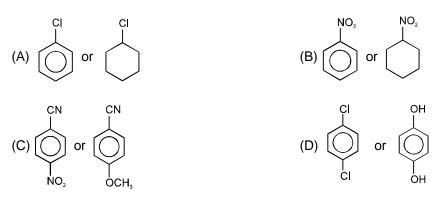
(B) Sodium sulphate

(C) Calcium chloride

- (D) Sodium bicarbonate
- 11. Which of the following statement is not true?
 - (A) Small aliphatic compound with at least two functional group which can form hydrogen bond are water soluble
 - (B) Most of the aromatic compounds are water insoluble due to large hydrophobic group of six carbon atom.
 - (C) Aromatic amines are soluble in aq. NaOH but insoluble in aq. HCl.
 - (D) Aromatic hydroxy compounds are soluble in aq. NaOH solution.
- 12. The correct orders about compounds I and II are :



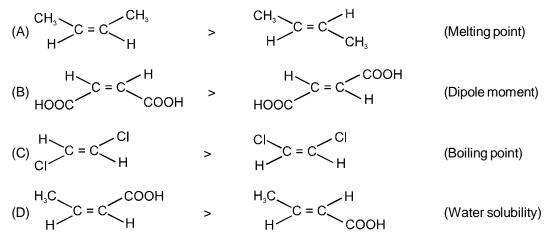
13. In which of the following pairs first has higher dipole moment than second ?



Physical properties of organic compounds & POC-II

14. The correct order for the given pair of isomers is :

CH₂ _H



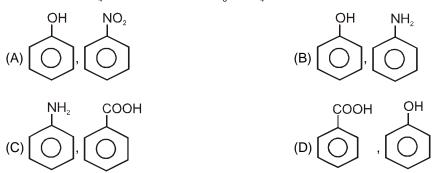
15. Which of the following is correct set of physical properties of the geometrical isomers ?

		& H С		
	Dipole moment	Boiling point	Melting point	Stability
(A)	>	>	>	>
(B)	>	>	>	>
(C)	>	>	>	>
(D)	>	>	>	>

CH

_CI

16. A mixture of organic compounds A & B when dissolve in NaOH, A is soluble and its residue B gives positive test with Zn/NH_4CI followed by AgNO₃ + NH₄OH, (mulliken's barker test). Identify A & B



17. Which is/are the correct method for separating a mixture of benzoic acid, p-methylaniline & phenol?

(A)aq. NaHCO ₃	→ aq. NaOH	(B) $\xrightarrow{aq. HCl} \xrightarrow{H_2C}$	
(C)aq NaOH	aq. NaHCO ₃	(D) $ \xrightarrow{aq. NaOH} ac$	A HCI
Anthracene is purifi (A) filtration	ed by : (B) distillation	(C) crystallisation	(D) sublimation
Which one of the fo (A) Phenol	llowing has the highest melti (B) para - Nitrophenol	ng point ? (C) meta - Nitrophenol	(D) ortho - Nitrophenol.
Which of the followi (A) Salicylaldehyde	ng molecules is most volatile		, <i>,</i> , , , , , , , , , , , , , , , , ,

(C) p-hydroxybenzoic acid

18.

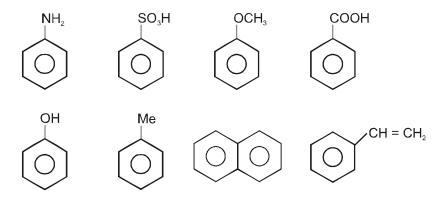
19.

20.

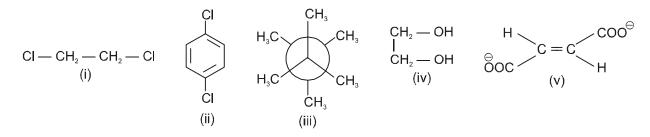
- (B) p-nitrophenol
- (D) m-hydroxybenzoic acid

PART - II : NUMERICAL TYPE QUESTIONS

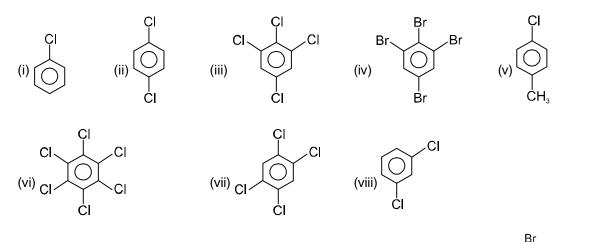
1. Amongst the following, the total number of the compounds soluble in aqueous NaOH is



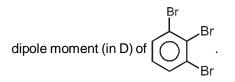
2. How many of the following compounds have zero dipole moment.



3. How many molecules of the following have non zero dipole moment :

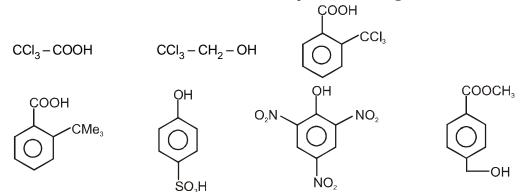


4. Considering benzene to be a planar symmetrical hexagon, if the dipole moment of () is 2D, find the



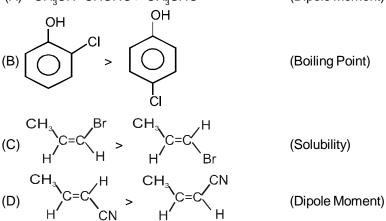
Physical properties of organic compounds & POC-II

5. How many acids (given below) react with NaHCO₃ and liberate CO_2



PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. In which of the following case/cases, is/are the order of indicated property correctly shown: (A) CH_CH=CHCHO > CH_CHO (Dipole Moment)



2. Which of the following has / have dipole moment of first compound greater than the dipole moment of second compound?

(A) NaCl and HCl (C) CH_3 -NO₂ and CH_3NH_2 (B) CFCl $_3$ and CHCl $_3$ (D) HF and BF $_3$

3. A water insoluble solid mixture of organic compounds containing p-Toluic acid, p-Toludine and naphthalene can be separated by using the sequence of reagents.

$$\begin{array}{c} (A) \xrightarrow{aq. \ NaCl} & \xrightarrow{aq. \ HCl} \\ (C) \xrightarrow{aq. \ HCl} & (B) \xrightarrow{aq. \ NaHCO_3} & \xrightarrow{aq. \ HCl} \\ (C) \xrightarrow{aq. \ HCl} & \xrightarrow{aq. \ NaHCO_3} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{aq. \ CH_3COOH} & \xrightarrow{aq. \ NH_4Cl} \\ (C) \xrightarrow{aq. \ HCl} & (D) \xrightarrow{a$$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension #1

The boiling point of a liquid is the temperature where its kinetic energy is sufficient to overcome the intermolecular attractive forces.

Boiling point depends on following :

(a) Intermolecular H-bonding.

- (b) Molecular weight attraction.
- (c) Dipole-dipole attraction.
- (d) Strength of vander Waal's forces.

Physical properties of organic compounds & POC-II

 $\begin{array}{c} {\rm CH}_2 - {\rm O} - {\rm CH}_3 \\ {\rm (C)} \begin{array}{c} | \\ {\rm CH}_2 - {\rm O} - {\rm CH}_3 \end{array} \end{array} \quad \begin{array}{c} {\rm O} - {\rm CH}_3 \\ {\rm (D)} \begin{array}{c} | \\ {\rm CH}_2 - {\rm O} - {\rm CH}_3 \end{array} \end{array}$

1. Which will have maximum boiling point?

$$\begin{array}{c} \mathsf{CH}_2-\mathsf{OH} \\ \mathsf{(A)} \mid \\ \mathsf{CH}_2-\mathsf{OH} \\ \end{array} \begin{array}{c} \mathsf{CH}_2-\mathsf{O}-\mathsf{CH}_3 \\ \mathsf{(B)} \mid \\ \mathsf{CH}_2-\mathsf{OH} \\ \end{array}$$

2. Which will have maximum boiling point?

3. Which will have maximum boiling point ? (A) CH₃-Cl (B) CH₂Cl₂

Comprehension #2

A water insoluble organic mixture contained following compounds

(C)

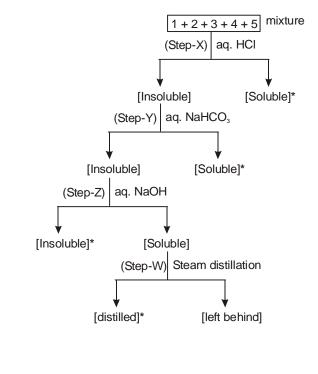
(C) CHCl₃

- (1) Benzoic acid (2) Salicylaldehyde
- (3) p-Hydroxybenzaldehyde (4) α -Naphthylamine
- The following sequence of reagents are used to separate this mixture

(D)

(D) CCl₄

(5) Naphthalene



Soluble compound at step X is formed by compound :

 (A) Benzoic acid
 (B) p-Hydroxybenzaldehyde
 (C) α-Naphthylamine
 (D) Naphthalene

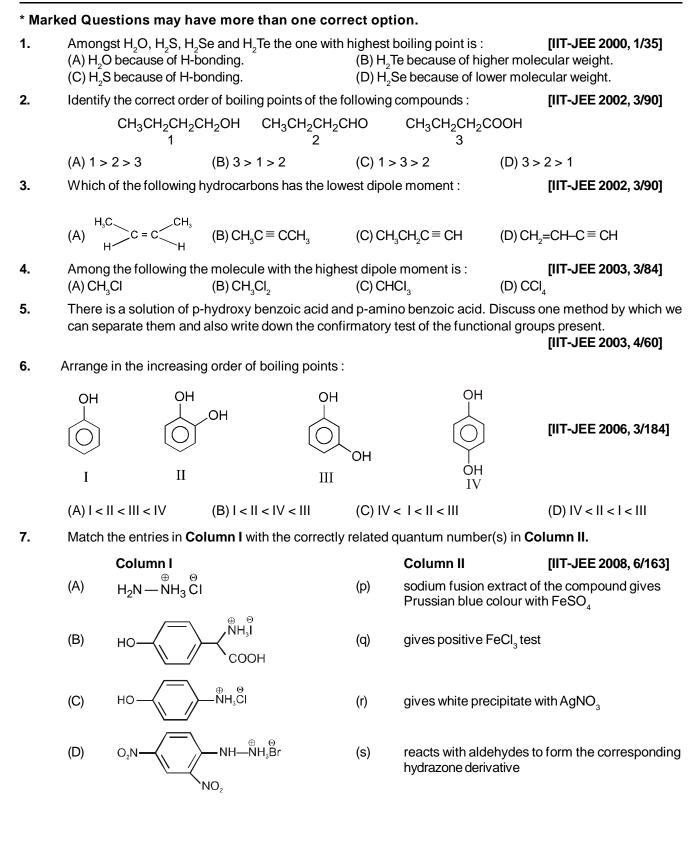
 Soluble compound at step Y is formed by compound.

- Soluble compound at step Y is formed by compound.(A) Benzoic acid(B) p-Hydroxybenzaldehyde(C) α-Naphthylamine(D) Naphthalene
- 6. Insoluble compound at step Z is formed by compound. (A) p-Hydroxybenzaldehyde (B) Salicyla
 - (C) α-Naphthylamine

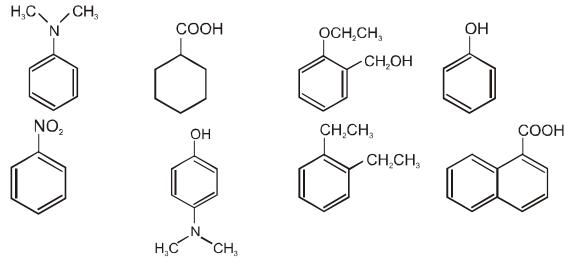
(B) Salicylaldehyde(D) Naphthalene

Exercise #3

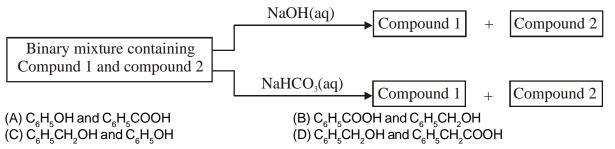
PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)



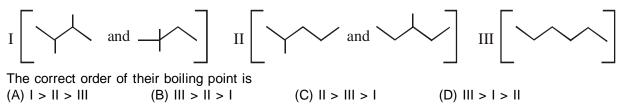
8. Amongst the following, the total number of compounds soluble in aqueous NaOH is: [IIT-JEE 2010, 3/184]



9. Identify the binary mixtures (s) that can be separated into the individual compounds, by differential extraction, as shown in the given scheme - [IIT-JEE-2012]

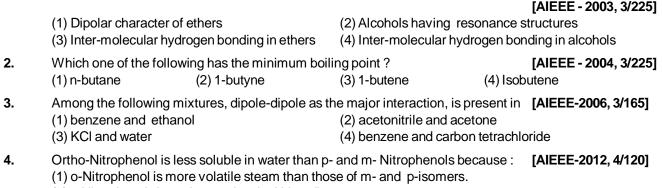


10. Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. [JEE(Advanced)-2014, 3/124]



PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

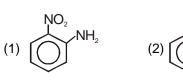
1. An ether is more volatile than an alcohol having the same molecular formula. This is due to -



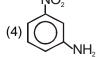
- (2) o-Nitrophenol shows Intramolecular H-bonding
- (3) o-Nitrophenol shows intermolecular H-bonding
- (4) Melting point of o-Nitrophenol is lower than those of m- and p-isomers.

Physical properties of organic compounds & POC-II

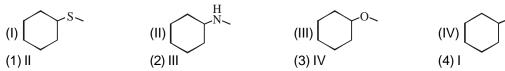
5. Which compound exhibits maximum dipole moment among the following [JEE(Main) 2015 Online(11-04-15), 4/120]



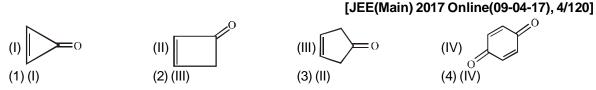




6. A mixture containing the following four compounds is extracted with 1 M HCI. The compound that goes to aqueous layer is : [JEE(Main) 2017 Online(08-04-17), 4/120]



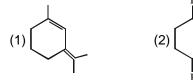
7. Which of the following compounds will show highest dipole moment ?

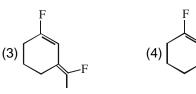


8. The increasing order of the boiling points for the following compounds is:-[JEE(Main) 2017 Online(09-04-17), 4/120]

$$\begin{array}{c} (I) C_2H_5OH \\ (I) C_2H_5CI \\ (I) (II) < (I) < (I) < (IV) \\ (I) < (IV) \\ (I) < (IV) \\ (I) < (IV) \\ (IV) \\ (IV) < (IV) \\ (IV) < (IV) \\ (IV) \\ (IV) < (IV) \\ (IV) \\ (IV) < (IV) \\ ($$

9. The most polar compound among the following is :-



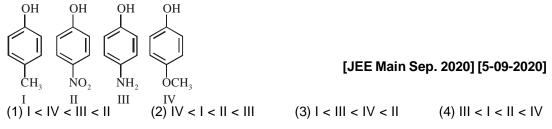


[JEE(Main) 2018 Online(16-04-18), 4/120]

- **10.** If dichloromethane (DCM) and water (H₂O) are used for differentaial extraction, which one of the following statement is correct ? [JEE(Main) 2019 Online(10-01-19), 4/120]
 - (1) DCM and H₂O will make turbid/colloidal mixture
 - (2) DCM and H₂O will be miscible clearly
 - (3) DCM and H₂O would stay as lower and upper layer respectively in the separating funnel (SF)
 - (4) DCM and H₂O would stay as upper and lower layer respectively in the separating funnel (SF)
- 11. Among the following four aromatic compounds, which one will have the lowest melting point ? [JEE(Main) 2019 Online(12-01-19), 4/120]



12. The increasing order of boiling points of the following compounds is :



ANSWER KEY

				EXER	CISE # 1				
				PA	RT - I				
A-1.	(A)	A-2.	(B)	A-3.	(C)	A-4.	(C)	A-5.	(D)
A-6.	(D)	B-1.	(C)	B-2.	(D)	B-3.	(B)	B-4.	(D)
B-5.	(D)	B-6.	(C)	C-1.	(C)	C-2.	(D)	C-3.	(D)
C-4.	(D)	C-5.	(A)	D-1.	(D)	D-2.	(C)	D-3.	(C)
D-4.	(B)	D-5.	(A)	E-1.	(B)	E-2.	(C)	E-3.	(A)
E-4.	(A)								
				PA	RT - II				
1.	(A) - r ; (B) -	• r ; (C) - p	; (D) - r	2.	(B)				
			I	EXER	CISE # 2				
				D۸	RT - I				
				FA	NT - T				
1.	(A)	2.	(A)	3.	(A)	4.	(D)	5.	(B)
6.	(C)	7.	(B)	8.	(A)	9.	(B)	10.	(D)
11.	(C)	12.	(D)	13.	(B)	14.	(B)	15.	(C)
16.	(A)	17.	(A)	18.	(D)	19.	(B)	20.	(A)
					RT - II				
	0	•						-	F
1.	3	2.	3 (ii, iii & v)	3.	5 (i, iii, iv, v, viii)	4.	4 D	5.	5
				PAF	RT - III				
1.	(AD)	2.	(ACD)	3.	(BC)				
				PAF	RT - IV				
1.	(A)	2.	(A)	3.	(D)	4.	(C)	5.	(A)
6.	(D)								

