CHAPTER – 1

INTRODUCTION

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1.1. General Introduction

"Dear colleague, leave the concept of large molecules well alone — there can be no such thing as a macromolecule". This advice was given to Hermann Staudinger just 50 years ago, after he delivered a lecture explaining evidences in favour of the macromolecular concept. Polymer chemistry plays stupendous role in our daily life and therefore, it is one of the most rapidly growing branch of science. For last 70 years polymers have gained tremendous attention of chemists, physicists and researchers in academics and industry. In today's world polymers are highly essential in each and every field viz. Clothing, packaging, medicine, and drugs, electronics, agriculture, communication, aerospace, entertainment equipment, defence, household products, healthcare products etc. That's why it is impossible to think of our life without polymers. Polymers have replaced all metals due to their unique properties e.g. good mechanical strength, light weight, good flexibility, special electrical properties, good chemical resistance, amenability for fabrication into complex shapes in a wide variety of colours etc.

Polymers can be converted into strong solid articles, flexible rubber-like masses, soft and resilient foams, smooth and fine fibers, clean and clear glass sheets, swollen jelly-like food materials and so on [1].

The origin of polymers leads us to the 18th century. Polymeric materials such as wood, skins, fibers, horn and bitumens were used by early man for transportation, tools and shelter. In 1839 Goodyear reacted natural rubber with sulfur to obtain vulcanized rubber. Cellulose nitrate as produced by Schönnbein in 1846 was more important as an explosive (guncotton) than as plastic because of difficulties and hazards associated with the processing of this polymer [2].

The first truly synthetic polymer resulted from Backland’s controlled condensation of phenol and formaldehyde in the very early part of the twentieth century. Few advances in polymer technology were recorded prior to the pioneering efforts of Staudinger, Carothers, Mark and many other modern polymer scientists who recognised the true structure and nature of macromolecules. In 1955 Staudinger was awarded the Nobel prize in recognition of his outstanding contributions to polymer science.

What are polymers? For one thing, they are complex and giant molecules and are different from low molecular weight compounds like say, common salt. Small molecules or monomers combined with one another by covalent
bonds to form a polymer. The interlinking of many units has given the polymer its name, poly meaning “many” and mer meaning “part” (in Greek). In simple words we can define polymer as, a large molecule built up by the repetition of small, simple chemical units.

1.2 Classification of Polymers :

As polymers are made up by same or different repeating units, they can have different molecular and chemical structures, physical and solution properties, thermal and mechanical behaviours etc. Because of these functional and structural diversity of polymers, they can be classified under following three major headings [3,4],

Based on
a) their origin
b) the mode of formation
c) geometric shape.

a) **Origin** :-

Depending on their origin, polymers can be divided into three main catagories.

i) Natural polymers :- These polymers are isolated from natural materials e.g. wool, silk, polysaccharide, protein, gums, rubbers etc.
ii) Semi synthetic polymers :- These are chemically modified natural polymers. e.g. cellulose nitrate, cellophane, leather etc.

iii) Synthetic polymers :- These polymers are prepared by polymerization of low molecular organic compounds e.g. polyethylene, poly vinyl chloride, polystyrene etc.

b) **Mode of Formation** :- Based on stoichiometry of the polymerization, the polymer can be classified into two main classes as ;

i) Condensation polymers :- In these polymers, the molecular formula of the structural unit(s) lacks certain atoms present in the monomer from which it is formed.

    e.g. polyesters, polyamides, polyurethanes etc.

ii) Addition polymers :- in which the molecular formula of the structural unit(s) is identical with that of the monomer from which the polymer is derived.

    e.g. polyethylene, polystyrene, polyacrylamide, polyacrylic acid etc.

c) **Geometric Shape** :- According to the shape of the macromolecules, polymers are classified into three major classes as illustrated in Fig 1.1.
i) Linear polymers :- In which carbon atoms joined together as a continuous sequence in a chain (Fig. 1.1a)
e.g. polyvinyl chloride, high density polyethylene, nylon-6 etc.

ii) Branched polymers :- This macromolecule does not consist solely of a continuous chain of catenated carbon atoms. Instead, other carbon atoms are attached to the polymer backbone at irregular spaced branch points. (Fig 1.1b)

e.g. low density polyethylene.

iii) Cross linked (Network) polymers :- These polymers are composed of polymer chains joined together with transverse chemical bonds or crosslinked (Fig 1.1c).

e.g. PF resin, vulcanized rubber etc.
Fig. 1.1. Schematic representation of the structure of (a) linear, (b) branched and (c) cross-linked or network polymers.
1.3 Liquid Crystals

**Definition and Nomenclature**

The classification of matter into solids, liquids and gases is not an absolute one. Many compounds of intermediate phases are known. It is well known that solids have well ordered arrangements of atoms, in liquids it is somewhat disordered while in case of gases, it is completely random or disordered. The liquid crystalline state is an intermediate state between the solid state and liquid state, the disorder being more than that of solid state but lower than that in liquid state. Thus "liquid crystals" can be defined as an intermediate state of matter which exists between crystalline solid and isotropic liquid.

Most of the organic solids have sharp melting points and when they are melted, the intermolecular attraction become so weak that the crystal structure becomes random and isotropic liquid is obtained. However, liquid crystal like substances pass through an intermediate stage upon heating, they first melt to a turbid, cloudy viscous liquid (the liquid crystalline state) which at higher temperature suddenly becomes optically clear isotropic liquid. Thus, in liquid crystalline stage the molecules still possess a certain degree of order.
Discovery of Liquid Crystals:

An Austrian botanist Friedrich Reinitzer was the first one who discovered liquid crystals [5]. In 1888, he experimented with a substance related to cholesterol and noted that it had two melting points. At 145.5° C it melted from a solid to a cloudy liquid and at 178.5° C it turned into a clear liquid. He also observed some unusual colour behaviour upon cooling, first a pale blue colour appeared as the colour liquid turned cloudy and second a bright blue-violet colour was present as the cloudy liquid crystallized. Reinitzer sent samples of this substance to Otto Lehmann, a professor of natural philosophy (physics) in Germany. Lehmann was studying the crystallization properties of various substances and had constructed a polarising microscope with a stage on which he could precisely control the temperature of his samples. Lehmann observed Reinitzer’s substances with his microscope and noted its similarity to some of his own samples [6]. He first referred them as soft crystals, later he used the term crystalline fluids. As he became convinced that the opaque phase was uniform phase of matter with properties of both liquids and solids, he began to call them “liquid crystals” [7]. Soon after, Gattermann and Ritschke [8] and Vorlander [9] investigated several liquid crystalline compounds. The culmination of all these efforts was the classification scheme by Friedel in 1922 [10]. Friedel
and Friedel [11] proposed the term ‘mesomorphic state’. Brown and Shaw [12] have used the term ‘mesomorphism’ for the title of their first review. The intermediate liquid crystalline state has been given many different names by different research workers such as “crystalline liquids” [7], “mesophase” [11,13] (Greek word “meso” means between), “anisotropic fluid”, “ordered liquid” etc. However, the term ‘liquid crystals’ is still more frequently used in the literature. Studies on the physical properties of liquid crystals were carried out in 1930’s, after which work on this field slowed down. Shortly, before 1960, it once again gained momentum and then the progress was swift and substantial. The discovery of discotic liquid crystals in 1977, by Chandrasekhar et al [14] gave a new dimension to the liquid crystals field.

Liquid crystals are classified into two major groups on the basis of their properties [15,16] and these are

1) Thermotropic liquid crystals and

2) Lyotropic liquid crystals.

Those liquid crystals whose phase transitions are brought by means of heat are referred as ‘thermotropic liquid crystals’. Those liquid crystals, that are formed by the force of solvents are termed as ‘lyotropic liquid crystals’.
Increasing the amount of heat or solvent leads to formation of an isotropic liquid for the thermotropic and lyotropic liquid crystals respectively. Gray and Winsor [17] prefer the terms “amphiphilic and “nonamphiphilic” for lyotropic and thermotropic liquid crystals respectively.

**Thermotropic Liquid Crystals:**

The long and rod-shaped molecules with one or more polar or/and polarizable groups favour the parallel alignment of the molecules. In a crystalline solid, if the conditions are favourable for mesomorphism, the order structure breaks down in stages, first passing into liquid crystalline state. This state has a certain degree of order and hence acquires anisotropic properties. Further heating destroys the orientation of the molecules and the mesophase finally changes to isotropic liquid. The mesophase obtained is termed ‘enantiotropic’ which takes place reversibly on heating and cooling, though the reversal to the solid phase is usually accompanied by super cooling. The schematic representation for enantiotropic mesophase is shown below:

<table>
<thead>
<tr>
<th>Crystalline Solid</th>
<th>( t_1 )</th>
<th>Liquid Crystalline or ( t_2 )</th>
<th>Isotropic</th>
</tr>
</thead>
<tbody>
<tr>
<td>State</td>
<td>⇄</td>
<td>Mesomorphic state</td>
<td>⇄</td>
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</table>
The transitions \( t_1 \) and \( t_2 \) take place at sharp definite temperatures and are precisely reversible. This type of transition in which \( t_2 \) is higher than \( t_1 \) is referred to as an enantiotropic mesophase. However, in some cases, a solid melts to an isotropic at temperature \( t_1 \), but on cooling, super cooling may occur and the temperature may fall considerably below \( t_1 \) and the mesophase may appear at temperature \( t_2 \) before the crystallization occurs. This type of mesomorphic state where \( t_2 \) is lower than \( t_1 \) and is observed only on cooling is known as monotropic mesophase. The schematic representation for monotropic mesophase is as under:

**Lyotropic Liquid crystals:** Liquid crystallinity formed by solution is referred as lyotropic liquid mesomorphism. The amphiphilic mesogens frequently form lyotropic mesophase either at room temperature or at higher temperature, which can incorporate into their structure considerable...
amounts of water and/or organic compounds [17]. Lyotropic liquid crystals were actually discovered long before their thermotropic counterparts were known. In 1850, their texture was noticed in a mixture of myelin and water. At the time of discovery, however, the significance of liquid crystals was not understood, so most research has been done on thermotropics. Only fairly recently have lyotropic liquid crystals begun to catch up.

The molecules that make up lyotropic liquid crystals are surfactants consisting of two distinct parts: a polar, often ionic, head and a nonpolar, often hydrocarbon tail. (Not all surfactants, however, form lyotropic liquid crystals.) Following the rule of "like dissolves like," the head is attracted to water, or hydrophilic, and the tail is repelled by water, or hydrophobic. When dissolved in high enough concentrations, the molecules arrange themselves so that the polar heads are in contact with a polar solvent and/or the nonpolar tails are in contact with a nonpolar solvent.

The first lyotropic substance ammonium oleate was reported by Lehmann [18]. McBain [19] has discussed the forms of mesomorphism in soap solutions. A number of cationic and anionic detergents also give mesomorphism phase when treated with water or other solvents [20,21]. Ostwald [22] has discussed the relationship between these liquid crystal states. Robinson [23] has reported an interesting observation that viscous
solution of poly-γ-glutamate in certain organic solvents are anisotropic. He has also reported lyotropic cholesteric phase and discussed the similarity between the lyotropic cholesteric phase and thermotropic cholesteric phase. Lyotropic liquid crystals are found in countless everyday situations. Soaps and detergents form lyotropic liquid crystals when they combine with water. In the kitchen, cake batters may harbor the liquid crystals as well. Most importantly, biological membranes display lyotropic liquid crystalline behavior.

1.4 Liquid Crystal Phases

The liquid crystal state is a distinct phase of matter observed between the crystalline (solid) and isotropic (liquid) states. There are many types of liquid crystal states, depending upon the amount of order in the material. Fig.1.2 shows Schematic representation of different phase transitions.
Nematic Phases

The word “Nematic” is derived from greek word “Nema” meaning threaded schlieren texture. The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction (along the director). In the following diagram (Fig.1.3), it can be noticed that the molecules point vertically but are arranged with no particular order.
Liquid crystals are anisotropic materials, and the physical properties of the system vary with the average alignment with the director. If the alignment is large, the material is very anisotropic. Similarly, if the alignment is small, the material is almost isotropic. The molecules in nematic phase are arranged with their long axis paralled, but they are not separated in layers and can be compared with long box of round pencils.

de Vries [25] proposed classification of nematic phases based on X-ray diffraction patterns as follows:

i) Skewed cybotectic nematic

ii) Normal cybotectic nematic

iii) Classical nematic.
The optical effects of the nematic threads have been studied by Zocher and Birstein [26]. Maier and Saupe [27] suggested in their theory that nematic-isotropic transition temperatures can be determined by calculation of free enthalpy of the phase involved at the transitions.

A special class of nematic liquid crystals is called chiral nematic. Chiral refers to the unique ability to selectively reflect one component of circularly polarized light. The term chiral nematic is used interchangeably with cholesteric.

**Smectic Phases**

The word "smectic" is derived from the Greek word “Smectose” meaning soap like and it was suggested first by Friedel [28]. This seemingly ambiguous origin is explained by the fact that the thick, slippery substance often found at the bottom of a soap dish is actually a type of smectic liquid crystal. Smectic mesophase is viscous, turbid liquid with reminiscent properties of soap. The smectic state is another distinct mesophase of liquid crystal substances. Molecules in this phase show a degree of translational order not present in the nematic. In the smectic state, the molecules maintain the general orientational order of nematics, but also tend to align themselves in layers or planes. Motion is restricted to within these planes,
and separate planes are observed to flow past each other. The increased order means that the smectic state is more "solid-like" than the nematic.

Fig.1.4 shows illustrated diagram of smectic phase.

![Photo courtesy Dr. Mary Neubert LCI-KSU](image.jpg)

Photo of a smectic phase (using polarizing microscope) [24]

The layer structure of the smectic phase was confirmed by x-ray analysis [29]. Smectic phase is identified by the focal-conic textures. Bragg [30] has given excellent account of the focal-conic structure and geometry involved, which provides further evidence for the layer theory of the smectic structure.

According to Hermann [31] and Saupe [32], smectic phases can be divided into two parts
a. Smectic phase with unstructured layers

b. Smectic phases with structured layers.

The most common smectics are in the first group which can be classified as smectic A and smectic C, while smectic B represents the second group. Many compounds are observed to form more than one type of smectic phase. As many as 12 of these variations have been identified, however only the most distinct phases are discussed here.

In the smectic-A mesophase, the director is perpendicular to the smectic plane, and there is no particular positional order in the layer. Similarly, the smectic-B mesophase orients with the director perpendicular to the smectic...
plane, but the molecules are arranged into a network of hexagons within the layer. In the smectic-C mesophase, molecules are arranged as in the smectic-A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane.

![Photo of the smectic C phase](using polarizing microscope)

In some smectic mesophases, the molecules are affected by the various layers above and below them. Therefore, a small amount of three dimensional order is observed. Smectic-G is an example demonstrating this
type of arrangement. Sackmann and Demus [33] and de vries [34] studied these smectic phases in detail.

**Cholesteric Phases**

The name “cholesteric” was derived for this type of mesophase because this phase was exhibited by cholesterol derivatives. The cholestreric (or chiral nematic) liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center [35,36]. The cholesteric phase is twisted nematic liquid crystals twisted about an axis perpendicular to the molecular layers, which lead to formation of helical structure. Gray [37] has reported an optically active deuterated compound exhibiting cholesteric phase. The addition of optically active materials to nematic liquid crystals also gives cholesteric liquid crystals [38].

Cholesteric liquid crystals have generally three textures.

1. Focal conic Textures.
2. Planar Textures.
3. Blue Phases.
Columnar Phases

Columnar liquid crystals are different from the previous types because they are shaped like disks instead of long rods. This mesophase is characterized by stacked columns of molecules. The columns are packed together to form a two-dimensional crystalline array. The arrangement of the molecules within the columns and the arrangement of the columns themselves leads to new mesophases.
Mesomorphism in Biological Systems:

Virchow [39] in 1854, first identified mesomorphism in the form of myelin in biological system. It was followed by some other reports of liquid crystallinity in nervous tissues [40] and red cells of haemoglobin and DNA [41,42]. Knapp and Nicholas first reported, mesomorphism in plants, which was observed in esters from banana peels and seeds of strychine producing plants [43]. Seddon and Templer [44] have published a very good review on liquid crystals and living cells. Chiral side chain for ferroelectric and antiferroelectric liquid crystals, which were obtained from preen gland wax of domestic goose were reported by Heppke et al [45].

1.5. Polymer Liquid Crystals

Introduction

Polymer liquid crystals (PLCs) are class of materials that combine the properties of polymers with those of liquid crystals. These “hybrid” show the same mesophase characteristic of ordinary liquid crystals, yet retain many of the useful and versatile properties of polymers.

Liquid crystalline polymers (LCPs) are an important extension to the science and technology of conventional polymers on the one hand and small organic molecules on the other. Recent development in the field of
polymers and fibers have shown that liquid crystalline order endows plastics and fibers with extraordinary physical properties. "Kevlar fiber" is such an example which has many fold tensile strength compared to other fibers. Hence the technological applications and possibility of large structural variations have given impetus for the synthesis and study of liquid crystalline polymers.

**Classification of Polymeric liquid crystals :-**

As proposed by Gray and Winsor [17], PLC macromolecules can be classified as amphiphilic or nonamphiphilic. The amphiphilic molecules, frequently forming mesophases with the participation of an amount of water and/or organic solvents, are defined as lyotropic liquid crystals. The nonamphiphilic mesogens are nonpolar or moderately polar organic compounds exhibiting highly geometrical anisotropy as a consequence of rod to disk like shape. The nonamphiphilic compounds form usually liquid crystalline phases after melting, and are defined as thermotropic liquid crystals.
Lyotropic Liquid Crystalline Polymers (LLCPs):

Lyotropic liquid crystals are formed by mesomorphic molecules in non-mesomorphic solvents. At low concentrations, an isotropic solution is formed. Such solutions become biphasic at intermediate concentrations. At still higher concentrations, a fully anisotropic solution or mesophase results. Two important prerequisites must be met before a polymer can form lyotropic mesophase.

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

(b) When in solution, the polymer chain must be extended and rigid [46].

The first commercial lyotropic LCP was Kevlar from Du pont, a fully aromatic polyamide, poly(p-phenylene terphthlamide), also known as aramide [47-51]. Fibers from such polymers with an extremely high tensile strength were obtained by wet spinning method in concentrated sulfuric acid solution. Aromatic polyamides (aramides) show lyotropic liquid crystalline behaviour in solvents like strong acids (e.g. sulfuric acid), ureas and dialkylamide-salt solutions. Polyamide is highly linear because of the rigidity and polarity of the amide linkage, fibers of ultra-high strength are spun from anisotropic nematic solutions.
Another well known LLCPS are polybenzazoles (PBZ), holds promise of extending not only mechanical properties but also the thermal capability closer to the limit of organic materials. Lyotropic rigid rod PBZ polymers have been processed into high performance fibers and films [52]. A PBZ solution in MSA (methane sulfonic acid) at above its critical concentration shows nematic texture when examined under a polarizing optical microscope. The US Air Force Ordered Polymer Program has devoted a considerable effort since the mid-1970s to the development of trans-poly(p-phenylenebenzobisthiazole) (PBT) and cis-poly (p-phenylene -
benzo bis oxazole) (PBO) for high performance applications. Poly (m-phenylene isophthalamide) (PmlA) is marketed by Du Pont under the trade name, Nomex. It is spun from hot DMA (Dimethyl acetamide) containing 3% calcium chloride. It can be wet- or dry-spun with the latter process giving the better mechanical properties. Nomex materials are used in yarns and fabrics for protective clothing for firemen, policemen and workers with petrol or rocket-based fuel or molten metals.

Numerous synthetic polypeptides also display liquid crystallinity, owing to their rigid, rod-like, helical conformation in helix-supporting solvents. The most widely studied and best characterized synthetic polypeptide is poly(γ-benzyl-L-glutamate) (PBLG) [53,54]. PBLG is a homopolymer of L-enantiomer of the benzyl ester of poly(glutamic acid). PBLG forms an
α-helix in several solvents, of which m-cresol has been the most popular but other ones, such as DMF, have also been used. PBLG forms cholesteric mesophase in solvents such as chloroform, dioxane, pyridine and DMF. The methyl and ethyl esters of poly (L-glutamic acid) also form lyotropic mesophase. A number of cellulose ethers and esters also display liquid crystalline behaviour in concentrated solution. Hydroxy propyl cellulose, for example shows cholesteric liquid crystalline behaviour in water, methanol or ethanol at a critical concentration of ~40 wt. % [55]. HPC is helical, because of intermolecular bonding and at high concentration the rigid rods aggregate to form a liquid crystalline mesophase.

Aharoni et al have reported several polyisocyanates which show lyotropic LC mesophase in chloroform and tetrachloroethane (TCE) [56,57]. Morgan has reported in his patent [58] that aromatic polyamide containing pyridine moieties gave liquid crystalline solutions in sulfuric acid and high tenacity fibers up to 18g/deneir could be obtained. Ogata et al.[59] had shown lyotropic properties of aromatic polyamides containing pyridine moiety in main chain. Apart from polyamides some other polymers are found to show lyotropic behavior in different polar solvents. Millaud and Strazielle [60,61] synthesized poly(azomethine)s from 1,4-phenylene-diamine and terephthaldehyde exhibiting lyotropic behaviour. Several references are
available in literature on lyotropic liquid crystalline polymers viz. polyquinolines form lyotropic mesophase in m-cresol/di-m-cresyl phosphate mixture [62], polyisocyanides [63,64], poly(aminobenzoic acid) [65], polybenzimidazoles (PBI) [66,67], polybenzothiazoles [68] and some substituted poly(organophosphazene)s [69] show lyotropic behaviour in polar solvents.

Some polyesters have also been reported till now which show lyotropic LC properties. Polk et.al [70,71] have synthesized block copolyesters containing cyclohexane rings and 1,4 or 1,3-phenylene rings, form a lyotropic LC phase in mixture of CH$_2$Cl$_2$ and o-chlorophenol at 25 wt% concentration. Polyesters consist of 2,2’-bis (methyl)-4,4’-biphenylene and PhTA units showed lyotropic phase or gelled bireferingence at 18-44 wt % concentration in diphenyl ether [72]. Lin et.al [73] have reported polyesters containing potassium sulfonate groups in the hydroquinone (HQ) and NO$_2$ groups in terephthalic acid (TA) moieties form a lyotropic LC phase in a number of polar solvents. These solvents include water, DMF, aqueous DMF and aqueous dimethyl sulfoxide (DMSO). An interesting polyester which contains highly substituted –O(CH$_2$CH$_2$O)$_2$CH$_3$ groups, form a lyotropic solution in pure water even at a critical concentration as low as 5 wt % w/v [74].
Synthesis of lyotropic LCPs:

The rigid rod lyotropic PLCs may be divided into three groups:

- Polyamides
- Heteroaromatic polymers
- Polymers having other structure.

The main goal is to obtain polymers which form lyotropic solutions and can be processed into high performance fibers or films. For this purpose, polymers with appropriate high-molecular masses having inherent viscosities around or above 2 dl/g are necessary.

Synthesis of Polyamides

Four types of reaction have been applied to the preparation of polyamides in general, but only one of these, the reaction of an acid chloride with an amine, has been broadly used to prepare lyotropic polyamides.

(1) The oxidative amidation reaction of aromatic amines and acids with phosphorous compounds, which is generally carried out in an amine or amide solvent with organic chlorine compounds as co-reactants, as in the following reaction scheme [75].
Lithium salts may be added to enhance the solubility of the polymer, and polymers with inherent viscosities well above 1.0 can be prepared by this route [76].

(2) The aminolysis of an active ester, such as those of substituted phenols and hydroxytriazoles, can be used to prepare aromatic and olefinic polyamides under relatively mild conditions in reasonably high molecular weights [77].

(3) Amidation reactions in the presence of imidazole or its derivatives, such as in the following reaction, have been used by organic chemists for some time to prepare amides in high yields [78].
(4) The low temperature polycondensation of diamines with bis-acid chlorides is still the simplest and most direct route to the preparation of high molecular weight polyamides. For this purpose, two reaction systems can be used: (i) interfacial polymerization in a two phase reaction system [79], and (ii) solution polymerization, either in an amide solvent, or in chlororocarbon salts with amines present to form ammonium hydrochloride salts [80].

Synthesis of Hetroaromatic Polymers:-
Polybenzimidazoles (PBI), polybenzoxazoles (PBO) and polybenzthiazoles are well known examples of this group. To synthesize these polymers, starting materials are terephthalic acid and hydrochlorides of tetra
substituted benzenes and two amine groups and additionally either two hydroxyl or two mercapto or two amino groups are taken. The polycondensation is carried out in polyphosphoric acid, PPA, at a stepwise increase of temperature from room temperature to 200°C [81,82]. As an alternative solvent to PPA, a mixture of methanesulfonic acid and phosphorous pentoxide was also used for synthesis of PBO [83].

Synthesis of other Lyotropic Polymers :-

Polymers of this group are poly(amide-hydrazide)s, polyhydrazides, polyoxamides and poly(fumaramide)s. Usually these polymers are synthesized similarly as aromatic polyamides in aprotic amide-type solvents at low temperature or by interfacial polycondensation [84].
1.6. Thermotropic Liquid Crystal Polymers (TLCPs)

Thermotropic LC polymers are most commonly grouped into two categories:

a) main chain liquid crystal polymers in which the mesogenic groups are linked to each other in a ‘head to – tail’ arrangement and

b) side-chain liquid crystal in which mesogenic groups are attached via a linking group to a polymer backbone.

In order for normally flexible polymers to display liquid crystal characteristics, rod like or disk-like elements (called “mesogens”) must be incorporated into their chains. The placement of the mesogens plays a large role in determining the type of PLC that is formed. Main-chain polymer liquid crystals or MC-PLCs are formed when the mesogens are themselves

\[
\text{MC-PLC} \quad \begin{array}{c}
\text{Mesogen} \\
\text{Polymer}
\end{array}
\]

\[
\text{SC-PLC} \quad \begin{array}{c}
\text{Mesogen} \\
\text{Polymer}
\end{array}
\]
part of the main chain of a polymer. Conversely, side chain polymer liquid crystals or SC-PLCs are formed when the mesogens are connected as side chains to the polymer by a flexible "bridge" (called the spacer). Generally long aliphatic alkyl chain (-CH₂-)ₙ can be used as spacers.

To form thermotropic liquid crystalline phase, compounds should contain following molecular structural features [85].

1. high length : breadth (axial) ratio.
2. Rigid units such as 1,4-phenylene, 1,4-cyclooctyl, 1,4-cyclohexyl, biphenyl etc.

\[
\text{1,4-phenylene} \quad \text{1,4-cyclohexyl} \quad \text{biphenyl}
\]

3. Rigid central linkage between rings -COO-, -CH=CH-, -CH=N-, -N=NO-, -N=N- etc.

4. anisotropic molecular polarization.
a) **Main Chain Polymer Liquid crystals:**

Main chain polymer liquid crystals are formed when rigid elements are incorporated into the backbone of normally flexible polymers. These stiff regions along the chain allow the polymer to orient in a manner similar to ordinary liquid crystals, and thus display liquid crystal characteristics. There are two distinct groups of MC-PLCs, differentiated by the manner in which the stiff regions are formed.

The first group of main chain polymer liquid crystals is characterized by stiff, rod-like monomers. These monomers are typically made up of several aromatic rings which provide the necessary size. The following diagram shows an example of this kind of MC-PLC.

![PHNA poly(hydroxynapthoic acid)](image-url)
The second and more prevalent group of main chain polymer liquid crystals is different because it incorporates a mesogen directly into the chain. The mesogen acts just like the stiff areas in the first group. Generally, the mesogenic units are made up of two or more aromatic rings which provide the necessary restriction on movement that allow the polymer to display liquid crystal properties. The stiffness necessary for liquid crystallinity results from restrictions on rotation caused by steric hindrance and resonance. Another characteristic of the mesogen is its axial ratio. The axial ratio is defined to be the length of the molecule divided by the diameter (x = 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.

This group is different from the first in that 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 following is a diagram of this type of main chain polymer liquid crystal. Notice the flexible spacer (methylene groups) and the stiff mesogen (aromatic ring and double bonds).
b) Side Chain Polymer Liquid Crystals

It is known that main chain polymer liquid crystals often cannot show mesogenic behavior over a wide temperature range. Side chain polymer liquid crystals, however, are able to expand this scale. These materials are formed when mesogenic units are attached to the polymer as sidechains. Side chain polymer liquid crystals have three major structural components: the backbone, the spacer, and the mesogen. The versatility of SC-PLCs arises because these structures can be varied in a number of ways.

*The Backbone:*

The backbone of a side chain polymer liquid crystal is the element that the side chains are attached to. The structure of the backbone can be very important in determining if the polymer shows liquid crystal behavior. Polymers with rigid backbones typically have high glass transition temperatures, and thus liquid crystal behavior is often difficult to observe.
In order to lower this temperature, the polymer backbone can be made more flexible.

*The Mesogen:*

Perhaps the most important part of a side chain polymer liquid crystal is the mesogen. It is the alignment of these groups that causes the liquid crystal behavior. Usually, the mesogen is made up of a rigid core of two or more aromatic rings joined together by a functional group.

*The Spacer:*

Like their main *chain* counterparts, mesogens attached as side groups on the backbone of side chain polymer liquid crystals are able to orient because the spacer allows for independent movement. The structure of the spacer is an important determining factor in side chain polymer liquid crystals. Generally, the spacer consists of two to four methylene (CH₂) groups attached together in a line. Accordingly, the spacer length has a profound effect on the temperature and type of phase transitions. Usually, the glass transition temperature decreases with increasing spacer length. Short spacers tend to lead to nematic phases, while longer spacers lead to smectic phases.
Structure for a typical polysiloxaneside chain polymer.
1.7. Some Examples of Mesogenic Main Chain Polymers

There are a large number of main chain thermotropic polymers. They can be classified again into two groups. One consist of rod-like moieties along the backbone of the polymer chain, known as wholly aromatic thermotropic LCPs, and have relatively stiff and extended conformations, and the other consist of regularly alternating rod-like moieties and flexible spacers in the main chain, known as semiflexible thermotropic LCPs. Polyesters [86], polyethers[86] and polyurethanes [87] are typical examples of latter class of thermotropic LCPS. Polyesters [86], poly(ester-amide) [88], poly(ester-imide)[89], poly(ester-anhydride) [90], poly(ester-carbonates) [91], poly(2,5-dialkoxyphenylenes) [92] and poly(2,5-dialkoxy-1,4-phenylene-2,5-thiophenes) [93] are notable examples of this class of polymer.

However by far the major contributions in this class of polymer have been made in the study of wholly aromatic, thermotropic polyesters because of their ease of processing in the nematic LC phase, and their excellent mechanical and thermal properties [94-96].

**Polyesters:**

**Synthesis of wholly aromatic thermotropic polyesters :-**

The synthesis of thermotropic polyesters of resonably high molecular weight is described in the literature [94,96,97]. Wholly aromatic,
thermotropic polyesters are prepared by condensation or step-growth polymerization reactions. These class of polymers can be synthesized by following methods:

(1) Some early polyesters were prepared by interfacial polycondensation or by high temperature solution polycondensation reactions from dicarboxilic acid chlorides. For higher temperature polycondensation reactions, the common solvents used are o-chlorobenzene, 1-chloronaphthalene, diphenyl ether and others. For these polycondensation reactions, the condensate, HCl, is removed from the reactor by an inert gas stream. Generally, low-temperature polycondensation reactions of aromatic diols and aromatic dicarboxylic acid chlorides give lower molecular weight polyesters than those obtained from high temperature polycondensation reactions. The chosen solvents for the low-temperature route include CH₂Cl₂, 1,1,2,2-tetra chloroethane and pyridine. In the chlorinated solvents, pyridine and triethyl amine are generally used as HCl acceptors [94,96,97].

Another method developed by Cottis et al. [98,99] and by Duska et al. [100] for synthesis of high molecular weight polyesters is carried out according to the following procedure. The requisite amounts of aromatic diols, aromatic dicarboxylic acid and/or aromatic hydroxy acid monomer and an excess of
acetic anhydride are refluxed in order to ensure an in situ acetylation of all hydroxy groups. After this period, the temperature of the resulting slurry in the reactor is gradually increased with the simultaneous distillation of acetic acid. Then the melt is cooled to form a solid product, which is ground to form a powder. Further polymerization of the fine powder is continued in the solid state under nitrogen flow until a higher molecular weight is attained.

The most common method for the preparation of thermotropic polyesters is reaction of diacetate derivatives of aromatic diols and/or acetoxy aromatic acid with aromatic dicarboxylic acids in the melt. This is known as the melt polycondensation reaction. This reaction is also called a transesterification or acidolysis reaction that generates acetic acid as a condensation product. The condensate is readily removed under vaccum. The common catalysts used for this reaction are usually the acetates of sodium, potassium, magnesium, zinc, manganese, cobalt and antimony (III) oxide [94,96,97].
Recently Kricheldorf and Lubbers [101] reported a relatively new method for the preparation of thermotropic polyesters from silylated aromatic dicarboxylic acids and diacetates of aromatic diols. This polycondensation can be carried out either in the melt or in the solution in which trimethylsilylacetae is a condensation product. Similarly, a thermotropic polyester can also be prepared from the reaction of silylated aromatic diols and aromatic diacid chlorides, either in the melt or in the solution that generates trichlorosilane as a condensation product [102].

(2) The second method involves the use of thionyl chloride and pyridine as an activating agent for the direct esterification reaction. This is the most effective method for this type of reaction [103].
The fourth method is an interfacial polycondensation reaction in which the aromatic diol is dissolved in the presence of a base, such as NaOH, and reacted with aromatic diacid chloride dissolved in a chlorinated solvent, such as CHCl₃ [79,105,106]. A phase transfer catalyst is usually used to accelerate the rate of reaction and to minimize side reactions such as hydrolysis of the amount of diacid chloride. In this polycondensation method, many factors can influence the molecular weight of the polyester. The most important factors are, for example, the concentration of the monomer in the aqueous and organic phase, and that of the phase transfer catalyst; solubility of the growing polymer chain, and the distribution of monomers, between the bulk and the interface and the stirring speed.
Structure – Property Relationships of wholly aromatic thermotropic polyesters

Aromatic polyesters are the most important thermotropic LC polymers developed for structural applications, and they serve as a good example of the ways in which chain modification can be used to control mesophase stability. Poly (4-oxybenzoate), poly(6-oxy-2-napthoate), poly(1,4-phenylene terphthalate), poly(1,4-phenylene 2,6-napthalenedicarboxylate), poly(4,4'-biphenylene terephthalate) and poly(4'-oxybipheyl-4-carboxylate) have, in principle, ideal structures for thermally stable homopolymers. These polymers are very rigid in nature and they have high crystal-to-nematic transition temperature, $T_m$, and, therefore, decompose before these transitions [107-109], making melting difficult. Also they are insoluble in most organic solvents. Therefore, several types of structural modifications are required to decrease the $T_m$ values of this class of polymers to a convenient level in order to prevent thermal degradation during processing from their nematic melts. The structural modifications that are commonly used to control the $T_m$ values of this class of polymers include following [110-113].

1. Copolymerization of different sizes of mesogenic (LC forming) monomers to lower the symmetry of the polyester primary structure.
[The common monomers are hydroquinone (HQ), 4,4'-biphenols (BP), terephthalic acid (TA), 4-hydroxybenzoic acid (HBA), 6-hydroxy naphthoic acid (HNA), naphthalene diol isomers (2,6-ND, 1,4-ND, 1,5-ND and 2,3-ND), naphthalene dicarboxilic acid isomers (2,6-NDA, 1,4-NDA, 1,5-NDA and 2,3-NDA) and 2,6-dihydroxyanthraquinone (2,6-AQ).]

2. The introduction of substituents of various sizes on either the aromatic dicarboxilic acid, the aromatic diol or both moieties to disrupt lateral packing.

3. The introduction of non-coplanar 2,2'-substituted-4,4'-biphenols and 2,2'-substituted-4,4'-biphenylenedicarboxylic acids, and other structurally similar monomers to cause a reduction of inter-chain interaction.

4. The introduction of kinked or bent (non-linear) monomers to lower the persistence length of the polyester in the LC phase and to disrupt lateral interaction in the solid state.

5. The incorporation of regularly disposed, flexible spacers between rigid rod-like units to give rise to a class of semiflexible polyesters which have low \( T_m \) and \( T_i \) values in contrast to wholly aromatic, thermotropic polyesters [114-119]. The commonly employed spacers are methylene,
oxyethylene, siloxane, trans-1,4-cyclohexyl and trans-1,4-cyclohexyl-
dimethylene units.

Additionally, there can exist an irregular distribution of rod-like units
and spacers in a thermotropic polyesters.

**Some examples of thermotropic polyesters:**

The very first condensation polymers of p-p'-dihydroxy-\(\alpha,\alpha'-\)dimethyl
benzalazine with diacylchloride to produce macromolecules with various
numbers of dimethylene groups between two ester groups were synthesized
by Roviello and Sirigu [120].

Research by Jackson and co workers in the Kingsport, Tennessee,
laboratories of Eastman Kodak in the 1970s led to the synthesis of rigid
random copolymers of aromatic polyesters. Jackson published a series of
papers, the first of which, with Kuhfuss in 1976 [121], really brought liquid
crystalline polymer to the attention of the community at large. Another
method of realizing liquid crystalline main chain polymer was applied by
same research group [122], starting with easy accessible poly(ethylene
terephthalate) (PET), rigid mesogenic elements are inserted into the
polymer backbone by transesterification with p-hydroxy benzoic acid
(PHB).
Later on Krigbaum et al. [123] have reported some homopolyesters of p-p'-bibenzoic acid with aliphatic diols. These polyesters show smectic mesophase.

Sinta et al. [12] made a range of liquid crystalline copolyesters where crystallinity has been eliminated using substituted 1,4-phenylene groups and 2,2'-disubstituted 4,4'-biphenylene groups.

Vora et al. have synthesized thermotropic LC Polymers from p-hydroxy benzoic acid, which exhibit nematic and smetic mesophases [125].

A series of TLC copolyesters were reported by Krigbaum [126] with halogen and phenyl substituted terephthalic acid or hydroquinone moiety. These polymers show melting below 400° C.

Heitz et al. reported copolyesters containig phenylalkyl substituted in the hydroquinone moiety to reduce T_m and for their ease of processing from the nematic phase [127,128].

Synthesis and properties of Liquid crystalline Polymers with laterally and terminally linked mesogenic units were studied by Roetz et. al.[129].

Many authors have reported polyesters that are modifications of poly(1,4-phenylene terephthalate) containing a relatively small to medium sized substituted such as methyl, methoxy, halogen , 1,1-dimethyl hexyl and tert-butyl, either in the HQ or TA moiety [126,130-133].
Schmidt [134] reported polyester containing 2,2'-bis (methyl)-4,4'-biphenylene unit in combination with phenyl TA moiety which has solubility in common organic solvents. The thermotropic polyester of BND (1,1'-binaphthalene-4,4'-diol) with PhTA and other two polyesters of either tert-butyl-HQ- or PhHQ with BNDA (1,1'-binaphthalene-4,4'-dicarboxylic acid) are soluble in CHCl₃ and THF [135].

An excellent review article based on thermotropic Liquid Crystalline Polyesters written by Bhowmik et al gives in depth information about the Liquid Crystalline Polyesters [136]

The effect of having more than two types of monomers in the polymer chains on the degree of randomness in the thermotropic liquid crystalline polyesters was studied by Carter [137] who reported that a high degree of randomness was possible by copolymerizing three monomers as compared with two monomers.

Recently Aksoy et al. [138] have reported synthesis and characterisation of fully aromatic TLC copolyesters containing m-hydroxy benzoic acid units. Thermal stability, degree of crystalinity, and Liquid Crystalline property etc. were reported.

Tendolkar et al. [139] synthesized a series of thermotropic random copolyesters based on ethoxy diethylene, oxyhydroquinone, ethylene glycol
and terephthaloyl chloride moieties and investigated the effect of flexible
dependent oxyethylene group on the thermal and liquid crystalline properties
of the copolyesters synthesized.

Previously, Han and coworkers [140,141] synthesized a thermotropic main
chain homopolyester poly[(phenyl – sulphonyl) – p- phenylene, 1,10 –
decamethylene bis (4-oxybenzoate)] and investigated its thermal transition
behaviour, domain texture and rheological behaviour.

An interesting random copolyesters was reported by Han et al [142]
containing flexible spaces of different lengths, one of which show
thermotropic as well as lyotropic liquid crystalline behaviour above 40%
solution in p-Chloro phenol.

**Copoly(ester-amides)**

In 1980 Jackson and Kuhfuss [143] reported properties of polyester amides
prepared from p-aminobenzoic acid and polyethylene terphthalate. McIntyre
and Milburu [144] have recognized that thermotropic polyesteramides could
be obtained from p-aminophenol with several monoalkoxyterephthalic acids
or p-carboxy phenoxy acetic acid.

Clauudann et al [145] have synthesized copoly (ester-amide)s from 2,6-
hydroxynapthoic acid, terephthalic acid, and 4-acetoxyanilid. Aharoni [146]
reported the synthesis of thermotropic liquid crystalline polyamide-ester incorporated with flexible methylene group in the main chain.

Kalyvas and McIntyre [147] investigated thermotropic liquid crystalline behaviour in some ply(ester-amide)s. Khan and coworker [148] have reported aromatic aliphatic polyesteramides having additional ether bonds in the macromolecules and studied the influence of the length of the aliphatic chain on the phase transition.

Recently, an interesting polyesteramide having a large aliphatic segment was synthesized by Pillai et al [149], which shows lyotropic as well as thermotropic Liquid Crystalline behaviour.

**Poly (ester-imide)s** :

Polyamides, a class of polymers, possesses a high degree of thermal stability and chemical resistance as well as good mechanical properties. Sun and Chang obtained thermotropic polymers by poly (imide carbonate) [150]. Poly(imide ester)s were prepared by Imajo et al from N,N'-dihydroxy pyromellitimide (DHPMI) using terephthaloyl, isophthaloyl, or adipoyl chloride in dimethyl acetamide (DMAC) in the presence of triethyl amine [151].

Mustufa et al. [152] have synthesized poly(imide-ester)s from DHPMI and various aliphatic diacyl chlorides.
Kricheldorf et al. [153] have reported liquid crystalline poly(pyromellitimide-ester)s from bis (hydroxy phenyl) pyromellitimide by melt condensation with the silyl esters of 2,6-naphthalene dicarboxylic acid and phenylthio terephthalic acid.

Kannan et al. synthesized poly(pyromellitimide ary1 phosphoramid e ester)s as flame retardant materials [154].

Kricheldorf et al. [155] have synthesized thermotropic poly (ester imide)s based on trimellitimide and diamino oligoether spacer. The presence of ether linkage on thermal and Liquid Crystalline properties were also studied.

**Polyurethane**

Thermotropic liquid crystalline polyurethanes have been prepared by Imure and Koide [156] by the reaction of 3,3'-dimethyl-4,4'-biphenyl diyl diisocyanates with Ⅵ,ω-alkanediols. Tanaka et al. [157] have synthesized polyurethanes with flexible spacer in the main chain. Stenhouse et al. [158] reported synthesis and properties of thermotropic poly (azomethine–urethane)s containing azomethine diols and different diisocyanates.
Polyethers

Percec and his coworkers [159,160], adopted successfully liquid-liquid phase transfer catalyzed polyetherification reaction and prepared liquid crystalline polyethers. A series of liquid crystalline polyethers were also synthesized by Keller [161] with azoxybenzene and acetylene diphenols. Hikmet et al. [162] have synthesized divinyl ethers by in situ cationic polymerization. Mechanical properties, phase behaviour and thermomechanical properties were studied. Percec and Yourd [163] have prepared main-chain polyethers having flexible mesogenic units and flexible spacers in backbone. These polymers are believed to exhibit monotropic liquid crystalline properties due to the dynamic equilibrium between anti and gauge conformations. Random aromatic liquid crystalline copolyethers of α-methyl stilbene and flexible alkyl spacer (5-14) were reported by Hoff et al. [164]. These polymers exhibit nematic LC behaviour and were also characterized using light scattering and TEM.

1.8 Characterization of Polymers

Polymers can be characterized by various techniques viz. FTIR, NMR, TGA, DSC, WAXD, solution properties, scanning electron microscopy
(SEM), transition electron microscopy (TEM) etc. In this chapter we have discussed some of these techniques in brief.

**Thermogravimetry analysis (TGA):**

The most common usage of TGA is in measuring the thermal and oxidative stability of polymers under working conditions. It is also used to investigate the thermal decomposition of polymers and associated kinetic parameters [165,166] i.e. the reaction order and activation energy. Evaluation of these parameters are important in elucidating the mechanism involved in polymer degradation.

Hsiao and coworkers investigated thermal stability of aromatic polyamides by TGA analysis. The $T_g$ of these polymers were observed in the range of 195-300°C, depending on the structure of the diamine component and decreased with decreasing rigidity and symmetry of the polymer backbone [167].

The thermal stability of the silicone-containing polyamides were studied by Maldar and coworkers [168] by TGA. They suggested that polyamides containing aromatic sulfone ether and silicone structures are highly thermally stable.
Bhaskar et al. [169] have investigated thermal stability by TGA thermograms of two copolyester series. No significant weight loss was observed below 375°C and thermal stability decreased with increasing content of the cycloaliphatic comonomers.

**Differential Scanning calorimetry (DSC):**

DSC has become an indispensable tool for polymer characterization over last few decades. Almost all physical or chemical change occurs with a change in enthalpy, all changes can be followed by calorimetry. DSC is an important tool in the identification of mesophases which no research group working in the field of liquid crystals can afford to be without. DSC reveals the presence of phase transition in a material by detecting the enthalpy change associated with each phase transition. The precise identity of the phase(s) can not be obtained, but the level of enthalpy change involved at the phase transition does provide some indication of the types of phase involved. Accordingly, DSC is used in conjunction with optical polarising microscopy, to determine the type of mesophase that a material exhibits.

When a material melts, a change of state occurs from solid to a liquid and this melting process requires energy (endothermic) from the surroundings. Similarly a crystallization of a liquid is an exothermic process and energy is
released to the surroundings. The DSC instrument measures the energy absorbed or released by a sample as it is heated or cooled. The melting transition from solid to liquid is a rather drastic phase transition in terms of the structural change and this is reflected by the relatively high energy of transition. However, DSC can be similarly used to detect much more subtle phase transitions that are involved in liquid crystalline materials. Such more subtle structural changes involved in liquid crystalline phase transitions are reflected by the relatively small enthalpy changes.

Ringsdorf and his group have reported the synthesis and thermal characterization of liquid crystalline polymers with methacrylate and acrylate backbones in which the mesogenic groups are in pendant side chains [170, 171].

Bhowmik et al. [172] have reported thermal study of thermotropic polyester. The polymer does not exhibit a distinct Tg but exhibits two distinct endotherms, T_m and T_i respectively.

Krigbaum et al. have studied thermal properties of a series of copolyesters and shown that polymers exhibit two endotherms, and enthalpy of isotropization for smectic mesophase is large [173].
Effect of annealing on thermal transitions was reported by Chang et al. for copolyesters [142]. These copolyesters show $T_g$, melting point and nematic-isotropic transition temperature ($T_{NI}$).

Imai and coworkers have synthesized a series of aromatic polyamides and their $T_g$ were determined by DSC and TMA techniques. The $T_g$'s for the polymer films determined by the TMA technique were somewhat lower than those observed by DSC [174].

**Wide angle X-ray Diffraction (WAXD):**

The x-ray diffraction technique is important to investigate morphological studies of polymer with bulk specimens. It has been applied primarily to crystalline or semicrystalline polymers and leads directly to structural interpretations in terms of two phases like crystalline and amorphous [175]. The diffraction of x-rays from crystalline polymers gives rise to sharp diffraction lines. The detail information on the state of order of a crystalline material may be obtained from the analysis of the intensity, position and line width of the diffraction lines. X-ray diffraction is becoming increasingly more important in the initial characterization of liquid crystals. Nematic and smectic samples yield comparatively simple diffraction when powder samples are run in the mesophase with no applied
external orienting field. The nematic phase exhibits a weak diffraction around 4.5 Å related to the average distance separating these paralleled rod-like molecules. In the smectic phase an additional maximum appears at lower angles which is related to the smectic layer thickness.

As for non-liquid crystalline polymers, x-ray diffraction techniques can be used to determine the degree of crystallinity of a liquid crystalline polymer. The degree of crystallinity of a thermotropic polymer correlates well with the crystal-to-nematic transition $T_m$, as determined by DSC. Generally, the higher the degree of crystallinity the higher the $T_m$ of a thermotropic polymer [176]. Additionally, this technique provides valuable information on the arrangement and type of packing of LC forming (mesophase) units, and the types of LC phase present in a specific polymer.

Blackwell et al. [177-180] reported the results of thermotropic polyesters in a series of papers, which are concerned with the elucidating the structures of various melt-spun LCP fiber at a molecular level by this technique.

Recently Guerra and coworkers have studied crystallinity of biodegradable poly(ester amide)s by powder x-ray diffraction methods. It was observed from their results that influence of crystallinity on mechanical behaviour is important at the very early degradation stages [181].
Crystalline nature of homopolyester of 4-hydroxy phenylacetic acid was reported by Prasad et al. [182] by WAXD technique. From different reflections they concluded that this polymer adopts a smectic-B-like hexagonal chain packing.

The mechanical properties exhibited by thermotropic liquid crystalline polymers/poly(ether imide) blends was extensively studied using x-ray diffraction, blend rheology and interfacial energy measurements [183].

Solution Property :-

Rheology is very important for polymer solution[184]. The most common and useful method used in solution property is the dilute solution viscosity. The solution viscosity is extremely helpful to determine molecular weight of polymers since the early work of Staudinger [185,186] and has continued to be useful even today. Solution viscosity is basically a measure of the size or extension in space of polymer molecules. It is empirically related to molecular weight for linear polymers [187]. This quantity provides innumerable information regarding the size of the polymer molecules in solution, including the effects upon chain dimensions of polymer structure, molecular shape, degree of polymerization and polymer-solvent interactions [188]. Limiting viscosity number or intrinsic viscosity [η], which characterizes the polymer in the state of infinite dilution is probably
the most frequently measured property for estimating the interaction and
solution parameters. The intrinsic viscosity depends on several factors viz.
the nature of the polymer and that of the solvent, polymer concentrations,
polymer's molecular weight and also the temperature [3].

Vangani and Rakshit reported the viscosity behaviour of homopolymers of
2-ethyl hexyl acrylate and its copolymers with acrylamide (AM),
acrylonitrile (AN) and methyl methacrylate (MMA) [189].

Kansara et al. [190] have studied the solution behaviour of poly(2-
methyloxy cyanurate) in various solvent systems to get an insight on the
conformational behaviour of this polymer.

The viscosity characteristics of polyamide solutions show unique
dependence on time [191]. Ismail et al. [192] have studied intrinsic
viscosity of terpolymers of Acrylamide, Acrylic acid and Acrylonitrile in
different solvents and at different temperatures. $\eta_{sp}/C$ values for these
polymers increased with dilution in water, DMF and water : DMF solvents
where the terpolymer behaves as polyelectrolyte.

Calundann and Jaffe [145] have reported inherent viscosity values for
Vectra™ family of thermotropic copolyesters with 0.1 % polymer solutions
in pentafluro phenol.
Pillai et al. [149] studied viscosity behaviour of lyotropic poly(ester amide). They concluded that viscosity values of polymer were found to increase in concentration, reaches maximum and then fall. It was also found that threshold viscosity values decreased with increasing shear rate. In thermotropic copolyesters containing m-hydroxybenzoic acid units viscosity was found to decrease with an increasing content of kink monomer units in the copolyester composition [138]. Solution properties of Methyl Methacrylate-Acrylonitrile copolymers were reported by Asaduzzaman et al. The activation parameters of viscous flow, voluminosity and shape factor were also calculated [193]. Solution viscosity of aromatic polyamides having pyridine moiety in concentrated sulfuric acid and mixed solvent of hexamethyl phosphortriamide (HMPA) and N-methyl -2-pyrrolidone (NMP) was studied [59]. The apparent solution viscosity of polyamide in HMPA/NMP was higher than that in sulfuric acid. Apparent solution viscosities of the polymer solution were also measured by a rotary viscometer at various rotation rates and temperatures.
1.9. Applications of liquid crystals

From the application point of view, liquid crystals is one of the most developing and fascinating field of current research. Liquid crystals have many odd and interesting physical properties which may be exploited for practical advantage, particularly in the area of electro optical applications and in biological systems. They are also used in chromatography, in display devices, in non-destructive testing, ultrasonic image detectors, as iridescent inks and as solvent for spectroscopy.

Liquid Crystalline materials have been used for display applications for nearly three decades. Table-1 list the current applications for liquid crystal displays [194].

Cholesteric liquid crystals exhibit a colour temperature response mechanism on the molecular scale. This effect has been made use of widely in thermography [195].

Cholesteric liquid crystals have also been used in aerodynamics testing, in disposable thermometers as temperature detector to detect tumors etc.. Ferroelectric liquid crystals have been widely explored for display applications due to its unique properties of bistability, speed and linear response with field.
In addition to these applications liquid crystals have been used as stationary phase in gas-liquid Chromatography and as solvents in Nuclear Magnetic Spectroscopy. They have also been used as solvents in many chemical reactions.

Liquid crystal displays have been widely used from simple numeric displays to large information displays because of their low driving voltage and current, high contrast ratio, low cost, compactness, readability in glaring sun light and easy interface with integrated circuits.

Currently, ferroelectric liquid crystals are becoming a subject of major interest for application in display and other opto-electronic devices as well as for basic studies due to their fast response and memory characteristics [196].

Surface stabilized ferroelectric liquid crystal geometry is needed for electro-optical switching devices. The ferroelectric liquid crystals of most interest for device applications are chiral smectic C phase.
TABLE – 1

Application for Liquid Crystal displays and Cholesteric Liquid Crystals.

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<td>1.</td>
<td>PDLC Electrically switchable holograms.</td>
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<td>TFT Xerox</td>
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<td>3.</td>
<td>TFT LCD 40 inch colour TV</td>
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<td>4.</td>
<td>Lyotropic Liquid Crystals in Pharmacy</td>
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<td>5.</td>
<td>Ferroelectric and Antiferroelectric LCDS : 24 inch black and White LCD display</td>
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<td>Dichromic LCD’s to display fuel and engine parameters on Fighter Aircraft</td>
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<td>LCDS in information board</td>
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<td>Dichroic Active Matrix LCD.</td>
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<td>Thermocromic LCDS in thermometric and novelty devices.</td>
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<td>12.</td>
<td>Medical thermography applied for detection of breast malignancy.</td>
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1.10. Scope of the Present Work

Polymers are extensively used in almost all fields of human life today. During last 50 years, polymer chemists and chemical engineers have greatly improved their ability to make broad range of polymer structure. Polymer physicists and mechanical engineers have learned to measure the significant and critical properties of these polymers. Production engineers and industrial designers have learned to use these materials in thousands of applications.

Aromatic polyamides (aramides) are very important polymers. They possess very high thermal resistance, chemical resistance and also very good flame retardancy. They are extensively used as high performance materials, films, polymer blends and composites. Due to very rigid structure in polymer backbone they show very limited solubility in common organic solvents. Aliphatic polyamides eg. nylon 6 10, 11 and 12, show good flexibility, good impact resistance and low surface friction, but show poor dimension stability. Polyamides are widely used in automotive components, gears, bearing, bushings, gaskets, printing roll cover, alkaline battery cases, electrical insulations, extruded films for food packaging, bus stop shelter and street signs.
Investigation of structure property relationship of polymers can prove to be an effective measure to optimize their performance for desired application. Structure modifications of aramide can lead to an increase in solubility in organic solvents and reduction in melting temperature.

We have synthesized mixed aromatic-aliphatic polyamides which are soluble in conc. H₂SO₄, m-cresol and dimethyl acetamide. These polymers show good thermal stability.

Liquid crystalline polymers are an important extension to the science and technology of conventional polymers on the one end and small organic molecules on the other. They offer a number of potential applications: high strength fibers, precision moulded small components, films exhibiting excellent barrier properties, novel composites, processing aids in melt etc. LC polyesters find application in electrical or electronic components, in cables and connectors in cable fiber optics, in equipment for chemical process, in components for aerospace industry and in applications with high requirement profile in vehicle engineering.

In the present study, different types of polymeric systems have been synthesized and these are characterized by various techniques. Results of investigation are presented and discussed. We have also studied structure-
property relationship, effect of different mesogens/chemical units on thermal properties and crystallinity. Modification in polymer backbone to lower melting point and achieve liquid crystalline property were reported. It is hoped that this would provide a comprehensive background for the fundamental understanding of polymer synthesis, characterization and studies of different properties viz. thermal, crystallinity, solution, liquid crystallinity etc.

In the first chapter of the thesis, a review of literature on liquid crystals, liquid crystalline polymers and their characterization by various techniques are presented, including the scope of the present work. The methods and materials with experimental techniques are presented in chapter two.

In the third chapter of the thesis, we have reported synthesis of poly(azomethine ester)s with different mesogenic units. These polymers were characterized by different techniques and their thermal, degree of crystallinity and liquid crystalline properties were studied. Effect of different mesogenic units on thermal and liquid crystalline properties were also investigated. In the fourth chapter, synthesis and characterization of four different series of copolyesters were reported. Studies of various properties viz. thermal, solution and liquid crystalline etc. were done.
Structure-property relationship to obtain LC behaviour and effect of flexible spacers in polymer backbone was also investigated.

Modifications of aromatic polyamides are useful to make them melt processable and soluble in common organic solvents. Hence, in the fifth chapter of thesis, we have described synthesis and characterization of mixed aliphatic–aromatic polyamides. Thermal properties were studied by TGA and DSC whereas solution properties i.e. solution viscosity in pure as well as in mixed solvents were reported.

In the last chapter of the thesis, a summary of our studies are reported.