INTRODUCTION

LIQUID CRYSTALS

1. GENERAL:

The liquid crystalline state has been discovered more than one hundred years ago. In the liquid crystalline state of matter, molecular order is intermediate between the ordered crystals and disordered liquids. Liquid crystals have become more popular due to their applications in electronic display devices, commonly known as "LCD" incorporated in common gadgets like watches, calculators etc.

Reinitzer (1), an Austrian botanist in 1888, for the first time observed that cholesteryl benzoate, in contrast to the normal behaviour of the organic compounds in general exhibited two "melting points" one at 145°C when the fluid has a coloured cloudy appearance and the other at 175°C when the melt exhibiting vivid colours vanishes like other compounds. The phenomenon is reversible. He referred this compound to Otto Lehmann (2) to investigate this phenomenon in detail. Otto Lehmann (2) synthesized many organic compounds which exhibited similar behaviour. This study gave birth to new phenomenon called liquid crystallinity. By 1970, the idea of application of liquid crystals in electronic display devices lead to great upheaval in this field and many scientists started working in this field of liquid crystalline materials.

The list of books and reviews (3-9) is indicative of interest in the field of liquid crystals.

Liquid crystals are classified into two major groups on the basis of the manner in which they are obtained (10-12) viz. Thermotropic liquid crystals and lyotropic liquid crystals. Those liquid crystals whose phase transitions are brought about by means of heat, are referred to as thermotropic liquid crystals. Liquid crystals, which are formed by the forces of solvents are termed as lyotropic liquid crystals. Increasing amount of heat or solvent results in the completely disordered state of an isotropic liquid or true solution for the thermotropic and lyotropic liquid crystals, respectively. Gray and Winsor (13) prefer the term 'amphiphilic' and 'non-amphiphilic' for lyotropic and thermotropic liquid crystals, respectively.

Though the terms "Liquid crystals" and "Crystalline liquids" have been widely used to designate these compounds from early times, objections have been raised to the nomenclature on the grounds that the state is neither true liquid nor true crystalline solid. Terms such as 'mesomorph', 'mesoform', 'mesophase', 'mesogen' and 'mesomorphism' are widely used in contemporary literature.

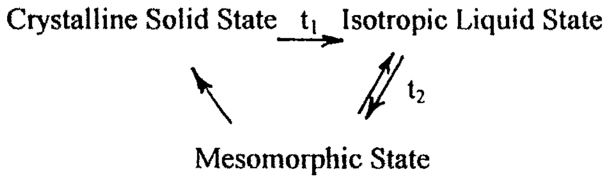
Brown and Shaw used (14) the term "mesomorphism". However, the term "liquid crystals" is still more frequently used.

2. Thermotropic Liquid Crystals

Liquid crystalline molecules are long and rod shaped or disc type having polar groups which are responsible for ordered alignments In a crystalline solid, if the conditions are favourable for mesomorphisms, the ordered structure breaks down in stages, first passing into liquid crystalline state. This state has a certain degree of order and hence acquires anisotropic properties. Further heating destroys the orientation of the molecules and the mesophase finally changes to isotropic liquid. The mesophase obtained is termed enantiotropic which takes place reversibly on heating and cooling, though the reversal to the solid phase is usually accompanied by supercooling. The schematic representation for enantiotropic mesophase is as under.

$$\begin{array}{ccccc} \text{Crystalline} & \overset{t_1}{\rightleftharpoons} & \text{Liquid-Crystalline} & \overset{t_2}{\rightleftharpoons} & \text{Isotropic} \\ & & \text{OR} & & \\ \text{Solid State} & & \text{Mesomorphic state} & & \text{Liquid state} \end{array}$$

The transitions t_1 and t_2 take place at sharp definite temperatures and are precisely reversible. However, in some instances, a solid melts to an isotropic liquid at temperature t_1, on cooling the temperature may fall considerably below t_1 and mesophase may appear at temperature t_2 before the crystallisation occurs. This type of mesomorphic state where, t_2 is at lower temperature than t_1 and is observed only on cooling is known as monotropic mesophase. The schematic representation for monotropic mesophase is as under:



The monotropic temperature t_2 is also reversible and if mesomorphic state is heated, isotropic liquid is obtained at temperature t_2.

On the basis of the molecular arrangements, Friedel (10) classified thermotropic liquid crystals into two broad classes - smectic and nematic. Often the cholesteric phase is described separately, but it is also known that this is a twisted nematic mesophase.

Liquid crystalline compounds may either exclusively be smectic and nematic or smectic and cholesteric or they may exhibit polymesophase. There may be more than one type of mesophase present in the same compound. The transition temperatures are always definite and define the stability of different mesophases. The change with increasing temperature may be represented as:

$$\begin{array}{c}\text{Crystalline}\\\text{Solid State}\end{array} \xrightleftharpoons{t_1} \begin{array}{c}\text{Smectic}\\\text{mesophase}\end{array} \xrightleftharpoons{t_2} \begin{array}{c}\text{Nematic or}\\\text{cholesteric}\\\text{mesophase}\end{array} \xrightleftharpoons{t_3} \begin{array}{c}\text{Isotropic}\\\text{liquid}\\\text{state}\end{array}$$

There are many substances possessing more than one type of the same phase. The Phenomenon is known as polymorphism and is commonly observed for smectic mesophase.

$$\begin{array}{ccccccccc} \text{Crystalline} & \xrightleftharpoons{t_1} & \text{Smectic} & \xrightleftharpoons{t_2} & \text{Smectic} & \xrightleftharpoons{t_3} & \text{Nematic} & \xrightleftharpoons{t_4} & \text{Isotropic} \\ & & \text{II} & & \text{I} & & \text{or} & & \\ \text{Solid State} & & \text{(smectic-B)} & & \text{(smectic-A)} & & \text{Cholesteric} & & \text{liquid} \end{array}$$

2.1 Smectic Liquid Crystals

The term "smectic" originated from the Greek word "smectose" meaning soap like and was coined by Grandjean (15) as smectic mesophase is viscous, turbid liquid with reminiscent properties of a soap. It was first used for ammonium oleate a soap salt.

The smectic phase is the most highly ordered with the molecules arranged in definite layers. These layers can slide over one another because the molecules are free to move from backward and forward, but not up and down. It is best illustrated as a box of penciles or cigars.

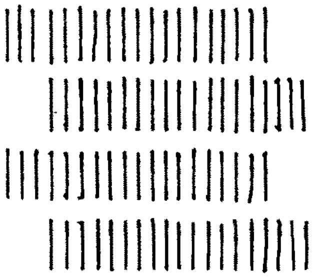


FIGURE 1 : A schematic representation of molecular arrangement in two plane smectic strata.

In the smectic phase the layers of molecules are quite flexible. If a single sheet could be suspended in space free from gravity it would take a form of a perfectly flat surface and side to side attraction of the molecules in the sheet would be the strongest on it. Apparently the cohesions between these layers would be relatively weak which accounts for the characteristic layer flow observed in the stepped drops. A number of such smectic sheets as laid on top of one another, like the pages of a book, will tend to adjust further so as to let ends of the molecules in one sheet fit in some characteristic way to the ends of the molecules in the adjacent sheet

A film of smectic phase stretched over a small hole in a plate gives the condition of parallel sheets. The resulting structure is optically extinct and is said to be homeotropic. The homeotropic phase is characterised by the formation of series of strata or terraces. These terraces are called the Grandjean terraces after their discoverer Grandjean (15). The stratified structure of the smectic phase was inferred from the formation of stepped drops observed under microscope and has been confirmed by X-rays (16).

When smectic phase is formed on cooling the isotropic liquid, it first appears frequently in the form of non-spherical characteristic elongated birefringent particles which are known as batonnets. These increase in number as the temperature falls, coalesce and show evidence of a focal conic texture, when examined in polarized light The focal-conic texture is originated due to lack of common orientation of the smectic sheets as they are formed Bragg (17) has given an excellent account of the focal-conic structure and geometry involved, which furnish further evidence for the layer theory of the smectic structure

Saupe (18) has classified smectic mesophases into two groups based on the proposal of Hermann (19); (a) smectic phases with unstructured layers and (b) smectic phases with structured layers. In the first group the distribution of the molecular centres within the layers corresponds to that of a two-dimensional liquid. It is without long range order. In the second group the layers are built up regularly so that the positions of the molecular centres lie on a two dimensional lattice. The most common smectics are in the first group which includes the phases classified as smectic-A and smectic-C. A representative of the second group is classified as smectic-B. The extensive work of Sackmann and Demus (20) and of de Vries (21) has revealed some of the details of the molecular arrangements of these phases. The most common smectic phases are designated as A, B and C. Sackmann and Demus (20) have classified smectics according to the texture observed in the mesophase (Table 1). They identified seven smectic phases from S_A to S_G (20) by miscibility studies. de Vries and Fishel (22) have reported the eighth possible smectic phase S_H.

Moreover, de Vries (23) has classified smectics into three main classes on the basis of X-ray studies. The class first contains smectic A, C, F and D; the class second contains smectic E, G and H; the class third contains the smectic B.

As suggested by Gray and Goodby (24) the thermodynamic ordering of known smectic polymorphic forms appears to be as follows:

$$\underset{\text{thermal stability decreases}}{\xrightarrow{\text{A, D, C,F, B, H, E, G,}}}$$

Smectic mesophases are optically positive and behave optically in the same way as uniaxial crystals. Gray (24) and Demus (25) have given an excellent review on the textures of different smectic phases with photographs

Table 1

Texture classification of smectic mesophases

Type of smectic mesophase	Structure	Texture
Smectic-A	Planar	i) Stepped drops
		ii) Oily streaks
		iii) Homeotropic
	Non-planar	i) Simple polygonal texture
	(DUPIN –	ii) Simple fan shaped texture
	-Cyclides)	iii) Batonnets
		iv) Bubbletextures
	Cylinders	i) Myelinic textures
Smectic-C	Planar	i) Homogenous texture
		ii) Stepped drops
		iii) Schileren texture
	Non-planar	i) Broken polygonal texture
	(DUPIN –	ii) Broken fan shaped texture
	-Cyclides)	iii) Batonnets
	Twisted	i) Planar texture
		ii) Schlieren texture
		iii) Straited fan shaped textures
Smectic-F	Planar	i) Schlieren texture
		ii) Stepped drops

	Non-planar (DUPIN-Cyclides)	i)	Stripped, broken fan shaped textures
Smectic-B	Hexagonal	i)	Mosaic texture
	Planar	ii)	Homeotropic texture
		iii)	Stepped drops
		iv)	Batonnets
		v)	Ovals
		vi)	Lancets
	Non_planar (DUPIN-Cyclides)	i)	Focal conic texture (Paramorphosis)
	Tilted	i)	Mosaic texture
		ii)	Planar texture (Optically active)
Smectic-E	Planar	i)	Mosaic texture
		ii)	Stepped drops
	Non-Planar	i)	Straited
		ii)	stripped fan shaped texture
Smectic-C	Planar	i)	Mosaic texture
		ii)	Stepped drops
Smectic-D	Cubic Bands	i)	Isotropic mosaic texture

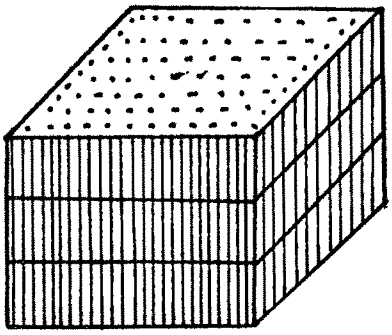


FIG. 2 SCHEMATIC STRUCTURE OF SMECTIC 'A'

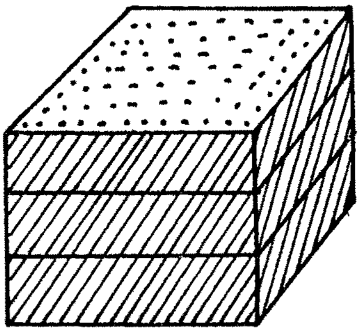


FIG. 3 SCHEMATIC STRUCTURE OF SMECTIC 'C'

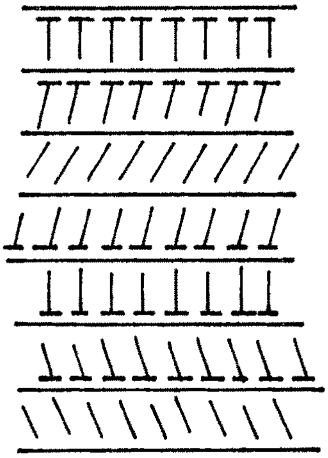


FIG. 4. SCHEMATIC STRUCTURE OF SMECTIC 'C'

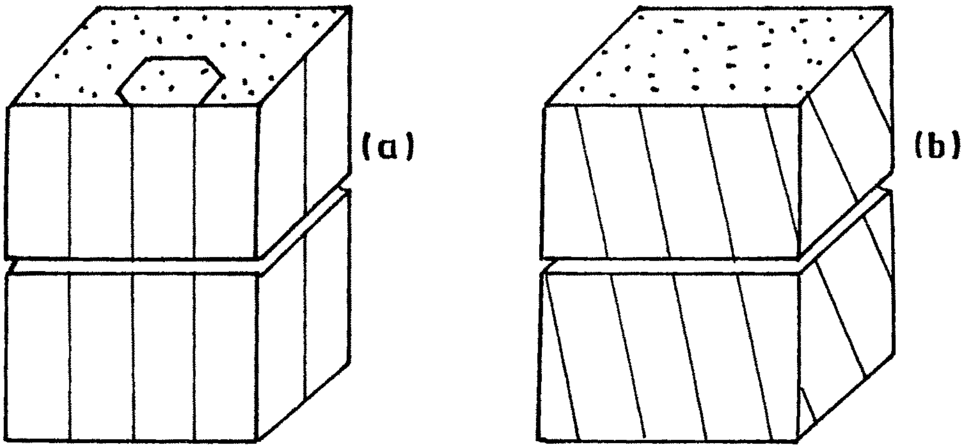


FIG.5 SCHEMATIC STRUCTURE OF **(a)** HEXAGONAL **(b)** MONO CLINIC SMECTIC 'B'

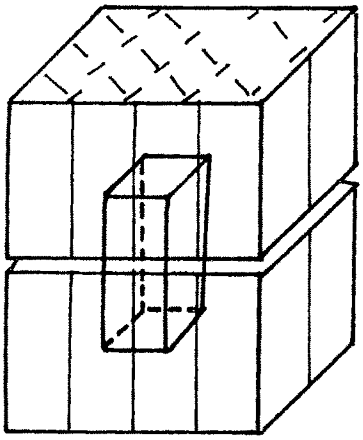


FIG.6. SCHEMATIC STRUCTURE OF SMECTIC 'E'

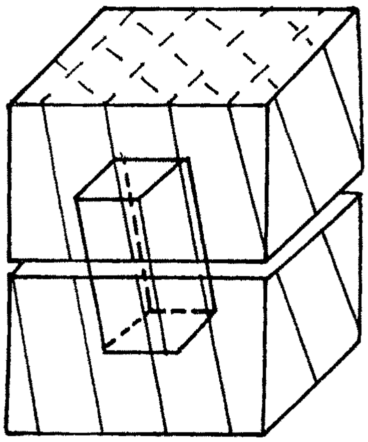


FIG.7 SCHEMATIC STRUCTURE OF SMECTIC 'G'

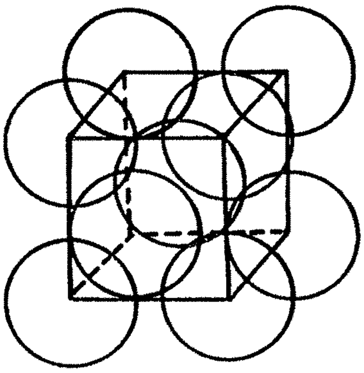


FIG. 8 SCHEMATIC STRUCTURE
OF SMECTIC 'D'

Schematic diagram of different smectic phases are shown in Fig.2 to 8.

In 1983, Levelut et al., (26) reported the existence of a new smectic phase O (or O* in the chiral spaces), and they proposed a structure for smectic O* (O) that was similar to smectic C*. In 1988, Chandani et al., (27,28) first observed a double hysteresis loop characteristic of antiferroelectric phases in several compounds. They called their new phase smectic C_A*. This was an important observation for the flat panels display technology because it introduced a novel way to expand the grey scale of ferroelectric displays.

2.2 Interdigited Smectics:

This new family with the structure of highly ordered smectic like phase is reported by de Vries et al., (29). The molecules are arranged in layers with their alkyl tails fully interdigited with the tail of molecules of adjacent layers. The currently known smectic phases are therefore suggested to be called as segregated smectics.

2.3 Nematic Liquid Crystals :

Compared to the smectic mesophases, nematic phase is less ordered as there is no layered arrangement of molecules. The word "Nematic" is derived from a Greek word "Nema" meaning threaded schlieren texture. The molecules in the nematic phase are arranged with their long axes parallel but they are not separated in layers and can be compared with a long box of round pencils. The molecules in nematic phase exist in the form of groups, each group containing about 100,000 parallel molecules. These groups are referred to as swarms, and the theory known as the "Swarms theory" was first proposed by E. Bose (30) in 1909, to explain the molecular arrangement and order in the nematic phases.

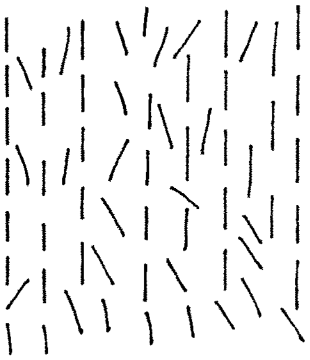


FIG 9 : Molecular arrangement in the nematic phase.

Nematic liquid crystals are optically positive and can be formed by compounds, which are optically inactive or racemic modification.

2.3.1 New Types of Nematic Liquid Crystals

Carbonaceous Mesophases

Generally, nematogens consist of rod like molecules whose longest axis tend to be parallel in the nematic phase discussed earlier. Albe (31), Onsagar (32) and Dreyer (33) suggested that in addition to such positive nematics, it is reasonable to expect that there might be negative nematics with planer molecules aligned with their shortest axis parallel to each other.

The carbonaceous mesophase is an original discotic nematic liquid crystal (34) which appears during liquid phase pyrolysis of many hydrocarbons. A careful study of this carbonaceous mesophase is also difficult because of the high temperature (400°C to 500°C) and of the lack of chemical stability of organic compounds in this temperature range.

Gasparoux (35) has studied carbonaceous mesophase in detail and reviewed properties of the carbonaceous mesophase. This mesophase exhibits many analogies with the classical nematic liquid crystal in particular the dynamic behaviours of some disclination. Chevastiak and Lewis (36) have observed that the mesophase solubility depends on the original material from which it is formed and that the percentage of the mesophases is not necessarily the same as the one of insolubles. Thus direct optical observations seem to be the way of evaluation of this percentage. Gasparoux (35) has compared the physical properties of carbonaceous mesophase with those of thermotropic nematic systems (disc-like and rod-like systems).

2.4 Discotic Liquid Crystals:

The first discotic liquid crystal was synthesized and identified in the year 1977 by the group working in the Raman Research Institute, Bangalore, India in pure compounds with disc like molecules (37). These phases are formed from molecules having more or less flat aromatic cores with usually six, but some times four lateral substituents, normally, alkoxy or esters (or more complex) groups, with atleast five carbon atoms. The thermodynamic, optical and X-ray studies (38) have lead to the conclusion that the compounds are entirely new type of liquid crystals. The structural arrangement of different disc-like molecules is schematically represented in Fig. 10 and 11.

The discs are periodically stacked in columns, the different columns forming a hexagonal array. The mesophase has been variously described as Discotic (39), Canonoic (40) and Columnar (40 & 41) phase.

The columnar structure has been confirmed by the excellent X-ray work of Levelut (38). It has been established also, that these mesophases exhibit a rich

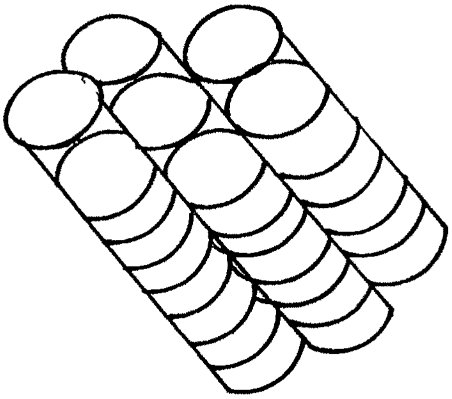


FIG. 10 SCHEMATIC REPRESENTATION OF THE TILTED COLUMNAR STRUCTURE

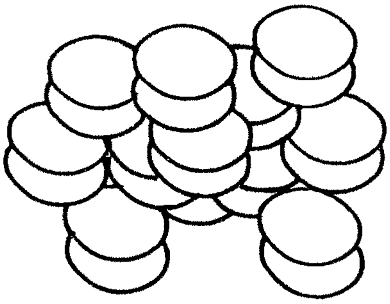


FIG. 11 SCHEMATIC REPRESENTATIONS OF THE NEMATIC PHASE OF DISC-LIKE MOLECULES

polymorphism comparable to the polymorphism observed in rod-like systems. Thus new and interesting area of research has opened up. Disc-like molecules (42, 43) with cholesteric properties are reported in literature. Reentrant phenomenon in disc-like liquid crystals (44) is also reported. Abied et al., (45) and Vora et al., (46) have reported disc-like molecules with only three substituents.

Number of examples are reported in the literature with typical structural unit which are varied and fascinating. Kawada et al., (47) have reported novel nematogenic benzene derivatives; N.N'-dialkanoyl-2,5,6-trimethyl-4-alkanoyloxy-1,3-benzene-diamines.

Kreuzer et al., (48) have reported discotic liquid crystals cyclic siloxanes with mesogenic side groups. Recently Takada et al., (49) have reported the discotic columnar liquid crystals in Oligo Saccharide derivatives. Plesnivy et al., (50) have synthesised star-like heptamers exhibiting a hexagonal columnar mesophase (D_h).

2.5 Cholesteric Liquid Crystals:

The name "Cholesteric" was derived for this type of mesophase because this phase was exhibited by cholesterol derivatives. The cholesteric phase is the twisted nematic phase as this possessed the structure of the layered nematic liquid crystals twisted about an axis perpendicular to the molecular layers, which results in helical structure. Typical nematic compounds having chirality, also exhibit cholesteric phase (51-53) hence they are called "Chiral nematics" Gray (53) has reported an optically active deuterated compound exhibiting cholesteric phase. The addition of optically active materials to nematic liquid crystals also gives cholesteric liquid crystals (54).

Recently Kobayashi and his co-workers (55) proposed a new method of preparing twisted nematic liquid crystal displays (TMLCDs), the non-rubbing technique in which the cells are made without rubbing. The liquid crystals are injected in the isotropic phase and then cooled down into the nematic phase. Randomly, distributed micro-twisted nematic domains were formed during the cooling process. The mode is called the amorphous twisted nematic (a-TN) liquid crystal display. Analytical simulations for the a-TN are also given by this group (56). The characteristics of the a-TNs are further investigated by Cheng and Sun (57).

The helical structure (Fig. 12) causes the cholesteric liquid crystals to behave in an unique and most striking way not shared by other types of liquid crystals i.e reflection of iridescent colours. Certain cholesteric compounds can selectively scatter light giving different colours. The colour is determined by (a) pitch of the helix, (b) the temperature, (c) the angle of incident beam. Physical effects which wind or unwind the helix such as temperature, mechanical disturbances like pressure or shear and traces of organic vapour, result in various colour changes. Cholesteric liquid crystals are optically negative while smectic and nematic compounds are optically positive. They generally have following three textures.

(a) Focal Conic Texture:

When an isotropic liquid is cooled, the texture obtained is focal-conic. The term is derived from the conic sections that are usually observed in case of smectics The focal-conic texture nucleates in discrete points from where it grows in all the directions. i.e. radial growth until whole film is covered.

(b) Plane Textures: (Planar Textures):

In this texture, the sample is uniformly aligned with the twist axis perpendicular to the plane of the film. However, alignment discontinuities can show reflected colours for perpendicular incidence of wavelength of light at the centre of reflection band which is equal to the length of the pitch multiplied by refractive index.

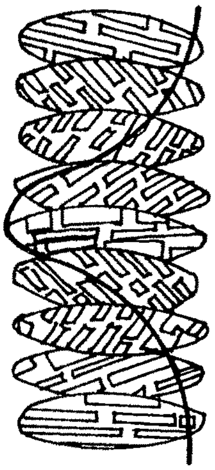


FIG.12 PROBABLE ORGANIZATION OF THE CHOLESTERIC PHASE. (N^*)

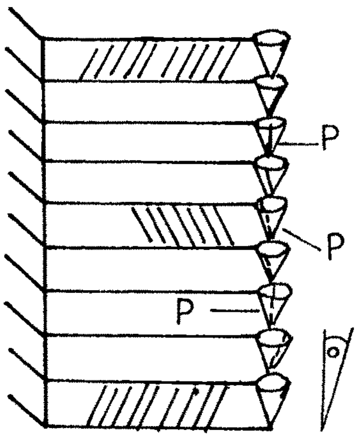


FIG.13 STRUCTURE OF THE SMECTIC C PHASE (C^*)

P= Direction of the spontaneous polarization

(c) Blue Phases:

Some cholesteric mesogens on cooling the isotropic liquid exhibit a phase which is visible to the eyes in reflected light, but is not visible microscopically, in transmitted light using crossed polaroids. This phase is known as a blue phase and its possible structure was determined by NMR spectroscopy (58). This type of cholesteric compounds have small pitches less than 700 nm. The temperature range of the blue phase is typically about 1°C during which sample reflects colours of light which would be associated with a cubic structure having lattice parameters about the same as the pitch of the cholesteric phase. This phase on further cooling changes to a birefringent texture.

Bergmann and Stegemeyer (59) have confirmed the blue phase of cholesteryl nonanoate by calorimetric and microscopic studies and they reported the existence of two polymorphic forms of blue phase. These phases are optically isotropic, exhibit Braggs (light), scattering an monocrystals may be grown showing distinct crystal faces. Stegemeyer et al., (60, 61) have observed two thermodynamically stable phases (Blue phase I and Blue phase II). It was suggested by Saupe (62) that these blue phases (I & II) have cubic structure. Crooker (63) has suggested possible amorphous "fog" phase (Blue Phase III) besides cubic phases (Blue phase I and Blue phase II).

Number of workers (64-69) studied the physical properties and their results provide further evidence that blue phase is a three dimensionally ordered system (64) and confirmed the cubic structure (65). Kitzerow (70) has presented an experimental review on electric field effects on blue phases

3.0 Re-entrant Behaviour of Mesophases:

The phenomenon in which nematic mesophase is observed at lower temperatures, then smectic mesophases is called a re-entrant nematic phase. This phenomenon was first observed by Cladis (71) in binary mixture at normal pressure. Certain cyano compounds with alkyl or alkoxy end groups exhibit re-entrant nematic and smectic A phase (72,73) at atmospheric pressure.

The explanation given for this unusual behaviour is that, the anti-parallel associations responsible for the bilayer smectic-A phase, also provide mechanism which accounts for the re-appearance of the nematic phase at some lower temperature. This phenomenon is also observed in the case of mixture (74), at atmospheric pressure (75) and at atmospheric pressure in pure compounds (72, 73).

$$\begin{array}{l}\text{Crystalline}\\ \text{solid}\end{array} \overset{95^\circ C}{\rightleftharpoons} SA \overset{96^\circ C}{\rightleftharpoons} N \overset{138.9^\circ C}{\rightleftharpoons} SA \overset{247^\circ C}{\rightleftharpoons} N \overset{283^\circ C}{\rightleftharpoons} I$$

Arora et.al., (76) have reported Re-entrant phenomenon in cyano substituted biphenyl esters having flexible spacer.

The mesogen 4-n-octyloxy benzoyloxy-4'-cyanostilbene was found to possess Re-entrant nematic and smectic phases (77).

Number of homologous series having terminal polar groups such as -CN, $-NO_2$, -Br, were studied by Destrade et al., (77,78) showing Re-entrant phenomenon in nematic and smectic phases. Demus et al., (79) have reported Re-entrant nematic phase in binary system of two terminal non-polar compounds. Re-entrant behaviour has also been observed in discotic materials (80), with phase appearing with change of temperature both above and below a columnar phase. Destrade et al , (78, 81) have reported re-entrant cholesteric phases in polar mesogens.

Re-entrant phenomenon in a new polar cyclohexane series has been reported by Nguyen (82).

Subramaniam et al., (83), have reported re-entrant isotropic phase in polypeptide solution, they have stated that existence of higher temperature isotropic phase is due to thermal disruption of long range orientational order of the elongated macromolecules and the lower temperature re-entrant isotropic phase is a result of an intramolecular helix to random coil transition which leads to a macromolecular conformation inconsistent with liquid crystallinity.

Trivedi and Thakkar (84) have reported first time a re-entrant nematic system having end formyl group in the naphthalene ring system. Number of theories are proposed to explain re-entrant phenomenon (85, 86).

4.0 Phase Type in Chiral Compounds:

Chiral compounds are able to form mesophases with structures related to those of non-chiral substances, however, with different properties Table 2 presents an overview of the most important phase types occuring in chiral compounds.

Due to the presence of chirality, the nematic phase is changed to the cholesteric phase. Formally it can be built up by nematic layers in which the preferred direction (director) is shifted by a constant angle coming from one layer to the next (Fig.12). This twisted or helical structure possesses several special optical properties which are very useful in practical applications. The outstanding optical activity makes it useful for electro-optical displays, the selective reflection of light is the basis of the thermographic use of cholesteric liquid crystals. Because of its symmetry properties, the cholesteric phase cannot be ferroelectric.

Table 2

Phase types of chiral liquid crystals

Nonferrolectric structures

N*	Helical nematic structure, optical activity, selective reflection

Ferroelectric phase types (Chiral tilted smectics)

Random molecular packing

C*	helix, optical activity, selective reflection,

Pseudo-hexagonal structre

I*	tilted to side	no layer correlation short in-plane correlation
F*	tilted to apex	helix structure, optical activity selective reflection
J*	tilted to apex	long-range layer correlation long range in-plane correlation
G*	tilted to side	no helix structure

Herring-bone molecular packing

K*	tilted to side	long-range layer correlation long-range in-plane correlation
H*	tilted to apex	no helix structure.

In a very small temperature region (about some tenths of a degree) between the cholesteric and the isotropic phase, compounds with sufficiently high twist can display up to three different types of "blue" phases as discussed earlier (87).

All smectic phases with tilted structure derived from chiral compounds exhibit ferroelectric properties, because of their low symmetry, they are able to form spontaneous polarisation and piezoelectric properties (88). The ferroelectric liquid crystalline phases have become very important for fast switching electro-optical displays. Most of these ferroelectric structures are differentiated from the non chiral analog by a twist of the layers with respect to the tilt direction. Fig. 13 shows the structure of the twisted C phase designated by *C. In the twisted form, the lateral dipole moments of the molecules are cancelled on average. By interaction with the walls (basis of the SSFLC displays) or in electric or magnetic fields, the twist can be unrolled and in this form the phase can show ferroelectric properties which originate from a summation of many lateral molecular dipole moments. The *C phases and also the other twisted structures compiled in Table 2, possess optical activity and selective reflection of circularly polarized light.

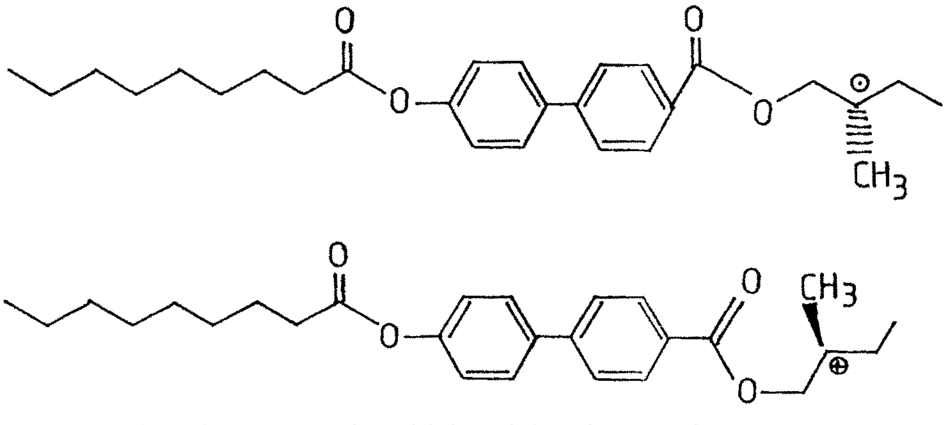
Recently several new types of ferroelectric liquid crystals have been described. In some chiral pyrimidine derivatives in the temperature region between the *C and *G phases a new phase has been detected with properties similar to those of the *C phase (89). In certain chiral biphenyl derivatives exist smectic phases with orthogonal arrangement of the molecules in the layers and a helical ordering of blocks of molecules designated smectic A* (90).

The smectic "O phase" is another new type in which adjacent layers of the molecules are oppositely tilted to give an antiferroelectric arrangement (91).

5.0 Ferroelectric, Antiferroelectric and Ferrielectric Phases:

The role of biaxial correlations between mesogens in producing chiral structure, nevel chiral instabilities and modulated structures in ferroelectric and antiferroelectric liquid crystals; the effect of chiral fluctuations in achiral phases and the phase behaviour of chiral-achiral mixtures; a demonstration of ferroelectricity in an achiral smectic with banana-shaped molecules; and new collective fluctuation modes in chiral liquid crystals.

The novel phenomena of antiferroelectricity and ferrielectricity have been observed (recently) in smectic *C phases (92-94). This behaviour has so far been found in materials where the degree of chirality is relatively high, for example in materials where the chiral centre is near to the rigid aromatic core of the molecule or where the peripheral aliphatic chain is relatively long. In this materials the motion of the chiral centres about the long axis of the molecule is damped and therefore the degree of chirality is increased. The increase in chirality over that in closely related systems is manifested in a shortening of the pitch length of the helix in chiral phases and a substantial increase in the spontaneous polarization.



[(S)-2-methylbutyl 4'-n-nonoyloxy biphenyl-4-carboxylate]

The proposed structure of the antiferroelectric is shown first (Fig. 14) because it is easier of the two new structures to rationalize. It is proposed that the layers are stacked in such a way that the polarization vectors in subsequent layers point in the opposite directions, thereby cancelling each other. This results in the spontaneous polarization falling to zero. On the application of a strong electric field this layer ordering is broken up and the phase returns to the normal ferroelectric structure; hence the polarization temperature curve returns to its usual form A schematic representation of the switching process is shown in Fig.15. In the unpoled antiferroelectric state, subsequent layers are tilted in opposite directions to one another If the antiferroelectric phase is subjected to a d.c. voltage the layer ordering will break up, and the molecules will be poled in one direction depending on the polarity of the applied electric field in order to give a ferroelectric phase. Switching from the antiferroelectric to ferroelectric phase occurs at a defined applied field; therefore, there is a sharp threshold for a switching. The switching process can be investigated by measuring the tilt angle as a function of the applied voltage.

A similar structure is proposed for the ferrielectric phase except that the layers are stacked in such a way that there is a net polarization, i.e the number of layers of opposite polarization direction are not equal. There might be for instance twice as many layers where the polarization is opposite to that of the other layer, as shown in Fig 16. However, it is also suggested that the stacking of the layers is regular so that the phase has two interpenetrating sub-lattices. For this stacking arrangement the ferroelectric phase will have a measurable polarization. This value will be lower than that of the ferroelectric phase, but it will not approach zero as in the Antiferroelectric phase

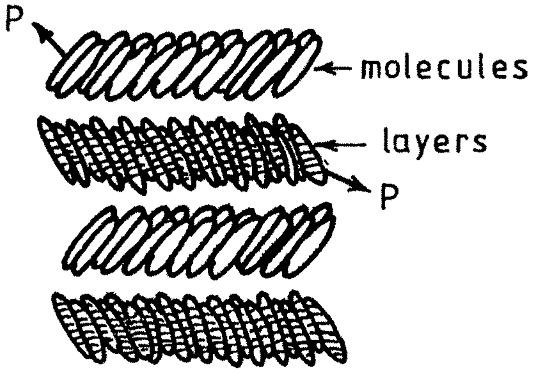


FIG.14 ANTIFERROELECTRIC SMECTIC C^* PHASE

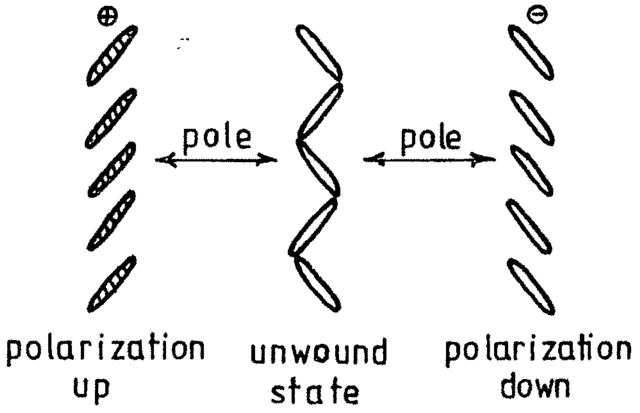


FIG.15. ANTIFERROELECTRIC-FERROELECTRIC SWITCHING

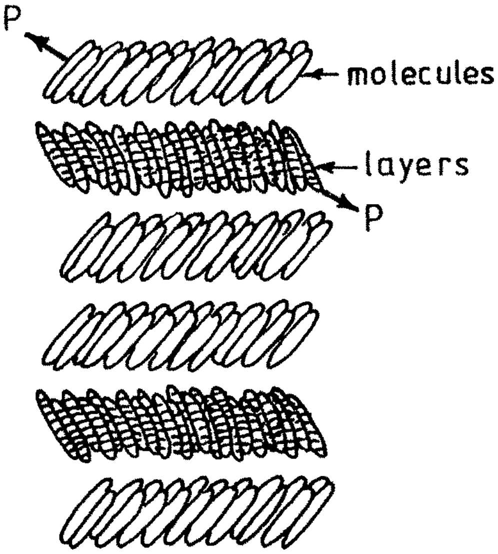


FIG. 16 FERRIELECTRIC SMECTIC C^*PHASE

6.0 Lyotropic Liquid Crystals (Amphiphilic Compounds)

Lyotropic liquid crystals are commonly obtained by the forces of a solvent on a solid. Ammonium oleate was the first lyotropic liquid crystal reported by Lehmann (95).

McBain (96) has discovered the forms of mesomorphism in soap solutions. Robinson (97) reported lyotropic cholesteric phase and discussed the similarity between the lyotropic cholesteric phase and thermotropic cholesteric phase. Vora et al., (98) have reported lyotropic mesomorphism using concentrated sulphuric acid as solvent in polymers. Lyotropic systems with polymers and different solvents are studied in details (99, 100). Recently Bruce et al., (101) have studied thermotropic and lyotropic mesomorphism of one of the ligands, 4-dodecyloxy-2-hydroxy benzoic acid (HDOBA).

7.0 Ionic Liquid Crystals:

There are only a few reports concerning ionic thermotropic liquid crystals. Some liquid crystal polymers with the pyridinium side chain (103) and those with alkyl ammonium salt as principal chain have been reported (104). Hydrogen-bonded liquid crystals have also been reported (105).

Recently Haramoto et al., (106) have reported the new type of ionic liquid crystal material shown in Fig. 17.

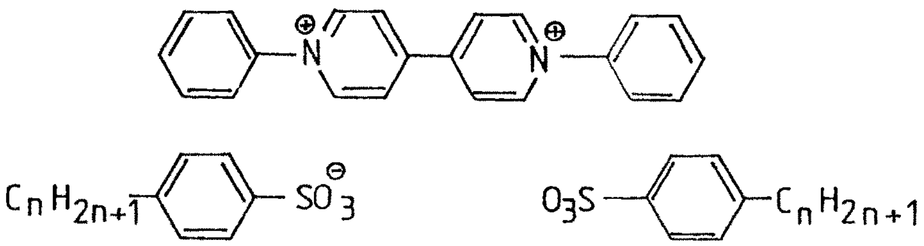


FIG. 17 : Chemical Structure of the new ionic liquid crystal compound

8.0 Mesomorphism in Biological Systems:

Liquid crystals play an important role in nature Mesomorphic property in the form of myelin in biological system was first shown by Wirchow (107) in 1854. The sense such as smell may be involved with substances exhibiting mesomorphic properties (108). This is based on the possible presence of cholesterol ester sensitive to small amount of vapours. Birefringence in the case of muscle was noted by Muralt and Edsall in 1930 (109).

From a study of structure of Heamoglobins, Perutz et al , (110) concluded that it could assume liquid crystalline form in the red cell. Until 1970, no one reported the presence of liquid crystalline compounds in plants. Knapp and Nicholas (111) reported the isolation of tetracyclic triterpene ester exhibiting smectic and cholesteric mesophase, from banana peels and from the seeds of strychnine producing plants. Livolant (112) has observed cholesteric phase of DNA in Vitro and in Vivo. Same author has reported the electron microscopic analysis of the highly concentrated liquid crystalline phase of DNA (113)

9.0 Physical Properties of Liquid Crystals:

Pioneering work on different physical properties has been carried out by a number of research workers.

In early seventies and eighties various physical properties of liquid crystalline materials have been studied in detail such as X-ray studies (114,115), Nuclear magnetic resonance (116), surface tension, (117) spectroscopic studies (118-120), elasticity and viscosity (121), dielectric constant (122,123), Mossbauer effect (124) chromatography (125,126), ultrasonic (127,128), magnetic susceptibility (129) and calorimetry (130-135)

A number of books and review papers have discussed the physical properties of liquid crystals, and their importance in the different technical applications (133-143) Viscosity and surface tension studies are important because of the sharp change in molecular orientation at the phase transitions. Liquid crystals, preferably with less number of unsaturation, are now used as solvents in infrared and ultraviolet spectroscopy (144). Malthete and Billard (145), have shown ferrocene derivative to be mesogenic, which are very useful in Mossbauer spectroscopy. X-ray studies are useful in understanding different textures and structures of mesophases, while gas chromatography and specific volume studies enables one to achieve purification of chemical substances and to evaluate order parameters for applications. Thus studies of physical properties decide the applicability of liquid crystals (146).

10.0 Applications of Liquid Crystals :

Day by day, liquid crystals are finding more and more importance due to their technological applications, hence, this field has become fascinating. Now a days liquid crystals are used in almost every field particularly in the field of electro-optical applications and in biological systems. Some of their applications are listed below:

10.1 Electro-optical Applications (147-150):

Electro-optical applications include seven segment display panel, electronic windows which go from clear to frosted with a flip of switch, numeric displays for watches, calculators, toys, games, point of scale advertising panels, flat screen television, temperature indicator, image-convertor and storage displays (151) The liquid crystal storage displays can record and reporudce the image. A laser addressed projection and a matrix addressed displays are also used Hareng et al., (152) have summarised the recent work on these two kinds of displays. Reflective type of liquid crystals display device is also reported (153) which is more readable than conventional ones.

A liquid crystal cell (device) is made by sandwitching a liquid crystal mixed with some dopent between two glass plates coated with some current conducting transparent material such as tin oxide. Improvements in or relating to liquid crystal display cell is described by Siemens (154). Electric and magnetic fields are capable of inducing molecular re-orientation in liquid crystals which are reflected in variety of optical changes i.e. by applying electric current to the plates the cell becomes opalescent and by switching it off, the cell again becomes transparent in microseconds. The advantages are low power consumption, ability to withstand high levels of light and low cost. Disadvantages are difficulty in cell fabrication, life time, response time and viewing angle considerations.

The visualization of acoustic images with a nematic liquid crystal is reported (155) which gives direct two dimensional acoustic images with good response time. The use of liquid crystals in IR video-camera has been reported (156, 157). Recently J.S.Patel (158) has discussed liquid crystal devices and devices for liquid crystals highlighting future potential of liquid crystals in communication applications.

10.2 Ferroelectric Liquid Crystals (Chiral Smectic *C) (159)

A promising way for overcoming difficulties of liquid crystal display is to use chiral smectic *C liquid crystals in a carefully chosen geometry. Displays based on FLCs using the chiral smectic *C (Sc*) phase are known as surface stabilised ferroelectric liquid crystal displays (SSFLCDs) (160). These media are ferroelectric and thus permit a very direct action by the external field. As reported below the resulting electro-optic device will show the following characteristic properties.

1) High speed even at very low voltage:

The electro-optical response is as much as 1000 to 10,000 times faster (for the smectic *C) than currently available electro-optical devices using liquid crystals.

2) Bistability:

The electro-optical response is characterised by two stable states, either of which may be selected by an appropriate electric field and either of which is stable in the absence of the field.

3) Threshold behaviour :

The change from no switching response to full switching response is made over a very small range in the amplitude and duration of the applied field.

4) Large electro-optical response :

The optical change induced by the electric field corresponds to a rotation through 20^0 to 60^0 angle of an uniaxial material having a refractive index and anisotropy Δn greater than 0.2. This response is 10 to 100 times larger than that attainable in other bistable electro-optical devices. Antiferroelectric liquid crystal are gaining considerable attention because of their characteristic tristable switching (161) applicability for display devices (162-164)

Shibaev et al., (165) were the first to report a ferroelectric liquid crystal polymer (PFLC) and the first report of electro-optical switching in Polymer Ferroelectric Liquid Crystals (PFLC) came from Uchida et al., (166). A number of switchable PFLCs have been designed and studied by many researchers (167).

10.3 Liquid Crystals as Temperature Detectors (168)

Cholesteric liquid crystals selectively reflect light in the visible region, depending upon the pitch of the helix. The pitch is temperature dependent and therefore can be used to detect the temperature via colour changes. This technique is also used to detect body temperature, to detect short circuits in electric equipments. Solvent vapours (in ppm) such as benzene or chloroform also affect the pitch hence they can be detected in the ppm concentration.

Coghlah (169) has reported that colour changing clothes for the human are designed and it has good potential for marketing. Patents have appeared with improved stability of the cholesteric mesophase in temperature sensing devices and also they claim long ranges of temperatures which can be covered (170-171).

10.4 Non Destructive Testing (13, 172, 173)

The property of cholesteric liquid crystals of exhibition of colours with the change in temperature is used in non-destructive testing. They can be used to reveal blockages in heat conducting systems, local overheating in metal surfaces due to eddy currents in wind-tunnel experiments, variation in heat transfer between well bonded and poorly bonded areas in honey-comb structures and to locate hot spots in integrated circuits. They are also used in mapping out heating elements in moulded rubber pads. Cholesteric liquid crystals have found use as temperature sensors in studies of heat flow and convection in weightless liquids and gases. These studies were made during the return flight from the moon of the space ship Appolo-14. New method (174) of sensing high hydrostatic pressure utilizing cholesteric liquid crystals as a sensing element and optical fibers for communication with high pressure region is proposed and demonstrated.

Cholesterol based liquid crystals are rapidly being replaced by chiral nematics in applications as cholesteryl derivatives are less stable and do not exhibit high birefringence. Against this chiral nematics are quite stable and exhibit very high birefringence.

10.5 Liquid Crystal in Medical Science:

Liquid crystals are also used as a diagnostic tool to detect carcinoma of the breast, study abnormal veinous patterns (including peripheral vascular disease) locate the placenta of fetus, diagnosis of pulmonary disease and detect primary or metastatic carcinoma in the skin. All of these tests utilise cholesteric liquid crystals, whose reflected colour changes with temperature. A cholesteric liquid crystal is used in the preparation of clinical thermometer which is used for the rapid detection of fever especially by oral temperature measurements.

In the medicine field liquid crystals are factors in at least three diseases. Hardening of the arteries is a result of the deposition of cholesterol esters on artery walls Cells involved sickel cell anemia has a liquid crystal structure and it has been proposed that gallstones might be treated by converting the hard material to liquid crystalline material so that it can be flushed from the body.

10.6 Liquid Crystals as Reaction Solvents:

Dewar and Nahlovsky (175) reported that for claisen rearrangement of cinnamyl phenyl ether in nematic solvent, no change of reaction product or rate is observed However, Bacon et al., (176) have reported that the thermal isomerization of 2,4,6 trimethoxy-s-triazine in nematic solvent proceeds faster and with smaller loss in entropy of activation than in isotropic phase.

Tottareli and Samori (177) have reviewed the applications of liquid crystals in chemistry. The structures of many small organic compounds can be established, using NMR, by dissolving the compound in a liquid crystal, such as p-azoxyanisole If some of the structural parameters of the solute molecules are known (e g by X-ray analysis), other parameters such as bond distance and bond angles can be established (178).

Liquid crystal systems are also used in oil recovery Such systems generally are ternary, involving water, oil and surfactant. At composition and concentration were the three components form a liquid crystalline phase, the oil is most highly solubilized. Use of such liquid crystal systems may double the amount of oil recovered

10.7 Liquid Crystals in Chromatographic Separation:

The use of liquid crystals as stationary phase in gas liquid chromatography is promising technique in separation of structural isomers (179,180). The selectivity of liquid crystalline phase is consequence of the molecular order, shape, polarity, polarizability, and flexibility of solute molecules. Vora et al., (181) and many other researchers (182-184) have reported the use of liquid crystals stationary phase in gas chromatography and have indicated their advantages for better separation of hydrocarbons. Richmond (185) used the liquid crystals for separation of position isomers of di-substituted benzenes. An inherent practical limitation of mesomorphous stationary phase is their restricted useful temperature ranges.

10.8 Liquid Crystals in Spectroscopic Studies

Liquid crystals are widely used in UV, IR, NMR and ESR spectroscopy (186). Information regarding the nature of the mesophase itself can be obtained (187) or liquid crystalline phase can be used as solvents which may provide information concerning bond lengths and preferred conformation of dissolved solute (188).

LIQUID CRYSTALLINE POLYMERS

11.0 General

One of the fascinating area of the current research in the field of liquid crystals deals with liquid crystalline polymers The development of 'Kevlar fiber" has stimulated research to find additional high modulus, high strength fibers and to investigate the structure and properties of high modulus polymers. Hence the technological applications and possibility of large structural variations have given impetus for the synthesis and study of liquid crystalline polymers.

In 1950 Oster (189) studied polymers with liquid crystalline order in aqueous solution of tobacco mosaic virus and in 1956 Robinson (190) reported polymeric liquid crystalline solutions of poly (γ-benzyl-L-glutamate) in various solvents. Number of synthetic polymers exhibiting liquid crystalline behaviour have been reported in the literature (191,192).

Number of patents and reports claiming the production of fibers (Kevlar fibers) from polymer solution existing in liquid crystalline state are known (193,194). These fibers have been reported to have tenacities which are greater in magnitude than those reported for steel on a weight basis. The liquid crystal states in polymers have been characterised most frequently by optical and electron microscopy, light scattering methods based on visible light, X-ray and electrons, thermal studies by DSC and TGA, spectroscopic methods (particularly IR and NMR), solution or melt viscosity behaviours, and by the study of the effect of electrical or magnetic fields on the molecular orientation. Many of these experimental methods rely on the fact that liquid crystal states are anisotropic and their properties are thermodynamically controlled.

For the first time Vora and Patel (195) have reported mesogenic polymers incorporating a monomer having symmetrically substituted triazine heterocyclic moiety and evaluated the effect of chemical structure on mesomorphism. Recently liquid crystalline polymers with novel structural units are reported in the literature (196-198)

11.1 Classification of Liquid Crystalline Polymers:

The phase behaviour and characteristic molecular structure of liquid crystalline polymers is given by Finkelmann (199). He stated that solid polymers with ordered structures are excluded and only homogeneous phases are considered that are in liquid crystalline state. Finkelmann (199) classified liquid crystalline polymers in its early stage. This classification can further be extended looking to the development of this field. Mesogenic polymers can be subdivided into the scheme given in Fig. 18.

It is most convenient first to describe the molecular structure of the monomer unit, following the classification of Gray and Winsor (134) for conventional liquid crystals. The monomer units can be either amphiphilic and non-amphiphilic Subsequently one can distinguish whether the mesogenic moiety forms a part of the polymer main chain or is attached to the side chain. A system can be lyotropic or thermotropic, depending upon whether mesophase is observed by variation of solvent or by temperature change. Siol (200) and Finkelmann (201), Kelker (202), and Elias (203) studied different mesogenic systems. The behaviour of lyotropic liquid crystalline side chain polymers in aqueous solution has been compared with phase behaviour of the corresponding monomers (204). Non-amphiphilic monomer units are characterized by their rigid rod-like molecular structure. Anisotropy of polymer is dependent on the nature of incorporation of the mesogenic groups which may be directly incorporated into the main chain (Fig.19a) or may be linked to the main polymer chain as side groups forming a "comblike" structure (Fig 19b).

Fig. 19a

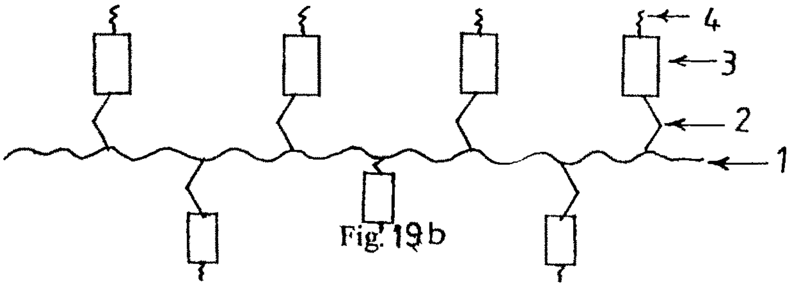


Fig. 19b

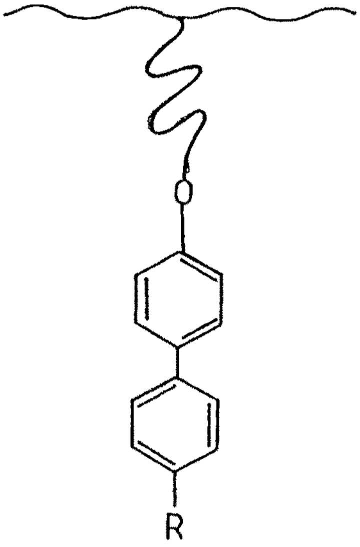


FIG. 20a ROD LIKE MESOGENS

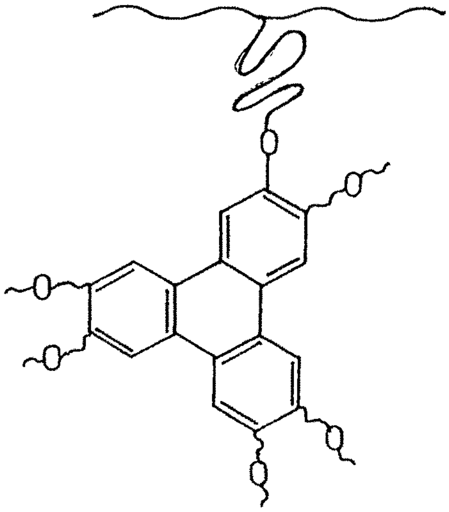
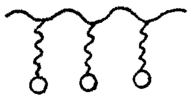
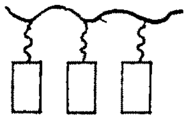
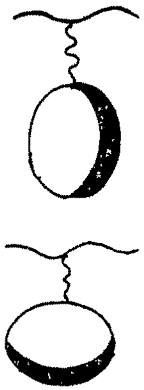
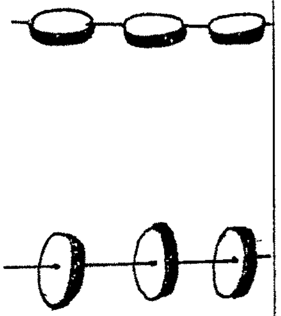


FIG. 20b DISC LIKE MESOGENS

MONOMER UNIT	 AMPHIPHILIC		 NONAMPHIPHILIC		 DISCOTIC	
POLYMER	 SIDE CHAIN	 MAIN CHAIN	 SIDE CHAIN	 MAIN CHAIN	 SIDE CHAIN	 MAIN CHAIN
PHASE BEHAVIOUR	LYOTROPIC	—	THERMOTROPIC	THERMOTROPIC LYOTROPIC	THERMOTROPIC	THERMOTROPIC

CLASSIFICATION OF MESOGENIC POLYMERS

FIGURE : 18

Scheme of the macromolecular structure of LC polymers

a) Mesogenic groups in the main chain	b) Mesogenic side groups
	1) Main chain
	2) Flexible Spacer groups.
	3) Rigid moiety of the mesogenic groups.
	4) Flexible tails.

Kreuder and Ringsdorff (205) classified these "comblike" polymers into different classes, depending on the nature of the side mesogenic moiety attached to the main chain polymers.

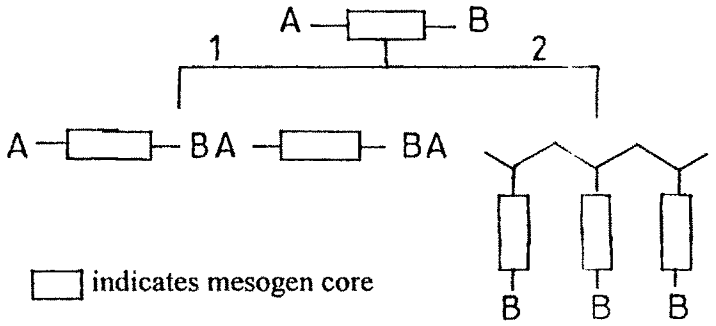
(a) When mesogenic groups are rigid chain (Fig. 20a)

(b) The mesogenic moieties are disc-like called "discotic" liquid crystalline polymers (Fig. 20b).

The molecular features responsible for mesomorphic thermotropic L.C. polymers are: 1) Introduction of the mesogenic groups in to a polymer backbone leads to main chain L.C. polymers (Fig. 20a). (2) Attaching mesogenic groups directly to a polymer backbone or through some flexible aliphatic chains leads to side chain L.C. polymers (Fig. 20b) (3) By blending of low molecular weight optically active molecules into the polymer.

11.2 Thermotropic Liquid Crystalline Polymers

For the synthesis of macromolecules which are expected to be liquid crystalline, a simple concept can be followed by using suitable mesogenic monomers which are able to build-up a liquid crystalline phase. If the mesogenic group of these molecules is substituted with appropriate functional groups A and B, macromolecules can be synthesised as shown in (Fig. 21).



Symbol ☐ indicates mesogen core

Fig. 21 Polymerization of a mesogenic monomer

(1) If A and B are able to perform a condensation reaction, the mesogenic group builds up the polymer main chain These polymers will be named "Liquid Crystalline Main Chain Polymers".

(2) If A is capable of performing an addition polymerization reaction, the polymer chain builds up by A and hence the mesogenic group are fixed like side chains to the polymeric main chain. These polymers can be called "Liquid Crystalline Side Chain Polymers".

For both polymers the original mesogenic moieties of the low molecular weight compound has been preserved which suggests the ideas, that the ability of forming a liquid crystalline phase can be preserved (204).

11.3 Synthesis of Polymers having Mesogenic Side Chain:

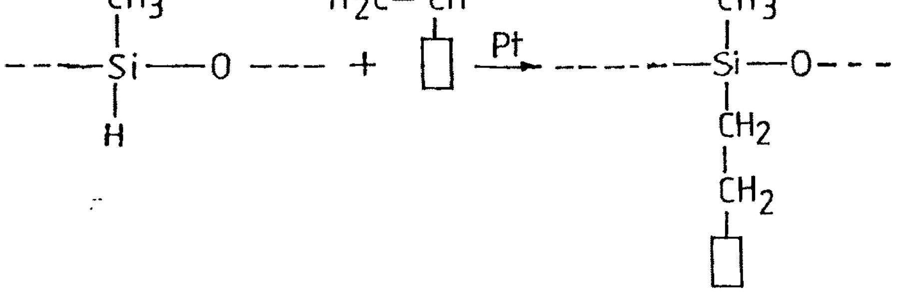
The mesogenic side chain polymers consist of two components, the mesogenic moieties and the polymer main chain to which they are attached A large number of known mesogenic molecules (206) can be used as components. Moreover, a variety of different polymer main chains are available The combination of these components allows manifold variation of different types of mesogenic side chain polymers. The polymers can be prepared by three different types of polymerization specified in Table3

The most convenient method is to introduce into a mesogenic molecule a reactive group capable of undergoing addition polymerization. A number of polymerizable monomers have been synthesized. They are summarized by Blumstein and Hsu (207a)and by Shibaev and Plate (207-b).In most cases the polymerizable groups are methacrylate or an acrylate, which form a flexible vinyl backbone.

The second possibility is to introduce into the low molecular weight mesogen, a reactive group capable of undergoing a poly condensation reaction. In this way polymers containing hetero atoms in the backbone can be synthesized.

Rech and Ringsdorf (208) reported liquid crystalline polymers having mesogenic side chains on the rigid backbone and on the backbone having flexible spacers.

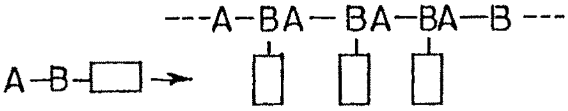
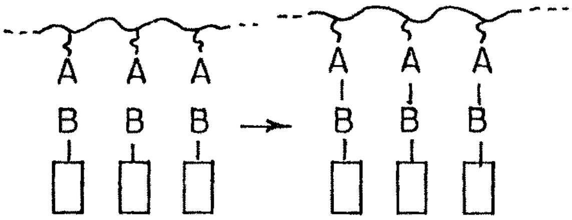
The third synthesis route starts with reactive polymers. They can be modified to mesogenic side chain polymers by using suitable reactive mesogenic monomers. An example of this type is the smooth addition of vinyl-substituted mesogenic monomers (209) to polyoxy (methylsilylene). Recently Choi et al., (196) have synthesized and designed a new side-chain liquid crystalline polymers by Metathesis Polymerization.



□ indicates mesogenic molecules

Table 3

Synthesis of Mesogenic Side

Principles		Examples
Addition Polymerization		Polyacrylates Polymethacrylates Polystyrene Derivatives
Condensation Polymerization		
Modification of Polymers		Polysiloxanes

11.3.1 Model Consideration:

Two extreme cases are considered : (1) in the first case, a polymer is dissolved in liquid crystal matrix. Apart from local anisotropic conformations of the polymer chain due to the anisotropic matrix, motions of the polymer segments and the mesogenic molecules are not coupled, as represented schematically in Fig. 22a. (2) In the second case, if rigid mesogenic side chains are directly attached to the polymer backbone (Fig. 22c) motions of the polymer segments and mesogenic groups are directly coupled. In the liquid state above Tg the polymer tends to adopt a statistical chain conformation that hinders anistropic orientation of the mesogenic side chains. Also, steric hindrance prevents mesogenic order. In addition to these extreme conditions intermediate states could be realized if the mesogenic groups were fixed to the polymer backbone via a flexible spacer as indicated in Fig. 22b. The flexible spacer decouples motions of the main chain and side chain and alleviates steric hindrance. Under these conditions the mesogenic side chains can be anisotropically ordered in the liquid state even though the polymer main chain tends to adopt a statistical chain conformation. Consequently, variation of the spacer length should clearly influence liquid crystalline order of the side chain.

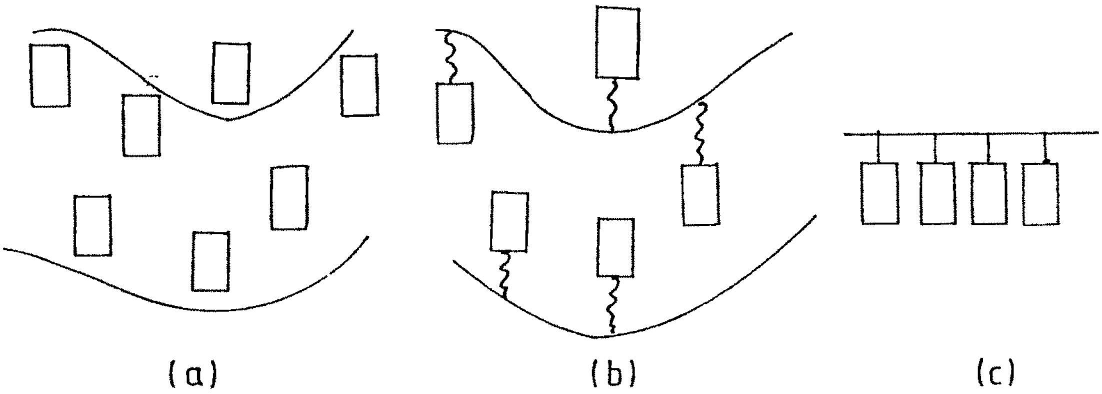


Fig 22 Liquid crystalline molecules
(a) dissolved in a polymer (b) linked to a polymer via a flexible spacer and (c) directly linked.

11.3.2 Influence of the chemical constitution on the type of Mesophase formed:

Linkage of mesogenic side chains to a polymer backbone also results in thermodynamically homogeneous thermotropic mesophases. However, because of the polymer main chain additional variations of the chemical constitution are possible. These are the chemical composition of the backbone, degree of polymerization, tacticity and the chemical constitution of the flexible spacer.

11.3.2.1 Variation of the Mesogenic Group:

A. Nematic and Smectic Polymers:

Following the model consideration, formation of the liquid crystalline phase has to be assumed to be more or less influenced by the polymer main chain of the mesogenic group, which is fixed via the flexible spacer to the polymer backbone. Therefore starting from a defined mesogenic group a nematic and smectic polymer phase should be determined by the substituents of the mesogenic moiety. For low molar mass derivatives it is well known that with increasing length of the alkyl substituents a smectic phase becomes stable (210). For the poly (methacrylates) when the short $-OCH_3$ substituent most distant from the polymer main chain is exchanged by a long $-OC_6H_{13}$ substituent, the nematic phase of polymer (with $-OCH_3$ substituent) changes to smectic phase in polymer with $-OC_6H_{13}$ substituent group (211, 212). This principle is also observed if the poly (methacrylate) main chain is exchanged by Siloxane main chain. Although their chemical and physical properties strongly differ, the order of the mesogenic side chain also changes from nematic to smectic with increasing length of the substituent (213).

Thus, the influence of the substituents upon the type of mesophase formed is essentially identical for low molecular weight mesogens and polymeric mesogens, so that polymeric nematic and smectic mesophases can be achieved by varying the length of the substituents.

B. Cholesteric Polymers:

Chiral molecules have to be present to obtain cholesteric (Chiral nematic) phase (214). Therefore, the substitution of chiral group to the mesogenic moiety described above should result in cholesteric homopolymers. Until now, however, only smectic phase was obtained when chiral molecules were polymerised (215).

Cholesteric phases can be achieved by using the well known concept of "induced cholesteric phases" (216). Assuming a direct analogy between polymer and low molecular weight liquid crystal, the cholesteric phase has to be induced if chiral molecules are added to the nematic polymer host phase. The validity of the concept has been proved by different systems (217).

Some condensation polymers are reported exhibiting cholesteric phase having one of the chiral monomer units in polymer main chain (218,219).

11.3.2.2 Variation of the Polymer Main Chain and Spacer Length:

According to the model consideration a flexible spacer decouples motions of the main chain and side chain. In reality there will be a more or less strong coupling of motions, resulting in varying interactions of the main chain and side chain. Two aspects should be considered. On the one hand, the linkage of the mesogenic moieties of the polymer backbone restricts translational and rotational motions. Motions of the mesogenic side chains are now correlated to motions of the neighbouring molecules via the backbone, which influences intersections of the mesogenic side chains. Consequently, the flexibility of the backbone, which can be characterized by the statistical chain length, directly affects the behaviour of mesophase. On the other hand, mobility of chain segments of the polymer backbone is strongly influenced by the bulky mesogenic groups. This directly affects the glass transition of the polymer.

An increasing flexibility of the backbone can also be achieved by copolymerization if the bulky mesogenic groups are replaced with small groups (220). By analogy to the previous results, lowering the glass transition temperature by increasing the flexibility of the main chain reduces the mesophase to isotropic transition temperatures. Flexibility of the side chain also can be changed by changing the spacer length. It has been also observed that increase in the spacer length stabilises smectic phases (210).

It has been found that the tacticity has little or sometimes no influence on the behaviour of the liquid crystalline phase (221).

11.3.2.3 Effect of Molecular Weight:

The average molecular weight of the polymer and the molecular weight distribution are specific properties of polymers, hence they have to be considered in connection with the properties of the mesogenic polymers.

Finkelmann (199) has compared the phase behaviour of a mesogenic monomer with that of the corresponding polymer and observed that (a) non-mesogenic monomer gives nematic polymer, (b) nematic monomer yields a highly ordered smectic polymer, the transition to the isotropic phase is strongly shifted to higher temperature, and (c) both monomer and polymer exhibit smectic and nematic phases, but the phase transition temperatures of the polymer are shifted to higher temperatures. Stabilization of the mesophase is observed for all monomer-polymer systems investigated. In principle, upon changing from monomer to polymer, the chemical constitution of the system, polarizability and form anisotropy should remain constant. Therefore, the strong shift of phase behaviour must be attributed to restriction of the translational and rotational motions of the mesogenic side chains. This suggested that a strong shift of phase behaviour is expected in changing from the monomer to the dimer, trimer etc. This shift should vanish when a chain length is reached for which no correlation exists between the motions of an additional monomer and the initial monomer. Investigation of the variation with molecular weight indicates no shift of phase behaviour at higher degree of polymerization.

11.3.3 Liquid Crystalline Elastomers:

Linkage of conventional low molecular weight mesogenic molecules to linear polymers has resulted in a new class of polymeric substances that combine the properties, characteristics of the mesogen and the polymer. Finkelmann et al (222) have prepared liquid crystal elastomers from polysiloxanes. Above glass transition temperatures, these polymers exhibit an almost free motion of the chain segments. Because of this mobility, the main chains are able to diffuse past each other, a property of the liquid state. On the other hand, in the liquid crystal state the mesogenic moieties fixed via spacers to the backbone create an ordered mesophase more or less independent of the main chain.

By analogy to linear liquid crystalline polymers; variation of the substituents of the mesogenic groups allowed synthesis of nematic, cholesteric and smectic elastomers. These liquid crystalline polymer networks have elastic properties typical of cross linked polymers. The mesogenic side chains can be macroscopically oriented by mechanical deformation, which results in interesting opto-elastic properties

Liquid Crystalline Elastomers containing polysiloxane, polyacrylate, polymethacrylate and also "combined" main chain / side chain polyesters were realized (223). Liquid Crystalline Elastomers exhibit exceptional physical properties due to the combination of rubber elasticity with the anisotropy of the liquid crystalline state. Meier and Finkelmann (224) have also discussed on "Liquid Crystalline Elastomers". Chiral smectic elastomers for piezoelectric/ pyroelectric sensors and discotic elastomers as photoconductors were studied by Kelly (225). Twomey et al., (226) have examined the effect of processing conditions, chain length of precursor siloxane polymer and thermal treatment on mesomorphic characteristics of LC elastomers.

11.4 Liquid Crystalline Main Chain Polymers:

In principle for the liquid crystalline main chain polymers, two different structures can be obtained, which depend on the chemical nature of the functional group A and B.

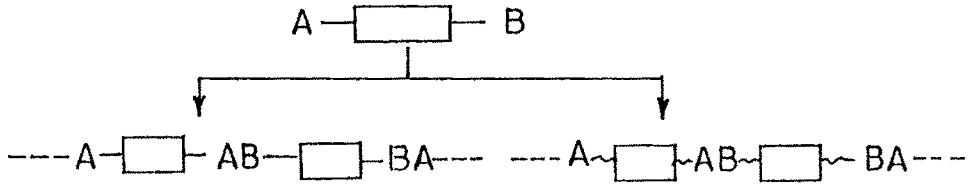


Fig.23 Structures of LC Main Chain Polymers

If A and B are directly linked to the rigid mesogenic moiety, a rigid rod-like structure is produced for the resulting polymer backbone. If on the other hand A and B are substituted via flexible spacers (e.g. flexible alkyl chain) to the mesogenic moieties, the resulting polymer main chain consists of alternating rigid segments (mesogenic groups) and flexible segments (e.g. alkyl chains). In contrast to the previous polymers the flexibility of the over-all polymer main chain can be regulated by using different chemical structure of different length of the flexible segments

11.5 Co-polymers:

The third type of liquid crystalline polymer is the random co-polyesters. These systems are suitable for high modulus application (227, 228)

Additional co-polyesters are described in the patent literature (229, 230). Krigbaum et al., (231) synthesized and studied nematogenic block co-polymers of rigid and flexible aromatic units Jackson et al., (232) synthesized liquid crystalline polyesters by using trans-4,4'-stilbene di-carboxylic acid and 1,3-propanediol Hoshino et al (233) studied liquid crystalline behaviour of polymeric glycols terminated with aromatic diester and diacid mesogenic groups

Scherowsky et al., (234) have presented the first examples of coloured ferroelectric liquid crystalline co-polymers exhibiting bistable electro-optical switching and prepared fluorescent ferroelectric liquid crystalline co-polyacrylates (235).

11.6 Lyotropic Liquid Crystalline Polymers (Diluted Systems):

The development of ultra high strength high modulus fibers based on lyotropic aromatic polyamides (236-238) by the DuPont company has increased the interest in the field of liquid crystalline polymers This "Kevlar" fiber was drawn by the solution spinning of an aromatic polyamides in the lyotropic liquid crystalline state

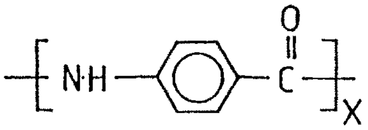
Two important prerequisite must be met before a polymer can form lyotropic mesophase:

(1) The polymer must be soluble enough in the solvent to produce solution above a critical concentration,

(2) While in solution the polymer chain must be extended and rigid (239).

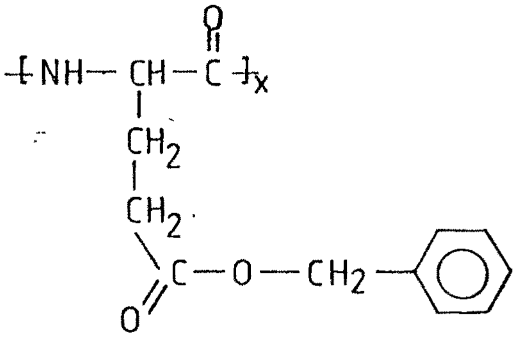
The most common lyotropic polymeric mesogens are synthetic polypeptides, cellulose derivatives, polyarylamides, polyesters, polyisocyanates and polyoxadiazoles. All of these materials exist in either extended linear or helical conformation in the solvents used to form the mesophase.

Polyamides, for example, show lyotropic liquid crystalline behaviour in solvents such as strong acids (e.g. Sulfuric acid), ureas and dialkylamide salt solutions Polyamide is highly linear because of the rigidity and planarity of the amide linkage and fibers of ultra-high strength are spun from anisotropic nematic solutions.



Poly (1,4-benzamide).

Numerous synthetic polypeptides also display liquid crystalline behaviour owing to their rigid; rod-like helical conformation in helix-supporting solvents. The most widely studied and best characterized synthetic polypeptide is poly(r-benzyl-L-glutamate) (PBLG) (240).



PBLG is a homopolymer of the L-enantiomer of the benzyl ester of poly(glutamic acid). PBLG forms cholesteric phases in solvents such as chloroform, dioxane, pyridine and dimethyl formamide which tend to support the helical structure of the macromolecule.

A number of cellulose ethers and esters also display liquid crystalline behaviour in concentrated solutions. Hydroxypropyl cellulose (HPC) (241) for example, displays cholesteric liquid crystalline behaviour in water, methanol or ethanol at a critical concentration of 40 wt % (242). HPC is helical, because of intramolecular hydrogen bonding and at high concentration the rigid rods aggregate to provide a liquid crystalline mesophase.

Some linear polyisocyanates have shown lyotropic as well as thermotropic mesomorphic behaviour (243). Recently Percec et al., (244) have reviewed the work done on "Liquid Crystalline Polymers".

11.7 Liquid Crystalline Polymers with Azo Central Linkage:

Heilmeir et al., (245) first reported "guest host effect" in nematic liquid crystal displays. The guest-host cell have many advantages such as coloured display, wide viewing angle and high brightness. If a small amount of elongated dye is mixed in liquid crystals, the dye molecules get aligned in the liquid crystal matrix and hence can be oriented from one position to other along with liquid crystal molecules on the application of electric field. The phenomenon of aligning the guest-host dyes molecules is called guest-host interaction.

Coloured polymeric liquid crystals with properties comparable to low molar mass guest-host systems can be obtained by copolymerization of mesogenic monomers and monomeric dyes (246, 247). Ringsdorf et al., (248) synthesized and studied phase behaviour of azo dye containing liquid crystalline side group co-polymers. They observed that these polymers showed the same electro-optical effects as low molar mass liquid crystals. Lipatov et al., (249) studied X-rays of polymers with side mesogenic groups based on p-hydroxy-p'-amyloxyazobenzenes and main chain of different types. Kozuyoski et al., (250) synthesized the thermotropic polyesters containing azo linkage. Mariam et al., (251) studied molecular structural effects on mesophase behaviour of monomers and polymers containing an azo group.

Recently photosensitive liquid crystalline polymer having azo linkage are reported which change from trans-to cis-to trans by exposing to UV and visible light (252) Levelut et al., (253) have studied X-rays of a homologous series of mesogenic azo compounds complexed with Palladium (II).

11.8 Applications of Polymeric Liquid Crystals:

Several methods have been designed to disperse liquid crystals in polymer matrices; permeating a microporous filter, emulsifying the liquid crystal in a water soluble polymer; and phase seperation techniques to create a dispersion of droplets in non-aqueous polymer materials. The later two methods have been widely employed in many new commercial products having potentially promising applications; for example, privacy windows, reflective displays, projection systems, and most recently, liquid crystal polymer dispersions have been refined to perform with active matrix technologies. The futures of these fascinating materials holds even more promise with further developments and increased interest in reflective display technologies (254), bistable capabilities of dispersed ferroelectric materials (255), and holographic applications where patterned phase separation techniques are employed to create spatial modulations in droplet densities (256).

(1) Ultrahigh Modulus and Ultra High Strength Fibers (228-236)

Closely packed ensemble parallel extended polymer chains should exhibit the highest achievable specific strength, which are the basis for the technology of ultrahigh strength organic polymeric fibers Polyamide fibers (Kevlar fibers) (257) are competitive with the lower modulus types of graphite fibers and rigid composites. Other specific applications include conveyor belts, V-belts, ropes and cables, body armor, interior trim and structural parts of air-crafts. The "Stilth" plane or invisible planes have coating of Kevlar fibers which absorbs microwaves, to mask the radar images. Another class of lyotropic fibers produced by dry jet-wet spinning, are the rigid rod polymers developed as part of the Air Force Ordered Polymer Programme (258-260).

Many patents have appeared for thermotropic liquid crystalline polymers which can be drawn in the fibers or cast into resins (216, 262). Poly (p-hydroxy benzoic acid) exhibits a thermotropic nematic phase, which is commercially known as "Ekonol", it is useful for high modulus fibers (263, 264).

(2) Liquid Crystalline Mouldable Resins (265)

M/s Dartco Mfg. Co. (USA) have developed a self reinforced liquid crystalline aromatic co-polymer that can be moulded on standard injection equipment. This resin is expected to replace metallic and other polymeric materials in such areas as telecommunication equipment, computers, aerospace and autoparts. Co-polyesters, such as p-hydroxy benzoic acid modified poly (ethylene terephthalate), 60/40 PHBA/PET (X7G) polymers, have been produced by the Tennessee Eastman Company (266-269). Other melt processable nematic thermotropic polyesters, based on combinations of 2,6-naphthalene dicarboxylic acid, 2,6-dihydroxynaphthalene and 6-hydroxy-2-naphthoic acid, and referred to as naphthalene thermotropic polymers have been produced by Celanese Corporation (269).

The self reinforcing polymers major attraction is its outstanding property profile, high strength at elevated temperatures, heat resistance to 354°C excellent dimensional stability and impact strength at continuous use temperature of -51°C to 241°C good burn resistance with minimum of smoke. Resistance to almost all solvents and chemicals.

(3) Electronic Optical Devices:

Number of liquid crystal polymers have shown good promise in storage and display devices. Liquid crystal polymers are extensively exploited as non-linear optical materials with exciting applications in the electronics. Epoxy resins can be used as a polymer binder. These types of displays can provide large display area with nice projection. Hence they can be used for overhead projection e.g, TV screen, computer output, etc. The Polymer Dispersed Liquid Crystals (PDLC) technology can be used from architectural point of view to prepare window-shutters, which can provide privacy. PDLC's can also be used in automobile industries to prepare dash board displays, sun-proof, side windows and rear windows (270). Cost effective liquid crystalline polymers are aimed at electronic applications (271).