CHAPTER 1

INTRODUCTION

Order and mobility are the two basic principles of nature, governs the structure of the condensed phase. The condensed phase, either solid or liquid, is an assembly of the ultimate particles (also called motifs) which may be atoms, ions, molecules or parts of molecules which represent the crystallographic repeat unit. In solids, motifs have fixed arrangement but exhibit randomness of highly mobile motifs. Depending upon the ordered or disordered arrangement of the motifs, solids are further classified as ‘crystalline’ and ‘amorphous’. While crystals have long-range positional and orientational order, the amorphous solids have only a short-range order. Going from the crystal to liquid, one loses order and glasses do not undergo melting instead they exhibit glass transition. There is no change in the order but a gain in molecular or conformational mobility occurs at the glass transition temperature. Crystalline, amorphous and liquid are the three conventional limiting states of the condensed phase. Crystalline and amorphous states exhibit almost no mobility whereas the liquid state possesses the maximum mobility of motifs. The amorphous and liquid states show a statistical disorder, in contrast to the crystalline state, which shows the three-dimensional long-range order of motifs.

Mesomorphic state, also called the fourth state of matter, represents a number of different states of matter whose degree of order lies between that of perfect crystals and isotropic liquids. Freidle proposed the term ‘mesomorphic’ in 1922 for the materials of a middle (Greek mesos) form
(Greek morphe). Because of their in between microscopic structure, the mesophase crystals (Greek phasis = appearance) will be in-between liquid and solid in macroscopic appearance. It thus becomes difficult to identify the mesophase as solid or liquid.

The renaissance of research activity in the area of polymer science, particularly in liquid crystals, is a direct result of the central importance of polymers in a wide variety of technology driven applications. The credit for the discovery of liquid crystals must go to Friederich Reinitzer (1888), a botanist of the institute for Plant Physiology of the German university of Prague who in 1888 described his observations of the colored phenomena occurring in melts of cholesteryl acetate and cholesteryl benzoate. He noted the “double melting” behavior in case of cholesteryl benzoate whereby the crystal transformed at 45.5ºC into a cloudy fluid which suddenly clarified on heating upto 178.5ºC. This work was followed up by Otto Lehman (1890), Donald and Windle (1992).

![Cholesteryl benzoate](image)

Cholesteryl benzoate

The most essential starting point for the advances in theoretical treatment of the liquid crystal state were the publication by Maier and Saupe (1958) on the mean field theory of the nematic state focusing attention on London dispersion forces as the attractive interaction amongst molecules and upon the order parameter.
Most materials exist in any of the three distinct phases: solid, liquid or gas. Of these basic phases, crystalline solids possess the highest degree of order in their molecular structure. Because of this high degree of order, crystalline solids often exhibit physical properties (properties like tensile strength, refractive index), which undergo considerable variation in different directions relative to the crystal axes. Though liquids are much less ordered, orientational ordering of molecules does occur in the liquid phase. This characterizes the liquid crystalline state; an intermediate phase of matter between isotropic liquid and a crystalline solid (Figure 1.1).

![Decreasing molecular order](image)

**Figure 1.1** Decreasing molecular order

### 1.1 THE LIQUID CRYSTALLINE STATE

Liquid Crystallinity is now accepted as a thermodynamically stable phase exhibiting the properties of both liquid and crystalline solid. Liquid crystallinity has been identified in a wide range of compounds that are capable of self-assembly to produce one or two dimensional ordering of the molecules. These molecules usually have a rigid, flat, lathe-like structure with high aspect ratio, or alternatively they have flat disk-like shapes. The majority of those identified are small molecules but these structure can be
incorporated into polymer forms that also exhibit LC phase, liquid crystallinity can be induced either thermally (thermotropic) or on addition of a solvent (allotropic).

In 1922 Friedel, suggested that the LC phase be called the mesomorphic phase. More recent work has suggested that the LC phase is only one of the three possible intermediate or mesomorphic states, the other two being plastic crystals and condis crystals. The distinction amongst these three phases relates to the type of disorder in the molecules on passing from the crystalline state into this intermediate region. Plastic crystals are said to show orientational disorder; that is, the molecules can be parallel or perpendicular to each other. Condis crystals show conformational disorder; that is, new degrees of freedom become available because bonds can now rotate more freely. Liquid crystals show only positional disordered, that is, the long axes of the molecules remain parallel to their neighbors but form structures with only one or two dimensional order. These distinctions are now overlooked and the terms liquid crystals and mesomorphic are used synonymously. Hence, molecules or groups that form LC phases are regularly referred to as mesogens.

1.1.1 Characteristics of liquid crystalline materials and requirements for liquid crystallinity

Liquid crystalline materials generally have several common characteristics. Among these, a rod-like molecular structure, rigidness of the long axis and strong dipoles and / or easily polarizable substituents. The distinguishing characteristic feature of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of
liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state used synonymously with the liquid crystal state. The term ‘mesophase’ is used to describe the “sub phases” of liquid crystal materials. Mesophases are formed by changing the amount of order in the sample, either by imposing order in only one or two dimensions, or by allowing the molecules to have a degree of translational motion. The molecules exhibit anisotropic behaviour in this phase (Gennes 1975). The mesogens joined by a rigid bridging group are linked to flexible spacers of varying length that separates the mesogens along the chain and induces the flow of the melt.

1.2 DESCRIPTION OF MESOPHASES

In a normal melting process, the degree of freedom of the molecules increases in three dimensions. Thus, the molecules those are ordered in the solid state tumble freely in the amorphous liquid. However, in the melting process mediated by mesophase behavior, there is a stepwise breakdown of the order and a concomitant selective increase in the number and type of degree of freedom. Each step in the breakdown of the order coincides with the formation of a thermodynamically stable mesophase. It is possible to propose six major types of mesophases. First, it is possible to keep orientational order but lose positional order. These “positionally disordered” crystals or “orientationally ordered” liquids are widely known as “Liquid Crystals”. The name liquid crystal was given because of the obvious liquid like flow of these materials. A typical LC structure is shown in Figure 1.2.
Next is the group of materials with a mesophase which shows “orientational disorder” but positional order. These crystals are widely known as “Plastic crystals” because of the ease of deformation of such crystals”.

The third group of mesophase materials represents the “conformationally disordered” crystals and is called “Condis crystals”. The physical properties of condis crystals, which largely maintain positional and orientational order, change in much too subtle a way from the fully ordered crystals so that a common property could be attached to their name.

Condis crystals consist of flexible molecules, which can undergo relatively easily hindered rotation to change conformation without losing positional or orientational order. While all the three mesophases have some degree of long-range order in common with crystals, they also have some degree of non-vibrational motion in common with liquids. As a result, all mesophases, like the liquid, show a glass transition when the crystallization to
a full order is prevented on cooling. At temperatures below the respective
glass transition one can thus have three further mesophases.

(i) Positionally disordered glasses or liquid crystal (LC) glasses.

(ii) Orientationally disordered glasses or Plastic crystal (PC)
glasses.

(iii) Conformational disordered glasses or Condis crystal (CD)
glasses.

The liquid crystalline state appears in the phase diagram between
the crystal and the liquid phases. It displays molecular organization pattern in
which orientational ordering is the dominant theme, while long range
positional ordering characteristic of crystal is absent and it combines the
properties of both crystalline and liquid phases. Liquid crystallinity may be
induced purely by thermal effect (Thermotropic systems), by the influence of
solvent (Lyotropic systems) or by the elevation of pressure (Barotropic
systems).

Almost all pure compounds exhibiting the thermotropic
mesomorphism have pronounced anisotropy of shape. The vast majority of
LC substances are based on lath like or rod like molecules. They are also
named as Calamitic (from Greek-red) and are conventionally classified into
three types: Nematic, Cholesteric and Smectic. In 1977, it was established that
relatively flat disc shaped molecules may also form stable liquid crystalline
phase representing the discotic phase. Recently, the formation of LCs from
pure compounds of Pyramid-like and Plasm-like (from the name of six legged
stick like insect) structures has been reported. Molecules with half disc like
structure are also found to exhibit thermotropic LC phases.

In liquid crystals one looks for the presence of orientational order
and the absence of three-dimensional long range positional order. Molecular
level orientational order can be best achieved with mesogens, which are rods, laths or discs. These shapes have a large length to width ratio. Macromolecules can form similar liquid crystals if flexible spacers link the mesogenic groups. The mesogenic groups can be attached to the macromolecules as side chains or as part of the main chain. Common to all liquid crystals is the fact that molecules are oriented approximately parallel to a preferred axis in space called ‘Director’.

1.3 THERMOTROPIC LIQUID CRYSTALS

Turning to macromolecules, Bawden and Pirie (1937) reported that when its concentration was increased, a solution of tobacco mosaic virus separated into two phases. One of which was birefringent. Robinson (1957) investigated the birefringent solution extensively and found that, it showed properties quite similar to those of low molar mass cholesteric liquid crystals. About the same time, Flory (1956) adopted conventional lattice model to a system of rigid, rod like particles. He predicted that a solution of hard asymmetric particles should separate into two phases, an ordered mesophase and an isotropic phase, above a threshold concentration. In the case of rod like polymers the axial ratio (length to diameter) of the macromolecules were found to govern the concentration at which phase separation occurs. However, only contemporaneous bipolymers could be cited as examples. In those cases, the required rigidity and large axial ratio were achieved by virtue of stable helical conformation of the macromolecules. Since these first studies on polymers, there has been growing interest in synthetic polymers that showed liquid crystalline order. In 1960s, researchers at Du Pont discovered that certain aromatic polyamides such as poly(p-phenylene terephthalamide) exhibit anisotropic properties in concentrated solution. As result of this work ultrahigh modulus Kevlar aramide fiber was developed and commercialized.
The first reported observation of thermotropic liquid crystalline behaviour in polymers was made by Roviello and Sirigu (1975) and independently by Kuhfuss and Jackson (1972). The material described in the later study was aromatic-aliphatic copolyester prepared by the reaction of p-acetoxybenzoic acid and poly(ethylene terephthalate). Since then, there has been considerable research on polymers of this type, which are called main chain liquid crystalline polymers (MCLCPs). Academic interest focused largely on characterizing these systems and understanding their structure-property relationships. Commercial interest has concentrated on thermotropic MCLCPs to permit melt processing particularly injection molding.

Since 1984, there is a large increase in the commercialization of MCLCPs. Dartco launched the first injection molding grade copolyester trade named “Xyder” derived from terephthalic acid, p-hydroxybenzoic acid and p,p’-biphenol. The following year Celanese launched the “Vector” series of the LC polyester based on p-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid. Other companies which produce MCLCPs are Unitika, Mitsubishi Chemical, crystalline and two crystalline LCPs. The advantage is that while the processing of LCPs is typically limited to injection molding, film/sheet extrusion, thermoforming, blow molding, or other techniques can process the amorphous LCPs.

It is well known that low molar mass liquid crystals (MLCs) can be ordered unidirectionally in an electric field; similarly, LCPs can also be ordered. This concept has received considerable attention in recent years and the side chain LCPs (SCLCPs) have been found to be particularly interesting in this aspect. In SCLCPs, the mesogenic groups are linked via suitable reactive substituents, to an existing polymer backbone. The mesogenic groups maintain a degree of orientational freedom depending on the coupling strength to the backbone and its alignment may be altered by the application
of electric field. The alignment takes place on a time scale orders of magnitude faster for SCLCPs than for MCLCPs. This allows the optical properties of SCLCPs to be altered readily by the use of an external electric field. This behaviour leads to a variety of potential applications for SCLCPs.

Two main features that make LCPs unique materials are (i) the combination of properties typical for MLCs and mesophases (optical properties, sensitivity to the external electric field) with engineering and foremost of all mechanical properties of polymer materials – plastics, films and fibers. (ii) Possibilities to fix and freeze any LC structure and texture by cooling the material below the glass point.

1.3.1 Nomenclature of thermotropic liquid crystalline polymers

LCPs are usually obtained by incorporating the mesogenic molecules to a polymer by suitable chemical reactions. If the mesogenic structure of single molecule is unchanged by polymerization and can be found in the monomer unit of the polymer, then it can be expected that polymer also exhibit liquid crystalline state.

The incorporation of mesogenic group is carried out either by connecting the mesogenic groups via flexible spacer thus forming semi flexible MCLCPs or in the case of SCLCPs, also called comb LCs, by fixing the mesogens via flexible spacers to polymer backbone. Starting from these two ‘classical’ types several variations of the macromolecular architecture of LCPs have recently been carried out by combining different structural elements and different building principles like for example, combination of disc and rod like mesogen in a single polymer chain, combined main chain and side chain polymers, polymers with laterally or terminally attached mesogenic groups, polymer with crossed mesogens etc.
The comprehensive classification scheme for the variety of LCPs based on structural modifications (Brostow 1990) is given in Table 1.1. The incorporation of the mesogens can be achieved in different ways.

1.3.2 Classification of thermotropic liquid crystals

1.3.2.1 Nematics (N)

The term nematic (from Greek nemato, thread-like) was introduced by Friedle on account of the linear discontinuities, twisted like threads, which are the optical feature characteristics of this type of liquid crystals. Nematic liquid crystals can be formed by compounds that are optically inactive or by racemic mixtures. The main features of molecular organization are as follows: (a) The distribution of the molecular centers of gravity is devoid of long range order. The correlations in position between centers of gravity of neighboring molecules are similar to those existing in the normal isotropic liquids except for the anisotropy $\zeta_\parallel \neq \zeta_\perp$ in the length scale (b). The molecules, however, tend to be parallel to some common axis. This axis of preferred molecular orientation defines the director, $n$, which may be treated as a vector, directions of which, $+n$ and $-n$ are equivalent. (c) The preferred axis of orientation $n$, usually varies from point to point in the medium. However, suitable treatment of the glass surface between which the nematic is observed, application of an external magnetic or electric field and viscous flow will result in a uniform alignment and give a monodomain which is optically uniaxial. Figures 1.3a and 1.3b shows the schematic representation of molecular arrangement in nematic phase.
<table>
<thead>
<tr>
<th>Table 1.1 Structural classifications of LCPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
</tr>
<tr>
<td>Longitudinal</td>
</tr>
<tr>
<td>Parallel</td>
</tr>
<tr>
<td>Network</td>
</tr>
</tbody>
</table>

Diagram notes:
- A: Longitudinal
- B: Orthogonal
- C: Parallel
- Ds: Biparallel
- Dr: Mixed
- E6: Double
- Ed: Network
- F: Desk comb
1.3.2.2 Cholesterics (Ch, N*)

If an optically active compound is dissolved in a nematic liquid, the structure acquires a spontaneous twist about an axis perpendicular to the director (Figure 1.4). The same twisted structure can also be found with
cholesteric derivatives. Hence the word cholesteric was proposed by Freidle to describe these types of mesophases. Locally, a cholesteric phase is similar to a nematic phase. Again, the molecular centers of gravity have no long-range order but there is some order in the direction of the molecules. The molecular long axes are approximately parallel to some common axis referred to as the director $n$. However, $n$ is not constant in the space. The structure is helicoidal with the “precession” of the director about the helical axis $Z$. The pitch of the helix $P$, is much larger than the molecular dimension.

Figure 1.4 Cholesteric phase
1.3.2.3 Smectics (S)

The term smectic (from smectos, soap like) liquid crystal is not particularly specific and is used for liquid crystals, which are neither nematic nor cholesteric. Smectic phases consistently exhibit a higher degree of order than nematics (Figure 1.5). They have fluid properties and are much more viscous than the other mesophases (Sawa 1979). Although the total number of smectic phases is not known, the existence of the following phases seems assured.

\[
\begin{align*}
S_C & \quad S_F & \quad S_G & \quad S'_G(S_J) & \quad S_H & \quad S'_H(S_K) & \quad S_I \\
S_A & \quad S_B & \quad S_D & \quad S_E \\
S'_C & \quad S'_F & \quad S_G & \quad S'_H & \quad S'_I
\end{align*}
\]

Refers to mesophases formed by optically active compounds or optically active mixtures. With the exception of \(S_D\), all smectic phases have lamellar structure with well-defined layer spacing. \(S_D\) has an overall cubic symmetry and is more like a plastic crystal. It is useful to make a subdivision on smectics. The smectic phases with unstructured layer, \(S_A, S_C, S'_C\) the hexatic smectics \(S_B, S_F, S'_F, S_I\) and \(S'_I\). The \(S_B, S_E, S_G, (S'_G), S_H, (S'_H), S_J, (S'_J)\) and \(S_K, (S'_K)\) which are identified as smectics on the basis of microscopic observations turned out to be crystals characterized by a very low yield stress.

A classification based on structure, symmetry and order established by X-ray was proposed by de Vries (1973).
1.3.2.4 Discotic mesophases

These phases are formed from molecules having more or less flat aromatic cores with usually six but sometimes four, lateral substituents, normally alkoxy or ester groups with at least five carbon atoms as shown in Figure 1.6.

The structure is based on the tendency of the molecular discs to align with their sort axis (which is normal to the average molecular plane) parallel. The steric driving force for this is as intuitively obvious as it is in the case of elongated molecules. However, the presence of disordered side chain is crucial to the formation of discotic mesophases. The particular molecular disc-like shape determines the basic types of liquid crystal formed and is used in the nomenclature that describes the phases. There are two fundamental types: nematic and columnar.
1.3.2.5 Columnar phases

These phases are characterized by stacked columns of molecules, the columns being packed together to form a two dimensional crystalline array (Gennes 1975 and Chandrasekar 1977). Within the columns, the molecular positions may have short or long-range order, but columns are not in register along their axis (Figure 1.7). So, these phases are not three dimensionally crystalline. The appearance of several orders of sharp spots on
X-ray photographs showing the two dimensional columnar packing strongly suggests that this two dimensional array has true positional long-range order. The columnar phases can thus be described as having two-dimensional long-range order and three dimensional bond orientation long-range order.

All the phases so far known can be characterized by the order (o) or disorder (d) of the molecular stacking in the columns and by the two-dimensional lattice symmetry of the columnar packing. D to denote discotic mesophases labels them all and the known phases are summarized below.

\[
\begin{align*}
D_{ho}, D_{bd} & \quad \text{Hexagonal ordered and disordered} \\
D_{rd} & \quad \text{Rectangular disordered} \\
P_{2/a} & \quad \text{Plane space group symmetries} \\
P_{2/a4} \\
C_{2/m} & \quad \text{Oblique disordered} \\
D_{obd} &
\end{align*}
\]

1.3.2.6 Banana-shaped LCs

Banana-shaped LCs are similar to calamitic LCs, but contain a molecular kink. They have an elongated shape, with the molecular length being significantly larger than the molecular breadth (Figure 1.8). These LCs as well as generating the mesophases associated with calamitic LCs, generate a set of their own mesophases. These mesophases have been given the nomenclature of B1-B7 depending on the order of discovery.
1.3.3 Textures of thermotropic liquid crystals

The microscopic observation of liquid crystals in linearly polarized light is widely used (Sackmann and Demus, 1963, 1973 and Saupe 1977). The texture observed in microscopic studies are valuable in classifying the liquid crystals. Combined with miscibility studies, differential thermal analysis and X-ray, a system of classification of liquid crystals has evolved. Textures of liquid crystals are usually observed with the liquid crystal placed between a glass slide and a coverslip in polarized light (crossed polarizers). The various textures in thermotropic liquid crystals are as follows:

- **Schlieren (Streaks) Textures**: Ordinary nematic liquid crystals often show the schlieren textures in layers 0.1mm or greater in thickness. The texture results from a homogeneous orientation of the molecules. The films show a large number of threads like disclinations (threads) in the structure.
• **Cholesteric –Nematic textures**: This type of orientation is generated spontaneously on preparation of the sample or can be generated by adjusting the cover glass slightly. Such a system shows a negative optical character.

• **Focal Conic textures**: The focal conic textures exhibit two modifications the fan shaped texture and the polygonal texture. The fan shaped texture shows disclination lines forming hyperbolae and the polygonal texture forms ellipses. The smectic A structure is an example of a simple focal conic texture.

• **Mosaic Texture**: A mosaic texture has different colored, optically homogeneous regions with irregular boundaries. In each region the molecular arrangement is uniform and the optical axes in different regions have different orientations. The optical homogeneity of the regions indicates that the layers of these textures are planar.

• **Isotropic Textures**: Liquid crystals with cubic packing of spheres generated by clusters of molecules are optically isotropic. Among liquid crystal structures the smectic D modification is an isotropic texture and is stable.

• One dimensional periodicity (Lamellar structure)

• Two dimensional periodicity: (a)Hexagonal Structure( regular and inverted) (b)Tetragonal Structure

• Three dimensional periodicity (Cubic structure – regular and inverted)
1.4 FACTORS AFFECTING LIQUID CRYSTALLINE BEHAVIOUR

1.4.1 Effect of the mesogenic cores

The mesogen is an important part of a side chain polymer liquid crystal. It can also be incorporated directly into the chain. Usually, the mesogen is made up of a rigid core of two or more aromatic rings joined by a functional group. Table 1.2 shows LCPs with mesogenic groups and spacers.

Table 1.2 LCPs with mesogenic groups and spacers

<table>
<thead>
<tr>
<th>Mesogenic Unit</th>
<th>Spacer Unit</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Mesogenic Unit 1" /></td>
<td><img src="image2.png" alt="Spacer Unit 1" /></td>
<td>6,8,10</td>
</tr>
<tr>
<td><img src="image3.png" alt="Mesogenic Unit 2" /></td>
<td><img src="image4.png" alt="Spacer Unit 2" /></td>
<td>10</td>
</tr>
<tr>
<td><img src="image5.png" alt="Mesogenic Unit 3" /></td>
<td><img src="image6.png" alt="Spacer Unit 3" /></td>
<td>2.4</td>
</tr>
<tr>
<td><img src="image7.png" alt="Mesogenic Unit 4" /></td>
<td><img src="image8.png" alt="Spacer Unit 4" /></td>
<td>2.4</td>
</tr>
<tr>
<td><img src="image9.png" alt="Mesogenic Unit 5" /></td>
<td><img src="image10.png" alt="Spacer Unit 5" /></td>
<td>5,6,8,10</td>
</tr>
<tr>
<td><img src="image11.png" alt="Mesogenic Unit 6" /></td>
<td><img src="image12.png" alt="Spacer Unit 6" /></td>
<td>2.4-6,10</td>
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<tr>
<td><img src="image13.png" alt="Mesogenic Unit 7" /></td>
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<td><img src="image15.png" alt="Mesogenic Unit 8" /></td>
<td><img src="image16.png" alt="Spacer Unit 8" /></td>
<td>23,5</td>
</tr>
<tr>
<td><img src="image17.png" alt="Mesogenic Unit 9" /></td>
<td><img src="image18.png" alt="Spacer Unit 9" /></td>
<td>9-11</td>
</tr>
</tbody>
</table>
They provide the necessary restriction on movement that allows the polymer to display liquid crystalline properties. The stiffness necessary for liquid crystallinity results from restrictions on rotation caused by steric hindrance and resonance.

Another characteristic feature of the mesogen is its axial ratio. The axial ratio is defined to be the length of the molecule divided by the diameter \((x = \frac{L}{d})\). Experimental results have concluded that these molecules must be at least three times long as they are wide. Otherwise, the molecules are not rod like enough to display the characteristics of liquid crystals. The mesogens are separated or “decoupled” by a flexible bridge called a spacer. Decoupling of the mesogens provides for independent movement of the molecules, which facilitates proper alignment.

The bridging units used in LCP are usually two member groups such as: carbonyl, amide, azo, azoxy, azomethine, 1, 2-ethylenyl and acetylene (Blumstein 1978, Makaruk and Furman 1997) synthesized MC-LC polysebacates containing mesogenic units with odd member bridging groups as well as mesogenic units elongated by introduction into bridging groups cyclohexanone or ferrocene units were synthesized. Bisphenols obtained from p-hydroxybenzaldehyde and various ketones by aldol condensation were used as a source of mesogenic units. Their investigations led to the conclusion that mesophase transition temperatures depended on the length and stiffness of the mesogenic unit, the length of the flexible spacers, and upon the intermolecular interactions. Introduction of a cyclohexanone ring into the bridging group slightly increases Tm and Ti. Polymers with azo-mesogenic structure possess higher melting temperature. The polarity of the azopolymer is important in mesophase behavior. Modifying rigidity and length of the mesogen can alter mesophase behavior.
Kumaresan and Kannan (2003, 2004) synthesized combined thermotropic liquid crystalline polyphosphates containing azobenzene moiety in the backbone as well as in the side chain having terminally substituted one (1). Both the main and side chain bearing the same mesogen with photoisomerization effect. Based on the terminal groups the effect of the mesogenic properties and the photoisomerization were varied.

\[
X = H, F, Cl, Br, I, CN, NO_2, CH_3, OCH_3
\]

(1)

Prajapati et al (2004) also synthesized a new mesogenic homologous series of naphthyl azomesogens with lateral chloro-groups. The study indicated that the lateral chloro groups adversely affected mesophase thermal stability.

Prajapati and Pandya (2005) synthesized and characterized two new mesogenic homologous series of azobenzene derivatives containing ethoxyethyl tails, as azobenzene derivatives are more stable compared to Schiff base derivatives.

1.4.2 Effect of Flexible Spacer

The flexible spacer molecule separates the mesogenic group along a liquid crystal polymer backbone by means of reducing the transition temperature and exposing the thermotropic mesophase in a convenient temperature range. The spacer would allow the flexibility necessary for the required movement. The chemical periodicity of the molecule is retained even though the length of the repeat unit is increased. The melting and the
isotropic transition temperature tend to be higher when an even number of CH₂ units are incorporated into the polymers as when compared to the odd number of –CH₂– units. This effect may be explained by assuming that the conformation of the even numbered –CH₂– spacer is all trans (planar zig zag). This conformation is straight and has lowest energy. Stability of the mesophase decreases with increasing spacer length.

The variation in spacer length affects both the freedom of the mesogenic unit from the polymer backbone and overall length of the MC-SC unity. Incorporation of higher polymethylene flexible spacer length on the properties of main chain LC polymers has been documented. These effects were observed in all cases, which can be summarised as follows:

- There is reduction of transition temperature (both Tm and Ti) with increasing spacer length.
- An odd even relationship exists for the transition temperatures of polymers.

Senthil and Kannan (2004) reported regarding the polymethylene spacer containing main chain liquid crystalline polymers (2). As the even number of the methylene spacers is increased from two to ten, the polymers tend to grow as larger mono-domain was improved while comparing the textures of polymers I-V. The alignment of mesogens takes up maximum

\[
\text{Polymers} \\
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Polymer} & I & II & III & IV & V \\
\hline
m & 2 & 4 & 6 & 8 & 10 \\
\hline
\end{array}
\]
unidirectional in melt condition, thereby forming a nematic phase. The polymers containing two, four and six methylene spacers show a micrograin phase, which may be attributed to the restricted mesogenic movement. The decrease in transparency of liquid crystalline texture with decreasing methylene chains was also observed. Studies on the Odd even effect of methylene spacers in Polypyromellitimide esters were carried out by Francisca Mary and Kannan (1998).

1.4.2.1 MCLCPs containing spacer groups

These polymers are made by the use of spacer groups to interlink low molecular weight mesogens. They form thermotropic nematic or smectic melts when heated above their m.p. A large variety of mesogenic units and flexible spacers of varying length and constitutions are used to prepare different kind of LCPs (Kwolex 1987). These polymers and characterized mainly by X-ray scattering, DSC, NMR, viscometric techniques and polarized microscopy, to determine $T_m$ the melting transition of an LC melt.

$T_m$ the melting transition to form an LC melt, $T_i$ the clearing of LC-isotropic melt transition the value of $\Delta H$ and $\Delta S$ of these transitions, phase diagram and rheological properties. The effect of electric and magnetic fields to produce orientation has also been studied (Ober et al 1984). Flexible spacer groups govern clearing temperatures and melting points. These polymers differ from low molecular weight compounds because of the coupled interaction of the mesogenic and spacer groups.

The rings in the mesogen may be joined by stiff polar linkages such as $\text{-CH=N-}$, $\text{-C=C-}$, $\text{-N=N-}$, $\text{-COO-}$, $\text{-N=N (O)-}$. These rings may be substituted by alkyl, aryl or halogen, provided the substituents are not too large because they interfere with the parallel organization of the mesogenic units in the LC phase. All types of the LC phases have been observed including cholesteric and
discotic melt phases. The larger spacer length, the LC phase may disappear. An interesting interpretation of this observation is that spacers act as solvents for the mesogenic units (Nuyken et al 1997).

As the molecular weight increases the transition temperature rapidly increases upto a molecular weight of $M_n$ 10,000, where it becomes a plateau (Ober et al 1984). Longer mesogens have higher $T_m$ and branching or substituents on mesogen lowers the $T_m$. Lowering of $T_m$ is important for molding or spinning LCPs without decomposition. $T_i$ varies with the length of the mesogenic groups and the LC range is quite short for low mesogenic group length. The amide group in the mesogen increases the transition temperature and the stability of the smectic and nematic states. The transition temperature is higher than the corresponding ester containing mesogens because of the hydrogen bonding. In the azomethine series two, three and four rings are present in the mesogenic groups where the $T_i$ is more sensitive to length than $T_m$. The mesomorphic range is as high as 100-200°C and clearing temperatures are too high and in some cases it's more than 400°C.

Most frequently used spacer groups are ethylene oxide and siloxanes. The transition temperatures are much lower for the polymer with siloxane spacer, followed by ethylene oxide spacers. The transition temperatures decrease progressively with increasing spacer length. Higher transition temperature is observed for a polymer containing even number of spacer atoms along the chain compared with values for the polymer with adjacent odd numbers of spacer atoms. Usually $T_i$ is not as sensitive to the odd-even effect as is $T_m$. This results in a broader mesomorphic range for the polymer containing odd number members of the series. The decrease in $T_m$ is greater for polymers with siloxane spacer groups. Some of these polymers are amorphous with a $T_g$ less than 0°C and are LC melt at ambient temperature.
Entropy change of LC-isotropic transition ($\Delta S_i$) can be calculated from DSC measurements. The value of $\Delta S_i$ was found to exhibit odd-even effect for members of polymethylene series (higher for polymer with even spacer atoms). This would imply a lower entropy and increased order in the melt for polymers with even spacer groups. It also correlates the observed odd-even alternation in the transition temperatures.

The $\Delta S_i$ values were lower for a series of polymers containing a poly(ethylene oxide) spacers than for the corresponding polymethylene series, as expected for flexible chains. A two-phase system can be postulated where such flexible groups are excluded from LC mesogenic phase and constitute a liquid unordered phase. Thus in the more flexible polymer containing poly(ethylene oxide) spacer, $\Delta S_i$ would be measured for the mesogenic groups. Thus spacer groups play an important role in determining the transition temperatures, mesomorphic range, entropy change and the nature of LC phases.

The nature and the direction of the linkage within the mesogenic group or those joining the mesogenic group with the spacer group can affect the transition temperature and nature of the LC phase. The direction of the ester groups within the mesogenic groups can change a polymer from LC melt to an isotropic melt. A specific case where the LC organization is effective is the smectic polyester prepared from HO-(CH$_2$)$_n$–OH and 4,4′-bibenzoic acid, compared with those prepared from HOOC- (CH$_2$)$_n$-COOH and 4,4′-biphenol. The latter exhibits a nematic phase for the odd values of n and broad smectic phase for even values.
1.5 POLYMER LIQUID CRYSTALS (PLCs)

PLCs are a class of materials that combine the properties of polymers with those of liquid crystals. These “hybrids” show the same mesophase characteristic of ordinary liquid crystals, yet retain many of the useful and versatile properties of polymers. Incorporation of the rod like or disk like mesogens into the flexible polymer chains results in the display of liquid crystal characteristics. The placement of the mesogens plays a large role in determining the type of PLC.

1.5.1 Structural classification of Polymer LCs

These are two main categories of thermotropic polymer liquid crystalline polymers:

1.5.1.1 Main Chain Liquid Crystal Polymers (MCLCP)s

Main Chain Liquid Polymers (MCLCP)s have mesogenic units linked to each other directly or through spacer units to form the polymer backbone. The schematic representation of MCLCP is given below:
1.5.1.2 Side Chain Liquid Crystal Polymers (SCLCPs)

SCLCPs have mesogens attached pendant to the polymer chain via an intermediate linking unit.

1.6 PHOTOINDUCED PROCESSES IN POLYMER MEDIA

Photochemical reactions of macromolecules are initiated by the absorption of light in the UV or visible region and hence they are fundamentally different from thermal (dark) reactions and proceed very rapidly (Timpe 1982). The absorption of light leads to an excited state (an electronic isomer of the ground state) due to charges of energy and spin state of some of the electrons. This excited state exhibits physical and chemical properties different from those of the ground state, which in many cases provides reaction pathway not possible by thermal activation.

Photochemical processes can be divided into three groups.

- Absorption step leading to the excited molecule
- Photophysical processes including vibrational, relaxation, internal conversion, intersystem crossing, fluorescence and phosphorescences (Michael Stephen and Joseph Straley 1982).
- Photochemical processes giving rise to chemical conversion and formation of new compounds.

1.6.1 Light Absorption In Macromolecules

The fundamental law of photochemistry states that only light absorbed by the molecule (i.e. also by a macromolecule) can initiate a photochemical process (Grothus Draw law). Two conditions are required for light absorption by a molecule.
1. The wavelength ($\lambda$) (or the frequency, $\nu$) of the light must correspond to the energy of a possible electronic transaction in the molecule as expressed by the equation,

$$hv = E_a - E_g$$

where $h$ - Planck constant

$E_a$ and $E_g$ - energies of the excited and ground states respectively

2. The interaction between electrical components of the incident light and the polymer molecule must lead to a change of either charge distribution or dipole moment of the molecule (i.e. transition moment integral must be non-zero).

These conditions may be effectively used to explain several fundamental aspects of photochemical as well as photo physical processes.

1.6.2 Reactivity Distribution in Photocrosslinking of Amorphous Polymers

In order to achieve photo cross-linking in the polymer chains, the inherent cross-linking groups should have high photosensitivity. The parameters that influence photosensitivity of the polymers are:

- concentration of functional groups
- their spatial distribution and mobility in the matrix
- mobility of the excitation energy
- presence or absence of energy or electron traps.

Thus, a broad reactivity distribution must exist.
1.7 PHOTOCROSSLINKABLE POLYMERS – A SURVEY

Photocrosslinking of polymers is a technology enjoying increasing interest due to its potentials for the study of polymer reactions and for a wide variety of applications. The rapid growth of this technology is reflected in recent progress in the development of both suitable macromolecules and related technical equipment.

The polymers, which exhibit mesomorphism in the melt and have the ability to undergo crosslinking by the influence of ultraviolet or visible radiation, form this special class of materials which include cinnamate esters, acetylene, stilbene, azide, arylidene and miscellaneous functional groups. The unique combination of liquid crystalline behaviour and photocrosslinking property makes these polymers useful in developing macroscopically ordered network systems like liquid crystal elastomers, liquid crystal thermosets, thin films with controlled polar orientation of functional groups, which are of interest in micro-electronics and opto-electronics (Griffin et al 1988), photorecorders (Vandewyer and Smets 1970), enzyme fixing materials (Ichimura and Watanabe 1980) high density data storage (Lin et al 1990 and Wu et al 1999) molecular addressing (Natensohn et al 1998, 1997). The photo-cross-linkable LCPs oriented macroscopically by various ways like by surface effect, by application of electric field etc. may be cross linked by irradiation either in the mesophase or in liquid crystalline glassy state to get macroscopically ordered network materials. This class of polymers is also demonstrated to be useful in optical data storage devices. Photochemistry of these polymers is of interest from topochemical aspects since the photochemical reactions take place in an organized environment.
1.7.1 Photocrosslinking processes

Crosslinking of polymers by light can be accomplished by two alternative methods:

- Excitation of the macromolecules by direct light absorption or sensitization. Here, chromophore groups capable of absorption of light must be present in the polymer (Ikeda et al 2004).

- Excitation of an initiation molecule, followed by reaction of the resulting photolytic products with the macromolecules. This type of process requires the presence of functionalities capable of dark reactions with free radicals or ionic species formed prototypically.

Both the main chain and side chain photocrosslinkable LCPs have been reported. All these polymers contain cinnamate moieties in their structure, which function both as a mesogen and photoactive group. It is well established that polymers with cinnamate ester groups, such as poly(vinyl cinnamate), are quite photo reactive and undergo a high yield cross-linking reactions which proceed by photo $2\pi + 2\pi$ cyclo addition between $\text{C=O}$ bond adjacent to the $\text{C=O}$ group of the cinnamate ester.

Photocrosslinkable polymers containing pendant chalconyl group has been synthesized by the acetylation of polystyrene followed by the condensation of resulting poly(p-vinylacetophenone) with benzaldehyde in the presence of an acid catalyst. The photocrosslinking ability was investigated by ultraviolet spectroscopy (Unrush 1959, Unrush and Smith 1960).
Photosensitive epoxy resins with improved thermal stability were prepared by the reaction of epichlorohydrin with \( \alpha,\alpha'- \)bis (hydroxybenzylidene) cycloalkanones (Koelbet Herbert et al 1974).

Griffin et al (1988) demonstrated for the first time the laser addressed optical recording on a freestanding film of the above polymer. Examination of the otherwise transparent film, after scanning with 325 nm laser light, showed clearly defined yellow laser-written tracks on a transparent background. Yellow coloration due to the absorption of the photo-Fries product, permits a reasonable positive contrast image. Absorption of laser light results in photo-Fries product formation as well as heat transfer to the film by radiation less deactivation of the excited state of the cinnamate chromophores. The heat transfer presumably can elevate the film temperature above the amorphous to nematic transition temperature. In addition, part of the film exposed to the laser is insoluble in solvents suggesting the occurrence of crosslinking through the cyclobutane ring formation. This process together with the generation of the LC phase by heat dissipation results in a write once laser track, which retains the integrity of the nematic glass. Formation of Photo-Fries product on photolysis leading to the yellowing of the film could be completely suppressed by replacing the aryl ester group of the cinnamate by fairly rigid cyclohexane moiety.


This polymer shows nematic phase between 35°C (Tg) and 120°C (Ti) and frozen glassy mesomorphic solid at room temperature. Photolysis experiments on the film of this polymer reveal that there are three types of photo-reactions that can take place: (i) trans to cis isomerization about C=C bond of the cinnamate ester-unit, (ii) crosslinking reactions through cyclobutane ring formation and (iii) photo-Fries rearrangement. Detailed
studies show that there is a unique wavelength dependence of photochemistry of these polymers. On irradiation of the polymer film at 366 nm, those chromophores present as aggregates react preferentially to form dimer (cyclo addition) while the unaggregated or isolated chromophores remain unreacted. However, irradiation at 313 nm produces both dimer and the photo-Fries products. Upon exhaustive irradiation at 366 nm the absorption due to the aryl cinnamate chromophores does not disappear completely. The residual absorption is due to the unreacted cinnamate which can be shown by the appearance of the absorption due to the photo-Fries product upon 313 nm irradiation of this exclusively 366 nm irradiated film. This effect is more pronounced in the glassy nematic phase, where greater fraction of the chromophores is aggregated. These observations tend to support that a significant fraction of chromophores are present in the aggregate and the dimerization is the only photoreaction that occurs upon specific excitation of these aggregates. Exhaustive irradiation at 366 nm converts all aggregate pairs to dimers and the remaining isolated chromophores, having very little absorption at 366 nm, are reactively insensitive to further 366 nm irradiation. However, 313 nm irradiation causes them to undergo an alternate unimolecular photo-Fries reaction.

Brzozowski Zbigniew et al (1989) obtained polyaryl sulfonates from cyclohexanone-2,6-diylidene or cyclopentanone-2,5-diylidene with 2,4-toluene disulfonyl chloride derivatives. They exhibited photocrosslinking ability under UV light.

Creed and coworkers (1990) reported the following siloxane based LCP with cinnamate ester group in the main chain (3).

\[
\begin{align*}
\text{(3)}
\end{align*}
\]
Gangadhara and Kishore (1993) synthesized and studied photocrosslinkable main chain liquid crystalline polymers (PC-MC-LCPs) containing bis(benzylidene) cycloalkanone (4) by solution polycondensation method. All the polymers exhibited a nematic mesophase in the range 120-170°C. The photocrosslinking was carried out in the form of thin film. Two kinds of photoreactions, namely photoisomerization and photo-crosslinking, operate in these polymers. The crosslinking proceeds by the 2π-2π cycloaddition reaction of the bis(benzylidene)cycloalkanone moieties. The crosslinking rate decreases with increase in the size of the cycloalkanone ring. In DSC, all the polymers show one endothermic peak at 350°C. This is due to thermal crosslinking in the chromophore contain mesogenic unit in the polymer backbone.

![Chemical Structure](4)

UV sensitive polyarylates were derived from photosensitive bisphenol with phthaloyl chlorides. Polyarylates obtained from bis(3-ethoxy 4-hydrobenzylidene)acetone and bis(4-dihydroxyphenyl)dichloroethylene have shown superior properties over other polyarylates (Brzozowski and Noniewicz 1995).

Kannan and Murugavel (1996) synthesized and characterized new photocrosslinkable flame retardant polyvanillylidene arylphosphate esters.

Ahmed (1998) synthesized and studied the photoreactive new homo and co-photosensitive polymers containing pendant chalcone moieties attached through hexamethylene spacer between the photosensitive group and backbone were studied (5). The polymers containing chalcone moieties...
directly attached to the backbone was characterized by maximum absorption at shorter wavelength ($\lambda_{\text{max}} = 312\text{nm}$) than the polymers containing extended chalcone moieties. After 65 min UV irradiation all the polymers were crosslinked.

![Chemical structure](image)

Four series of photocrosslinkable poly (benzylidene phosphoramidate ester)s (6) were synthesized by Kannan and Murugavel (1999). The rate of crosslinking decreases with increase in the size of the alkanone ring. The LOI values are in the range of 27-38 depending on the structures. Halogen containing polymers showed higher LOI values than the non-homogenate polymers.

![Chemical structure](image)
Marian et al (2000) reported photocrosslinkable copolyesters (7). 1,4-phenylene bis(acrylic acid) is a thermally stable diacid, which can be incorporated into polyesters. The phenylene bisacrylate structural units undergo rapid photochemical reaction in the solid state to form crosslinks. They were analyzed the Tg, Tm and Ti by DSC. The 20,10,5% PET copolymers show a Tg 5°C higher than that of the PET homopolymer and the 50% copolymers shows a Tg approximately 30°C higher than the homopolymer.

Kamal and Ahmed (2000) synthesized the main chain liquid crystalline poly(arylidene ether)s containing cyclopentanone polymers (8). All the polymers are freely soluble in conc. H$_2$SO$_4$ and methanesulphonic acid due to the unstability of the polymers. The methoxy-substituted polymers possess better solubility than the unsubstituted polymer. Anisotropic properties of all polymers were exhibited at higher temperature under polarized optical microscope and showed nematic textures. The electronic spectra showed absorption broad band and also small bathochromic shifting with $\lambda_{\text{max}}$ near 273-285 nm due to the $\pi-\pi^*$ transition within the benzenoid system and the $\lambda_{\text{max}}$ near 334-409 nm due to $\pi-\pi^*$ excitation of -C=C- group present the polymer backbone.
Sung et al (2005) studied the photocrosslinkable chalcone moiety (9). The copolymerization was carried out in DMF solution in the presence of AIBN as the initiator. The photocrosslinking studies were carried out in the form of thin film. The visible range absorption increased gradually by the UV irradiation, which is ascribed to the generation of the open merocyanine from the closed spyrooxazine form.

Kodak et al (1968) developed a light sensitive coating materials consisting of a polycarbonate from divanillal cyclopentanone with phosgene.

Anwar and Mohamed (1991) reported arylidene polymers (10) containing cyclopentanone moiety. All the polymers were prepared by solution polycondensation method at 140°C, to obtained yield of 95.1%. The electrical conductivity of polymer was measured by the Arrhenius method, which gave a value of \( 3.2 \times 10^{-13} \ \Omega^{-1} \text{cm}^{-1} \) at 300K. The introduction of the nitro group at positions 2 and 19 increases the energy difference between the cis- form and the abundant trans -form from 51.068 to 129.76 kcal mol\(^{-1}\).
Unsaturated polyamides and imides were prepared by condensing 2,6-bis (3-aminobenzylidene) cyclohexanone with terephthaloyl chloride, pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride, maleic anhydride or nadic anhydride to yield a bismaleimide and bisnadimide which were utilised as new polymer precursors (Mikroyannidis 1992).

Poly[bis(benzylidene ester)s containing bisbenzylidene cycloalkanone groups have been synthesized and studied for their liquid crystalline and photochemical properties. The bis(benzylidene) alkanone group in the polymer backbone acted as a mesogen as well as photoreactive centre. They exhibited nematic mesophase behaviour (Gangadhara and Kishore 1995).

Shih et al (1999) prepared several binary copolycarbonates by polycondensation of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (11) with methylhydroquinone, isosorbide using interfacial polycondensation method. The exo-cyclic double bond gets completely crosslinked within 20min. After crosslinking, the polymers were insoluble.

Nayef (2003) synthesized a new interesting class of linear unsaturated polyesters and copolyesters based on dibenzylidenecyclo alkanones (12) by the interfacial condensation at ambient temperature. Inherent viscosities were found with in the range 0.28-0.65dLg⁻¹. 3,3’azobenzene linkage are more soluble than 4,4’azoazobenzene linkage. The polymers based on the meta-azo linkage are less thermally stable than para-
azobenzene linkage. Electrical conductivity measurements of the polymers gave values in the range of $10^{10}$-$10^{12}$ Ω cm$^{-1}$.

Sakthivel and Kannan (2005) synthesized a new class of main chain liquid crystalline photodimerizable vanillylidene containing cyclopentanones with various alkylphosphorodichloridates by solution polycondensation (13). They also studied the photocrosslinking of these polymers by UV spectroscopy.

Percec et al (1988) reported that synthesis and characterization of liquid crystalline copolymethacrylates copolyacrylates and copolysiloxanes containing 4-methoxy-4′-hydroxy-α-methylstilbene and 4-hydroxy-4′-methoxy-α-methyl stilbene constitutional isomers as side groups.

Sakthivel and Kannan (2004) reported the novel thermotropic liquid crystalline cum photocrosslinkable polyvanillylidene allyl / aryl phosphate esters.
1.8 PHOTOISOMERIZATION IN AZO POLYMERS - A SURVEY

Polymers that have sufficient energy following the absorption of a photon may be homolytically cleaved to get free radicals. These polymers may then undergo secondary reactions such as cyclization, hydrogen abstraction, or fragmentation. Polymers capable of these photoreactions are called photosensitive polymers. Trans-cis isomerization, ring opening-closing, tautomerism and valence isomerization reactions may take place in photochromic reactions. Photochromic polymers have covalently bound photochromic groups in the main or side chain. These polymers are more conductive on irradiation, and hence have been used in electrophotography, solar cells, semiconductors and molecular - sized electron devices (Reiser 1989). Polymers that incorporate azo-functionalities in the backbones or pendant to the chain undergo cis-trans photoisomerization during capture of light energy (Rau 1990). The azobenzene chromophore can exist in two configurations: the cis form and the more stable trans form.

Zimmerman et al (1958) suggested that the photoisomerization of azobenzene involves the thermal reactions between the excited trans and cis states in which a lower energy barrier separates. This was later confirmed by Fischer and Malkin (1962) who showed the temperature dependence on quantum yield for trans-cis isomerization.

Chen and Morawetz (1976) studied the rate of photoisomerization where the energy barrier is low. When irradiated with light of appropriate wavelength, the stable trans form undergoes a reversible photoisomerization i.e. \( \text{trans} \leftrightarrow \text{cis} \leftrightarrow \text{trans} \). This cis-trans isomerization can occur thermally or/and photochemically to yield a photostationary composition and its wave length is temperature dependant (Neoborne and Weiss 1978, Rau and Luddecke 1982). The azo dye molecules are predominantly in the trans state at room temperature and are isotropically distributed. The structural and
dipolar properties of the azo unit and its content in the sample are factors that play an important role during the orientation process. When excited by a linearly polarized blue green light (488 nm), preferential molecular excitation and the associated photoisomerization process results in an orientational whole burning i.e. orientational re-distribution of the dye molecule with respect to the polarization direction of the irradiating light (Viswanathan et al 1999). This leaves the trans- isomers predominantly oriented perpendicular to this direction (Figure 1.9).

\[ \text{trans isomer} \rightarrow \text{cis isomer} \rightarrow \text{trans isomer} \]

**Figure 1.9  Photoisomerization of azobenzene groups by polarized light**

Successive photoisomerization cycles result in net dichroism and birefringence induced in the material due to the absorbance and refractive index difference in the parallel and perpendicular directions (to the incident polarization direction). Makushenko et al (1971) showed that a reversible
reorientational photoisomerization and photodichroism takes place in aromatic azo compounds. Due to the mobility of the azo dye molecules, the photoisomerization process results in an easy change in its orientation due to the polarized optical field and this effect has been observed even in high Tg polymer matrices. These phenomena of birefringence and dichroism in azo polymer materials are known to be due to the Weigert effect (Ebralidze and Ebralidze 1992) and were reported by Eich et al (1987). Zhong-Fan Liu et al (1992) studied the kinetics of the thermal cis-trans isomerization of an azo compound in the assembled monolayer film.

Iimura et al (1981) reported the synthesized of thermotropic liquid crystalline polymers-azoxy and azotype polyesters. Photoinduced trans ↔ cis ↔ trans isomerization of the azobenzene group is usually completely feasible and reversible in the solution phase (Sudesh and Neckers 1985). Stilbenes undergo irreversible photochemical side reactions dimerization by [2+2] cycloaddition and oxidative cyclization leading to phenanthrene derivatives. These side reactions limit the applications of stilbene type molecules (Feringa et al 1993). This is an example of irreversible photoresponse. A mechanistic study of the trans ↔ cis isomerization of the azobenzene moiety bound on a liquid crystalline polymer was studied by Chao et al (2001).

The property of photoisomerization and photoinduced anisotropy of the azobenzene groups has made it a potential component in many technological applications such as optical information storage and processing (Xie et al 1993 and Hvilsted et al 1995), optical switching devices (Ikeda and Tsutsumi 1995 and Tsutsumi et al 1998), polarization splitters (Lee et al 1999), non-linear optical devices (Zentel 1989) digital holographic storage (Natansohn et al 1997). A novel class of banana shaped azo compounds exhibiting anti-ferroelectric switching behavior was identified by Veena Prasad et al (2001).
The versatility of these photoactive systems in the azo-group is that they can be selectively attached either to the main chain, side chain or chain ends of a wide range of polymer systems. In recent years, the azobenzene containing LC polymers systems have received increased attention and a variety of LC azopolymers have been synthesized in which the azobenzene moiety plays a vital role both as a mesogen and as a photosensitive chromophore (Natansohn and Rochon 2001). The properties of photoinduced critical opalescence and reversible all optical switching in photosensitive liquid crystals was studied by Tabiyran et al (2003, 2004).


Bach and Hinderer (1973) synthesized various polypyromellitimides of high stability and good mechanical strength containing azobenzene, azobihenyl and p-phenoxyazobenzene units.

Ishihara et al (1982) synthesised photoresponsive polymeric adsorbent containing amphiphilic polymer with azobenzene moiety and studied its application of cell adhesion chromatography. The polarity of the surface of the polymeric adsorbent was increased by UV irradiation because of trans-cis isomerization of azobenzene moiety.

Reck and Ringsdorf (1985, 1986) and Reiger (1989) characterized some of the chemical structures of main chain and side chain mesogens containing azobenzene and azoxybenzene, and observed that they may influence the molecular packing and order of the mesophase.
Theocharis (1987) described the synthesis of coordination polymers containing 2,5-dibenzylidene cyclopentanone segments, capable of forming metal complexes as well as possessing photocrosslinking properties.

Eich et al (1987) developed reversible optical data storage and holographic optical storage in polymeric liquid crystals (14) using azobenzene in the side chain was used as a storage medium. The strong dielectric anisotropy was due to the cyano dipoles linked to the mesogenic units.

![Image of azobenzene molecule](image1.png)

Armelle Vix et al (1988) synthesized thermotropic main chain liquid crystalline polymers composed of azobenzene or azoxybenzene mesogens and flexible spacers with or without a phenyl side pendant group (15).

![Image of polymer structures](image2.png)

Allcock and Kim (1989) reported in high polymeric liquid crystalline phosphazene with cyclic trimeric systems (16). The polymer bears with methoxy terminated azobenzene as mesogen. They have reported microcrystalline structure for polymers and nematic schlieren texture for cyclic trimer.

\[
\begin{align*}
\text{OR} & \quad \text{OR} \\
\begin{array}{c}
P = N \\
\text{OR}
\end{array} \\
R = -(\text{CH}_2\text{CH}_2\text{O})_3-\text{N}=\text{N}-\text{N}=\text{N}-\text{OCH}_3
\end{align*}
\]

(16)

Robello (1990) synthesized three acrylic monomers bearing 4-dialkylamine-4′-nitrostilbene and azobenzene dyes. These dyes were homopolymerized and copolymerized with methyl methacrylate using a free radical initiator to produce polymers for non-linear optics. During polymerization some cross-linking process occurred with stilbene monomers presumably through internal double bond in the dyes.

Angeloni et al (1991) emanated the synthesis of two new series of the structurally isomorphic polyacrylates with azobenzene moiety. Laterally methyl substituted azobenzene causes a drop of 50-100K in the stability of the mesophase with respect to the corresponding samples of the unsubstituted methyl series. The polymer showed interdigitated smectic structures.
Xie et al (1993) reviewed the developments and recent applications of the photochemical and thermal cis-trans isomerization of aromatic azogroups covalently linked with polymers such as liquid crystallinity, non-linear optical properties, monolayer assemblies and the linear induced birefringence and dichroism.


![Chemical structure diagram](image)

(17)

The photoresponsive properties of optically active (meth)acrylic homopolymers with pendent L-lactic acid or L-alanine connected to 4-aminoazobenzene were studied by Angeline Altomare and Roberto Solaro (1995).

Oberski et al (1995) prepared liquid crystalline polymers containing photosensitive arylene vinylene segments in the main chain for their structure property relationship study and light emitting applications.

Anderle et al (1996) reported the azobenzene dyes dissolved in a glassy polymeric matrix or liquid crystalline polymers to the backbone as side groups are induced by light (18). In particular, dye/matrix combinations giving rise to nonlinear holographic responses, two photon holography, and transient holographic modes applicable for holographic displays.
Haitjema et al (1996) synthesized the new azobenzene based monomers with (CH₃) (basic) and COOH (acid) substituents. For some of these compounds, a new synthetic route has been developed especially for azobenzene monomers (19).

Tsutsumi et al (1998) reported the photochemical nematic to isotropic (N-I) phase transition and the thermal I-N phase transitions behavior of polymer azobenzene LCs with donor acceptor substituents at the 4,4'-position (20). They explored the effect on the structure of the main chain of the polymer on the phase transition behavior of the side chain azobenzene LCs.
Lee et al (1999) synthesized a new series of combined LC polymers involving side chain azobenzene moiety with varying the length of the methylene spacer (21). All the polymers exhibited nematic phases in melt.

Sanford et al (1999) reviewed the synthesis of conjugated polymers of arylidenecycloalkanones namely poly (2,5-arylidene cyclopentanone) and poly (2,6 arylidine-cyclohexanone) by condensation of cyclopentanone or cyclohexanone with terephthalal-aldehyde using catalytic amounts of alcoholic potassium hydroxide.

Chen et al (1999) synthesized an azocarbazole based polyimide from an azocarbazole diamine monomer and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride by a two step polycondensation reaction (22).
Francisca Mary and Kannan (1999) synthesized poly (pyromellimide ester)s and (imide-urethane) s containing azobenzene units (23). On characterization of these polymers, she showed that Tg values decreases linearly as the number of methylene spacer was increased, while Tm showed the odd-even effect.

Yiliang et al (2001) synthesized three novel polyurethanes containing donor acceptor type azobenzene groups in the main chain and studied the donor-acceptor effect on photoisomerization.

Hasegawa et al (2002) synthesized three kinds of photoresponsive polyurethanes containing slightly different azobenzene moieties and studied their birefringence behavior. Despite the slight difference in the chemical structure of the azobenzene moiety, a large difference in the growth behavior of the photoinduced birefringence was observed. Hence, it was concluded that isomerization behavior of the azobenzene moiety was the main factor for this difference.

Kang et al (2002) synthesized and studied the properties of polynorboranes with azobenzene chromophores using optical multichannel
analyzor with Xe lamp as well as UV –Vis spectroscopy with high pressure mercury lamp. It was found that rate of photoisomerization and relaxation depended on the structure of the azobenzene chromophore rather than the polymer backbone.

Kumaresan and Kannan (2003) reported liquid crystalline organophosphorus polymers (24) and the incorporation of phosphorus were conformed by $^{31}$P-NMR spectroscopy. The char yield of the polymers was around 26-38%. The above data reveals that the high char for these polymers is an indication to behave as fire retardant polymers via condensed phase mechanism.

Angiolini et al (2003) studied the photochromic and photoresponsive behavior of optically active polymers containing side chain azobenzene moieties. These copolymers were studied using UV spectroscopy under irradiation at 348 nm.

Gaub et al (2003) synthesized a multiple photo reactive azobenzene groups incorporated in the backbone. The reversible optical switching of the individual polymer molecules was observed using molecular force spectroscopy. The switching between the trans - and cis - azo configurations with 420 and 365 nm wavelength respectively. They characterized a polyazopeptide, observed reversible length changes of single chains as induced by light of different wavelengths and studied this process under the

Ramesh Babu and Kannan (2004) studied new combined type liquid crystalline polyphosphate esters, containing α-methylstilbene and substituted azobenzene, respectively \((25)\). The main chain and side chain mesogens were attached to the phosphorous through decamethylene spacers. All the polymers were thermally stable up to 260ºC. The melting transition appeared in the range 138-150ºC and this is attributed to transitions caused by segmental motion of the main and side chain moiety.

\[
\begin{align*}
\text{X} & = \text{H, F, Cl, Br} \\
\text{(25)}
\end{align*}
\]

1.9 CHARACTERIZATION TECHNIQUES

Organic chemists have successfully used the spectroscopic methods for the structural elucidation of polymers. Some of the techniques used are elaborated in this section.

1.9.1 Infrared Spectroscopy

IR spectroscopy is one of the most powerful analytical techniques, which offers the possibility of chemical identification. This is based on the fact that a chemical substance shows marked selective absorption in the infrared region. The structural elucidation of organic compounds makes use
of the region 4000-400 cm\(^{-1}\). The various bands present in the IR spectrum correspond to characteristic functional groups and bonds present in the chemical substance. This technique helps to identify the presence of impurities and water in the sample. It also helps in the deduction of the shape of symmetry of the molecule. The development of the Fourier transform instrumentation has accelerated data acquisition and improved characteristics.

1.9.2 Nuclear Magnetic Resonance Spectroscopy

Proton NMR is one of the investigative tools for the structural identification of monomers and polymers. It is an absorption spectrometry under appropriate conditions in a magnetic field; a sample can absorb electromagnetic radiation in the radio frequency region at frequencies governed by the characteristics of the sample. Absorption is a function of certain nuclei in the molecule. A plot of frequencies of the absorption peaks versus peak intensities constitute the NMR spectrum. The success of this application depends on the measurements of chemical shifts and percentage of hydrogen distribution.

\(^{13}\)C-NMR spectroscopy is a tool used for the investigation of polymer structure. Since the natural abundance of C-13 is only 1.1% that of C-12 and its sensitivity is only about 1.6% that of \(^1\)H, the overall sensitivity of \(^{13}\)C compound with \(^1\)H is about 1/5700. Because of this reason it is necessary to use highly sophisticated NMR spectroscopy like FT instrumentation for determining the effect of neighboring electron of these nuclei.

1.9.3 Ultra violet spectroscopy

This technique is generally used to characterize aromatic compounds and conjugated olefins. It can also be used to detect impurities in organic compounds since bands due to impurities are very intense and the
$\lambda_{\text{max}}$ values for the impurities can be easily identified. The molecular absorption in the ultraviolet region of the spectrum is dependent on the electronic structure of the molecule. The absorption of energy results in the elevation of electrons from orbitals in the ground state to higher energy orbitals in an excited state. This technique is also useful in the study of photocrosslinking ability of the polymers and also in the study of kinetics of the reaction.

### 1.9.4 Differential Scanning Calorimetry (DSC)

DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analyzer is designated such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will flow to it than the reference to maintain both at the same temperature. Whether more or less heat must flow to the sample depends on whether the process is endothermic or exothermic. DSC may also be used to observe subtle phase changes, such as glass transitions. It is possible to observe the fusion and crystallization events as well as glass transition temperatures (Tg). This technique has been found to be a complimentary method to optical methods in the study of liquid crystal transitions. As transitions between solid and liquid take place, it often goes through a third state, which displays properties of both phases. This anisotropic liquid is known as a liquid crystalline or mesomorphic state.
Using DSC, it is possible to observe the small energy changes that occur as transition takes place from a solid to a liquid crystal to an isotropic liquid.

1.9.5 Thermogravimetric Analysis (TGA)

TGA is an analytical technique used to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight changes that occurs as a specimen is heated. It can detect changes in weight of 1 µg. The measurement is normally carried out in air or in an inert atmosphere, such as Helium or Argon, and the weight is recorded as a function of increasing temperature. Sometimes, the measurement is normally carried out in a clean oxygen atmosphere (1-5% O₂ in N₂ or He) to slow down oxidation. In addition to weight changes, some instruments also record temperature difference between the specimen and one or more reference pans (differential thermal analysis or DTA) or the heat flow into the specimen pan compared to that of the reference pan (DSC). TGA has also been used to determine decomposition weight loss, combustion analysis, thermal stability, moisture content and reaction mechanism.

1.9.6 Polarized Optical Microscopy

Although much neglected and undervalued as an investigative tool, polarized light microscopy provides all the benefits of bright field microscopy and yet offers a wealth of information, which is simply not available with any other optical microscopy technique. As well as providing information on absorption color and boundaries between minerals of differing refractive indices obtainable in bright field microscopy, polarized light microscopy can distinguish between isotropic and anisotropic materials. The technique exploits the optical properties of anisotropy to reveal detailed information about structure and composition of materials, which are invaluable for identification and diagnostic purposes.
Isotropic materials, which include gases, liquids, unstressed glasses and cubic crystals, demonstrate the same optical properties in all directions. They have only one refractive index and no restriction on the vibration direction of light passing through them. Anisotropic materials, in contrast, which include 90 percent of all solid substances, have optical properties that vary with the orientation of incident light with the crystallographic axes. They demonstrate a range of refractive indices depending both on the propagation direction of light through the substance and on the vibrational plane coordinates. More importantly, anisotropic materials act as beam splitters and divide light rays into two parts. The technique of polarizing microscopy exploits the interference of the split light rays, as they are re-united along the same optical path to extract information about these materials.

The polarizer and analyzer are the essential components of the polarizing microscope. The other desirable features include:

- A rotating specimen stage to facilitate orientation studies with centration of the objectives and stage with the microscope optical axis to make the center of rotation coincide with the center of the field of view.
- Strain free objectives-stress in assembly can produce optical effects under polarized light, a factor that could complicate observations.
- An eyepiece fitted with a cross wire graticule to mark the center of the field of view. Often, the cross wire graticule is substituted for a photomicrography graticule that assists in focusing the specimen and composing images with a set of frames bounding the area of the view field to be captured either digitally or onto the field.
- Bertrand lens to enable easy examination of the objective rear focal plane, to allow accurate adjustment of the illuminating aperture diaphragm and to view interferences (Figure 1.10).

- A slot to allow the insertion of compensators/retardation plates between the polarizer, which are used to enhance optical path differences in the specimen. In most modern microscope designs, this slot is placed either in the microscope nosepiece or an intermediate tube positioned between the body and eyepieces tubes. Compensation plates inserted into the slot are then situated between the specimen and the analyzer.

The polarizers illustrated below are actually filters containing long chain polymer molecules that are oriented in a single direction. Only the incident light that is vibrating in the same plane as the oriented polymer molecules is absorbed, while vibrating at right angles to the plane is passed through the first polarizing filter.

![Diagram of polarized optical microscope](image-url)
The microscope configuration uses crossed polarizers where the first polarizer (termed: the polarizer) is placed below the sample in the light path and the second polarizer (termed: the analyzer) is placed above the sample, between the objective and the eyepieces. With no sample on the microscope stage, the analyzer blocks the light polarized by the polarizer and no light is visible. When samples that are birefringent are viewed on the stage between crossed polarizers, the microscopist can visualize aspects of the samples through light rotated by the sample and then able to pass through the analyzer.

1.10 AIM AND OBJECTIVES OF THE CURRENT STUDY

In recent years, the azobenzene containing LC polymer systems have received increasing attention because of their unique properties that allow various applications triggered by light with their mechanical properties and processability. A variety of LC azo polymers with new architectures have been synthesized lately, in which azobenzene moiety plays vital role both as mesogen and photosensitive chromophore (Natansohn and Rochon 2001).

The versatility of the photoactive systems in the azo groups can be selectively attached to the side chain, main chain or chain ends of a wide class of polymer systems. Appropriate substitution of the azobenzene chromophores may be used to tune the chromatic features from UV through the visible spectrum. The possibility of efficient optically induced effects even with low incident light is advantageous.

Liquid crystalline-cum-photocrosslinkable polymers have found wide applications such as display and optical storage device, LC thermosets, thermoplastics and LCD, optical and electro optical applications, Fabricating anisotropic networks and thin films, photoresists to make large scale integrated circuits and printing plates.
Considerable work is being done by incorporating the azo-moiety in the side chain. However, the work done by incorporating the azo group in the main chain is rather less when compared to its side chain counterpart. The liquid crystalline benzylidene containing alkanone polyesters with the azogroup in the main chain are hitherto unreported in the literature.

In an attempt to achieve these objectives, the present investigation comprises of:

1. **Synthesis of arylidenes**
   - 2,5-bis (benzylidene) cyclopanone (BCP)
   - 2,6-bis (benzylidene) cyclohexanone (BCH)
   - 2,5-bis (vanillylidene) cyclopanone (VCP)
   - 2,6-bis (vanillylidene) cyclohexanone (VCH)

2. **Synthesis of m-bromoalkanols**
   - 6-bromo-1-hexanol
   - 8-bromo-1-octanol
   - 10-bromo-1-decanol

3. **Synthesis of monomers, namely,**
   - 2,5-bis [4-(m-hydroxyalkyloxybenzylidene)] cyclopanone
   - 2,6-bis [4-(m-hydroxyalkyloxybenzylidene)] cyclohexanone
   - 2,5-bis [4-(m-hydroxyalkyloxyvanillylidene)] cyclopanone
   - 2,6-bis [4-(m-hydroxyalkyloxy vanillylidene)] cyclohexanone
     \( m = 6, 8, 10 \)
4. Synthesis of 4,4'-azobenzenedicarbonyl chloride

5. Characterization of monomers by FT-IR, $^1$H-NMR, and $^{13}$C-NMR spectroscopy.

6. Polymerization by using solution polycondensation method at ambient temperature.

7. Characterization of polymers by solubility, intrinsic viscosity, FT-IR, $^1$H, $^{13}$C NMR spectroscopy.

8. Thermal stability by TGA and DSC.

9. Liquid crystalline properties by HOPM and DSC.

10. Photocrosslinking studies by UV spectroscopy.