INTRODUCTION

LIQUID CRYSTALS

LIQUID CRYSTALS

The field of liquid crystals is one which has attracted physicists, chemists, biologists and technologists alike. Their concerted efforts continue to yield rich rewards in the domain of science and of technological applications. In fact this field is expanding so fast that it is appropriate to quote the red queen Alice encounters in her wonderland - " Now, here you see, it takes all the running you can do to keep in the same place. If you want to get somewhere else, you must run twice as fast".

1. DEFINITION AND NOMENCLATURE:

Liquid crystalline phase has been known to exist in low molecular weight systems since the end of the nineteenth century. Now liquid crystalline phases have been termed the fourth state of matter. Liquid crystals are highly associated liquids, that occur over various temperature ranges in melts or solutions of certain organic molecules and compounds. Liquid crystallinity is an intermediate state of matter, existing between the usual crystalline solids and isotropic liquids.

Under appropriate conditions of temperature and pressure, matter may exist in three possible states of aggregation - solid, liquid and gaseous state. In the solid state or crystalline state, the molecules are fixed and rotations are not possible. In liquid state, the molecules are mobile in three directions and can rotate about three axes perpendicular to one another. In liquid crystalline state, molecules are mobile in two directions and can rotate about one axis.

The melting of normal solids is associated with the collapse of overall possitional order of the lattice array and makes the beginning of essentially free rotation of the particles (1). Two intermediate phases of matter have been identified when only one or other of these two freedom (freedom of position or freedom of rotation) has been at least partially obtained. These are termed liquid crystals and plastic crystals. These mesophases (intermediate states) do not satisfy all the properties of either solid or liquid and in fact exhibit many physical properties that are characteristics of both. For example, liquid crystals flow but their optical properties such as birefriengence are those usually expected of regular solids. Molecules within plastic crystals have rotational and diffusional mobilities approaching that of liquid phase although the solid condition is maintained. In liquid crystals, molecules are free to move but their rotational mobility is restricted. In plastic crystals the molecules are free to rotate in place and to some extent change lattice sites, but they still form a regular crystalline superstructure. The phenomenon of mesomorphism is essentially dependent on molecular shape.

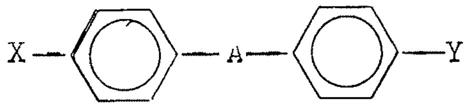
Rinne (2) classified matter as exhibiting either ataxy (disorder or amorphous structure) or eutaxy (an ordered structure).

In 1888, Reinitzer (3) observed peculiar melting behaviour for an ester of cholesterol. He found that the crystals of the substances melted sharply to form not an isotropic melt but gave an opaque melt. The conclusion drawn from this observation was that some type of order still existed in the molten state. Reinitzer furthermore observed that opacity vanished at a higher temperature called the clearing temperature. Lehmann (4) and others (5) have shown that the liquid crystalline state is truly intermediate state of matter.

Lehmann introduced the term " Flüssige Krystalle" (liquid crystal) to describe this strange behaviour of the fluid state. Friedel (6) proposed the nomenclature for these phases as mesophases. Mesophases may arise as a result of temperature variations, the term thermotropic mesophase is used for such mesophases. Mesophases may, however, also result from the changes of the concentration of solutions. With increasing concentration, a transition from a non-ordered isotropic solution to an ordered anisotropic solution can take place. For such systems, the term " Lyotropic liquid crystals" is used. Eventhough, the term thermotropic and lyotropic are widely used, Gray and Winsor (7) preferred the term amphiphilic and non-amphiphilic. The amphiphilic mesogens frequently form mesophases at room temperature or at higher temperature which can incorporate considerable amount of water and/or organic compounds into their structure. So they have been called lyotropic, i.e. solvent induced mesophases. The non-amphiphilic mesogens have mainly been studied as pure compounds with emphasis on the transition temperatures. Thus, non-amphiphilic mesophases are commonly called thermotropic, i.e. temperature induced. A mesomorphic phase characterized by a reversible phase transition is referred to as "enantiotropic".

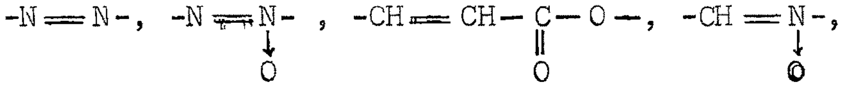
2. CHARACTERISTIC PROPERTIES OF MESOMORPHIC THERMOTROPIC LIQUID CRYSTALS:

There exists a close relationship between the symmetry of the molecules and its capacity to form liquid crystals. In general, the molecules of a liquid crystalline compound are elongated, rod- or lath-shaped and possess middle and terminal polar groups. The shape of these elongated rod-like molecules facilitate to set themselves parallel to one another leading to the closest possible packing in the crystalline or liquid crystalline state, the molecules being held together by local attachment due to the polar groups and non-specific Van der Waals attractions. On raising the temperature, the cohesion between the molecules previously holding them together in the crystalline arrangement, do not break down uniformly in all directions. There may be some residual force still operating which will tend to hold the molecules together in the groups. Thus, for a liquid crystal to be formed, the cohesion forces operating between elongated molecules must be both anisotropic and of suitable magnitude. Another criterion for the formation of liquid crystals is the rigidity of the elongated molecules. If the molecules lack rigidity, flexing may occur along its length and this may prevent the formation of liquid crystals. The introduction of unsaturation in the chain makes the molecules more rigid due to Sp^2 hybridization and thus mesomorphism is attained in number of such compounds. For example, the majority of the thermotropic liquid crystals are aromatic in nature. Aromatic molecules are polarizable, planner, rigid and if substituents are placed at proper positions can give rise to mesomorphism. For benzene nuclei the substituents may occupy p-,p'-positions and be of such kind that they link up at least one other benzene ring which also carries a p-substituent. It is preferable that the linking group between the two benzene nuclei should be of rigid nature. This is represented as follows (8).

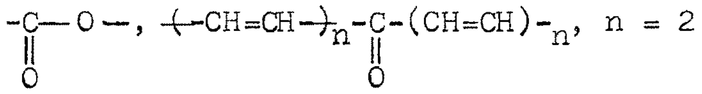


where X and Y are terminal substituents and A is the central linkage. Thus the usual central linkages are,

$-CH{=}CH-,\ (-CH{=}CH-)_n,\ -C{\equiv}C-,\ -CH{=}N-,$

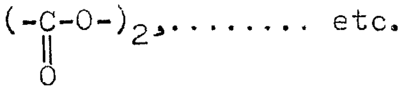


$-N{=}N-,\ -N{=}\underset{\substack{\downarrow\\ O}}{N}-,\ -CH{=}CH-\underset{\substack{\|\\ O}}{C}-O-,\ -CH{=}\underset{\substack{\downarrow\\ O}}{N}-,$



$-\underset{\substack{\|\\ O}}{C}-O-,\ (-CH{=}CH-)_n-\underset{\substack{\|\\ O}}{C}-(CH{=}CH)-_n,\ n = 2$

$-CH{=}N-N{=}CH-,\ \ -CH_2-CH_2-,\ \ -O-CH_2-CH_2-O-,$



$(-\underset{\substack{\|\\ O}}{C}-O-)_2$, ... etc.

The linkage between benzene nuclei through ortho- or meta- positions is not favourable to the liquid crystal formation, because the molecules then become non-linear. However, linearity and rigidity are increased by linking up the benzene nuclei directly and thus biphenyl system provides a rich source of liquid crystals, which are thermally more stable than the benzene substituted analogues. It is observed that benzene nucleus in general or any aromatic (characterizing) system plays an important role in the formation of liquid crystals. However, recently some alicyclic analogues of biphenyl or other aromatic systems are reported to be mesomorphic (9). With the increase in the number of aromatic rings, the stability and the phase length of the mesophases are increased. The replacement of aromatic ring by saturated alicyclic ring gives reduction in the thermal stability of the system whereas in some other systems alicyclic system gives thermally stable phases.

In the crystalline state of mesogen the bonding forces exist between the molecules. However, thermal agitation disturbs these bonds and on heating weaker bonds break first leaving the solid with some degree of relative movement before sufficient thermal energy has been acquired to overcome, in any great degree, the tendency for them to set themselves parallel to one another. Thus, the solid melts to a fluid but remains mesomorphic because of the preferred orientation of the molecules. On further heating the thermal vibrations are increased to a greater extent and the isotropic liquid is obtained. The step-wise thermal break-down in 'Liquid crystallines' may be expressed as follows:

$$\underset{\text{solid state}}{\text{Crystalline}} \xrightleftharpoons{t_1} \underset{\text{mesomorphic state}}{\text{Liquid crystalline or}} \xrightleftharpoons{t_2} \underset{\text{state}}{\text{Isotropic liquid}}$$

The transition t_1 and t_2 take place at sharp definite temperatures and are precisely reversible. But reversal from mesomorphic state into the crystalline state is usually accompanied by supercooling. This type of transition in which t_2 is higher than t_1 is referred to as an enantiotropic mesophase. However in some instances, a solid melts to an isotropic liquid at temperature t_1, but on cooling, supercooling 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 temperature t_2 is lower than t_1 and is observed only on cooling is known as monotropic mesophase. The schematic representation for monotropic mesophase is as under:

$$\begin{tikzcd}
\text{Crystalline solid state} \arrow[rr, "t_1"] & & \text{Isotropic liquid state} \arrow[dl, shift left] \\
& \text{mesomorphic state} \arrow[ul] \arrow[ur, shift left, "t_2"] &
\end{tikzcd}$$

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

2.1 Smectic, Nematic, Cholesteric and Discotic Liquid Crystals:

Friedel (6) carried out detailed optical studies of liquid crystals and conveniently divided them into three types - smectic, nematic and cholesteric. Smectic and nematic mesophases are the most common type of mesophases. The transition temperatures are always definite and define the stability of different mesophases. The change with increasing temperature may be represented as :

Crystalline solid state $\xrightleftharpoons{t_1}$ Smectic mesophase $\xrightleftharpoons{t_2}$ nematic mesophase or cholesteric mesophase $\xrightleftharpoons{t_3}$ Isotropic liquid state

(Fig.1 is a schematic representation of phase transitions in a liquid crystal.)

Hence the transition from completely ordered solid-crystal through the smectic and nematic structures to the true liquid may be outlined as follows:

(i) Three dimentional crystal :Apart from vibration, the centres of gravity of all lattice units are fixed, rotations are not possible.

(ii) Crystals with rotating molecules: The centres of

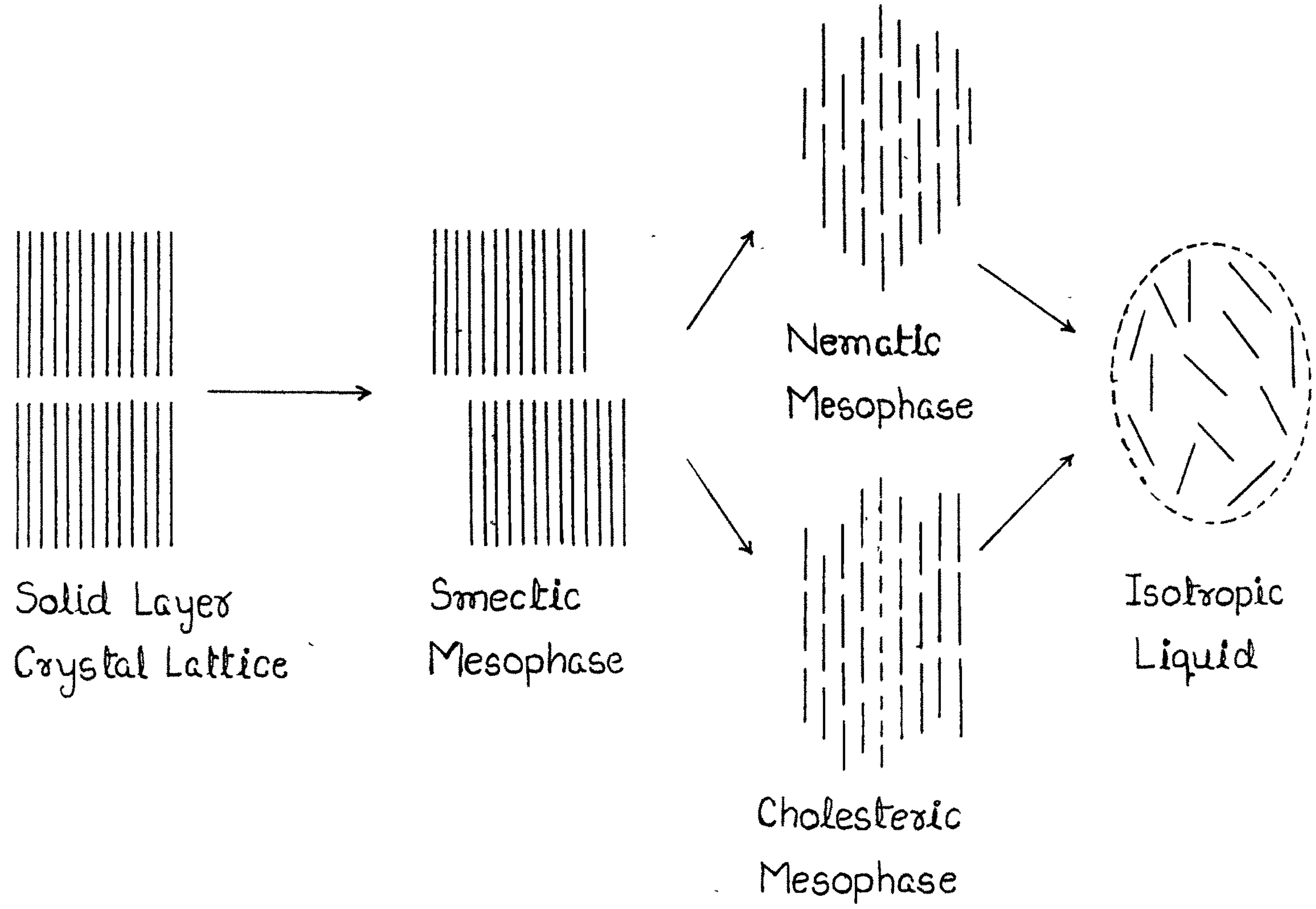


FIG. 1: Schematic Representation of Phase Transitions.

gravity of all the lattice units are fixed, rotations about one or more axes is possible.

(iii) Smectic structure: The centres of gravity of the units are mobile in two directions, rotation about one axis is permitted.

(iv) Nematic structure: The centres of gravity of the units are mobile in three directions, rotation about one axis is permitted.

(v) True liquid : The centres of gravity of the units are mobile in three directions, rotations about three axes perpendicular to one another is possible.

The number of mesogens are known possessing more than one mesophase of the same type. The phenomenon is known as polymesomorphism and is commonly observed for smectic mesophase. In this case also the temperature range and the stability of the different mesophases are sharply defined.

$$\begin{array}{c}\text{Crystalline}\\ \text{solid state}\\ \end{array} \xrightleftharpoons{t_1} \begin{array}{c}\text{Smectic}\\ \text{II}\\ \text{(Smectic B)}\end{array} \xrightleftharpoons{t_2} \begin{array}{c}\text{Smectic}\\ \text{I}\\ \text{(Smectic A)}\end{array} \xrightleftharpoons{t_3} \begin{array}{c}\text{Nematic}\\ \text{or}\\ \text{Cholesteric}\end{array} \xrightleftharpoons{t_4} \begin{array}{c}\text{Isotropic}\\ \text{liquid}\\ \end{array}$$

Later development in the field of liquid crystals has added one more new class of liquid crystals commonly known as discotic (columnar) (10) or cannonic (11) mesophase, exhibited by the disc-like molecules.

2.1.1 Smectic Liquid Crystals:

The term "Smectic" is in fact derived from the Greek word "Smectos" meaning soap-like and has no special significance. It was first used for ammonium oleate, a soap salt, it being the first substance known. Many common soaps exhibit smectic phases at elevated temperatures ($\sim$ 200°C) or in the presence of water.

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 side to side, or backward and forward, but not up and down. The best illustrated as a box of pencils or cigars (Fig.2.)

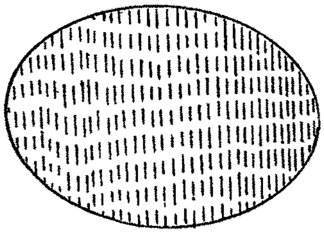


Fig.2: A schematic representation of molecular arrangement in two plane smectic strata.

A film of smectic phase stretched over a small hole in a plate gives the conditions 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 (12). Smectic phase is identified by the focal-conic texture. It extends all over the specimen and when examined in polarized light, gives a fan-like appearance. The focal-conic texture is originated due to lack of common orientation of the smectic sheets as they form. Bragg (13) has given an excellent account of the focal conic structure and the geometry involved which provides further evidence for the smectic structure.

Saupe (14) has divided smectic phase into two groups based on the proposal of Hermann (15); (i) Smectic phases with unstructured layers and (ii) 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 representitive of the second group is classified as smectic B. The extensive work of Sackmann and Demus (16) and de Vries (17) has revealed some of the details of the molecular arrangements of these phases. At least nine different modifications of the smectic mesophases have been identified or proposed (18,19). Much work on the classification of smectics has been done by Sackmann and Demus (16) and Demus and Richter (20). They have examined a number of pure compounds and their mixtures with one another and have assigned structure to the smectic mesophases. They classified smectic mesophases according to the textures observed (20) (Table-1).

Sackmann and Demus (16) proposed seven smectic phases, A through G. These are identified by miscibility studies. However, de Vries (17) has classified the smectic into three main classes called α , β and γ on the basis of X-ray studies. The class α contains smectic types A, C, F and D, class β contains the smectic B and class γ contains the smectic E, G and H.

2.2 Nematic Liquid Crystals:

The term nematic meaning thread like (Greek-'noma'= thread") is used because of the mobile thread like lines which are observed in nematic mesophase. The optical effects of the nematic threads have been studied by Zocher and Birstein (21). Frank (22) has named these lines as disclinations. The molecules in the nematic phase are

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 (DUPIN cyclides)	i. Simple polygonal texture.
		ii. Simple fan shaped texture.
		iii. Batonnets.
		iv. Bubble texture
	Cylinders	i. Myelinic texture.
Smectic C	Planar	i. Homogeneous texture.
		ii. Stepped drops.
		iii. Schlieren texture.
	Non-planar (DUPIN cyclides)	i. Broken polygonal texture.
		ii. Broken fan shaped texture.
		iii. Batonnets.
	Twisted	i. Planar texture.
		ii. Schlieren texture.
		iii. Streated fan shaped texture.
Smectic F	Planar	i. Schlieren texture.
		ii. Stepped drops.
	Non-planar (DUPIN Cyclides)	i. stripped, broken fan shaped texture.
Smectic B	Hexagonal, planar	i. Mosaic texture.
		ii. Homeotropic texture.
		iii. stepped drops.
		iv. Batonnets.
		v. Ovals.
		vi. Lancets.

Table - 1 (contd)

Type of smectic mesophase	Structure	Texture
	Non-planar (DUPIN cyclides)	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	Isotropic.
	Bands	Mosaic texture.

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 the 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 "Swarm Theory", was first proposed by E.Bose (23) in 1909, to explain the molecular arrangement and order in the nematic phase. Zocher (24) proposed the distortion hypothesis which is now referred to as the continuum theory of liquid crystals.Luckhurst (25) applied both the swarm and distortion theories of the nematic mesophase to the study of magnetic resonance experiment and has shown that they lead to isomathematical conclusions.

The schematic representation of the order in a nematic phase is shown in Fig.3.

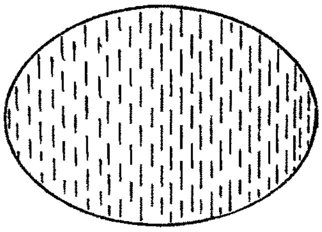


Fig.3 : A schematic representation of molecular arrangement in nematic phase.

The appearance of the textures which are formed after the completed transition, often depends considerably on the layer thickness. Thicker nematic layers may show the typical threaded texture. The well-defined thread-like structure may move and float around in the nematic liquid. The term nematic refers to these features.

In contrast to the smectic phase generally there is considered to be only one nematic phase, although de Vries (26) has proposed three types of nematic phases based on X-ray diffraction pattern, the type of the preceeding smectic phase, and the microscopic studies. These three nematic phases are (i) skewed cybotactic nematic, (ii) normal cybotactic nematic and (iii) the classical nematic phase observed in bis(4'-n-octyloxybenzal)-2-chloro-1,4-phenylenediamine.

Nematic liquid crystals are optically possitive. The nematic liquid crystals can be formed by compounds that are optically inactive or by racemic modifications.

2.2.1 New Types of Nematic Phases:

Generally nematogens consist of rod-like molecules whose longest axes tend to be parallel in the nematic phase as discussed earlier. Alben (27), Onsager (28) and Dreyer (29) suggested that in addition to such positive nematics, it is reasonable to expect that there might be 'negative' nematic with plannar molecules aligned with their shortest axes parallel to each other.

2.2.1a Carbonaceous Mesophase :

This mesophase was obtained by Zimmer and White (30) during the process of coking and carbonization. The mesophase transformation usually occurs in the range of 400 to 500°C.

2.2.1b Re-entrant Nematic Phase:

Cladis (31) obtained the nematic phase at lower temperature than the smectic phase in a binary mixture at normal pressure. Previously it was general assumption that nematic mesophase being less ordered than smectic phase, should be obtained at higher temperatures only, 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 phase (32, 33). The explanation given is that the anti-parallel associations responsible for the bilayer smectic A phase also provide mechanism which accounts for the reappearence of the nematic phase at some lower temperatures. This phenomenon was also observed in the case of mixtures (34) at atmospheric pressure, at higher pressure (35) and at atmospheric pressure in pure compounds (33,34).

Number of workers have worked on the different aspects of re-entrant nematic mesophases (36-53).

2.3 Cholesteric Liquid Crystals:

The cholesteric phase is the twisted nematic phase, as this possesses the structure of the layered nematic liquid crystals twisted about an axis perpendicular to the molecular layers, which results in a helical structure (Fig. 4). The term is derived from cholesterol as most of the compounds exhibiting this type of mesomorphism are related to cholesterol or sterol type of skeleton. However, cholesterol itself is non-mesogenic. Substances which possess the general requirements of typical nematic structure but are chiral, also exhibit cholesteric phase (54). This class of liquid crystals is referred to as "chiral nematic" to distinguish them from those derived from cholesterol or sterols. Gray (55) has provided an example of the limiting case in which an optically active deuterated compound was shown to be cholesteric. The addition of optically active materials to nematic liquid crystals also give cholesteric liquid crystals (56), though thermal transformation between the nematic and cholesteric phases do not occur. The preparation of many low melting "chiral nematic" compounds have been described (57,58). The optically active smectic liquid crystal was reported by Helfrich and Oh (59). Electric and magnetic fields can force a cholesteric mesophase into the nematic arrangement.

The helical structure causes the cholesteric liquid crystals to behave in a unique and most stricking way not

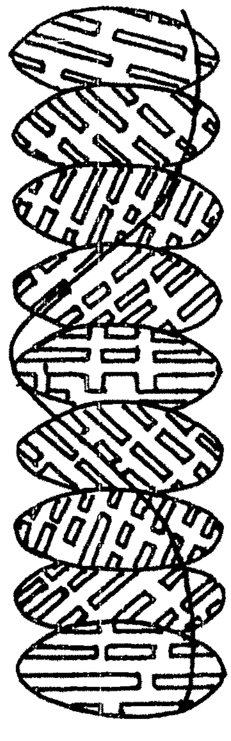


FIG. 4: Probable Organization of Cholesteric Phase.

shared by the other types of liquid crystals, i.e. reflection of iridescent colours. Certain cholesteric compounds although colourless themselves, are able to selectively scatter light into different colours. The colour of the reflected light is determined by (a) pitch of the helix (b) the temperature and (c) the angle of the 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.

In contrast to both smectic and nematic, cholesteric liquid crystals are optically negative. They generally have the following three textures.

2.3.1 Focal-conic Texture:

When an anisotropic liquid is cooled, the texture obtained is focal-conic. The term is derived from the conic sections that are usually observed in the case of smectics. The focal-conic texture nucleates in discrete points from where it grows in all directions, forming circular areas, until finally the whole film is covered.

2.3.2 Planar of Plane Texture:

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

The focal-conic texture may change to plane texture by disturbing the cover glass.

2.3.3 Blue Phase:

Certain 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 blue phase. This phase on further cooling changes to a birefringent texture. Due to this, the transition temperatures on cooling isotropic cholesteric liquid are not really 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 (60). Bergmann and Stegemeyer (61) have confirmed the blue phase of cholesteryl nonanoate by calorimetric and microscopic studies and they reported the existance of two polymorphic forms of blue phase (62-67).

Blue phase has created great interest in the scientists and number of researchers have tried to understand the blue phase and now it has been reported that they are of more than one type (62-69,70,71).

2.4 Discotic Mesophases:

Chandrasekhar et al. (10) have reported for the first time mesophase in a pure compound with disc-like molecules. They have suggested the structure which has transitional periodicity in two dimensions and liquid like disorder in the third. Number of mesogens (72-77) have been synthesized and some of them exhibit two or three discotic mesophases. Different phases for disc-like liquid crystals are described on the basis of optical textures (78).

Billard (79) and Destrade (80) have suggested nomenclature for different type of discotic phases.

As a molecular structural point of view, these molecules possess a central part and flexible chains and having two fold axis parallel or perpendicular to the director, it is possible for disc-like systems to imagine a more diversified symmetry.

In the last three years many discotic compounds are synthesized which correspond, for example, to benzene, triphenylene, truxene, ruffigalol, anthraquinone, naphthalenetrisfuran, trithiatruxene and cyclohexane derivatives (Fig. 5).

Most of these compounds exhibit a hexagonal or trigonal symmetry, but some of them are characterized by a binary or by a tetragonal symmetry. An exhaustive investigation of the symmetry of these systems have been presented by Billard (79) (Fig. 6). In one of the homologues ($R=C_6H_{13}O$), the columnar phase is believed to be tilted (80) (Fig.7,8).

The discotic mesophases attracted different scientists and number of aspects of this mesophase are brought out by recent studies (81-86).

3. LYOTROPIC LIQUID CRYSTALS:

Lyotropic liquid crystals are commonly obtained by the action of a solvent on a solid. They are further divided into several categories, according to their structure. They often are two component systems composed of water and amphiphilic compounds. However, multicomponent systems also are common in lyotropic liquid crystals. An example similar to liquid crystal found in living systems is a mixture of lecitinin, cholesterol, bile salts and water.

Generally, the compounds possessing two groups with large solubility differences are characterized as amphiphilic compounds (87) and they are (a) hydrophilic group which tends to be water soluble and hydrocarbon insoluble and (b) a lyophilic group which tends to be hydrocarbon soluble and water insoluble. Two common types of molecular geometries are found. Sodium stearate is typical of one type of

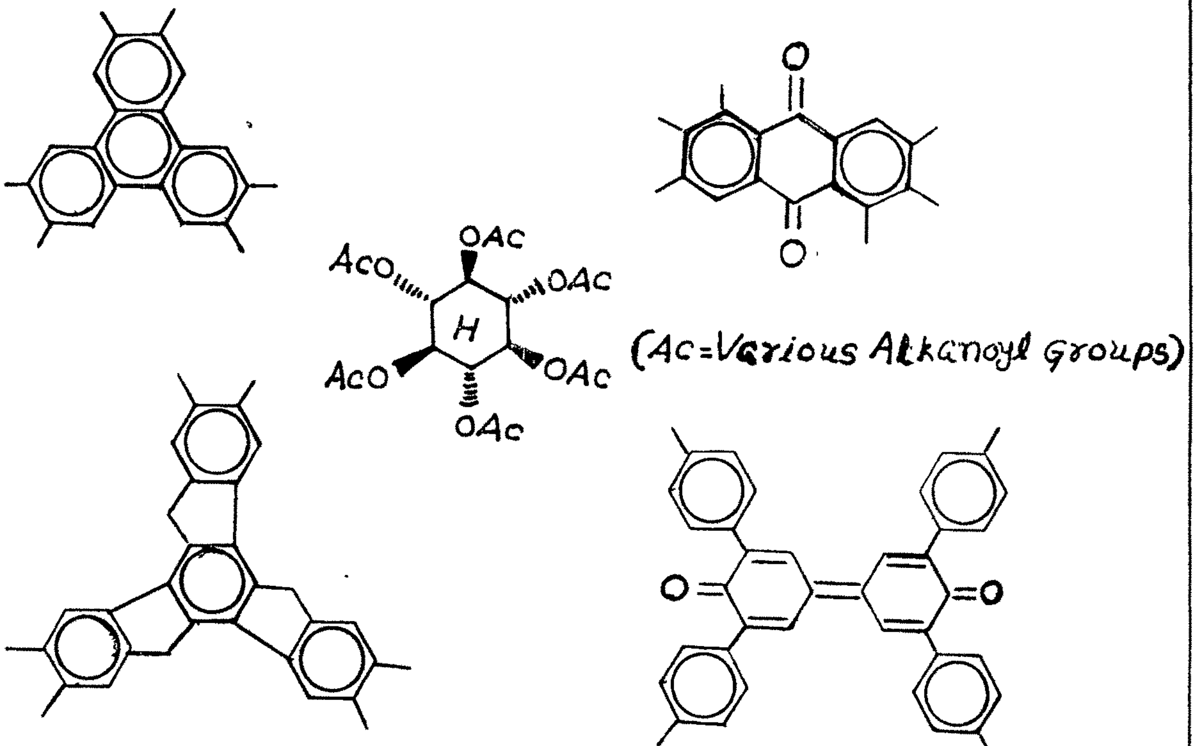
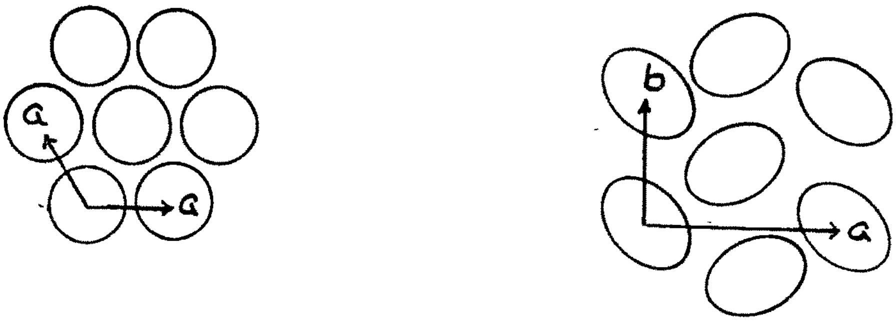


FIG. 5 : Examples of Cores Which Lead to Disc-like Mesogens.



(a)

(b)

FIG. 6 : (a) Hexagonal and (b) Rectangular Modification of the Columnar Structure.

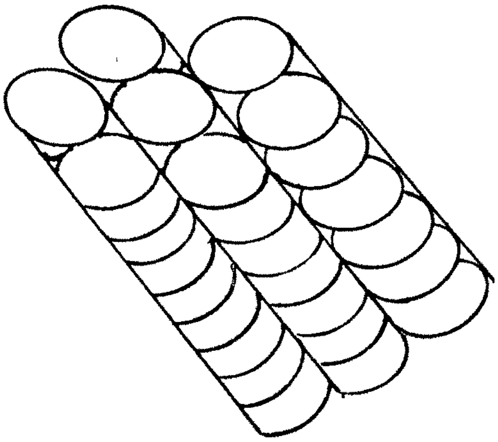


FIG. 7 : Schematic Represention of the Tilted Columnar Structure.

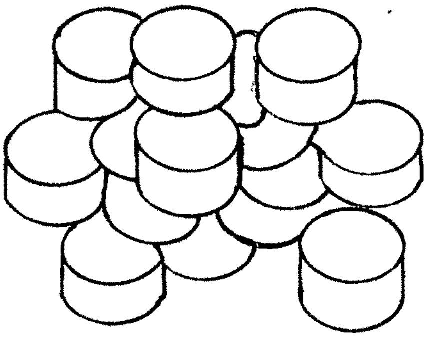
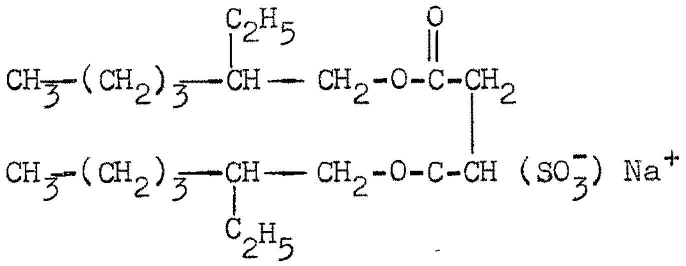


FIG. 8 : Schematic Represention of the Nematic Phase of Disc-like Molecules.

molecule, in which the molecule's polar head is attached to one long hydrophilic tail. A second type of molecule has its polar head attached to two hydrophilic tails. The hydrophilic groups either lies side by side in a "clothespin" structure or at an acute angle to each other to form a wedge-shaped molecule. An example of the latter type of molecule is dioctyl sodium sulfosuccinate (Aerosol OT).



$$\begin{array}{l} CH_3-(CH_2)_3-\overset{C_2H_5}{\overset{|}{CH}}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2 \\ CH_3-(CH_2)_3-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-O-C-CH\ (SO_3^-)\ Na^+ \end{array}$$

McBain (88) has discussed the form of mesomorphism in soap solutions. A number of cationic and non-ionic detergents have also been shown to give anisotropic phases when they are treated with solvents and in particular with water (83-91). Ostwald (92) has discussed the relationship between these liquid crystalline states and truly colloidal states. Robinson (93) has reported lyotropic cholesteric phase and has discussed the similarity between the lyotropic cholesteric phase and thermotropic cholesteric phase.

Lyotropic systems are also thermotropic and the combined action of temperature and solvents enables them to pass successively from the solid crystalline state to the liquid crystalline state and further to isotropic liquid or dissolved state. The constitutional analogies between amphiphilic, non-amphiphilic and plastic crystals have been discussed in detail by Gray and Winsor (94).

4. MESOMORPHISM IN BIOLOGICAL SYSTEMS:

Liquid cyrstals play an important role in nature. Brown and Shaw (95) have pointed out that the mesomorphic modifications are of important biological significance, as slight changes in composition and in physical and chemical properties can materially affect the formation, continuation or cessation of the mesomorphic state, a delicate balance characteristic also of many biological processes. Catalytic process in biological systems could readily find favourable environment in the structure of the mesomorphic state. As Bowden (96) has put it, this state seems to be especially suited to biological functions and may possibly be the basis of vital activity.

Mesomorphic properties in the form of myelin in biological systems was first shown by Wirchow (97) in 1854. Biological systems are multicomponent and contain numurous types of macromolecules, inorganic ions etc. It has been reported that tobacco mosaic virus exhibits lyotropic mesomorphism (98). One of the first demonstrations of liquid crystalline phenomenon in a well characterized biological system was given by Bernal and Fankuchen (99) who used X-ray diffraction to investigate solution of tobacco mosaic virus. Rod-like particles of 152 A° diameter and 300 A° in length occur which associate in parallel alignment in aqueous solutions, giving rise to characteristic diffraction pattern. Birefringence in the case of muscle was noted by Muralt and Edsall in 1930 (100). The brilliant work of Engstrom and Finean (101) on the structure of nervous tissue shows the presence of two components in optical opposition and in the concentric multilayers of lipid or lipoprotein forming the myelin sheath. From a study of structure of Heamoglobins, Perutz et al. (102) concluded that it could assume liquid crystalline form in the red cell. Robinson (93) in 1956 showed conclusively that the polypetide poly-r-benzyl-L-glutamate existed in organic solvents as a cholesteric liquid crystalline spiral. Knapp and Nicholas (103,104) reported the isolation of tetracyclic triterpene ester, exhibiting smectic and cholesteric mesophase from banana peels and from the seeds of strychnine producing plants.

Recently Livolant (105) has observed cholesteric phase of DNA in vitro and in vivo.

5. PHYSICAL PROPERTIES OF LIQUID CRYSTALS:

Better attention for studying the physical properties of liquid crystals including X-ray application, study of UV, IR, Raman, NMR spectra, surface tension, viscosity, differential thermal analysis, calorimetry has been paid in the recent past. Pioneering work on different physical properties have been carried out by number of workers Van der Lingen (106), Hückel (107), de Broglie and Friedel (108), Bernal and Crowfoot (109) and Brown et al. (110) carried out X-ray studies. Nuclear magnetic resonance study was carried out by Spence et al. (111,112.), Lippmann et al.(113) and Saupe and Englert (114). The studies of ultraviolet and infrared spectroscopy were carried out by number of workers (115,116). Early viscosity studies were carried out by Schenk (117) and Porter and Johnson (118). Kast (119) has given a critical summary of dielectric study in the field of liquid crystals upto 1931. Bhide and Bhide (120) lateron carried out dielectric study. The Mössbaur effect was studied in the smectic liquid crystal state for the first time by Uhrich et al. (121). Dewar et al.(122) and Kelkar (123) initiated the use of liquid crystal stationary phase in chromatography. Chow and Martire (124) carried out more detailed study on chromatography.

Early magnetic susceptibility studies were carried out by Mauguin (125), Foex (126) and Tsvektov et al. (127).

In recent years various physical properties of liquid crystalline materials have been studied in great detail such as X-ray studies (128-130), Nuclear magnetic resonance (131), surface tension (132), spectroscopic studies (133-135), Elasticity and Viscosity (136), dielectric constants (137-138), Mössbauer effect (139), chromatography (140-141), ultrasonics (142,143), magnetic susceptibility (144) and calorimetry (145-150).

Number of books and review papers have discussed the physical properties of liquid crystals and their importance in the different technological applications (151-161). Viscosity and surface tension studies are of importance and interest because of the sharp change in molecular orientation at the phase transitions. Liquid crystal preferably with less number of unsaturation, are now used as solvents in infrared and ultraviolet, spectroscopy (133). Malthete and Billard (162) have shown ferrocene derivatives to be mesogenic, which are very useful in Mössbauer spectroscopy. X-ray studies are useful in understanding different textures and structures of mesophases, while gas chromatography and specific volume studies enable one to achieve purifications of chemical substances and to evaluate order parameters of liquid crystals. Dielectric studies decide about the field of application. Thus studies of physical properties decide the applicability of certain liquid crystals.

LIST OF SOME REPRESENTATIVE LOW MOLECULAR WEIGHT LIQUID CRYSTALLINE COMPOUNDS (163):

Sr. No.	Liquid Crystalline Compound	Transition Temperatures(°C)		
		Smectic	Nematic	Isotropic
1	4-n-pentylbenzoic acid	-	88.0	126.0
2	4-methoxy-4'-methyl thiobenzoate	-	65.5	73.6
3	2,7-di(4'-methoxybemzoyloxy)- 1,5-dimethoxy naphthalene	-	236.0	275.0
4	2,5-bis(4-n-pentyl phenyl)-pyrazine	143.3*	182.2	191.3
5	Di-iso-butyl-silandiol	89.5	-	101.5
6	3-β-hexyloxy cholesten(5)	-	68.0**	79.0

* K 143.3°C S_C 173.6°C S_A 182.2°C.

** Cholesteric phase.

6. APPLICATION OF LIQUID CRYSTALS:

Watching a little TV on our wrist-watch may not be much fun, but certainly this device marketed by Seiko, the Japanese giant electronic industry, turned out to be one of the most eye-catching high-tech products to reach the US market last year. This technological fact became possible due to liquid crystals the same material which is used to display numbers, and symbols in pocket calculators, wrist-watches and electronic games.

Some liquid crystals are very sensitive to temperature, changing colour with even slight temperature changes. These help in diagnosing ailments such as breast cancer, that are associated with small changes in the skin temperature. Other liquid crystals have given us synthetic fibres and composite materials of exceptionally high strength, which are being used for making body armour, parachute shrouds and even tennis rackets.

6.1 Electro-optical Applications (164-167):

Electro-optical applications include seven segment display panel, electronic windows which go from clear to frosted with flip of a switch, numeric displays for watches, calculators and games. Point of scale advertising panels, flatscreen television, temperature indicator and image-convertor and storage displays (168). The liquid crystal storage displays can record and reproduce the image. A laser addressed projection display and a matrix addressed display are also used. Hareng et al. (169) have summarized the recent work on these two kinds of displays. Reflective type of liquid crystals display device is also reported (170) 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. Improvement in or relating to liquid crystal display device is described by Siemens (171). 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 use of liquid crystals in the IR, video-camera has been reported (172,173). The visualization of acoustic images with a nematic liquid crystal is reported (174), which gives direct 2-dimensional acoustic images with good response time.

Some of the advantages of liquid crystal displays are low operating voltage, low power consumption, ability to withstand high levels of light (liquid crystals scatter light rather than generate their own light) and low cost.

Disadvantages are difficulty in cell fabrication, lifetime, response time and viewing angle considerations.

Gray (175) 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 (168). As mentioned earlier Hareng et al. (169) have discussed two types of display applications of the thermotropic effect in semctic A liquid crystal phase.

6.2 Chiral Smectic C* (Ferroelectric liquid crystal) as a New Material for High Speed Bistable Liquid Crystal Devices (176):

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 electric 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 the insufficient non-linearity in 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 lead to increasingly impractical production costs for flat-panel displays with potential use in computer terminals, oscilloscopes, radar and TV 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.

1) High Speed even at very low voltages:

   The electro-optical response is as much as 100 to 1000 times faster (for the smectic C*) than currently available electro-optical devices using liquid crystals.

2) Bistability:

   The electro-optical response is characterized by two stable stages, 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 a 20° to 60° angle of a uniaxial materials having a refractive index and anisotropy Δn of greater than 0.2. This response is

10 to 100 times larger than that attainable in other bistable electro-optical devices.

In addition, grey-scale control is possible by pulse amplitude and width modulation, switching between two birefringence colours (or between several, with superposed samples) is also possible.

6.3 Liquid crystals in chromatographic separation:

The use of liquid crystals as stationary phases in gas liquid chromatography separation of structural isomers is studied extensively (122,177,178). The selectivity of liquid crystalline phases is a consequence of the molecular order, shape, polarity, polarizability and flexibility of solute molecules. Number of workers have reported (140,141,179) the use of liquid crystal stationary phases in gas chromatography and have indicated their advantages for better separation of hydrocarbon and for the analysis of compounds of ecological and biological interest.

An inherent practical limitation of mesomorphous stationary phase is their restricted useful temperature ranges.

6.4 Liquid crystals as temperature detector (180);

Cholesteric liquid crystal selectively reflects light in the visible region, depending on the pitch of the helix. The pitch is temperature dependent and therefore, may be used to control the temperature via colour changes. This technique is used to detect short circuit and also in medical area of the measurements of body temperature for the detection of skin tumors etc. Solvent vapours (in ppm) such as benzene or chloroform also affect the pitch. This provides a means of solvent detection in ppm concentration.

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 (181,182).

6.5 Liquid Crystals in Sepctroscopic Studies:

Liquid crystals are widely used in UV, IR, NMR and ESR spectroscopy (183). Information regarding the nature of the mesophase itself can be obtained (184) or liquid crystalline phase can be used as solvents which may provide information concerning bond lengths and preferred conformation of the dissolved solute (185).

6.6 Non-Destructive Testing (186,187):

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 eddy currents in wind-tunnel experiments, variation in heat transfer between well-bonded and poorly 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. This studies were made during the return flight from the moon of the spaceship Appolo-14.

6.7 Liquid Crystals as Reaction Solvent:

Dewar and Nahlovsky (188) reported that for Claisen re-arrangement of cinnamyl phenyl ether in nematic solvent, no change of reaction product or rate is observed. However, Bacon et al.(189) have reported that the thermal isomerization of 2,4,6-trimethoxy-s-thiazine in nematic solvent proceeds faster and with a smaller loss in entropy of activation than in isotropic phase.

Gottarelli and Samori (190) have reviewed the applications of liquid crystals in chemistry.

6.8 Liquid Crystals in Medical Science (19):

Liquid crystals also are used as a diagnostic tool to detect carcinoma of the breast, study abnormal venous patterns (including peripheral vascular disease), locate the placenta of a fetus, diagnose 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.

Also 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 wall. Cells involved in sickle 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 materials so that it can be flushed from the body.

LIQUID CRYSTALLINE POLYMERS

LIQUID CRYSTALLINE POLYMERS

1. GENERAL:

Different classes of organic compounds with different homologous series exhibiting liquid crystallinity have been studied upto date. However, it is only in the last few years that liquid crystalline order has been recognized in polymer systems. Because of the direct industrial exploitation possible in ever increasing polymers and plastic technology, scientists are in continuous search of liquid crystallinity to be obtained in the synthetic polymers (191). Thus the activity in the field of liquid crystalline polymers is growing apace and the study of liquid crystal properties in polymer systems holds out much promise for the future, not only because of such systems will provide us with new knowledge about both polymers and liquid crystals, but also from the stand point of their technological importance.

The field of liquid crystalline polymers (LCP) has become one of the fascinating area of the current research. The development of Kevlar fibers has stimulated research to find additional high modulus, high strength fibers and to investigate the structure and properties of high modulus polymers. As this research evolved, the connection between these new mesogenic polymers and low molecular weight liquid crystals became more evident. Prior to these

(iii) Comb-like polymers, whose side-chains contain long aliphatic substituents, which are capable of forming an interchain crystalline phase.

Number of patents and reports claiming the production of fibers (Kevlar fibers) from polymer solutions existing in liquid crystalline state are now known (208-210).

Recent books "Liquid Crystalline Order in Polymers" edited by Blumstein (211), "Polymer Liquid Crystals" edited by A. Ciferri et al. (212) and "Recent Advances in Liquid Crystalline Polymers" edited by L.L. Chapoy (213) provide detailed account of mesomorphic polymers.

Vinyl oleate has been polymerized by different workers in liquid crystalline and isotropic phases (214,215). Hardy and co-workers (216-218) have studied kinetics of polymerization of cholesteryl acrylate and other monomers. Billard et al. (219-221) have studied binary phase diagrams of thermotropic mesomorphic polymers with low molecular weight mesogens and have observed miscibility behaviour similar to two low molecular weight mesogens.

The copolymer obtained by condensing terephthalic acid, ethylene glycol and p-hydroxybenzoic acid exhibits thermotropic mesomorphism and have improved mechanical and physical properties (222,223). These results lead to the synthesis of number of other polymers where p-hydroxybenzoic acid is substituted by other hydroxy aromatic acids (224).

The literature survey reveals that homopolymerization of p-hydroxybenzoic acid gives thermally stable polymer (225-227). One of the patent, reveals that first an oligomer was prepared from p-hydroxybenzoic acid and then this oligomer was polymerized at 260°C to obtain a highly ordered heat resistant polymer (225).

Number of addition polymers have been reported which exhibit lyotropic mesomorphism (216,228). Recently number of condensation polymers exhibiting thermotropic mesomorphism have been synthesized (229-232). In many cases the repeating unit is consisted of an extended segment and a more flexible segment, following the suggestion of de Gennes (233). Krigbaum et al. have reported mesogenic homopolyesters incorporating different rigid units (234-236). Roviello and Sirigu (230) and Blumstein and co-workers (237) used different rigid units with flexible segments. Griffin and Havens (238) prepared polymers having quite long repeating units.

For the first time Vora and Patel (239) have reported mesogenic polymers incorporating a monomer having symmetrically substituted triazine heterocyclic moiety and evaluated the effect of chemical structure on mesomorphism.

2. CLASSIFICATION OF LIQUID CRYSTALLINE POLYMERS:

Mesogenic polymers exhibiting liquid crystalline behaviour can be synthesized in a variety of different ways, as indicated by the increasing number of publications in the past few years.

Finkelmann (240) has classified the liquid crystalline polymers to describe their characteristic molecular structure and the phase behaviour. He has stated that if solid polymers with ordered structures are excluded and only homogeneous phases are considered that are in liquid crystalline state, mesogenic polymers can be subdivided into the scheme given in Fig. 9.

It is most convenient first to describe the molecular structure of the monomer unit, following the classification of Gray and Winsor (241) for conventional liquid crystals. The monomer units can be either amphiphilic or 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 third distinction involves the phase behaviour. The system can be lyotropic or thermotropic, depending upon whether the mesophase is observed by variation of solvent content or by variation of temperature.

At present time there have been only a few synthetic investigations of the polymers having lyotropic repeating units. Some papers are summarized by Kelkar (242) and Elias (243). Soil (244) has investigated polymerization of amphiphilic monomers. The phase behaviour of lyotropic liquid crystalline side chain polymers in aqueous solution has recently been compared with the phase behaviour of the corresponding monomers (245).

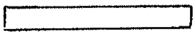
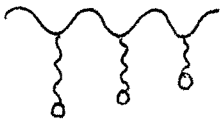
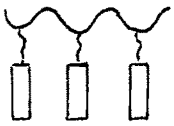
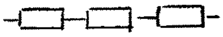
Monomor unit	 Amphiphilic		 Non-amphiphilic	
Polymer	 Side chain	 Main chain	 Side chain	 Main chain
Phase behaviour	Lyotropic		Thermotropic	Thermotropic, Lyotropic

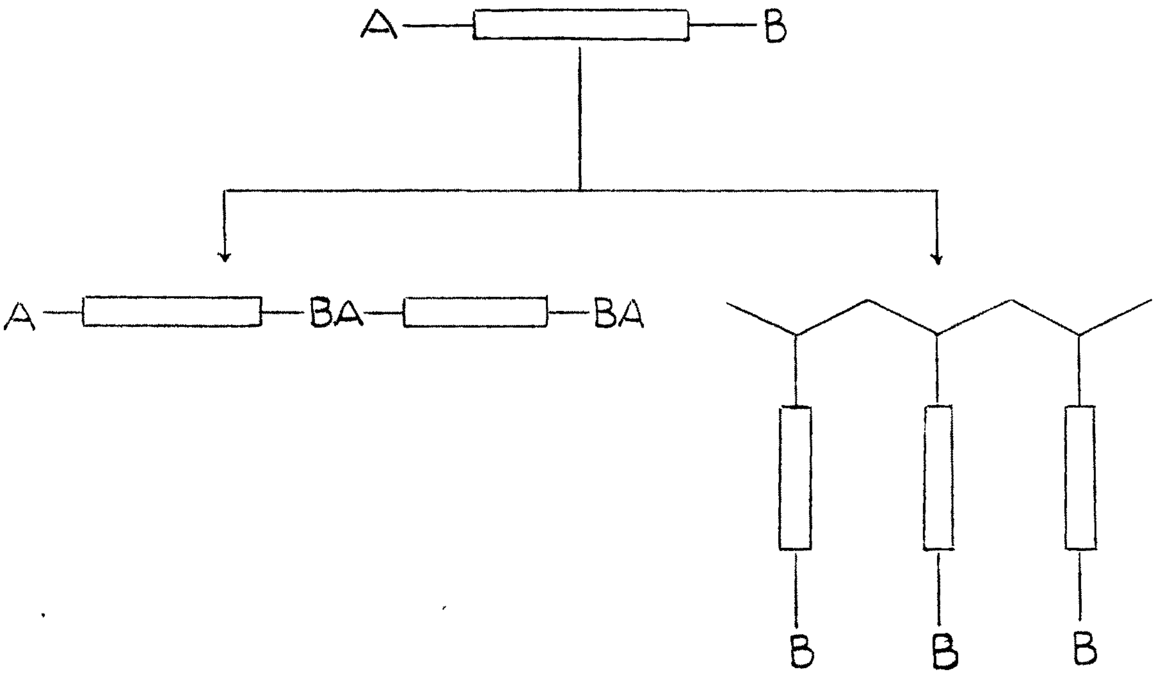
Fig.9. Classification of Mesogenic Polymers.

Non-amphiphilic monomer units are characterized by their rigid rod-like molecular structure typical of low molecular weight liquid crystals. If these monomer units are joined to form the main chain, the polymer backbone itself becomes rigid and rod-like. The non-amphiphilic mesogenic moiety can also be attached to the side chain. In contrast to the previously described mesogenic main chain polymers, in the liquid crystalline state only the original mesogenic side chains are responsible for the liquid crystalline order. This order is more or less independent of the conformation of the polymer main chain. Therefore it would be assumed that these "mesogenic side chain polymers" are very similar to the conventional low molecular weight mesogens.

3. THERMOTROPIC LIQUID CRYSTALLINE POLYMERS:

Looking for the literature with key words "Liquid crystal" and "polymer" a mushrooming number of papers are available. In most cases, however, polymers are described, which exhibit an anisotropic structure in the glassy state but not the liquid crystalline state above the glass transition temperature (196,246-248). Only some papers remain, which deal with thermotropic liquid crystalline polymers; where the macromolecules can be obtained in the liquid crystalline state like a low molecular weight liquid crystals. These polymers could be realised just in the last few years.

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 & B, macromolecules can be synthesized (Fig. 10).



(Symbol ▭ indicates mesogen core)

FIG. 10 : Polymerization of a Mesogenic Monomer.

(i) If A and B are able to perform a condensation reaction, the mesogenic groups built up the polymer main chain. These polymers will be named "Liquid Crystalline Main Chain Polymers". (ii) If A is capable of performing an addition polymerization reaction, the polymer chain build up by A and the mesogenic groups are fixed like side chains to the polymer main chain. These polymers will 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 idea, that the ability of forming a liquid crystalline phase can be preserved (249).

4. SYNTHESIS OF POLYMERS HAVING MESOGENIC SIDE CHAIN:

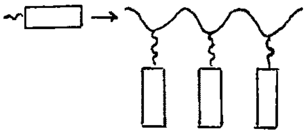
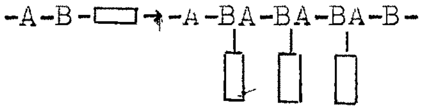
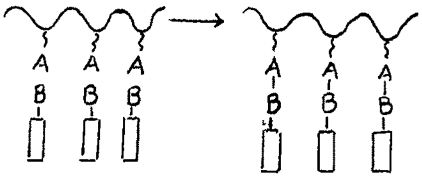
The mesogenic side chain polymers consist of two components, the mesogenic moieties and the polymer main chain to which they are attached. A large number of known mesogenic molecules (250) can be used as components. Moreover, a variety of different polymer main chains are available. The combination of these components allows a manifold variation of different types of mesogenic side chain polymers. These polymers can be prepared by three different types of polymerization specified in Table - 2. The most convenient method is to introduce into a mesogenic moiety, a reactive group capable of undergoing addition polymerization. A number of polymerizable monomers have been synthesized. They are comprehensively summarized by Blumstein and Hsu (251) and by Shibaev and Plate (252). 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 polycondensation reaction . In this way polymers containing heteroatoms in the backbone can be synthesized. Recently Reck and Ringsdorf (253) reported liquid crystalline polymers having mesogenic side chains on the rigid backbone and on the backbone having flexible spacers. The structure of these polymers is given in Table-2.

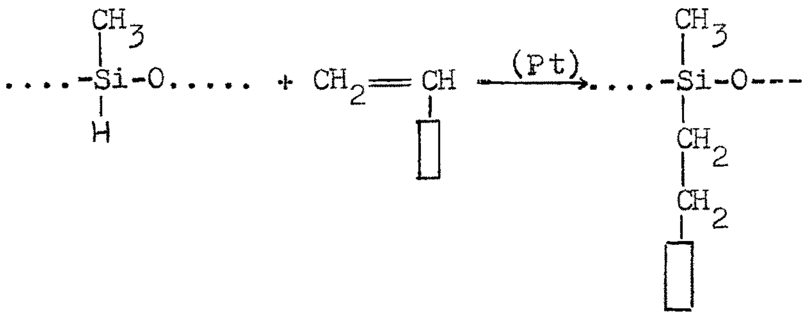
The third synthesis route starts with reactive polymers. They can be modified to mesogenic side chain polymers by using suitable reactive mesogenic monomers (254 - 256). An example

Table - 2

Synthesis of Mesogenic side:

Principles	Examples	
Addition Polymerization		Polyacrylates, Polymethylacrylates, Polystyrene derivatives
Polycondensation Polymerization		Nuclearly substituted polyesters
Modification of polymers		Polysiloxanes

of these type is the smooth addition of vinyl-substituted mesogenic monomers (255) to poly oxy(methylsilylene) :



$$\cdots\text{-}\underset{\displaystyle H}{\overset{\displaystyle CH_3}{Si}}\text{-}O\cdots\cdots + CH_2{=}\underset{\displaystyle \square}{CH} \xrightarrow{(Pt)} \cdots\text{-}\underset{\displaystyle CH_2CH_2\square}{\overset{\displaystyle CH_3}{Si}}\text{-}O\text{---}$$

▭ = mesogenic molecule

The large number of variations mentioned above suggest that it should be easy to prepare polymers with mesogenic side chains. Several experiments, however, have demonstrated that the direct linkage of rigid mesogenic groups to a polymer backbone is generally not sufficient to obtain a mesogenic polymer. In most cases only isotropic polymer melts are observed or solid polymers with a liquid crystalline structure. The latter structure vanishes irreversibly if the polymer is heated above its glass transition temperature (T_g). When these polymers are subsequently cooled below T_g, isotropic glasses are obtained. Thus direct linkage of mesogenic groups to the polymer main chain results in a different system than the low molecular weight liquid crystals. In fact , because of the covalent linkage to the main chain, motion of the mesogenic groups is drastically reduced. Transitional diffusion is no longer independent of the neighbouring molecules. As space filling model show, large mesogenic groups are prevented from attaining parallel alignment because of strong steric hindrance. This also causes a stiffening of the polymer chain which is often indicated by an increase of T_G compared to the same polymer without a mesogenic side chain.

Subsequently a simple model will be described (246) which enabled the systematic synthesis of liquid crystalline side chain polymers. According to these model considerations some aspects of the properties of these polymers will be described.

4.1 Model Considerations

In the liquid crystalline state of the polymer two aspects have to be considered. The polymerization chain exhibits a high mobility of the chain segments and a tendency towards a statistical chain conformation. On the other hand, the mesogenic groups tend towards an anisotropic orientation. Both techniques are conflicting and it will depend on the molecular structure which tendency predominates. The crucial point, whether a liquid crystalline polymer or an isotropic polymer melt will appear, is the chemical structure and property of the linkage between polymer main chain and the rigid mesogenic group. Two extreme limiting conditions for this linkage can be considered (Fig. 11).

(A) The rigid rod-like mesogenic group is directly coupled to the polymer main chain (Fig. 11A). The tendency towards a statistical chain conformation hinders the anisotropic orientation of the mesogenic side groups. Furthermore, due to their voluminous molecular structure a steric hindrance suppresses the formation of the liquid crystalline order. Under these conditions, above the glass transition temperature only an isotropic polymer melt will be observed.

(B) The rigid rod-like mesogenic group is decoupled by the polymer main chain (Fig.11B). This fictitious condition can be approximately achieved by a flexible space between polymer main chain and mesogenic side chain. Due to this indirect linkage, the motion of the polymer main chain do not affect the anisotropic orientation of the mesogenic groups. The polymer will exhibit the liquid crystalline state.

The actual conditions for the linkage will be between the extremes of the complete decoupling and the direct coupling of the mesogenic group to the polymer main chain.

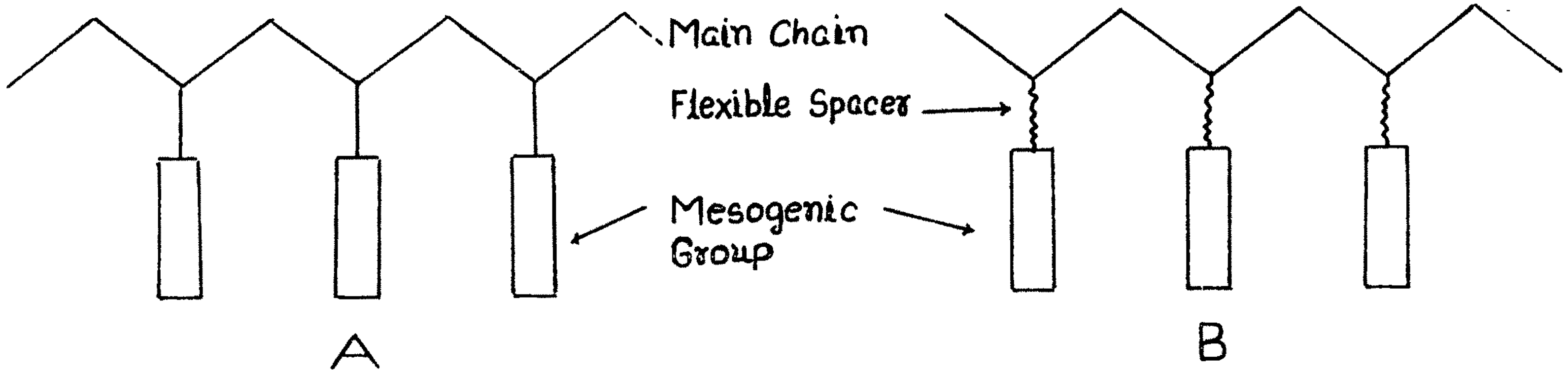


FIG. 11 : Linkage of the Mesogenic group of the Polymer main chain A directly, B via the Flexible spacer.

Therefore the main chain will influence more or less the motion of translation and motion of the mesogenic group and vice-versa, compared with a low molecular weight molecule in the liquid crystalline state. The mechanism of these interaction will depend on the chemical nature of the polymer main chain, the spacer and the mesogenic group.

4.2 Phase Behaviour of Mesogenic Polymers:

The phase behaviour of conventional low molecular weight mesogens has been investigated by both theoretical and experimental methods (242). One can ask how this phase behaviour will be influenced by linkage of the mesogenic molecules to the polymer main chain, and whether there are still analogies to the low molecular weight mesogens. Furthermore, the polymeric behaviour is of interest.

The essential features of the phase behaviour of the mesogenic polymer can be established by differential scaning calorimetry (DSC), which turns out to be an appropriate and convenient method. DSC measurements reveal the characteristic combination of properties for mesogenic polymers (i) a glass transition; characteristic of the polymer backbone, and (ii) a phase transformation from mesophase to the isotropic phase due to the mesogenic side chain. Complementary studies with a polarizing microscope reveal a very important property of the polymers, the texture observed in the liquid crystalline state of the polymer can be frozen without change in the glassy state. This procedure may have practical applications, because it allows the preservation of information given by the texture in the glassy state.

So far, DSC measurements indicate combination of properties of polymer and mesogens. A typical property of conventional semi-crystalline polymers is their biphasic character due to coexisting crystalline and amorphous domains. This raises the question of whether an anisotropic mesophase is thermodynamically homogeneous or should be defined in a way similar to the partially crystalline polymer. Pressure, volume and temperature measurements give more detailed insight into the phase behaviour of the mesogenic polymers.

5. INFLUENCE OF THE CHEMICAL CONSTITUTION ON THE TYPE OF MESOPHASE FORMED:

For low molecular weight mesogens, extensive theoretical and experimental studies have been performed to relate the type of mesophase and the chemical constitution, the data is recently compiled (242). Linkage of mesogenic side chains to a polymer backbone also results in thermodynamically homogeneous thermotropic mesophase. 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.

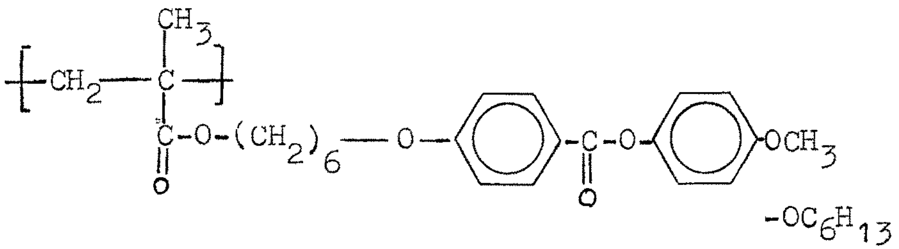
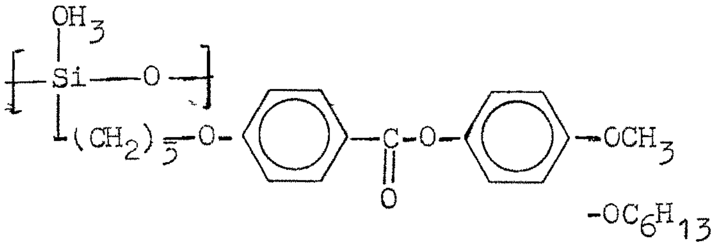
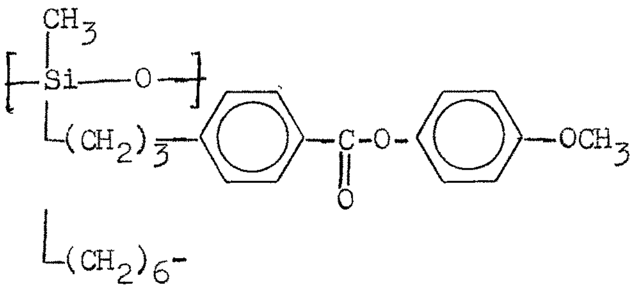
5.1 Variation of the Mesogenic Group:

5.1.1 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, is fixed via the flexible spacer to the polymer backbone. Therefore, starting from a defined mesogenic group a nematic and a smectic polymer phase should be determined by the substituents of the mesogenic moiety. In Table-3 some typical polymers are summarized with the benzoic acid phenylester as mesogenic group. For low molar mass derivatives it is well known, that with increasing length of the alkyl substituents a smectic phase becomes stable (260, 261). This tendency is also obtained for the polymers. For the poly (methacrylates) the short $-OCH_3$ substituent most distant from the polymer main chain is exchanged by a long $-OC_6H_{13}$ substituent (polymer-2) and the nematic phase of polymer-1

Table - 3

Nematic and Smectic side chain Polymers;

No	Polymer	Phase transition (°K)	Ref.
1		g309n374 i	(257,258)
2		g303s374 i	
3		g288n334 i	(259)
4		g288s385 i	
5		g288n 334 i	(260,256)
6		g278s319n391 i	

changes to the smectic phase in polymer-2. This principle is also observed if the poly(methacrylate) main chain is exchanged by a 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 (polymer-3 and 4). But not only the substituent, which is most distant from the polymer backbone, influences the structure of liquid crystalline phase. This is indicated with polymer-5 and 6. In this case the substituent most distant from the main chain remains constant. Here again with increasing length of alkyl substituent of the mesogenic moiety of a low temperature, smectic phase becomes stable for polymer-6.

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

5.1.2 Cholesteric Polymers:

Chiral molecules have to be present to obtain cholesteric (Chiral nematic) phase (262). Therefore, the substitution of chiral substituent to the mesogenic groups described above should result in cholesteric homopolymers. Until now, however only smectic phase was obtained when chiral molecules were polymerized (251, 263).

Cholesteric phases can be achieved using the well known concept of "induced cholesteric phases" (264). Assuming a direct analogy between polymer and low molecular weight liquid crystal, the cholesteric phase has to be induced if chiral monomers are added to the nematic polymer host phase (Fig.12). The validity of this concept has been proved by different systems, which are listed in Table-4(265).

Recently some condensation polymers are reported exhibiting cholesteric phase having one of the chiral monomer units in polymer main chain (266-270).

5.2 Variation of the Polymer Main Chain and Spacer Length:

The orientation of the mesogenic side groups, which are decoupled by flexible spacer, follow the principles similar to that of low molar mass liquid crystals, forming nematic, smectic and cholesteric phases. It would be supposed, that the main and side chain are essentially decoupled as expected by the model consideration. Actually however, the tendency towards a higher ordered phase is always observed if the monomer is converted to polymer (251, 263). If nematic polymers are obtained, in most cases the corresponding monomers exhibit none or only monotropic

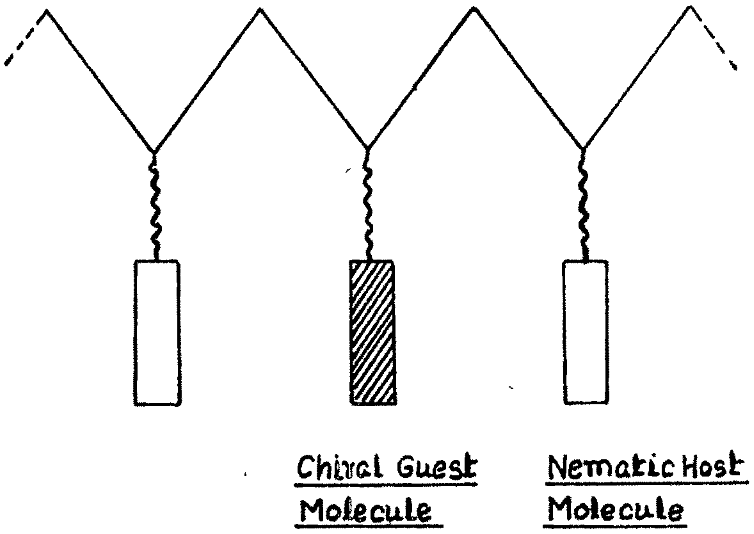
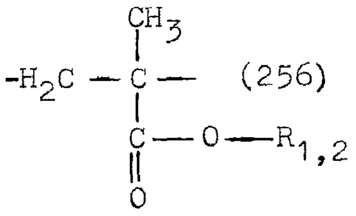
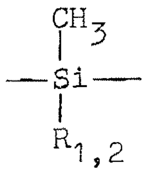
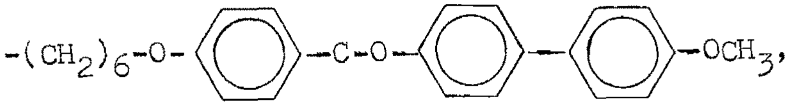
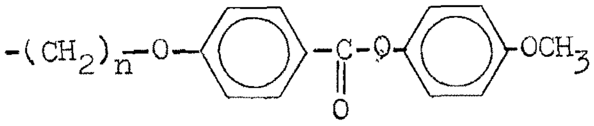
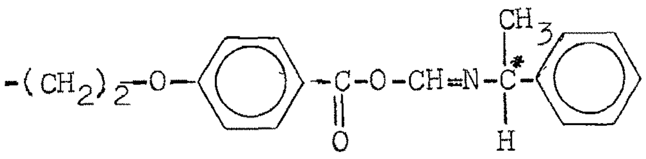
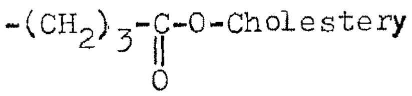


FIG. 12 : Schematic Representation of an "Induced Cholesteric Phase."

Table - 4

Induced cholesteric Polymer chain:

Polymer main chain	 $-H_2C-\overset{\overset{CH_3}{\vert}}{C}-$ (256) $\quad \underset{\underset{O}{\Vert}}{C}-O-R_{1,2}$	 $-\overset{\overset{CH_3}{\vert}}{\underset{\underset{R_{1,2}}{\vert}}{Si}}-$ (264)
Nematic group		
Chiral group	 ,	 $-(CH_2)_3-\underset{\underset{O}{\Vert}}{C}-O-$Cholestery

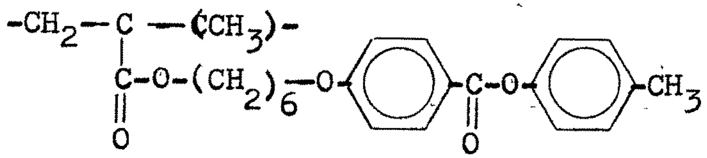
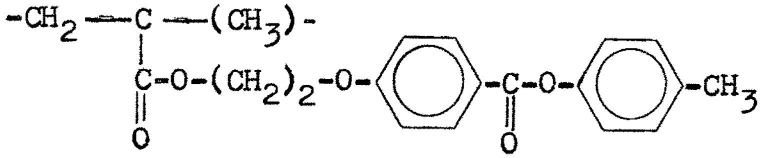
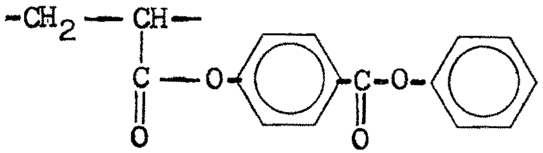
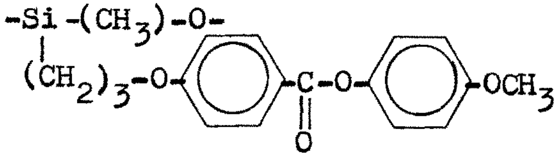
phase. Starting with nematic monomers mainly smectic polymer phases are obtained. Only very few examples exist, where a nematic monomer becomes a nematic polymer at the same temperature (258). For the polymers, however, the phase transitions nematic-isotropic are always observed at higher temperatures than for the corresponding monomers. This tendency towards a stabilization of the liquid crystalline state has to be perceived, because the conditions for the motions of transition and rotation of the mesogenic groups had been changed. Detailed measurements have to be made to get a quantitative insight into these mechanisms.

Corresponding to the model consideration a limiting case can be supposed. The mesogenic groups are just able to build up an anisotropic aggregation, whereas, on the other hand, the polymer main chain disturbs a macroscopical order, which is known for conventional liquid crystals. This has to be expected for little or no decoupling by a flexible spacer. In Table-5 some polymers are listed with decreasing length of the number of atoms between the main chain and the rigid mesogenic moiety.

In order to obtain a liquid crystalline polymer, the flexible spacer as well as the flexibility of the polymer main chain have to be considered. It has been found that the tacticity has little or no influence on the structure and behaviour of the liquid crystalline phase (271).

Table-5

Nematic Polymer With Different Spacer Length:

No	Spacer length	Polymer	Phase	$\Delta\eta$	Ref.
1	9		Nem	+	(258)
2	5		Nem	-	(257) (272)
3	2		Nem	-	(273)
4	4		Nem	+	(259)

5.3 Effect of Molecular Weight:

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

Finkelmann (240) has compared the phase behaviour of a mesogenic monomer with that of the corresponding polymer and observed that (i) non-mesogenic monomer gives nematic polymer, (ii) nematic monomer yields a highly ordered smectic polymer, the transition to the isotropic phase is strongly shifted to higher temperatures, and (iii) 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 suggests 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 degrees of polymerization.

6. 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, characteristic of the mesogen and the polymer. Finkelmann et al.(274) have prepared liquid crystal elastomers from polysiloxanes (Fig. 13). Above glass transition temperatures, these polymers exhibit an almost free motions 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 moities fixed via spacers to the backbone create an ordered mesophase more or less independently 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 an interesting opto-elastic properties.

7. LIQUID CRYSTALLINE MAIN CHAIN POLYMERS:

In principle for the liquid crystalline main chain

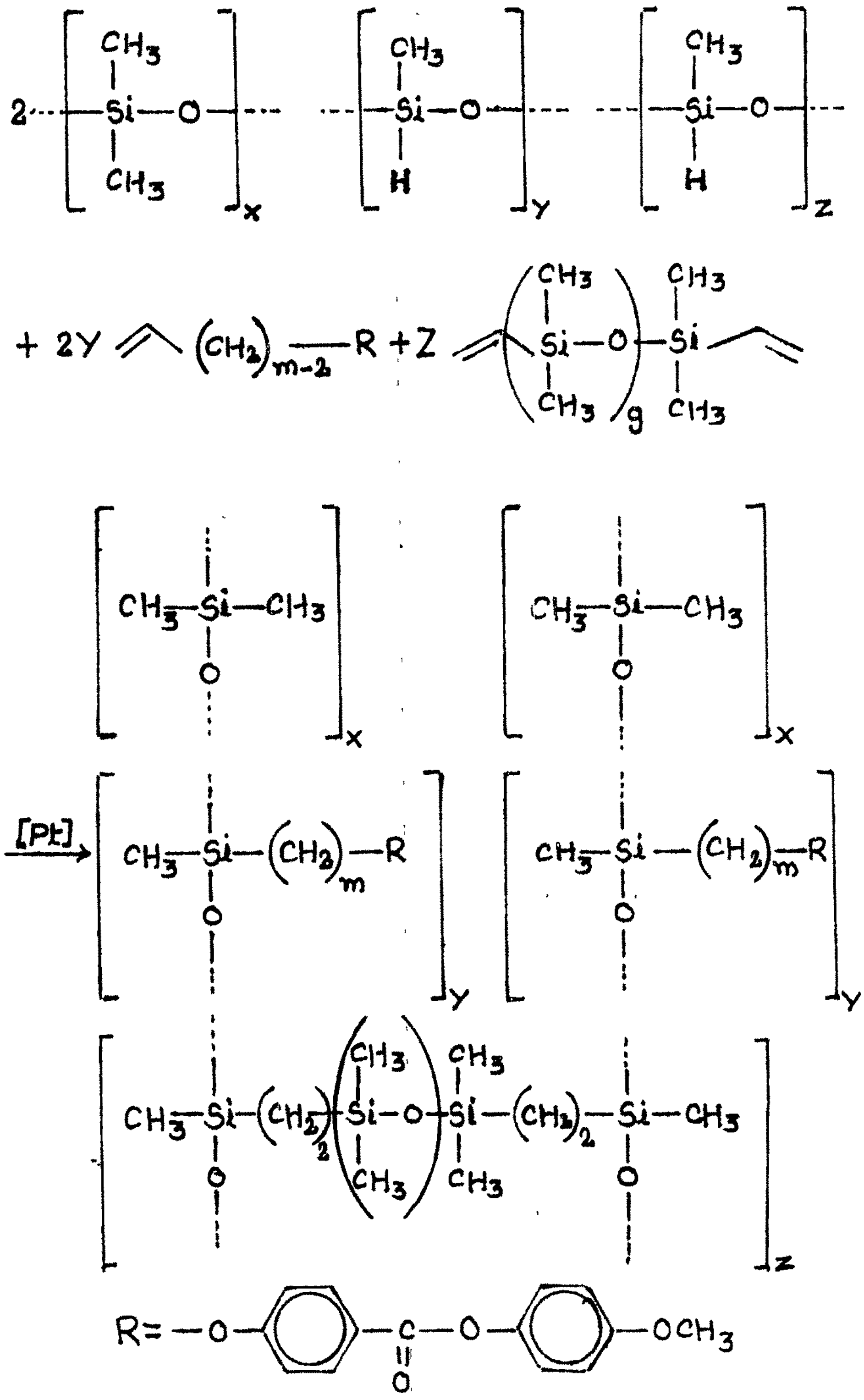


FIG. 13: Synthesis of LC Polysiloxane Network.

polymers, two different structures can be obtained, which depend on the chemical nature of the functional groups A and B (Fig. 14).

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 spaces (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 be previous polymers the flexibility of the over-all polymer main chain can be regulated by using different chemical structure or different length of the flexible segments.

7.1 Theories:

Already in 1949 Onsager (275) and in 1951 Ishihara (276) treated theoritically the packing of rigid rod-like molequles. They calculated the excluded volume as a function of the orientation of the molecules. In 1956 Flory (277) has overcome the restriction to dilute solution using the lattice model as convenient method and calculated the statistics of packing of monodisperse macromolecules and solvent molecules without considering any dispersion interactions. If a critical concentration is reached for the polymer in solution, a lyotropic liquid crystalline phase is observed. This critical concentration depends on

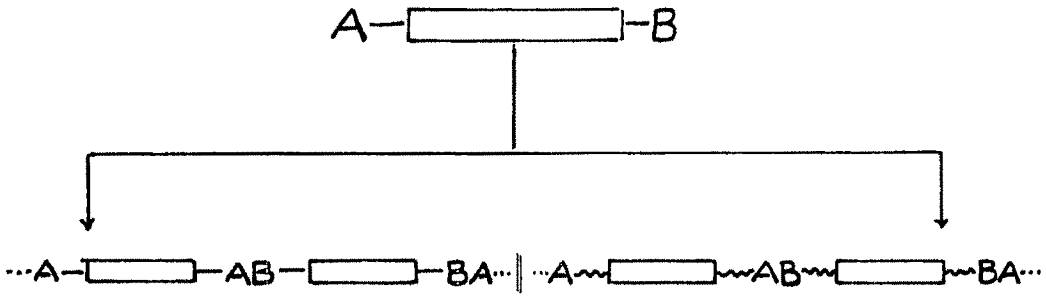


FIG. 14: Structures of LC Main Chain Polymers

the molecular weight and the flexibility of the macromolecules. In case of low molecular weight, a high concentration is needed to obtain the liquid crystalline phase. With increasing flexibility of the polymer backbone, the critical concentration increases upto limit where even in bulk no liquid crystalline phase can exist. Liquid crystalline polymers based on these principles have been reviewed by Papkov (278). Following these theories, thermotropic liquid crystalline polymers are obtained in the limiting case of no solvent being present. de-Gennes (233) and Di Marzio (279) pointed out that in the case of stable lyotropic phase of rigid rod-like molecules, the solvent molecules can be withdrawn and replaced by flexible polymers. The theories should still be valid even if the flexible polymers are tied to the end of the rigid rod-like molecules which result in thermotropic liquid crystalline polymers with flexible and rigid segments.

7.2 Some Examples and Properties of Mesogenic Main Chain Polymers:

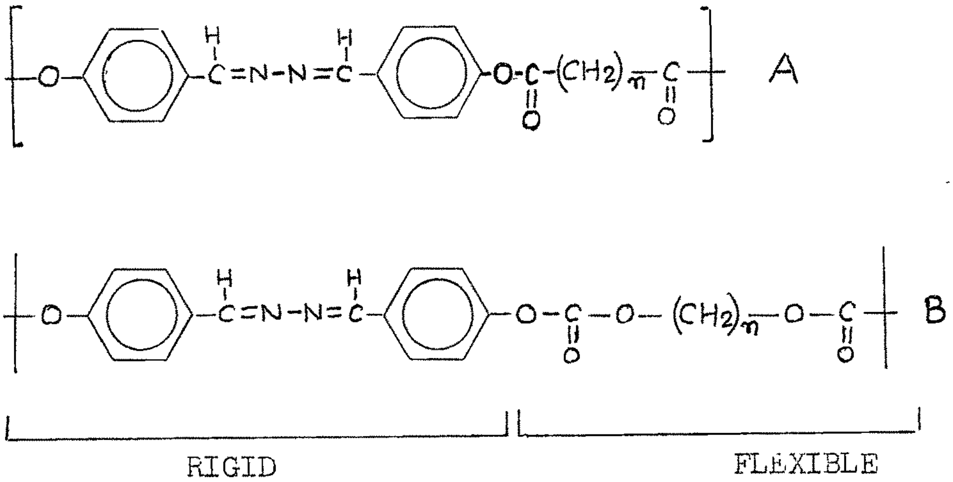
Some typical features of the liquid crystalline main chain polymers will be marked out by some arbitrarily chosen examples. The very first condensation polymers of p-p'-dihydroxy-α, α'-dimethylbenzalazine with diacyl chloride to produce macromolecules with various numbers of dimethylene groups between two ester groups were synthesized by Roviello and Sirigu (280). Looking at the structure, the polymers consist of rigid mesogenic segments and flexible segments formed by the alkyl chains (Table-6).

According to the theories the stability of the liquid crystalline phase is decreased with increasing over-all flexibility of the polymer main chain for constant molecular weight. This is confirmed by those polymers, where the length (n) of the flexible segments is varied. With increasing length (n) of the alkyl chain the examples show a decreasing phase transition temperature; liquid crystalline (LC)⟶ isotropic for the esters A as well as for the carbonates B (Table-6). Blumstein et al. (281) indicated that smectic and nematic phases can be prepared depending on the chemical structure of mesogenic moieties. Using chiral elements in the polymer backbone even cholesteric polymers are described by Blumstein (282).

Another method of realizing liquid crystalline main chain polymer was applied by Jackson and Kuhfuss (283). Starting with the easy accessibly poly(ethylene terephthalate) (PET), rigid mesogenic elements are inserted into the polymer backbone by transesterification with p-hydroxybenzoic acid (PHB). If a sufficient stiffness of the polymer main chain is reached, the anisotropic phase becomes stable. The mechanical properties of these polymers which point out the very important features of these materials were

Table - 6

Phase Transitions of Liquid Crystal Polymers(280):



A : n	Tc (°K)
8	568
10	529
12	514

B: n	Tc (°K)
10	530
12	508
14	486
16	467

also investigated.

Initial studies indicated that it is difficult to orient liquid crystalline polymers by magnetic field (283) but recent studies show that they can be oriented by magnetic field (284).

7.2.1 Undiluted Systems:

(A) Rigid Homopolyesters:

Completely rigid polymers of high symmetry such as poly (p-hydroxybenzoic acid) and poly(p-phenyleneterephthalate) (285) (Fig.15a) exhibit melting temperature too high (467°C) to be conveniently handled (286). This type of polymers could exhibit lyotropic behaviour only if suitable solvent existed.

Less symmetric structures allow a reduction of melting temperature below the decomposition temperature. Examples taken from the patent literature (287-289) are given in (Fig.15b).

(B) Semirigid Homopolyesters:

1. Nematic System:

A quite different situation is observed with the homopolyester in which the repeating unit was rigid segments, which are often mesogenic even before polymerization and flexible spacers. Roviello and Sirigu (290) prepared aliphatic esters of 4,4'-dihydroxy-α-methylstilbene (Fig.15c). Members with (n) between one and four exhibited nematic mesophases with T_{CN} between 107°C and 53°C and T_{NI} between 113°C and 97°C, both transition temperatures decreasing with (n), as often observed with low molecular weight liquid crystal.

Even the compound without the ester bond (Fig.15d) is a nematogen with T_{CN}=105°C and T_{NI}=121°C (291).

2. Smectic and Cholesteric Systems:

Krigbaum et al. (231) and Meurisse et al. (292) have reported some homopolyesters of p-p'-bibenzoic acid with aliphatic diols (Fig.15e).

These homopolyesters exhibited smectic mesophase and the polymer with n=6 exhibited batonnets of smectic A mesophase growing into a fan shaped texture upon cooling at 205°C.

Meurisse et al.(292) also investigated the behaviour of terphenyl derivatives (Fig.15f). These polymers with n=5,6 and 10 showed more definite smectic phases.

Krigbaum et al.(293) investigated homopolyesters containing the α -methylstilbene unit (Fig.15g) and copolymers containing both the adipic acid residue.

The mesophase of the homopolyester (T_{CCh}=110°C,

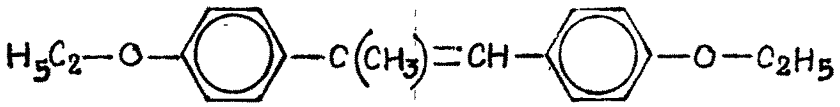


FIG.15d

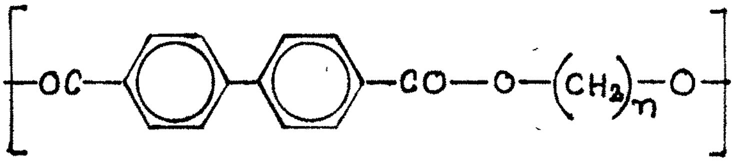


FIG.15e

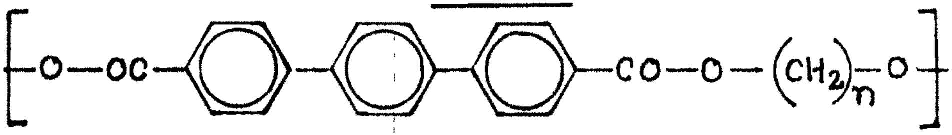


FIG.15f

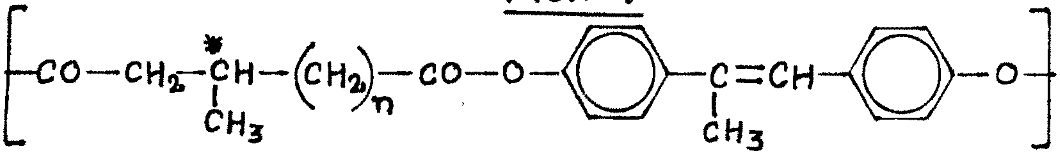


FIG.15g

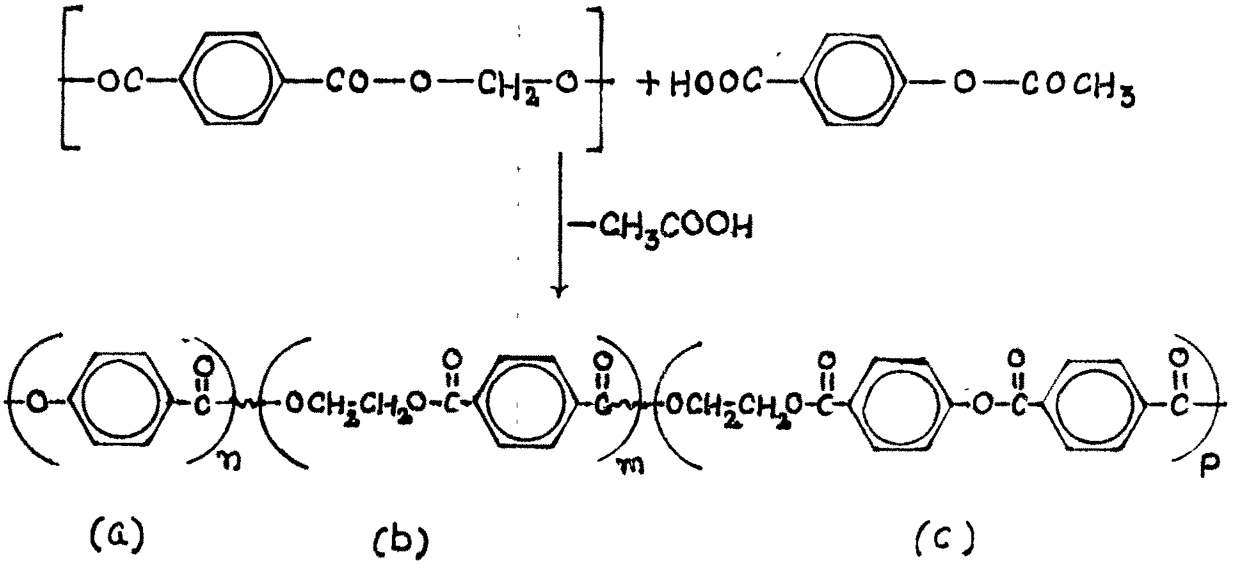


FIG.15h

T_{ChI}=250°C), exhibited fan like structure, suggesting a pitch of the cholesteric helix smaller than the wavelength of visible light.

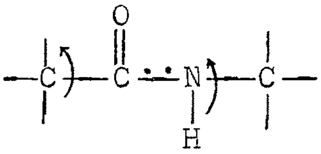
(C) Copolymers:

The third type of liquid crystalline polyester is the random copolyester. These systems are suitable for high modulus applications.

The copolymers prepared by Tennessee Eastman investigators (224,294,295)are formed by trans-esterification of poly(ethylene terephthalate) with p-acetoxybenzoic acid (Fig.15h). The final copolymer contains segments of PET (b) in addition to segments (a) and (c). Incorporation of more than 30% of oxybenzoyl units give stable mesophase.

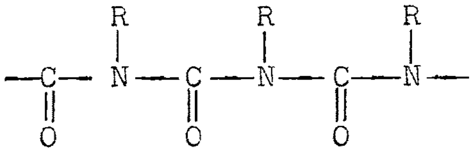
8. ASYMMETRIC MOLECULES:

Typical polymers consist of a linear sequence of monomer residue in which main chain bonds undergo extensive internal rotation. The resulting molecular shape is that of familiar rather symmetric random coil (296). However, an asymmetric shape may be obtained by using special solvents or particular types of bond. The role of flow and other external field is explained by Krigbaum (297). Solvents may induce asymmetry by promoting aggregation, by altering the potentials of internal rotation, or by favouring intramolecular hydrogen bonding. For instance, poly(γ-benzyl-L-glutamate) (PBLG) contains a peptide bond fixed in its planar trans configuration by its double bond character (298) and two adjacent rotating bonds, which generally assure random coil behaviour to the chain. However, in helicogenic solvents, all rotatable bonds are forced into equivalent positions by hydrogen bonding.



$$-\overset{|}{\underset{|}{C}}-\overset{O}{\overset{\|}{C}}\cdots\underset{\underset{H}{|}}{N}-\overset{|}{\underset{|}{C}}-$$

Asymmetric confirmations may alternatively be obtained using monomer that irrespective of the solvent give rise to main chain bonds with severely restricted internal rotations. Some poly(alkyl isocyanate) forming liquid crystals (299) may be a relevant example. The molecule contains a sequence of amide groups, none of which is free to rotate because of the partial double bond character and to steric interference between the n-alkyl chain and the carbonyl group (300).



$$-\underset{\underset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-\underset{\underset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-\underset{\underset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-$$

These amide groups form a sequence of alternating cis and trans planar configurations giving rise to a rather rigid structure (301). Asymmetric structures may also be obtained using bonds for which internal rotation occurs but has no effect on flexibility. The best known examples of polymer liquid crystals, the para-linked aromatic polyamides and polyesters, fall into this category.

8.1 Controlling the Melting Temperature:

In the search for polymer liquid crystals intended for both scientific investigation or industrial applications, one may be inclined to select the monomers that give rise to the most rigid, extended structures. Unfortunately, the requirement of a completely rigid structure must be mitigated with the requirements of polymers with accessible melting temperatures or sufficient solubility. Rigid structures such as poly(p-hydroxybenzoic acid), cellulose and poly(p-phenyleneterephthalamide) are untractable as undiluted systems, since melting temperature is close to the decomposition temperature. The latter polymers are only tractable as a diluted system, but in rather exotic solvents. The high melting behaviour of extended structure is related to low melting entropy. However, as long as the primary application of rigid and semirigid mesogens remains that of polymers with superior mechanical properties, conventional crystal nematic transition temperatures (T_{CN}) should be of the order of 250°C-350°C.

The general methods of aiming at an increase of the melting entropy are illustrated in Table-7,

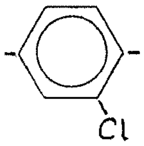
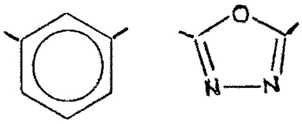
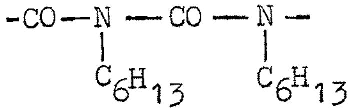
8.2 Determining Chain Rigidity:

In main chain polymeric mesogens, the problem of a general nature is the quantitative characterization of the degree of chain extension. The simplest case would be that in which internal rotation is totally inhibited giving rise to rigid rod-like molecules (Fig.16a) in which the rod-length is equal to the contour length L and much greater than the diameter 'd'. Semirigid chains may instead be modeled as a continuously bending worm-like chain (Fig.16b) or as a collection of rigid rods connected by flexible joints (Fig. 16c). The flexible joint may sometimes involve a sequence of flexible bonds as in Fig. 16d.

In most cases the so-called persistance length 'q' furnishes a measure of chain extension. Suppose a freely rotating chain is located at the centre of a cartesian coordinate system with its first link along Y. Then 'q' is the average sum of the projections of the remaining bonds along Y, and is a measure of the memory of the direction taken by the first segment (296). This parameter can be calculated theoretically from conformational analysis, or can be determined experimentally using techniques such as light scattering, viscosity, and flow birefringence, all of which are sensitive to chain dimensions. Concerning

Table - 7

Methods used for Depressing T_{CN}:

Copolymerization	
Asymmetric units	
Kinks or bends	
Flexible bonds	$-O-$, $-CH_2-$, $-NH-NH-$
Flexible Sequences	$\cdots-CH_2-CH_2-CH_2-\cdots$
Flexible side chains	 $-CO-N(C_6H_{13})-CO-N(C_6H_{13})-$

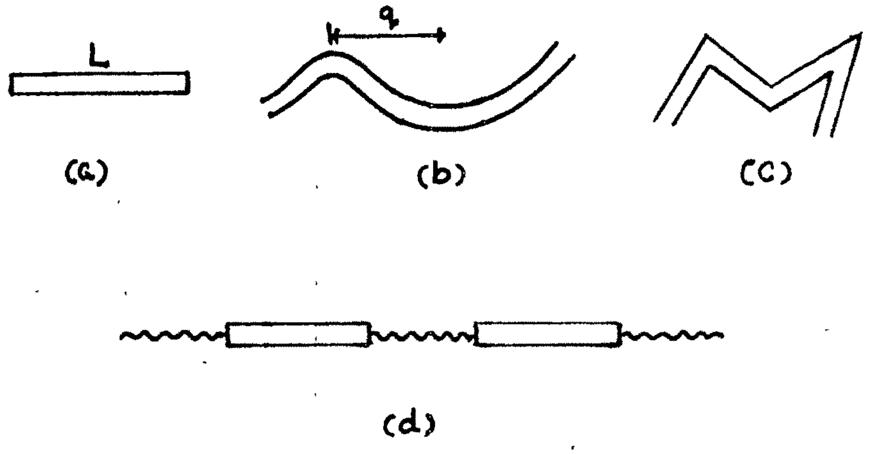


FIG. 16 : Models for Rigid and Semirigid Chains.

the possibility that a semirigid polymer may assume an overall more extended conformation in the anisotropic than in the isotropic phase suggests that mesophase formation is controlled by the axial ratio of the rigid, persistent segment at the transition point and not by the overall conformation (212).

8.3 Recognizing the Mesophase:

For both diluted and undiluted systems it is often difficult to assess the occurrence of the mesophase and contradictory assignments are sometimes reported. Often the microscopic texture characteristics of low molecular weight mesogens (302) is not seen in polymers which appears to be an anisotropic, birefringent liquid phase may be associated with gelation (crystallization) in concentrated solution (303) or with a disappearence of higher melting crystallities in a partially molten polymer (304). Moreover, time effects are often present both in solution (303) and in the melt. Especially when the T_{CN} and T_{NI} temperatures are close to each other, the formation of the texture may be observed on cooling, but not on heating (305).

The preferred technique for studying liquid crystalline mesophases, optical polarized microscopy, is therefore only really useful when a texture develops. In favourable circumstances textures typical of low molecular weight liquid crystal have been observed for polymers.

Differential scanning calorimetry (DSC) is also employed not only for melts (306), but also for solutions (307). However, its interpretation is often complicated by multiple peaks due to recrystallization or to several crystalline forms (304). Annealing and comparision of a heating and cooling curves with regard to the evolution and supercooling of peaks may sometimes help in the assignment of the transitions.

When the nematic texture is not observed and DSC not informative, the occurrence of the mesophase can be established by developing electrohydrodynamic instabilities in the polymer sample (308). This technique and other techniques based on flow and magnetic fields are explained by Krigbaum (297). Small angle light and X-ray scattering techniques (309) and IR and NMR spectroscopy have also been employed.

Finally, an extremely useful and available tool for assessing the type of mesophase is the determination of the phase diagram of the polymer with a reference mesogen. The compatibility of similar mesophases allows the determination of the unknown mesophase from the extrapolation of mutual solubility lines (220,310). Use of the contact method (311) allows greater rapidity in the assessment of the phase diagram.

9. DILUTED SYSTEMS (LYOTROPIC POLYMERS):

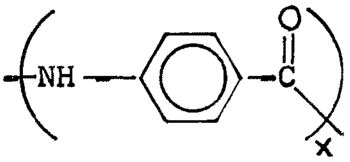
It is now more widely appreciated that a number of high molecular polymeric substances can form a liquid crystal or mesomorphic state (211,312-315). This new interest is due to part to recently recognised practical applications of polymer liquid crystals. Noteworthy are new technological advances in the fabrication of temperature resistant and ultrahigh fiber materials that depend upon a liquid crystal precursor organization of macromolecules. This application alone has provided considerable impetus to further consideration and characterization of the properties of large molecule of liquid crystals.

Polymer in fact would seen predisposed to liquid crystallinity since they may adopt an extremely elongated shape necessary for the long-range orientational order of these special fluids. It is possible in some cases by design of the monomer to optimize polymer rigidity while retaining useful thermal or solubility properties. These optimal factors occur most noticeably in the rod-like structure of helical polypeptides. These polymers form lyotropic liquid crystals at sufficiently high concentration in appropriate solvents.

Two important prerequisites must be met before a polymer can form lyotropic mesophase (a) The polymer must be soluble enough in the solvent to produce a solution above a critical concentration. (b) When in solution, the polymer chain must be extended and rigid (316).

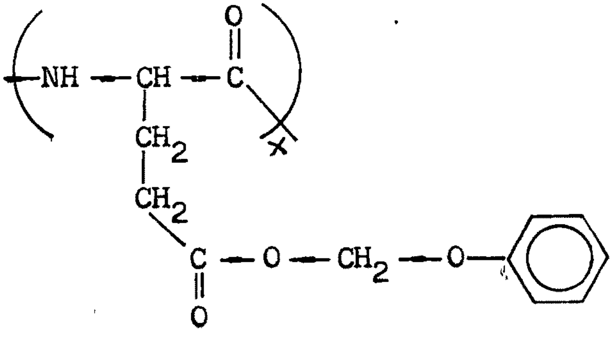
The most common lyotropic polymeric mesophases are synthetic polypeptides, cellulose derivatives, polyarylamides, polyesters and polyisocyanates. All of these materials exist in either an extended linear or a helical conformation in the solvents used to form the mesophase.

Polyamide, for example, shows 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) (313).



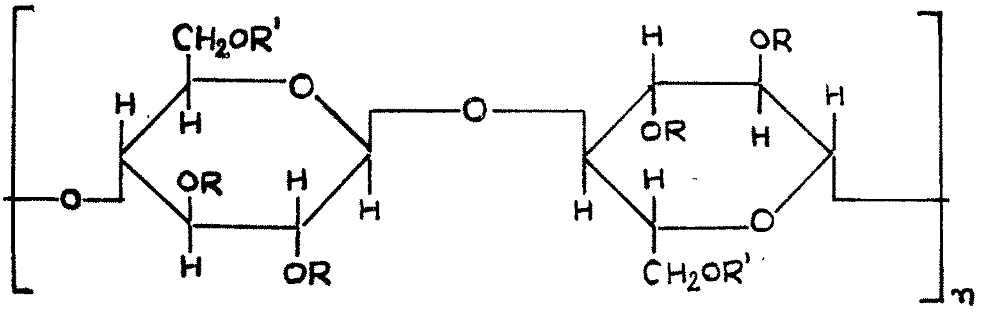
Poly(γ-benzyl-L-glutamate)

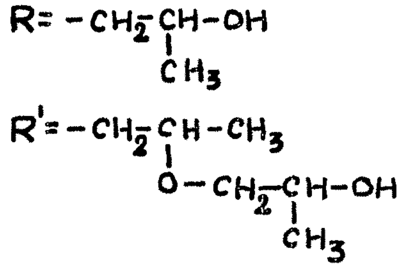
PBLG is a homopolymer of L-enatiomer of the benzyl ester of poly(glutamic acid). PBLG forms cholesteric mesophases in solvents such as chloroform, dioxane, pyridine and dimethyl formamide (DMF) which tend to support the helical structure of the macromolecules (313,317). The methyl and ethyl esters of poly(L-glutamic acid) also form lyotropic mesophases. In the cholesteric mesophase of PBLG there are three levels of chirality; the assymetric carbon in the amino acid, the helical polypeptide, and the macroscopic helical cholesteric mesophase.

A number of cellulose ethers and esters also display liquid crystalline behaviour in concentrated solution. Hydroxypropylcellulose, for example, displays cholesteric liquid crystalline behaviour in water, methanol, or ethanol at a critical concentration of ~40 wt % (318). Fig.17 shows a structure of hydroxypropyl cellulose (HPC) with an average of three hydroxypropyl group per anhydroglucose residue.

HPC is helical, because of intramolecular 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 (319).





$$R = -CH_2-\underset{\substack{|\\ CH_3}}{CH}-OH$$

$$R' = -CH_2-\underset{\substack{|\\ O-CH_2-\underset{\substack{|\\ CH_3}}{CH}-OH}}{CH}-CH_3$$

FIG. 17: Hydroxypropyl cellulose (HPC) Structure with an average of three Hydroxypropyl groups per Anhydroglucose residue.

10. POTENTIAL OF MESOGENIC POLYMERS:

Liquid crystalline polymers have created considerable interest in the last few years.

(i) These polymers can be considered as model system for isotropic amorphous polymers where semiordered regions have been proposed to exist and for drawn amorphous polymers, where by the drawing process a high degree of orientational order can be introduced.

(ii) Polymers that form partially ordered melt or parallel ordered solution can be processed in such a way that fibers with very high degree of orientational order are obtained. This specific structure leads to superior mechanical properties of the materials.

(iii) Polymers with ordered melt are of technological importance for the same reason that low molecular weight systems with anisotropic melts are widely used today in technical products, such as electrical displays. Additional advantages are expected for polymer systems, since parameters such as side groups structure formations or copolymer formation will lead to a large variety of properties of semiordered melts.

(iv) If the polymerization is carried out in semiordered liquid phase of monomer or in semiordered solutions, it is possible to study the polymerization process in ordered system. This will allow a deeper insight to the reaction mechanism. Also by this procedure, macroscopically ordered polymers may be obtained if the monomer phase is macroscopically ordered, for instance, due to an external field or due to forces exhibited by specific surfaces. In this case interesting optical properties are expected for the polymeric systems.

The very first time qualitative investigations (320) were carried out on a copolymer, which contain the polar component to achieve high dielectric anisotropy. For this polymer with increasing voltage, the response time decreases down to a value smaller than 200 ms for 10 V. Alghough no defined boundary conditions were used, these investigations indicate the high mobility of mesogenic groups, quantitative measurements of the orientation of the polymer in electric field will give detailed insight into their electric properties and the mechanism of the investigation of polymer main chain and mesogenic side chain.

In small molecule liquid crystal mesophases, the highly ordered liquid crystalline molecule or ordered- solute chromophore shows strong linear dicroism in nematic and smectic phases and circular dichroic effect in cholesteric mesophases (321). Linear and circular dichroism spectra provide information concerning the polarization of electronic transitions and the detection of hidden transition and they are a probe for monitoring the microscopic environment of the chromophores within polymeric systems. Liquid crystal-induced circular dichroism (LCICD) has been observed for several achiral molecules, such as anthracene, dissolved in birefringent concentrated solution of poly(γ-benzyl-L-glutamate) in helix-supporting solvents. More recently it was observed that achiral $CS_2Pt(CN)_4$ shows extrinsic circular dichroism when organised in hydroxypropyl cellulose cholesteric mesophases (322). This is first time that a chiral inorganic crystal has been resolved by use of a chiral liquid crystal polymers host.

The liquid crystalline order in a polymer solution or melt is of great importance, because the most perfect polymer crystals are formed from such solutions or melts, and thus this is indispensable in obtaining high strength, high modulus, fibers, and that is the most delighting feature of mesomorphism in polymers.

Wooten et al.(224) have observed that 30 mol % of p-hydroxybenzoic acid (PHB), a mesogenic moiety in PET (polyethylene terephthalate) increases the aromaticity and rigidity of the polymer chain while decreases the melt viscosity inducing liquid crystallinity in PET. This is indeed a unique effect and offers a solution to the problem of the decreasing processability which normally accompanies increasing polymer performance. In Fig. 18a, the melt viscosity of PET-PHB copolymer is plotted as a function of the p-hydroxybenzoate content at different shear rate.

Similarly, starting with PET the tensile strength increases rapidly, if the amount of PHB is larger than 35 mol.% because of the influence of the liquid crystalline order (224,285). The mechanical behaviour exceeds the mechanical behaviour of conventional materials and gives reason for their increasing technical application. In Fig.18b the tensile strength of PET is plotted over the amount of PHB, which was inserted into the main chain by transesterification.

The mesogenic polymers are reported to be more useful as 'pyroelectric Detector' (323) while the other types of pyroelectric detectors are difficult to prepare. The mesogenic polymers are light in weight, hence such pyroelectric detectors are more useful in the space technology.

11. SYNTHETIC ROUTES TO LIQUID CRYSTALLINE POLYESTERS POLYAMIDES AND COPOLYESTER:

In recent years the phenomenon of liquid crystalline behaviour has received considerable attention, as witness some excellent reviews of this subject. However, the study of condensation polymers as they relate to the liquid crystalline state has received relatively little attention until recently, possibly because of a lack of demonstrated utility.

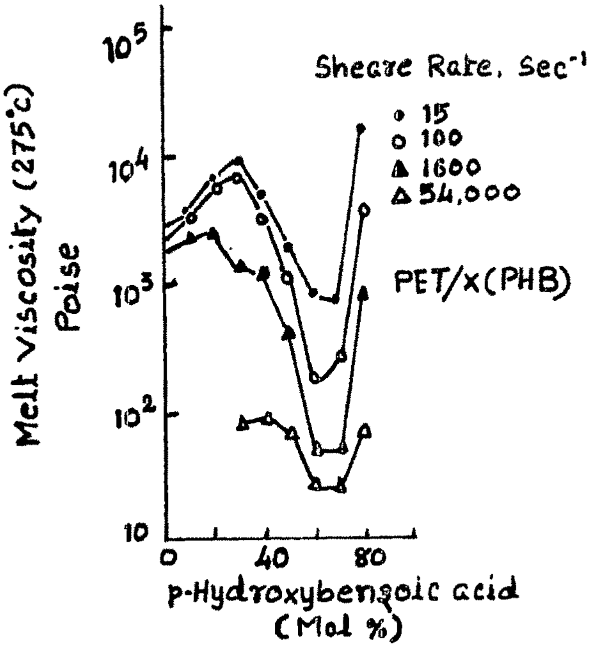


FIG.18a: Melt Viscosity of PET Modified With p-Hydroxybenzoic acid

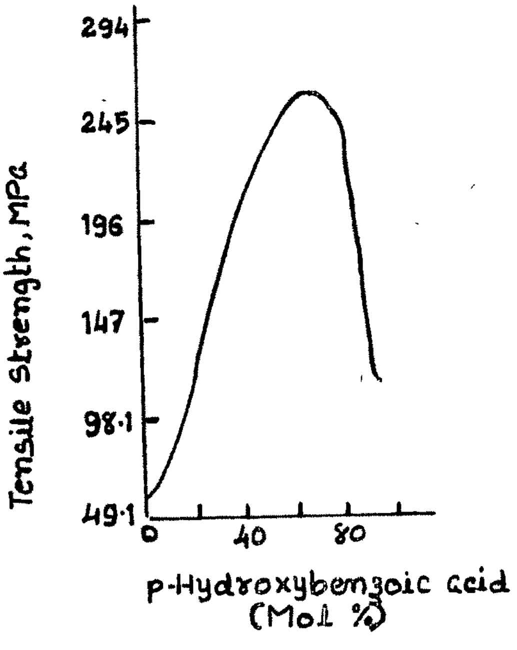


FIG.18b: Tensile Strength of PET Modified With p-Hydroxybenzoic acid

Earlier, the use of liquid crystalline solution of poly (r-benzyl-L-glutamate) made it possible to spin this polymer more rapidly than isotropic solution (324,325).

The practical application of lyotropic polyamides preceded that of thermotropic polyesters by at least ten years. Indeed, the development of Kevlar fibre by the du-Pont Company, by the solution spinning of an aromatic polyamide in the lyotropic states, probably provided most of the early incentive for research on thermotropic polyesters (326,327). An aromatic copolyester containing biphenol terephthalate and p-oxybenzoate units which is capable of forming a thermotropic melt (328,329) is marketed for ceramic-like plastics, and a family of oxybenzoate-ethylene terephthalate copolyesters has been intensively studied for the use in injection molded thermoplastics (330). Polyesters which are closely related in structure to the 'Kevlar' polyamide have not been realised commercially yet.

11.1 Aromatic Polyamides:

Morgan (331) has reviewed the historical development of the preparation of fibre-forming aromatic polyamides. He reported that the first polyamide of the non-peptide type, which was found to form liquid crystalline solutions, was poly(1-4-benzamide). Subsequent investigations revealed that other molecular structures which retained the linearity and rigidity of the p-phenylene group, could also lead to lyotropic polyamides, including the 2,6-naphthalene, trans-1,4-cyclohexylene, and p,p'-biphenylene. In addition, p-phenylene units can be connected by trans-azo- or trans vinylene groups and still retain their linear, rigid conformations. The molecular structures of such units, as complied by Morgan, are shown in Table-8 (331).

Four types of reactions have been applied to the preparation of polyamides in general, but only one of these, the reaction of an acid chloride with an amine, has been broadly used to prepare lyotropic polyamides. The direct amidation of acids and amines through a crystalline salt intermediate, as used for the preparation of aliphatic polyamides (332) (termed nylon salt) is not applicable for aromatic amine-acid monomer pairs, but three other types of reactions have recently been developed for the polyamides; these are:

1) The oxidative amidation reaction of aromatic amines and acids with phosphorous compounds, which is generally carried out in an amine or amide solvent with organic chlorine compounds as co-reactants, as in the following scheme (333,334):

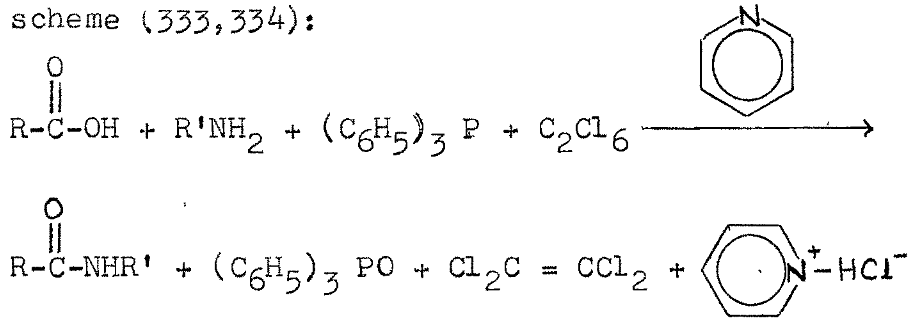
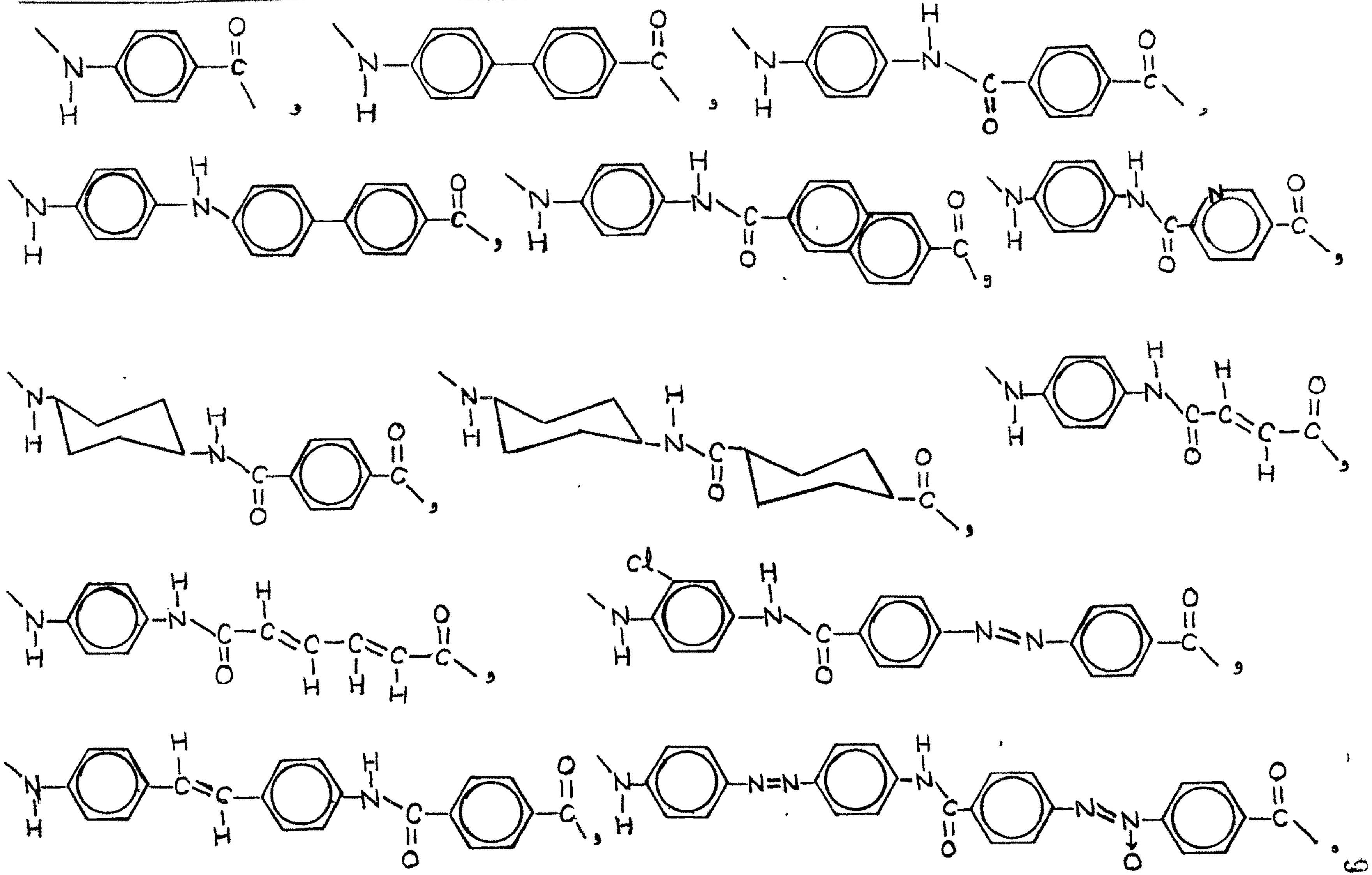


Table-8

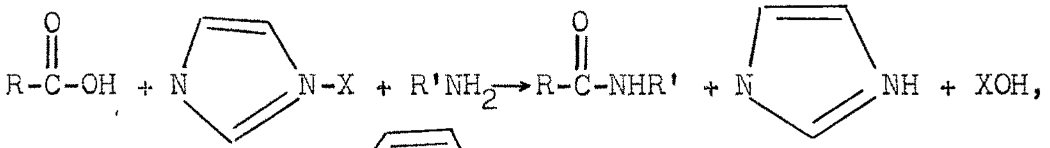
Repeating Units of Polyamides which form Lyotropic Solutions:

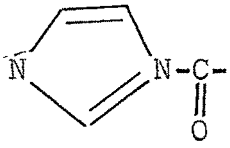


Lithium salts may be added to enhance the solubility of the polymers, and polymers with inherent viscosities well above 1.0 can be prepared by this route (335).

(2) The aminolysis of an active ester, such as those of substituted phenols and hydroxytriazoles, can be used to prepare aromatic and olefinic polyamides under relatively mild condition in reasonably high molecular weight (336).

(3) Amidation reactions in the presence of imidazole or its derivatives such as in the following reaction, have been used by organic chemists for sometime to prepare amides in high yields, but only recently has advantage been taken of this reaction for the preparation of polyamides (337, 338).



in which X is -H,  and other groups.

While it is likely that these reactions will find increasing utility, the low temperature polycondensation of diamines with bis-acid chlorides is still the simplest and most direct route to the preparation of high molecular weight polyamides. For this approach, two reaction systems can be used (i) interfacial polycondensation in two-phase reaction system (339) and (ii) solution polymerization, either in an amide solvent (with or without lithium salts to increase polymer solubility), or in chlorocarbon salts with amines present to form ammonium hydrochloride salts (340). Salts of the latter type may be added to the reaction to increase polymer solubility (331), and reaction temperature and solvent are particularly important in preventing premature precipitation, which could make the end groups of the aromatic polyamides inaccessible before high molecular weight can be achieved. Solvents for aromatic (or other rigid-rod) polyamides which may be used to process these polymers for films or fibres are compiled in Table-9 (341).

11.2 Aromatic Polyesters:

The problems of polymer solubility is particularly important and can be a limiting factor, in the preparation of high molecular weight, aromatic polyesters because such rigid-rod polymers have in general, both very high melting points and very low solubilities in all presently available reaction solvents. As a result of these characteristics, and in order to achieve very high molecular weights, aromatic polyesters must be prepared by a two step sequence involving first either a homogeneous solution polymerization reaction or a melt polymerization reaction, to form a polymer of intermediate molecular weight followed by a final reaction of the polymer in the solid state. This latter reaction,

Table - 9

Solvents for Aromatic Polyamides:

Solvent	Solvent activity
Amide Solvents (with or without Li or Ca salts):	
N,N-dimethylacetamide	strong (toxic)
Hexamethylphosphoramide	strong (toxic)
N-methylpyrrolidone	strong with salts
N,N,N',N'-tetramethylurea	strong
N-methyl caprolactum	weak
N-acetylpyrrolidone	weak
1,3-Dimethylimidazolidinone	strong
N-methylpiperidone	weak
N,N-Dimethylpropionamide	weak
N,N,N',N'-tetramethylmalonamide	
Acid solvents:	
Sulphuric acid (100.6% oleum)	very strong
Hydrofluoric acid	strong
Chlorosulphonic acid	strong

often referred to as 'solid-stating' occurs presumably in the non-crystalline phase of the semicrystalline polymer at a temperature slightly below its melting point and, if carried out under high vacuum, is capable of generating very high molecular weight polymers (342,343).

A great many aromatic polyesters and copolyesters which show thermotropic behaviour have now been reported, particularly in the patent literature (344). This copolyesters may contain either combinations of different types of mesogenic units or combinations of mesogenic and non-mesogenic (non-linear) units. The structures of many of the different types of monomers used to form liquid crystal aromatic polyesters and copolyesters are shown in Table-10 (344).

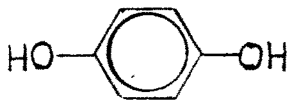
There are four basic reactions which can be used for the synthesis of aromatic polyesters of intermidiate molecular weights, as follows (345):

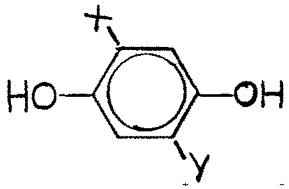
(1) The Schotten-Baumann reaction of an aromatic acid chloride with a phenol, which can be carried out either in solution at elevated temperature (generally in a chlorocarbon solvent with a tertiary amine present to react with the HCl liberated to form an ammonium salt), or by interfacial polycondensation at room temperature (again a chlorocarbon solvent is generally used for the phase containing the acid chloride and a base is present as an 'HCl-acceptor' in the

Table-10

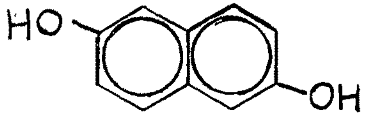
Monomers Used in the Synthesis of Liquid Crystal Aromatic Polyesters:

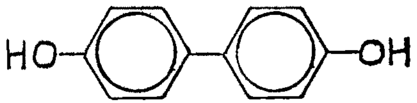
Aromatic diol

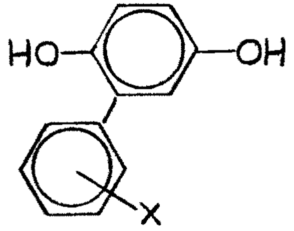




(x, y = halogen or alkyl)

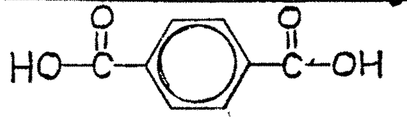


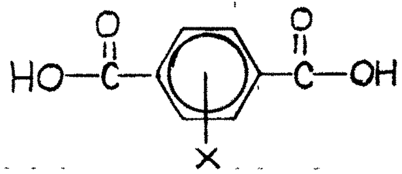




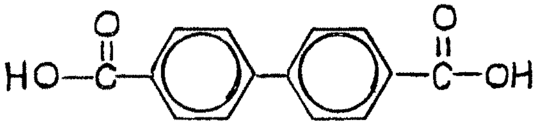
(x=halogen, alkyl)

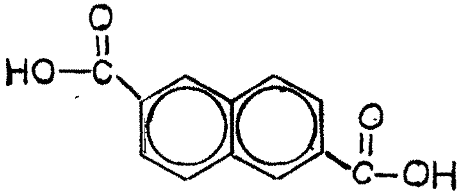
Aromatic dicarboxylic acid

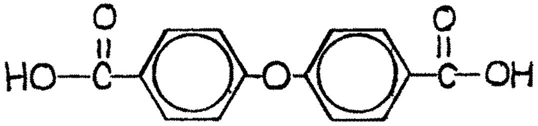




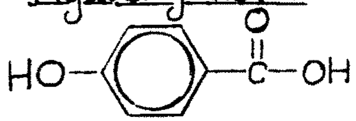
(x= halogen, alkyl)

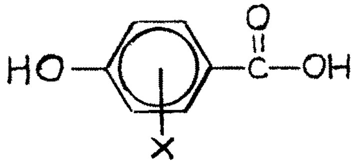




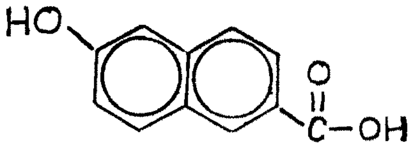


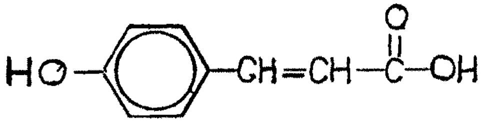
Hydroxy acid





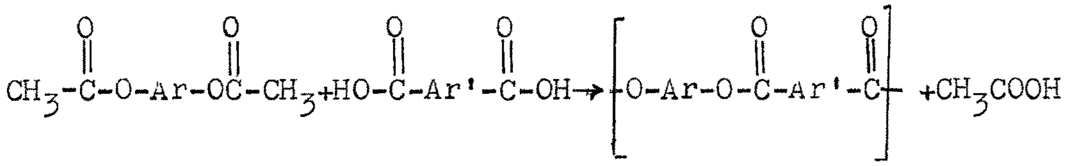
(x = halogen, alkyl)





aqueous phase containing the difunctional phenol), or as a melt reaction, in which the HCl liberated is removed by an inert gas stream or by maintaining the reaction mixture under vacuum (346).

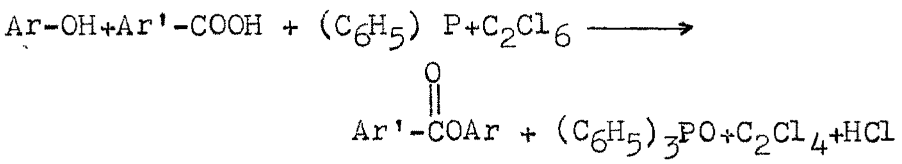
(2) Ester interchange reactions in the melt at high temperatures of either of two different types (a) reaction of a diphenyl ester of the aromatic dicarboxylic acid monomer with the difunctional phenol monomer to liberate phenol, which is removed under vacuum (347-349) or (b) reaction of a diacetate ester of the functional phenol monomer with the dicarboxylic acid monomer by an "acidolysis" reaction to liberate acetic acid, which is readily removed under vacuum (350, 351).



$$CH_3-\overset{O}{\overset{\|}{C}}-O-Ar-O\overset{O}{\overset{\|}{C}}-CH_3+HO-\overset{O}{\overset{\|}{C}}-Ar'-\overset{O}{\overset{\|}{C}}-OH\rightarrow\left[O-Ar-O-\overset{O}{\overset{\|}{C}}-Ar'-\overset{O}{\overset{\|}{C}}\right]+CH_3COOH$$

Both of these reactions may, of course, be equally applied to the polymerization of hydroxyacid monomers.

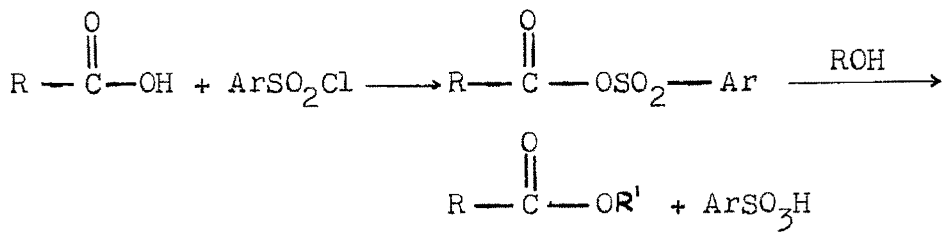
(3) The oxidative esterification reaction of an aromatic carboxylic acid with a phenol in the presence of a phosphorous compound and a chlorocarbon, as illustrated below (352).



$$Ar-OH+Ar'-COOH+(C_6H_5)\ P+C_2Cl_6\longrightarrow Ar'-\overset{O}{\overset{\|}{C}}OAr+(C_6H_5)_3PO+C_2Cl_4+HCl$$

This type of reaction was first applied to the preparation of polyamides, as discussed above, for which it is somewhat more effective in forming high molecular weight polymers, but it has now been used for the synthesis of a wide variety of aromatic polyesters, either by the self-condensation of hydroxyacids or by the co-condensation of dicarboxylic acids and difunctional phenols (353). A fairly wide variety of phosphorous compounds can be used as reducing or dehydrating agents, chlorophosphates, phosphates, polyphosphates and phosphazones (354). In most cases, lithium chloride is added and the reaction is run in either pyridine or an amide solvent system. The reaction has also been found to be catalyzed by tertiary amine salts (355).

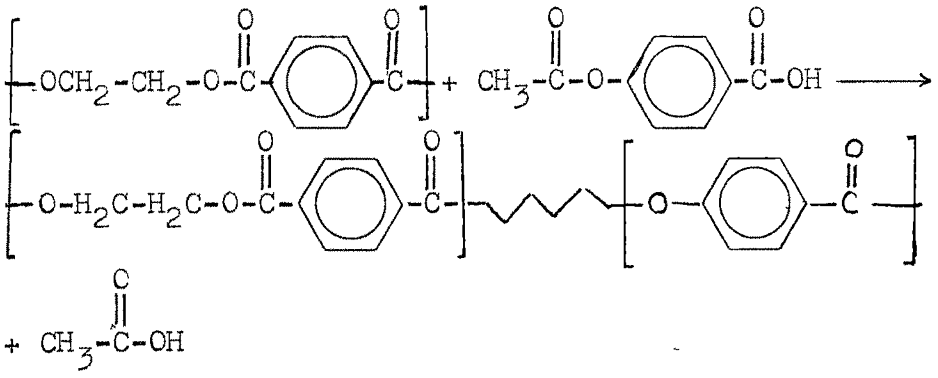
(4) Polymerization reactions involving the use of mixed anhydrides, formed in situ, have been reported to give fairly high molecular weight polymers, as for example in the recent report of the use of arylsulphonyl chlorides to effect the direct polycondensation of aromatic dicarboxylic acids with biphenols, presumably through the intermidiate formation of mixed sulphonate - carboxylate anhydride as follows (356):



$$R-\overset{O}{\overset{\|}{C}}-OH + ArSO_2Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-OSO_2-Ar \xrightarrow{ROH} R-\overset{O}{\overset{\|}{C}}-OR' + ArSO_3H$$

11.3 Copolyesters:

All of the reactions listed above can be equally applied to the preparation of aromatic copolyesters from almost any combination of hydroxyacids, dicarboxylic acids and biphenols of the type listed in Table-3. In general, the copolymers so obtained are random or statistical in composition. Furthermore, the acidolysis reaction has been successfully applied to preparation of random copolyesters by interchanging monomers and high molecular weight polymers, most notably in the preparation of poly(ethylene terephthalate-co-oxybenzoate) by the insertion reaction of p-acetoxybenzoic acid with preformed poly(ethylene terephthalate), as follows (357):



A problem can arise if this type of high melting semi-crystalline aromatic copolyester is maintained at temperatures at or near its melting point for a prolonged period of time. Under these conditions, the initially random copolymers can slowly reorganize to multiple block structures by a process termed the 'crystallization induced reaction' copolyester(358) of the oxybenzoate copolymer mentioned above and several other types of aromatic copolyesters were studied (359). The ester interchange reorganization reaction can apparently occur either in the solid state at temperatures close to the melting point or in the liquid crystalline phase of thermotropic copolyesters.

12. APPLICATION OF POLYMERIC LIQUID CRYSTALS:

12.1 Ultra high Modulus and Ultra high Strength Fibers (212)

A closely packed ensemble of parallel extended polymer chains should exhibit the highest achievable specific strength. These unique characteristics of uniaxially oriented polymers are the basis for the technology of ultrahigh strength organic polymeric fibers. In reality, fibrous structures of significant dimensions that approach their theoritical maximum strength have not yet been prepared. However, the gap between the theoritical limit and experimental results has been greatly reduced during recent years.

It was the discovery of very strong polyaramid fibers produced from anisotropic solution, and the realization of the importance of the liquid crystalline state in the preparation of highly ordered extended chain fibers that provided an unprecedented impetus to the research in ultrahigh strength fibers.

The stress-strain curves for the ultrahigh strength/high modulus fibers show a strong similarity to those for glass and steel on a specific basis (i.e. taking into account the lower specific gravity of the fibers from rod-like aromatic polymers in comparision to glass and steel).

These fibers are seen to be stronger and stiffer than glass and steel. Taken together, these properties suggest that these fibers should be quite useful in the reinforcement of rigid and flexible composition. Thus, Kevlar fiber (208-210) 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 (360) has been shown to be competitive with the lower modulus types of graphite fibers and in rigid composites. Other specific end use applications include conveyor belts, V-belts;ropes and cables; body armour, interior trim, exterior fairings, control surfaces, and structural parts in aircraft.

The use of para-oriented fibers for applications where flame resistance and dimensional stability are required include; industrial protective clothing, e.g. paints, shirts, coats and smocks for workers in laboratories, foundries, chemical plants and petroleum refineries; welder's clothing and protective shields; fire department turnout coats, paints, shirts, jump suits for forest fire fighters, and for military pilots.

Many patents have prepared for thermotropic liquid crystalline polymers which can be drawn in the fibers or cast into resins (361,362).

Recently U.S.A. defence department is known to have secret planes which are called 'invisible' planes, which means that they can not be detected by radars. The reason for non-detection is the Kevlar coating or fabrication which is said to absorb microwaves, hence the image of plane can not be seen on radar. This is very exiting application of Kevlar fibre.

12.2 Liquid Crystalline Mouldable Resins (363):

Recently, M/S Dartco Mfg.Inc.(U.S.A.) have developed a self-reinforcing liquid crystalline aromatic copolymer that can be moulded on standard injection equipment. Existing tooling designed for conventional engineering thermoplastics can be used for material evaluation and frequently for production. This liquid crystal resin is expected to replace metals, ceramics, glass, composites, thermoset and thermoplastic resins, and other materials in such areas as telecommunication equipments, computers, aerospace and auto parts.

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 temperatures of-51°C to 241°C; good burn resistance with minimal smoke generation; resistance to virtually all chemicals, including polar and nonpolar solvents and hydrocarbon fuels; resistance to high levels of ionizing and cobalt-60 radiation; UV resistance; lubricity; machinability and extremely low outgassing. Moreover, the materials' thermal stability is such that it can be used at high regrind ratios.

13. FUTURE:

Future applications of the liquid crystal polymers will take adventage of the fact that soluble thermotropic polymers can be coated from solution. Initially, applications will be limited to those where liquid crystals themselves are being used. Potential technological applications of liquid crystal polymers are in optical displays and devices. In optical displays they may serve as aligning as well as electroactive layers. They can also be used as polarizing film (linear or circular). Novel lyotropic linear polymer should continue to provide a variety in high-strength fibers. It is anticipated that scientific applications of liquid crystal polymers in optical spectroscopy will be more fully explored.

Thus, synthesis and characterization of novel polymers with liquid crystalline behaviour is an emerging area of scientific endeavour. Mesomorphic polymers, both lyotropic and thermotropic, of the smectic,nematic, and cholesteric types are becoming common place. These novel polymeric materials offer an opportunity and a challange for the synthetic as well as physical polymer chemists.