CHAPTER 1

INTRODUCTION
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1.1 HISTORICAL BACKGROUND AND NOMENCLATURE:

"Liquid crystalline" phenomenon was discovered in the later part of the last century by F. Reinitzer and O. Lehmann. Lehmann was the first to investigate the properties of liquid crystalline state\(^1,2\). Lehmann observed with Reinitzer's sample of cholesteroyl benzoate that a turbid liquid was formed on heating, which flowed readily like oil but still preserved many of the characteristics of crystals. He suggested the name "liquid crystals" to describe those substances which are liquid in their mobility and crystalline in their optical properties\(^3-7\).

Early this century, G. Friedel investigated liquid crystalline phases by optical microscopy and concluded that the substances are neither perfect crystals nor perfect liquids. He proposed the more logical terms "mesomorphs" or "mesoforms", since the properties are intermediate between very well defined phases\(^8\). Other names proposed for the mesomorphic state are discussed by Rinne\(^9\).

The term "liquid crystal" refers to the phase which lies between the highly ordered solid phase, with no translational mobility of component molecules, and the isotropic phase having molecular mobility and a general lack of molecular order\(^10,11\). Liquid crystalline compounds can be classified into two groups. In the first group, the ordered arrangements of molecules are formed by solvent-induced microphase separation between molecules.
having different polarity. This group is termed "amphiphilic". Examples of amphiphilic compounds are lipophosphates as well as non-ionic or ionic detergents. In the second group containing "non-amphiphilic" liquid crystals, the Carnal element for the origin of liquid crystalline order is the high geometric anisotropy and rigidity of the molecular moieties which may be present in the form of rigid rods or disks.

1.2 LIQUID CRYSTALLINITY: THE REQUIREMENTS

Thermotropic liquid crystals display the liquid crystalline state on heating, while lyotropic liquid crystalline state is observed on solvation\textsuperscript{12-14}. Friedel, Lawrence and Jelly suggested a nomenclature to classify the liquid crystalline state. Solutions of rod-like entities in a normally isotropic solvent often form liquid crystal phases at sufficiently high solute concentration. These anisotropic solution mesophases are lyotropic liquid crystals. The rod-like entities are usually quite long. Compared to typical thermotropic liquid crystal "mesogen" [see sec. 1.3] their axial ratios, i.e. length-to-diameter ratios are greater than 6.7.

In thermotropic liquid crystals, transitions involving mesophases are most naturally effected by a change in temperature. Axial ratios of the materials showing thermotropic liquid crystal phases are usually between 4-8.

The structural requirements discussed in the latter sections relate to the thermotropic liquid crystal phases only.
Certain molecular features are essential to generate liquid crystallinity in general. The molecules of liquid crystals possess in common some geometric features, notwithstanding the compounds be chemically of diverse types such as anils, azos, azoxies, cholesteric esters, etc.

The geometric and polar requirements have been well established through extensive research involving synthesis and optical characterization. The axial ratio of the molecule should be large. The compound should have geometric asymmetry and molecular rigidity along its molecular axis. Aromatic ring structure and double bonds increase rigidity. In addition, molecular interactions such as dipole-dipole interaction, ion-dipole interaction, induced dipole interaction and possibly hydrogen bonding play an important role. The presence of strongly polar and/or strongly polarizable groups on the molecular axis and weakly polar terminal groups enhances stability of the liquid crystalline state. The differently polarizable groups present in the molecule induce nonuniformity in cohesive forces between the elongated (rod-like) molecules.\textsuperscript{11,15,16}

The molecular architecture common to most liquid crystalline compounds is presented below.

\[
\begin{array}{c}
\text{Y} \quad \text{O} \quad \text{X} \quad \text{O} \quad \text{Y}
\end{array}
\]

It consists of two or more planar ring systems, such as 1,4-phenylene / 2,6-naphthalene / trans (1,4-cyclohexyl), linked together with central group (X) and appropriate terminal group.
The central and terminal groups determine the attractive forces between the molecules. The variation in cohesive forces is important for the molecule to display different liquid crystal mesophases. These mesophases are discussed in section 1.4.

1.3 THE MESOGEN

The term "mesogen" is assigned to the section of a molecule which is indeed responsible for the formation of capable of liquid crystalline state. It comprises, in general, rigid segments and nonoscillating linear linking functional groups. A mesogen must consist of at least two rigid units made up of aromatic / cycloaliphatic rings interconnected at the para positions by a short rigid functional group which does not disturb the coplanarity of the aromatic rings such that the overall length remains much greater than the diameter of the aromatic ring. The ratio of mesogen (considering the cylindrical mesogen) length to diameter usually is called the "axial ratio". Mesogens are further subclassified on the basis of the number of rigid units. The terms "diad" and "triad" refer to mesogens with two and three rigid aromatic units respectively.

Flory had developed theories which predict that rod like molecules with an axial ratio between 3.0 and 6.4 are capable of displaying thermal transition from the liquid crystalline state to isotropic liquid state prior to degradation. The compounds with large axial ratios melt at too high a temperature to generate liquid crystalline state. They either pass directly into isotropic state or decompose without melting at such high
temperatures. In these systems, liquid crystalline state can only be obtained by dissolution in a suitable solvent composition.

1.4 LIQUID CRYSTALLINE PHASES

Friedel classified thermotropic liquid crystals into three different types on the basis of optical observations. These are:

1.4.1 Smectic phases,
1.4.2 Nematic phases, and
1.4.3 Cholesteric phases.

If the cohesion between the molecules within a layer is stronger than that between molecular layers, crystal breaks down on heating or on solvation to generate lamellar arrangement of molecules having well defined layer spacings. The mesophases thus formed are called "smectics" and are usually characterized by high viscosity and characteristic low angle X-ray patterns from which the thickness of the strata can be determined. Further heating decreases the level of cohesion between molecules within a stratum and at certain temperatures the molecules would acquire an additional degree of translational freedom, which may give rise to rather poorly organized smectic phase, such as smectic A, or a nematic mesophase. In nematic mesophases, a large scale disappearance of positional order takes place. The unidirectional orientational order is preserved, however, on still further heating, the orientational cohesion of molecules breaks down with the appearance of isotropic fluid phase. Such passages, on heating, initially from crystal to a mesophase, then possibly from one mesophase to another and finally from the mesophase to
an isotropic liquid are all first order transitions which can be observed by differential scanning calorimetry. These phase transformations on heating are represented diagrammatically in Fig.1.

If a nematic arrangement of molecules has chiral centers, of a certain optical sign, the nematic arrays become twisted generating a helical arrangement normal to the molecular plane. The pitch of helix depends on the optical rotating power of the chiral group. Such twisted nematic phases are called cholesteric phases.

These mesophases are discussed in the following sections.

1.4.1 SMECTIC PHASES

The molecules in smectics have a layered arrangement resulting in a stratified structure. In molecules displaying more than one liquid crystalline phase, the smectic phase always occurs at lower temperatures in the heating mode and can be recognized by optical microscopy. The centers of gravity of molecular units can move in two directions, and rotation about one axis is permitted.

Systematic study of smectic liquid crystals had been undertaken by Sackmann, Arnold, Demus et al.\textsuperscript{17}. Smectic phases are classified on the basis of miscibility rules. Two smectic liquid crystals are of the same type if both are miscible in all proportions. The phases are also identified by x-ray diffraction
CRystal

SLIDING OF SMECTIC LAYERS AT K→S TRANSITION (SMECTIC)

ADDITIONAL TRANSLATIONAL FREEDOM AT S→N TRANSITION (NEMATIC)

ISOTROPIC LIQUID

FIG. 1.

MOLECULAR ORIENTATION IN SEVERAL LIQUID CRYSTAL PHASES
patterns and microscopic textures. The Halle group\textsuperscript{17} identified a number of smectic phases from smectic A through smectic G. Smectic H phase was added by de Vries et al.\textsuperscript{18}

1.4.1.1 SMECTIC A

This is the least ordered of all smectic phase. The molecules in smectic A phases are arranged in layers. The long molecular axis is perpendicular to layer planes. The molecules within each layer have considerable rotational and translational freedom around their long axes. The resultant loose arrangement of molecules makes the layer somewhat flexible and often results in complex curved organization\textsuperscript{19} (Fig.2).

1.4.1.2 SMECTIC C

Smectic C phases are very much identical to smectic A phases. The only difference is that the molecules in smectic C phases are tilted with respect to layers (Fig.2).

1.4.1.3 SMECTIC B & SMECTIC H

In this phase molecules have ordered structure within the layer. Harmann and Krummacher suggested that the molecules are grouped by rotating around their long axes, to effectively generate cylindrical units\textsuperscript{20}. The close packing of cylindrical units results in hexagonal organization. Smectic B phases are further divided into two subphases i.e. B\textsubscript{n} or B\textsubscript{t} (H phase) where the subscript n stands for normal and t for tilt. In B\textsubscript{n} phase molecules are normal to the layer as in smectic A and in B\textsubscript{t} phase molecules are tilted as in smectic C (Fig.2).
a) SMECTIC A STRUCTURE

b) SMECTIC C STRUCTURE

c) SMECTIC B STRUCTURES

FIG. 2.

SCHEMATIC DIAGRAM OF SMECTIC (A,C,B) STRUCTURES
1.4.1.4 SMECTIC D

This phase is intermediate between smectic A and C. The structure suggested for this phase is that of a cubic lattice. The sites in smectic D are occupied by multimolecular spherical units (micelles). The structure of smectic D has been the subject of considerable discussion\textsuperscript{135-137} (Fig.3).

1.4.1.5 SMECTIC E

The first x-ray diffraction pattern reported for smectic E phase showed highly ordered structure without hexagonal lattice and an alignment of molecules perpendicular to the layers\textsuperscript{21}. The stable texture of smectic E phase is a mosaic texture and is reported to be optically uniaxial (Fig.3). The tilted E phase designated by $E_t$ is also possible.

1.4.1.6 SMECTIC F

Smectic C and smectic F phases are almost similar. In fact, at the present time there is little clarity as to what the major difference between the two are. The tilt of the molecules with respect to the layer in smectic F is somewhat greater than that in smectic C.

1.4.1.7 SMECTIC G

The smectic G phase has an ordered arrangement of molecules within the layer. The molecules appear to be tilted, and three dimensional lattice probably exists within the layers (Fig.3).
a) SMECTIC D STRUCTURE

b) SMECTIC E STRUCTURE

c) SMECTIC G STRUCTURE

FIG. 3.
SCHEMATIC DIAGRAM OF SMECTIC (D,E,G) STRUCTURES
The structures $B^*$, $E^*$, $G$ and $H$ are very closely related. Smectic phases are broadly subclassified as (i) smectic phase with structured layers and (ii) smectic phase with unstructured layers. The interlayer attractions in smectics are weak compared to the lateral forces between the molecules in a layer. The layers are able to slide over easily. The smectic phases have fluid properties but are more viscous than other mesophases. Smectic phases occur at lower temperatures due to higher degree of order. Smectic A and C phases are unstructured smectic phases. Smectic B is a structured smectic phase. In compounds exhibiting more than one smectic phase the smectic A phase is observed at higher temperatures than the other smectic phases.

In polarized optical microscopy smectic phases with unstructured layers show focal conic fan shape texture and structured smectic layers display mosaic texture. The physical conditions to be met in order to form smectic phases are:

i) terminal intermolecular attractive forces in the crystal must be relatively weak compared to lateral intermolecular forces and

ii) the lateral intermolecular attractive forces must be sufficiently strong to maintain the layered structure.

1.4.2 NEMATIC PHASE

Nematic liquid crystals differ structurally from isotropic liquids due to spontaneous orientational abilities of their molecules along the long axes. This spontaneous alignment or orientation process generates highly birefringent material,
with dissimilar refractive indices for polarized light along and perpendicular to the optical path. The most common textures observed under polarizing microscope is the schlieren or threaded texture. Specific heat, compressibility and thermal volume expansion in nematics are similar to those in normal liquids (Fig.4).

1.4.3 CHOLESTERIC PHASE

Cholesteric liquid crystalline phases are observed in rectilinear compounds with optically active carbon. These are essentially nematic planar structures in which successive planes are twisted. Hence, cholesteric phase is often termed as "twisted nematic mesophase". The planes are stacked in a uniformly twisted fashion. The direction of the local optical axis lies in the plane perpendicular to the twist axis. The axis of the adjacent plane is shifted uniformly by an angle \( \theta \) generating a helical arrangement of planes along the twist axis. The distance for a 360° turn is called the pitch. Cholesteric mesophase can also be obtained by mixing a nematic liquid crystal with a miscible optically active compound. Cholesteric liquid crystals are miscible with nematic liquid crystals and the thermodynamic properties are very much similar. This phase displays batonnet texture under polarizing optical microscope\(^2\) (Fig.5).

1.5 CHARACTERISTICS OF LIQUID CRYSTALS

The orientation order in nematic liquid crystalline state is intermediate to that observed in crystalline solids and in normal liquids. The extent of orientation is represented by
FIG 4.

SCHEMATIC DIAGRAM OF A NEMATIC PHASE
FIG. 5.

SCHEMATIC DIAGRAM OF CHOLESTERIC PHASE SHOWING PITCH $P$ AND DISPLACEMENT ANGLE $\theta$
the order parameter, $S$ as defined by the expression (1).

$$S = \frac{1}{2} < 3 \cos^2 \theta >$$  \hspace{1cm} (1)

where $\theta$ is the angle between the molecular axis and the preferred direction and brackets $<$ $>$ indicate an average value of the quantity enclosed. The average value of $\cos^2 \theta$ is used to calculate order parameter, $S$. The value of order parameter varies between zero for an isotropic liquid and one for a perfect crystal. The order parameter near the clearing point is generally 0.3-0.4 but at lower temperatures may become as high as 0.8 for a nematic mesophase.

A number of liquid crystals exhibit both smectic and nematic mesophases. Compounds forming only one of them are named smectogenic or nematogenic on the basis of the mesophase they form. The temperature at which compounds undergo a phase change is known as the transition temperature. Transition temperatures are usually recognized on the basis of the phases involved in a transition, such as crystal - smectic, crystal - nematic, smectic - nematic and nematic or smectic - isotropic transition temperatures. The temperature for the phase change from a mesophase to an isotropic liquid is often called clearing temperature ($T_c$). Thermotropic liquid crystals, on heating, undergo a sequence of characteristic phase changes at the transition temperatures (Fig. 1), and the three dimensional geometric organization of the molecules gradually collapses. This gradual breakdown of molecular organization is obviously related to the asymmetric nature of the intermolecular attractive forces operating between sides, planes and terminal groups of the
molecules. The various intermolecular attractive forces of unequal strength have been shown schematically in Fig. 6. When the forces operating along the three axes of a molecule are identical, the three dimensional crystalline arrangement will naturally collapse at the same temperature to form a normal liquid without displaying mesophases in between. It is, therefore, essential that these three intermolecular forces be not identical and also be strong enough to maintain partially ordered molecular organization against thermal vibrations. Systems are known in which mesomorphic states are not formed during heating cycle but are only observed on cooling from the isotropic melt. These are termed monotropic mesophases. "Monotropic smectic" or "monotropic nematic" phases are known. Mesophases are termed "enantiotropic" when they are observed in heating as well as in cooling cycles\textsuperscript{26-28}.

1.6 POLYMERIC LIQUID CRYSTALS

KEVLAR, the first generation liquid crystalline polymer, is a lyotropic system. It is infusible and is soluble only in concentrated sulfuric acid. Its capabilities as high strength fiber can be harnessed only by part wet / part dry jet spinning from its solution in concentrated sulfuric acid. Composites can be made by reinforcing with epoxy resins.

The second generation liquid crystalline polymers are thermotropic liquid crystalline systems. These are melt processible and have intrinsic bone-flesh character suitable for in situ generation of composites.
FIG. 6.
SCHEMATIC DIAGRAM OF INTERMOLECULAR FORCES (a, b, c) ACTING BETWEEN MOLECULAR LAYERS
1.6.1 MESOGENIC POLYMERS

Existence of mesomorphic order in polymer melts was first described in open literature in 1968 \(^{134}\) and patents were filed on commercially pertinent systems in 1974 \(^{29}\). Polymer liquid crystals (mesogenic polymers) are classified on the basis of nomenclature adopted for low molecular weight liquid crystals described in sections 1.1 and 1.4. Further classification is made on the basis of the location of the mesogenic units in the molecular chain. In main chain liquid crystalline polymers the mesogenic unit is a part of the molecular chain. In side chain liquid crystalline polymers mesogenic units are linked to polymer backbone as pendants (Fig. 7).

Interest on polymeric liquid crystals originated with the prime objective of coupling film forming properties of polymers with the electro-optical properties of liquid crystals to form better display devices. The objective remained unfulfilled, however. The anisotropy of the main chain polymeric liquid crystalline state opened attractive prospects for the production of high strength materials \(^{30-36}\). The anisotropy is maintained if processed in liquid crystalline state, resulting in materials of greater strength in the direction of orientation \(^{37}\).

1.6.2 LYOTROPIC LIQUID CRYSTALLINE POLYMERS

These liquid crystalline polymers are not discussed as extensively in the literature as thermotropic mesomorphic systems. Aromatic polyamides are most important polymers of this class \(^{38-43}\). The solvents for these polymers are either aprotic
a) MAIN CHAIN LCPs

b) SIDE CHAIN LCPs

FIG. 7.
SCHEMATIC DIAGRAM OF MAIN CHAIN AND SIDE CHAIN LCP STRUCTURES
dipolar solvents (dimethyl acetamide containing 2-5% of lithium or calcium chloride) or strong acids (100% sulfuric acid, chloro, fluoro- or methane sulphonic acid). Important factors determining mesomorphic state formation are molecular weight, concentration of the polymer in solution, solvent composition and solution temperature. Hydrogen bonding capability of amide group enhances the ability to form lyotropic solutions.

1.6.3 THERMOTROPIC LIQUID CRYSTALLINE POLYMERS

Thermotropic liquid crystalline polymers have received considerable attention in the recent past. Rigid rods like poly(hydroquinone terephthalate) and poly(4-oxy benzoate) are non-melting high temperature polymers with decomposition temperature in excess of 500°C. Considerable research efforts have focussed on structurally modifying these polymers to generate melt processible mesomorphic polymers which can be processed by conventional processing equipments.

A variety of approaches have been made to reduce the crystal perfection and the crystal lattice energy with the objective of reducing the melting temperature ranges of the rigid rod polymers and thus generating liquid crystallinity at suitably lower temperature. These include (i) use of non-rigid groups (flexible spacer) in the main chain to reduce the axial ratio of mesogen, (ii) placement of substituents on the mesogenic group to disrupt regularity of the repeating unit, (iii) use of non-linear cycloaliphatic comonomers (kinks), (iv) incorporating crankshaft monomers, and (v) copolymerization of mesogens.
Random placements of repeat units can lower the transition temperatures still further\(^{68}\).

The three flexible spacers used predominantly are polymethylene\(^{69-73}\), poly(ethylene oxide)\(^{74-76}\) and polysiloxane segments\(^{77,78}\). Liquid crystalline polymers with alkyl, alkoxy, halo, nitro, phenyl, cycloalkyl or cyano substituted on 1,4-phenylene ring are reported in literature\(^{79-82}\). 1,4-Phenylene or 2,6-naphthalene based liquid crystalline polymers were extensively studied and discussed. Homopolymers based on these aromatic moieties are crystalline and non-melting. The melting ranges are reduced by incorporating 1,3-phenylene, 2,5- or 1,4-naphthalene rings in the polymer chain\(^{34,83-86}\). Modification of rigid rod system by incorporating flexible spacer to reduce transition temperatures affect the mechanical behavior of the system due to dilution and randomization of directional vectors associated with the mesogens. Copolymers of 1,4-benzene / 2,6-naphthalene moieties with slight loading of either 1,3-benzene / 2,5-naphthalene units in the main chain result in thermotropic liquid crystalline polymers without much compromise on the mechanical performance of linear rigid homopolymer\(^{87}\). Thermotropic liquid crystalline polymers generally comprise non hydrogen bonding groups e.g. esters as central linking units.

The monomers most frequently used in the synthesis of liquid crystalline polyesters are listed in Table 1. The generalized skeleton structure of a main chain liquid crystalline polymer is presented in Fig. 8. The central linking unit must ensure that the linearity of the rigid unit is maintained which
TABLE 1

MONOMERS FOR SYNTHESIS OF LCPS

<table>
<thead>
<tr>
<th>a) DICARBOXYLIC ACIDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-C-(\text{--O--OH})</td>
</tr>
<tr>
<td>HO-C-(\text{--O--C--OH})</td>
</tr>
<tr>
<td>HO-C-(\text{--O--OH})</td>
</tr>
<tr>
<td>HO-C-(\text{--O--C--OH})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>b) DIOLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-(\text{--OH})</td>
</tr>
<tr>
<td>HO-(\text{--OH})</td>
</tr>
<tr>
<td>HO-(\text{--OH})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>c) HYDROXY ACIDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO-(\text{--C--OH})</td>
</tr>
<tr>
<td>HO-(\text{--C--OH})</td>
</tr>
</tbody>
</table>

X = Halogens, Alkyl, -
FIG. 8.
GENERAL STRUCTURE OF MAIN CHAIN LCPs (52)
is possible provided that the two rings are separated by the odd number of chemical bonds. It is "1" for biphenyls, "3" for ester,azo, azoxy, azomethine, amide groups and "5" in case of alazines$^8$.

1.7 STRUCTURE - PROPERTY RELATIONSHIP

The thermal behavior, especially the transition temperature, is probably most discussed in the study of thermotropic liquid crystalline polymers. The thermal transitions are related to structural parameters such as the nature of aromatic rings, central link units, substitution on mesogen, the flexible spacer type and the number of carbon atoms in the flexible spacer. Polyesters have been investigated extensively since these can be synthesized by low temperature polycondensation and high temperature melt transesterification reaction from easily available or readily synthesizable monomers$^3$. The structure-property relationships discussed under the following three subsections are pertinent to liquid crystalline polyesters. These are:

1.7.1 Effect of mesogenic structure,
1.7.2 Effect of flexible spacer, and
1.7.3 Copolymerization.

1.7.1 EFFECT OF MESOGENIC STRUCTURE

Factors related to mesogenic structure which affect the thermal behavior of mesomorphic polymers are: a) number of rings in the mesogen, b) intramesogenic link, and c) substitution on the mesogen.
1.7.1.1 NUMBER OF RINGS IN MESOGEN

Transition temperatures of mesomorphic polymers are enhanced by an increase in number of aromatic rings in the main chain. However, the presence of a large number of rings would result in non-melting polymers.

Crystal-mesomorphic, mesomorphic-isotropic transition temperatures and temperature range over which mesophase is stable are higher for polymer 2. This is attributed to the additional aromatic ring in the polymer, which increases the length and hence the axial ratio of the mesogen. Similar trend is observed in the thermal characteristics of polymers 3 and 4.

<table>
<thead>
<tr>
<th>No.</th>
<th>STRUCTURE</th>
<th>Trans. Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>POLYMER 1.</td>
<td>-CO-(\text{O})-COO+CH_2\text{CH}_2*-O</td>
<td>C154, LC160I</td>
</tr>
<tr>
<td>POLYMER 2.</td>
<td>-CO-(\text{O})-COO+CH_2\text{CH}_2*-O</td>
<td>C256, LC311I</td>
</tr>
<tr>
<td>POLYMER 3.</td>
<td>-O-(\text{O})-OCO-(\text{O})-COO+CH_2\text{CH}_2*-CO-</td>
<td>L237, LC294I</td>
</tr>
<tr>
<td>POLYMER 4.</td>
<td>-O-(\text{O})-OCO-(\text{O})-COO+CH_2\text{CH}_2*-CO-</td>
<td>L236, LC265I</td>
</tr>
</tbody>
</table>

Polymer 3 has only one intramesogenic link. The diad mesogenic ester shows directional sense. The thermal behavior of polymer 3 is related to the manner in which the flexible spacer -(CH_2)_10- is linked.
As discussed in the section 1.5, the mesomorphic properties like mesophase transition behavior and mesophase thermal stability are affected by the intermolecular attractive forces. The nature of central ring changes mesophase stability and transition temperature of mesomorphic compounds. In low molecular weight liquid crystals the trend in transition temperature may be related to the nature of the central ring as\textsuperscript{90-93}:

\[
\begin{align*}
\text{O} & \rightarrow \text{N} \\
\text{N} & \rightarrow \text{N} \\
\text{N} & \rightarrow \text{C} \\
\text{C} & \rightarrow \text{C} \\
\text{C} & \rightarrow \text{C}
\end{align*}
\]

The central ring can be differentiated into three major groups a) aromatic b) unsaturated cyclic and c) cycloaliphatic.

Incorporation of hetero atoms in aromatic ring reduces the mesophase transition temperature. In case of diene ring systems, location of double bond plays a significant role in mesophase stability. The non-planarity of 1,3-cyclohexadiene ring makes it harder for the molecules to pack into a regular structure which results in lower mesophase transition temperature. The greater packing efficiency of bridged bicyclo compound results in thermally stable mesophases. Thus, the thermal stability of mesomorphic compound with unsaturated cyclic central ring is intermediate between those with aromatic and cycloaliphatic central rings. Rings other than 1,4-benzene and 2,6-naphthalene may completely destroy liquid crystallinity by disturbing molecular linearity\textsuperscript{94}.
1.7.1.2 INTRAMESOGENIC LINKS

The intramesogenic links are the group of atoms that connect two aromatic rings of the mesogen. The type and the linking direction in unsymmetrical intramesogenic links of the mesogen have a pronounced effect on the thermal behavior of mesogenic polymers. The extensively investigated intramesogenic link units are a) azo b) azoxy c) ethene or substituted ethene d) azomethine or substituted azomethine e) substituted or unsubstituted alazine and g) ester. A few selective examples of polyesters with different intramesogenic link units are listed below.\textsuperscript{68,75,95-100}

![Chemical structures](image)

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>INTRAMESOGENIC LINK</th>
<th>TRANS. TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.</td>
<td>NONE</td>
<td>C 154 LC 160 I</td>
</tr>
<tr>
<td>6.</td>
<td>-CH=CH-</td>
<td>C 197 LC 200 I</td>
</tr>
<tr>
<td>7.</td>
<td>-N=N-</td>
<td>C 210 I</td>
</tr>
<tr>
<td>8.</td>
<td>-ON=N-</td>
<td>C 200 I</td>
</tr>
<tr>
<td>9. [ RANDOM ]</td>
<td>-C=O-</td>
<td>NON LC</td>
</tr>
<tr>
<td>10. [ ORDERED ]</td>
<td>O</td>
<td>MONOTROPIC NEMATIC</td>
</tr>
<tr>
<td>11.</td>
<td>-C=CH-</td>
<td>C 200 LC 222 I</td>
</tr>
<tr>
<td></td>
<td>[ CH_3 ]</td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>-C=N=N=C-</td>
<td>C 217 LC 242 I</td>
</tr>
<tr>
<td></td>
<td>[ CH_3 ]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ CH_3 ]</td>
<td></td>
</tr>
</tbody>
</table>
Polymers 5 to 8 are rigid rod-flexible spacer type polymers with diad mesogenic group. The intramesogenic links are different. The thermal behavior of the polymers can be related to the intramesogenic link unit. The unit is altogether absent in polymer 5. This polymer has been selected for comparing the thermal behavior of other polymers with identical flexible spacer. Additional factor in ester linkages is the direction during linking of two rings together. This can be either head to tail (random) or head to head (ordered) sequences. The random arrangement in polymer 9 generates non-mesomorphic character whereas ordered arrangement in polymer 10 generates monotropic nematic behavior. Thus, structure randomization affects the crystal packing efficiency dramatically, resulting in either non-mesomorphic or poorly defined mesophases.

Similar observations are recorded for liquid crystalline polyesters with triad mesogenic unit and decamethylene flexible spacer. The polymer 13 appears to form smectic phase and polymer 16 showed poorly defined smectic phase. In polymers 13 and 14 as well as in polymers 15 and 16 the intramesogenic ester units are interchanged. The axial ratios are identical. The difference in these polymers is in the crystal packing efficiency and intermolecular forces due to the interchange of the ester linkages. These factors affect mesophase transition temperatures of polymers 13 and the clearing temperatures of polymers 15.
1.7.1.3 SUBSTITUTION ON MESOGEN

Substitution on mesogenic unit increases diameter of the mesogen, which decreases the axial ratio. It also reduces the orientation of the adjacent mesogen and disrupts its packing efficiency. The phase transition temperature is decreased as a result. Polar substituents enhance dipolar interactions between neighbouring chains, which lead to an increase in transition temperatures. In polymers with mono or disubstituted mesogenic units the nature and relative position of substituted groups governs the thermal behavior\textsuperscript{101,102}.
The diol monomers used in these polymers are 4,4'-dihydroxy azoxybenzene (polymer 17), 4,4'-dihydroxy-3,3'-dimethyl azoxybenzene (polymer 18) and 4,4'-dihydroxy-2,2'-dimethyl azoxybenzene (polymer 19). It is observed that the introduction of substituent into mesogen unit results in depression in both $T_m$ and $T_c$ of the polymer, where $T_m$ and $T_c$ are mesophase transition and clearing temperature respectively. In polymers 18 and 19 the methyl group positioning is altered. The greater disturbance of the coplanarity of the mesogen is observed in polymer 19.

A series of substituted liquid crystalline copolyesters were investigated by R.W.Lenz et al. These copolyesters are based on the structure given below.

![Chemical Structure]

The polar effect is of less importance than steric constraints in governing the thermal behavior. Substituents X, Y are either halogen atoms or alkyl groups. The transition temperatures are presented in Table 2.

<table>
<thead>
<tr>
<th>POLYMER</th>
<th>A</th>
<th>B</th>
<th>TRANS. TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.</td>
<td>H</td>
<td>H</td>
<td>C 216 N 265 I</td>
</tr>
<tr>
<td>18.</td>
<td>H</td>
<td>CH₃</td>
<td>C 196 N 218 I</td>
</tr>
<tr>
<td>19.</td>
<td>CH₃</td>
<td>H</td>
<td>C 118 N 163 I</td>
</tr>
</tbody>
</table>
The thermal transitions of liquid crystalline polymers from substituted mesogens are affected by four factors.

1) BOND LENGTH :-

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Bond Length (Å)</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.1</td>
<td>20, 21</td>
</tr>
<tr>
<td>CH₃</td>
<td>1.53</td>
<td>22</td>
</tr>
<tr>
<td>Cl</td>
<td>1.7</td>
<td>23</td>
</tr>
<tr>
<td>Br</td>
<td>1.89</td>
<td>26</td>
</tr>
</tbody>
</table>

The phase transition temperatures decrease with an increase in bond distances between mesogenic units and with incorporation of substitution on the unit.

2) BULKINESS OF THE SUBSTITUENT GROUP :-

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Bond Length (Å)</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>21, 24, 25</td>
<td></td>
</tr>
<tr>
<td>C = N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The phase transition temperature decreases as the bulkiness of the substituent group increases.

3) POLARITY OF THE SUBSTITUENT :-

<table>
<thead>
<tr>
<th>Substituent</th>
<th>Bond Length (Å)</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxy</td>
<td>28, 21</td>
<td></td>
</tr>
<tr>
<td>Methyl</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The presence of oxy group between mesogenic part of the chain and substituent in polyester 28 destroys liquid crystallinity.

4) SYMMETRY OF THE MESOGENIC SUBSTITUTION :-

Thermotropic liquid crystalline polymeric systems with
symmetrically disubstituted mesogen unit (2,5-disubstituted-1,4-phenylene) have higher transition temperatures than monosubstituted analogs (polymers 27 and 23). The packing efficiency is enhanced in the presence of symmetric disubstitution.

1.7.2 EFFECT OF FLEXIBLE SPACER

Polymethylene, polyethylene oxide and polysiloxane units are incorporated as flexible spacer in main chain thermotropic polymers to bring down the transition temperatures.

1.7.2.1 POLYMETHYLENE SPACERS

\[
\text{[MESOGEN] - \{CH}_2\}^n
\]

The mesophase transition temperatures and mesophase thermal stabilities (\(\Delta T\) i.e. \(T_{c}^{m} - T_{m}\)) decrease with increase in the number of carbon atoms, in an odd-even or zig-zag manner. The transition temperatures of polymers with even number of carbon atoms are higher. Polymers with spacers greater than eight carbon atoms display smectic phases. The higher flexibility of the polymer chain in the presence of long spacers permits the mesogenic units to orient themselves into highly ordered structures. The odd-even effects in both crystal - liquid crystal and liquid crystal - isotropic transition temperatures are yet to be quantified theoretically for polymeric liquid crystals. Similar effects have been observed for low molecular weight liquid crystalline compounds with alkyl end groups and in polymers with polymethylene substituted mesogenic units. Trans
conformations encourage liquid crystallinity while gauche conformations decrease the stability of mesophase order. The number of molecular conformations permissible increases with increase in the spacer length. At higher temperatures the larger concentration of gauche conformations in the terminal group of low molecular weight liquid crystals disturbs the cylindrical shape of the molecule and destroys the liquid crystalline order\textsuperscript{105,106}.

Incorporation of flexible spacer dilutes the chain rigidity. This dilution effect is dependent on the number of carbon atoms in flexible spacer. Branched flexible spacer lowers the transition temperature even further. If the Van der Waals radii of a substituent is less than the interchain distance, the substituent can be packed between the chains without an appreciable disruption of the crystalline lattice and interchain forces\textsuperscript{107}. Chiral flexible spacer induces cholesteric mesophases.

1.7.2.2 POLYETHYLENE OXIDE (PEO) SPACERS

\[ \text{MESOGEN} \rightarrow \{\text{CH}_2-\text{CH}_2-\text{O}\}_n \]

The polar oxygen atom, in polyethylene oxide spacer strengthens the lateral intermolecular attraction which promotes the formation of smectic mesophases. The mesophase type changes with the number of PEO units in the flexible spacer\textsuperscript{74-76}.

\[(\text{PEO})_n \rightarrow \begin{array}{ccl} 1 & 2 & 3 \\ \text{TYPE} & \text{NEMATIC} & \text{MONOTROPIC} \end{array} \]

\[(\text{SMECTIC}) \]

\[ \ldots \ldots \]

\[ \quad \]
1.7.2.3 POLYSILOXANE SPACERS

The two major thermal characteristics observed for polysiloxane spacer\textsuperscript{77,78} are that the phase transition temperatures are lower and that in some cases a glassy liquid crystalline state is observed. This behavior is attributed to the higher flexibility, bulky structure and conformational irregularity of the spacer.

1.7.3 COPOLYMERIZATION

Copolymerization of para aromatic / cycloaliphatic monomers with meta substituted aromatic monomers increases the dilution of mesogenic segment. This reduces the molecular packing efficiency and mesogenic symmetry. This type of systems can be divided into:

i) wholly aromatic and

ii) aliphatic - aromatic systems.

Wholly aromatic copolymers synthesized with the incorporation of small amounts of non-linear (1,3/1,2-benzene or naphthalene) monomers with rigid angular elements\textsuperscript{53,109-111} display lower thermal transition temperatures with only a marginal compromise on mechanical performance. The mesophase - isotropic transition temperatures of copolymers vary almost linearly with copolymer composition whereas crystal - mesomorphic transition temperatures pass through a minimum at some intermediate composition, generally at equimolar concentrations of the comonomers. The onset of thermotropic liquid crystallinity on copolymerization of monomers (building blocks) of non-
mesogenic homopolymers with the monomers of mesophasic polymers varies from system to system and depends on monomer symmetry, linearity and ability of the monomer to form ordered structures. The minimum requirements to form mesomorphic polymers have been established for industrially important systems.\(^5\)

Liquid crystalline polymers exhibit "anomalous" flow phenomena which include the excessive shear thinning at relatively lower shear rate range, a transient negative normal stress, the occurrence of a yield stress, a large secondary shear stress maximum after start up of steady shear flow.\(^1\) The steady shear viscosity for such polymers in the nematic phase is lower than in the isotropic phase, despite the lower temperatures of measurement in the former case.\(^2\) At the onset of nematic behavior the melt viscosity of a mesomorphic copolyester is less than that of a similar but non-mesogenic polymer by over three orders of magnitude.\(^3\) Melt viscosity is also composition dependent. Melt viscosity of PET-oxybenzoate copolyester decreases in the composition range over which the copolyesters exhibit liquid crystallinity as seen in Fig. 9. The melt viscosity increases up to 30 mole percent of oxybenzoate, which marks the onset of liquid crystallinity. Above 30 mole percent of oxybenzoate the melt viscosity decreases steadily until a minimum at 60 mole percent is reached.

Similar effect of composition is observed in the copolyester of chlorohydroquinone, terephthalic acid (TA) and isophthalic acid (IA). The onset of liquid crystallinity is observed at 15 mole percent and the melt viscosity levels off at
EFFECT OF COMPOSITION ON MELT VISCOSITY (Jackson and Kuhfuss)
The polymers reported and discussed in the literature are mostly copolyesters. They are suitable since the continuous alteration of composition is very facile, permitting great flexibility in the design of polymer system suited to optimal processing and property characteristics.

1.8 POLYMER SYNTHESIS

The four routes used in the synthesis of polyester are i) direct esterification ii) ester exchange/ transesterification, iii) self polycondensation and iv) Schotten-Baumann reaction.47,114,115,121

Direct polyesterification of diols with dicarboxylic acids generates polyesters with the elimination of water. The second method of direct polyesterification is through the formation of diphenyl chlorophosphate - pyridine complex in presence of lithium halide. The complex reacts with diacids to generate polyesters. A number of strategies adopted to synthesize polycondensation products through such complexes are discussed by Higashi et. al.116-120. Synthesis of polyesters by transesterification catalysis is well documented. The catalysts used in transesterifications are reviewed by R. E. Wilfong123. Self polycondensation procedures are applicable only in the case of hydroxy acids. Schotten - Baumann reactions performed between carbonyl halides and hydroxy compounds in the presence of an appropriate acid acceptor, are discussed in section 1.8.1.

The reactants must be extremely pure, present
FIG. 10.

EFFECT OF COMPOSITION ON MELT VISCOSITY
(Griffin and Cox)
stoichiometrically and the viscosity of polymerization medium should not hinder removal of the side product in order to generate high molecular weight polyesters.

A number of chemical structural units are available for use in the design and synthesis of liquid crystal polymers as described in section 1.6.3. Main chain liquid crystal polymers are synthesized by two strategies. These are (i) polymerization of rigid core with appropriate flexible spacer and (ii) monomer design by the incorporation of the flexible segment into the rigid core and subsequent polymerization. These routes are schematically represented in Fig. 11. Syntheses of such liquid crystalline copolyesters by (a) acid halide route and (b) transesterification are described in the following sections.

1.8.1 ACID HALIDE ROUTE

This route is divided, on the basis of reaction temperatures, into low and high temperature polycondensations. The most extensively used halide is chloride. The low temperature polycondensation technique has advantages over high temperature method in the polymerizations of thermally and conformationally unstable reactants. In addition, the polycondensation can be conducted in melt, solution or by interfacial methods.

1.8.1.1 MELT POLYCONDENSATION

The polycondensation is completed in two stages to obtain high molecular weight polyesters. In prepolymerization, acid dihalide and diol are heated above the melting point and
SCHEMATIC DIAGRAM FOR TWO STRATEGIES SYNTHESIS OF MAIN CHAIN LCP WITH FLEXIBLE SPACER
maintained isothermally at this temperature under inert atmosphere.

The second step, postpolymerization, is conducted under

\[
\text{PRE: } X - [A] - C - X + HY - [B] - YH \xrightarrow{\text{N atm}} T_m < t, -HX \xrightarrow{} (C - [A] - C - Y - [B] - Y)_n
\]

\[
\text{POST: } C \xrightarrow{\text{High vacuum}} \text{High Mol. wt. Polymer} \quad T_m < t < T_c
\]

high vacuum. The temperature is maintained somewhere between the mesophase transition and clearing temperatures of the polyester.

1.7.1.2 SOLUTION POLYCONDENSATION

In this technique diol dissolved in polar aprotic solvent – acid acceptor mixture is added to acid halide dissolved in aprotic polar solvent. The reactants are taken in stoichiometric amounts and the reaction is allowed to proceed under inert atmosphere at room temperature or at an elevated temperature.

\[
X - [A] - C - X + HY - [B] - YH \xrightarrow{\text{Solvent, acid acceptor}} \xrightarrow{N \text{ atm, RT}} \xrightarrow{} (C - [A] - C - X - [B] - X)_n
\]

The experimental parameters which influence the
molecular weight of the polyester are: (i) reactivity of the monomer, (ii) solvent system, (iii) acid acceptor, (iv) monomer purity and stoichiometry, (v) stirring rate, and (vi) reaction temperature.

1.8.1.3 INTERFACIAL POLYCONDENSATION

The reaction is conducted in two immiscible liquid phases, of which one is aqueous and the other is organic. Acid halides are taken in the organic phase, and diol, acid acceptor and phase transfer catalyst are taken in the aqueous phase. The two phases are intimately mixed in to induce polycondensation. Important factors governing interfacial polycondensation reactions are: (a) chemical reaction rate, (b) precipitation rate of polymer, (c) reactant and solvent purity, (d) stirring rate, (e) concentration of monomers in two phases, (f) hydrolysis of acid halide, (g) solution viscosity, (h) interfacial energy barrier, and (i) partition of reactants in the two liquid phases.

<table>
<thead>
<tr>
<th>PHASE-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACID HALIDE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PHASE-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIOL / DIAMINE</td>
</tr>
<tr>
<td>+ ACID ACCEPTOR</td>
</tr>
<tr>
<td>PHASE TRANSFER CATALYST</td>
</tr>
</tbody>
</table>
1.8.2 TRANSESTERIFICATION

The ester exchange or transesterification reactions can be subclassified, on the basis of the by-product eliminated, into:
a) alcoholysis, b) acidolysis and c) double ester interchange. Alcohol is generated as a by-product in alcoholysis while acid, in acidolysis technique. The double ester interchange is rarely used, since the rates are very slow. The reaction schemes for transesterification are shown below.

a) ALCOHOLYSIS:

\[
\text{CH}_3\text{O} - \text{C} - \text{A} - \text{C} - \text{O} - \text{CH}_3 + \text{HO} - \text{B} - \text{OH} \xrightarrow{\Delta} \left( \text{C} - \text{A} - \text{C} - \text{B} - \text{O} \right)_n
\]

b) ACIDOLYSIS:

\[
\text{HO} - \text{C} - \text{A} - \text{C} - \text{OH} + \text{CH}_3\text{O} - \text{B} - \text{O} - \text{C} - \text{CH}_3 \xrightarrow{\Delta} \left( \text{C} - \text{A} - \text{C} - \text{B} - \text{O} \right)_n
\]

c) DOUBLE ESTER INTERCHANGE:

\[
\text{R}_2\text{O} - \text{C} - \text{A} - \text{C} - \text{O} - \text{R}_2 + \text{R}_1\text{O} - \text{B} - \text{O} - \text{C} - \text{R}_1 \xrightarrow{\Delta} \left( \text{C} - \text{A} - \text{C} - \text{B} - \text{O} \right)_n
\]

1.8.3 INDUSTRIAL PROCEDURES

Main chain aromatic liquid crystal polyesters are manufactured through catalyzed transesterification reaction\textsuperscript{124-130}. The reaction schemes for two liquid crystalline copolyesters are shown in Fig. 12. The diols are acetylated and reacted with diacids in the presence of a catalyst under inert atmosphere at high temperatures. Post polymerization processes such as solid state polymerization are conducted to increase molecular weights.
FIG. 12.

REACTION SCHEMES FOR TWO COMMERCIALY IMPORTANT POLYMERS (57)
The monomer purity and reaction conditions significantly influence the molecular weight of the polyester.

Catalysts used in the transesterification technique are a) antimony trioxide/glycol phosphate, b) zinc acetate/antimony trioxide, c) titanium calcium oxalate, d) dibutyl tin oxide, e) tin acetate, f) sulfosalicylic acid, g) tetrabutoxy titanium and h) potassium titanium oxalate.

Liquid crystalline copolyesters are also synthesized from poly(alkylene ester) in two stages. The first stage involves depolymerization of poly (alkylene ester) into its low molecular weight oligomers. This, in the next stage, on condensation with dihydroxy compound generates poly (alkylene-arylene ester). This process is used in the modification of poly(ethylene terephthalate) with bisphenols or aromatic dihydroxy compound or aromatic hydroxy acid\textsuperscript{131}.

1.9 SCOPE OF THE RESEARCH WORK

The present investigation is aimed at the synthesis and study of some novel main chain thermotropic crystalline copolyesters with mesogens of differing axial ratios, wherein rigid rods are joined together by various aliphatic and cycloaliphatic units, known as flexible spacers. The effect of changes in the structural elements such as flexible spacer type, mesogen and composition of copolyesters on the thermal and morphological properties and also the degree of crystallinity has been investigated. The influences of (a) substituted mesogen, (b) substituted spacer, (c) variation in spacer length, (d)
cyclic nature of spacer, and (e) ratio of rigid to flexible units, on the properties have also been evaluated.

Three new series of thermotropic liquid crystalline copolyesters were synthesized by room temperature solution polycondensation technique using pyridine as acid acceptor and 1,2-dichloro ethane as solvent. These are:

i) Copolyesters of terephthalic acid, hydroquinone and flexible diols.

ii) Copolyesters of terephthalic acid, methyl hydroquinone and flexible diols.

iii) Copolyesters of terephthalic acid, chloro hydroquinone and flexible diols.

The flexible diols used were 1,2-ethanediol, diethylene glycol, 1,2-propanediol, 1,4-butane diol, (cis)1,4-cyclohexane diol, (cis+trans) 1,4-cyclohexane dimethanol. Within each system, the relative ratio of a rigid diol (hydroquinone, methyl hydroquinone, chloro hydroquinone) to a flexible diol was varied to alter the composition of the copolyesters.

The copolyesters were isolated and purified. The mesomorphic (crystal-liquid crystal) transition temperatures of the copolyesters were observed on a Koffler hot stage polarizing microscope. The relationship between chemical structure and thermal transition temperatures was established.

The wide angle x-ray scattering of the copolyesters, in the form of powders, was investigated in the 2θ range of 5 to 40
degrees. Scans of scattering intensity were obtained as a function of $2\theta$.

The copolyesters were characterized for their non-isothermal degradation behaviour in air by thermogravimetric analysis and differential thermogravimetry.

Scanning electron microscopy studies were performed on unsheared thin films of a few selected copolyesters. The micrographs of the sample surface were obtained using the secondary electron topographic image technique.

A phenomenological model was developed to correlate the structural elements with the thermal properties. The model took into consideration the following variables:

1) The axial ratio of mesogen
2) The symmetry elements in the mesogen and flexible spacer
3) The mole fraction of mesogen per repeat unit
4) The functional group ratio