CHAPTER 1

INTRODUCTION
1.1. Development of Liquid Crystal Polymers from evolution of Polymer Science

Upto the end of 19th century, metal and ceramics provided the conductors and refractory materials. Insulation was based on natural products such as wood, paper, shellac and gutta purcha. Since the early 1900's one of the most fruitful developments in materials has been the discovery and exploitation of synthetic high polymers.

These are substances produced originally in chemical laboratories, which consists of long chains or networks built up by the repeated linkage of small reactive molecules. When the chain gets long enough, new properties appear, such as hardness, stiffness and mechanical strength.

Depending on the detailed chemistry and spatial arrangement of the chains and their crosslinks, the following can be produced. These include plastics, rubber, adhesives, coatings and fibres.

There may be many hundreds of possible substances in each of these classes but not all of them possess sufficiently useful properties.

Liquid Crystal Polymers have captured the excitement and imagination of contemporary polymer scientists and engineers. These materials exhibit many unique properties that present not only challenges for basic research but also numerous opportunities.
These polymers are able to form partially ordered melts or solutions and hence they are expected to produce materials with higher degree of molecular orientation and order which should result in superior mechanical strength.

Although the technical application of low molar mass liquid crystals and liquid crystalline polymers are relatively recent developments, liquid crystalline behaviour has been known since 1888 when Renitzer (1) observed that cholesteryl benzoate melted to form a turbid melt that eventually cleared at a higher temperature. The term 'liquid crystal' was coined by Lehmann (2) to describe these materials. The first reference to a polymeric mesophase was in 1937 when Bowden and Pirie (3) observed that above a critical concentration a solution of tobacco mosaic virus formed two phases, one of which was birefringent. A liquid crystalline phase for a solution of a synthetic polymer, poly(γ-benzyl-L-glutamate) was reported by Elliot and Ambrose (4) in 1950.

There has been increased interest in liquid crystal polymers especially after the development and subsequent commercialization of high strength fibres from poly(phenylene terephthalamide), PPTA by Du Pont de Nemours Co. in the 1970's. For the past 20 years a tremendous growth and numerous development in this field has been continued.

Liquid Crystal Polymers

'Liquid Crystal' is a term that is now commercially used to describe materials whose molecular arrangement either in solution or in melt is intermediate between the three dimensionally ordered
crystalline state and completely disordered fluid state. Phases with positional or/and orientational long-range order in only one or two dimensions are termed as mesophases or liquid crystalline phases. The rigid units responsible for the formation for the liquid crystalline behaviour is referred to as mesogens. Several years of liquid crystal research have revealed thousands of mesogens that belong to very different classes of chemical compounds. The mesogenic unit usually consists of linked phenylene groups but can include cyclohexyl, biphenyl or triphenyl groups which can be used independently or in conjunction with the phenylene groups. Typically two or four aromatic or cyclic groups compose the mesogenic structure. The bridging groups in mesogens are azo, azoxy, nitro, cyano etc.

1.2. Classification of LCP

Classification of liquid crystal polymers can be made in various modes, one of which is the mode of attachment of the mesogen to the flexible polymer chain. The basic monomer units are low molar mass mesogens, either rodlike or disclike. They may be attached to the backbone in the mainchain itself and is termed as main-chain liquid crystal polymer. Recent development in this field have included the use of naphthalene, stilbene and related structure in addition to the traditional phenylene groups to produce the required rigid main chains. On the other hand the mesogen may be connected to the flexible polymer chain as pendent through flexible spacers and referred the polymer as side-chain liquid crystal polymers. One of the important features of side chain LCPs is that the mesogenic group, not the main chain determines the mesophase order. Therefore, a wide
variety of backbone polymers can be used with this strategy for LCP formation.

Among the recently developed LCP's with intriguing possibilities for novel behaviour are those which contain mesogenic cores in both the side chain and main chain. The presence of mesogenic cores in both side chain and main chain have a significant effect on the properties and organization of the mesophase. Nematic phases only occur where there is a mismatch between the length of the spacers in side chain and the main chain. Otherwise, smectic phases predominate. The polymers have been prepared in both linear thermoplastic and crosslinked elastomeric forms.

Examples of some main chain and side chain LC polymers are shown in Figures (1.1-1.5).

Figs. (1.1-1.3) represent the main chain polymers and Figs. (1.4-1.5) represent the side chain polymers.

Liquid crystal polymers are broadly classified into four types: nematic, cholesteric, smectic and discotic. The common structural feature of low molecular weight LC-compound is asymmetry of molecular shape, manifested either as rods, characterised by a uniaxial order with an axial ratio usually greater than 3 or by thin platelets with biaxial order. Some illustrative structures follow Figures (1.6-1.9).

The nematic liquid crystal has a high degree of long range
Molecular architecture in Liquid Crystal Polymers

<table>
<thead>
<tr>
<th></th>
<th>Rod-like mesogenic group</th>
<th>Disc-like mesogenic group</th>
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<tbody>
<tr>
<td>LC main chain polymer</td>
<td><img src="lc_main_chain.png" alt="Diagram" /></td>
<td><img src="lc_main_chain.png" alt="Diagram" /></td>
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<tr>
<td>LC side chain polymer</td>
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<tr>
<td>LC side chain elastomer</td>
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<td><img src="lc_side_elastomer.png" alt="Diagram" /></td>
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<tr>
<td>LC thermoset</td>
<td><img src="lc_thermoset.png" alt="Diagram" /></td>
<td><img src="lc_thermoset.png" alt="Diagram" /></td>
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16. Nematic: \[ \text{CH}_3\text{O} - \text{O} - \text{N} = \text{N} - \text{O} - \text{OCH}_3 \]
   p-azoxianisole

17. Smectic: \[ \text{CH}_3 - (\text{CH}_2)_3 - \text{O} - \text{CH} - \text{N} - \text{O} - (\text{CH}_2)_7 - \text{CH}_3 \]
   N-(p-butoxybenzylidene)-4-octylaniline

18. Cholesteric:
   \[ \text{CH}_3 - (\text{CH}_2)_7 - \text{C} - \text{O} \]
   Cholesteryl nonanoate

19. Discotic:
   \[ \text{C}_6\text{H}_{13} - \text{C} = \text{O} \]
   \[ \text{C}_6\text{H}_{13} - \text{C} = \text{O} \]
   \[ \text{benzenehexa-n-heptanoate} \]
orientational order of the molecules, but no long range translational order, thus it differs from the isotropic liquid in that the molecules are spontaneously oriented with their long axes approximately parallel (Fig. 1.10a).

The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules. As a consequence the structure acquires a spontaneous twist about an axis normal to the preferred molecular directions. The twist may be left handed or right handed depending on the molecular conformation (Fig. 1.10b).

The smectic phase exhibits both orientational and some positional order. The positional order ensures that on average the centre of the molecules are arranged in planes which are themselves perpendicular to the mean orientation direction of the layer or place. In the simplest smectic phase (smectic A or S_A phase) the molecular packing within the plane is disordered. The molecular packing in any one layer may be ordered and leads to be higher order smectic phases (S_B with hexagonal close packing and S_E with an orthorhombic array respectively within the layers). S_C phase may be developed by introducing tilted director within each layer. Smectic phases are generally more viscous than the nematic phases since their mobility comes essentially from the ability of the planes to slide one over the other rather through each other (Fig. 1.10c).

Liquid crystals of disc shaped molecules, generally referred to
Figure 1.10. Schematic representation of molecular arrangement in a) nematic, b) cholesteric and c) Smectic phase.
as discotic liquid crystals, were identified in 1977 (53). Since then a large number of discotic compounds have been synthesised and a variety of mesophases discovered. Structurally most of them fall into two distinct categories, the columnar and the nematic. The columnar phase in its simplest form consists of discs stacked one on top of the other aperiodically to form liquid-like columns. The nematic phase has an orientationally ordered arrangement of the discs without any long range translational order. A cholesteric phase has also been identified. A smectic-like lamellar phase has been reported but the disposition of the molecules in the layers has not yet been resolved (Fig. 1.11).

Figure 1.11. Disc-like mesogens form (a) columnar and (b) nematic mesophase
Stiff rodlike or platelet molecules organize in LC domains in such a way that molecular alignment occurs in a preferred directions along their long axes. This results in birefringent solution (lyotropic) or melts (thermotropic). Lyotropic liquid crystals are made up of two or more components. Generally one of which is an amphiphilic (containing a polar head group attached to one or more long hydrocarbon chains) and another is water. Examples of such systems include polypeptides, cellulose and its derivatives, synthetic aramids, e.g. poly(1, 4-benzamide), polyoxamides, polyhydrazides, polyisocyanates etc.

When the liquid crystalline or mesophase is induced as a function of temperature, the polymer is known as thermotropic LCP. Generally rigid units (paraoriented aromatic rings) alternate with flexible spacers, produce thermotropic liquid crystallinity. The first thermotropic LCP was reported in the mid 1970's by Roviello and Sirigu (5) and Jackson and Kuhfuss (6). In 1980's several thermotropic copolyesters were commercialized. Tennessee Eastman Company had developed the first commercial thermotropic copolyester (p-hydroxy benzoic acid modified polyethylene terephthalate) (7). In recent years, thermotropic LCPs are getting much more attention compared to its lyotropic counterpart because unlike the lyotropic LCPs which must be processed from solution, thermotropic LCPs can be melt processed from the mesophase. The retention of liquid crystallinity after processing generates high strength fibres and moulded objects.
1.3. Theory of liquid crystallinity

The formation of liquid crystals is solely a consequence of molecular asymmetry. It is not due to intermolecular attractions but is dominated by intermolecular repulsions, i.e. the fact that unites in two molecules can not occupy the same space. There is a limit to the number of rodlike chains that can be accommodated in random arrangement in solution or in melt. When this limiting concentration is exceeded, a crystalline phase or liquid crystalline phase separates.

Let us consider a fluid of long thin rods without any force between them other than the one preventing their interpenetration. At sufficiently low densities the rod can assume all possible orientations and the fluid will be isotropic. As the density increases, it becomes increasingly difficult for the rods to point in random directions and intuitively one may expect the fluid to undergo a transition to a more ordered anisotropic phase having uniaxial symmetry.

This phase separation phenomenon was treated semiquantitatively in an early theory proposed by Onsager (8) and is valid only for very long rods with an axial ratio of about 100, and are therefore not applicable to low molecular weight nematics.

The proposed lattice theory of Flory (9,10) is widely applicable for quantitative treatment of phase transition phenomenon in solution of rod like chain polymers, including melts. At a concentration $V_{p}^{*}$, i.e. volume fraction of polymer, athermal solutions of hard rods of axial ratio $x$ show incipiency of metastable order. 

$V_{p}^{*} \approx (8/x)[1-(2/x)] \approx 8/x$ at high values of $x$. 
The calculated minimum values of $x$ for stable nematic order in a melt of hard rods is 6.42.

Theory predicts that $V_p$ and $V_p'$, the volume concentration of polymer in the isotropic phase and anisotropic phase are at equilibrium in monodisperse systems. In real systems, polydispersity encountered and polymer-solvent interaction can change the axial ratio or modify chain stiffness. This theory is also not applicable to low molecular weight nematics for which the axial ratio is usually 3 and 5 (11).

The first molecular field theory of nematic state was proposed in 1916 by Born (12) who treated the medium as an assembly of permanent electric dipoles and demonstrated the possibilities of a transition from an isotropic phase to an anisotropic one as the temperature is lowered. The most widely used treatment based on the molecular field approximation is that due to Maier and Saupe (13). The theory begins with the assumption that the most important force between liquid crystal molecules is the dispersion force. This force occurs between two molecules that possess no permanent electric dipoles, but that can possess induced electric dipoles, which tend to keep the molecules aligned. The theory produces a prediction for how the order parameter vary with temperature in the nematic phase.

1.4. Molecular structure of LCP

Specific structural features of LCP's usually involve a succession of para oriented ring structures to give a stiff chain with a
high axial ratio (ratio of length of molecule to its width) x. The common structural features of LC compounds are manifested either as rods characterised by a uniaxial order with an axial ratio usually greater than 3 or by their platelets with biaxial order. Long, narrow rod shaped molecules have the most suitable geometry for forming a liquid crystalline phase. The vast majority of liquid crystalline substances are based on the following structure,
They possess,
1. Two or more aromatic (or, more rarely heteroaromatic and/or cycloaliphatic) rings, usually benzene ring,
2. One or two bridging groups, -A-B-, that bind the ringstogether,
3. Two terminal groups, X and Y, usually on the long axis of the molecule.

Following this structural principles, first formulated by D. Varlander (14), the known molecular building blocks are listed in Table (1.1) to (1.3). Most of these occur only in experimental cases and then in combination with the more usual groups found in liquid crystals.

Design of LCP structure:
Mesogens:
The 1,4-disubstituted benzene ring forms the standard building block from which the majority of liquid crystal molecular structures are derived. It is highly polarizable and determines the basic rod shaped structure. The angular molecules, derived from 1,2- or 1,3-disubstituted benzenes have small tendency to enter the mesomorphous
Table 1.1. Aromatic and heteroaromatic rings in mesogens

- Standard unit
- Next most frequent unit

\[ n > 3 \]

- \( R' \): Cl, Br, I, OH, OAlk, OOCAlk, CH\(_3\), CN, NO\(_2\)
- \( R \): F, Cl, Br, OCH\(_3\), CH\(_3\), NO\(_2\), NH\(_2\)

Rare unit
Table 1.2. Bridging groups that connect the mesogens

<table>
<thead>
<tr>
<th>Common units</th>
<th>Rare units</th>
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<td><img src="image1" alt="Common units" /></td>
<td><img src="image2" alt="Rare units" /></td>
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Table 1.3. Terminal groups in mesogens (R=n-alkyl, R'=branched or unsaturated alkyl).

<table>
<thead>
<tr>
<th>Standard Units</th>
<th>Common Units</th>
<th>Rare Units</th>
</tr>
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<tbody>
<tr>
<td>-OR</td>
<td>-Cl</td>
<td>-H</td>
</tr>
<tr>
<td>-OOOCR</td>
<td>-NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-F</td>
</tr>
<tr>
<td>-COOR</td>
<td>-COR</td>
<td>-Br</td>
</tr>
<tr>
<td>-CN</td>
<td>-COR</td>
<td>-Br</td>
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<table>
<thead>
<tr>
<th>Standard Units</th>
<th>Common Units</th>
<th>Rare Units</th>
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<tbody>
<tr>
<td>-NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-N=C=S</td>
<td>-N=C</td>
</tr>
<tr>
<td>-NHCHO</td>
<td>-N=N</td>
<td>-N=N</td>
</tr>
<tr>
<td>-SR</td>
<td>-OR'</td>
<td>-OR'</td>
</tr>
<tr>
<td>-HgCl</td>
<td>-COOR'</td>
<td>-COOR'</td>
</tr>
<tr>
<td>-R&lt;sub&gt;Si&lt;/sub&gt;</td>
<td>-OCOR</td>
<td>-OCOR'</td>
</tr>
<tr>
<td>-O(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;n&lt;/sub&gt;OR</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH</td>
</tr>
</tbody>
</table>
The fact also holds true for cases where the binding is caused by an angular bridging group as well as for naphthalene derivatives e.g.

Molecules with two bends on aromatic rings do not exhibit liquid crystallinity.

Introduction of heteroatoms in the benzene or naphthalene rings also produce liquid crystallinity. Some heterocyclic mesogens which form lyotropic solutions are illustrated,

\[
\text{poly}[2,6-(1,4-phenylene)-4-phenyl quinoline)}
\]

\[
\text{poly}[1,1'-(4,4'-biphenylene)-6,6'-bis(4-phenylquinoline)]
\]
Bridging groups:

Linear bridging groups have a structural angle of 180°. Angular bridging groups with parallel configuration exhibit greater thermal stability.

This structure includes azomethines, azo compounds, azoxy compounds, carboxylic acidesters, stilbenes, carboxylic acidamides, benzylphenylamines etc. Angular bridging groups with nonparallel configuration are much less likely to form liquid crystal compounds. They have a W-shaped central configuration with an odd number of atoms in the chains. Hydrazones or distyryl ketones are the examples of nonparallel bridging groups.

Aside from rod shaped molecules, a plane shaped molecule was long considered to have significant tendency toward the formation of the mesomorphic state. Nonplanar structure of many liquid-crystalline aromatic azomethines has been confirmed.
Terminal groups:

The $-\text{CH}_2-$ group and its homologues can be introduced in a bridging or terminal group, e.g.,

$$\text{C}_2\text{H}_5\text{O} \xrightarrow{\text{N} = \text{N}} \text{OOC(C}_{\text{H}_2}\text{nCH}_3$$

D. Vorlander found that the introduction of a branched alkyl group, $-\text{R'}$, such as $-\text{OR'}$, $-\text{OOCR'}$ or $-\text{CH}=\text{CH}-\text{COOR'}$, strongly depressed the clearing points as compared to the analogous $\text{n-alkyl isomers}$. 

Since the ether function plays an outstanding role as a terminal group, ethers containing more than one oxygen atom have been investigated,

$$\text{CH}_3\text{OCH}_2\text{O} \xrightarrow{\text{CH}=\text{N}} \text{CH}=\text{CHCOOC}_2\text{H}_5$$

All the terminal groups with a second oxygen atom lower the clearing points of smectics and nematics. The depression strongly depends on the oxygen's position in the chain.

The increase in molecular breadth due to substitutions on the aromatic rings normally reduce the anisotropy of molecular shape, thus depressing the stability of both nematics and smectics. The following examples give the clearing points of some nematics.
The above discussion gives evidence that the prime requirements for long range selfordering in a mesophase come from molecular geometry.

1.5. Properties of LCP

Liquid crystals are highly anisotropic fluids that exist between the boundaries of the solid and conventional isotropic liquid phase. Within certain ranges of temperature in melts and solutions, some organic substances are solid in terms of flow, the other fluid aspects to their physical states still exist. This dualism of physical properties of liquid crystal polymers results in an unusual combination of mechanical, thermal and chemical properties.

Biphasic behaviour of LCPs implies the presence of two distinct phases between the melting and clearing transitions. These two phases
being typically liquid crystalline phase or mesophase and isotropic melt. In most cases the biphase can be explained on the basis of a distribution of molar masses in a LC-polymer. Upon analysis (15) the nematic component was shown to be of a higher molar mass than the isotropic phase. Recently (16), the critical and experimental work has been demonstrated the effect of chemical heterogeneity as a cause of the triphase. Chemical heterogeneity has been shown to cause a low degree of crystallinity at low temperatures and an extended clearing transition at high temperature in random copolyesters (17,18). Low molar mass LC-polymers would be expected to be biphasic over a wide temperature range.

A characteristic feature of LCPs in the melt is the sharp reduction in viscosity which makes it possible for easy processing. The melt viscosity of an LC-polymer is sensitive to thermal and mechanical histories. If an LC-polymer is subjected to a shear or elongational flow, the mesomorphic domains are oriented in the direction of flow. Thermotropic main chain LCPs are known as 'self reinforcing' polymers because oriented parallel rod molecules are 'frozen' on cooling and retained in the solid state, the polymer is then reinforced with fibrills of the same material. The anisotropy in morphology results in an unusual combination of physical properties, viz, excellent mechanical properties, very low coefficient of linear thermal expansion along with outstanding dimensional stability. Coupled with these properties, high chemical resistance, flame retardance and ease of processing open up many new applications for LCP.
1.6. Synthesis of LCP

The traditional way to synthesise liquid crystalline main chain polymers is to connect two or more aromatic or cycloaliphatic rings in the para-position by short links as esters, amino, vinylene, azo, azoxy etc. There are two main routes for polyester synthesis. One uses a transesterification reaction between the phenyl esters and the diacids with aryl diols evolving phenol. The other uses an acidolysis reaction between the free diacids and the acetylated aryl diols at relatively high temperatures. The polymerization may be carried out with or without any catalyst. In general anhydrous sodium or potassium acetate are used as catalyst. Other catalysts are bisalts, tertiaryamines, phosphine etc.

Vacuum or purging with nitrogen or argon volatilises the acetic acid, resulting in higher molecular weight. Direct condensation of chlorohydroquinone, quinitol, or p-hydroxy benzoic acid is impractical because of thermal decomposition. Direct condensation of dihydric phenols and aromatic dicarboxylic acids catalyzed by tin, titanium or antimony compounds has been described (19). Condensation of p-acetoxy- benzoic acid with preformed PET is highly effective. PET is degraded by acidolysis and then built up as a copolymer (20).

Polymers with mesogenic side groups are prepared by polymerizing a monomer containing an active vinyl double bond attached by way of a spacer group to a mesogenic group. Methacrylates and acrylates are convenient starting materials. Another method is by addition of a vinyl mesogenic compound to
a silyl group on a preformed polymer (21).

Some homopolymers and copolymers exhibit a wide variety of LC structure. Crosslinking of such systems leads to mesogenic thermosets and elastomers (22). Disc like mesogens may also be used (23).

Synthesis of most liquid crystal polymers involve a high reaction temperature and a long reaction time. The synthesis of the polyesteramides from p-acetamidobenzoic acid and polyethylene terephthalate was carried out at 275°C for 4 hrs. as was reported by Jackson and Kuhfuss (6). LC-polyester from p-acetoxybenzoic acid and polyethylene terephthalate was synthesised at 275°C under reduced pressure in presence of nitrogen (24). Khan et al. synthesised polyesteramides from p-acetamidophenylacetate and bis(p-carboxyphenoxy)alkane at 282°C under reduced pressure (25). A typical method for preparation of polyamide and polyester involves a reaction temperature of 100°C in the presence of triphenylphosphine according to the direct polycondensation technique developed by Higashi (26). A typical method for preparation of polyamide by direct polycondensation was described by Moriyuki Sato et al. (27). Some typical polycondensation methods have also been followed to carry the polymerization reaction under mild conditions (28). Some phosphorilating agents have been chosen for this purpose. Triphenyl phosphine or Triphenyl phosphine dichloride could initiate direct polycondensation at ambient temperature to produce either polyester or polyamide. Various bisphenols such as bisphenol A or resorcinol and
aliphatic diols were used with dicarboxylic acid such as isophthalic acid or 2,5-pyridine dicarboxylic acid as monomers for direct polycondensation for the synthesis of polyester using the combination of triphenyl phosphine and a polyhalo compound as initiators. N. Ogata (29) reported the synthesis of polyamides and polyesters using triphenyl phosphine and hexachloroethane initiator system by a low temperature polycondensation method. C.K. Ober et al. (30) synthesised polyesters from the dihydroxy compounds by polymerizing the diacidchlorides at 50°C for 24 hrs. in inert atmosphere using pyridine as proton acceptor. LC-polyesters were prepared by C. Ramireddy and coworkers (31) by using pyridine as catalyst and HCL scavenger, which was produced as a byproduct of the esterification reaction with acidchlorides. The reaction was allowed to proceed for 48 hrs. at room temperature under cry nitrogen. Polyesteramides with exactly desired structure can be synthesised from monomers with proper structure and functional groups. Danuta Sek et al. (32) synthesised the desired monomers and carried out the polymerization reactions in boiling chlorobenzene at 130°C in the presence of pyridine in an argon atmosphere. The reaction variables have strong influence on the molecular weight of the polymer as was observed by James Economy (33).

1.7. Modification of LCP

Fully aromatic main-chain LCPs, such as poly(p-oxybenzoate) or poly(p-phenylene terephthalate) are intractable due to their high melting points and decomposition before melting. Hence, less perfect structure having lower melting points and easier processibility were
developed. The stability of the mesophase depends on the rigidity of the molecular chain which in turn related to the type of the mesogen and the spacer. According to Corradini and Vacetello (34) rigidity of the chains impart mesophase stabilization. Longer mesogenic unit increases the rigidity of the chain and stabilize the mesophase as well. For fixed mesogenic length longer flexible spacers favour the formation of an isotropic phase. Several approaches have been taken in an attempt to lower the transition temperature of the polymers to enable their processing at more convenient temperature. Reduction of the transition temperature of LCPs can be achieved by a number of ways. These modifications were used either individually or in combination. The replacement of rigid links in the polymer main-chain by flexible groups, in order to reduce the rodlike nature of the chain was suggested by Rovilolo and Sirigu (5) to be one of the effective modifications. Incorporation of metallinkages has also been undertaken in order to obtain bent rigid units (35). Copolymerization of para-substituted monomers which differ in structure and length, use of rodlike arylene moieties of different length and / or shape. (e.g. p-phenylene in conjugation with p, p’-triphenylene or 2, 6-naphthalene) or unsymmetrically substituted arylene moieties are the other methods adopted for reducing the transition temperature of LC-polymers (36).

Substitution on the flexible spacers generally causes changes similar to those produced by adding substituents to the mesogenic groups, therefore reduced transition temperature and reduced crystallinity are commonly observed (37). If optically active spacers
properties, good chemical resistance and almost zero water regain and small coefficient of thermal expansion.

Thermotropic melt polymers give films with superior properties especially in the machine direction. Since, LCPs offer a low viscosity for impregnation of carbon fibres and excellent chemical resistance, LCP-carbon fibre composites have been developed and used as secondary composites for the aerospace industry.

1.9. Characterization of LCP

The traditional techniques employed for the mesophase characterization include NMR, X-ray diffraction, optical microscopy, thermo-optical analysis and thermal analysis. Structural organization and chemical composition of the LCPs have been determined by quantitative as well as qualitative infrared spectroscopy.

IR analysis: Infrared spectroscopy is an extremely powerful analytical technique for both quantitative and qualitative analysis. The chemical composition of a polymer can be determined by the definite absorption bands obtained in the spectrum. The quantitative composition of the polymer can also be evaluated from the percent absorbance of the peaks utilizing the internal standardization method (40). IR spectroscopy is also very useful for analysing the molecular interactions among the polymer chains.

WAXD analysis: One of the physical methods used to characterise polymer and polymer morphology, Wide-angle-X-ray diffraction
are used, that is with substituents on the spacer which produce an asymmetric centre, then cholesteric or twisted smectic A phases can result from polymers that otherwise form nematic or smectic C mesophases respectively. A wide variety of substituents has been incorporated into both the linking groups forming the mesogenic structure (38). The substituents have a variety of effects on the polymer, but they generally interfere molecular packing and reduce transition temperatures of the polymers and lead to a decreased order in the mesophase i.e., smectic polymers may become nematic on substitution (39). Polymers that have an even number of atoms in the backbone of the spacer exhibit substantially higher transition temperature than their homologues with an odd number of atoms. Polymers with substituted benzene mesogens required a spacer of 12 methylene groups to give the widest range of mesophase stability (40).

On the other hand, incorporation of rigidity into the main chain increases the interchain bonding which tends to increase crystalline phase stability and elevate the melting temperature of the polymer. The effect of replacement of an ester linkage with an amide linkage in thermotropic copolyester was studied by Khan et al. (25). In the crystalline solid isomorphous replacement was found to occur and the amide group was found to enhance the stability of the mesophase and raise the transition temperature owing to strong interaction based on H-bonding. The melting temperature of polymers linked with ethers between the spacers and the mesogens are typically higher than those with esters. This is probably due to the fact that the ether-linked polymer has a spacer two atoms shorter, with the
carboxyl groups. Typically the clearing transitions of the ether linked polymers occur at higher temperatures.

1.8. Application of LCPs

The LCPs have found major applications in the electro-optical fields. Compared with a monomeric system there are a few drawbacks with currently developed LCPs due to their high viscosity. Technological problems with LCPs in electro-optical applications, including data storage, information display, laser writing and coating for optical fibers could be overcome by the use of smectic polymers. LCPs offer at least a few advantages over PBT in electronic applications, such as low mould shrinkage, fast cycling time, capability of moulding thin parts, better chemical and mechanical properties etc.

LCPs are also useful in other various fields like plastics, resins, fibres, films etc. High mechanical strength, excellent creep and fatigue resistance make LCP fibres important in industrial applications. Excellent cut/tear resistance and thermal insulation make LCP fibres desirable for gloves and protecting clothing. As LCP fibres are light weight, strong, non-abrasive, dimensionally and thermally stable, they are widely used as rubber and plastic reinforcement in radial tyres, space applications, boats, aircraft interior and propellor etc. It is also used as cement reinforcement in building materials.

LCP rods have been used to replace steel wire. This is because LCP rods are light weight, flexible, have excellent tensile
technique is the most valuable one since it provides concrete information regarding the conformation of the single polymer chain and its orientation as well as about the short and long range order of the polymer chain in the solid. It also permits qualitative and quantitative determination of crystalline components of semicrystalline polymers which is of particular importance in relation to ultimate properties of polymers. Liquid crystalline mesophases are sufficiently organised at the molecular level to produce Bragg diffraction (42). WAXD experiments on liquid crystalline polymers are useful for mesophase identification and measurement of the mesogenic unit length. The combination of X-ray diffraction with thermal data and texture examination under the optical microscope is considered the most effective means of identifying specific mesophase type. The most commonly occurring mesophase in thermotropic liquid crystalline polymers is the nematic mesophase. X-ray diffraction has been used to identify this mesophase in many thermotropic polymers (43, 44). Smectic mesophases have now being identified in several main-chain LC-polymers by X-ray diffraction methods. Nematic mesophases were identified for polymers with odd number of methylene units in the spacer while smectic mesophases were observed for polymers with even number of methylene units. Nematic mesophases can be identified by X-ray diagram exhibiting one broad ring arises from the short range ordering of molecular chains parallel to each other. X-ray diagram typical for smectic phases consists two rings, the inner ring results from the periodicity normal to the smectic layers and the outer ring arises from the parallel arrangement of the polymer chains. Blackwell and coworkers (45) have successfully reproduced the X-ray diffraction
pattern of a liquid crystalline aromatic copolyester of 4-hydroxybenzoic acid, 2,6-dihydroxy naphthalene and terephthalic acid by theoretical calculation. S. Hanna and coworkers (46) studied the crystalline phase transition of random copolymer from HBA/HNA with increasing temperature. They have also studied the effect of annealing on crystalline phase transition of the above mentioned copolymer. They observed the pseudo-hexagonal phase of a random copolymer sample from HBA/HNA, which has been cooled from its melt, transformed to orthorhombic one after annealing.

Optical microscopy: Polarising microscope is widely used for studying the morphology of liquid crystals. The term 'texture' denotes the microstructure of a thin liquid crystalline specimen viewed under bright field conditions between cross-polars. The optical texture of liquid crystalline materials under a polarising microscope is characteristic of different mesophase (47) and the observed texture is compared against an atlas of standards (48) obtained from materials for which the symmetry of molecular order is known.

The homogeneous texture occurs when the optical axis lies parallel to surface boundary of the layer. Sometimes the term 'planar texture' is also used. The homogeneous texture occurs in the nematic and only in very special cases smectic phases. 'Homeotropic texture' occurs when the long axes of the molecules are at right angles to the boundary surface.

The nematic phase derives its name from its characteristic dark
threads, so called 'schlieren texture'. Schlieren texture appears in the smectic C and B phases as well as in the nematic phase (49). The nematic schlieren textures are exhibited by the copolyester from a 50/25/25 mol% mixture of terephthalic acid, pyrocatechol and methyl hydroquinone as reported by C. Noel (50-52). If the polymer is cooled to 122-123°C, a nematic to smectic A transformation was found to take place. Another variant of nematic homogeneous texture called 'marbled' texture exhibits sharp, straight bordered areas that imparts a rocklike appearance. Nematic droplets characterize a type texture of the nematic phase since they occur no where else. Upon cooling an isotropic melt, the nematic phase begins to separate at the clearing point in the form of typical free form droplets with cylindrical symmetry called point symmetry.

The so-called mosaic texture is typically encountered with the smectic B phase. It is recognizable by its curved grain boundaries and very different interference colours. Smectic A and C phases, the most frequently observed of the presently known smectic phases, are recognised by the typical fan shaped or focal conic texture. Smectic C phases show the fan texture less distinctly. H. Sackman called them 'broken-focal-conic texture' (54). The so-called batonnets are closely related to the focal-conic texture. Batonnets are rod shaped with cylindrically symmetrical protrusions and are formed when an isotropic melt of a smectic phase cools just before separation of the smectic C phase as a whole. The remaining smectic phases, such as the cubic D phase, E phase and others are yet to give diagnostic criteria for their identification. According to publications of H. Sackman, the
possible textures of the mesophases are patterned in the following scheme.

Table 1.4. Optical textures exhibited by liquid crystal polymers

<table>
<thead>
<tr>
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<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nematic</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
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<tr>
<td>Cholesteric</td>
<td>+</td>
<td>+</td>
<td>-</td>
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<tr>
<td>Smectic A</td>
<td>+</td>
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<tr>
<td>Smectic C</td>
<td>+</td>
<td>-</td>
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<td>Smectic D</td>
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<td>Smectic E</td>
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</tr>
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</table>

1. Homogeneous texture
2. Homeotropic texture
3. Schlieren texture
4. Focal-conic, broken focal-conic and fan-like texture
5. Mosaic texture
6. Terrased drops
7. Isotropic texture

Thermo-optical analysis:
The measurement of the transmission of polarised light through a sample of a polymer by a polarizing microscope fitted with a hot-stage
is known to be a useful technique for investigating the microstructure and crystallization behaviour of semicrystalline polymers. Magill studied the crystallization rate of isotactic polypropylene by measuring the intensity of transmitted light in an appropriate system (55). Zlabicki reported on the theoretical analysis of light depolarization in a system of parallel, birefringent plates embedded in either an isotropic or anisotropic medium (56). For liquid crystalline compounds, Cameron studied the depolarization factors for various low molecular weight liquid crystals and observed that rapid changes in depolarization factors occurred at phase transitions indicating that similar changes had occurred in the size and anisotropy of the mesophase elements (57). The use of light transmission technique for liquid crystalline polymers to study phase transitions had also been reported by several investigators (58-60). Wunder and coworkers studied the change in transmitted light intensity as a function of temperature for three LC-copolyesters, which formed nematic mesophases (61). The work reported by Bhattacharya and Lenz (62) involved the measurement of the total transmitted intensity for an LC-copolyester and a blend of an LC with a non-LC polymer, both as a function of temperature. The transition temperatures observed by light transmission studies closely matched those obtained from DSC and optical microscopic studies. The temperature range in which an LC-phase existed as a part of a triphase it was observed that the transmission intensity increased almost linearly until complete isotropization occurred. It may be possible to calculate the approximate nematic to isotropic composition of the triphase as a function of temperature. In the case of blends the transmission intensity was found to increase linearly and
the onset of isotropization of the mesophase component was found to depend on the composition of the blends. For some slowly crystallizable liquid crystalline polymers, the DSC thermograms of the cooling cycle generally give little information about the formation of the liquid crystalline or crystalline phases. Hence, the light transmission studies may be more useful for studying such systems.

**Thermal analysis**:

The thermal analysis methods of polymers are significant not only for the fact that the thermal properties of polymers are important but also that the technological properties of polymers depend upon their thermal history to a great extent. The major thermal analysis techniques include Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA).

**TGA**:

Thermogravimetry by definition is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to controlled temperature program. It has been widely used for studying thermal stability of the material. TGA is also used as a technique to perform chemical analysis either qualitatively or quantitatively. The analysis include the onset temperature of decomposition, end temperature of decomposition, temperature at 50% of the weight loss etc. In order to examine the thermal decomposition of the polymers in greater detail, the temperature corresponding to 5%, 10% and 50% weight loss have to
be evaluated. The decomposition temperature for 5-10% weight loss represents the thermal resistance of a polymer under experimental conditions. This has been defined as the temperature of incipient thermal degradation accompanied by the evolution of volatile products (63). Another definition has been proposed by Arnold (64). He used the inflation temperature of the thermo-diagram as the decomposition temperature of the polymer.

Thermal stability of the thermotropic LCPs mostly depend on the nature of the mesogens and flexible spacers present in the polymer chain. The coplanarity and colinearity of the mesogenic part influence the effective molecular alignment and in turn the molecular packing, therefore affect the mesophase stability. Longer mesogenic units lead to polymers with higher mesophase stability. Thermal stability of the polymers depend on their ionic counit content as was determined by Ostroa-Gumkowska et al. (65). They studied the thermal degradation of anionically modified polyethylene terephthalate in nitrogen and air. For the copolyesters with higher content of the ionic-counits, the characteristic temperature of decomposition are reduced, especially at the beginning of the main degradation step. The rate of decomposition and weight losses are more pronounced in a nitrogen environment than in air. Thermogravimetric analysis was carried out for polyesters based on 2, 5-thiophenedi-carboxylic acid, terephthalic acid and isopthalic acid by Rubin Cai and coworkers (66) in order to compare their thermal stability. All polyesters remain stable upto 450°C. Thermal stability of two series of LC-polymers, both with mesogenic triads connected by aliphatic spacers
varying in length, have been studied by C. Ramireddy and his coworkers (31). According to their result, replacement of the aromatic ring of terephthalic acid by a tricyclopentane cage led to a very substantial depression in the polymer stability.

DSC:

Differential scanning calorimetry (DSC) is of particular importance for polymer characterization. It permits the amount of heat to be determined that are taken up from or emitted to the surroundings per unit time during heating or cooling or isothermal procedure. In this manner heat capacities, melt enthalpies, transition temperatures, specific heat etc. can be measured and from these information further indications regarding phase transitions, crystallization process etc. can be derived. It is also possible to observe kinetic process, viz., melt and recrystallization process, isothermal crystallization process etc.

Most thermotropic polymers, unlike semicrystalline polymers in general, possess more than one melt transitions. On heating, at a certain temperature a thermotropic LCP passes into a mesophase where spontaneous flow and molecular order are found to coexist. On further heating a number of inner mesophase transitions may occur depending on the molecular conformation of the polymer in the mesophase. Ultimately the polymer transforms into a completely disordered isotropic melt at the isotropization temperature. At this critical temperature an equilibrium exists between the anisotropic and isotropic melts.
In order to calculate the change in the molar entropy of transition, the temperature and heats of transition have to be measured. The entropy of clearing transition is associated more with the type of spacer than the type of mesophase formed (67). In a series of high molecular weight thermotropic polymers, the odd-even effect show a striking regularity, but there also exists a molecular weight dependence on the melting and the clearing transitions (68). Both of these transition temperatures increase with molecular weight until a plateau reaches at higher polymer molecular weight (69). S.M. Aharoni (68) noticed substantial odd-even effect of a large family of strictly alternating, highly regular polyesteramides on their transition temperatures, where the polyesteramides with even numbered methylene groups exhibit higher melting points than their odd-numbered neighbours. DSC heating traces for phenyl- hydroquinone polyesters exhibit several minor and major endotherms that correspond to multistage transition, as reported by Rubin Cai et al. (66). The odd-even effect on the transition temperature is very much prominent in the studies of C. Ramireddy and coworkers (31) while working with two series of liquid crystalline polyesters.

Combined optical and thermal analysis:

Thermal transitions of liquid crystalline polymers are normally studied by a combination of DSC and visual observation on a hot-stage polarizing microscope. While DSC is run in a recorded manner and the actual transitions are determined from the recorded curve, an analysis by microscopy is generally based on subjective evaluations and descriptions of the observations.
Typical polarised optical micrographs of the molten liquid crystalline poly(ester-co-carbonate) (PEC) were presented by M. Kawbe et al. (70). A characteristic threaded texture of nematic mesophase were observed over the investigated composition range. The liquid crystalline transition temperature of PECs were found significantly low, compared with those of copolyesters based on biphenylene terephthalate and HBA. C. Ramireddy (31) has studied the liquid crystalline nature of the polymers by using a polarising microscope. Liquid-crystalline phase can be observed during both the heating and cooling of the material. Polymers containing terephthaloyl unit showed the formation of nematic mesophase, i.e. threaded schlieren texture. Polymers containing tricyclopentane unit were monotropic, i.e., the mesophase transition could be observed upon cooling from the isotropic melt. Barbera et al. (71) have synthesized five main-chain polymers containing benzene rings and conjugated double bonds in their structure and their phase behaviour was studied by optical microscopy and DSC. The polymers above their melting points afforded threaded schlieren optical texture for nematic melt. A series of thermotropic hydrocarbon liquid crystalline polymers based on triphenyl mesogen have been reported by Sung et al. (72). The polymer with n>2 exhibited smectic B and/or smectic E mesophases. DSC thermogram clearly indicated the transition from smectic E to smectic B phase and from smectic B to isotropic phase. For a series of polymers based on cyclo-octyl units with varying length of methylene units, only smectic phases could be detected (73). The morphology of two thermotropic polyesters with mesogenic units and flexible spacers along the backbones during isotropic and liquid crystallization transitions
were studied by Wang and his coworkers (74) by means of polarizing microscopy. These transition processes were found to be composed of the initiation of a new phase at local places of the old phase matrix and growth of the new phase domains.

1.10. Kinetics of Crystallization

1.10.1. Kinetics of crystallization of polymers:

To properly understand the origin of the structural features of polymers, consideration must be given to the mechanism and kinetics of crystallization.

The overall rate of crystallization is a function of the rate of nucleation and the rate of growth of the nuclei. The rate of nucleation generally increases with degree of undercooling (temperature increment below melting point). The rate of growth depends on the rate of diffusion of polymers from the molten phase to the growing nucleus and attains a maximum value fairly below melting point.

In kinetic measurements, which form the basis of crystallization studies, it is obviously vital to know the form of the development and if several forms are present the nature of the dominant one. Thus, if spherulites can be seen to develop in a crystallizing polymer at the same time as do crystallites, then if the latter grow more rapidly than the former, it is the nucleation and the growth of the spherulites which is of prime importance, because these are the rate determining steps.
Theories of polymer crystallization:

During crystallization of a polymer from the bulk, several experimental findings form the basis of three theories of polymer crystallization kinetics.

The first of these theories is based on work of Avrami (75). The second theory was developed by Keith and Padden (76) providing a qualitative understanding of the rates of spherulite growth. Most recently Hoffman and coworkers (77-81) developed the kinetic nucleation theory of chain folding and this theory continues to be developed even now. Together, these theories provide insight into the kinetics, not only of crystallization but also of several molecular mechanism taking part.

Type of nucleation:

Both homogeneous and heterogeneous nucleation are known in polymer crystallization. But the latter is the most predominant one as there are very few cases which involve extensively homogeneous nucleation where local order is created among small number of molecular units in neighbouring chains and to act as nuclei. Sporadic nucleation refers to nuclei formed homogeneously from the melt. Predetermined nucleation results from the number of heterogeneous nuclei present in the polymer. Often, integral values of Avrami Index \(n\) is also observed which complicates understanding of crystallization mechanism. In some cases nucleation can be partly homogeneous and partly heterogeneous.
Effect of temperature on crystallization rate:

In addition to nucleation effects, temperature can influence the crystallization rate by its effect on melt viscosity. As the melt viscosity increases, the mobility of the polymer chain decreases and crystal growth slows down. There is an optimum temperature for crystallization for many polymers. Above this temperature crystallization is limited by slow nucleation and below high viscosity. This selection of temperature in crystallization kinetic study is very much important.

Effect of thermal history on crystallization rate:

The rate of crystallization of a polymer can also be affected by its previous thermal history. There is evidence (82) that molecular order persists after the bulk of the polymer has melted and that their elements aid the nucleation process upon subsequent cooling.

Other factors affecting crystallization rate:

Heterogeneous nucleation (83) on the presence of heterogeneous medium in the polymer melt increases crystallization rate in general as has been observed by change in crystallization temperature and exotherms in isothermal crystallization measurements. Mechanical stress promotes crystallization by aligning polymer molecules, thus it can also affect crystallization rate (84, 85). Shear stresses has also been observed to increase the nucleation rate (86). Hence the bulk kinetics will follow a different course from the case where the nucleation is homogeneous.
1.10.2. Crystallization kinetics of liquid crystalline polymers:

The transition kinetics of liquid crystal polymers appear to be of great interest in order to control the effect of processing conditions on the morphology as well as the final properties of the material. Segmented liquid crystal polymers, having flexible spacers in the main chain have been extensively investigated because of their accessible transition temperatures and improved solubilities. These materials are semicrystalline and undergo the following phase transitions - crystallization from the mesophase and liquid crystallization from the isotropic liquid phase and also transitions between mesophases, if polymorphism exists.

The flexible polymers generally follow a chain folded mechanism, whereas rigid or semirigid polymers which frequently display mesophases, crystallize from their melt via aggregation of chain molecules (87).

The macroscopic overall crystallization process is based on the theory developed by Avrami. The theory stands on the following assumptions,

1) isothermal transition conditions, 
2) random nucleation, and 
3) growth rate of a new phase is dependant only on temperature, not on time.

Considering the nucleation rate and the growth geometry, the Avrami equation is expressed as,

\[ X(t) = 1 - \exp \left(-Kt^n\right), \]  

(1.1)
where \( X(t) \) is crystallinity percent at time \( t \),

\( K \) is a constant to the growth rate and

\( n \) is dependent on the nature of nucleation and geometry of crystal growth process.

Different Avrami exponent have been reported for different LCPs ranging from 1 to 4. This indicates that the crystallization kinetics of LCPs is influenced by the liquid crystalline phase itself. When \( n \) is equal to 1, it is often described as a process of instantaneous nucleation and rodlike growth. However, when \( n \) is within 2 to 4, it is described as a process of disclike or spherelike growth. This concept has been used to characterise the liquid crystallization of some nematic polymers. Since the smectic phase possesses two-dimensional order, the liquid crystallization of a smectic mesophase is often characterised by the \( n \) values ranging from 2 to 4 (88).

The kinetics of the liquid crystallization from the isotropic liquid and the kinetics of crystallization from different mesophases have been studied by various authors (89-100). The kinetics of phase transitions from isotropic state to the nematic mesophase of a thermotropic main-chain liquid crystalline polymer has been studied by Bhattacharya and coworkers (89) using DSC and optical microscopy. Avrami analysis of the data gives an exponent close to 1.0 which suggests a rodlike nucleation controlled growth. The values of the exponent \( n \) have been determined from the experiments performed by Lin and coworkers (90) with an aromatic thermotropic polyester to be
4 and 1 for crystallization and liquid crystallization respectively. Compared to crystallization, liquid crystallization rate showed a very weak temperature dependence in their work. It has generally found that massive structural rearrangements do not occur during crystallization and the structure of the solid crystals closely resembles that of the liquid crystals (91). The nematic to solid transition occurs with negligible volume change. Studies of the kinetics of mesophase formation and the three dimensional ordering from the mesophase of poly (alkyl terephthaloyl bis-(4-oxybenzoate)) with trimethylene and decamethylene spacers have been reported by Pracella et al. (93). Polyesters with same mesogenic units and hexa and decamethylene spacers have been studied by Joo and Kim (94). When the spacer is a trimethylene glycol, n was found to be 2 and for the decamethylene glycol polyester, it was found to be between 3 and 4. Hence the crystallization kinetics of LCPs is related to the length of the spacer and the efficiency of packing. Two series of very low n values have been reported by S.Z.D. Cheng (95) working with HBA/HNA copolyesters. They have suggested a diffusion controlled growth rate of the crystals. The crystallization process does not follow a constant radial crystal growth when it is diffusion controlled and in this case the apparent coefficient is considered as 0.5 n. Hence for one dimensional crystal growth n becomes 0.5 and for two and three dimensional growth it becomes 1.0 and 1.5 respectively. J. Grebowicz et al. (96) found similar values for n while working with PTFE. Jonsson et al. (101) reported that the process of crystallization follows the Arrhenius equation with an activation energy value of about 400-800 KJ/mole. The transition entropies and enthalpies of the copolymers were found
surprisingly low as reported by S.Z.D. Cheng. If the crystallization rate is high enough one may expect only nucleation (aggregation) as the rate determining step and the value of n must be close to 2 as previously reported by Warner and coworkers (102).

1.10.3. Data analysis for crystallization kinetics

The overall rate of bulk crystallization was analysed in terms of the previously stated Avrami equation,

\[ X(t) = 1 - e^{-Kt^n} \]

The parameters in equation (1.1) can be determined by taking double logarithm of this equation,

\[ \ln[-\ln(1-X(t))] = \ln K + n \ln t \]

Consequently a plot of double logarithm of the amorphous content as a function of logarithm of time permits the determination of n from the slope of the straight line. The method for determining K involves the use of crystallization half-time method. On normalized basis, the crystallization half-time \( t_{0.5} \) is defined as the time at which the normalized crystalline content is 0.5. The crystallization half-time method using equation (1.1) at \( t = t_{0.5} \) consists of the determination of n and K.

\[ S_{t_{0.5}} = \frac{n \ln 2}{2} \]

\[ K = \left( \frac{\ln 2}{t_{0.5}^n} \right)^{\frac{1}{n}} \]
$S_{t_1}$ is the slope of the curve of amorphous content as a function of logarithm of time at $t=t_1$.

The activation energy values involved in the phase transition processes were evaluated by using the Arrhenius equation

$$\frac{-dn}{dt} = Z.e^{-E/RT} \quad (1.5)$$

The negative slope of the $\ln(1/t^*)$ vs $1/T$ line represents the activation energy value where $1/t^*$ is the time at which the rate of crystallization is at maximum and $T$ is the crystallization temperature.

1.11. Effect on annealing on polymer morphology

1.11.1. Annealing of polymers

The annealing of polymers can be defined as a secondary process wherein the polymer is brought to a certain temperature, kept there for a time and then cooled to room temperature. The annealing of semicrystalline polymers may change the crystal structure, the degree of crystallinity, the perfection of the crystals, the orientation of both the crystalline and amorphous phase, their contiguous structural morphology and the number of tie chains between the crystallites (103, 104). Direct morphological changes are also observed on annealing bulk crystallised samples below their equilibrium temperature.

Polymorphism may result due to annealing crystalline polymer as its one crystalline form transforms into another. These transformation
may be due to a true crystal-crystal transformation or to partial melting and recrystallization, i.e., reorganisation of metastable crystallites. Several types of reorganisation process may be involved which in turn help to develop different crystalline forms in polymers. Thus, one form may consist of reorganised material while the other may have little organisation but still not be completely unaltered.

Annealing process is time and temperature dependent. At low annealing temperatures, which may appear to lie below the melting range the evidence of melting is less obvious though partial melting and recrystallization is operative involving low melting crystals. It melts first and recrystallizes at annealing temperature (105). It involves the concept of chain mobility within the crystals. But a different molecular mechanism has often been supported in this condition known as solid state thickening. The higher the annealing temperature, the longer is the recovery but it is always faster than the time for isothermal crystallization from the unperturbed melt at the same temperature. These leave little doubt that at least at these high temperatures, annealing behaviour is indeed a consequence of melting followed by recrystallization around residual crystallites acting as seeds.

1.11.2. Effect of annealing on liquid crystal polymers

Annealing of liquid crystal polymers between the glass transition temperature and the melting temperature leads to increased level of crystallinity and increased crystalline perfection analogous to the
behaviour of conventional semicrystalline polymers. Annealing at or above the melting point also leads to enhanced crystallinity and crystalline perfection. The effect of annealing at different temperature region on liquid crystalline polymers have been reported by various authors. The effects of annealing on the structure of liquid crystalline copolyesters have been studied extensively by A. Kaito and coworkers (106). In the course of annealing, not only is the lateral order of the random copolyester improved but also the random sequences crystallize into ordered crystals with higher melting temperatures. Jung-II-Jin et al. (107) worked with a series of sequentially ordered copolyesters prepared from terephthalic acid and isomeric naphthalenediyl bis(4-hydroxy benzoate)s. All the polymers were subjected to thermoannealing and accompanying changes in properties were examined by DSC, WAXD and solution viscosity. According to their findings molecular weight, melting temperature and degree of crystallinity have been increased by annealing the polymers at high temperature. M. Kawbe et al. (70) suggested that the lateral order and overall perfection of the crystalline structures can be developed by annealing the thermotropic LCP at a few degree below the liquid crystalline transition temperature for a long period. Butzba et al. (108) had reported a sharp increase in crystallinity during extended annealing of the PHB/HNA(58/42) copolymer. J. Economy and coworkers have annealed a sample of HBA/HNA(50/50) copolymer at 210°C for 24 hrs and examined by DSC. DSC thermogram showed an approximate 4x increase in transition enthalpy indicating an increased crystallinity. It was reported by L. Carpento et al. (109) that on increasing the annealing
temperature, a recrystallization of the mesogenic polyester in a more perfect form was observed and the melting temperature increased until it superimposed onto the clearing temperature. Makhija et al. (110) have studied the effect of annealing at temperatures below and above the melting point on the morphology of the copolyester of p-hydroxybenzoic acid, isophthalic acid and hydroquinone.

1.12. Effect of nucleating agents on Polymer morphology

Nucleation is of fundamental importance in crystallization which itself determines the basic characteristics of almost half of the modern polymeric materials.

It is generally admitted (111) that nucleation in polymers is of the predominated heterogeneous type and that crystallization from the melt initiates the heterogeneities such as catalyst residues and residual crystal fragments.

Several attempts (111-115) have recently been made to control the rate of crystallization and the morphology by the addition of very finely divided substances which promote abundant nucleation. The mechanism of action of these nucleating agents has not yet been understood clearly, though several attempts at modelisation (111-112) have been made.

The majority of the technical nucleating agents used are mica, talc and salts of inorganic and organic acids (e.g. sodium
benzoate) with a very high melting point. These nucleating agents do not behave as heterogeneous substrates in lowering the energy barrier towards crystal nucleation but dissolve in the polymer and react as true chemical reagents with the molten macromolecules to form the nucleating species. Considerable number of studies has been reported on the crystallization of PET, there is still a lack of sufficient information to understand the nature and mechanism of crystallization in nucleated PET (116). Recently, a few organic nucleating agents have been developed (117) which generally melt along with the polymer while being processed. Very few work has been reported so far on this type of nucleating agent used in crystalline polymers. Mitra and Mishra (118) have evaluated the effect of such an organic nucleating agent, dibenzylidene sorbitol (DBS) on PET. It has been found that DBS when incorporated into the polyester at a 0.5-1.0 wt% level, significantly lowers the induction period and reduces the half-time of crystallization. Mercier and coworkers (119) have established the new mechanism of nucleation on the basis of the effect of Sodium-2-chlorobenzoate on polyethylene terephthalate. They also observed similar behaviour between a range of reactive alkali metal salts and PET. In each case, the infrared spectra indicated the formation of ionic end group from which the nucleated polymer remelted. Mitra and Mishra (120) have also established the fact that the same nucleating agent when used beyond a certain level does not nucleate crystallization process. This is probably due to the formation of agglomerates of the nucleating agent beyond this level of incorporation.
It has recently been discovered (121), cojointly in the "Laboratoire des Hants Polymers" of the Université Catholique de Louvain (Belgium) and "I.C.I. Petrochemicals and Plastics Division Research Department" (Welwyn Garden City), that the mechanism of action of organic nucleating agents such as sodium benzoate and its derived salts, completely differs from the anticipated model, at least in the case of polyesters.

1.13. Main theme of the present work

One of the newly introduced members in the arena of high performance materials is the thermotropic liquid crystalline polymers. They overshadow their lyotropic counterpart because of their ability to produce highly oriented melt processed objects and to avoid the problem for selection of solvents. There is a variety of thermotropic LPCs with the variation in the constitutional units, i.e., the mesogens, the bridging groups and the functional end groups. The range of thermal stability of these mesomorphic materials can be altered according to demand by introducing flexibility or rigidity in the molecular chain. Several modes of such structural alteration are in practice. Generally the synthesis of liquid crystalline polymers involves a very high reaction temperature and a prolonged reaction time. At high temperature the sequential order is broken and other side reactions take place. In addition a suitable synthesis process should be developed to overcome the high energy requirements for polycondensation. Characterization of the polymers is also essential in order to control their performance characteristics in the field of application.
The morphology of liquid crystalline polymers are directly related to their crystallization behaviour. A knowledge of phase transitions and a study on the crystallization kinetics are essential for determining and controlling the morphology as well as the properties of the LC-polymers. The effect of annealing on these crystallized materials, particularly the frozen in strain and the change in crystallinity has established its importance in the area of present day research works.

Morphology of the LC-polymers can be controlled by the use of certain additives, which are often known as nucleating agents. Though there is a wide variety of nucleating agents available today, the selection of right type of these agents, their concentrations and the corresponding morphological changes should be investigated particularly with the development of newer type of LC-polymers.

In the light of the above discussion the following work has been undertaken in the present study.

A set of controlled structure thermotropic LC-polyesters with suitable mesogen and flexible spacers have been synthesised. A low temperature polycondensation technique has been adopted to maintain the chain regularity. The polymers have been characterized by conventional LCP-characterization techniques, which include FTIR spectroscopy, WAXD analysis, DSC and TGA, optical microscopy, thermo-optical analysis etc. for determining their chemical structure,
thermal stability, crystalline behaviour, phase behaviour and thermal transitions etc.

A systematic study has also been made on the crystallization behaviour of these polymers. The various parameters related to the kinetics of isothermal crystallization and the mechanism of nucleation and crystal growth have been ascertained.

Annealing study on these polymers has also been made at different temperatures and for different residence times in order to study the polymorphic transitions of the polymers and to improve their crystalline behaviour.

The use of nucleating agents on the morphology of these LC-polymers and their effect on nucleation has also been investigated.

Finally a new technique has been developed to manipulate the phase transition behaviour and the mesophase stability of the synthesised polyesters by introducing a small fraction of the amide linkage during synthesis. The resulting polyesteramides show good mesophase temperature control without affecting the thermal stability significantly.