

Solutions

**CMR
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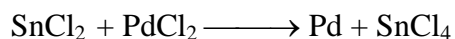
Sub:	Engineering Chemistry			Code:	15CHE22				
Date:	09/05/2017	Duration:	90 mins	Marks:	50	Sem:	II	Branch:	All

Internal Assessment Test II – May 2017

1. (a) Explain electroless plating of copper on PCB with relevant reactions . (06 Marks) (CO3, L3)

Solution: Deposition of metal or alloy over a conducting or non-conducting substrate surface by **chemical reduction of the metal ions by use of reducing reagent** and without the use of electrical energy is called electroless-plating.

Treatment with SnCl₂ leaves a thin layer of SnCl₂ and later treatment with acidified PdCl₂ leads to deposition of Pd.

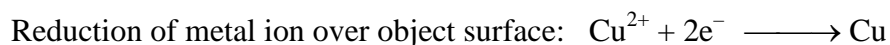
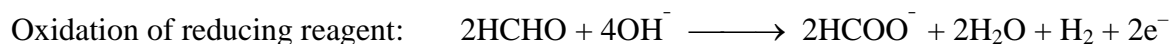


Electroless-plating of Copper:

Substrate surface needs to be cleaned by suitable cleansing methods (solvent degreasing, acid pickling, alkali pickling, mechanical polishing, etc.). However, when the object is non-conducting or insulator material such as, plastics, PCBs, glass, etc. it needs to be activated by treatment with acidified SnCl₂ and then with acidified PdCl₂. Following bath compositions are used for plating.

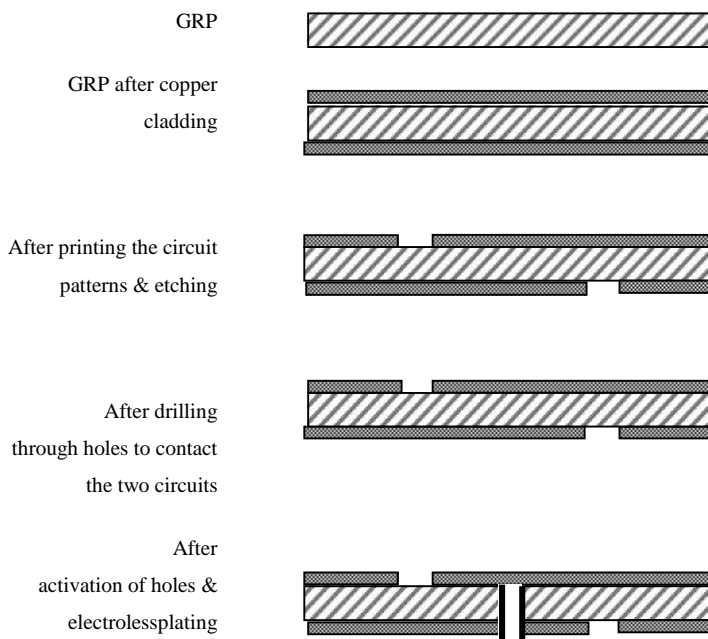
Constituents	Amount	Purpose
CuSO ₄	12 g/L	Provides metal ions
H-CHO	8 g/L	Reducing reagent
Rochelle salt	14 g/L	Complexing agent
NaOH	15 g/L	Provides alkaline medium
EDTA	20 g/L	Exaltant & complexing agent
pH	11.0	
Temperature	25°C	

Reactions:





- A coating of copper on both sides a glass reinforced plastic (GRP) sheet/board is accomplished by cladding two thin foils of copper.
- Necessary circuits will be drawn (or printed) on either sides using etch-resistant ink. The board is etched in acidified solution of FeCl_3 . Only the circuit parts will be left and rest other copper is etched away.
- Holes are drilled wherever, contact between the two circuits is necessary.
- Hole surfaces are activated by treatment with acidified SnCl_2 and then with acidified PdCl_2 . Electroless plating of copper is carried out in a suitable bath as mentioned above to establish the contact between two circuits through the holes.



(b) What is reformation of petrol? Describe catalytic reformation with reactions. (04 Marks) (CO4, L1,L2)

Solution: "Reforming of petrol (or gasoline) is defined as the process of increasing the octane number of petrol by structural modifications or molecular rearrangements of hydrocarbons". Structural modifications refer to linear hydrocarbons being converted into more compact branched hydrocarbons or into cyclic hydrocarbons or into alkenes or into aromatics.

Process conditions-

Feed stock: Virgin gasoline

Catalyst: Pt supported on alumina or silica base

Temperature: 475-525C

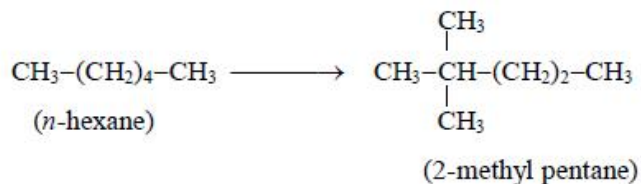
Pressure: 15-50 atm.

Description- Feed stock vapour, free from sulphur and nitrogen content (which otherwise would poison the catalyst) is mixed with hydrogen, preheated, compressed and passed over catalyst in a series of reformers and the products are fractionated to get **stabilised gasoline**. Reforming reactions

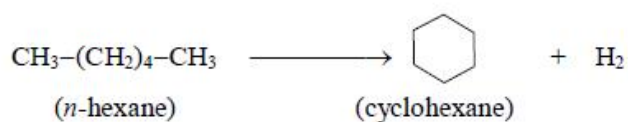
are as follows:

Reforming reactions:

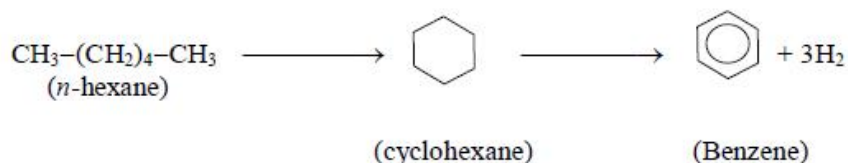
(i) Isomerization: Conversion of straight hydrocarbon into branched chain hydrocarbon.



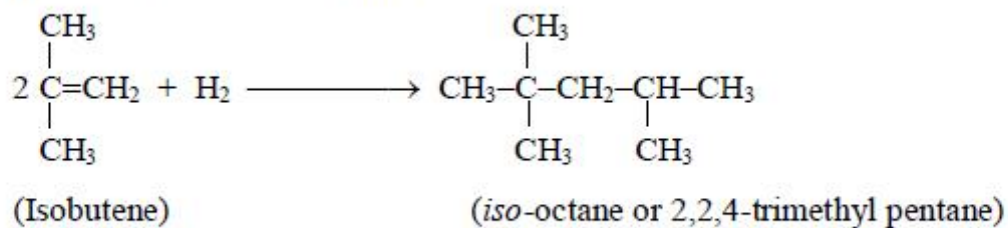
(ii) Cyclization: Conversion of straight chain hydrocarbon into cyclic compounds.



(iii) Cyclization and dehydrogenation: Conversion of straight chain hydrocarbon into aromatic compounds.



(iv) Polymerization & hydrogenation:



2. (a) Explain the process of electroplating of chromium for engineering applications. Indicate the reason for not employing chromium as anode. (05 Marks) (CO3, L3)

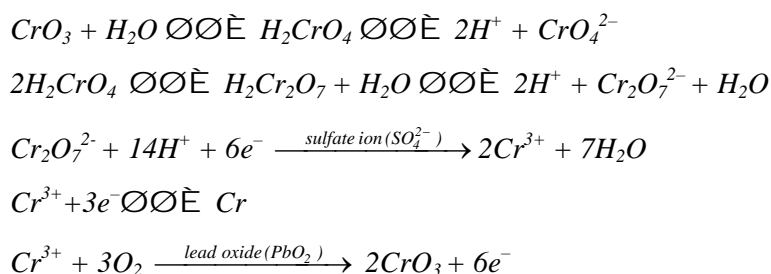
Solution: Electroplating of Chromium:

Chromium is employed for either decorative purposes (as a thinner coat) or engineering purposes (as a thicker hard coat). Mentioned below are coating specifications.

Bath composition	CrO ₃ (chromic acid) : H ₂ SO ₄ = 100: 1 ratio
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Temperature	45 – 60 °C
Current density	100 – 200 mA/cm ²
Current efficiency	17 – 21 %
Anode material	Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating)
Cathode material	Surface cleaned object metal
Reaction at anode	$\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
Reaction at cathode	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$

- Active chromium anode is not used because, the anode efficiency is nearly 100% and that of the cathode is only around 20% at the best. There will be increase in concentration of Cr^{3+} ions which results in poor quality electrodeposits (black deposits).
- A thin coating of chromium is porous and thicker coating leads to cracking. Therefore, Cr-plating over steel is applied with an undercoat of copper and nickel. Copper is known to offer better finishing. Coverage of nickel and hence chromium is better with copper below. Also, lower thickness of nickel can be opted with an undercoat of copper. Chromium gives decorative & pleasing finish, nickel offers corrosion resistance and copper extends good coverage and better adhesion.
- There is a complex sequence of reactions which control the concentration of Cr^{3+} in the plating bath. Sulfate ion is said to catalyse the conversion of Cr^{6+} into Cr^{3+} and PbO_2 catalyses the conversion of Cr^{3+} into Cr^{6+} .



Chromium plating is a hard, attractive coating, with low coefficient of friction exhibiting wear resistance, abrasion resistance and also good corrosion resistance (with an undercoat of nickel and copper)

(b) Define cracking. Describe fluidized bed catalytic cracking. (05 Marks) (CO4,L1,L2)

Solution: Cracking is defined as the process of breaking of less useful, higher molecular weight hydrocarbons into more useful lower molecular weight hydrocarbons like kerosene, petrol etc. It involves rupture of C-C & C-H bond and produces low boiling alkanes & alkenes.



Fluidised bed catalytic cracking:

Process conditions:

Feed stock: light gas oil or heavy gas oil

Catalyst: Y-type of zeolite activated with rare earth oxide + ZSM-5 type of zeolite (to increase O.N.) into a matrix of aluminium silicate

Temperature: 500-550°C

Pressure: slightly above ambient pressure

Description:

- Oil preheated to about 300 °C is sprayed into the reactor through riser column.
- The reactor contains the finely powdered catalyst at 700°C.
- Cracking takes place in fluidized state with a contact time of 3 seconds.
- Temperature in the reactor falls to about 530 °C.
- Cracked hydrocarbons are removed from top, condensed and fractionated to get gasoline. Heavy residues are taken for second stage cracking to improve the cracking efficiency.
- After some time due to accumulation of oil and deposition of carbon, catalyst gets inactivated.
- Thus it is sent to oil stripper where, oil is removed using a blast of steam.
- Then, it is sent into regeneration chamber to remove C. Carbon is burnt off in presence of hot air and flue gases escape from a vent.
- Regenerated catalyst is mixed with fresh feed stock and returned to cracking chamber.

Advantages of fluidized bed catalytic cracking:

- The process is continuous unlike fixed bed cracking. Catalyst usage and regeneration are separate and simultaneous.
- Cracking efficiency is higher because, **feed in the vapor form and catalyst in the fluid form come in good contact with each-other.** Thermal cracking efficiency is lesser.
- Octane rating of fuel is higher (80-85) than in thermal cracking (66-68).

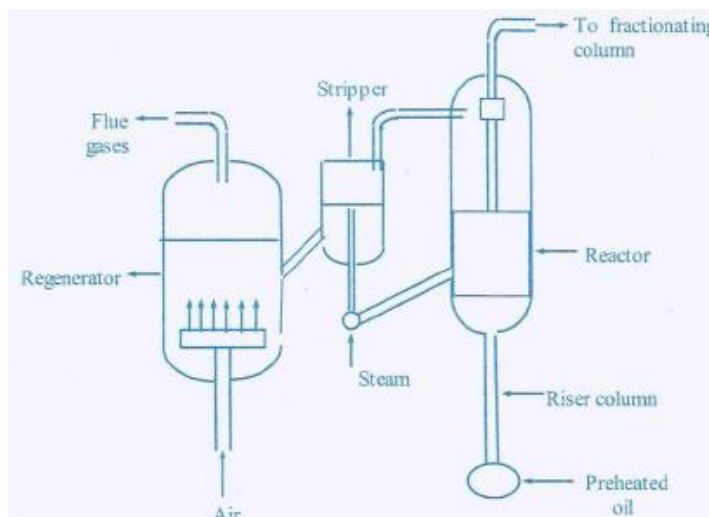


Fig. Fluidized bed catalytic cracking

3. (a) A 0.6g of coal sample (carbon 90%, H₂ 3% and ash 7%) was subjected to combustion in a bomb calorimeter. Mass of water taken in the calorimeter was 2000g and the water equivalent of calorimeter was 400g. The rise in temperature was 3°C. Calculate the gross and net calorific value of the sample. Given specific heat of water is 4.187kJ/kg/°C and latent heat of steam is 2545kJ/kg. (06 Marks) (CO4, L3)

Solution: Given

$$\begin{aligned}
 m &= 0.6 \times 10^{-3} \text{ kg} \\
 W_1 &= 2000 \times 10^{-3} \text{ kg} = 2 \text{ kg} \\
 W_2 &= 400 \times 10^{-3} \text{ kg} = 0.4 \text{ kg} \\
 (T_2 - T_1) &= 3^\circ\text{C} \\
 \%H &= 3 \\
 s &= 4.187 \text{ kJ kg}^{-1} \text{ }^\circ\text{C}^{-1} \\
 L_q &= 2457 \text{ kJ/kg}
 \end{aligned}$$

$$\begin{aligned}
 GCV &= \frac{(W_1 + W_2)(T_2 - T_1) s}{m} \text{ kJ kg}^{-1} \\
 &= \frac{(2 + 0.4)(3) 4.187}{0.0006} \\
 &= 50244 \text{ kJ kg}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 NCV &= GCV - 0.09 \times \%H \times L_v \text{ kJ kg}^{-1} \\
 &= 50244 - 0.09 \times 3 \times 2457 \\
 &= 50244 - 663.39 \\
 &= 49580.61 \text{ kJ kg}^{-1}
 \end{aligned}$$

(b) Explain the influence of the following factors on the nature of electrodeposit (a) Current density (b) pH of the medium. (04 Marks) (CO3, L3)

Solution: (a) Current density: Current density is the current per unit area expressed as A cm^{-2} (or mA cm^{-2} or A m^{-2} or A ft^{-2}). Rise in current density, increases electrodepositon rate till a limiting value. At low current densities, surface diffusion is faster compared to electron transfer to metal ions resulting in coarse-grained deposits (fewer nuclei are formed). When current density is increased, opposite phenomena is observed and leads to fine grained deposits (with more of nuclei). However, at very high current densities, bad deposits with rough and powdery texture (or burnt deposits) are formed, which are poorly adherent to object surface. Fast depletion of metal ions may represent hydrogen evolution and presence of oppositely charged hydroxide ions, result in deposition of hydroxides or oxides of the metal. Therefore, optimum current densities are employed.

(b) pH of the medium: Generally, higher pH leads to precipitation of metal hydroxides / carbonates and lower pH leads to H₂ liberation and burnt deposits. Generally, moderate pH of 4 to 8 is preferred. Buffers are used to maintain the required pH, e.g., borate buffer is used for maintaining pH = 4.0 – 4.5 in

Ni-plating, citrate buffer is used in Au-plating, etc. However, cyanide baths employ relatively higher pH = 9 – 13 without precipitation of metal. Metal is kept in the dissolved state in such plating solution by getting it complexed with complexing reagents. Variation of pH beyond the predetermined ranges is known to give poor quality deposits.

4. (a) Explain the synthesis of petrol by Fischer Tropsch process. (05 Marks) (CO4, L3)

Solution:

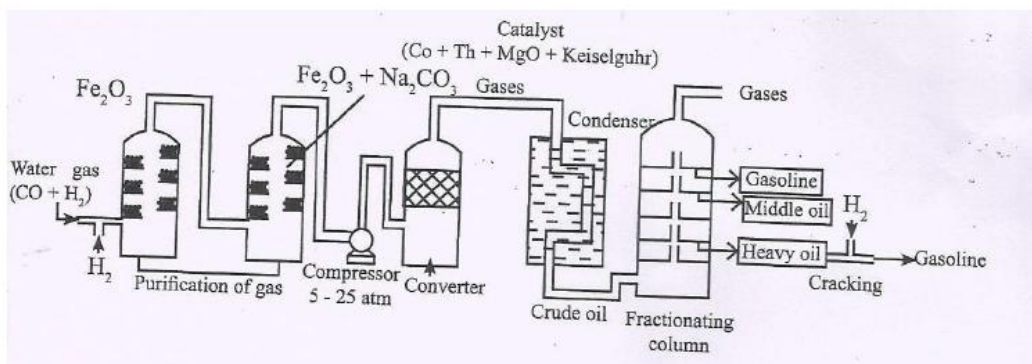
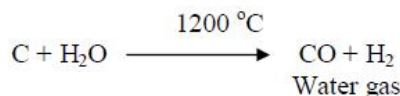


Fig. Synthesis of petrol by Fischer-Tropsch process

- Synthetic petrol refers to a laboratory manufactured petroleum substitute (Prepared from nonpetroleum resources).
- This process is a catalysed chemical reaction in which coke is converted into hydrocarbon.
- Water gas is produced by passing steam over red hot coke.



- Water gas is mixed with H₂ to get synthetic gas.

$$\text{CO} + \text{H}_2 + \text{H}_2 \longrightarrow \text{CO} + 2\text{H}_2$$

Synthetic gas
- The gas is purified by passing through Fe₂O₃ (to remove H₂S) and then into a mix of Fe₂O₃, Na₂CO₃ (to remove organic s compounds).
- The purified gas is compressed to 5 – 25 atm and then led through a converter which is maintained at 200 – 300 °C and contain mixture of 100 parts Co, 5 parts Thoria, 8 parts magnesia and 200 parts Keiselguhar earth.

• The Reactions are-



- The outgoing gaseous mixture is led to a condenser or cooler where the liquid crude oil is obtained.
- The crude oil is fractionated to yield gasoline and heavy oil.
- The heavy oil is used for cracking to get more gasoline.

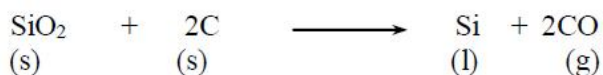
(b) Explain the production of solar grade silicon by Union carbide process. (05 Marks) (CO1, L3)

Solution:

Preparation of Solar grade Si is essential for use in PV cells. Solar grade Si has high purity (99.9999%) after several steps of refinement. The several steps involved are:

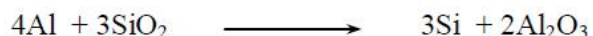
I. Preparation of Metallurgical Grade Silicon from Naturally Occurring Quartz:

A mixture of quartz (SiO_2) and carbon (from coke or coal) is struck by electric arc in a furnace using carbon electrodes.



CO is oxidized to CO_2 and escapes into the atmosphere.

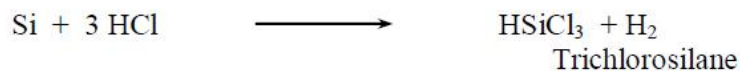
Silicon is obtained in the molten state and is contaminated with aluminium, calcium and magnesium. The impurities could be removed as slag by the addition of silica. Following reactions take place there.



The oxides of aluminium, calcium and magnesium combine with additional silica to form the corresponding silicates and are removed as slag. The silicon left behind is called *metallurgical grade silicon* (98.5 %).

II. Synthesis of Silane (Silicon Hydride- SiH_4) from Silicon:

Metallurgical grade silicon is heated to $300\text{-}350^\circ\text{C}$ and dry hydrogen chloride is passed. Trichlorosilane and a small amount of tetrachlorosilane are formed as given below



The compounds can be separated by simple distillation. Then, tetrachlorosilane is converted to trichlorosilane by treating with hydrogen at 1000°C in a reactor.



Trichlorosilane is passed through ion exchange resin containing quaternary ammonium salts to give dichlorosilane and tetrachlorosilane. Dichlorosilane subsequently forms trichlorosilane and silane (silicon tetrahydride).



The products are again separated by distillation. Tetrachlorosilane is hydrogenated to trichlorosilane, which in turn is passed through ion exchange resin. The process is continued to get silane (silicon tetrahydride).

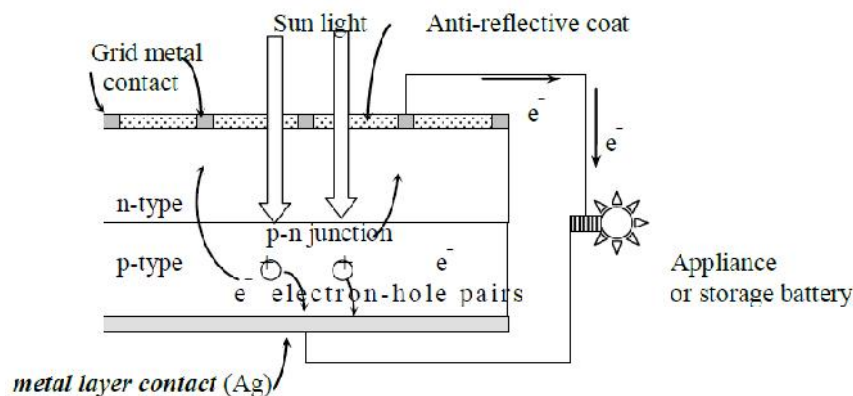
III Purification of Silicon Hydride (Silane) & Deposition of Silicon:

Silicon hydride or silane obtained above is further purified by distillation. Silane is passed into a reactor containing heated silicon seed rods. Silane gets pyrolysed to form polysilicon (semiconductor grade silicon)



5. (a) Define photovoltaic cell. Explain the construction and working of photovoltaic cell. (05 Marks) (CO1, L1, L3)

Solution: Photovoltaic cells are devices that convert solar energy into DC current. They are also called as solar cells and have semiconductor diodes (p-n junction) for utilization of solar energy.



Photovoltaic cell is made of a semiconductor diode (p-n junction). The diode has two electrical contacts. A metallic grid is used on one side and on the other side; a layer of noble metal such as Ag is used. Ag is nobler than the Si-semiconductor and this contact is called as back contact. The metal grid permits the light to fall on the diode between the grid lines. An antireflective coating is used to enhance the light trapping (absorption) by p-n junction.

$$E = \frac{hc}{\lambda}$$

where E is the energy of photon absorbed; h is the Planck's constant, c is the velocity of the light and λ is the wavelength of the light.

When electromagnetic radiation (sunlight) having energy sufficient to overcome the barrier potential falls normal to the surface of the p-n junction, electron - hole pairs are created. The electrons move towards the n-region as it is positively charged now and holes move towards p-region as it is negatively charged now. The electrons are driven into the external circuit and an appliance can be run using it or the energy can be stored in a battery. The stored energy could later be used for various applications such as lighting purposes, telecommunication, etc.

(b) What is glass transition temperature? Explain the following factors affecting glass transition temperature (a) Chain flexibility (b) Intermolecular forces. (05 Marks) (CO5, L1, L3)

Solution: All amorphous polymers, when cooled below a certain temperature, become stiff, hard, brittle and glassy but above this temperature, they are soft, flexible and rubbery. This transition temperature of a polymer is called "glass transition temperature".

(a) Chain flexibility: The factors which lower chain flexibility of polymer increases Tg. Linear polymer chain made of C-C, C-O and C-N single bonds have higher degree of freedom of rotation, increases chain flexibility and thus decrease Tg. Presence of rigid structures in polymer chain such as aromatic or cyclic structure hinder freedom of rotation thus lowering of chain flexibility and increase in Tg.

E.g. Tg of polyethylene -110C

Tg of polystyrene 100C

(b) Intermolecular forces: Strong intermolecular cohesive forces restrict molecular mobility. This leads to an increase in Tg.

Eg: Tg of polypropylene -18C

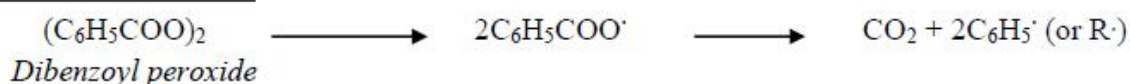
Tg of nylon 66 57C

For polyethylene, Tg is quite low because strong intermolecular cohesive forces are absent. The substituent group on C atoms is only hydrogen which is not bulky at all. On the other hand, Nylon6, a polyamide has a high Tg (50oc). It is because of the presence of large number of polar groups in the molecules, leading to strong intermolecular hydrogen bonding.

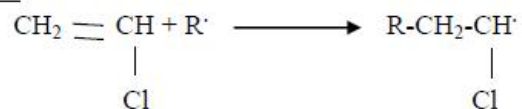
6. (a) Explain the free radical mechanism for addition polymerization by taking vinyl chloride as an example. (06 Marks) (CO5, L3)

Solution:

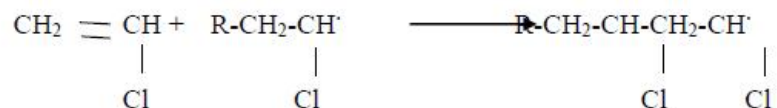
Generation of free radicals



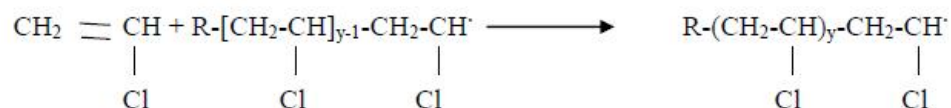
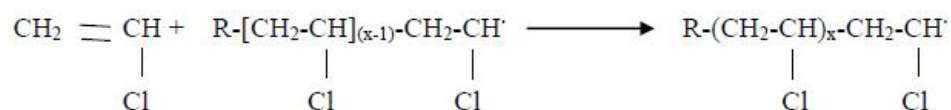
Initiation



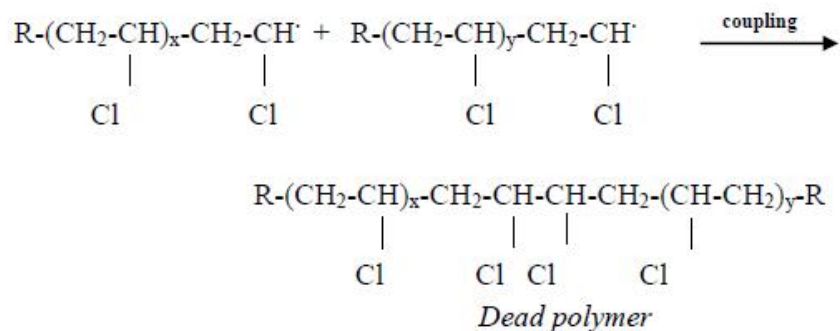
Propagation



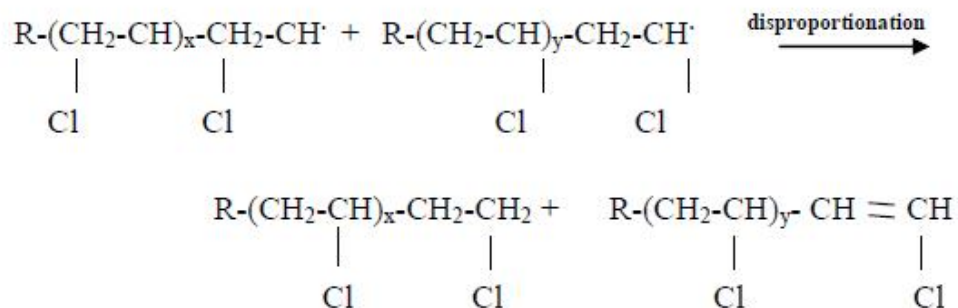
Or in general,



Termination by coupling (by the combination of two radicals)

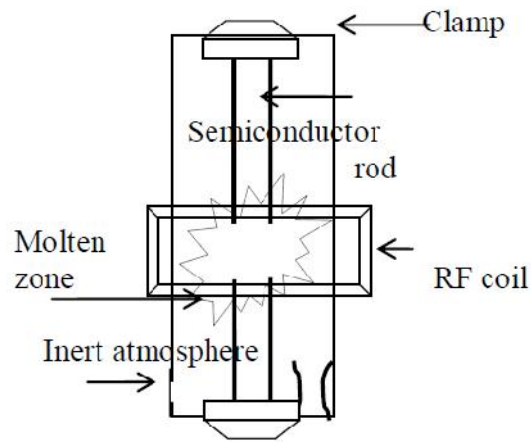


Termination by disproportionation



(b) Explain the purification of silicon by zone refining. (04 Marks) (CO1, L3)

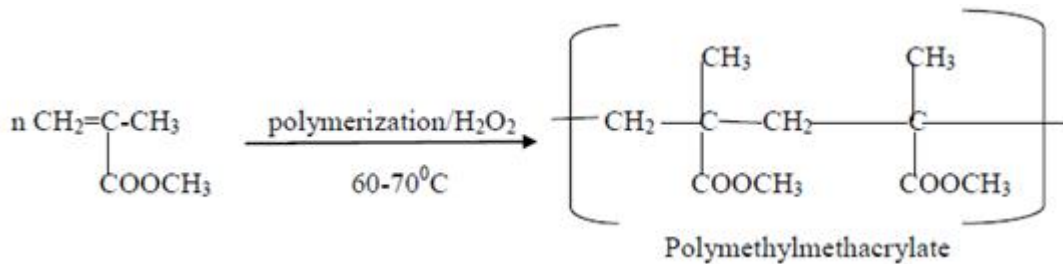
Solution:



Silicon of 99.999999% purity can be obtained by zone refining. It is based on the principle that impurities are more soluble in molten material than in the solid material. A vertical zone refiner is used in the purification of silicon. A rod of silicon to be purified is clamped and is heated by a RF coil to the melting point of silicon. The heater is moved very slowly from top to bottom. This is said to be one zone pass. Impurities move with the molten part of the material as the RF coil moves down. Pure silicon solidifies at the upper portion. The process is repeated number of times to get ultrapure silicon. When the process is complete, the bottom portion where the impurities are concentrated is removed.

7. (a) Write the synthesis and applications of the following polymers. (a) PMMA and (b) Polycarbonates. (05 Marks) (CO5, L2)

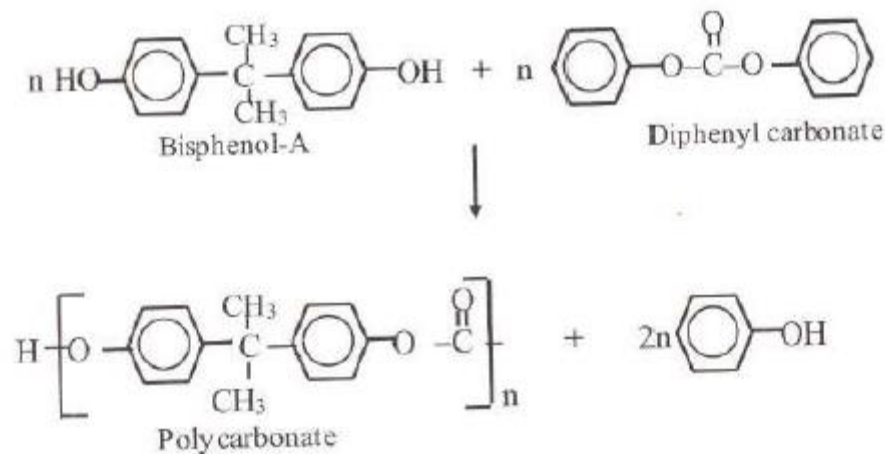
Solution: (a) PMMA:



Applications: (i) For making lenses, air craft windows, artificial eyes, TV screens, attractive sign boards etc.

(ii) It is also used for making transparent bottles, tubes etc.

(b) Polycarbonates:



Applications: (i) They are used in making industrial safety glasses, because of optical clarity.
(ii) They are used in machinery hoses due to its resistance to abrasion and chemicals.

(b) In a polymer sample 20% of molecules have molecular mass of 15000g/mol, 35% molecules have molecular mass of 25000g/mol, and remaining molecules have molecular mass of 20000 g /mol. Calculate the number average and weight average molecular mass of the polymer. (05 Marks) (CO5, L3)

Solution: Given,

$$N_1=20 \qquad M_1= 15000\text{g/mol}$$

$$N_2=35 \qquad M_2= 25000\text{g/mol}$$

$$N_3= 100- (20+35) = 45 \qquad M_3= 20000\text{g/mol}$$

$$\begin{aligned} \text{We know that, } M_n &= (N_1M_1+N_2M_2+N_3M_3)/ (N_1+N_2+N_3) \\ &= (20*15000+35*25000+45*20000)/(20+35+45) \\ &= 20750 \end{aligned}$$

$$M_n=20750 \text{ g/mol}$$

$$\begin{aligned} M_w &= (N_1M_1^2+N_2M_2^2+N_3M_3^2)/ (N_1M_1+N_2M_2+N_3M_3) \\ &= [20*(15000)^2+35*(25000)^2+45*(20000)^2]/(20*15000+35*25000+45*20000) \\ &= 21385.54 \end{aligned}$$

$$M_w= 21385.54\text{g/mol}$$