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Unit- IV

ADVANCED POLYMERIC MATERIALS FOR ENGINEERING APPLICATIONS

(From the Academic year 2022-23 onwards for ME Stream)

POLYMERS

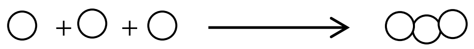
Polymers are of various types to meet our requirements. Polymers find a wide range of applications in the field of technology because of its unique and wide range of properties.

Some of the important properties are

- They do not re act with chemicals like acids and bases. They are inert to most of the chemicals.
- They are soft and flexible. Many are hard and rigid.
- They are bad conductors of electricity. Some of them conduct electricity.
- They are available in wide range of colors.
- They are easy to fabricate.
- Some plastics are hard and rigid.
- Some are transparent; some are opaque.
- They are lightweight.
- They do not undergo corrosion.
- They can be recycled after use.

Polymers: Polymers are high molecular weight material formed by the covalent linkage of several small repeating units called as monomers.

$$nM \longrightarrow -(M)_n-$$



Monomers Polymer

The word polymer is a combination of two Greek words ‘Poly’ means many and ‘mer’ means part. The process of forming a polymer is called *polymerization*.

Classification of polymers:

Polymers can be classified in several ways based on

1. Occurrence
2. Structure
3. Effect of heat on polymer

1. Based on the occurrence the polymers are classified as *natural* and *synthetic* polymers.

Polymers isolated from natural materials are called natural polymers.

Eg: cotton, silk, wool *etc*.

Polymers synthesized from low molecular weight compounds are called synthetic polymers.

Eg: Plastics - polyethylene, polyvinyl chloride, polystyrene and teflon

Synthetic rubbers - Buna-S, neoprene and butyl rubber

Synthetic fibers - Nylon 6, Nylon 6, 6 and Terylene

2. Based on the structure the polymers are classified as *linear* polymers, *branched* polymers and *cross-linked* polymers.

In linear polymers, the monomers are linked linearly.

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–M–M–M–M–M–
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Eg: HDPE (high density polyethylene)

In branched chain polymers the linear chains may branch out, forming a branched structure.

```
– M–M–M–M–M–
     |
     M
     |
     M
```

Eg: LDPE (low density polyethylene), Polybutadiene.

Cross-linked polymers, under certain conditions, the linear chain will undergo branch formation leading to three-dimensional structure.

```
 |  |  |  |  |
–M–M–M–M–M–
 |  |  |  |  |
–M–M–M–M–M–
 |  |  |  |  |
–M– M–M–M–M–
 |  |  |  |  |
```

Eg: Phenol- formaldehyde resin (Bakelite)

3. Based on the effect of heat, polymers are classified into *thermoplastic* and *thermosetting polymers.*

Thermoplastics: they become soft on heating and hard on cooling repeatedly. They retain their structure even when subjected to heat and pressure. Hence they can be repeatedly remoulded into new shapes without any loss of their physical properties.
Eg: PVC, PE, PMMA, Polypropylene

Thermosetting polymers: plastics which get hardened during moulding process and cannot be softened by reheating are called thermosetting polymers. They cannot be remoulded into new shapes.
Eg: Phenol-formaldehyde resins, Urea-formaldehyde resins

DIFFERENCES BETWEEN THERMO-PLASTICS AND THERMO-SETTING PLASTICS

THERMO-PLASTICS	**THERMO-SETTING PLASTICS**
become soft on heating and hard on cooling reversibly	get *hardened* during *molding* process and cannot be softened by reheating
can be repeatedly remolded into new shapes without any loss of their physical properties	cannot be remolded into new shapes as they lose their physical properties
are soft and less brittle	are hard and more brittle
contain long chain linear monomer units	contain cross-linked monomer units
soluble in some organic solvents	insoluble in organic solvents
Eg: PVC, PMMA and Polypropylene	Eg: Phenol- formaldehyde resin, Urea-formaldehyde resin

Polymerization: The process in which several simple and small molecules called monomers are linked together to form a single large molecule of high molecular weight under temperature, pressure and in the presence of catalyst is called *polymerization*.

Eg: Formation of polyethylene

$$\underset{\text{Ethylene}}{n\ CH_2{=}CH_2} \longrightarrow \underset{\text{Polyethylene}}{-\!\!\left(CH_2{-}CH_2 \right)_n\!\!-}$$

Types of polymerization:

Addition polymerization or chain polymerization:

The process in which several unsaturated molecules called monomers linked together through the double bond to form a polymer without the elimination of small molecules like water, ammonia, HCl, *etc*., is called addition polymerization.

Example1: Formation of polyethylene

$$n\,CH_2{=}CH_2 \longrightarrow -\!(CH_2{-}CH_2)_n\!-$$

Ethylene Polyethylene

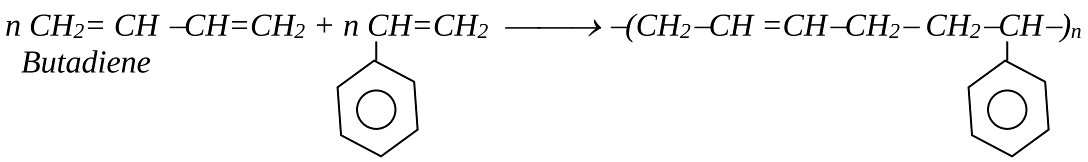
Example 2: Formation of PVC

$$n\,CH_2{=}\underset{\displaystyle Cl}{\underset{|}{CH}} \longrightarrow -\!(CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}})_n\!-$$

Vinyl chloride Polyvinyl chloride

Copolymerization - *It is a kind of addition polymerization in which two or more different monomers linked together to form a polymer.*

Eg: Formation of Buna-S



Styrene *Buna-S*

Condensation polymerization or stepwise polymerization:

This type of polymerization takes place between monomers having two reactive functional groups in them. The linking of the monomers takes place through pairs of functional groups of two different monomers. Most of the times, polymerization is accompanied by the release of simple byproducts like H_2O, HCl *etc*, along with the polymer.

Polymerization takes place in a stepwise manner hence it is also called as *stepwise* polymerization.

Eg: Formation of Nylon 6,6

$$\begin{array}{cccc} HO & OH & H & H \\ | & | & | & | \end{array}$$

$$n\ OC{-}(CH_2)_4{-}CO\ +\ n\ H{-}N{-}(CH_2)_6{-}\ N{-}H$$

Adipic acid Hexa methylene diamine

$$\downarrow$$

$$-(OC\ -(CH_2)_4-CO-HN\ -(CH_2)_6-\ NH-)_n\ +\ 2n\ H_2O$$

Nylon 6,6

Differences between addition polymerization and condensation polymerization

Sl. No	***Points***	**Addition polymerization**	**Condensation polymerization**
1	Type of molecule involved	Unsaturated molecule	Molecules with two functional groups
2	Type of reaction	Chain /Addition reaction	Condensation reaction
3	By products	No by-products	Most of the times yield byproducts
4	Molecular weight of polymer	Equal to sum of molecular weight of monomers	Not equal to sum of molecular weight of monomers
5	Hardness	Soft and flexible	Hard and rigid
6	Examples	Polyethylene synthesis	Nylon 6,6 synthesis

Free radical mechanism of addition polymerization:

The polymerization of unsaturated monomers involves a chain reaction. The free radical mechanism of addition polymerization is explained by taking the formation of polyvinyl chlroride from vinyl chloride as a monomer.

The polymerization takes place in three steps namely

(I) Initiation

(II) Propagation and

(III) Termination

(I) **Initiation:** Initiation step involves, (i) Formation of free radicals and

(ii) Attack of free radical to monomer

Initiation of the polymer chain growth is brought about by adding materials called *initiators* which on heating decompose into *free radicals* (which may be defined as organic molecules having unpaired electrons). Most frequently used initiator is dibenzoyl peroxide (DBP). Dibenzoyl peroxide (DBP) undergoes homolytic decomposition in presence of heat or sun light to produce free radicals.

$$\underset{\text{(DBP)}}{C_6H_5\,CO{-}OO{-}CO\,C_6H_5} \longrightarrow \underset{\text{Benzoyloxy radical}}{2C_6H_5\,COO^{\bullet}} \longrightarrow \underset{\text{Phenyl radical}}{2\,C_6H_5^{\bullet}} + 2CO_2$$

It can be written as

$$\underset{\text{Initiator}}{R\text{-}R} \xrightarrow{\Delta \text{ or } h\nu} \underset{\text{free radical}}{2R^{\bullet}} \qquad (R = C_6H_5^{\bullet})$$

The free radicals so formed are highly reactive and can attack double bonds of unsaturated monomers and thus initiate the chain reaction.

$$R^{\bullet} + \underset{\substack{| \\ Cl}}{CH_2{=}CH} \longrightarrow \underset{\substack{\qquad\;\;| \\ \qquad\;\;Cl}}{R{-}CH_2{-}C^{\bullet}H}$$

Now the monomer is linked to the free radical unit. The free radical site is shifted from free radical to the monomer unit.

ii) Propagation:

The free radical formed in the initiation step successively attacks a fresh monomer molecule resulting in the linking of the second monomer unit to the first and transfer of the free radical site from the first monomer unit to the second and so on and the propagation of chain reaction sets in.

$$R{-}CH_2{-}\underset{\substack{| \\ Cl}}{C^{\bullet}H} + CH_2{=}\underset{\substack{| \\ Cl}}{CH} \longrightarrow R{-}CH_2{-}\underset{\substack{| \\ Cl}}{CH}{-}CH_2{-}\underset{\substack{| \\ Cl}}{C^{\bullet}H}$$

Or

$$R{-}CH_2{-}\underset{\substack{| \\ Cl}}{C^{\bullet}H} + n.\,CH_2{=}\underset{\substack{| \\ Cl}}{CH} \longrightarrow R{-}(CH_2{-}\underset{\substack{| \\ Cl}}{CH})_n{-}CH_2{-}\underset{\substack{| \\ Cl}}{C^{\bullet}H}$$

Propagation continues until the growing chain is terminated (deactivated).

iii) Termination:

Termination is commonly due to the reaction of a long chain free radical with another long chain free radical. The products formed are dead or non-reactive and hence further chain propagation is not possible.

Termination can take place in two ways.

a. Combination or coupling
b. Disproportionation

Termination by Coupling or Combination: The two growing chains unite by the coupling of the lone electron present in each chain to form an electron pair and thus nullify their reactiveness. Since this process involves the coupling of two lone electrons. This kind of termination is known as ‘Termination by Coupling’.

$$\mathrm{R{-}(CH_2{-}\underset{\underset{Cl}{|}}{CH})_n{-}CH_2{-}\underset{\underset{Cl}{|}}{C^{\bullet}}H \;+\; \underset{\underset{Cl}{|}}{C^{\bullet}}H{-}CH_2{-}(\underset{\underset{Cl}{|}}{CH}{-}CH_2)_n{-}R}$$

$$\downarrow \text{Coupling}$$

$$\mathrm{R{-}(CH_2{-}\underset{\underset{Cl}{|}}{CH})_n{-}CH_2{-}\underset{\underset{Cl}{|}}{CH}{-}\underset{\underset{Cl}{|}}{CH}{-}CH_2{-}(\underset{\underset{Cl}{|}}{CH}{-}CH_2)_n{-}R}$$

(Dead polymer)

Termination by Disproportionation: In this case, one H from one growing chain is abstracted by the other growing chain and utilized by the lone electron for getting stabilized, while the chain which had donated H gets stabilized by the formation of a double bond. This termination process results in the formation of two polymer molecules of shorter chain length, one is saturated and another one is unsaturated end group.

$$\mathrm{R{-}(CH_2{-}\underset{\underset{Cl}{|}}{CH})_n{-}CH_2{-}\underset{\underset{Cl}{|}}{C^{\bullet}}H \;+\; \underset{\underset{Cl}{|}}{C^{\bullet}}H{-}\underset{\underset{H}{|}}{CH}{-}(\underset{\underset{Cl}{|}}{CH}{-}CH_2)_n{-}R}$$

$$\downarrow \text{ Disproportionation}$$

$$\mathrm{R{-}(CH_2{-}\underset{\underset{Cl}{|}}{CH})_n{-}CH_2{-}\underset{\underset{Cl}{|}}{CH_2} \;+\; R{-}(CH_2{-}\underset{\underset{Cl}{|}}{CH})_n{-}CH{=}\underset{\underset{Cl}{|}}{CH}}$$

Saturated polymer Unsaturated polymer

During polymerization termination is possible due to either reaction. The actual mode depends on the experimental conditions.

Number average and weight average molecular weight

The molecular weight of a polymer influences its properties. Low molecular weight polymers are soft and gum like resins. The high molecular weights are tough and more heat resistant. Polymers are polydisperse i.e., contain all kinds of molecules (different chain lengths and molecular weights). The molecular weights of polymers are thus averages.

Number average molecular weight (Mn): Number average molecular weight is defined as the total mass (W) of all the molecules in a polymer sample divided by the total number of molecules present. Thus it is represented as,

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \text{----------} + n_iM_i}{n_1 + n_2 + n_3 + \text{---------} + n_i} = \frac{\sum N_iM_i}{N_i}$$

Weight average molecular weight (Mw)**:** It depends on the total weight of the polymer in a given volume of a solution. It can be determined from light scattering and ultra-centrifugation techniques, which depend on the weights of molecules present. The molecular weight is averaged according to the weight of molecules of each type.

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2 + \text{--------} + n_iM_i^2}{n_1M_1 + n_2M_2 + n_3M_3 + \text{---------} + n_iM_i}$$

The weight average molecular weight is always greater than number average molecular weight.

It gives an index of polydispersity.

Calculation of number average molecular weight and weight average molecular weight:

1. If a polymer sample has population of:

10 molecules of molecular mass each = 5000

20 molecules of molecular mass each = 7500

20 molecules of molecular mass each = 10000

25 molecules of molecular mass each = 15000

20 molecules of molecular mass each = 20000

5 molecules of molecular mass each = 25000

Solution: Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \text{----------} + n_iM_i}{n_1 + n_2 + n_3 + \text{---------} + n_i} = \frac{\sum N_iM_i}{N_i}$$

$$M_n = \frac{(10 \times 5000) + (20 \times 7500) + (20 \times 10000) + (25 \times 15000) + (20 \times 20000) + 5 \times 25000)}{10+20+20+25+20+5}$$

$$M_n = \frac{1.3 \times 10^6}{100}$$

$M_n =$ **13,000**

Weight average molecular weight

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2 + \text{--------} + n_iM_i^2}{n_1M_1 + n_2M_2 + n_3M_3 + \text{---------} + n_iM_i}$$

$$M_w = \frac{10 \times (5000)^2 + 20 \times (7500)^2 + 20 \times (10000)^2 + 25 \times (15000)^2 + 20 \times (20000)^2 + 5 \times (25000)^2}{10 \times (5000) + 20 \times (7500) + 20 \times (10000) + 25 \times (15000) + 20 \times (20000) + 5 \times (25000)}$$

$$M_w = \frac{2.0125 \times 10^{10}}{13 \times 10^5}$$

$M_w =$ **15,480.76**

2. A polymer of polypropylene is found to have following composition

$$R\,[-CH_2-\underset{\displaystyle CH_3}{\overset{}{CH}}-]\,R_{400} \quad 20\ \%$$

$$R\,[-CH_2-\underset{\displaystyle CH_3}{\overset{}{CH}}-]\,R_{500} \quad 30\ \%$$

$$R\,[-CH_2-\underset{\displaystyle CH_3}{\overset{}{CH}}-]\,R_{600} \quad 50\ \%$$

Calculate the number average molecular weight and weight average molecular weight of the polymer. (Given atomic mass of C =12, H =1, neglect mol. mass of R)

Solution: Molecular weight of propylene monomer = 42 (3C + 6H= 3x12 + 6x1= 36+ 6 = 42)

$M_1 = 42 \times 400 = 16800$

$M_2 = 42 \times 500 = 21000$

$M_3 = 42 \times 600 = 25200$

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

$$= \frac{20(16800) + 30(21000) + 50(25200)}{20+30+50}$$

$M_n =$ **22,260**

Weight average molecular weight

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2}{n_1M_1+n_2M_2+n_3M_3}$$

$$= \frac{20(16800)^2 + 30(21000)^2 + 50(25200)^2}{20(16800) + 30(21000) + 50(25200)}$$

M_w = **22,715**

3. Calculate the number average molecular weight and weight average molecular weight of the given polymer with different compositions (neglect the mol. mass of R).

Polyethylene

R [–CH_2 –CH_2–] R $_{250}$ 50 %

R [–CH_2 –CH–] R $_{450}$ 30 %

R [–CH_2 –CH–] R $_{500}$ 20 %

Solution: Molecular mass of the monomer = (2x12 + 4x1) = 28

M_1 = 28 x 250 = 7000 n_1 = 50

M_2 = 28 x 450 = 12600 n_2 = 30

M_3 = 28x 500 = 14000 n_3 = 20

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

$$= \frac{50(7000) + 30(12600) + 20(14000)}{50+30+20}$$

$$= \frac{350000+378000+280000}{100}$$

= 1008000/100 = **10,080**

Weight average molecular weight

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2}{n_1M_1+n_2M_2+n_3M_3}$$

$$= \frac{50(7000)^2 + 30(12600)^2 + 20(14000)^2}{50(7000) + 30(12600) + 20(14000)}$$

$$= \frac{2450000000 + 4762800000 + 3920000000}{1008000}$$

$$= \frac{1.11328\text{x}10^{10}}{1008000} = \mathbf{11,044.44}$$

4. Calculate the number average molecular weight and weight average molecular weight of the given polymer with different compositions (neglect the mol. mass of R).

Polyvinyl bromide

$$R\,[-CH_2-\underset{|}{\overset{Br}{CH}}-]\,R_{400} \quad 45\ \%$$

$$R\,[-CH_2-\underset{|}{\overset{Br}{CH}}-]\,R_{400} \quad 25\ \%$$

$$R\,[-CH_2-\underset{|}{\overset{Br}{CH}}-]\,R_{600} \quad 30\ \%$$

Solution: Molecular mass of single unit = (2x12 + 3x1 + 1x80) = 107

M_1 = 107 x 400 = 42,800

M_2 = 107 x 400 = 42,800

M_3 = 107 x 600 = 64,200

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

$$= \frac{45(42,800) + 25(42,800) + 30(64,200)}{45 + 25 + 30}$$

$$= \frac{1926000 + 1070000 + 1926000}{100}$$

= 4922000/100 = **49,220**

Weight average molecular weight

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2}{n_1M_1 + n_2M_2 + n_3M_3}$$

$$= \frac{45(42,800)^2 + 25(42,800)^2 + 30(64,200)^2}{45(42,800) + 25(42,800) + 30(64,200)}$$

$$= \frac{2.51878\text{x}10^{11}}{4922000} = \mathbf{51,173.91}$$

5. Calculate the number average molecular weight and weight average molecular weight of the given polymer with different compositions (neglect the mol. mass of R).

Polyvinyl chloride

Cl

$$R\,[-CH_2-\underset{Cl}{\underset{|}{C}}H-]\,R_{200} \quad 20\ \%$$

$$R\,[-CH_2-\underset{Cl}{\underset{|}{C}}H-]\,R_{300} \quad 30\ \%$$

$$R\,[-CH_2-\underset{Cl}{\underset{|}{C}}H-]\,R_{400} \quad 50\ \%$$

Solution: Molecular mass of single unit = (2x12 + 3x1 + 1x35.5) = 62.5

M_1 = 62.5 x 200 = 12500

M_2 = 62.5 x 300 = 18750

M_3 = 62.5 x 400 = 25000

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

$$= \frac{20(12500) + 30(18750) + 50(25000)}{20+30+50}$$

$$= \frac{250000+562500+1250000}{100}$$

$= 2062500/100 =$ **20,625**

Weight average molecular weight

$$M_w = \frac{n_1M_1^{\,2} + n_2M_2^{\,2} + n_3M_3^{2}}{n_1M_1+n_2M_2+n_3M_3}$$

$$= \frac{20(12500)^2 + 30(18750)^2 + 50(25000)^2}{20(12500) + 30(18750) + 50(25000)}$$

$$= \frac{(3125x10^6) + (1.0546x10^{10}) + (3.125x10^{10})}{2062500}$$

$$= \frac{(4.4921x10^{10})}{2062500} = \mathbf{21{,}779.87}$$

6. Calculate the number average molecular weight and weight average molecular weight of the given polymer with different compositions (neglect the mol. mass of R).

Polystyrene

$$C_6H_5$$
$$|$$

R [–CH_2 –CH–] R $_{100}$ 30 %
C_6H_5

R [–CH_2 –CH–] R $_{200}$ 30 %
C_6H_5

R [–CH_2 –CH–] R $_{300}$ 40 %

Solution: Molecular mass of single unit = (8x12 + 8x1) = 104

M_1 = 104 x 100 = 10400

M_2 = 104 x 200 = 20800

M_3 = 104 x 300 = 31200

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3}{n_1 + n_2 + n_3}$$

$$= \frac{30(10400) + 30(20800) + 40(31200)}{30+30+40}$$

$$= \frac{2184000}{100} = \mathbf{21,840}$$

Weight average molecular weight

$$M_w = \frac{n_1M_1^{\,2} + n_2M_2^{\,2} + n_3M_3^{\,2}}{n_1M_1+n_2M_2+n_3M_3}$$

$$= \frac{30(10400)^2 + 30(20800)^2 + 40(31200)^2}{30(10400) + 30(20800) + 40(31200)}$$

$$= \frac{(5.51616x10^{10})}{2184000} = \mathbf{25257.14}$$

7. Calculate the number average molecular weight and weight average molecular weight of a polymer consisting of 10% by weight of macromolecules of molecular mass 1000 and 90% by weight of macromolecules of molecular mass 10,000.

Solution: n_1 = 10; n_2 = 90; M_1 = 1000; M_2 = 10,000.

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2}{n_1 + n_2}$$

$$= \frac{10(1000) + 90(10000)}{10+90}$$

$$= \frac{910000}{100} = \mathbf{9,100}$$

Weight average molecular weight

$$M_w = \frac{n_1M_1^{\,2} + n_2M_2^{\,2}}{n_1M_1+n_2M_2}$$

$$= \frac{10(1000)^2 + 90(10000)^2}{10(1000) + 90(10000)}$$

$$= \frac{(9010000000)}{910000} = \mathbf{9901.1}$$

Synthesis, properties and applications of polymers

Teflon (Polytetra fluoro ethylene - PTFE):

Polymerization is carried out by the suspension polymerization. It is prepared by heating tetrafluoro-ethylene (monomer) under pressure in presence of ammonium persulphate initiator in a steel autoclave. The reaction is exothermic and proper dissipation of heat is necessary.

$$\underset{\text{Tetra fluoro ethylene}}{n\ CF_2{=}CF_2} \xrightarrow[\Delta]{\text{Amm. persulphate}} \underset{\text{polytetrafluoroethylene}}{-\!\!(CF_2{-}CF_2)_n\!\!-}$$

Properties:

i) It is tough flexible material with waxy surface.

ii) It is not wetted by oil and water. Excellent non-stick property.

iii) It is extremely resistant to chemical attack.

iv) It has excellent electrical insulating properties.

v) Its density is 2.1- 2.3 g/cm^3

vi) Melting point is 327 ^oC.

Applications: It is used in manufacture of

i) Electrical goods like wire and cable insulation, insulation for motors, generators, transformers, coils and capacitors.

ii) Gasketing, belting, pump and valve packing, laboratory equipments.

iii) It is used for coating food processing and cooking utensils.

Polymethyl methacrylate (PMMA) or plexi glass:

The monomer methyl methacrylate [an ester of methyl acrylic acid, $CH_2=C(CH_3)COOH$] undergoes polymerization in presence of 5% hydrogen peroxide at 60 - 70 ^oC to produce a acrylic polymer PMMA.

$$n\ CH_2=\underset{\displaystyle COOCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}} \xrightarrow[60\text{-}70\ ^oC]{H_2O_2} -\!\!\left(CH_2-\underset{\displaystyle COOCH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\right)_n$$

Methyl Methacrylate PMMA

Properties:

i) **It is a colorless transparent plastic. Percentage transmittance is 92 with an excellent outdoor life.**

ii) It is hard and rigid with a melting point of 120 ^oC.

iii) It is resistant to many inorganic reagents, including dilute acids and alkalis, sun light and weather.

iv) The mechanical and thermal properties are good.

v) It has low scratch resistance.

Applications:

i) It is used to make attractive sign boards and durable lenses for automobile lighting.

ii) It is used in buildings for decorative purposes.

iii) It is used in the manufacture of lenses, optical instruments, windshields, sign boards.

iv) It is used for surface coating of automobiles.

Polymer Composites:

Structural materials required by the modern technology should have the properties such as,

i) low density

i) high strength

ii) abrasion and impact resistance

iii) corrosion resistance.

Any single metal, alloy, ceramic or polymeric materials cannot have the above properties, because a strong material is relatively dense. Then new material called polymer composites are developed.

Definition: Two or more distinct components which combine to form a new class of materials with entirely different properties suitable for structural applications are referred to as composite materials.

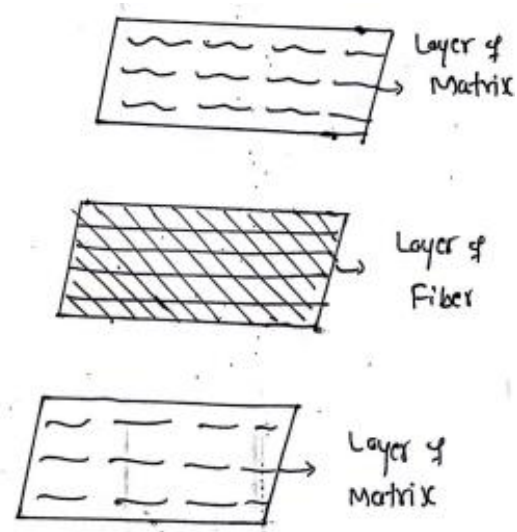
Polymer Composites are obtained by using a polymer with other kind of materials its identity and the mechanical properties of the polymer Composite material is superior to their constituents.

Polymer Composites are generally made of two components, namely **i) matrix and ii) fiber.**

The fiber is embedded in the matrix to make the matrix stronger. The polymer matrix generally used is thermosetting polymeric resins like epoxy, polypentadiene and polythene.

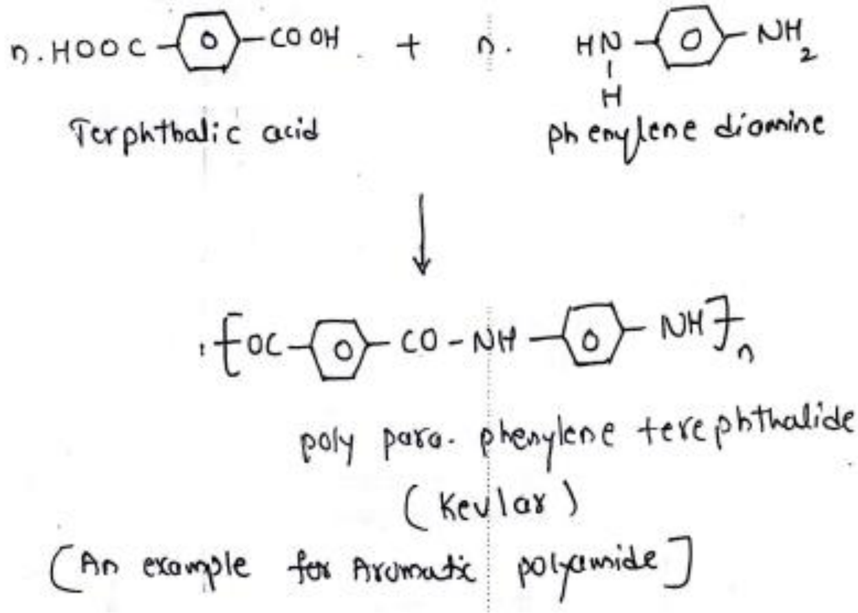
The fibers used include glass fibers, Kevlar and carbon fiber.

Fiber- reinforced composites are strong and light. They are stronger than steel but weight is less. Hence these composites can be used to make automobiles lighter.



Synthesis of Kevlar:

Kevlar belongs to a family of aramides. It is an aromatic polyamide with the name poly para-phenylene terephthalide.



Properties: Kevlar has high strength and forms better fibers than non-aromatic polyamides like nylon 6, 6. It has higher tensile strength and modulus than fiberglass. Kevlar fibers are used to get good stiffness, high abrasion resistance and light weight.

Applications: it is used in making light weight boat hulls, pressure vessels, high performance race cars, bullet proof vests and puncture resistant bicycle tyres.

Applications of polymer composites:

(1) Aerospace: they are used in making wings, antennae, helicopter blades, landing gears, seats, floors rocket motor cases.

(2) Automobiles: used in making body panels, bumpers, gears, bearings

(3) Boats: used in making hulls, decks, masts.

(4) Chemical: used in making piper, tanks, pressure vessels, hoppers, valves, pumps.

(5) Domestic: used in making interior and exterior panels, chairs, tables.

(6) Electrical: used in making panels, housings, switchgears, connectors.

Polymer nanocomposites:

Polymer nanocomposites are materials in which nanoscopic inorganic particles are dispersed in an organic polymer matrix to improve the performance properties of the polymer. They consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. These may be of different shape (platelets, fibers, spheroids), but at least one dimension must be in the range of 10-100 A.

Properties:

i) Polymer nanocomposites have shown drastic enhancements in the mechanical, electrical, optical and thermal properties.

ii) They have excellent stiffness and strength, increased dimensional stability, improved flame retardance, improved solvent and UV resistance.

iii) Rheological properties of nanostructured polymer/clay nanocomposites are strongly influenced by the morphology of the materials, which depends on the clay dispersion in the polymer matrix.

iv) They exhibit good anti-bacterial properties and its property has been used for food packaging obtained by titanium nanoparticles.

Applications:

i) Used in microelectronic devices, sensors and biomedical sciences.

ii) Used as electrolytes, anodes in lithium-ion-batteries and super capacitors.

iii) Used in organic solar cells and intrinsic conductive polymers.

iv) They are the good substitute for more expensive technical parts like gear systems in wood drilling machines, wear resistance materials and in the production of barrier plastic film for food industry.

v) Fe_2O_3 polymer nanocomposites are used as advanced toner materials for high quality colour copiers and printers and as contrast agents in memory devices.

vi) Polymer nanocomposites containing ferrites are increasingly replacing conventional ceramic magnetic materials because of their mouldability and reduction in cost.

vii) They are also potential materials for microwave absorbers, sensors and other aerospace applications.

1. Calculate the number average and weight average molecular mass of polystyrene sample containing 20%, 35%, 30% and 15% of polymer chains with the degree of polymerization 10^3, 10^4, 10^5 and 10^6 respectively.

Molecular weight monomer = 104

M1=104x10^3

M2=104x10^4

M3=104x10^5

M4=104x10^6

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + n_4M_4}{n_1 + n_2 + n_3 + n_4}$$

$$= \frac{20(104x1000)+35(104x10000)+30(104x100000)+15(104x1000000)}{20+35+30+15}$$

=1910480000/100

Mn=**19104800**

(1) Weight average molecular weight

$$M_w = \frac{n_1M_1^{\,2} + n_2M_2^{\,2} + n_3M_3^2 + n_4M_4^2}{n_1M_1+n_2M_2+n_3M_3+n_4M_4}$$

$$= \frac{20(104x1000)^2+35(104x10000)^2+30(104x100000)^2+15(104x1000000)^2}{1910480000}$$

M_w =**86639416.44**

2. Calculate the number average and weight average molecular mass of polystyrene sample containing 20%, 25%, 40% and 15% of polymer chains with the degree of polymerization 10^4, 10^5, 2x10^5 and 5x10^5 respectively.

Molecular weight monomer = 104

M1=104x10^4

M2=104x10^5

M3=104x2x10^5

M4=104x5x10^5

Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + n_4M_4}{n_1 + n_2 + n_3 + n_4}$$

$$= \frac{20(104x10000)+25(104x100000)+40(104x2x100000)+15(104x5x100000)}{20+25+40+15}$$

=1892800000/100

M_n=**18928000**

Weight average molecular weight

$$M_w = \frac{n_1M_1^{\,2} + n_2M_2^{\,2} + n_3M_3^2 + n_4M_4^2}{n_1M_1+n_2M_2+n_3M_3+n_4M_4}$$

$$= \frac{20(104x10000)^2+25(104x100000)^2+40(104x2x100000)^2+15(104x5x100000)^2}{1892800000}$$

M_w = $\underline{6.0591232x10^{16}}$

1892800000

M_w = **32011428.57**

Calculate the number average and weight average molecular mass of polystyrene sample containing 20%, 35%, 30% and 50% of polymer chains with the degree of polymerization $10^3, 10^4, 10^5$ and 10^6 respectively.

Molecular weight monomer = 104

M1=104x10^3

M2=104x10^4

M3=104x10^5

M4=104x10^6

(2) Number average molecular weight

$$M_n = \frac{n_1M_1 + n_2M_2 + n_3M_3 + n_4M_4}{n_1 + n_2 + n_3 + n_4}$$

$$= \frac{20(104x1000)+35(104x10000)+30(104x100000)+15(104x1000000)}{20+35+30+50}$$

=104x10^3(20+350+3000+15000)/100

Mn=19104800

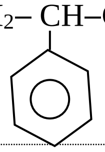
(3) Weight average molecular weight

$$M_w = \frac{n_1M_1^2 + n_2M_2^2 + n_3M_3^2 + n_4M_4^2}{n_1M_1 + n_2M_2 + n_3M_3 + n_4M_4}$$

$$= \frac{20(104x1000)^2+35(104x10000)^2+30(104x100000)^2+15(104x1000000)^2}{19104800}$$

M_w =86639416.44

Questions

1	What are polymers? How are they classified?
2	What is polymerization? Discuss the types of polymerization.
3	*Explain* the free radical mechanism of addition polymerization taking polymerization of vinyl chloride as an example.
4	Compute the synthesis of i) Polymethyl methacrylate ii) Teflon
5	Distinguish between thermoplastics and thermosetting polymers.
6	*Calculate* the number average and weight average molecular masses of a polymer with the following composition. (Given: Atomic weight of H = 1, C = 12 & Cl =35.5) $[-CH_2-\overset{\overset{Cl}{\vert}}{C}H-]_{250}$ is 50% ; $[-CH_2-\overset{\overset{Cl}{\vert}}{C}H-]_{450}$ is 30% ; $[-CH_2-\overset{\overset{Cl}{\vert}}{C}H-]_{500}$ is 20%
7	Compute the synthesis, properties and applications of Kevlar.
8	Mention the applications of polymer composites.
9	What are nanocomposites? How are they prepared?
10	Discuss the applications of nanocomposites.
11	Calculate number average and weight average molecular mass of polythene having the following composition. (a) $-(-CH_2-CH_2-)_{200}$ 35% (b) $-(-CH_2-CH_2-)_{750}$ 65%
12	Calculate number average and weight average molecular mass of polypropylene having the following composition. (a) $-[-CH_2-CH(CH_3)-]_{200}$ 25% (b) $-[-CH_2-CH(CH_3)-]_{750}$ 75%
13	Calculate number average molecular mass of PVC having the following composition. (a) $-[-CH_2-CH(Cl)-]_{250}$ 20% (b) $-[-CH_2-CH(Cl)-]_{650}$ 80%
14	Calculate the number and weight average molecular mass of Buna-S having the following composition. $-(CH_2-CH=CH-CH_2-CH-CH_2-)_{50}$ 
15	Calculate the number and weightage average molecular mass of Nylon 6, 6 having the following composition. $-(OC-(CH_2)_4-CO-HN-(CH_2)_6-NH)_{30}-$

LIQUID CRYSTALS

Matter exists in three different physical states namely solid, liquid and gas. Each physical state is named by a terminology so called phase.

<u>Example 1. Water system:</u> Water exists in three different phases namely ice, water, and water vapour. With rise in temperature ice melts to water, water evaporates to water vapour. Here solid is converted to liquid, liquid is converted to gas. The change is reversible on cooling.

Ice <----------→ water <-----------→ water vapour

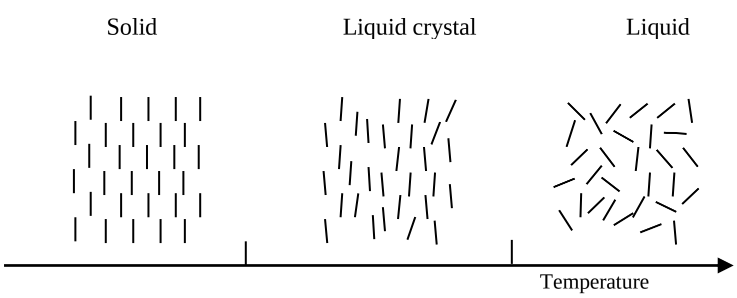
$0^{o}C$ $100^{o}C$

2. When cholestryl benzoate (solid) is heated slowly, the solid melts to liquid, but the liquid obtained is very cloudy and not a clear liquids like water. If it is further heated, the cloudy liquid turns into a clear liquid (like water). On cooling, the clear liquid turns into a cloudy liquid state and later into a solid. These changes takes place at definite temperature and is called as phase transition temparature and therefore the cloudy liquid state must be a phase different from solid and liquid phase. This phase is called *liquid crystal phase.*

Cholestryl benzoate < <u>$145.5^{o}C$</u> > Cholestryl benzoate < <u>$178.5^{o}C$</u> > Cholestryl benzoate

(Solid) (Cloudy liquid) (Clear liquid)

Molecular ordering: It is the arrangement of molecules. In case of solid, the molecules are properly arranged and hence the molecular ordering is proper or fixed. In liquid, the molecules are randomly arranged and hence the molecular ordering is random. Where as in case of liquid crystals the molecular ordering is in between solids and liquids.

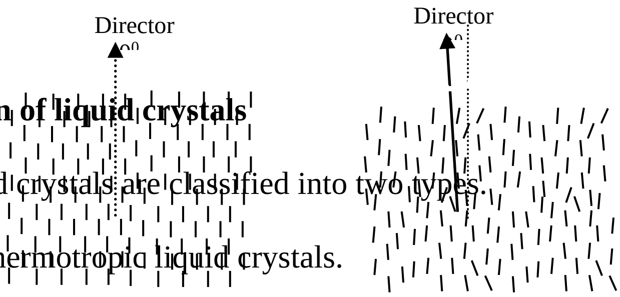


Liquid crystal state is a distinct state in which the molecular ordering is in between perfectly crystalline solid and liquid state.

Director:

The molecular ordering in a liquid crystal is studied using an imaginary axis called *director*. Director is generally represented by an arrow.

In liquid crystals, each molecule is inclined or arranged or placed at some angle with respect to the director. Therefore, the average angle is considered or taken as amount of order. The angle will be closer to zero when the molecules are highly ordered. If the angle is 57 it means that there is no orientational order. If the angle is less than 57 it means that there is orientational order.



Classification of liquid crystals

Liquid crystals are classified into two types.

1. Thermotropic liquid crystals.
2. Lyotropic liquid crystals.

1. Thermotropic liquid crystals.

These are the chemical compounds which exhibit liquid crystal behavior upon heating.

Eg: Cholesteryl Benzoate & p-azoxyphenetole.

2. *Lyotropic liquid crystals*

These are the chemical compounds which exhibit liquid crystal behavior upon mixed with another substance.

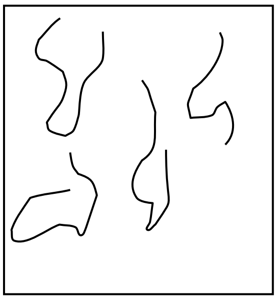
Examples: (i) soap (soap - water mixture) molecules (ii) phospholipids

Classification based on Molecular ordering in liquid crystals

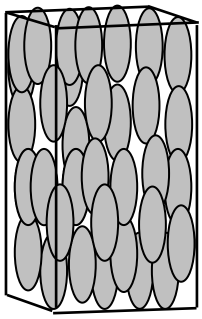
Nematic liquid crystals (Greek, nema = thread):

These are the liquid crystals in which the molecules are arranged parallel to each other due to intermolecular force. Since these liquid crystals shows thread like structure and hence are commonly called as nematic liquid crystal phase (nema = thread).

Example: Paraazoxy anisole (PAA) shows liquid crystal behavior between 118-135^{o}C. These molecules are optically inactive.



Thread like structure



Chiral nematic phase or Cholestric liquid crystals: (Chiral = twist)

These are the liquid crystals having twisted structure. As a result of twisting, the molecules arrange themselves in such a way that a group of molecules align at different angles with respect to their adjacent group. Therefore, the director is not fixed.

Eg: Cholesterol benzoate and cholesteryl myristate.

Smectic liquid crystals (Smectose = soap)

These are the liquid crystals in which the molecules are arranged or positioned in between nematic liquid crystal and Chiral nematic phase or Cholestric liquid crystals. These are having soap-like structures.

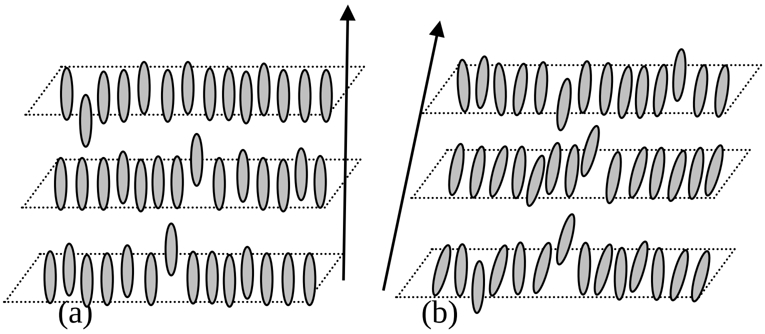
There are three different smectic liquid crystal phases. Smectic A, Smectic B, and Smectic C.

In Smectic A phase, the director is perpendicular to the plane.

In Smectic C phase, the director makes an angle other than 90^{O} to the plane.

In Smectic B phase, the director is perpendicular to the plane but the molecules are arranged themselves in a network of hexagonal layer.

Examples: 4-n butyloxybenzilidene amino propiophenone (smecticA); terphthalylidene-bis-4-n-butylaniline (smectic B) 4,4'-di-n-heptyloxyazoxybenzene (smectic C)

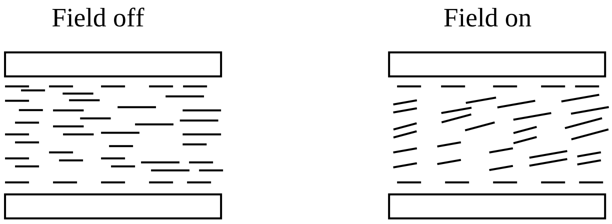


Schematic representation of smectic where molecules lie on regularly spaced planes (in the form of layers). (a) smectic A where the director is perpendicular to the planes (b) smectic C where the director is tilted

Electro - optic effect

Electric field effect on liquid crystals

In liquid crystals, the molecules are freely arranged in all possible directions. When a thin film of liquid crystal is placed between two parallel plates, the direction of arrangement of molecules depends on the application of external electric field. In the absence of an electric field, the molecules are aligned parallel to the surfaces giving a homogeneous texture. Whereas in the presence of an electric field the molecules near to the surface are arranged parallel to the surface and the remaining are free to orient themselves or randomly arranged. As a result of this, the liquid crystal undergoes deformity. This transition (deformity) is important in the operation of the liquid crystal displays (LCD) because the transition brings about a significant change in the optical characteristics of the liquid crystal.



Effect of light on Liquid crystals:

Terminologies: Unpolarized light: The light which travels in all possible directions.

Polarized light: The light which travels in only one direction.

Polarizer: It is a component made up of colored glass sheet or plastic sheet which converts unpolarized light into polarized light.

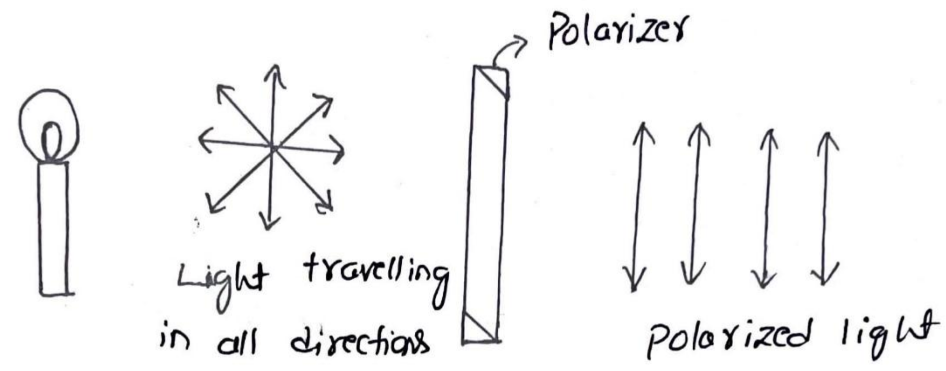


Figure: Polarization of light

When light is incident on two crossed polarizers, no light emerges because the light emerging from the first polarizer is completely absorbed by the second polarizer and hence appears dark.

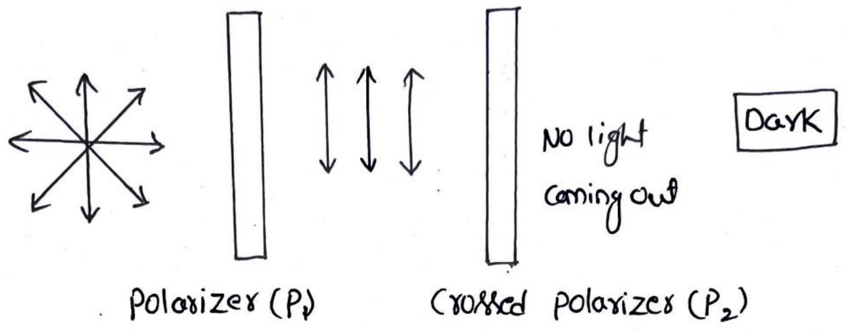


Figure: Light incident on two crossed polarizers

A thin film of liquid crystal is placed between two glass plates and is introduced between the crossed polarisers. The molecules between the glass plates are made to lie parallel to the surface. The director is forced to twist by 90^o.The polarization direction of light is therefore rotated by 90^o and strikes the second polariser. This polariser allows light to pass through it and appears bright (silvery grey). This property is made use in liquid crystal displays.

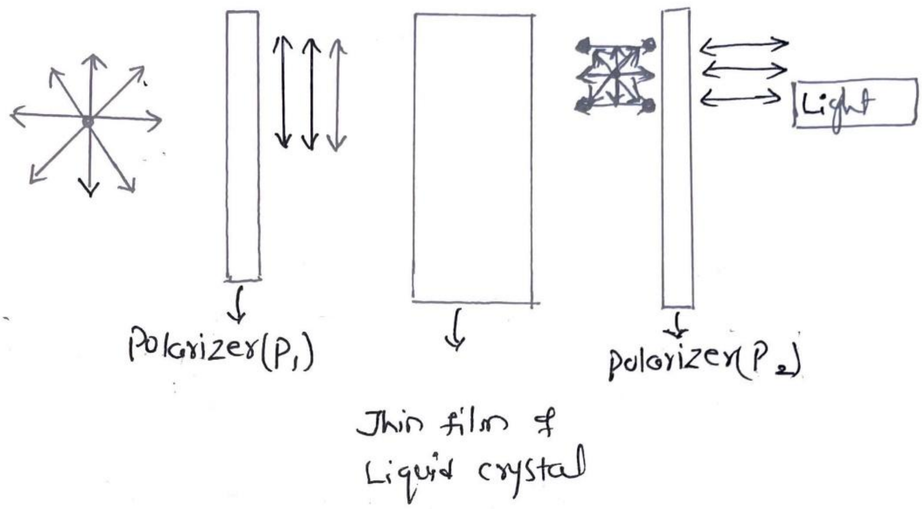


Figure: Light incident on thin film of liquid crystal

Applications of liquid crystals in liquid crystal display (LCD)

Principle

Liquid crystal displays (LCD) use nematic liquid crystals.

Note: Nematic (Greek = thread like) liquid crystals are formed by compounds that are optically inactive. The molecules have elongated shape and are oriented parallel to the director.

The advantage of nematic liquid crystals is that there are weak inter molecular forces between their molecules which can be easily disrupted. Hence the molecules in a nematic phase can be readily realigned along new directions. Both electric field and light can bring about such realignments (electro optic effect). LCDs use the ease of molecular reorientation to change the area of display from light to dark.

When a voltage is applied to a set of electrodes in some area of display, the liquid crystal molecules reorient along a new direction. In the absence of electric field, the molecules return to their original position.

Liquid Crystal Displays are used to display numeric, alphanumeric and graphic images. Electro-optic property of liquid crystals is made use in liquid crystal displays. Information is passed on to the user using liquid crystals which control the brightness / darkness of the parts of a display. Numeric display has seven segments (also called pixels) whereas alphabets are displayed in fourteen-segment display.

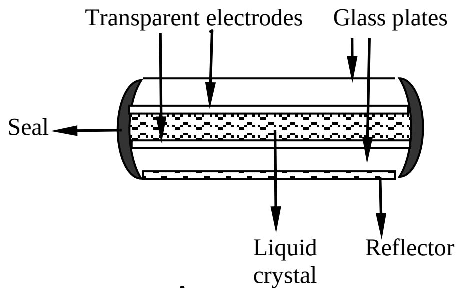
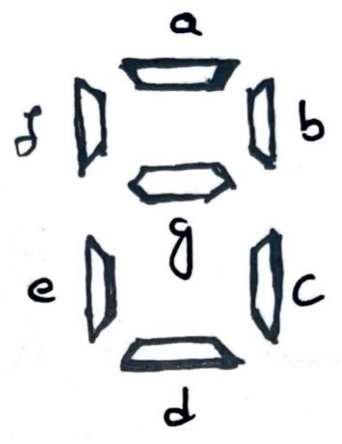
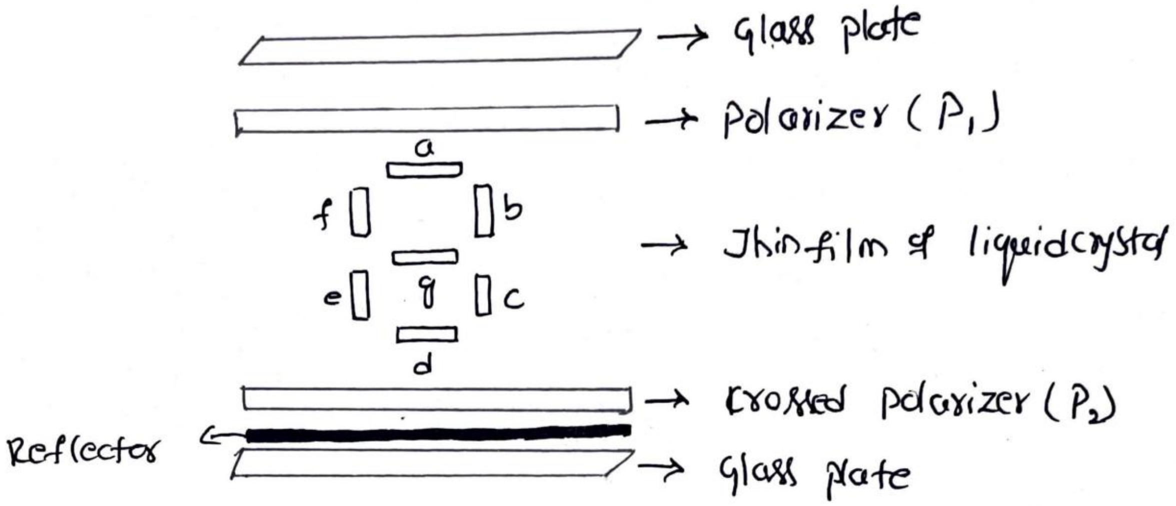


Figure: Schematic representation of a liquid crystal display (reflection mode pixel) where the liquid crystal is embedded between two glass plates

In a 7-segment display the segments are addressed a, b, c, d, e, f and g. Each segment represents a liquid crystal. Light from the area of each of the seven segments or pixels is controlled independently and creation of any of the nine digits becomes possible.



In each segment a thin film of liquid crystal (twisted nematic) between glass plates is placed between two crossed polarizers. The molecules are forced to lie parallel to the glass surface. The director is forced to twist by 90°. The polarization direction of light is therefore rotated by 90^o and it strikes the second polarizer. This polarizer allows light to pass through it and the reflector reflects the light 90^o twist the liquid crystal once again so that all this light pass through the first polariser. All the segments (screen) appear silvery grey.



The situation is different when voltage above threshold voltage is applied through a transparent electrode to the required segments. For example, when we switch on the calculator, number 0 (zero) is displayed on the screen. Because the power from the battery through the electrodes is supplied to outer six (a, b, c, d, e, f) segments, avoiding the middle segment (i.e. g). When power is supplied to outer segments, due to electric effect, they tend to change their orientation by 90^o. So that, the polarized light cannot pass through these 6 outer segments. And no light reaches the bottom polarizer. Since no light reaches back areas, that particular area appears dark, against those areas without an applied voltage appears silvery grey. By electro-optic effect 0 (zero) is displayed.

Suppose, if number 1 is to be displayed, voltage is applied to the two segments b and c. (other segments a, d, e, f, are relaxed.) Applied voltage changes the director configuration from one twist to the reformed state. And no light reaches the bottom polariser. Since no light reaches back areas with an applied voltage appears dark against those areas without an applied voltage appears silvery grey.

Liquid crystals displays are used in

a) Calculators, watches, mobile telephones, laptops computers, etc.

b) Indicators used in automobiles dashboards; airplane cockpits, traffic signals, advertisement boards and petrol pump indicators.

c) Blood pressure instruments, digital thermometers and TV channel indicators.

d) pH meters, conductometers, colorimeters, potentiometers and other analytical instruments.

2. Light-emitting diode (LED): A Light Emitting Diode (LED) is a semiconductor device, which emits light when an electric current passes through it. To emit the light, holes from p-type semiconductors recombine with electrons from n-type semiconductors.

Figure: Light emitting diode

Light-emitting diodes are heavily doped p-n junctions. Based on the semiconductor material used and the amount of doping, an LED emits the colored light at a particular spectral wavelength when forward biased. As shown in the figure, an LED is encapsulated with a transparent cover so that emitted light can come out.

The LED symbol is the standard symbol for a diode, with the addition of two small arrows denoting the emission of light.

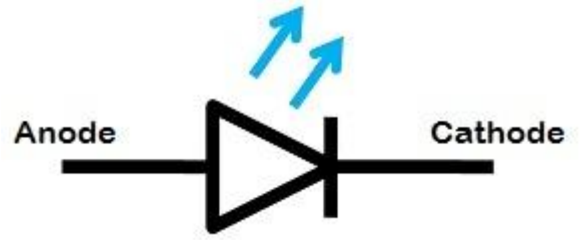


Figure: LED symbol

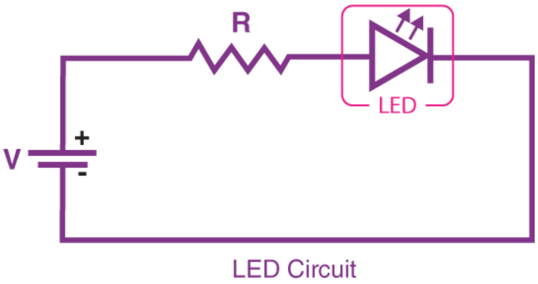


Figure: LED circuit.

Working of LED

The construction of LED is very simple because it is designed through the deposition of three semiconductor material layers over a substrate. These three layers are arranged one by one where the top region is a p-type region, the middle region is active and finally, the bottom region is n-type. In the construction, the p-type region includes the holes; the n-type region includes electrons whereas the active region includes both holes and electrons. LEDs work on the principle of *Electroluminescence*. On passing a current through the diode, minority charge carriers and majority charge carriers recombine at the junction and release energy in the form of photons.

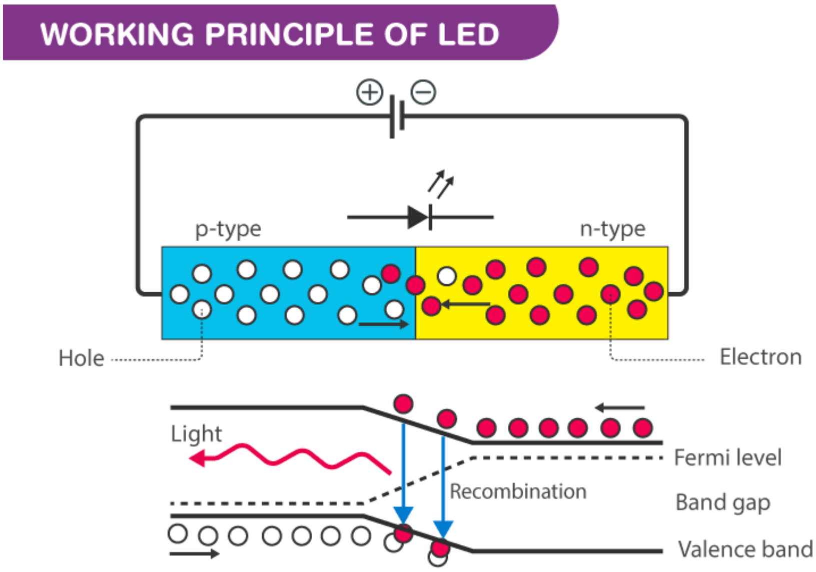


Figure: Working of LED

When the voltage is not applied to the LED, then there is no flow of electrons and holes so they are stable. Once the voltage is applied then the LED is forward biased, so the electrons in the n-region and holes from p-region move towards the active region. This region is also known as the depletion region. When the diode is forward biased, the minority electrons are sent from p → n while the minority holes are sent from n → p. At the junction boundary, the concentration of minority carriers increases. The excess minority carriers at the junction recombine with the majority charges carriers. Because the charge carriers like holes include a positive charge whereas electrons have a negative charge so the light can be generated through the recombination of polarity charges. In forward bias, the electrons and holes are moving fast across the junction and they are combined constantly, removing one another out. Soon after the electrons are moving from the n-type to the p-type silicon, it combines with the holes, then it disappears. Hence it makes the complete atom, which is more stable and it gives the little burst of energy in the form of a tiny packet or photon of light.

Properties of LEDs

- LEDs consume less power, and they require low operational voltage.

- No warm-up time is needed for LEDs.
- The emitted light is monochromatic.
- They exhibit long life and ruggedness.

Uses of LEDs

LEDs find applications in various fields, including optical communications, alarm and security systems, remote-controlled operations, robotics, *etc*. It finds usage in many areas because of its long-lasting capability, low power requirements, swift response time, and fast switching capabilities. Below are a few standard LED uses:

- Used for TV back-lighting
- Used in displays
- Used in Automotives
- LEDs used in the dimming of lights

Types of LED's

1. **Organic Light Emitting Diodes (OLEDs)**

OLEDs are thin film devices consisting of a stack of organic layers sandwiched between two electrodes. OLEDs operate by converting electrical current in to light *via* an organic emitter. It is an electroluminescent device that uses organic molecules as a source of light emission. Light is emitted by organic material when an external field is applied across it.

Properties:

1. **Thinness and flexibility:** OLEDs are very thin and flexible, suitable for use in curved or flexible displays.
2. **High contrast:** OLEDs have a high contrast ratio, which produce deep blacks and bright whites, resulting in images with vivid and rich colours.

3. **Fast response time:** OLEDs have a fast response time, resulting in smooth and seamless motion in video content.
4. **Wide viewing angle:** OLEDs have a wide viewing angle, with which the image quality is maintained even when viewed from different angles.
5. **Energy efficiency:** OLEDs are energy efficient as they do not require a back light like traditional LCD's, resulting in lower power consumption. Applications:

1. Flat-panel TV screens
2. Digital cameras
3. Mobile phones

2. Quantum Light Emitting Diodes (QLED's)

QLED is an electroluminescent device that uses quantum dots (QD's) as a source of light emission.

Properties:

1. **Accurate and vibrant colours**: QLEDs are capable of producing highly accurate and vibrant colours due to their use of quantum dots, which emit light of a specific colour when they are excited by a light source or an electrical current.
2. **Energy efficient**: QLEDs are more energy-efficient than traditional LCD displays because they do not require as much back lighting.
3. **High contrast**: QLEDs have high contrast ratios, which means that the difference between the darkest and brightest areas of the display is greater, resulting in more detailed and life like images.
4. **Long life span**: QLEDs have a longer life span than traditional LCD displays because they do not suffer from the back light burnout or colour fading over time.
5. **Fast response times**: QLEDs have fast response time, which mean that they can

display fast-moving images without motion blur or ghosting.

6. **Flexibility**: QLEDs can be made on flexible substrates, which allows for the creation of flexible displays that can be bent or curved.

Applications:

1. Flat-panel TV screens
2. Digital cameras
3. Mobile phones

3. Light emitting electrochemical cells (LEEC's)

A light-emitting electrochemical cell (LEC or LEEC) is a solid-state device that generates light from an electric current (electroluminescence). LECs are usually composed of two metal electrodes connected by (e.g. sandwiching) an organic semiconductor containing mobile ions.

Properties:

They operate with low voltages, which allows for high power efficiencies.