Total No. of Questions – [4] Total No. of Printed Pages 2

G.R. No.	

Paper Code - U127-105B (T2)

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F. Y. B.TECH. (COMMON) (SEMESTER - II)

COURSE NAME : Engineering Chemistry

(2017 PATTERN)

Time : [1 Hour] [Max. Marks : 30]

solution

(*) Instructions to candidates:

1) **Answer Q.1 OR Q.2, Q.3 OR Q.4**
2) **Figures to the right indicate full marks.**
3) **Use of scientific calculator is allowed**
4) **Use suitable data where ever required**

Q.1) a) i) Define GCV and NCV

ii) A sample of coal contains: C= 92%, H = 6% and ash = 2%. The following data were obtained when above coal was tested in bomb calorimeter:

Weight of coal burnt = 0.9 gm

Weight of water taken = 546 gm

Water equivalent of bomb calorimeter = 2250 gm

Rise in temperature = 2.4 ^{0}C

Acid correction = 50 cal

Fuse wire correction = 15 cal

Calculate GCV and NCV assuming latent heat of condensation of steam as 587 cal/gm

Ans:

i) *Gross calorific value is defined as the amount of heat liberated after complete combustion of unit mass or volume of fuel and products of combustion are cooled to room temperature (15 ^{0}C).*

Net or lower calorific value is defined as the amount of heat liberated after complete combustion of unit mass or volume of fuel and products of combustion are allowed to escape.

ii)Solution:

Given: Weight of fuel = 0.9 gm

Weight of water = W = 546 gm

Water equivalent of calorimeter = ω = 2250 gm

Rise in temperature = $t_2 - t_1$= 2.4^{o}C

Acid correction = t_a = 50 cal

Fuse wire correction = t_f= 15 cal

%H = 6 %

$$\text{GCV of fuel (L)} = \frac{(W+\omega)(t_2 - t_1 + t_c) - (t_a + t_f)}{x} \text{ cal/gm or kcal/kg}$$

$$= \frac{(546 + 2250)(2.4) - (50 + 15)}{0.9}$$

$$= \frac{(2796)(2.4)-(65)}{0.9}$$

$$= 7383.78 \text{ cal/gm}$$

$$\begin{aligned} NCV &= GCV - 0.09 \times H \times 587 \text{ cal/gm} \\ &= GCV - 0.09 \times 6 \times 587 \\ &= 7383.78 - 316.98 \\ &= 7066.8 \text{ cal/gm} \end{aligned}$$

b) Define cetane number. Explain cetane number determination with example. Explain effect of chemical structure on cetane number. Explain improvement of cetane number. [

Ans: *Cetane number of diesel oil is defined as percentage of cetane (hexadecane) in the mixture of cetane and 2-methyl naphthalene which matches with the fuel under test in ignition characteristics.*

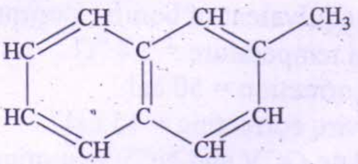
Cetane number of diesel:

- Antiknocking tendency of diesel oil is decided by cetane number. Higher the cetane number, lesser the knocking in diesel engine.
- **Cetane ($C_{16}H_{34}$) or hexadecane** have very less ignition delay hence have very low knocking tendency. Therefore it is considered to have cetane number **100**.

$$CH_3-(CH_2)_{14}-CH_3$$

Cetane

- **2-methyl naphthalene** have very high ignition delay hence have very high knocking tendency. Therefore its cetane number is considered to be **0**.



2-Methyl naphthalene

- By mixing cetane and 2- methyl naphthalene in various proportions, primary reference fuels are prepared which will have cetane numbers from 0 to 100.
- Primary reference fuels are burnt in standard diesel engine. Diesel under test is also burnt in the same diesel engine. Its ignition characteristics (knocking tendency) are matched with that of primary reference fuels of known cetane number.

For e.g. if a sample diesel oil gives same ignition characterestics in standard diesel engine as that of a mixture of 35% cetane and 65% 2-methyl naphthalene, then cetane number of diesel under test is considered to be 35.

Chemical structure and cetane number:

The relation of chemical structure of hydrocarbon and cetane number can be given as follows: Straight chain alkanes>cycloalkanes>alkenes/olefins>branched chain alkanes>aromatics.

Improvement in cetane number:

Cetane number in diesel can be improved by addition of small quantity of pre-ignition dopes like ethyl nitrite, ethyl nitrate, isoamyl nitrate, acetone peroxide etc.

c) Analysis of a fuel gave C=85%, H = 3%, O = 1.5%, S = 0.5%, H_2O = 0.2%, N= 0.6% and remaining ash. Calculate minimum weight of air required for complete combustion of 1 kg of fuel. [

Solution: For 1 kg of fuel, C = 0.85 kg, H = 0.03 kg, O = 0.015 kg, S = 0.005 kg

Constituents which take part in the combustion can be considered for calculation of oxygen

Sr. No.	Combustion reaction	Volume of O_2 required
1	$C + \frac{1}{2}O_2 \rightarrow CO_2$ 12kg 32 kg	$0.85 \times \frac{32}{12} = 2.267$
2	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ 2 kg 16 kg	$0.03 \times \frac{16}{2} = 0.24$
3	$S + O_2 \rightarrow SO_2$ 32 kg 32 kg	$0.005 \times \frac{32}{32} = 0.005$
		Theoretical amount of oxygen required = 2.512

O_2 required = Theoretical O_2 - O_2present in fuel
= 2.512 – 0.015
= 2.497

$$\text{Quantity of air} = \frac{\text{Oxygen quantity in kg}}{23} \times 100 \text{ kg}$$

$$= \frac{2.497}{23} \times 100$$

= 10.856 kg

OR

Q.2) a) Give 6 difficulties in storage and transportation of hydrogen

Solution:

Following difficulties are observed for the storage and transportation of hydrogen:

i)H_2 is colourless, odourless, lighter than air. Its leakage is difficult to detect.

ii)H_2 forms explosive mixture with atmospheric oxygen.

iii)Its ignition temperature is low hence highly flammable. Thus H_2 is riskey for storage and transportation.

iv) H_2 can be stored in compressed form. Large energy is required to compress H_2. Compressed H_2 satisfying driving range require large tank which add to weight.

v)H_2 can be stored in liquefied form at cryogenic temperature. Large energy is required to liquefy H_2. Insulation of tank to prevent losses adds to cost.

vi)H_2 can be stored in the form of metal hydride which require higher temperature to release H_2.

b) Define power alcohol. Give 3 advantages and 3 disadvantages of power alcohol.

When ***ethyl alcohol is blended with petrol (about 20-25%)*** *and is used as a fuel for internal combustion engine , it is called as power alcohol.*

1) Advantages of power alcohol: (any 3)

i)Alcohol has higher octane number (about 90) as compared to petrol with octane number about 60 -70. Addition of alcohol to petrol thus improves octane number.

ii)Alcohol burns clean, hence when blended with petrol, reduces fuel emission.

iii) Alcohol acts as a solvent. It helps in reducing gummy depositions and carbon deposits on the internal parts of engine.

iv) Alcohol acts as a coolant. It reduce chances of overheating of engine.

v)Alcohol is a renewable source of energy. It reduces dependency on foreign countries for petrol

vi)Alcohol is capable of absorbing moisture, hence it removes traces of moisture present in petrol.

2) **Disadvantages of power alcohol: (any 3)**

i)Alcohol lowers calorific value of petrol because calorific value of alcohol is only two third as that of petrol.

ii)Alcohol may get easily oxidized to acetic acid which may cause corrosion of various engine parts.

iii)Alcohol has high surface tension, hence it is difficult to atomise, particularly at low temperature causing starting trouble.

iv)Alcohol has oxygen atom, hence air required for combustion is less than petrol. Modification of engine for air inlet is thus required.

c) Volumetric analysis of producer gas used as a fuel is as, H_2 = 20%, CO = 18%, N_2 =50%, CH_4 = 2%, CO_2 = 10%. If 25% excess air is used, find the volume of air actually supplied per m^3 of the gas. [

Solution:

For 1 m^3 of gaseous fuel, CO = 0.18 m^3, CH_4= 0.02 m^3, H_2 = 0.20 m^3 and N_2 = 0.50 m^3

Gases which take part in combustion are to be considered for calculation of oxygen.

Sr. No.	Combustion reaction	Volume of O_2 required
1	$CO + \frac{1}{2}O_2 \rightarrow CO_2$ 1 vol ½ vol	0.18 x ½ = 0.09
2	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ 1 vol 2 vol	0.02 x 2 = 0.04
3	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ 1 vol ½ vol	0.2 x ½ = 0.1
		Total volume of oxygen required = 0.23

$$\text{Volume of air} = \frac{\text{Volume of oxygen in } m^3}{21} \times 100\ m^3$$

$$= \frac{0.23}{21} \times 100\ m^3$$

$$= 1.095\ m^3$$

As 25 % excess air is supplied,

$$\text{Quantity of air actually supplied} = \text{Theoretical air} \times \frac{(100 + \%\ \text{excess air})}{100}$$

$$= 1.095 \times \frac{(100+25)}{100}$$

$$= 1.369\ m^3$$

Q.3) a) Define crystallinity of polymers. Explain any five factors affecting on it. [

Ans:

Crystalliny of the polymer is the extent to which molecules of a polymer are arranged in orderly pattern with respect to each other.

Factors affecting: (any 5)

1) Branching of polymer chain:

Branched polymers are more difficult to crystalline than linear polymer. Linear polyethylene (High density polyethylene – HDPE) has crystallinity 90%, whereas branched polyethylene (Low density polyethylene- LDPE) has 40%. Linear polymer will have high cystallinity, because the atoms along the chain permit closer approach. Branching imparts irregularity to the molecular structure and reduces the ability of the molecule to get themselves packed closely.

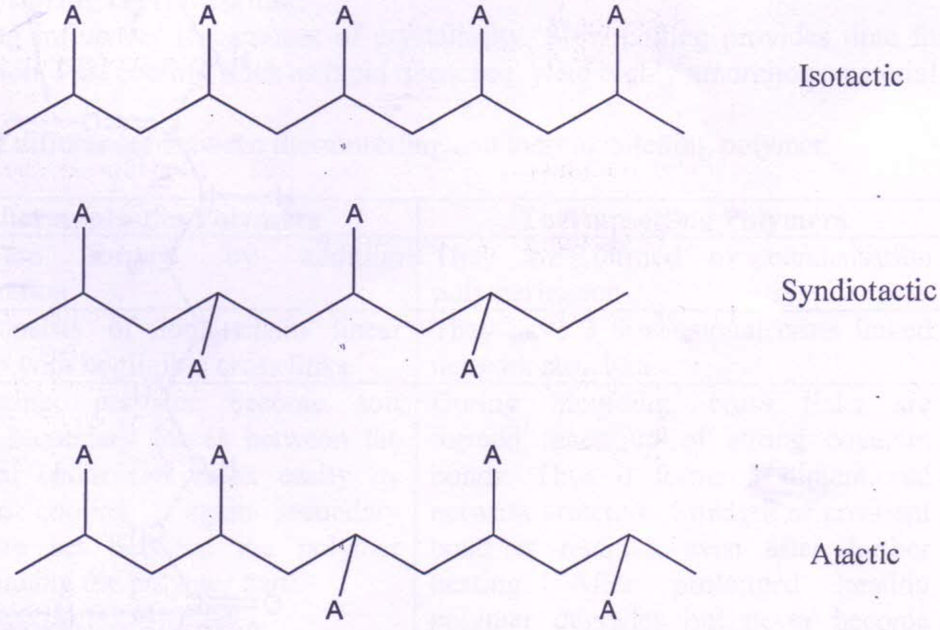
2) Tacticity (Stereo isomerism) : Tacticity gives the orientation of monomeric units in polymer chain.

When all functional groups (side groups) are on the same side of the chain, it is called isotactic polymer.

When the arrangement of functional groups (side groups) is in alternating fashion, it is called syndiotactic polymer.

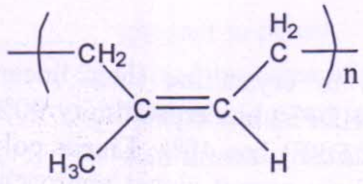
When the arrangement of functional groups (side groups) are at random around the main chain, it is called atactic polymer.

Tactacity

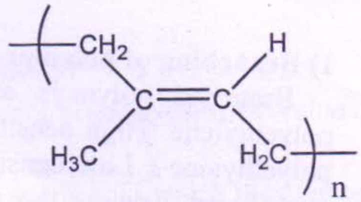


Isotactic and syndiotactic polymers crystallize relatively easily as geometrical regularity allows chain to fit together. Atactic polymers are difficult to crystallize therefore are amorphous. For e.g. : Isotactic and syndiotactic polystyrene are more crystalline whereas atactic polystyrene, in which the substituents are arranged in random manner are less crystalline (amorphous)

3) Cis and trans isomers (Geometric isomers): A good example to illustrate effect of geometry on crystallinity is natural rubber and Gutta- Purcha. Both are polyisoprens. Natural rubber is cis- polyisoprene and Gutta-Purcha is trans polyisoprene.



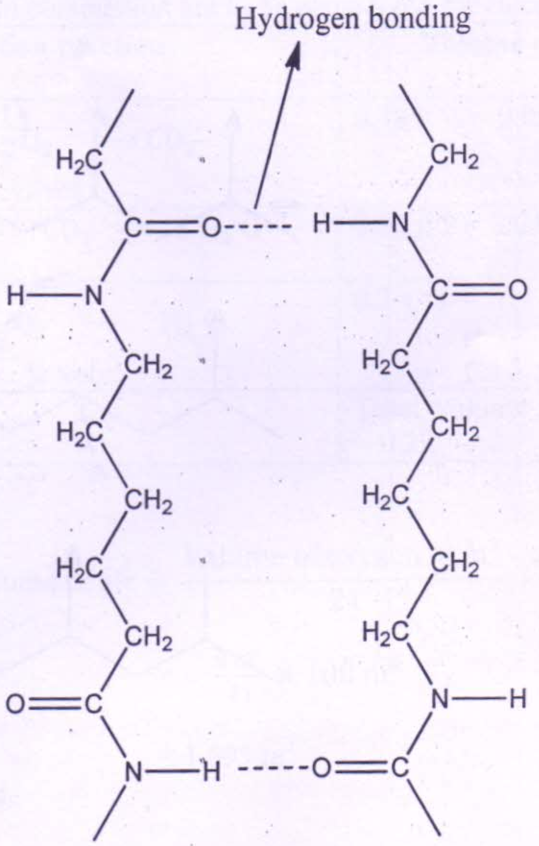
Cis- 1,4 polysisoprene
Natural rebber (Less crystaline)



Trans- 1,4 polysisoprene
Gutta Purcha (More crystaline)

Natural rubber is coiled structure whereas Gutta-Purcha give a rod like structure to the molecule. A rod like structure enables Gutta-Purcha molecules to orient themselves in an orderly manner and pack up closely therefore Gutta-Purcha is more crystalline.

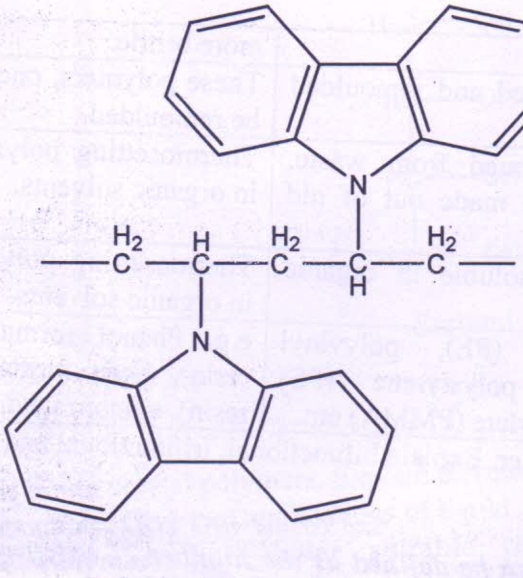
4) Intermolecular forces : High crystallinity in Nylon 6 attributes to its polarity. Polar groups in the molecule leads to the formation of hydrogen bonds between the adjacent chains. This increases interchain/ intermolecular forces of attraction and facilitates tighter packing and perfect bonding of the chain elements with each other increasing crystallinity.



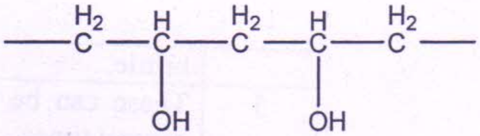
Hydrogen bonding in Nylon 6

5) Bulky side groups: If the side groups are bulky, polymer finds it difficult to crystallize because bulky side groups come in the way of closer molecular packing. For e.g. Polyvinyl carbazole is amorphous.

If the side groups are relatively small, for e.g. Polyvinyl alcohol, polymer can easily crystallize.



Polyvinyl carbazole
(bulky side groups)



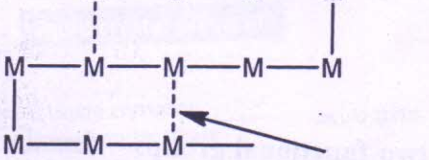
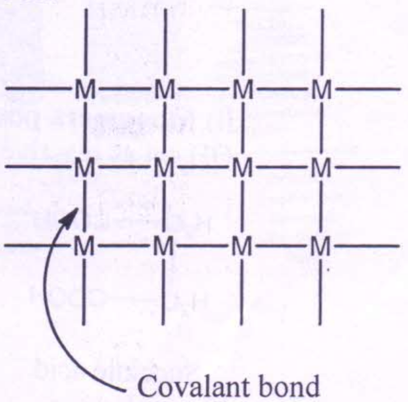
Polyvinyl alcohol
(smaller side groups)

6) Rate of cooling during crystallization:

The rate of cooling influences the amount of crystallinity. Slow colling provides time for greater crystallization. Fast cooling, such as rapid quenches, yield highly amorphous material.

b) Give four points of differences between thermosetting and thermosoftening polymer.

Ans: (any 4)

Sr.No.	Thermoplastics Polymers	Thermosetting Polymers
1	They are formed by addition polmerization	They are formed by condensation polymerization
2	They consists of long chain linear polymers with negligible cross links.	They have 3 dimensional cross linked network structure.
3	On heating, polymer become soft because secondary forces between the individual chain can break easily by heat. On cooling , again secondary bonds are set between the polymer chains making the polymer hard.  ('M' represent monomer)	During moulding, cross links are formed made up of strong covalent bonds. Thus it forms 3 dimentional network structure. Strength of covalent bond is retained even after further heating. After prolonged heating polymer degrades but never become soft.  'M' represents monomer
4	These polymers are soft, weak and less	These polymers are hard, strong and

	brittle.	more brittle.
5	These can be moulded and remoulded several times.	These polymers, once moulded, cannot be remoulded.
6	They can be reclaimed from waste. (New article can be made out of old one).	Thermosetting polymers are insoluble in organic solvents.
7	Thermoplastic are soluble in organic solvents.	Thermosetting polymers are insoluble in organic solvents.
8	e.g. Polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) polymethyl methacrylate (PMMA) etc.	e.g. Phenol formaldehyde resin (PF resin), Urea formaldehyde resin (UF resin), silicones etc.

c) Define functionality of monomer. Explain bifunctional, trifunctional and tetrafunctional monomers with examples.

Ans:

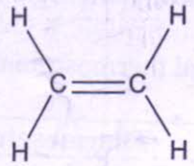
Functionality of monomer can be defined as the number of reactive sites/ bonding sites/ functional groups present in the molecule.

Bifunctional monomers:

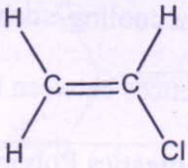
When monomer possesses two reactive sites, then it is known as bifunctional monomer.

For e.g.

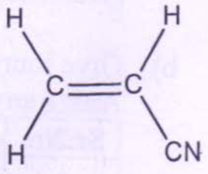
i) **Monomers possessing double bond in the structure** (vinyl monomers) – opening of one of the double bond will give two reactive sites.



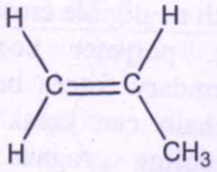
Ethylene



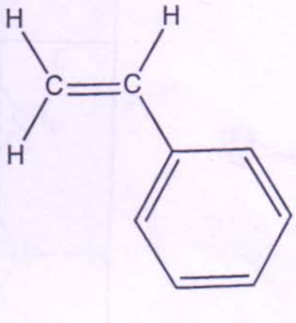
Vinyl chloride



Acrylonitrile

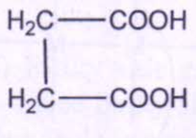


Propylene



Styrene

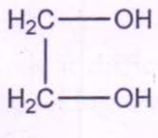
ii) **Monomers possessing two functional groups** – functional groups like –NH2, -COOH, -OH act as reactive sites.



Succinic acid

$HOOC-(CH_2)_4-COOH$

Adipic acid



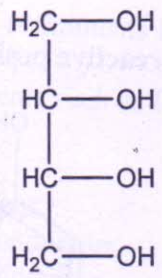
Ethylene glycol

$NH_2-(CH_2)_6-NH_2$

Hexamethylene diamine

Trifunctional monomers:

When monomer possesses three reactive sites, then it is known as trifunctional monomer.



Sorbitol

OR

Q.4) a) Define liquid crystal polymers. Explain thermotropic and lyotropic liquid crystal polymers with example. Give two applications of liquid crystal polymers. [

A polymer that under suitable conditions of temperature, pressure and concentration, exist as liquid crystal is known as liquid crystal polymer.

There are two types of liquid crystal polymers –

1) Thermotropic liquid crystal polymers:

The polymers which have tendency to align their polymer chains (mesogens) over a large distance before their crystallization from the melt, is called as thermotropic liquid crystal polymers. For e.g. : Vectra, Victex, Xyder etc.

2) Lyotropic liquid crystal polymers:

The polymer which have tendency to align their polymer chains (mesogens) over a long distance before their crystallization from the solution is called as lyotropic liquid crystal polymers. For e.g. Kevlar

There are three states or structural forms of liquid crystal structure. Based on that, they are further classified as,

i) Smectic liquid crystal polymers:

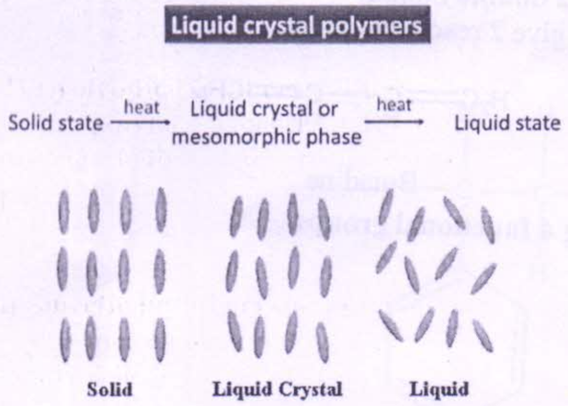
Polymer chains (mesogens) maintain orientational order, but also tend to align themselves in layers i.e. mesogens are arranged in parallel and lateral order.

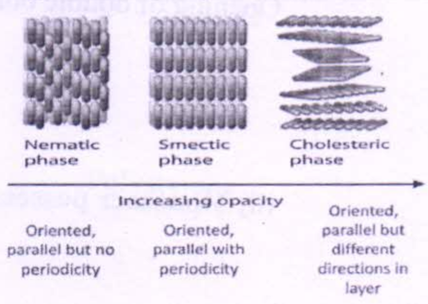
ii) Nematic liquid crystal polymers:

The polymer chains (mesogens) are arranged in parallel order but not in lateral order.

iii) Cholesteric liquid crystal polymers:

This is a modified nematic phase. In this, mesogens are oriented parallel to one anothers (just like nematic phase) but the directions vary from one layer to another.



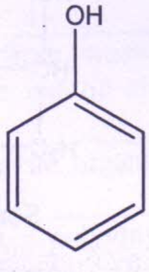


Applications: (any 2)

Liquid crystal polymers find uses

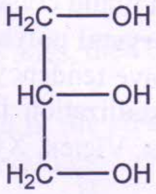
For eg.

i) **Monomer possessing 3 reactive positions-**



Phenol

ii) **Monomers possessing 3 functional groups-**



$$\begin{array}{l} H_2C-OH \\ HC-OH \\ H_2C-OH \end{array}$$

Glycerol

Tetrafunctional monomers:

When monomer possesses four reactive sites, then it is known as Tetrafunctional monomer.

For eg.

i) **Monomer possessing triple bond-**

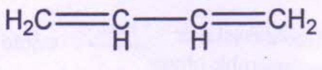
Opening of one bond gives 2 reactive sites, opening of another bond gives 2 more reactive sites.

$HC\equiv CH$

Acytylene

ii) **Monomer possessing 2 double bonds-**

Opening of double bonds give 2 reaction sites each.



$$H_2C=\underset{H}{C}-\underset{H}{C}=CH_2$$

Butadine

iii) **Monomer possessing 4 functional groups-**

1) In electronic and electrical equipments like flat panel displays, switches, computer memory modules etc.
2) In optoelectronics components such as Fibre optic cables.
3) In data storage discs.
4) In chemical appliances.
5) In encapsulation of IC devices.
6) In housing for light wave conductors.
7) In variety of aerospace applications.
8) As filler for composite material.
9) In military communications.

b) Define glass transition temperature. Discuss the effect of side groups, intermolecular forces and molecular weight on Tg of polymer.

Ans:

The temperature below which a polymer is hard, brittle, glassy and above which it is soft, flexible and rubbery is called 'glass transition temperature' (Tg)

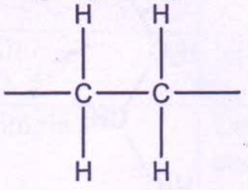
Factors affecting glass transition temperature (Tg) –

Tg of polymer depends on size, chain geometry, chain flexibility and type of molecular aggregates formed.

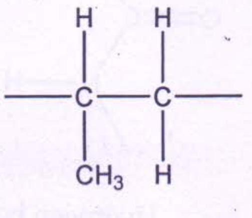
1) Presence of bulky side groups –

Bulky groups increases the Tg of polymer.

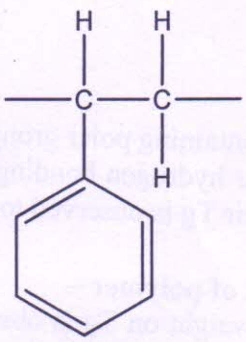
Higher the freedom to rotate, more is flexibility to chain segments, lower is Tg. Presence of aromatic or bulky side groups on backbone chain hinders the freedom for rotation, reducing flexibility, exhibiting higher Tg.



Polyethylene



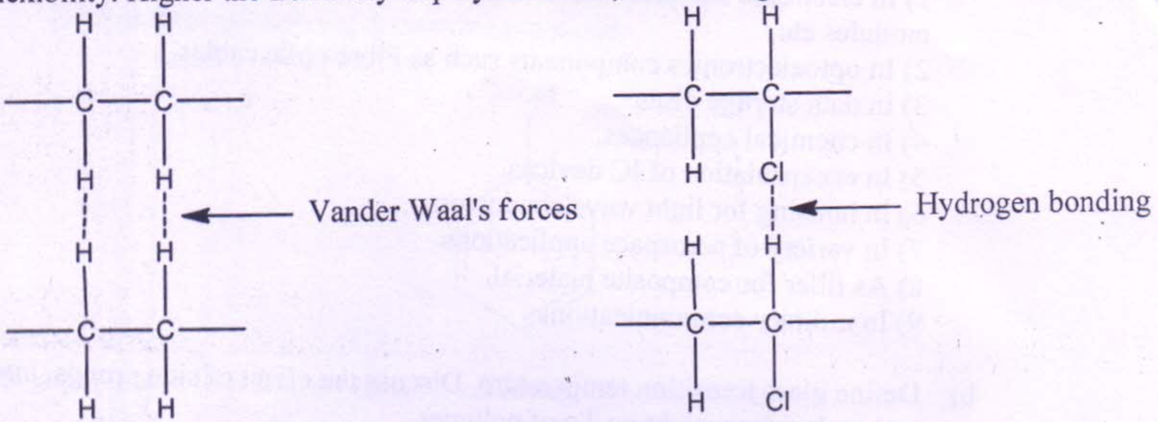
Polypropylene

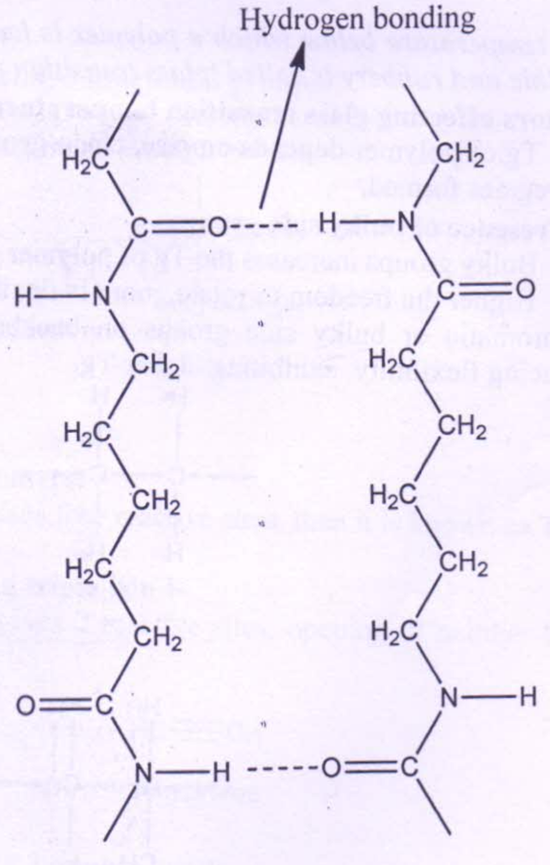


Polystyrene

2) Intermolecular forces –

In case of polyethylene, only Vander Waal's forces act on neighbouring chains, hence molecular aggregates are not strong. Chain can easily slip one over the other showing higher flexibility. Higher the flexibility of polymer chain, lower is Tg.





Hydrogen bonding in Nylon 6

Polymer chain containing polar groups are held more strongly by neighbouring dipoles as well as intermolecular hydrogen bonding and are unable to move easily. As the flexibility of the chain reduces, their Tg is observed to be higher.

3) Molecular weight of polymer –

Effect of molecular weight on Tg is observed for the values of average molecular weight up to 20000. Lower molecular weight polymer show lower Tg. Wher as higher molecular weight polymer show high Tg.

c) Compare suspension polymerization and emulsion polymerization techniques

Ans: (any 4)

Sr.No.		Suspension Polymerization	Emulsion Polymerization
1	Medium	Water and a stabilliser	Water and emulsifying agent
2	Catalyst/ Initiator	Should be soluble in monomer	Should be water soluble.
3	Dissipation of Heat and Temperature Control.	Rapid heat dissipation because of water medium. Less temperature control is required.	Rapid heat dissipation because of water medium. Less temperature control is required.
4	Purity of polymer	Less pure	Less pure
5	Molecular weight of polymer	Low	Low
6	Safely hazards	Nil	Nil
7	Separation from medium and drying	Simple	Coagulation and after processing is required