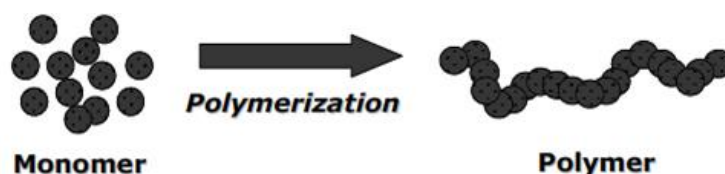


Definition: “Polymers are carbonaceous materials with large molecular masses obtained by covalent linkages of several small repeating units called monomers.

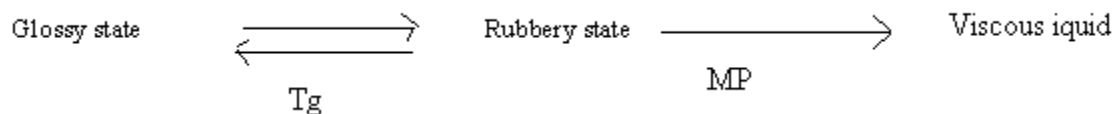
Polymerization: “Polymerization is union of two or more smaller and simpler molecules of similar or different types with or without elimination of any part of the molecule resulting in the formation of new covalent linkages.”



• GLASS TRANSITION TEMPERATURE (T_g)

Unlike in metal article fabrication, the polymers are not melted to the liquid form to fabricate, but heated just to its softening temperature. This is referred to as glass transition temperature.

Definition of T_g : “The temperature at which a polymer abruptly transforms from glassy state (hard state) to a rubbery state (soft state) is called Glass Transition Temperature and denoted by T_g .”



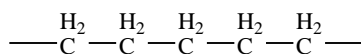
This transition from hard solid state to soft and flexible state corresponds to the beginning of chain motion or rotation about C-C single bonds in polymers. Below T_g polymer is said to be in frozen state.

Parameters affecting T_g:

a) **Chain flexibility:** Free rotational motion imparts flexibility. Rigid structure in the polymer chain or with bulky side chains hinder the freedom of rotation and decrease in flexibility and increase T_g. Hence, highly flexible polymer will have low T_g value.

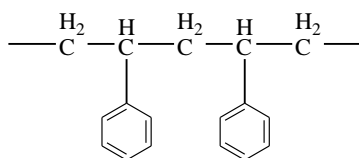
Ex; T_g of polyethylene is -110 °C

T_g of polystyrene is 100 °C



Polythylene

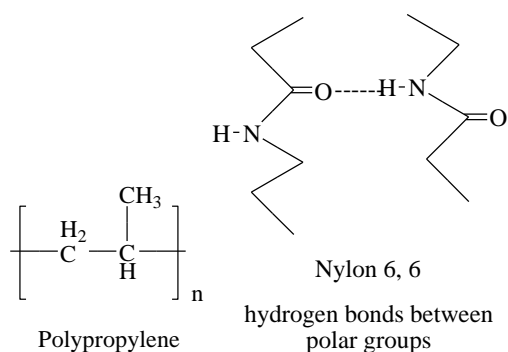
Free rotation of C chain possible



Polystyrene

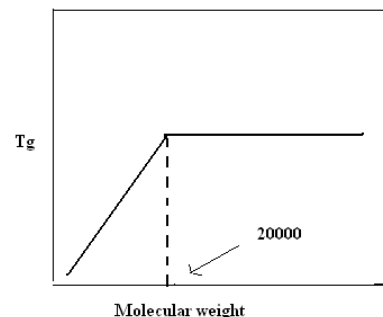
Free rotation of C chain hindered

b) **Intermolecular forces:** Presence of large number of polar groups in molecular chain lead to strong inter molecular forces such as hydrogen bonding, Van der Waals forces etc., and they restrict molecular mobility and hence increase T_g. Hence higher the intermolecular forces higher will be the T_g.



c) **Branching and Cross linking:** A high degree of branching and cross linking in the polymer, brings the molecular chains closer, lowers the free volume reducing chain mobility. This will increase T_g. Hence highly branched and cross linked polymers will have higher T_g.

- a) **Molecular weight:** High molecular weight polymers have greater density and increase in T_g. However, T_g is not significantly affected by the molecular mass if the degree of polymerization is above 250 or molecular mass is above 20000. (graph)

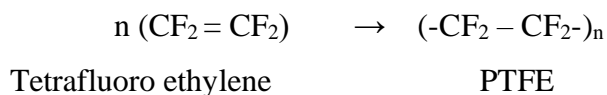


Significance of T_g:

- i) T_g can be used to evaluate the flexibility of a polymer and predict its response to mechanical stress.
- ii) Many polymers change their other physical properties like viscosity, elastic nature, etc., also at T_g. Hence, the use of a polymer at T_g with respect to other properties can be decided.
- iii) Different fabrication works like moulding, shaping, calendaring, etc., can be conveniently carried out with knowledge of T_g, as the entire machinery can be pre-set to that temperature.

• Synthesis, Properties, Applications of TEFLON (Poly tetra fluoro ethylene – PTFE)

Synthesis: It is made by addition polymerization of water emulsion of Tetra fluoro ethylene in aqueous or alkaline medium at 55-240° C in presence of Benzoyl peroxide as catalyst at 1000 PSI pressure.



Properties: 1. High degree of crystallinity of 93-98 %, high melting point of 327° C and high density of 2.3 g cm⁻³.

2. Insoluble in most solvents and chemicals
3. Not wetted by oil and water
4. High thermal stability, strength and insulating properties.

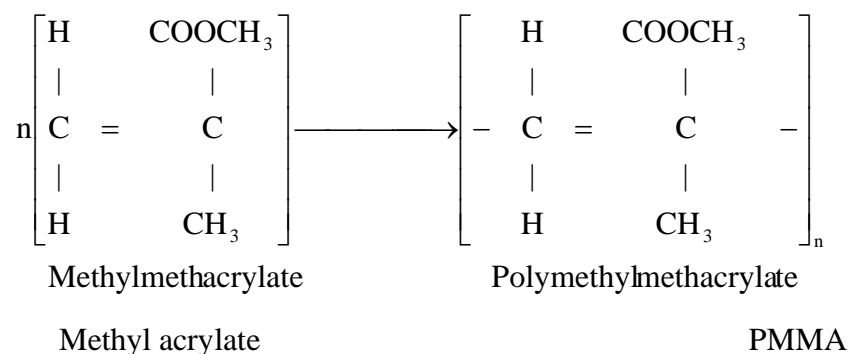
Applications: 1. For insulation in motors, transformers coil and capacitors

2. Making industrial filters, gaskets and belts
3. As non-sticky coating on bakery trays and frying pans
4. As anti-corrosive coating
5. As non-lubricated bearing.

- Synthesis, Properties, Applications of PLEXI GLASS (Poly methyl methacrylate)**

PMMA

Synthesis: it is made by bulk or emulsion polymerization of Methyl meth acrylate in presence of H_2O_2 as initiator at $60\text{-}70^\circ\text{C}$ under atmospheric pressure.



- Properties:**
1. Highly transparent, thermoplastic, softening at 120°C .
 2. Excellent optical properties
 3. Not affected by sunlight but affected by many chemicals and some organic solvents
 4. Has good dimensional stability.

- Applications:**
1. For making lenses, aircraft parts and light fixtures
 2. Used in jewelry, wind screens and TV screens.
 3. For making artificial eyes and denture.
 4. Used in emulsion paints.

- Conducting Polymers**

Most of the polymers are insulators, with desirable properties such as light weight, processability, durability, and low cost. By designing the molecular structures of polymers, chemists have developed new materials that exhibit electrical conductivities comparable to metals while retaining the advantages of polymers. Generally, these electrically conducting polymers are composed of conjugated polymer chains with π -electrons delocalized along the backbone. The polymers are converted to the electrically conductive, or doped, form via oxidation or reduction reactions that

create delocalized charge carriers. Charge balance is accomplished by incorporating an oppositely charged counter ion into the polymer matrix.

An organic polymer with highly delocalized pi-electron system, having electrical conductance of the order of a conductor is called a conducting polymer.

Synthesis:

An organic polymer can be converted into a conducting polymer if it has

- ⇒ Linear structure
- ⇒ Extensive conjugation in polymeric back bone (pi-back bone)

The conducting polymers are synthesized by doping, in which charged species are introduced in organic polymers having pi-back bone. The important doping reactions are:

- ⇒ Oxidative doping (p-doping)
- ⇒ Reduction doping (n-doping)
- ⇒ Protonic acid doping (p-doping)
- ⇒ Normally electron in a polymer are localized and do not take part in conducting but doping can create delocalized electrons and responsible for conduction.

Mechanism of conduction:

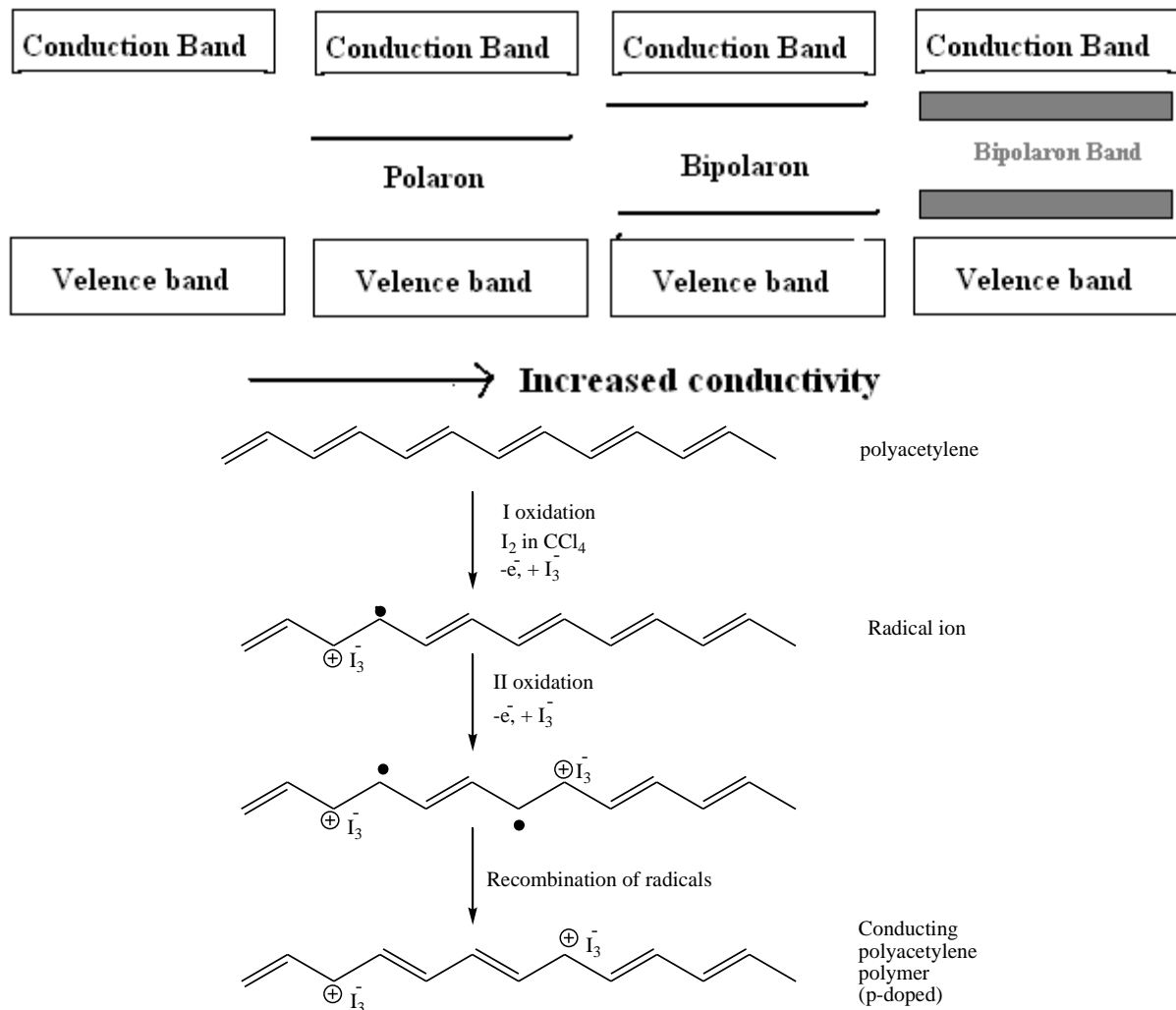
- ⇒ Band theory of solids has been used to explain the conduction mechanism in conducting polymers. The neutral polymer (insulator) be transferred into a conductor by doping with electron donar (reducing dopant such as sodium naphthalide) or an electron acceptor (Oxidative doping (p-doping) - like iodine vapor, FeCl_3 , iodine in CCl_4 , HBF_4 , perchloric acid, etc and benoquinone)

The removal of an electron from the polymer pi-back bone using a suitable oxidizing agent leads to the formation of delocalized radical ion called polaron.

A second oxidation of a chain containing polaron, followed by radical recombination yields two charge carriers on each chain. The positive charge sites on the polymer chains are compensated by anions (I_3^-) formed by the oxidizing agent during doping.

The delocalized positive charges on the polymer chain are mobile, not the dopant anions. Thus, these delocalized positive charges are current carries for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction. On doping polyacetylene

using iodine in CCl_4 , for partial oxidation, the conductivity increases from $10^{-5} \text{ S. cm}^{-1}$ to $10^3\text{-}10^5 \text{ S.cm}^{-1}$.



Question Bank on polymers:

1. Give the synthesis, properties and applications of:
 - (i) Teflon
 - (ii) PMMA
2. What is glass transition temperature? Mention its significance. Explain any two factors that affect the glass transition temperature of a polymer.
3. What are conducting polymers? Explain the mechanism of conduction in polyacetylene.

Unit -5 Liquid crystals

Q- What /define are liquid crystals? Explain molecular ordering positional and orientational order in solid, liquid and liquid crystals. Mention general applications of liquid crystals.

Definition: Liquid crystals (LCS) may be defined as *the distinct state of matter, in which the degrees of molecular ordering (positional and orientation order) is lies between ordered anisotropic crystalline state and completely disordered isotropic liquid state.*

The terms *mesophase* and *mesogen* also refer to the liquid crystal state. Liquid crystals exhibit optical anisotropy, i.e., they possess different optical properties when light is incident in different directions. Liquids, however, exhibit optical isotropy i.e., they exhibit the same optical property irrespective of the direction of the incident light. All LCS are organic molecules with *rod* or *disk* shape.

Positional and orientational order in solids, liquids and liquid crystals:

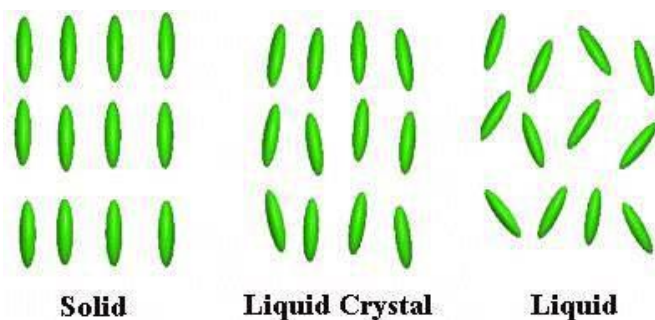


Figure 1: Positional and orientational order in solids, liquids and liquid crystals

In solid crystal state, the molecules are highly ordered. Each molecule occupies a definite position in a more or less rigid arrangement and in immobile rigid arrangement and orient in a preferred direction.

In liquid state, the molecules neither occupy specific positions nor remain oriented in a particular manner. The molecules are overcome with cohesive forces of attraction and are somewhat free to move at random colliding with one another and change their position abruptly.

Intermediate state between the solid state and the liquid state exists another metastable state is called Liquid crystalline phase, wherein the molecules are free to move but are oriented in a particular manner.

For example: Solid cholesteryl benzoate (CB) on heating becomes hazy liquid, which on further heating turns into a clear and transparent liquid. On cooling these changes were observed exactly at the same temperature. Between 145 °C and 179 °C the temperature at which it converts into the liquid crystalline state is called *phase transition temperature*. The temperature at which the transition from liquid crystalline state to isotropic liquid (179 °C) state is called clearing temperature.

The structure of cholesteryl benzoate is given below.

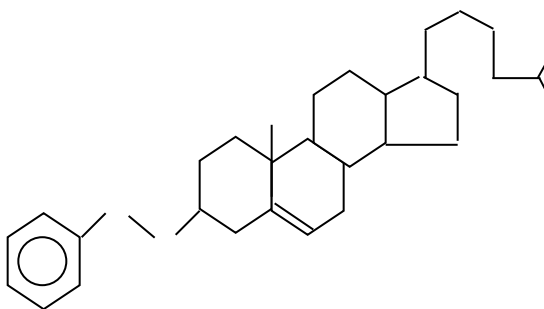


Figure 2: Structure of cholesteryl benzoate

General applications of liquid crystals: liquid crystal find application in areas of science and engineering, particularly in display systems. Devices using liquid crystalline displays (LCD) have the advantages of low power consumption at lesser cost and hence widely used in electro-optic displays like mobile communication, high-resolution T.V displays, calculator, aircraft cockpit etc. Liquid crystal also finds application in temperature sensors, thermography, pressure sensor etc.

Q- What is Director? Explain its significance.

- **Director and its significance:** In a liquid crystal the molecule passes orientational order i.e. the molecule tends to remain a particular direction. *The direction of preferred orientation of molecules*

in a liquid crystalline phase is called a director. Since molecules are in constant motion and they spend more time pointing along the director than any other direction. Hence the extent of orientational order can be described by taking an average angle Θ made by different molecules with the director.

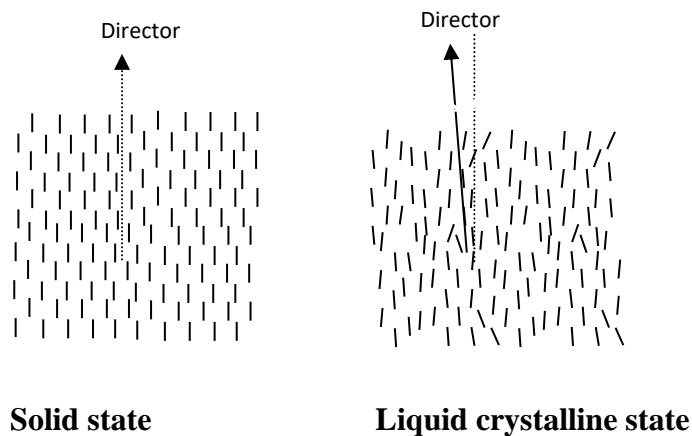


Figure 3 : Director in solid state and liquid crystalline state

Significance of director :

1. An average angle of 0° indicates perfect orientation and can be expected in solid crystals.
2. Liquid crystals exhibit a smaller average angle ($0 - 5^\circ$) with the director.
3. An average angle greater than 45° indicates no orientational order as found in liquids.

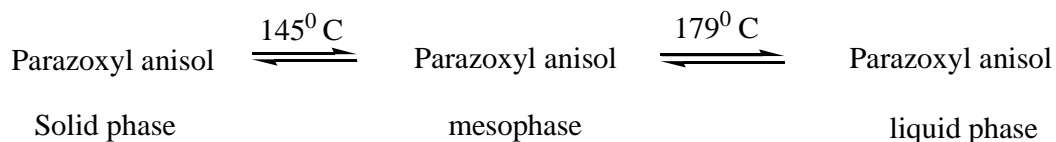
Q- Discuss the classification of liquid crystals with suitable example

Or Explain the molecular ordering in Thermotropic, Lyotropic and columnar liquid crystals.

Classification of Liquid crystals: Liquid crystals are classified into three main categories namely

- (i) Thermotropic
- (ii) Lyotropic
- (iii) Columnar

(i) Thermotropic liquid crystals: The class of compounds that exhibits crystalline behavior or variation of temperature alone is called thermotropic Lcs. More no. of thermotropic Lcs are formed from organic molecules with a rod like shape.



Thermotropic liquid crystals are obtained by raising the temperature of solid and by lowering the temperature of the liquid. Thermotropic LCS are further classified into 3 phases

- (a) Nematic
- (b) Smectic
- (c) Cholesteric (chiral or twisted)

(a) Nematic mesophase: The liquid crystalline phase is made up of optically inactive rod - like molecules. In this phase, the molecules have no layered structure. The molecules in nematic phase possess intermolecular forces such that they are parallel to one another and hence nematic phases are characterized by the total loss of positional order and their behavior is very close to their anisotropic liquid phase. When the nematic phase is observed in polarized light the molecule appears to have thread like texture.

Example: P-azoxy anisole (PAA) which is stable between 118 -135 $^{\circ}\text{C}$

Applications: Nematic phase liquid crystals are widely used for displays. This is based on change of plane polarization during the application off the electric field.

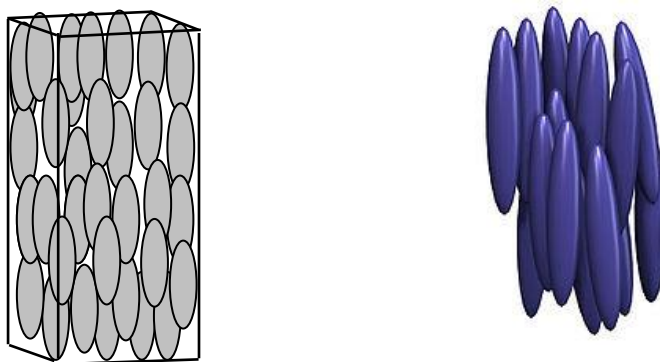


Figure 4: Nematic liquid crystal

(b) Smectic mesophase: Smectic phased molecules are cigar-shaped molecule and are arranged in layers. In this mesophase, the molecules possess a small amount of positional order and orientational order. The molecules tend to point along

the direction and can move forward and backward but not up and down i.e. 2-dimensional motion can be possible. Based on the orientation of the director there are 9 types of smectic phases identified [smectic A to I]

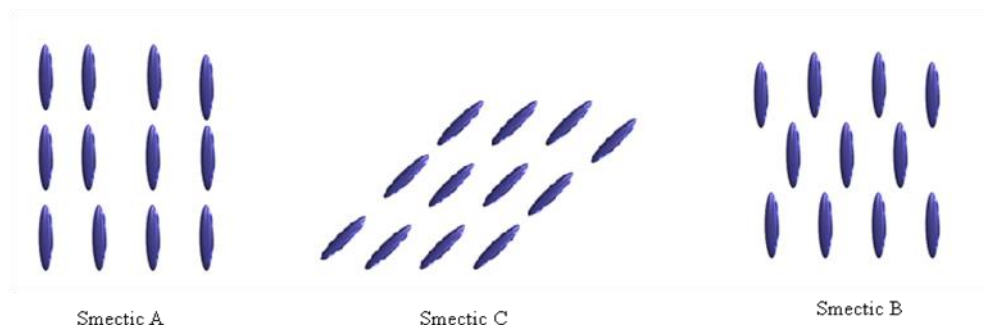


Figure 5: Smectic mesophase

Example: 4-n-butyloxy benzylideneamino-propiophenone (Smectic C)

4,4'-di-heptyloxyazoxybenzene. (Smectic C)

(c) Cholesteric or chiral or twisted mesophase: They are formed from optically active compounds having chiral (twisted) centers. In this mesophase, all the molecules stay parallel to one another and arrange themselves at different angles with respect to their adjacent groups. In this mesophase the director rotates throughout the sample forming a helical pattern as it changes just like a nut screwed on a bolt. The distance covered by a director as it completes one full turn (360°) is called the 'pitch' of the liquid crystal. The pitch repeats throughout the substance.

The pitch length of a cholesteric varies sensitively with temperature, pressure, impurities, electric field. The most striking feature of cholesteric mesophase is strong optical activity and selective reflection, which are attributed to the twisted structure.

The twist present in these mesophases makes them to exhibit spectacular optical properties, which are made use of in displays. A cholesteric Liquid Crystals rotates the direction of linearly polarized light. The pitch length is temperature dependent and hence cholesteric liquid crystals are used in thermography.

Example: cholesteryl benzoate, cholesteryl formate

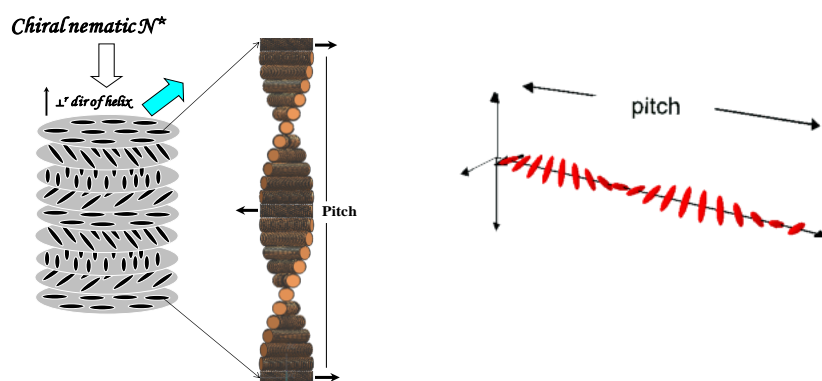


Figure 6: Cholesteric or chiral or twisted mesophase

(ii) **Lyotropic liquid crystals:** Liquid crystals that are obtained by mixing the two components - organic solids compound (amphiphilic) and polar solvent. Increasing the concentration of the one of the components till liquid phase is obtained such liquid

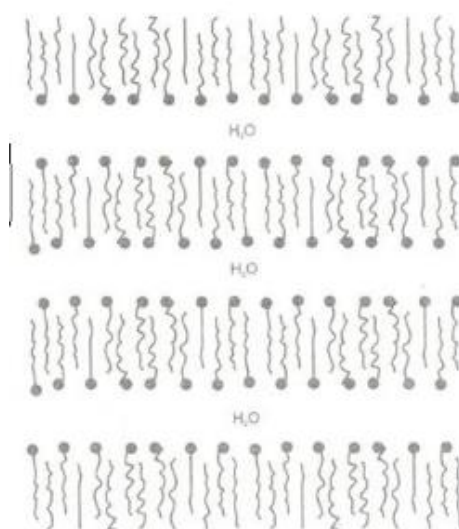


Figure 7: Lyotropic mesophase

crystals are called lyotropic liquid crystals. The amphiphilic or amphiphile compound possesses two groups that differ greatly in their solubility properties. One part of the molecule has 'hydrophilic head' which is highly soluble in H_2O . While other part has hydrophobic or lyophobic tail which is highly soluble in hydrocarbon solvents.

In the lyotropic phase, the water is sandwiched between the polar heads of adjacent layers of amphiphilic molecules. Example:

1. Soap water mixture
2. DNA
3. Synthetic polypeptides
4. Biological compounds such as proteins, nucleic acid, also exhibit lyotropic type of liquid crystalline behaviour in water.

(iii) Discotic or Columnar Liquid Phase

The liquid crystal phases so far discussed are usually made of rod-like (elongated) molecules. Liquid crystals are also formed by molecules which have disk like or plate like structure. These are referred to as *discotic* or *columnar* liquid crystals.

The simplest discotic phase is also called the *nematic discotic* phase because there is orientational order but no positional order (Fig. 1.7a). There is random motion of the molecules, but on an average, the axis perpendicular to the plane of each molecule tends to orient along the director. In the *smectic discotic* or *columnar* phase, in addition to the orientational order present in the nematic discotic phase, most of the molecules tend to position themselves in columns (Fig. 1.7b). The columns are arranged in a hexagonal lattice resembling a set of coins stacked as shown below (note: the coins in a stack have a great deal of positional order i.e., the coins are equidistant whereas the molecules in a columnar phase are stacked in random fashion).

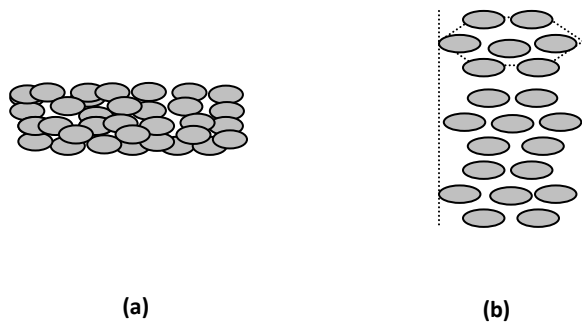


Fig. 8 Schematic representation of disc like molecules arranged in (a) nematic discotic (b) smectic discotic (columnar) liquid crystal phases

Q- What are the requirements for an organic molecule to exhibit Liquid crystalline behaviour ?

The requirements of a molecule to form liquid crystal are:

- (i) the molecules should be elongated in shape and
- (ii) appreciable part of the molecule should have rigidity with preferably flexible ends. In some liquid crystals the central part of the molecule is rigid with flexible ends (See Figure below).
- (iii) in some others, rigid segments are attached along its length by short flexible segments as in polymers. The flexible part twists its way throughout the substance causing the molecules to lose its positional order.

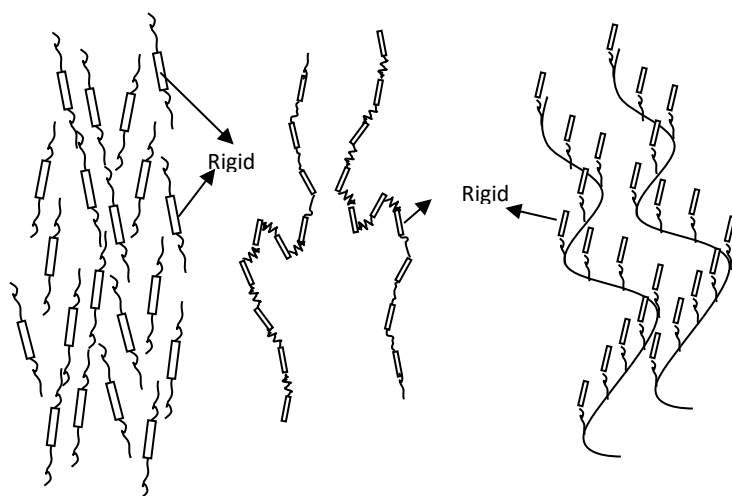
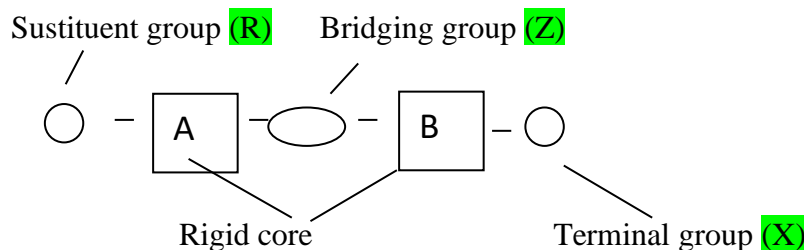


Figure 9. Orientational order in liquid crystals – illustration of how rigid segments help in maintaining orientational order in (a) molecules with rigid central part and flexible ends (b) chains where rigid groups are attached through flexible segments and (c) flexible chains with side chains carrying rigid segments

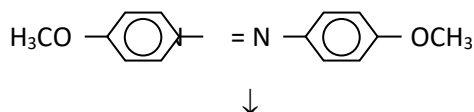
But, the rigid segments in the molecule attempts to maintain the orientational order typical of liquid crystals. In addition, elongated molecules have strong attractive forces when they are aligned parallel to one another. The collision of the molecules with one another is less and all of them tend to point in one direction and thus the mesophase is stabilized. The flexibility of the ends allows a molecule to position itself more easily between other molecules when they move about.

Q- Explain the basic structure of liquid crystals.

For many liquid crystals, their chemical structure can be represented as follows:



Ex:



In the structure, R is called substituent group, A & B are aromatic groups/rings. Z is linking group and X is terminal group.

Side Chain [R] (Substituent group): Three commonly used side chains are: (i) Alkyl group
(ii) Alkoxy group (iii) Alkynyl group (iv) alkynyl oxy group

The length (the number of carbon atoms) and flexibility of the substituent group affect the phase transition and type of mesogenic phase. When the number of carbon atoms in the side chain is less (3-5, lower order) show the nematic phase. When the number of carbon atoms in side chain is more (9-12, higher - order) shows only smectic phase. When the number of carbon atoms in side chain is more (6-8, middle - order) show nematic and smectic phases.

Linking group or bridging group: it contributes to the phase transition temperatures and physical properties of liquid crystalline phase. Several linking groups have been used:

Aromatic rings [A & B]: most of the compounds exhibiting liquid crystalline phase, consists of one or more aromatic rings. These aromatic rings may be phenyl, biphenyl, terphenyl or a combination of the above rings.

Usually longer the rigid core, the higher is the transition temperatures.

Terminal group (X): Several terminal groups have been used like Alkyl group, Alkoxy group, Alkynyl group, Alkynyl oxy group, halogens,, Nitro (-NO), amino, sulphide cyano (CN) etc

Q- What is homologous series? Explain liquid crystalline behavior in homologous PAA series?

A series of compounds of the same type wherein successive members differ in their molecular formula by CH_2 group is called homologous series. The composition of any homologous series can be expressed by a general formula C_nH_{2n+1} .

The thermal stability of a liquid crystal compound is depending on the structure. Therefore, the thermal stability of members of a homologous series changes with change in the number of C-atoms in the chain. On heating a liquid crystalline compound, they undergo change from highly ordered arrangement in solid state to disordered isotropic liquid through anisotropic liquid crystalline state. It is interesting to study the phase transition that occurs on heating in homologous series of a liquid crystal.

When the transition temperatures are plotted for a homologous series against the number of C-atoms in the n-alkyl chain of the molecule, certain smooth transition curves are obtained. For a given series, the upper curve represents the transition from liquid crystalline state to the isotropic liquid state (clearing temperature) and the lower curve shows the transition from solid state to liquid crystalline state (transition temperature). The region between two curves gives the range of temperature at which the liquid crystalline state exists.

Generally, the first few homologous are purely nematic, the middle will form both nematic and smectic mesophases and the higher homologous does not show significant variation.

PAA homologous series: The liquid crystal of para azoxy anisole (PPA) is stable between 118°C and 135°C . PAA has more than 12 homologous which are formed when $-CH_2$ groups are added to its side chain. Plot of the transition temperature against the number of C-atoms in the PAA is shown in fig.

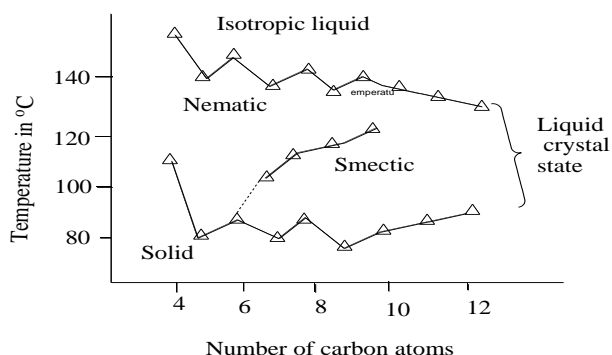
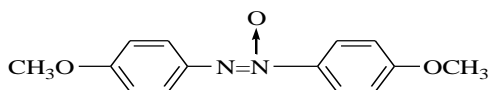


Figure 9: Phase transition temperature against the number of C-atoms in PAA

From the Figure, the phase transition of PAA is given by

1. When the group (side chain) contains 1-5 C-atoms, the transition is from solid to nematic, nematic to isotropic liquid.
2. Homologous containing 6- 10 C-atoms shows a transition from solid to smectic, smectic to nematic before melting to a liquid.
3. When the number of C-atoms is greater than 10, shows a transition from solid to smectic, smectic to liquid.

Q- Explain the display mechanism in liquid crystals. Or Explain the electro-optic effect of liquid crystals. How is it utilized in display systems?

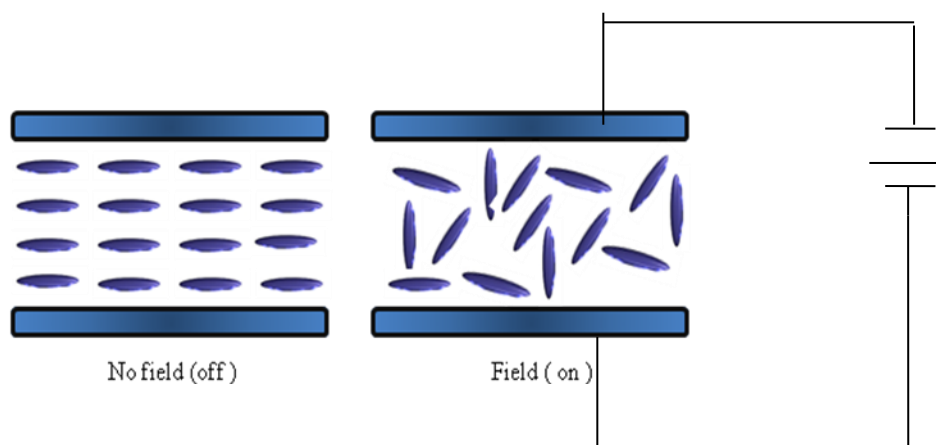


Figure 10 : Electrooptic effect in Nematic liquid crystals.

Effect of light on chiral liquid crystals: 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.

When a thin film of chiral liquid crystal is placed between two crossed polarizers, in absence of electric field the pitch in chiral liquid crystal acts like a wave and gradually rotates the plane polarization of light by 90° . Hence a linearly polarized light incident on the cell emerges as bright light. The 90° twist in the cell is lost when the sufficiently strong electric-field is applied to the \propto till it looks dark. The following conditions are necessary to show electro optic effect in the chiral liquid crystals.

1. The plane polarization of the light should be parallel to the surface of the first polarizer

The product of the optical anisotropy ' Δn ' (the difference in the refractive indices parallel and perpendicular to the director) and pitch ' p ' should be greater than the wavelength of the incident light.

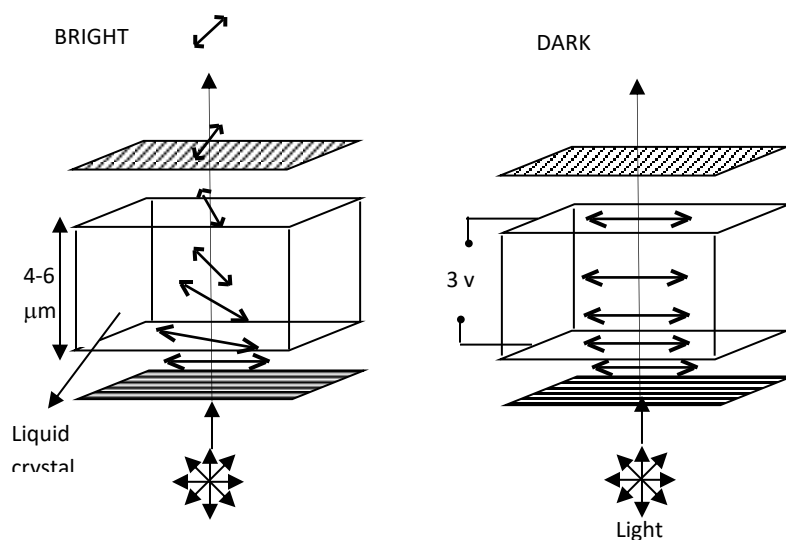


Figure 11: Electrooptic effect in chiral liquid crystals.

Application in Display systems

This is used in information display systems, where liquid crystals control the brightness or darkness of parts of a display device. Numbers can be created in numeric displays which have seven segments (also called pixels). Alphabets can be displayed on a fourteen segment arrangement.

A numeric display consists of seven segments for each digit. Each segment is a liquid crystal. Light emitted by each crystal can be independently controlled so that any digit can be displayed. When an electric field is applied to a segment, the liquid crystal is deformed and when polarized light is incident, it gets brightened. By using dichroic dyes, the contrast between bright and dark areas can be enhanced and required colours can be obtained.

One of the most important effects of electrooptic effect (of nematic and chiral liquid crystals) is in liquid display systems (LCD). Electro-optic effect of liquid crystal controls brightness and darkness of emergent light.

LCD requires a very small current. Most of the display in LCD watches and calculators composes of 7 segments. Each seven segments section can display one number. The 14- segments LCD are used of alphabets. Light from the area of each segment are controlled independently and creation of any digits or alphabets is possible. 5x7 matrix segments are used for numbers, letters and figures.

A 7-segment display (Figure 14) consists of seven segments for each digit (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 ten digits becomes possible. When an electric field is applied to a segment, the liquid crystal in that segment undergoes deformation (is activated) and when polarized light is incident, the segment gets brightened. A typical liquid *crystal display cell* (reflection mode) and the electrical circuit with four rows and two columns for a digit to appear is shown in below Figures.

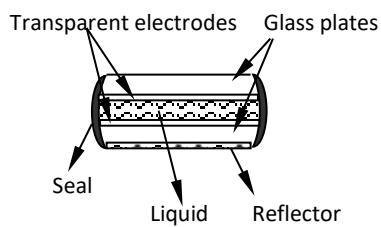


Figure 12: Representation of a liquid crystal display (reflection mode pixel) where the liquid crystal is embedded between two glass plates

In the Figure 14, when voltage applied to

- i) Row 1 column I activate the liquid crystal in an area **a** which gets brightened.
- ii) Row 2 column I activates the liquid crystal in an area **d** which gets brightened.
- iii) Row 3 column I activates the liquid crystal in an area **e** which gets brightened.
- iv) Row 1 column II activates the liquid crystal in an area **b** which gets brightened.
- v) Row 2 column II activates the liquid crystal in an area **c** which gets brightened.
- vi) Row 3 column II activates the liquid crystal in an area **f** which gets brightened.
- vii) Row 4 column II activates the liquid crystal in an area **g** which gets brightened.

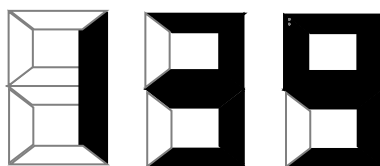
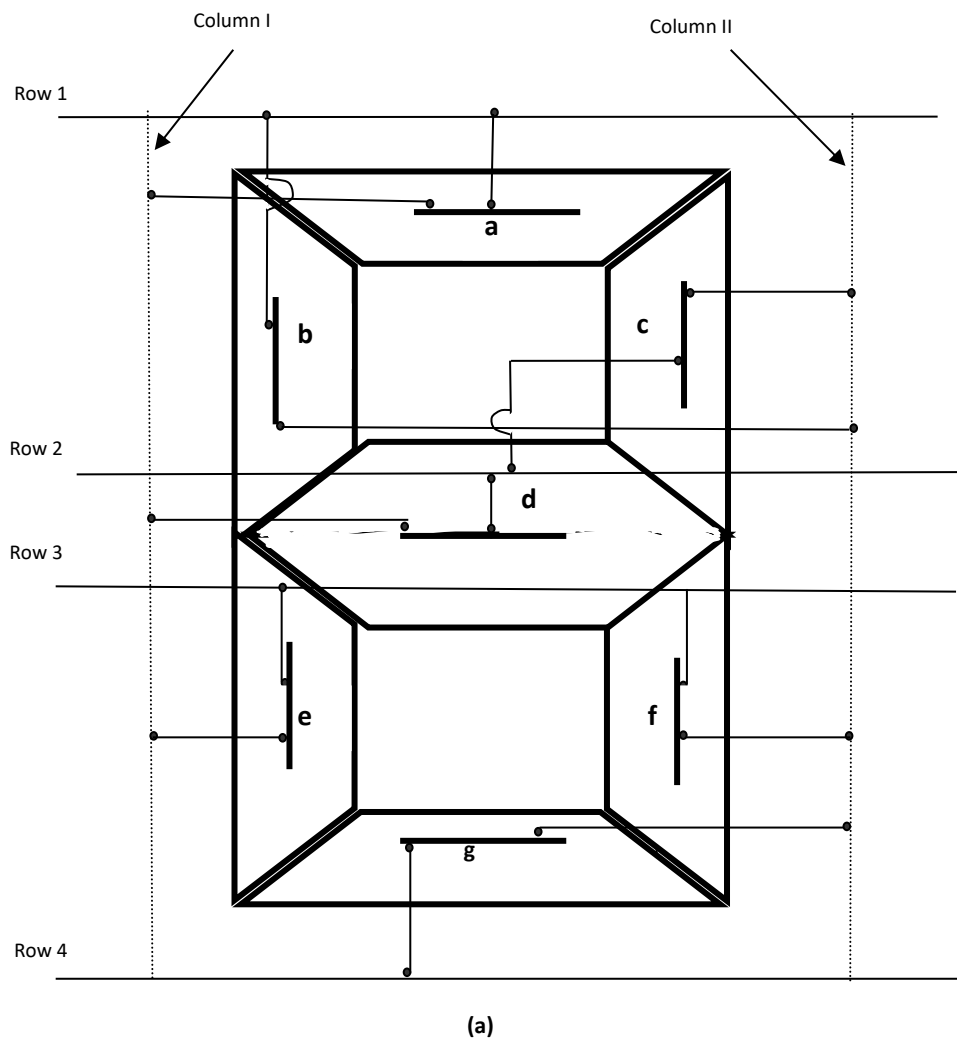


Figure 13: Seven segment LCD for a digit; each row is connected to two segments and each column is connected to three or four segments; a, to g are the LCD cells. (b) display of number 139

For example, to get a number 139 on the display (Fig.b) an electric field is applied between row 2 and column II (operation v) and between row 3 column II (operation vi) to give '1'

In the second digit operations (i), (v), (vi) and (vii) give '3'

In the third digit operations (i), (ii), (iv), (v), (vi) and (vii) give '9'. Thus the digits 139 appears on the display.

To enhance the difference in the brightness between dark (turned OFF, voltage removed) and bright areas (turned ON, voltage applied), dyes are used. Dyes used in liquid crystal displays are called *dichroic dyes* and give desired colours to the displays with a good contrast.

Various electric equipment's use LCD's:

1. Calculators, watches, mobile, telephones, laptops.
2. Indicators used in traffic signals, advertisement boards, petrol pump indicators etc.
3. In analytical instruments like pH-meter, conductometer, colorimeter, potentiometer etc.

Question Bank on liquid Crystals

1. What are liquid crystals? How are they classified? Give examples.
2. What is a director in liquid crystal terminology? Explain its significance
3. Distinguish between thermotropic and lyotropic liquid crystals
4. Distinguish between nematic discotic and smectic discotic phases
5. Explain the molecular ordering in the following liquid crystal phases (a) Nematic phase (b) Chiral mesosphere (c) Smectic phase (d) Discotic or Columnar Liquid Phase

6. Explain the liquid crystalline behavior in PAA homologous series.
7. Explain the electro-optic *effect* of liquid crystals. How is it utilized in display systems?