INTRODUCTION

LIQUID CRYSTALS

1. General :

Mesogenic materials, whether comprised of small molecules or macromolecules, have attracted scientists and technologists alike due to their fascinating properties and versatile applications. Mesogens (Liquid Crystals) are known to common man more due to their applications in electronic display devices. LCD displays used in watches, calculators etc. have taken these mateials through the length and breadth of the globe.

Almost before a century, an Austrian botanist Reinitzer (1) noted unusual melting behaviour of cholesteryl benzoate. He referred it to Otto Lehmann (2) to investigate the phenomenon in detail. This gave the birth to new phenomenon called liquid crystallanity. Eventhough there were objections (3-5) to consider this ordered phase as a distinct phase having mechanical properties of a liquid and optical properties of a crystalline solid, the objections did not stand grounds and soon it was established by number of scientists (6-14) that liquid crystallanity is a pure state of matter and it's a distinct phase intermediate between crystalline solid and the isotropic liquid. Lehmann (2) called the substances exhibiting this phenomena as "Flussige Krystalle" i.e. flowing crystals. However, lat eron they were known as "Liquid Crystals" (2). Initially some scientists (15-17) objected the

nomenclature as it was a paradoxical nomenclature. However some scientists (16,17) suggested that liquid crystals better be named as mesogens and the phenomenon should be considered as "Mesomorphism" i.e. an intermediate phase. However the popular name liquid crystals still prevails.

There was great upheaval in the early twentieth century in the field of liquid crystal research. However, after 1933, the research work in the field of mesogenic materials decreased. The field was revived in 1966 by organising International Liquid Crystal Conference at Kent State University, Kent, Ohio, U.S.A. Prof. G. H. Brown took lot of pains to see that this conference activates others and he lured many scientists.

Liquid crystals are classified into two major groups on the basis of the manner in which they are obtained(6,18,19). Thus liquid crystals are divided into two major groups 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 (20) prefer the terms

'amphiphilic' and 'non-amphiphilic' for lyotropic and thermotropic liquid crystals, respectively.

2. Thermotropic Liquid Crystals :

The long and rod-shaped molecules with one or more polar or\and polarizable groups favour the parallel alignment of the molecules. In a crystalline solid, if the conditions are favourable for mesomorphism, the ordered structure breaks down in stages, first passing into liquid crystalline state. This state has a certain degree of order and hence acquires an isotropic 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 super-cooling. The schematic representation for enantiotropic mesophase is as under : Crystalline t_1 Liquid-Crystalline t_2 Isotropic Solid state ~ Mesomorphic state Liquid state

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 , but on cooling, super-cooling may occur and the temperature may fall considerably below t_1 and mesophase may appear at temperature t_2 before the crystallization occurs. This type of mesomorphic state where t_2 is at lower

temperature than t₁ and is observed only on cooling is known as monotropic mesophase. The schematic representation for monotropic mesophase is as under :

Crystalline Solid State t_1 Isotropic Liquid State t_2

Mesomorphic State

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

3. Thermotropic Mesophases :

On the basis of the molecular arrangements Friedel (6) 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 polymesophases. 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 :

Crystalline t_1 Smectic t_2 NematicOR t_3 IsotropicSolid state \longleftarrow mesophaseCholestericLiquidMesophasestate

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.

Crystalline t₁ Smectic t₂ Smectic t₃ Nematic t₄ Isotropic $II \rightleftharpoons I \swarrow I \backsim Or \backsim Liquid$ Solid state (Smectic-B) (Smectic-A) cholesteric Liquid 3.1 Smectic Liquid Crystals :

The term smectic originated from the Greek word "Smectose" meaning soap like and was coined by Friedel (6) as smectic mesophase is viscous, turbid liquid with reminiscent properties of soaps.

Smectic liquid crystal compounds are stratified and the melting process evidently disrupts end to end molecular cohesion, but the temperature at which the mesophase is stable, is not sufficient to break apart lateral association and the layers remain essentially intact. Smectic liquids therefore, maintain a good deal of two dimensional order, best illustrated as a pencils in box or cigars.

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

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 characterized by the formation of series of strata or terraces. These terraces are called the Grandjean terraces after their discoverer Grandjean (21). 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 (22).

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 battonnets. These increase in number as the temperature falls, coalesce and show evidence of a focalconic 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. The study and explaination of the focal-conic texture are largely due to G. Friedel (6). Bragg (23) has given an excellent account of the focal-conic structure and the geometry involved, which furnish further evidence for the layer theory of the smectic structure.

Based on Hermann's (24) classification, Saupe (25) has classified the smectic phase into two classes; smectic phase with unstructured layers and smectic phase with structured layers. The extensive work of Sackmann **a**'

Type of smectic Structure Texture mesophase Smectic -A Planar i) Stepped drops. ii) Oily streaks. . iii) Homeotropic Non-Planar Simple polygonal.texture. i) (DUP IN ii) Simple fan shaped texture. . Cyclides) iii) **Batonnets** iv) Bubbletextures. Cylinders i) Myelinic textures. Smectic - C Planar i) Homogenous texture ii) Stepped drops , . Schlieren texture. iii) Broken polygonal.texture. Non-Planar i) (DUP IN ii) Broken fan shaped texture. Cyclides) iii) Batonnets. Twisted Planar texture i) ii) Schlieren texture. Straited fan shaped textures. iii) Smectic-F Planar i) Schlieren texture ii) Stepped drops. Non-Planar i) Stripped, broken fan shaped (DUPIN textures Cyclides). Smectic - B Hexagonal Mosaic texture. i) Planar ii) Homeotropic texture. Stepped drops. iii) iv) Batonnets. v) Ovals. . vi) Lancets. Non-Planar Focal conic texture i) (DUP IN (Paramorphosis) Cyclides) .

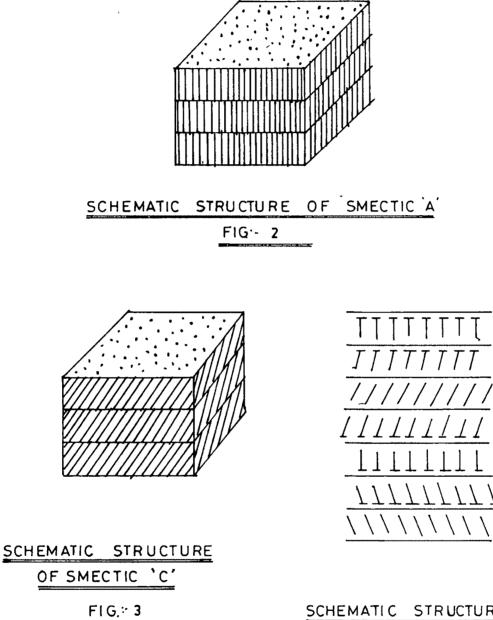
Table : 1Texture classification of smectic mesophases.

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Type of smectic mesophase	Structure		Texture		
	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 shapped texture		
Smectic - G	Planar	i)	Mosaic texture.		
		ii)	Stepped drops.		
Smectic – D	Cubic Bands	i)	lsotropic mosaic texture.		

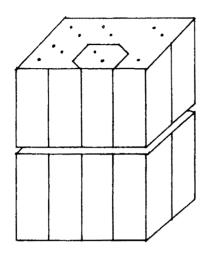


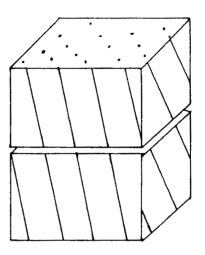
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SCHEMATIC STRUCTURE

OF SMECTIC 'C' FIG. '- 4

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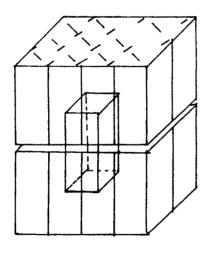
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SCHEMATIC STRUCTURE OF HEXAGONAL <u>SMECTIC 'B'</u> <u>FIG: 50</u>

SCHEMATIC STRUCTURE
OF MONO CLINIC
SMECTIC B
FIG = 5b.

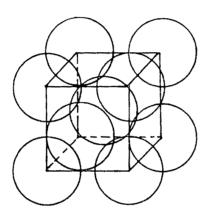
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SCHEMATIC STRUCTURE OF
SMECTIC 'E'
FIG · 6

IATIC	ST	RL	JC T	URE
SME	СТ	۱C	`G	'
F	IG	-	7	
	SME	SMECT	SMECTIC	ATIC STRUCTI SMECTIC G FIG - 7



SCHEMATIC STRUCTURE OF SMECTIC 'D'

FIG.- 8

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and Demus (26) and of de Vries (27) has revealed some of the detail^{ed} arrangements of these phases. The most common smectic phases are designated as A, B and C. Sackmann and Demus (26) have classified smectic phase according to the texture observed in the mesophase (Table-1). They identified seven smectic phases from S_A to S_G (26) by miscibility studies. de Vries and Fishel (28) have reported the eighth possible smectic phase S_H .

Moreover, de Vries (29) has classified smectic 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 (30 a), the thermodynamic ordering of known smectic polymorphic forms appears to be as follows :

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

Smectic mesophases are optically positive and behave optically in the same way as uniaxial crystals. The books "Texture of liquid crystals and smectic liquid crystals (30 a,b) provide detailed accounts of all smectic phases.

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

3.2 Interdigited Smectics :

This new family with the structure of highly

ordered smectic like phase is recently reported by de Vries et al., (31). 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

3.3 Nematic Liquid Crystals :

The word "Nematic" is derived from a Greek word 'Nema' meaning threaded schlieren texture. The optical effects of the nematic threads have been studied by Zocher and Birstein (32). Frank (33) named these lines as disclinations. The molecules in nematic phase are arranged with their long axis parallel, but they are not separated in layers and can be compared with a long box of round pencils.



FIGURE ; 9 Molecular arrangement in the nematic phase.

de Vries (34) proposed classification of nematic phases based on X-ray diffraction patterns as follow :

- i) Skewed cybotectic nematic
- ii) Normal cybotectic nematic
- iii) Classical nematic.

Maier and Saupe (35) mentioned in their theory that nematic-isotropic transition temperatures can be determined by calculation of free enthalpy of the phase involved at the transitions. Nematic liquid crystals are optically positive and can be formed by compounds, which are optically inactive or by racemic modification.

3.3.1 New Type of Nematic Liquid Crystals: Carbonaceous Mesophases:

Generally nematogens consist of rod like molecules whose longest axis tend to be parallel in nematic phase. Alben (36), Onsagar (37) and Dreyer (38) suggested that in addition to such positive nematics, it is reasonable to expect that there might be negative nematics with planar molecules aligned with their shortest axis parallel to each other.

The carbonaceous mesophase is an original discotic nematic liquid crystal (39), which appears during liquid phase pyrolysis of many hydrocarbons.

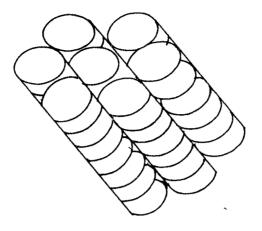
The chemistry of the liquid phase carbonization is very complicated, but the understanding of the formation of microstructure in cokes and graphites was substantially improved since the role of the mesophase transformation was recognised first by Brooks and Taylor (40) and Zimmer and White (41). During the carbonization, the transformation takes place in graphitizable organic materials at temperatures between 350 °C to 550 °C. During the transformation, the large planar molecules formed by the action of thermal cracking and aromatic polymerization orientate more or less parallel to form an optically anisotropic phase called carbonaceous mesophase. Gasparoux (42) has studied this mesophase in detail and reviewed its properties. This mesophase exhibits many analogies with the classical nematic liquid crystal, in particular the dynamic behaviour of disclinations. The study of this phase is difficult because of the high temperature (350 °C to 550 °C), and lack of chemical stability of organic compounds in this range.

3.4 Discotic Mesophase\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, Banglore, India in pure compound with disc like molecules (43). 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 (44) 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 & 11.

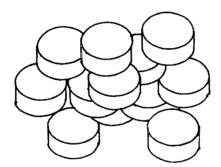
The discs are periodically stacked in columns, the different columns forming a hexagonal array. This mesophase has been variously described as Discotic (45),

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SCHEMATIC REPRESENTATIONS OF THE TILTED COLUMNAR STRUCTURE

FIG. 10



SCHEMATIC REPRESENTATIONS OF THE NEMATIC PHASE OF DISC-LIKE MOLECULES

FIG. = 11 .

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Canonoic (46) or Columnar (46,47) phase.

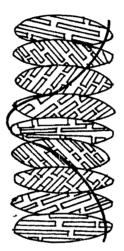
The columnar structure has been confirmed by Xray. It has been established that these mesophases exhibit a rich polymorphism comparable to polymorphism observed in rod-like system. Disc like molecules (48,49) with cholesteric properties are reported in literature.Re-entrant phenomenon in disc like liquid crystals (50) is also reported. Abied et. al., (51) and Vora et. al., (52) have reported disc like molecules with only three substituents.

Number of examples are reported in the literature with typical structural units which are varied and fascinating. Kawada et al., (53) have reported novel nematogenic benzene derivatives; N,N'dialkanoy1-2,5,6-trimethy1-4-alkanoyloxy-1,3benzenediamines.

Recently Kreuzer et al., (54) have reported discotic liquid crystals cyclic siloxanes with mesogenic side groups.

3.5 Cholesteric Liquid Crystals :

The cholesteric phase was observed in cholestrol derivatives hence they derived this name cholesteric phase. It is twisted nematic phase as it possesses the structure of layered nematic liquid crystals twisted about an axis perpendicular to the molecular layers, which results in helical structure. Nematogens with chiral centre also exhibit cholesteric



PROBABLE ORGANIZATION OF THE CHOLESTERIC PHASE

FIG:-12

phase (55-57) hence, they are called "chiral nematics". Gray (57) 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.

Cholesteric liquid crystals have helical structure (Fig. 12) hence they behave in unique and in most striking way not observed in other types of liquid crystals i.e. reflection of iridescent colours. Certain cholesteric compounds can selectively scatter light into different colours. The colour of the reflected light can be determined by (a) pitch of helix (b) by temperature (c) the angle of the incident beam. Physical effects which wind or unwind the helix, such as temperature, mechanical disturbance like pressure or shear and traces of organic vapours, result in various colour changes. In contrast to smectic and nematic compounds cholestric liquid crystals are optically negative. They generally have three types of textures:

(i) 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.

(ii) Plane Texture or Planar Texture :

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 the wavelength of light at the centre of the reflection band is equal to the wavelength of the pitch multiplied by refractive index.

(iii) Blue Phases:

These phases, named for their visual appearance, often appear in a narrow range of temperature (less than 0.5 °C) between cholesteric and isotropic liquid. Some cholesteric mesogens on cooling the isotropic liquid exhibit phase which is visible to the eyes in reflected light, but it is not visible microscopically in transmitted light using crossed polaroids. This phase is known as blue phase. This type of cholesteric compounds having blue phase have small pitches which are less than 700 nm. A blue phase sample reflects the colours of light that would be associated with a cubic structure having a lattice parameter about the same as the pitch of the cholesteric phase. This phase on further cooling changes to a bireferingent texture. Due to this, the transition temperatures on cooling isotropic liquid-cholesteric, not readily observed optically and one gets the impression that supercooling is occuring. The nuclear magnetic resonance

spectroscopy was used to determine the possible structure of the blue phase (58).

Bergmann and Stegemeyer (59) have confirmed the blue phase of cholesteryl nonanoate by calorimetric and microscopic studies and they reported the existence of two polymorials forms of blue phase. These phases are optically isotropic, exhibit Braggs (light) scattering and monocrystals may be grown showing distinct crystal faces. Stegmeyer 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 III).

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). Recently, Kitzerow (70) have presented an experimental review on electric field effects on blue phases.

4. Re-entrant Behaviour of Mesophases :

Cladis (71) was the first to observe the phenomenon of Re-entrant nematic in a binary mixture at normal pressure. Previously it was believed that nematic phase being less ordered than smectic phase, should be obtained at higher temperature. In contrast to this, she observed nematic phase at lower temperature than the smectic phase. The nematic phase obtained at lower temperature than smectic phase is called Re-entrant nematic phase. Now it is known that certain cyano compounds with alkyl or alkoxy end groups exhibiting the bilayer smectic A phase also exhibit Re-entrant nematic phases (72,73). The explaination 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 temperatures. This was observed also in case of mixture (74) at atmospheric pressure, at high pressure (75) and at atmospheric pressure in pure compounds (72,73).

Arora et al., (76 a) have reported recently Reentrant phenomenon in cyano substituted biphenyl esters having flexible spacer.

Much work in the field of re-entrant behaviour has been carried out ever since its first discovery (77- 93). 4-n-Octyloxybenzoyloxy-4'-Cyanostilbene exhibits Re-entrant nematic and smectic phases (78).

Number of homologous series having terminal polar groups such as -CN, $-NO_2$, -Br were studied by Destrade (77-79) et al., showing Re-entrant phenomenon in nematic and smectic phases. They have discussed the relation between the molecular structure and the influence of the central group and of electron withdrawing terminal groups such as -CN, $-NO_2$ and -Br.

-22

They (77) have also discussed the influence of the alkyl, alkoxy and alkanoyl terminal substituents on the Re-entrant phenomenon. Demus et al., (86) 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 (94), with phase appearing with change of temperature both above and below a columnar phase. Destrade et al., have reported Re-entrant cholesteric phases in polar mesogens. (79,80).

Re-entrant phenomenon in a new polar cyclohexane series has been reported by Nguyen (89).

Subramaniam et al., (82) have reported re-entrant isotropic phases 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 intermolecular helix to random coil transition which leads to macromolecular conformation in consistent with liquid crystallinity.

Trivedi and Thakkar (92) 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 (93,95).

5. Lyotropic Liquid Crystals :

In lyotropic liquid crystals (amphiphilic

compounds) mesophases are obtained by the forces of solvation. Ammonium oleate was the first lyotropic liquid crystal reported by Lehmann (96). McCBain (97) has discussed the form of mesomorphism in soap solutions. Lyotropic mesophases are further divided into several categories according to their structures. They are often two component systems composed of water and amphiphilic compounds. However, multi-component systems are also common in lyotropic liquid crystals. Small et al., (98) have studied lyotropic mesomorphism of ternary and quaternary systems of Lecithin, cholesterol and water.

Lawson and Flautt (99) have studied NMR spectroscopy of smectic and waxy mesophases in various surfactant systems, such as sodium palmitate - water system. Robinson (100) has reported lyotropic cholesteric phase and discussed similarities between lyotropic cholesteric and thermotropic cholesteric phase. The constitutional analogies between amphiphilic, non-amphiphilic and plastic crystals have been discussed in detail by Gray and Winsor (101). Tobacco Mosaic virus exhibits this type of mesomorphism (102). Recently, Vora et al., (103) have reported lyotropic mesomorphism using concentrated sulphuric acid as solvent in polymers.

6. Plastic Crystals :

Timmermann (104) was first to observe and

recognize the plastic crystals as compact globular molecules. A plastic crystal possesses long range positional order but orientationally completely disordered, whereas liquid crystal has orientational order and zero (or reduced) positional order. The basic difference between two classes of the compounds is the molecular shape and geometry. Liquid crystalline compounds are long, rigid and rod like whereas plastic crystals are globular and compact. A primary determining factor of mesomorphism is length to breadth ratio of molecular frame which is denoted by R. If R >>1, than possibility of liquid crystal formation is there, if $R\approx 1$ then plastic crystal may form.

7. Mesomorphism in Biological Systems :

It seems that there can not be life without lyotropic mesomorphism. The biological membranes function through gel and liquid crystalline phases. The effect of drugs, toxic materials etc. are reflected in these phase changes of membranes which play vital role in different functions keeping life throbbing.

As early as 1854, Virchow (105) was the first scientist to observe the mesogenic properties in the form of myelin in biological system. Living sperms composed in part of protein, nucleoproti@ns and albumines have been shown to possess a mesomorphic state (106, 107). The sense such as smell may be involved with substance 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).

The brilliant work of Engstorm and Finean (110) on the structure of nervous tissue shows the presence of two components in optical opposition and in the concentric multilayer of lipid or lipoprotein forming themyelin sheath.

From a study of structure of Hemoglobin, Perutz et al., (111) concluded that it could assume liquid crystalline form in red cell. Robinson (112) in 1956 showed conclusively that polypeptide poly-r-benzyl-tglutamate existed in organic solvents as a cholesteric liquid crystal spiral.

Untill 1970, no one reported the presence of liquid crystalline compounds in plants. Knapp and Nicholas (113) reported the isolation of tetracyclic triterpene ester exhibiting smectic and cholesteric mesophase, from banana peals and from the seeds of strychnine producing plants. Livolant (114) has observed cholesteric phase of DNA in vitro and in vivo. Recently, same author has: reported the electron microscopic analysis of the highly concentrated liquid crystalline phase of DNA (115).

Physical Properties of Liquid Crystals :
 Pioneering work on different physical

properties has been carried out by a number of research workers. Van der Lingen (116) and Huckel (117), de Broglie and Friedel (118), Pohl et al., (119) and Brown et al., (120) carried out X-ray studies. NMR study was carried out by Spence et al (121, 122). Lippmann et al., (123) and Saupe and Englert (124). The studies of ultraviolet and infrared spectroscopy were carried out by number of researchers (125,126). Viscosity studies were also carried out by Schenk (127) and Porter and Johnson (128). Kast (129) and Bhide et al., (130) have given a critical summary of dielectric study. The Mössbauer effect was studied in smectic liquid crystalline state for the first time by Uhrich et al., (131). The use of liquid crystals as stationary phases in chromatography was initiated by Dewar et al., (132) and Kelker (133). The detailed study on chromatography was carried out by Chow and Martire (134). Recently Vora et al., (135) used few liquid crystalline compounds as a stationary phases in gas chromatography. Magnetic susceptibility studies were carried out by many scientists (136-138).

A number of books and review papers have discussed the physical properties of liquid crystals and their importance in the different technical applications (139-154). Viscosity and surface tension studies are important because of the sharp change in molecular orientation at the phase transition. Liquid crystals, preferably with less number of unsaturation are now used as solvents in infrared and ultraviolet spectroscopy (155). Malthete and Billard (156) have shown ferrocene derivatives to be mesogenic which are very useful in Mössbauer spectroscopy. Thus the study of physical properties is important as it decides the applicability of liquid crystals and they can be exploited for their practical advantages.

9. Mesomorphic polymers :

Study of organic compounds exhibiting liquid crystallanity dates back. However, it is only in the last thirty years that liquid crystalline order has been recognised in polymer system. In 1950, Oster (157) studied polymers with liquid crystalline order in aqueous solution of tobacco mosaic virus and in 1956 Robinson (112) reported polymeric liquid crystalline solutions of poly (r-benzyl-L-glutamate) in various solvents.

The polymerization of non-mesogenic monomer within liquid crystalline solvents has been reported by Amerik and co-worker (158), Tanaka et al., (159) and Blumstein et al., (160). Organisation of the monomer within a mesomorphic solvent was found to have a considerable influence on the kinetics of polymerization and molecular weight. The polymerization of liquid crystalline monomers, the structure and the thermotropic liquid crystalline behaviour of the resulting polymers were studied by Perplies et al., (161,162) and by

Wendorff et al., (163). The polymerization of mesogenic monomers were studied in the mesomorphic state, the isotropic liquid state and in isotropic solutions. The polymers obtained were thermotropic mesomorphic in nature.

Polymerization of non-mesogenic monomers having mesophase conducive side chain may result in polymer with thermotropic liquid crystalline properties (164-166). Number of patents and reports claiming the production of fibers (Kevlar fibers) from polymer solutions existing in the liquid crystalline state are now known (167-169). These fibers have been reported to have tenacities which are greater in magnitude than those reported for steel on a weight basis. Kevlar fiber has been shown to be useful as a tire cord, as a replacement for glass and steel belts in bias-belted and radial belted tires. Kevlar-49 has been shown to be competitive with the lower modulus types of graphite in rigid composites. Willfong and Zimmermann (170) have discussed relationship of Kevlar properties to end use applications. The para oriented aramid fibers are used in flame resistant clothing. Liquid crystalline polymers are mainly classified as main chain liquid crystalline polymers and side chain liquid crystalline polymers. Classification of liquid crystalline polymers is given in Table -2.

Recently, number of synthetic polymers

<u>Classification of Mesogenic Polymers</u> (176)

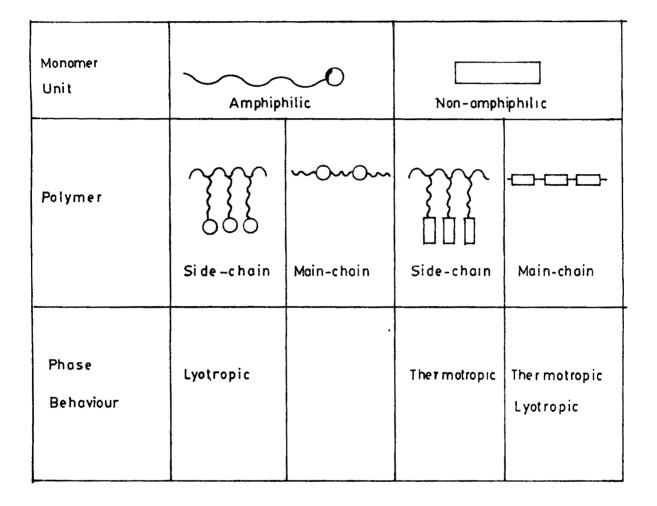


TABLE - 2

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exhibiting liquid crystalline behaviour have been reported (171,172). West et al., (173,174) have used liquid crystal epoxides in haze free "Polymer Dispersed Liquid Crystals". Number of books have appeared which provide detailed account of mesomorphic polymers (175-177). The presence of liquid crystalline structure in polymers has created great upheaval in the field of polymer chemistry which has led to different types of studies in polymer chemistry including synthesis of mesogenic polymers, the characterization of mesogens, determination of orderliness and exploitation for technological uses (176, 178-180).

10. Mixed Mesomorphism :

Liquid crystals with low crystal-mesophase transition temperatures and with wide phase length have been primary goal of organic chemists in recent years. Since the occurance of single component, room temperature liquid crystal with wide mesophase range is rare, it is necessary to mix two or more low melting materials which may give room temperature mesomorphic mixture with wide mesophase range. Number of workers have studied and reported the formation of mixed liquid crystals in the case where one or both the components are non-mesogenic (181-185). Dave and Vora (186) have reviewed the work of Dave et al., (182,183) on mixed mesomorphism and have derived an order of end group efficiency in the nematic mesophase as under : $NO_2 > OEt > OMe > n-Pro > N Me_2 > Me = Cl > F = Br > H$

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Many mixtures have been reported where a mesogen or other compounds were added to a low melting mesogens, either to decrease the melting point, or to increase the mesophase range or to change the electric conductivity and dielectric anisotropy (187-191). Domon and Billard (192) and Hulme and Raynes (193) have used a numerical technique to predict the eutectic compositions of liquid crystalline mixtures.

Majority of binary systems reported so far have components, one or both of which may be either nematogenic or non-mesogenic. Recently extensive studies have been carried out for mixed mesomorphism of smectic type. Dave et al., (194) studied some binary systems comprising of a smectogen and non-mesogenic schiff bases. They observed nonlinear behaviour (maxima) in the case of mesogenic-isotroic transition temperature curve when the non-mesogenic schiff bases had a terminal nitro or chloro substituents. Similar behaviour was also observed when one of the component was polymesomorphic in which nematic mesophase was eliminated and the smectic-isotropic transition temperature curve showed non linear behaviour (maxima). Similar behaviour was observed by Schroeder and Schroeder (195) in the mixture of alkoxy azoxybenzenes with nitro substituted nonmesogenic schiff bases. Vora and Chhangawala (196) and Padmini et al., (197) reported binary systems consisting of a smectogen exhibiting polymorphism and non-mesogenic

schiff bases, in which they observed that smectic phase was changed to nematic phase even when the concentration of the non mesogenic schiff-base. was lower. Arora et al., (198) and Neubert et al., (199) have reported creation of nematic phase in smectogen by the addition of the second component which is also a mesogen. This work has vindicated the results of Vora et al., who reported such behaviour of the binary phase diagram for the first time.

Griffin et al., (200, 201) have studied number of binary systems where one or both the components have strongly polar terminal groups (-CN or NO₂). They have attributed the enhancement of smectic mesophases in such systems to the bimolecular smectic structure present in such mesogens. Shashidhar et al., (202) for the first time, observed a new kind of smectic A - A transition in binary mixtures of terminally substituted cyano and nitro compounds. Recently, Heppke et al., (203) reported Re-entrant nematic phase in the mixtures of isothiocyanato and cyano compounds. Vora and Dixit (204) have studied binary systems exhibiting linear and nonlinear thermal behaviour. Vora and Gupta (205) and Sarma et al., (206) have studied the binary mixtures of mesogenic and non-mesogenic compounds.

Cladis and Brand (207) reported for the first time an inverted cholesteric phase surrounded by different types of smectic A phase in a binary system. Lee et al., (208) have used fourier transformation

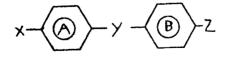
infrared absorption (FTIR) to study the binary mixture of discotic liquid crystals.

11. The Effect of Chemical Constitution and Mesomorphism

There exists the close relationship between the molecular structure and the mesomorphism of a compound. For finding correlation between molecular structure and liquid crystalline properties considerable interest has been shown from the very beginning. The accumulation of the information as per the literature indicates that there are host of the compounds which exhibit liquid crystalline properties and it is very difficult to classify all of them in a general way. However, emerging picture can be summerized based on the literature survey as under :

The compounds can be aromatic, alicyclic, heterocyclic and with different combinations.

The rings A and B can be alicyclic or aromatic, X and Z are terminal para substituents and Y is the central linkage. X and Z are terminal substituents such as alkyl, alkoxy, cyano, -CNO, nitro etc. The usual central linkages are -CH=N-, -C=C-, -CH=CH-,-(CH=CH)_n-, -COO-, -CH = CHCOO-. -CH₂-CH₂-, -O-CH₂-CH₂-O, -N=N-, -NHCO- etc..



The examples of exhibition of mesomorphism in

AROMATIC COMPOUND :-

Ref: 209

 $H_{21} C_{10} O = CH - O - CH = N - O - C_{10} H_{21}$ $K \xrightarrow{73 \ C} S_{G} \xrightarrow{120 \ C} S_{F} \xrightarrow{150 \ C} S_{I} \xrightarrow{156 \ C} S_{C} \xrightarrow{190 \ 8 \ C} S_{A} \xrightarrow{192 \ 4 \ C} Isotropic$

<u>FIG > 13:a</u>

ALICYCLIC COMPOUND :

H45 C2700C C00 C27 H45

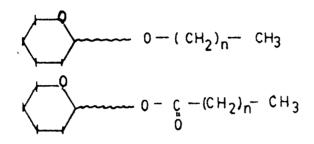
C27H45 - Cholesteryl group

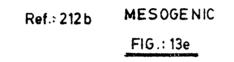
K 125 °C S 197 °C Ch 232 °C Isotropic

Ref: 210

FIG: 13.b

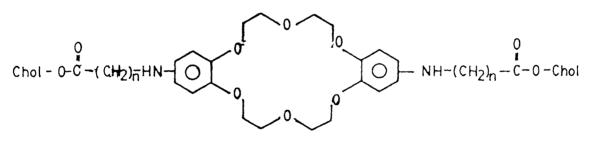
CARBOHYDRATE LIQUID CRYSTALS





Many Scientists have reported mesogens with typical molecular geometry challenging the present beliefs of relationship between molecular structure and mesomorphism, few rexamples are:

1)



Ref - 213

FIG > 13 f

HETEROCYCLIC COMPOUND

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ORGANOMETALLIC COMPOUND

CH₃ 0
$$-$$
 CH= N $-$ O $-$ Hg $-$ OCO $-$ CH₃
K $\frac{177^{\circ}C}{N}$ N $\frac{180^{\circ}C}{15}$ Isotropic

Ref. : 212 a

FIG : 13.d

5 ~ ~ ~

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RO - OF CH = CH - COOH

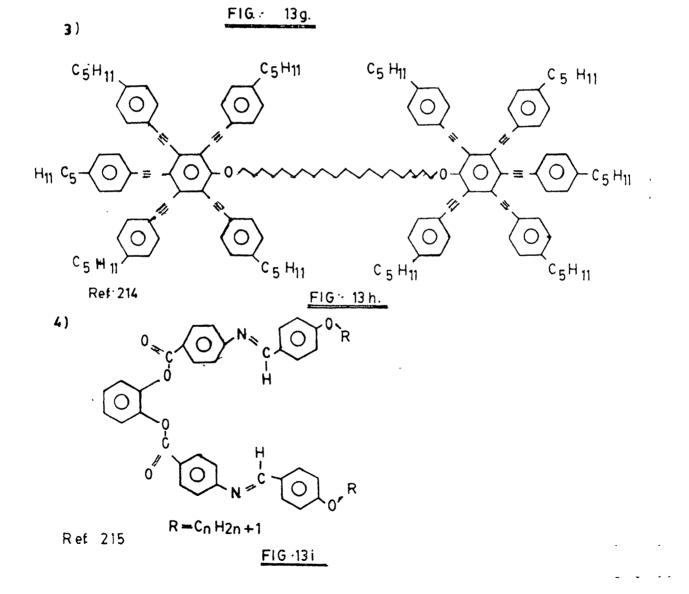
R = Linear alkyl chains with C4 to C8 atoms

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•

INS

2)



different types of compounds are listed in figure 13-a to 13.

11.1 The Effect of Terminal Substituents on Mesomorphism

Terminal groups present in the molecule have got their own importance because of their polarity. It has been found that, terminally substituted compounds exhibit more stable mesophases compared to unsubstituted mesogenic compounds. However, for smectic liquid, crystals, certain terminal groups reduce the thermal stability. As the carbon chain of alkoxy or alkyl group is lengthened, the tendency of depressing the melting points is increased. Liquid crystals of moderate chain lengths are normally purely nematic, increasing the length of the carbon chain gives both smectic and nematic mesophases and very long chain lengths usually exhibit only smectic phases. Gray (216) has discussed in detail the effect of increase in alkyl chain in a mesogenic homologous series. Gray (217) obtained group efficiency order in nematic and smectic system5. Gray (218) and Dave and Vora (219) have studied the effect of substitution in cholesteryl benzoates, and obtained a group efficiency order for the different substituents in the cholesteryl systems.

From application point of view the end group in mesogen has become quite important, as mesogens with

positive or negative dielectric anisotropy are used in display devices. A highly dipolar end group, whose dipole works across the long axis of the molecules endows the mesophase with a negative dielectric anisotropy whereas if the dipole is acting along the long axis of the molecules, then it exhibits positive dielectric anisotropy. Consequently many mesogenic compounds having cyano, nitro and halogen as lateral or end groups are synthesized (220-223).

Schroeder and Schroeder (224) have reviewed the liquid crystalline compounds with free phenolic or amino groups and have also synthesized number of compounds exhibiting liquid crystalline properties having free phenolic and amino groups. Vora and Gupta (225) have reported for the first time an extensive mesogenic homologous series having phenolic end group. They have pointed out that not only intermolecular hydrogen bonding of the end phenolic group is present but additionally the hydrogen bonding of end phenolic group with azomethine schiff base linkage also takes place giving secondary structures. The infrared spectra gave clear indentification for such molecular arrangement. Mc2 Millan and Labes (226) have reported mesogens with terminal amino groups and alkyl amino groups. Hirata et al., (227) have described some ortho hydroxy substituted liquid crystals which are stabilized through hydrogen bonding.

Coates and Gray (228) have evaluated the effect

of the end trifluoromethyl group on mesomorphism, and have found that compared to other end groups it is less conducive to mesomorphism. Vora et al., (229) have also studied the effect of trifluoro methyl group on mesomorphism. Demus et al., (86,230,231) have studied the effect of β cyanoethyl and -CH = C COOR

terminal groups in binary mixtures and discussed re-entrant behaviour in terminally nonpolar substituted binary mixtures. Destrade et al., (77,232) have reported the influence of the terminal substituents on the re- entrant phenomenon and found that the alkoxy group appears to be more suitable to induce the re-entrant mesophase phenomenon than alkyl terminal group.

Dabrowski et al., (233) have reported new homologous series with the isocyanato terminal group. They have found that the mesogenic properties of the compound with the -CNO terminal group depend strongly on the structure of the rigid core of the molecules and more strongly than the analogous compounds with the cyano terminal group. Chung et al., (234) have synthesized thermotropic mesogenic compounds having two terminal units and central flexible spacers.

Demus et al., (235) have synthesized terminally swallow tail type compounds and established that by selecting proper geometry of molecules, the liquid crystalline property can be maintained in such systems. Recently, in search of chiral smectic *C phase, number of mesogens are synthesized by different researchers

where terminal alkoxy groups are chiral in nature (236-239).

11.2 The Effect of Lateral Substituents on Mesomorphism

Lateral substituents may force apart the molecules and may thus reduce the intermolecular lateral cohesions but at the same time side substituents may increase the molecular polarizability which in turn may increase the intermolecular attractions. Normally, the first effect predominates i.e. a lateral substituent decreases the mesophase thermal stabilities. However, if the substituents do not have fullest breadth increasing effect as in the case of the 5 - substituted -6 -nalkoxy-2-naphthoic acids (240) then the second effect predominates i.e. the thermal stabilities of substituted mesogens increases. An order of the substituent effect in decreasing the smectic and nematic thermal stabilities for the lateral substitution is as follows which was given by Gray (217).

Smectic Order : H<F<Cl<Br = NO₂<Me<I
Nematic Order : H<F<Me<Br<I = NO₂

The effect of lateral methyl group on benzylidene anilines was studied by Gardlund et al., (241). While effect of lateral -Br, -CN and -F groups on mesomorphism was studied by Dubois et al., (242). Griffin et al., (243) have investigated the effect of lateral trifluoro methyl group on mesomorphism and correlated it with a lateral methyl group. Arora and coworkers (244) have synthesized a series of phenylene esters in which the effect of a lateral methyl group on the transition temperatures was investigated. The introduction of the lateral methyl group results in a decrease in the transition temperatures of all the phases. This has been attributed to the broadening of the molecules, as well as to the change in molecular conformation. The increased dissymetry resulting from the methyl group, leads to less effective packing in crystal lattices and therefore lowers the crystal mesomorphic transition temperatures.

Mesomorphic properties of 2,6-; 1,5-, and 1,4-; substituted naphthalene derivatives were studied by Gray and Jones (240), Wiegand (245) and Dave et al., (246,247). These studies show that the order of mesophase thermal stabilities in naphthalene ring substitution is as :

2,6- > 1,5- > 1,4-

Increase in the molecular breadth have three pronounced effects :

- (i) Lowering of the temperature at which mesophase appears.
- (ii) Decreasing the stabilities of the mesophase.
- (iii) Destroying any smectogenic property regardless
 of alkoxy or alkyl group chain length.
 Vora et al., (248,249) have studied number of

homologous series with bulky methoxy group as a lateral-

Å3

substituent. They have found that contrary to common observations lateral methoxy group does not depress much crystal-mesomorphic transition temperatures, but the mesomorphic -isotropic transitions are drastically reduced.

Demus et al., (250-252) have reported compounds with lateral long chain substituents and established new molecular concept for liquid crystals. They have found that the nematic state is mainly stabilized by steric repulsions and that the attractive forces play only a second role. Bapat and Ghatage (253) have synthesized number of laterally substituted mesogenic compounds and used in gas liquid chromatography. They have found that laterally substituted liquid crystals are showing tremendous advantages over earlier liquid crystals in separation of intricate mixtures of isomeric product. Recently, Takenaka et al., (254) have reported ferroelectric liquid crystals with lateral long alkoxy group.

Surendranath et al., (255) have studied the effect of the lateral methoxy group on the re-entrant phenomenon. Gray et al., (256-258) have reported laterally chloro and fluoro substituted compounds. Chloro substituted compounds could be expected to be useful in two frequency switching devices, due to its greater polarity.

11.3 Mesomorphism in Homologous Series :

Many homologous series of liquid crystals containing different functional groups are synthesized and a systematic study of change in the basic molecular structures and its effect on various physical properties have been investigated by many workers in the field. For a homologous series, when the mesomorphic transition temperatures are plotted against the number of carbon atoms in the alkoxy chains, smooth curves can be drawn for even and odd carbon atoms. The upper curve corresponds to even and lower curve to odd number of carbon atoms. The curves usually have the falling tendency as the series is ascended. This is referred to as an odd even effect. For a system with n-alkyl group attached directly to the phenyl ring, the reverse situation arises because the oxygen of ether linkage in the alkoxy group is equivalent stereo-chemically to a methylene unit. This also decreases all the transition temperatures. Although transition temperatures follow a some what regular trend, the prediction as to crystal mesophase transition temperatures can not be made.

As carbon chain is lengthened, the transition temperatures are generally lowered. The amplitude of this change decreases with increasing carbon chain length, and the two curves merge later in the series. Usually the smectic-nematic transition temperatures do not exhibit the odd-even effect but lie on a smooth curve which rises at first, then levels off and may or may not merge with the falling nematic-isotropic curve.

However, there are few cases in which the odd-even effect is observed for smectic-nematic and smecticcholesteric transition temperatures. Gray and Goodby (259) have observed that the extended carbon in a biphenyl system has striking effect on the incidence of the smectic 'C' mesophase.

12. Applications of Liquid Crystals :

Due to the versatile applications of mesogenic materials, they are finding more and more importance day by day, hence, it has become fascinating field of current research. Now a days liquid crystals are used in almost every field particularly in the field of electrooptical applications and in biological systems. Their applications are listed below.

12.1 Electro-Optical Applications (260-263)

Electro-optical applications include seven segment display panel, electronic windows which go from clear to frosted with a flip of a switch, numeric displays for watches, calculators, toys, games, point of scale advertising panels, flat screen television, handheld TV and terminals, heart monitoring devices, jewellery, house-hold appliances, pens, temperature indicator, image convertor and storage displays (264). The liquid crystal storage displays can record and reproduce the image. A laser addressed projection displays and a matrix addressed displays are also used. Hareng et al., (265) have summarised the recent work on

these two kinds of displays. Reflective type of liquid crystal display device is also reported (266) which is more readable than conventional one. A liquid crystal device is made by sandwiching a liquid crystal mixed with some dopent between two glass plates coated with some current conducting transparent materials such as tin oxide. 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 becomes transparent in microseconds. The advantages of liquid crystal displays are low operating voltages, 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 (267), which gives direct 2-dimensional acoustic images with good response time. The use of liquid crystals in the IR video-camera has been reported (268,269). Gray (270) has reviewed the current state of art of dyes used with liquid crystals for electro-optical display devices. The use of smectic phases in display devices is discussed by Thomson (264). Hareng et al., (265) have discussed two types of display applications of the thermotropic effect in smectic liquid crystal phase.

12.1 Ferroelectric Liquid Crystals (Chiral Smectic*C) (271)

Current liquid crystal devices (LCD) are based on dielectric alignment effects in nematic or cholesteric phases in which, by virtue of the dielectric anisotropy, the average molecular long axis takes up a preferred orientation in an applied field. Since the coupling of an applied electric field by this mechanism is rather weak the electro optical response time for these devices is too slow for many potential applications. The slow response and insufficient nonlinearity of "LCD"s have been the serious limitations. The lack of speed becomes especially important in proportion to the number of elements that have to be addressed in a device. This leads to increasingly impractical production costs for flat-panel displays with potential use, in computer terminals, oscilloscopes, radar and T.V.screens.

A promising way for overcoming these difficulties is to use chiral smectic '*C' liquid crystals in a carefully chosen geometry. 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

High speed even at very low voltage : (i) 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.

(ii) 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.

(iii) 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.

(iv) Large electro-optical response :

The optical change induced by the electric field corresponds to a rotation through 20 to 60 angle of a uniaxial material having a refractive index and anisotropy \triangle n of greater than 0.2. This response is 10 to 100 times larger than that attainable in other bistable electroptical devices. Recently, antiferroelectric liquid crystals are gaining considerable attention because of their characteristic tristable switching (272) applicability for display devices (273-275).

12.3 Liquid Crystals as Temperature Detectors (276) 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 electronic equipments, for the mapping of breast cancer region before operation as cancerous tissues have higher temperature than normal tissues. Solvent vapours (in ppm) such as benzene or chloroform also affect the pitch hence they can be detected in the ppm concentration.

Recently (277), it has been 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 (278,279).

12.4 Non Destructive Testing (217,280,281) :

Cholesteric liquid crystals can be used for the non destructive testing of materials in many ways. They can be used to reveal blockages in heat conducting systems. Local overheating in metal surfaces due to currents in wind tunnel experiments, variation in heat transfer between well bonded and poor bonded areas in honeycomb 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

50

return flight from the moon of the space ship pools if a fight of the space ship high of the space sh

12.5 Liquid Crystals as Reaction Solvents :

Dewar and Nahlovsky (283) 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., (284) have reported that the thermal isomerization of 2, 4, 6 trimethoxy-sthiazine in nematic solvent proceeds faster and with smaller loss in entropy of activation than in isotropic phase.

Tottareli and Samori (285) 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 (286).

Liquid crystal systems are also used in oil recovery. Such systems generally are ternary, involving water, oil and surfactant. At composition and concentration where 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.

12.6 Liquid Crystals 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.

12.7 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 (132,287,288). The selectivity of liquid crystalline phases is consequence

. 52

of the molecular order, shape, polarity, polarizability and flexibility of solute molecules. Vora et al., (135) and many other researchers (289-291) have reported the use of liquid crystals stationary phase in gas chromatography and have indicated their advantages for better separation of hydrocarbons. Richmond (292) 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.

12.8 Liquid Cystals in Spectroscopic Studies

Liquid crystals are widely used in UV, IR, NMR and ESR spectroscopy (293). Information regarding the nature of the mesophase itself can be obtained (294) or liquid crystalline phase can be used as solvents which may provide information concerning bond lengths and preferred conformation of dissolved solute (295).

12.9 Application of polymer Dispersed Liquid Crystals (PDLC) (296)

Uniform liquid crystal droplets in a polymer binder can be achieved by several different phase separation processes making possible electrically switched light shutters with wide range of applications. These applications include large scale flexible displays that do not require polarizers and are simple to fabricate. 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 PDLC technology can be used to form architectural point of view to prepare window shutters which can provide privacy. PDLC's can also be used in automobiles industries to prepare dash board displays, sun roof, side windows and rear windows.

There is a search for organic non-linear materials as they can be easily processed. Liquid crystalline non-linear materials have great opening in "LC Display" world. A non-linear liquid crystal material provides conditions of single crystal. Search for good optically non-linear material is on, and one day we might have ideal liquid crystal for application.