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Synthesis and characterization of low-melting thermotropic liquid crystalline poly(ester-imide)s.

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SYNTHESIS AND CHARACTERIZATION
OF
LOW-MELTING THERMOTROPIC LIQUID CRYSTALLINE
POLY(ESTER-IMIDE)S.

SUNNY JACOB
AUGUST, 1994

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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ACKNOWLEDGMENT

I would like to sincerely thank Dr. Jerry M. Adduci for his encouragement and guidance towards the successful completion of this thesis project. I thank very much the members of my oral committee, Dr. Gerald Takacs, Dr. Kay Turner and Dr. Andreas Langner for their suggestions on the preparation of this thesis report. Additionally I thank the faculty and the staff of the Chemistry Department at RIT for their generous support and willingness to answer my questions. Above all I express my sincere thanks to the Department of Chemistry at RIT for providing the financial assistance.
Abstract

Two new series of low-melting liquid crystalline poly(ester-imide)s, (PEIM(s)) containing biphenyldiimide mesogen with a high aspect ratio was prepared by the polycondensation of 11-(3,3',4,4'-biphenyltetracarboxydiimido)-bis undecanoic acid with various aliphatic diols and methyl esters of hydroquinone and 4,4'-biphenol by melt polymerization. The mesogenic diimide diacid was prepared by reacting 3,3',4,4'-biphenyltetracarboxylic dianhydride with 11-amino undecanoic acid using the method of Augl and Wrasidlo. The synthesized polymers were characterized by Gel Permeation Chromatography (GPC), IR Spectroscopy, Dilute Solution Viscosity, Thermogravimetry (TGA), Differential Scanning Calorimetry (DSC) and Polarizing Light Microscopy (PLM). The data obtained from GPC indicated the presence of a wide distribution of molecular weights. The infrared spectra of the polymers showed multiple peaks due to the vibrational coupling of the imide carbonyl groups. The inherent viscosities ranged from 0.5 g/dL to 1.65 g/dL. Thermogravimetric analysis showed that these PEIM(s) have high thermal stability in both oxidizing and inert atmosphere. DSC and PLM studies indicated that these poly(ester-imide)s are semi-crystalline and the degree of crystallinity can be increased by annealing above glass transition. They showed all major thermal transitions. The DSC curves of these polymers showed crystal ordering exotherm(s), glass transition and melting endotherm(s). The glass transition temperature of the polymers decreased with increase in the number of methylene units. The melting point of the even polymers decreased from 136 °C (n = 4) to 122 °C (n = 12) and interestingly an opposite trend was noticed for 'odd' polymers. The melting point of the 'odd' PEIM(s) were lower than the 'even' ones. These polymers showed a definite odd-even effect in melting point. An additional melting endotherm was observed in the DSC heating curves obtained after annealing the samples at the crystal ordering temperature. This indicated that the title polymers exhibited an enantiotropic liquid crystalline behavior. The optical micrographs of the 'even' PEIM(s) observed between crossed polarizers after annealing indicated the presence of an ordered smectic phase below Tm2 and a less ordered smectic phase around Tm2. Formation of droplets near the clearing temperature followed by the formation of a coarse texture at a lower temperature in the case of 'odd' PEIM(s) are indicative of the presence of a nematic phase, below the isotropic transition temperature. Poly(ester-imide)s containing aromatic diols showed higher transition temperatures than those containing aliphatic diols. Multiple endotherms were evident in the DSC thermograms of poly(ester-imide)s containing aromatic diols. The optical micrographs of the aromatic polymers taken at temperatures around Tm were comparable to the fine scale versions of
the Schlieren texture. PLM studies and analysis of the cooling traces revealed that poly(ester-imide)s containing aliphatic diols have slow crystallization kinetics. The 'odd' PEIM(s) can be quench cooled from the isotropic melt to the isotropic glass. The rate of crystallization was found to be much faster in the case of polymers containing aromatic diols. The even and the aromatic poly(ester-imide)s were found to be more crystalline than the 'odd' ones. The poly(ester-imide) derived from aliphatic diol n = 7 showed unusual results in the DSC and PLM studies which is explained as a result of cross-linking or branching due to side reactions.
INTRODUCTION

*Liquid crystal* is a term that is now commonly used to describe materials that exhibit partially ordered fluid phases that are intermediate between the three dimensionally ordered crystalline state and the disordered or isotropic fluid state. Liquid crystallinity is often referred to as the fourth state of matter. Phases with positional and/or orientational long range order in one or two dimensions are called *mesophases*. The word meso was derived from the Greek word μησος, meaning middle. A material in this state is strongly anisotropic in some of its properties and yet shows a certain degree of fluidity of liquids. Molecules that have relatively rigid, elongated, or disc-like structure show propensity in forming mesophases. Depending on the detailed molecular structure, the system may pass through one or more mesophases before it is transformed into an isotropic liquid. The term mesomorphic is used to describe the structural attributes of a liquid crystalline phase, while the rigid groups that are capable of forming liquid crystalline phases are called mesogens.

Liquid crystalline (LC) order is a consequence solely of molecular shape anisotropy, such as found in rigid rod-shaped molecules or relatively stiff chain segments. Molecular asymmetry is a feature common to all LC materials. Asymmetry of molecular shape may be augmented by anisotropic inter-molecular forces. When the molecule contains aromatic units, the polarizability anisotropy of the phenylene group causes the intermolecular attractions which results in the parallel intermolecular alignment of the mesogens. For mesogenic molecules, there is a limit to the number of molecules that can arrange randomly in
solution or melt. When this critical concentration is exceeded, either a
crystalline or an ordered, liquid crystalline phase forms.

The wide spread application of low molecular weight (LMW) LCs
and liquid crystalline polymers (LCP's) lies in the fact that they possess
some unique properties not found in liquid or crystalline solid state. For
example, their morphology may be influenced by external magnetic or
electric fields, sometimes they change color with temperature, and some
exhibit extremely high optical rotation. At the same time LCs exhibit
fluidity of liquids and opaqueness of crystalline materials. One of the
major difference between liquid crystals and true isotropic liquids is that
liquid crystals appear cloudy where as isotropic liquids are clear. The
cloudiness is the result of scattering of light due to the fluctuation of the
preferred orientation of the molecules.

The electro- and/or magneto-optic properties of the different liquid
crystalline phases are exploited in the applications of LMW LC's. These
materials need only amazingly low energy to order and re-orient
themselves and are useful for detectors and indicators which require low
power consumption and detect very low energies with good resolution.
Liquid crystals are now used in displays for watches, clocks, calculators,
panel meters, and other digital displays, as well as point-of-purchase and
point-of-sale displays. Also, they are useful laboratory tools for gas-
liquid chromatography, absorption spectroscopy, and nuclear magnetic
resonance spectroscopy. They have been used in toys, artistic and
decorative materials.

Applications of liquid crystalline polymers usually depend on their
solid state structure and properties. The largest market for LCP's is
structural fibers, principally poly(p-phenylene terphthalamide), PPTA.
The desirable characteristics of PPTA fibers are high strength, low density, nonabrasiveness and dimensional and thermal stability. Applications of LCP fibers include protective fabrics such as bullet-proof vests and gloves, industrial fibers (ropes and thread), rubber reinforcement (radial tires), plastics reinforcement (structural composites), and asbestos replacements (brake linings, clutch facings, gaskets and packing). Molded LCP's have been used in electrical applications as surface mounted and fiber-optic connectors. Other uses of thermotropic LCP's include applications where chemical resistance is needed (tower packing, pumps and valves) and mechanical components requiring good wear resistance (pulleys, bushings and seals).

1.1 History

In March 1888, a young botanist named F. Reintzer,\(^1\) observed that esters of cholesterol appeared to have two melting points between which the liquid showed iridescent colors and birefringence. This observation was reported to Otto Lehman who was professor of physics at Aachen, who worked for some time in the field of crystal transitions, and above all had developed a polarizing microscope with a hot stage. He confirmed Reintzer's observations, and their collaborative work over the next few years laid the foundations of liquid crystal science. In 1889 Lehmann described the material as 'flowing fluids' and the following year as 'crystalline liquids'.\(^2\) The first synthetic liquid crystalline compound reported was p-Azooxyanisole, \(^1\)\(^3\)
In 1922, the year of Lehmann's death, Friedel published a monumental paper in which he introduced the terms 'nematic', 'smectic', and also 'mesophase', under the generic title 'liquid crystals' on the basis of optical studies. Liquid crystal science continued to mature, and synthetic chemists, particularly Vorlander, demonstrated the principles of molecular design which underpin the field. He thought about the possibility of liquid crystalline state in rigid polymer molecules, and as early as 1923 he pursued the concept of a liquid crystalline polymer. He studied the effect of increasing the length of liquid crystalline molecules by synthesizing rods with one, two and three benzene rings para linked through ester groups and noted their increasing transition temperature. He also found that poly(p-benzamide) would not melt, and reported it as a birefringent powder which chars without softening. In many respects, Vorlander can justifiably be considered as the father of polymeric liquid crystals.

During these years, there was an increasing interest in natural rod-like macromolecules which formed liquid crystalline phases when present in solution (lyotropic phases). Bawden and Pirie in 1937 made a key observation that solutions of tobacco mosaic virus (TMV), formed two phases one of which was birefringent. In the next 20 years or so, other naturally occurring viruses such as cucumber virus and potato virus were also added to the list. In 1941 Bernal and Fankuchen examined the liquid crystalline phase with X-ray diffraction while Oster in 1950 carried out light scattering experiments. In the same year Elliot and Ambrose reported the first synthetic liquid crystalline polymer, poly(γ-benzyl-L-glutamate) (PBLG) which showed liquid crystalline phases in solution. Although PBLG fibers were spun from the lyotropic phase by
Ballard in 1958, they were not developed into a product. The first commercially successful liquid crystalline polymer, Kevlar, an aromatic amide was developed in 1960’s by Kwolek of DuPont. Vorlander’s effort to make liquid crystalline polymers which would be stable without the addition of solvents was frustrated by the fact that the crystal melting points of the rigid chains increases rapidly with increasing chain length. The first thermotropic liquid crystalline polymer was synthesized by Jackson and co-workers at Tennessee Eastman in 1976.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{O} & \quad \text{C} \\
\text{CH}_{2} & \quad \text{CH}_{2} \\
\text{O} & \quad \text{O}
\end{align*}
\]

It was a co-polyester of PET and hydroxybenzoic acid. In the same year, Rovieli and Sirigu reported another thermotropic liquid crystalline polymer which was synthesized from a thermotropic monomer, p, p'-dihydroxy-α,α'-dimethylbenzaline with the corresponding acyl chlorides. There are now, in the 1990’s a number of mouldable liquid crystalline materials available in the market, The Vectra series from Hoechest Celanese being a leading example.

It was realized by Bernal and Fankuchen, that the mechanism of formation of liquid crystalline phases was associated with the high-aspect-ratio rigid character of the virus particles of the TMV suspensions. The first theoretical prediction that accounted for the observed behavior was given by Onsager in 1949. By using a viral expansion, he explained the observed biphasic nature of solutions of rigid molecules. This was followed up in papers by Isihara in 1951 and by Flory in 1956. Flory who adapted a some what different approach in which he
adapted his lattice model of conventional polymers to the rigid rod situation. They predicted that rod-like molecules would spontaneously order above a critical concentration that depended on the aspect ratio of the molecule. Later these theories were modified to include other effects such as polydispersity and partial rigidity.17

The involvement of polymeric materials has been largely a matter of adding active rod-like groups, onto flexible polymer chains. They can be added either as side chains or into the backbone itself. In 1978 Ringsdorf 18, Finkelmann and co-workers realized that rod-like side chains would only readily form mesophases if they were decoupled from the backbone by means of a short length of flexible chain acting as a spacer. Side chain liquid crystalline polymers is an interesting topic of current research and is now marked by a recent collection of papers edited by McArdle.19 Recently new thermotropic polymers have been developed with mesogenic cores arranged not only in the main chain or the side chain, but with rigid mesogenic groups parallel to the chain.20 Even discotic, or disc shaped mesogenic cores have been incorporated into polymers.21 It is now known that even "all hydrocarbon polymers" (polymer with no heteroatom on the backbone) with mesogenic groups and no polar groups show liquid crystalline properties.22, 23

1.2 Classification of Liquid Crystalline Systems

In order to understand the structure and properties of polymeric liquid crystals it is necessary to briefly describe and define several aspects of liquid crystallinity in small molecule compounds. Liquid crystallinity also known as mesomorphism can be broadly classified as lyotropic and thermotropic. Lyotropic liquid crystalline phases contain
non-mesogenic solvent molecules in addition to the mesogenic ones and the anisotropy is observed when the material is present in a suitable solvent above a critical concentration. Thermotropic materials give in bulk anisotropic melts in a particular temperature range on heating or cooling. Thermotropic liquid crystals can be further divided into two classes, *enantiotropic* and *monotropic*. Enantiotropic liquid crystals form mesophases upon heating from the solid phase where as monotropic liquid crystals form mesophases only upon super cooling the isotropic liquid phase below the melting temperature. In the former case, the mesophase is thermodynamically stable and can be observed on both heating and cooling. But in the latter case, the mesophase is metastable with respect to the solid and is seen only in the cooling regime.

Depending on the structure of the mesogen(s), the rigid molecules or the stiff chain segments can be oriented in the mesophase in more than one way giving rise to different liquid crystalline order. Following the nomenclature proposed originally by Friedel, they are classified broadly into three types: *nematic, cholesteric and smectic*.

The nematic liquid crystalline phase has a high degree of long range orientational order of the molecules, but no long range translational order (fig. 1. a). It differs from the isotropic liquid in that the molecules are spontaneously aligned with respect to a vector known as the director (n) which is denoted by an arrow. The degree of orientational order in liquid crystals is described by an order parameter S, which is an average of the function $1/2(3 \cos^2 \theta - 1)$. Where $\theta$ is the angle between the molecular axis and the preferred direction. The preferred orientation of the molecules usually varies from point to point in the medium (fig. 2).
Molecular arrangements in the three major Friedelien classes of liquid crystals: (a) nematic; (b) cholesteric (with a horizontal twist axis) and (c.i) smectic A and (c.ii) smectic C.

As shown in the figure in each domain the molecules are oriented with respect to the local director $n$, and the domains are then oriented with respect to the global director $N$. A uniformly aligned sample will be optically uniaxial, positive and strongly birefringent.

In the light microscope, nematic liquids show characteristic 'threaded' textures which originated from the Greek word ὑφέμια. The molecules in this case possess intermolecular forces that allow them to stay parallel to one another. For nematic, the order parameter range from 0.3 to 0.8. X-ray studies indicate that some nematics possesses a lamellar type of short-range order. The cholesteric phase is illustrated in fig. 1.b. It is equivalent to nematic which has been twisted periodically about an axis perpendicular to the director. The twist in a cholesteric arises spontaneously when the mesogenic molecules have a chiral center. The
twist may be right-handed or left-handed depending on the molecular conformation. The cholesteric phase is characterized by the order parameter (S) and the pitch (P). The pitch is the distance it takes the director to undergo a 360 degree rotation. The spiral arrangement of molecules in the cholesteric is responsible for its unique optical properties, viz., selective reflection of circularly polarized light and a rotatory power about a thousand times greater than that of an ordinary optically active substance. Optically inactive or recemic mixtures result in a helix of infinite pitch, and a nematic rather than cholesteric arrangement will be the result.

Smectic liquid crystalline phases, are named because their basic layer structure gives them a soapy feel which is derived from the Greek word σμέγμα. In reality, many soap and detergent molecules show lyotropic smectic phases. These structures arise from the amphiphilic nature of the molecule. The smectic phase, which is the most ordered, is characterized by both orientational and positional order. i.e., they have stratified structures, but a variety of molecular arrangements are possible within each stratification. The two most common variants are known as smectic A and smectic C and are shown in fig. 1.c. In smectic A, the molecules are upright in each layer with their centers irregularly spaced in a 'liquid-like' fashion. The inter layer attractions are weak as compared with the lateral forces between molecules and in consequence the layers are able to slide over one another relatively easy. Hence, this mesophase has fluid properties, though it is much more viscous than the nematic. Smectic C differs from smectic A in that the director of each layer is inclined at an angle \( \omega \) to the layer normal, this angle being identical for all layers. Additional smectic variant are also known, in which there is
increasing order. For instance in smectic B phases, the packing within the layer is on a two dimensional lattice, but again there is no lateral correlation between layers. Over a dozen other distinct modifications have been identified. In their book on smectic liquid crystals, Gray and Goody\textsuperscript{27} identify the following types of smectic phases:

\begin{itemize}
  \item A, A\textsubscript{1}, A\textsubscript{2}, A\textsubscript{d}, \tilde{A}
  \item B, B\textsubscript{hex}, B\textsubscript{2}, B\textsubscript{A}, B\textsubscript{C}
  \item C, C\textsubscript{1}, C\textsubscript{2}, \tilde{C}, C\textsuperscript{*}
  \item D, E, F, F\textsuperscript{*}, G, G\textsuperscript{*}, H, H\textsuperscript{*}, I, J, K
\end{itemize}

From geometrical considerations, Herrmann\textsuperscript{28} argued that there should be 18 distinct mesomorphic groups between the perfectly ordered crystalline arrangement and truly amorphous ones.

The liquid crystals of disc-shaped molecules generally referred to as discotic liquid crystals fall into two distinct categories, the \textit{columnar} and the \textit{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 different columns constitute a two dimensional lattice (fig. 3.a). The nematic phase has an orientationally ordered arrangement of the discs without any long range order (fig. 3.b). Unlike the classical nematic of rod-like molecules, this phase is optically negative.

![Fig. 3. Structural representation of: (a) the columnar phase and (b) the nematic phase of disc-like molecules.\textsuperscript{29}](image-url)
The above classification holds good for liquid crystalline polymers (LCP's) also. In fact, in LCP's the rod-like or disc-like small mesogenic molecules are fused into the main chain or side chain of the polymers. The nature of the mesophase depends rather sensitively on the backbone, the mesogenic unit and the spacers. With rod-shaped repeating units, mesophases similar to nematic, cholesteric and smectic types are observed.\textsuperscript{30} As with small-molecule liquid crystals the most simple polymeric mesophase is the nematic. Polymer molecules that are completely rigid rarely form mesophases (fig. 4.a), some examples such as poly(p-phenylene) and poly(p-phenyleneterephthalamide), PPTA exist. A chain that is too flexible will not form a LC phase, but given sufficient rigidity the chains will align with each other (fig. 4.b). Even though the chains wander to some extent in the mesophase, they will be straighter than would be expected for an isolated molecule, or in an isotropic liquid under the same conditions. The diagrams suggest that the distribution of orientation about their director will be more restricted in the polymer so that the quality of alignment will be better. Theoretical and experimental \textsuperscript{31, 32} indications suggest that the quality of alignment in the mesophase defined by the order parameter $S$, will be a direct function of the stiffness.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{diagram.png}
\caption{Schematic diagrams of nematic organization of molecules: (a) a nematic polymer with rigid chains; and (b) a nematic liquid crystalline polymer with semi-rigid chains. n is the director.\textsuperscript{33}}
\end{figure}
Another type of nematic phase has been recently discovered known as the so-called *biaxial nematic*. In this case the chain molecules with anisotropic cross sections are so organized in a mesophase that there is long range orientational order about all three orthogonal axes. In other words, not only do the molecules lie with their chain axis parallel, but there is also rotational correlation about this axis. This concept is illustrated for lath-like chains or fibrils in fig. 5.

![Fig. 5. Schematic representation of a biaxial nematic phase.](image)

As in the case of small molecules, the cholesteric mesophase is mainly shown by polymers that have chiral centers in the main chain. Fig. 6 shows the twist of the successive layers about an axis normal to the molecular director which thus follows a helical path. The pitch of the helix depends on the temperature and, in the case of lyotrophic systems, the polymer concentration. Cholesteric behavior can be induced in an otherwise nematic polymer by the addition of small-molecule chiral compounds. Such cholesteric polymer phases are called *induced cholesterics*. In the case of side-chain liquid crystalline polymer, the addition of side groups which are cholesteric as well as mesogenic onto a flexible chain tends to introduce too much order with the result that a smectic rather than a cholesteric phase is produced.
Fig. 6. The helical arrangement of the layers resulting from the twist of the successive layers about an axis normal to the chain axis.\textsuperscript{33}

Fig. 7.a & Fig. 7.b, respectively, shows the smectic organization of the mesogens in the back bone and the side chain of a polymer. At first sight it might seem that in smectic polymers, the chains could simply be aligned each other, in the same way as small molecules, although the lamellae would be much thicker. This does not generally occur for two
reasons. In the first place, unlike small mesogenic molecules, polymers have a distribution of molecular lengths so that any exact segregation of the ends of rigid chains into sharply defined layers is impossible. Secondly, as most liquid crystalline polymer molecules are not rigid rods on the scale of their length, the distance between the ends is likely to be shorter than their maximum length and variable. Smectic phases occur in polymers because of molecular details which are not apparent in a smooth worm-like model of a simple chain. Main-chain polymers in which rigid mesogenic sequences are separated by flexible sequences can show smectic behavior, as the two different types of sequence segregating so that they form layers normal to the chains. In the case of polymers with mesogenic side groups attached to the backbone through some flexible spacers, the backbone is likely to be accommodated in the regions between the mesogenic layers as shown in fig. 7.b.
With disc-shaped repeating units, some new kinds of mesophase structures have been found. For example, a polyester with (disc-shaped) triphenylene as the repeating unit in the main chain separated by flexible spacers forms a hexagonal columnar structure (fig. 8.a). On the other hand, rigid aromatic polyamides and polyesters with disc-shaped units in the main chain exhibit a different type of mesophase which has been described as a 'sanidic' (or board-like) nematic (fig. 8.b).

Fig. 8. Schematic representation of the mesophases of discotic polymers: (a) the hexagonal columnar phase; (b) the "sanidic" nematic phase made up of boards stacked parallel to one another; and (c) the columnar nematic phase.
The addition of electron acceptor molecules to discotic polymers results in the formation of charge transfer complexes which stabilize - or in certain non-mesomorphic materials, induce - mesophases. A new type of induced meso phase identified in such systems is the 'columnar nematic' shown in fig. 8.c.35

1.3 Molecular Design and Synthesis of LC Polymers

The structural requirements for the molecular design of low molecular weight liquid crystalline materials are also applicable to high molecular weight LC polymers. These include:

1) the presence of a rigid segment such as 1,4-phenylene, 1,4-bicyclooctyl, 1,4-cyclohexyl, etc,
2) a high length : breadth ratio (axial ratio or aspect ratio),
3) rigid central linkages such as -COO-, -CH=CH-, -CH=N-, etc,
4) presence of polar terminal groups such as -CN, -OCH3, -NO2, etc,
5) absence of bulkier substituents on the rigid segments, for e.g. lateral substitution causing a steric effect that results in twisting of the molecular structure about the inter-ring bond in a biphenyl derivative causes a very large decrease in nematic and smectic thermal stabilities,
6) branching of the terminal alkyl chains diminishes the liquid crystal tendencies,
7) an increase in the aspect ratio elevates the nematic - isotropic transition temperature,
8) crystallinity can be enhanced by attachment of weak polar groups such as C=O to the rigid segment,
9) the molecule must be flexible enough to have a low transition temperature, and
10) anisotropic molecular polarization.

The most basic construction is to simply link the mesogenic groups end to end to form a rigid polymer chain. They are known as *rigid-rod* LCP's. But this type of materials have a high melting point ($T_m$) and high liquid crystal - isotropic transition temperature ($T_{lc}$) and thermal degradation of the polymer often prevents the mesophase being observed at all. e.g. poly(hydroxybenzoic acid), PHBA \textsuperscript{36}

\[ \text{[---]} \text{--o--C--} \text{---]}_n \]

3

The reduction of transition temperatures into a useful working range without destroying the stability of the mesophase is the most important concern in the design of liquid crystal polymers. There are various pathways to solve the problem. Fig. 9 illustrates the wide range of molecular architectures that can be created through the combination of mesogens and other type of sequence within a polymeric system. One route is to make semi-flexible LCP's, by introducing flexible spacers between the mesogenic groups. Mesogenic monomers with terminal functional groups can undergo polycondensation to form the polymer. The polymerization step is chosen appropriate to the monomer used and products produced. For example, solution polymerization, melt polymerization\textsuperscript{37}, inter-facial condensation and ester exchange reaction can be used to synthesize polyesters. The interested reader is referred to a recent review by R. W. Lenz \textsuperscript{38} for more details. Other routes involve making the chains less stiff by introducing mobile linking units in between the rigid groups or attaching bulky groups or chains to the
Fig. 9 Different approaches in the design of Liquid Crystalline polymers.\textsuperscript{39}
mesogens. LC polymers of this kind, with the mesogenic group in the backbone are called *main-chain liquid crystalline* polymers.

Yet another important approach is to design *side chain LCP's* by incorporating the mesogenic groups as side chains of a flexible main chain through some flexible spacers. These polymers can be prepared by three different methods: 1) by the chain-growth polymerization of the corresponding vinyl derivatives, 2) addition of pendant mesogenic moieties to a preformed polymer, and 3) condensation polymerization of difunctional monomers that has pendant mesogenic groups. Many of the property differences observed between the side chain LCP's and main chain LCP's are due to the fact that the mesogenic group has much greater mobility in the side chain, resulting in a polymer chain that is also much less restricted in its motions.

Another way to bring down the transition temperature is to make it lyotropic by the addition of low molecular weight solvents. Among the novel designs, LCP's with mesogens both in the main chain and side chain are worth mentioning. These polymers have been prepared in both linear thermoplastic and cross linked elastomeric forms. 40

According to Finkelmann, nematic polymers are obtained in most cases, if the corresponding monomers exhibit either no mesophase or a monotropic nematic phase. Nematic monomers give mainly smectic polymers. This indicates that an increase in LC order and transition temperature occurs on passing from monomer to polymer and that we should be looking for monomers that only just favor the formation of nematic phases. In the case of combined side-chain main-chain polymers, nematic phases only occur when there is a mismatch between the length
of the spacer in the side chain and the main chain. Otherwise, smectic mesophases predominate.

1.4 Chain Modification and Structure Consideration on the Stability of LCP's

This section discusses briefly how Vorlander's idea for making LC polymers by linking LMW molecules can be extended so that liquid crystalline stability is observed in an optimum temperature range (a temperature range where the transitions can be observed far below the decomposition temperature, a temperature range where the polymer is easily tractable). This range mainly depends on the end use of the polymer. For example, a moldable LC polymer for a high temperature application would ideally have a melting point between 350 °C and 400 °C. It would have a LC melt between T_m and upper isotropic transition temperature without any thermal degradation. For low temperature applications such as optical fibers or as the active element of a non-linear optical device, where low temperature processing is possible, the polymer would be designed to have a T_m in the region of 200 °C with LC phase stability range at least 50 °C above this temperature.

Let us consider first the chain structure and equilibrium behavior of main chain liquid crystalline polymers. In thermotropic LCP's, the liquid crystalline phase transitions are observed only in a particular temperature range. It lies between the crystal melting point T_m or the glass transition temperature T_g (in cases where crystallinity is absent), and the upper isotropic transition temperature T_i. According to Flory and Ronca 41, for an undiluted system, a critical value of the axial ratio (length to diameter) is given by
\[ \chi_{\text{crit}} = \frac{L}{d} = 6.417 \]  

For straight and rigid polymer molecules, the value of \( \chi_{\text{crit}} \) will be far in excess of 6.4. But the question is, how the chain flexibility affects the effective axial ratio? In such cases another term, persistence ratio, \( \chi_p \), is commonly used.(\( \chi_p = \frac{q}{d} \) where \( q \) is the persistence length and \( d \) is the molecular diameter. Persistence length, \( q \), is a measure of the straightness of a chain molecule and is defined as the average projection of the end-to-end distance on an infinite chain in the direction of the first link. It is normally measured using the methods of either light scattering or small angle X-ray scattering with the polymer in dilute solution.) Table I. shows the pertinent values for some polymers. In fact, HPC and PBLG

<table>
<thead>
<tr>
<th>Table I. Persistence length, ( q ), and persistence ratio, ( \chi_p ) of some selected polymers</th>
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<tbody>
<tr>
<td>Polymer</td>
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<tr>
<td>Poly(vinyl acetate)</td>
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<td>Cellulose nitrate</td>
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<td>Hydroxypropyl cellulose</td>
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<td>Poly(benzyl-L-glutamate)</td>
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<td>Poly(p-benzamide)</td>
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shows LC properties whose $\chi_p$ values are way above 6.4. The crystallinity in PBA persists up to the decomposition temperature masking the liquid crystallinity. Others do not show any LC behavior. In cases where the axial ratios are smaller than the critical value, hard rod repulsion is not sufficient to explain the stability of the mesophase. According to a recent Flory-Ronca theory,\textsuperscript{42} asymmetric attractive interactions must be added to asymmetric repulsion.

Ordinary polymers are made up of linear sequences of monomer residues in which the main chain bonds undergo extensive internal rotation resulting in a symmetric random coil. Asymmetric shape can be obtained by using a flow field, special solvents, or by incorporating particular types of bonds. In PBLG,\textsuperscript{9} the peptide bond is fixed in its planar trans configuration by the double bond character and helicogenic solvents force all rotatable bonds into equivalent positions through hydrogen bonding resulting in liquid crystallinity. Asymmetric conformations observed in poly(alkyl isocyanates),\textsuperscript{10} is the result of severely restricted internal rotations.\textsuperscript{43}

\begin{center}
\begin{tikzpicture}
\node[draw,rectangle,inner sep=1pt] (node1) at (0,0) {O};
\node[draw,rectangle,inner sep=1pt] (node2) at (0.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node3) at (1,0) {O};
\node[draw,rectangle,inner sep=1pt] (node4) at (1.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node5) at (2,0) {O};
\node[draw,rectangle,inner sep=1pt] (node6) at (2.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node7) at (3,0) {O};
\node[draw,rectangle,inner sep=1pt] (node8) at (3.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node9) at (4,0) {O};
\node[draw,rectangle,inner sep=1pt] (node10) at (4.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node11) at (5,0) {O};

\draw[thick] (node1) -- (node2);
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\draw[thick] (node8) -- (node9);
\draw[thick] (node9) -- (node10);
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\end{tikzpicture}
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\begin{center}
\begin{tikzpicture}
\node[draw,rectangle,inner sep=1pt] (node1) at (0,0) {R};
\node[draw,rectangle,inner sep=1pt] (node2) at (0.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node3) at (1,0) {R};
\node[draw,rectangle,inner sep=1pt] (node4) at (1.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node5) at (2,0) {R};
\node[draw,rectangle,inner sep=1pt] (node6) at (2.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node7) at (3,0) {R};
\node[draw,rectangle,inner sep=1pt] (node8) at (3.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node9) at (4,0) {R};
\node[draw,rectangle,inner sep=1pt] (node10) at (4.5,0) {N};
\node[draw,rectangle,inner sep=1pt] (node11) at (5,0) {R};

\draw[thick] (node1) -- (node2);
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\draw[thick] (node9) -- (node10);
\draw[thick] (node10) -- (node11);

\end{tikzpicture}
\end{center}

10
The free rotation of the chain is hindered by the partial double bond character of amide groups and the steric interference between the n-alkyl side chain and the carbonyl group.

Asymmetric structures may also be achieved using bonds for which internal rotation occurs, but has no effect on flexibility. Para linked aromatic polyamides, 11, and polyesters are excellent examples of this kind. Rotation about the adjacent Ph-C and N/O-Ph bonds doesn't cause a bending of the chains. The chain is naturally extended like crankshaft with all the axes of rotation parallel to each other. Here again the amide

![Diagram](image)

or the ester bond is fixed in its planar trans configuration by the partial double bond character. Thus the presence of rotating and non-rotating bond in succession is key point that assures chain extension and asymmetry.

At the melting point, Tm, the crystal phase is in equilibrium with the melt and it is possible to write

$$T_m = \frac{\Delta H}{\Delta S}$$

(2)

Rigid-rod LC polymers which are made up of rigid mesogens typically possess very high melting points which makes melt processability difficult. The high melting point of rigid extended structures is related to the low conformational entropy and high value of $\Delta H$ resulting from
'better' intermolecular bonds in the crystal. The fact that the liquid phase in equilibrium with the crystal at $T_m$ may be a mesophase with long range orientational order is likely to have relative little influence on $\Delta S$ and $\Delta H$ for crystal melting. The melting temperature $T_m$ will be reduced, if the entropy change, $\Delta S$, on melting can be increased or the enthalpy change, $\Delta H$, is decreased or both.

There is no limit to the number of ways by which polymer chains can be modified to achieve this end. An effective way of decreasing $\Delta H$ is the addition of modifying units at random positions along the chain to give a random copolymer or the use of asymmetrical units at regular intervals along the chain to depress the diffusion of the crystalline solid by reducing the probability of finding a run of the crystalizable unit. Kinks or bends in the main chain (e.g. ortho or meta bisphenols, phathalic acid) act in a similar manner. The destruction of chain periodicity reduce both crystallinity, and melting point without much loss of mesogenity and upper transition temperature.

The effectiveness of co-polymerization in modifying the LC properties of polyhydroxybenzoic acid, PHBA is well known.44, 45, 46, 47 The xydar series 45 of moldable L. C. polymers, employs biphenyl units for modifying the benzoic ester molecules. Another example for a commercially available thermotropic system is the vectra series 46 of moldable polymers, in which naphthoic units are introduced at random along the backbone of PHBA. A very good example 47 showing the efficiency of random co-polymerization in reducing the $T_m$ is provided by the system based on p-hydroxybenzoic acid and equal amounts of terephthalic acid and ethylene glycol. Polymers based on p-hydroxy benzoic acid modified by random co-polymerization with isophthalic acid
and hydroquinone is a good method of introducing kinks in the backbone. Bisphenol A in which the adjacent phenylene groups are joined through a single tetrahedrally co-ordinated atom is very effective in introducing kinks. One important advantage of introducing kinked units, is that the crystallinity can be reduced to very low levels, and probably eliminated altogether. As a consequence, the mesophase stability is increased and the temperature necessary for melt processing is correspondingly decreased without the loss of any mechanical properties.

Introduction of another mesogenic group at alternating positions (e.g. use of hydroxynaphthoic or biphenyl in benzoic unit ) is not very effective in decreasing Tm. A substantial reduction can be achieved by alternating the basic mesogenic units with similar units which are singly substituted on the p-phenylene rings, and the effect is much enhanced when the side group is substituted either at the 2- (or 6-) position or the 3- (or 5- ) position. This effectively increases the chain diameter (decrease the persistence ratio ) and reduce the efficiency of chain packing within the crystal and hence the melting point and upper transition temperature. Berger and Ballauff studied the effect on Tm and Tlc-i of adding different length alkyl side chains on the ring of poly(phenyleneterephthalate) and were found that the transition temperature lowered on increasing the side chain length. For n > 16, a separate low transition was identified with the melting of segregated side chain material. In some respects, it is possible to view the side chain as a sort of bound solvent. Reduction of the volume fraction and lowering of the anisotropic interaction can be taken as the cause for the reduction of transition temperatures. Another approach is to use the (-CH2-)2 group as
the alternating unit. The trans conformation of this flexible unit does not bend the molecule, at the same time reduce the Tm.

One important way of increasing ΔS is by increasing the conformational freedom (conformational entropy) within the mesophase at the melting point. This is normally done by incorporating aliphatic flexible groups such as, methylene (-CH2-), ethylene oxide -CH2-CH2-O-, or siloxane [-Si(CH3)2-O-] in between the mesogens. By this approach, the chemical periodicity of the molecule is preserved although the repeat distance is increased.

Table II illustrates the effect of flexible spacers on the transition temperature of 4,4'-diethoxy-α-methylstilbene. The data can be looked upon in two different ways. The flexible spacers in the backbone can be considered as small molecule mesogens connected together leading to an increase in Tm by 93 °C and in Tlc-i of 102 °C or otherwise the flexible spacers can be seen as reducing the high transition temperature of a polymer built from the mesogenic core alone. The number of (-CH2-) units in the spacer has a marked influence on Tm and Tlc-i. Fig. 10 is a

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tm</th>
<th>Tlc-i</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>199 °C</td>
<td>223 °C</td>
</tr>
<tr>
<td>13</td>
<td>106 °C</td>
<td>121 °C</td>
</tr>
</tbody>
</table>
plot of $T_m$ and $T_{lc-i}$ against the number of (-CH$_2$-) units in the spacer of homopolyesters of 4,4'-dihydroxy-a-methylstilbene and aliphatic acids.

Fig. 10. Plot of $T_m$ (●) and $T_{lc-i}$ (○) against the number of -CH$_2$- units, n in the flexible spacer of homopolyesters of 4,4'-dihydroxy-a-methylstilbene and aliphatic acids.

The odd even effect of the spacers is obvious from the graph. Both $T_m$ and $T_{lc-i}$ are higher when there are even number of -CH$_2$- units. This can best be understood by the close packing of the all-trans conformation of even numbered -CH$_2$- units. The planar zig-zag conformation is straight and has the lowest energy of any conformations, and is the most likely conformation in both crystalline and LC phases. As shown in fig. 11,

Fig. 11  Diagram showing the necessity of an even number of -CH$_2$- units to keep the axes of the mesogens parallel.
only the all trans even sequence can connect two mesogens without introducing a kink. Also it is evident that the mesophase stability decreases with increasing length of the spacer, and at n=12, Tlc-i the first dips below Tm and the LC phase is lost.

Polyethylene oxide 51, 52 spacer gives much the same trend as that of methylene spacers. Polysiloxanes because of their greater flexibility and larger diameter, appear to be much more effective in reducing the transition temperatures than the methylene and ethylene oxide spacers.

While these modifications are suitable for decreasing the Tm and increasing the melt processability of the polymers, they have an adverse effect on the mechanical properties such as tensile strength, flexural modulus, flexural strength, etc. The mechanical properties as well as the melting point (Tm) and glass transition (Tg) decrease significantly as the length of the flexible spacer increases.

Several studies have shown the importance of monomer sequence distribution on mesophase behavior and stability. Changing of the direction of the ester linkages in a chain affects the transition temperatures, the range of mesophase stability and in some cases even the mesophase texture.53, 54

Upon mesophase formation, the melt viscosity of the thermotropic LCP's will be reduced considerably. Fig. 12 shows the effect of temperature on the melt viscosity of poly(butylene 2,6-naphthalenedicarboxylate), PBN/50 mol% trans-4,4'-stilbenedicarboxylic acid, SDA thermotropic co-polyester.55 The minimum in the melt viscosity - temperature plot indicates the temperature at which there is maximum mesophase order. The lower melt viscosity is advantageous for
melt processability such as injection molding since less pressure would be required to produce more detailed parts. The morphology of the melt processed articles is dependent on deformation and thermal histories. Extensional flow produces fibrillar structures with high orientation in the machine direction. Flows with complicated stress distribution and temperature gradients yield complicated morphologies. Chung 56 and Ide 57 have discussed about the melt extrusion of LCP rods and films, respectively.

1.5 Characterization of Liquid Crystalline Polymers

Identifying the mesophase is an important step in the characterization of a liquid crystalline polymer. A single method cannot give a conclusive idea about the mesophases in a LC polymer. More than one technique may be needed to correctly identify the phase transitions, stability regions, and the morphology of the LC phases. Differential scanning calorimetry (DSC), optical microscopy, X-ray diffraction,
miscibility studies and induced molecular orientation studies are some of the common techniques used to gather information about the mesophases.

1.6 Differential Scanning Calorimetry (DSC)

DSC is a standard technique used for measuring transition temperatures and also enthalpy changes at these transitions. Phase transitions such as crystal $\leftrightarrow$ nematic, or liquid crystal $\leftrightarrow$ isotropic which occurs either by an input of additional thermal energy or output of excess thermal energy show up in the DSC thermogram as endotherms or exotherms on heating or cooling. Although transition temperatures can be easily found from the DSC traces, obtaining quantitative data for $\Delta H$, may not always be straightforward, as in most cases the peaks may not be baseline resolved. The position of the maximum of the peak is commonly taken as the transition temperature. The area under each peak after baseline correction gives the value of enthalpy change at that temperature.

As shown in fig. 13, the differential scanning calorimeter consists a reference pan, and a sample pan containing a few milligrams of the

![DSC schematic](image)

Fig. 13. Schematic representation of a typical DSC measuring cells.
material under study. The two pans are provided with individual heaters so that they can be maintained isothermally as they are heated or cooled at a linear rate. The differential power thus indicates the heat absorbed or liberated by the specimen on heating or cooling, and the output of the equipment is a plot of $\delta H/\delta t$ against time. In the case of constant heating or cooling rates, it is effectively $\delta H/\delta T$ against temperature.

The DSC thermogram of the thermotropic co-polyester formed by the transesterification of poly(ethylene-1,2-diphenoxyethane-p,p'-dicarboxylate) with p-acetoxy benzoic acid is given in fig. 14.58 As seen in the figure, the DSC curves of LCP's may show the glass transition, cold crystallization exotherm, melting endotherm and mesophase-isotropic liquid transition endotherm. The mesophase-isotropic, mesophase-mesophase and mesophase-solid transitions are reversible on cooling, where the mesophase-solid transition is seen to be much more

![DSC curve](image)

**Fig. 14.** DSC curve of Co-polyester formed by transesterification of poly(ethylene-1,2-diphenoxyethane-p,p'-dicarboxylate) with p-acetoxy benzoic acid.
prone to super cooling than the isotropic-mesophase transition (See fig. 15). Only the lowest temperature mesophase can be frozen into the glassy state. The mesophase-isotropic transition is not much affected by changes in heating or cooling rates. 59, 60

Many polymers have $\Delta S$ and $\Delta H$ values at $T_m$ and $T_{ic-i}$ larger than those determined for LMW molecules. 61, 62 This indicates that at least a portion of the flexible spacers participate in the ordered regions of the macromolecule. In most cases, the melting transition shows a surprisingly small $\Delta H$ of melting which indicates that the crystal structure of the polymer cannot have a high packing density or order in the solid state. 59 LCP's show dramatic annealing effects with the loss of solid-solid transition and changes in temperature, shape and area of the endothermic/exothermic peaks. The longer relaxation times for polymers
and the lack of positional 'memory' of polymer segments result in this behavior. Monotropic mesomorphism is rarely found in LCP's.

Transition from the solid to the first LC phase may be accompanied by several first order transitions (See figure 15). Multiple transitions may be due to i) interconvertible forms of the polymer, which differ only in the degree of crystal size and perfection. ii) differences in crystal morphology (e.g., folded-chain crystals and partially extended chain structure) iii) true polymorphism or iv) solid- mesophase and mesophase-mesophase transitions. This makes it difficult to arrive at a conclusion regarding the nature of the transitions based only on the DSC data. The true nature of the transitions can be established only through a combination of optical studies and/ or X-ray diffraction investigation or some other supporting data.

1.7 Polarizing Light Microscopy

The polarizing light microscopy (PLM) can be used to identify the liquid crystalline phases, characterize molecular order and quantify the distribution of defects in the LC polymer. The textures observed with light microscopes provide some clues regarding the molecular order in the LCP's. The term, texture as used by Friedel, designates the picture of a thin layer of LC material sandwiched between glass plates observed by means of a microscope usually in a linearly polarized light. The details of the optical textures are highly dependent on the mesophase type, sample thickness, and surface treatment of the glass among other factors. The features of the various textures are caused by the existence of different kinds of defects. For preliminary characterization, PLM studies are now commonly used to identify the LC phases in LMW LC's and LCP's. The
observed texture is compared against an atlas of standards obtained from materials for which the symmetry of molecular order is known already.63, 64

When LC specimens are viewed between crossed polarizers, it is the position of extinction bands, and how the positions change as the crossed polars are rotated, that is used to find the point-to-point variation in molecular orientations. Consider a monodomain sample viewed between crossed polars in monochromatic light (fig. 16). The elliptical outline represents the intersection between the optical indicatrix and specimen plane. The SS and FF lines in fig. 16 shows the slow and fast vibration directions in the sample. \( \theta \) is the angle that the polarized light makes with the principal axes of the specimen. The light transmitted by the polarizer is resolved into the vibration directions of the specimen. Propagation through the sample introduces a phase difference between the component rays, because the two vibration directions are associated with different refractive indices, \( n_1 \) and \( n_2 \). Both the components are resolved into the transmission direction of the crossed analyzer and are

![Diagram showing the geometry](image)

**Fig. 16.** Representation of the geometry relevant to deriving equation (3).65
transmission direction of the crossed analyzer and are then superimposed.

The transmitted light intensity, I, for light of unit intensity and wavelength L on the specimen of thickness d is given by

\[ I = \sin^2(2\theta) \sin^2 \left[ \frac{\pi d}{\lambda (n_2 - n_1)} \right] \]  

(3)

The difference \( n_2 - n_1 = \Delta n \) is known as the birefringence. From this equation, an anisotropic material in which \( n_2 - n_1 \) has a definite value is expected to appear light when viewed under crossed polars. The differences in the refractive indices in the perpendicular and parallel directions is responsible for the different textures. The above equation predicts that a sample between crossed polars will appear dark, if i) the specimen is optically isotropic, i.e. \( n_2 - n_1 = 0 \). It will also remain dark if it is tilted about a horizontal axis, ii) the specimen is optically anisotropic and is being viewed along an optic axis, here again the birefringence is zero, But it will transmit light when tilted about an axis, iii) the specimen is anisotropic and its vibration directions are parallel to the transmission direction of the polars. The sample should appear light if the crossed polars are rotated or the specimen is rotated, iv) the specimen is optically anisotropic and is being viewed in monochromatic light and the combination of specimen thickness and birefringence represents a path difference of integral wavelength for the two refracted rays, i.e. \( d(n_2 - n_1) = m \lambda \). The specimen should appear light if the illuminating wavelength is changed.

The energy required to deform an LC material is so small that even the slightest perturbation can distort the structure profoundly. So when a LC material placed in between glass plates is examined under a
polarizing microscope, one rarely see the familiar interference figures expected from the anisotropic structures shown in fig. 1.a, b and c. Instead one usually obtains a rather complex optical pattern.

The identification of LC phases in a LCP use the same methods developed for small-molecule mesophases. The nematic phase exhibits threaded and/or schlieren texture (fig. 17) when viewed under the PLM. 67, 68, 69

On cooling the isotropic melt, the nematic phase begin to separate near the clearing temperature in the form of typical droplets, which after further cooling, grow and coalesce to form large domains. Nematic droplets characterize a type-texture of the nematic phase. The schlieren textures display dark brushes which corresponds to the extinction positions of the mesophase, i.e., line defects along which there is no local

![Fig. 17. A Schlieren texture typical of a nematic phase seen between crossed polars. Points A and B shows the two fold and four fold brush arrangements.](image-url)
director. It can be seen from fig. 17 that, at certain points two brushes meet (point A), at others there are four brushes meeting (point B). These points indicates singularities, i.e. disclinations in the structure. In an LC, a disclination is a discontinuity in the orientation.

The disclination strength ISI, is related with the number of dark brushes meeting at one point as

\[
\text{ISI} = \frac{\text{number of brushes}}{4} \quad (4)
\]

The characteristic appearance of a disclination under crossed polar is a stationary point singularity from which two or four brushes radiate, and the brushes rotate as the polars are rotated. The sign of S is positive when the brushes rotate in the same direction as the rotated polarizers and negative when they turn in the opposite way. Observation of points with \( S = \pm 1/2 \) can unambiguously be taken as a nematic phase, even though some nematic schlieren textures have \( S = \pm 1 \). Close analysis of the disclination lines in some polymeric nematic phases exhibiting threaded structures showed that a massive organization of macromolecules occurs as the temperature is raised.\(^{70, 71, 72}\) On increasing the temperature, a large number of threads are observed soon after melting, and they become loose and decrease in number on increasing the temperature of the melt. At elevated temperature most of them form closed loops.

Other characteristics of nematic phase are, the intense movement within the melt and scintillation effects due to Brownian motion. Another texture called homeotropic texture \(^{69, 71, 72}\) is observed when the long axes of the mesogenic molecules are at right angles to the glass surfaces. Such samples show no birefringence in orthoscopic observations when viewed vertically. On slightly touching the cover glass, the dark field of
view brightens instantly, distinguishing the homeotropic from the isotropic texture. All textures observed for nematic can easily be quenched and super cooled to room temperature.\textsuperscript{68, 69, 71, 73}

Some main chain thermotropic co-polyesters \textsuperscript{74, 75} that are found to be nematic, seldom show clearly defined optical textures. These textures are on such a fine scale that most of the optical microscopes cannot resolve them as seen in fig. 18.\textsuperscript{76} In some circumstances these textures may appear as the fine scale versions of the schlieren texture. The absence of obvious point singularities may be explained as the lack of sufficient resolution. The textures are reluctant to coarsen in the melt although they can be seen to be mobile at sufficiently high temperature. X-ray diffraction studies \textsuperscript{77} indicate that the samples are anisotropic both

![Optical micrograph of a typical fine scale texture of a random co-polyester. crossed polarizers.](image)

in regard to structure and properties, even though the polymers show a lack of overall preferred orientation of the optically anisotropic regions.

Biaxial nematics (one in which there are correlation of molecular orientation about all three axes) can be readily identified from the biaxial
symmetry of their optical properties. The standard method of determining whether a crystal is optically uniaxial or biaxial is through observation of interference figures in the polarizing microscope using transmitted light. The figures are observed by illuminating the specimen with highly convergent light and inserting a so-called Betrand lens below the eyepiece; this permits observation of back-focal plane. The optical diffraction pattern of the sample is known as a conoscopic image. For a uniaxial material, the figure (fig. 19. a) consists of a four-fold dark cross coupled concentric circles, and for a biaxial sample the symmetry of the conoscopic image is two-fold (fig. 19. b). For more details the reader is referred to optical crystallography by E. E. Wahlstrom.78

![Fig. 19. Optical interference figures of: (a) a uniaxial sample viewed along the optic axis of; (b) a biaxial sample viewed along the bisector of the angles between the two optic axes. The crossed polars are aligned orthogonally with the page.]

The high viscosity of the smectic melts makes it difficult to achieve identifiable characteristic textures. LCP's show several variants which closely resemble the focal conic (fig. 20.a ) and fan shaped (fig.20.b) of smectic A and C modifications of LMW LC's.79, 80, 81, 82
Fig. 20. Typical smectic A and smectic C textures: (a) the focal conic - polygonal texture; (b) Simple fan shaped texture.

Frequently, a fine granulated texture of ordered domains as shown in fig. 21 is observed. This texture coarsens on annealing into a focal-conic fan texture. This is characteristic of smectic A phase. Addition of chiral compounds to certain smectic C polyesters cause the formation of the typical twisted smectic textures (fig. 22. a & 22. b).
Fig. 22. Twisted smectic texture obtained by the addition of: (a) terephthalidene-bis-(4-(+)-4'-methylhexyloxy) aniline; (b) 4'-
(2-methylhexyloxy) biphenyl-4-carboxylic acid to the SC
phase of a homopolyester.

The striations can be explained as the periodicity of layers with equal
twist angle. the separation of the stripes corresponds to the half-pitch of
the smectic screw.

In the case of polyester of p,p'-bibenzoic acid with hexamethylene
diol, the smectic liquid comes from the isotropic one in the form of
batonnets (fig. 23) which coalesce and grow into focal-conic texture.79, 85

Fig. 23. Smectic batonnets observed at 229 oC for a homopolyester of p-p'
bibenzioic acid with hexamethylene glycol as seen through
crossed polarizers.
These observations are true for smectic A or smectic C mesophase, but, usually the smectic C batonnets show regions with different interference colors.

A Chevron texture 79 (fig. 24) also called myclinic texture with typical transition bars are observed on cooling from the nematic state of a polyester prepared from di-n-propyl-p-terphenyl-4,4'-carboxylate and tetramethylene glycol. Such texture generally appears in the temperature range immediately below the nematic-SA or nematic-SC transition. Bosio et al 86 identified the nematic and S_A mesophases for some polymers based on p-terphenyl mesogens.

![Chevron Texture](image)

Fig. 24. Chevron texture observed upon cooling from the nematic state of polyester prepared from di-n-propyl-p-terphenyl-4,4'-carboxylate and tetramethylene glycol.

Cholesteric LCP's are characterized by a planar texture with oily streaks as shown in fig. 25. 87 In the planar structure, they can show bright reflection colors. Some cholesteric materials 88 with high twist may yield non planar fan-shaped, focal conic or polygonal textures. This
makes it difficult to identify cholesterics or smectics based on texture. However, by adding either a low molecular weight nematogen or a nematic polymer, the cholesteric pitch can be increased and planar texture can be observed.

As there is much room for misinterpreting the observed contrast, PLM is seldom used as a conclusive method of characterizing the mesophases of LCP's. Some of the limitations are, i) in the case of multi-component systems, a liquid crystalline phase can only be detected microscopically, if the volume fraction and the degree of coarsening result in a resolvable micro structure, ii) in some occasions, the specimen shows a paramorphotic texture - a texture that is inherited from the parent phase. As the transitions between LC phases are the result of instantaneous molecular rearrangements, the immediate post-transition texture may not be easily distinguishable from its pre-transition counterpart. Stable textures characteristic of the new phase may require long time, sometimes weeks to form, iii) some materials crystallize to give a
micro structure that may be mistaken for the mosaic texture of smectic D. This can be tested by reheating the sample as soon as the mosaic texture is formed. If the transition is not reversed at a closer temperature, the texture formed can be attributed as due to crystallization.

All these ambiguities can be clarified by using some complimentary characterization techniques like X-ray diffraction as it gives a direct measure of the order at the molecular level.

1.8 X-ray Diffraction

The structure of an ordered crystal can be easily described using three positional parameters and appropriate thermal parameters per atom. These parameters are normally obtained from a detailed X-ray, electron or neutron diffraction studies.

X-ray diffraction is one of the most powerful technique for revealing the internal structure of materials where the radiation wavelength is of the order of intermolecular spacing, diffraction patterns can give readily interpretable information about the presence of long range positional order, the relative molecular position, the quality of preferred orientation with respect to an external axis and details of crystal structure and perfection. X-rays are preferred in most cases, as they require comparatively unsophisticated equipment and need only sample dimensions on the millimeter scale.

One of the principal equations of crystal diffraction is the well-known Bragg equation,

\[ n\lambda = 2d \sin \theta \]  

(5)

where \( n \) is the order of diffraction, \( \lambda \) is the wavelength, \( d \) is the distance between the diffracting planes and \( \theta \) is the diffraction angle (fig. 26.a).
Incident beam

Semi-apex angle of diffracted cone = \( \frac{30}{3} \)

Poly cryos Hine ample

Diffracted cones of radiation correspond to differently spaced planes in the crystal structure

Fig. 26. Illustration of: (a) the phenomenon of diffraction; and (b) diffraction in a polycrystalline sample.

The equation is based on the fact that the ray will diffract through a defined angle after interacting with a set of standing waves in electron density, i.e. the planes. A monochromatic beam directed at a perfect single crystal at an arbitrary orientation is unlikely to produce any diffraction patterns. However diffraction patterns can be obtained, if one uses a sample which consists of many crystals in all possible orientations, as a result of diffraction by the correctly oriented crystals. Such diffraction patterns (fig. 26.b) appear as a set of concentric circles. The radius of each circle gives the value of \( \theta \), from which \( d \), the spacing of the diffracting planes can be calculated.

For powder samples the well-known Debye-Scherrer technique is used. In powder diffractometry, the one dimensional pattern corresponds to the radial scan through the rings. It gives all the reticular spacing but no information about the spatial orientation of the planes. An example of such a pattern is given in fig. 27.89 When the sample is non-crystalline and possesses only short range positional order, the diffracting maxima
Fig. 27. Powder diffraction pattern and molecular packing in the ordered crystal phase of Isobutyl-4-[4-phenylbenzilideneamino]cinnamate. This substance shows the phase behavior: crystal-SE-SB-SA-N for the ordered crystal phase. Molecular packing and diffraction pattern are very diffuse, even though the mean molecular spacing can be obtained from the peak positions. For isotropic liquids, only diffuse diffraction peaks are observed and the structure can only be described in terms of a radial distribution function, which for a molecular liquid contains no atomic detail. By convention, the axis on the diffraction pattern parallel to the rotation symmetry axis of the sample is known as the meridian, and the one at right angles is called the equator.

Based on the X-ray diffraction patterns observed at large diffraction angles, the mesophases can be divided into three groups. The first group is made up of the disordered phases (N, SA and SC) which give only one diffuse, broad diffraction maxima. SE, SB, SH and SG form the second group, whose diffraction patterns one or few sharp Bragg reflections instead of a diffuse ring. The SF and SI have intermediate properties between the two groups. By large diffraction angles mean,
angles of the order of $20^\circ$ and small diffraction angles are taken to be the order of $3^\circ$.

Diffraction is a powerful technique for the characterization of LCP's where the sample has some degree of preferred orientation with respect to an external axis. A single diffraction pattern can provide information about the layers, their orientation and the perfection of their positional and orientational order.

X-ray diffraction patterns of unoriented LCP samples can be very useful in distinguishing between a number of mesophases, but this is not always true. X-ray patterns of semi-flexible main chain polymers are often too diffuse to be of help for identification of mesophases, especially in the case of unoriented nematic and cholesteric. Nevertheless, the literature reports X-ray diffraction patterns which are compatible with a nematic structure.\textsuperscript{52, 58, 73, 92, 93} They are characterized by a diffuse halo (fig. 28) at wide angles arising from the intermolecular spacing perpendicular to the long axis of the molecules. At small diffraction

![Fig. 28](image)

Fig. 28  Typical X-ray pattern of an unoriented nematic liquid crystal.
angles nematic patterns may contain a diffuse ring corresponding to the distances which are close to the maximum molecular length. Such diffuse rings indicate that there is no order in the direction of the long molecular axis. Blumstien et al.\textsuperscript{93} reported from X-ray studies that even more ordered smectic phases exist in semi-flexible main chain LCP's. They reported from X-ray patterns that poly(p-p'\textsuperscript{'}-benzilidiene aminophenylsebacate) and poly(4,4'-diphenylsebacate) exhibit a S\textsubscript{B} and its tilted modification. The patterns were characterized by a sharp central and outer ring which indicate a periodic order within the lamellae. But this assignment is in conflict with Strzelecki's work\textsuperscript{94}, which reported poly(4,4'-diphenylsebacate) to be nematic. Based on texture observation and X-ray studies Bosio et al.\textsuperscript{86} reported a smectic C smectic A and nematic phases for the semiflexible main-chain polyesters based on terphenyl mesogens. The X-ray diffraction pattern showed a sharp inner ring along with four sharp outer rings which are consistent with the formation of such a highly ordered mesophase.

Ambiguities regarding the mesophases in unoriented samples can be removed to some extent by analyzing the X-ray patterns of oriented samples where ever possible. If the sample can be obtained in the form of an oriented monodomain, the X-ray pattern will give more detailed structural information.\textsuperscript{90, 91} Oriented nematic phase \textsuperscript{58, 95} can be prepared by cooling the isotropic liquid in a strong magnetic field. Oriented S\textsubscript{A} and S\textsubscript{C} may be prepared by careful cooling from the nematic phase. Another method for preparing monodomains of more ordered phases is by careful melting of either a single crystal or an oriented fiber.
Fig. 29 shows the typical X-ray pattern of the main types of oriented nematic phase.

Fig. 29. Schematic X-ray pattern of a classical oriented nematic phase.96

The anisotropy is clearly indicated from the two symmetry directions. The dominant feature is that the outer diffuse halo in the case of powder samples is split into two crescents symmetrical about the equatorial plane. These features are qualitatively the same for all materials studied, but differ quantitatively in the length of the arc, which indicates the degree of parallel orientation. The scattering about the meridian differs qualitatively between the different types of materials showing that the molecular packing in the nematic phase varies with the polymer. Along the meridian usually one can see arcs or short bars which are due to intramolecular scattering and their position correspond to repeat distances of the order of the repeat unit length. As their intensity is smaller than that of the strong equatorial crescents, over exposure of the films is needed to clearly see them in the pattern.58, 95, 97 X-ray diffraction studies have revealed some other interesting aspects (e.g. the identification of a different nematic phase known as cybotactic phase) about the nematic phase.58, 95, 98
Fig. 30 shows the relationship between a smectic C structure and the various features of resulting fiber diffraction pattern.99

![Diagram showing relationship between smectic C structure and fiber diffraction pattern.]

Fig. 30. A schematic diagram showing the relationship between a smectic C structure and the various features of the resulting fiber diffraction pattern.

The diffuse equatorial maxima indicates short range positional order of the chains within the smectic layers. The degree of arcing is related to the order parameter. The thin, concentric diffraction arcs from layers indicated long range positional order. The two sharp small angle reflections along the meridian can be attributed to the regular smectic layer distance.

The X-ray patterns of well aligned samples of polyester prepared from di-n-propyl-p-terphenyl-4-4'-carboxylate and diols, obtained by the careful melting of oriented fibers were essentially the same as that for a smectic A phase.86 The layer spacing was found to be significantly smaller than the repeat unit length, suggesting a tilt angle relative to the normal. The smectic phase of the polymer was miscible with the smectic
C of standard materials, which is again an indication of the smectic C configuration.

Fig. 31 is a powder diffractometer scan of a liquid crystalline polymer which has partially crystallized. The sharp peaks represent the crystalline component, where as the diffuse maxima corresponds to the LC matrix. The relative areas under the diffuse and sharp parts of the scan can give the degree of crystallinity.

![Diffractometer Scan](image)

**Fig. 31.** A powder diffractometer scan of a thermotropic liquid crystalline polymer.

### 1.9 Miscibility Studies

Another important method for identifying the mesophase of a liquid crystalline material is by studying the miscibility of the unknown with a LMW reference compound of known mesophase. This method was developed by Sackman, Arnold and Demus and is based on the postulate that isomorphism is indicated, if a binary system exhibit a liquid crystalline phase that extends without interruption over the entire composition range. On the other hand, complete miscibility of the same type may not occur for every binary system, perhaps due to endothermic
endothermic mixing. So an uninterrupted miscibility or formation of heterogeneous regions cannot always be taken as due to the presence of two separate mesophases. Hence the identification procedure consists of developing isobaric temperature-composition phase diagrams with several known mesogens until one is found that gives an uninterrupted miscibility over the entire composition range. The reference compound can be chosen by comparing the DSC data and microscopic observation of the sample and reference. The phase diagrams for the liquid crystalline mixtures can be generated from the thermal data or by the contact method\textsuperscript{103} (which involves the observation of microscopic texture of the mesophases between crossed polarizers).

In the case of polymers, the lower solubility may create some additional problems to miscibility studies compared to LMW LC's. Nevertheless, it has been used successfully in several instances for the identification of nematic the phase.\textsuperscript{104, 105} A. Fayolle et al \textsuperscript{106} have identified the smectic C of polyester based on terphenyl units by constructing a binary phase diagram with terphthalidene-bis-(4-n-butylaniline), TBBA. The mutual miscibility studies didn't work in identifying the presumed SE phase \textsuperscript{86} and SH phase \textsuperscript{80} of similar polyesters. The reason for immiscibility is not clear in the case of these polymers. Literature review indicates that miscibility studies are worth doing for the identification of nematic and smectic phases of low order.

1. 10 Induced Molecular Orientation

Induced alignment of the mesophases by physical methods such as external electric field, magnetic field and/or viscous flow is well known. Macromolecules capable of forming mesophases are characterized by
asymmetrical shapes and would be expected to have anisotropic magnetic susceptibilities and dielectric constants. These properties help the polymer chains to become aligned when placed in a magnetic field or electric field. The intensity of the field needed to induce orientation in the mesophase is much lower than the isotropic liquid state. Therefore, a significant drop in the field strength required to produce orientation as temperature is increased or decreased is an indication of mesomorphism.

The effect of electric fields on main-chain liquid crystalline polymers has been less extensively studied. Two reviews by Iizuku 107, 108 are worth mentioning in this regard. Martin and Stupp 109 studied the effect of electric field orientation on the crystallization process of random copolyesters of hydroxybenzoic acid. It was found that there was a significant increase in the enthalpy of melting and transition temperature was shifted to higher temperatures.

Magnetic fields are more readily applicable to bulk samples than electric field, although very big magnets may be needed to achieve the required field strength. Noel et al 110 was the first to investigate the effect of a magnetic field on a nematic main-chain co-polyester prepared by the acidolysis reaction between hydroquinone bis-acetates and terephthalic acid. A recent review describes much of this work in detail.111 Hardouin et al 112 studied the effect of varying the length of flexible spacers with the measurements of viscosity and alignment of polymers in a series of polyesters. For n =12, no alignment was observed and showed a high melt viscosity. They suggested that the higher viscosity of the polyester might hinder the molecular alignment. For n=5, the orientation time increases rapidly as the inherent viscosity is increased from 0.29 to 0.54 dL g$^{-1}$. Generally low molecular weight polymers orient easily even in
even in low strength magnetic fields while high molecular weight polymers are difficult to orient.\textsuperscript{113}

Fig. 32. a and fig. 32. b\textsuperscript{114} show the fracture surface of an oriented sample in a field of 1.1 Tesla (T) and an unoriented sample of the same material respectively. The molecular orientation in the oriented sample is evident from the high level of fibrillar alignment with the magnetic axis.

![Fig. 32. Micrograph of the fracture surface of: (a) a sample oriented in a magnetic field of 1.1 T; (b) a similar sample given the same heat treatment but without the magnetic field.](image)

\textbf{Review on Poly(ester-imide)s}

Polyimides are a class of most stable and environmentally resistant polymers currently available for use at high temperatures up to 300 °C. Their outstanding mechanical properties and appreciable thermal and oxidative stability make them suitable substitutes for metals and glass in high performance applications in the electrical, electronic, automotive, aerospace and packaging industries. They are marketed as films, moldings, molding powders, wire coating enamels, adhesives and laminating resins. There are two general types of commercial polyimides:
laminating resins. There are two general types of commercial polyimides: those cured by condensation, and cross linked polyimides. Cross-linked polyimides are derived from a preformed imide monomers or oligomers such as bismaleimides and the reverse Diels-Alder (RDA) polyimide PMR-15. Condensation polyimides are derived from dianhydrides or dianhydride derivatives and diamines. Most of the wholly aromatic polyimides are intractable and they are commonly prepared by the post curing of polyamic acid precursors at elevated temperatures to cause imidization.

Considerable effort is still being devoted to improvement of these materials without a concomitant loss in the thermal stability. Among these include the use of kinked dianhydrides, dianhydrides and diamines containing aliphatic structures or ether linkages. Another method of decreasing the processing temperature without affecting the mechanical integrity of the polymers is the design of poly(ester-imide)s (PEIMs) containing flexible methylene spacers. They are a class of co-polyesterimides in which the aromatic system provide the rigidity necessary for mechanical integrity and the flexible spacers increase the tractability of the polymers. In this design, improved mechanical properties can be achieved if the aromatic system(s) is(are) asymmetric enough to show mesomorphism so that the polymer retains its preferred molecular orientation in the melt upon cooling. These thermotropic liquid crystalline polymers have the capability of attaining appreciably higher tensile strength and flexural properties in the direction of orientation in injection-molded specimens.

PEIMs are commonly prepared by the direct polycondensation of (i) a dianhydride or trimellitic anhydride with a mixture of diamine and
diol, (ii) a dicarboxylic acid containing preformed imide units with diols, (iii) a diphenol containing imide groups with a diacid or diacid dichloride, (iv) a dianhydride containing ester groups with a diamine or diisocyanate, and (v) a α,ω-diamine containing an ester linkage with a dianhydride.

In 1985, Kricheldorf and Pakull synthesized a series of polyesterimides by condensing N-(4-hydroxyphenyl)-trimelletic acid imide with 4-hydroxybenzoic acid or terephthalic acid and hydroquinone or 1,4-cyclohexane diacid and hydroquinone.

Similar to the fully aromatic imides, these polymers had a very high melting point and no mesomorphism was observed below 420 °C. In the following year, the same authors prepared some PEIMs containing variable number of -CH2- units by condensing the diimide diacid prepared from trimellitic anhydride and α,ω-diaminoalkanes with acetyl derivatives of various biphenols.
PEIMs containing biphenyl rings showed liquid crystalline properties and had a broad range of mesogenic phase (70 °C-170 °C) and a high degree of crystallinity. In the case of polymers containing hydroquinone or naphthalene rings, only those containing unsubstituted hydroquinone, tetrachlorohydroquinone and 2,6-dihydroxynaphthalene formed a mesogenic melt. These polymers were reported to show smectic behavior from DSC, PLM and X-ray studies.

In 1989, J. Adduci and J. Facinelli synthesized two series of polyesterimides by reacting N-[(4-chloroformyl)phenyl]-4-(chloroformyl)-phthalimide 16 or N-[(3-chloroformyl)phenyl]-4-(chloroformyl)-phthalimide 17 with various α,ω-diols by solution polymerization. The meta substituted series was found to be amorphous, showing no birefringence where as the para substituted series containing even number of methylene units showed anisotropic properties in the
melt. Later, the even numbered para substituted polymers were further characterized by DSC and X-ray diffraction and were found to show a smectic mesophase.\textsuperscript{119, 120}

\[ \{ \text{\begin{array}{c} \backslash C O \text{N} \backslash C O \backslash ( \text{CH}_2)_n \backslash O \\ n = 4 \cdot 10, \text{and } 12 \end{array}} \} \]

Kricheldorf and co-workers\textsuperscript{121} also reported an identical series of PEIMs with even number of methylene units prepared by the melt polymerization of dimethylester of N-(4-carboxyphenyl)-trimellitimide acid with \( \alpha,\omega \)-dihydroxy alkanes to exhibit smectic mesophases. They prepared isomeric PEIMs\textsuperscript{122} \textsuperscript{18} and observed that the isomers exhibited different liquid crystalline properties. They formed a nematic melt.

\[ \text{\begin{array}{c} \backslash C O \text{N} \backslash C O \backslash ( \text{CH}_2)_n \backslash O \\ n = 3 \cdot 11 \end{array}} \]
The work 123, 124 was extended by using various substituted and unsubstituted diphenols instead of α,ω-dihydroxyalkanes. See structures 19 & 20. A mobile nematic melt was observed for the polyester of 4,4'-dihydroxydiphenyl ether, 2,7-dihydroxynaphthalene, phenyl and (phenylthio)hydroquinone. All others showed either an immobile birefringent phase or an isotropic melt.

![Diagram of structure 19]

![Diagram of structure 20]
In a separate study by the same authors, semi-rigid PEIMs were prepared by condensing N-(4-hydroxy phenyl)-4-hydroxy phthalimide with derivatives of terephthalic acid instead of \(\alpha,\omega\)-aliphatic diacids 21.

![Chemical structure of PEIMs](image)

Optical studies revealed that most of these polymers indicated a nematic phase above Tg. The PEIMs of unsubstituted terephthalic acid was reported as a semicrystalline material showing birefringence up to a temperature of 500 °C, but didn't show any texture characteristic of LC materials.

Some other studies by Kricheldorf et al 126, 127 include incorporation of phosphate or phosphonate groups, carborane 1,7-dicarboxylic acid or isophthlic acid into polyesterimides. These co-polyesters were found to be amorphous. All these studies indicated that the trimellitimide group or the trimellitimide-ester-phenyl combination has good mesogenic properties and incorporation of bulky side groups or non-planar modifiers disrupt the liquid crystalline properties of the poly(ester-imide).
In another study 128 Kricheldorf and his group used a highly symmetric diimide diester 22 and prepared PEIMs 23 containing variable number of methylene units by the transesterification of the dimethylester 22 with aliphatic diols.

\[
\begin{align*}
\text{CH}_2\text{--CO--CH}_4\text{--N} & \quad \text{CO} \\
\text{CO} & \quad \text{N} \quad \text{CH}_4\text{--CO--OCH}_3
\end{align*}
\]

22

\[
\begin{align*}
\left[ \text{CO--CH}_4\text{--N} & \quad \text{CO} \\
\text{CO} & \quad \text{N} \quad \text{CH}_2\text{--CO--O} \quad (\text{CH}_2)_n \quad \text{O} \right]
\end{align*}
\]

23

These polymers were found to possess a layered super molecular structure in the solid state and they didn't form a fluid mesophase. Other diimide mesogens considered include the diimide diacids prepared from pyromellitic dianhydride 129 and benzophenone-3,3',4,4'-tetracarboxylic dianhydride 130 and \(\omega\)-aminoacids. These diimides showed mesogenic properties only in the polyesters made by condensing them with aromatic diols.

In 1992, J. Adduci and E. Freeman 131 prepared a series of chiral PEIMs 24 by condensing 2-(4-carboxyphthalimido)propionic acid prepared from trimellitic dianhydride and D,L-alanine with \(\alpha,\omega\)-dihydroxyalkanes. DSC analysis showed that these polyesters are amorphous with \(T_g\) and \(T_m\) values very close to one another.
The imide diacids, the imide diols or the imide alcohol acid required for the synthesis of all the PEIMs discussed above were prepared by the reaction of the respective anhydride with a suitable \( \omega \)-amino acid or \( \omega \)-amino alcohol. Another route for the synthesis of PEIMs reported by C.V. Avadhani and co-workers \(^{132}\) involved the reaction of an ester diisocyanate with pyromellitic anhydride. The ester diisocyanates were prepared from the ester dicarboxylic acids via the Curtius rearrangement.
2.0 OBJECTIVES

The objectives of the study were the following: (i) to synthesize two new series of liquid crystalline poly(ester-imide)s with low melting point having the general structure 25, 26;

\[
\begin{align*}
25a &- j \\
n = 3 - 12
\end{align*}
\]

(ii) to demonstrate the liquid crystalline properties of the new polymers; (iii) to investigate the odd-even effect and the effect of rigid diols on the LC transitions, stability and the type of mesophase exhibited by the polymers; and (iv) to investigate the effect of annealing on the liquid transition temperatures and enthalpy of transitions.
The first phase of the project involved the synthesis of three mesogenic diimide diacids \(6,6'-(3,3',4,4'-\text{biphenyltetracarboxydiimido})\)-bis-hexanoic acid, 27, (BPDI-6A), \(11,11'-(3,3',4,4'-\text{biphenyltetracarboxydiimido})\)-bis-undecanoic acid, 28, (BPDI-11A), and \(4,4'-(3,3',4,4'-\text{biphenyltetracarboxydiimido})\)-bis-benzoic acid, 29, (BPDI-BA) whose structures are given below.

They were prepared by reacting one equivalent of \(3,3',4,4'-\text{biphenyltetracarboxylic dianhydride}\) with two equivalents of 6-aminohexanoic acid, 11-aminoundecanoic acid or 4-aminobenzoic acid using the method of Augl and Wrasidlo 133 to give the corresponding
diimide diacids shown above. The monomers were characterized by elemental analysis, melting point and infrared spectroscopy. The diimide diacid 28 was then condensed with various \( \alpha,\omega \)-dihydroxyalkanes to give the 25 series. The 26 series was prepared by the melt polycondensation of 28 with 1,4-diacetoxybenzene and 4,4'-diacetoxybiphenyl.

In the second phase, the synthesized polymers were characterized by Infrared spectroscopy, thermogravimetric analysis, dilute solution viscosity, gel permeation chromatography, differential scanning calorimetry and polarizing light microscopy.
3.0 RESULTS AND DISCUSSION

3.1 Synthesis of monomers

The mesogenic diimide diacids 27, 28 and 29 were prepared by refluxing 3,3',4,4'-biphenyltetracarboxylic dianhydride with the corresponding ω- amino acids in DMF in the presence of acetic anhydride. The reaction proceeded in two steps as shown in Scheme I. The percentage yield of the products ranged from 60 to 96%. Monomers 27 and 28 were soluble in dioxane, DMF and DMAc and were insoluble

\[
\text{3,3',4,4'-biphenyltetracarboxylic dianhydride} + 2\text{H}_2\text{N}-(\text{CH}_2)_n-\text{COOH} \quad n = 5, 10
\]

\[
\text{ω-amino acid}
\]

\[
\Delta \text{DMF}
\]

\[
\text{HOOC}-(\text{CH}_2)_n \quad \text{N} \quad \text{OH} \quad \text{C} \quad \text{OH}
\]

\[
\text{amic acid}
\]

\[
-2\text{AcOH} \quad \text{Ac}_2\text{O}
\]

\[
\text{Scheme I}
\]
in benzene, toluene, methylene chloride and diethyl ether. Acceptable melting point range and better percentage recovery were obtained when recrystallization was performed from a mixture of dioxane and water. The melting point determined by a UNI-MELT™ capillary melting point apparatus ranged from 217-220 °C for 27 and 170-172 °C for 28. The IR spectra of 27 and 28 (fig 43 & 44) showed peaks characteristic of cyclic imides in the region 1777 - 1788 cm⁻¹ and 1685 - 1719 cm⁻¹ due to the symmetric and asymmetric vibrational coupling of the imide carbonyl groups. The ring closure imidization was further confirmed by elemental analysis. See Table III.

The diacid 29 was insoluble in all common organic solvents except DMSO. Hence recrystallization was carried in DMSO. The compound didn’t show a melting in the UNI-MELT™ capillary melting point apparatus instead it became dark brown around 460 °C. Thermogravimetric analysis of the sample showed no melting peaks and decomposed at a temperature of 471 °C. The TG/DTA thermogram is given in fig. 45. The IR (fig. 46) showed peaks characteristic of the cyclic imides. But the elemental analysis results showed slight differences in the calculated and found percentage compositions. (See Table III.) The observed percentages were found to be in between an otherwise ring open amide and the supposedly ring closed imide. The differences in the composition may also be due to the presence of DMSO in the product which has not been removed even after the rigorous drying conditions. To bring the melting point to a reasonably low range, attempts were made to convert the diacid into a dichloride or a diacetate using the methods suggested in the literature.118, 119, 121 All methods tried were a failure
Table III. Percentage yields and the general properties of monomers.

<table>
<thead>
<tr>
<th># name</th>
<th>IUPAC name</th>
<th>Molecular Formula</th>
<th>Molecular Weight</th>
<th>Yield</th>
<th>Melting Point °C</th>
<th>Elemental Analysis</th>
<th>Major IR Peaks cm⁻¹</th>
<th>Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>6,6'-(3,3',4,4'-biphenyl tetracarboxydiimido)-bis-hexanoic acid</td>
<td>C₂₈H₂₀O₈N₂</td>
<td>520.53</td>
<td>93</td>
<td>217 - 220</td>
<td>Calc. 64.61, 5.38, 5.42</td>
<td>1769, 3300 - 2500</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found. 64.69, 5.60, 5.45</td>
<td>1706, 1710</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>11,11'-(3,3',4,4'-biphenyl tetracarboxydiimido)-bis-undecanoic acid</td>
<td>C₃₈H₄₈O₈N₂</td>
<td>660.79</td>
<td>95</td>
<td>170 - 172</td>
<td>Calc. 69.07, 4.24, 7.32</td>
<td>1770, 3300 - 2300</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Found. 68.86, 4.53, 7.44</td>
<td>1698, 1712</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>4,4'-(3,3',4,4'-biphenyl tetracarboxydiimido)-bis-aminobenzoic acid</td>
<td>C₃₀H₁₆O₈N₂</td>
<td>532.28</td>
<td>60</td>
<td>No melting</td>
<td>Calc. 67.68, 5.26, 3.03</td>
<td>1777, 3250 - 2500</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Td = 471</td>
<td>Found. 65.77, 4.96, 3.18</td>
<td>1683, 1721</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HyDaC</td>
<td>C₁₀H₁₀O₄</td>
<td>194.19</td>
<td>87</td>
<td>121 - 122</td>
<td></td>
<td>1760, 1230, 1175</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BPhDaC</td>
<td>C₁₆H₁₄O₄</td>
<td>270.21</td>
<td>85</td>
<td>158 - 159</td>
<td></td>
<td>1755, 1245, 1200</td>
<td></td>
</tr>
</tbody>
</table>
and the diacid was found to be insoluble and unreactive. The idea of using 29 as a monomer was dropped.

Hydroquinone and 4,4'-biphenol were acetylated by digesting with acetic anhydride in presence of conc. H₂SO₄ in the cold. The methyl esters were recrystallized from ethanol. The melting points of the acetoxy derivatives were found to be 118 - 120 °C (lit. 121 - 122 °C ) and 158 - 159 °C (lit. 160 - 161 °C) respectively. The properties of the monomers are listed in Table III. The infrared spectra of the methylesters are given in figures 47 & 48.

3.2 Polycondensation of Aliphatic Poly(ester-imide)s

In this study the diimide diacid monomer 28 was used for polycondensations. Poly(ester-imide)s 25 a - j were prepared by the melt polymerization 38 of 28 with excess α,ω-dihydroxyalkanes in the presence of tetraisopropyltitanate as the catalyst. Excess diols were used to get high molecular weight polymers. The initial products of polymerization are low molecular weight ester-imide oligomers end capped with hydroxyl groups. Transesterification reaction between the oligomers under vacuum removes the excess diol. As more and more diol is removed, the average degree of polymerization increases and results in a high molecular mass polymer. The reactions involved are shown in scheme II. They formed as lightly colored viscous melts which can be spun into long fibers at the end of polymerization. Polymers were purified by dissolving them in methylene chloride and reprecipitating from cold methanol. Inherent viscosities were determined from a 0.5 g/dL
solution of the polymers in m-cresol. The percentage yields and the general properties of the aliphatic PEIM(s) are listed in Table IV.

The yields ranged from 67 to 92%. The main loss occurred during mechanical separation from the reaction flask. Poly(ester-imide) 25 a n = 3 showed the lowest inherent viscosity (0.5 dL/g) and a value of 1.6 dL/g was calculated for 25 e (n = 7). The inherent viscosity values
Table IV. Percentage yields and general properties of poly(ester-imide)s 25 a - j. a = peak value of the first endotherm at a heating rate of 10 °C/min; b = melting point obtained from a Fisher Meltemp apparatus; c = viscosity from a 0.5 dL/g solution of the polymers in m-cresol.

<table>
<thead>
<tr>
<th># name</th>
<th>n</th>
<th>Yield %</th>
<th>Tg °C</th>
<th>Tm a °C</th>
<th>Tm b °C</th>
<th>η inh dL/g</th>
<th>Td °C</th>
<th>Major IR Peaks cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alcohol</td>
</tr>
<tr>
<td>25 a</td>
<td>3</td>
<td>83</td>
<td>15.9</td>
<td>63.0</td>
<td>66.5</td>
<td>0.51</td>
<td>487</td>
<td>3457, 1397 1723, 1265 1717 1174</td>
</tr>
<tr>
<td>25 b</td>
<td>4</td>
<td>81</td>
<td>11.7</td>
<td>135.5</td>
<td>135.0</td>
<td>0.56</td>
<td>485</td>
<td>3464, 1397 1725, 1260 1706 1174</td>
</tr>
<tr>
<td>25 c</td>
<td>5</td>
<td>84</td>
<td>12.7</td>
<td>69.9</td>
<td>65.5</td>
<td>0.75</td>
<td>485</td>
<td>3457, 1390 1723, 1238 1709 1173</td>
</tr>
<tr>
<td>25 d</td>
<td>6</td>
<td>90</td>
<td>4.9</td>
<td>131.6</td>
<td>132.5</td>
<td>0.62</td>
<td>481</td>
<td>3472, 1394 1720, 1235 1712 1173</td>
</tr>
<tr>
<td>25 e</td>
<td>7</td>
<td>68</td>
<td>17.0</td>
<td>119.9</td>
<td>64.0</td>
<td>1.65</td>
<td>488</td>
<td>3456, 1394 1727, 1238 1712 1184</td>
</tr>
<tr>
<td>25 f</td>
<td>8</td>
<td>90</td>
<td>2.7</td>
<td>125.0</td>
<td>127.5</td>
<td>0.53</td>
<td>482</td>
<td>3460, 1389 1730, 1240 1716 1177</td>
</tr>
<tr>
<td>25 g</td>
<td>9</td>
<td>86</td>
<td>2.4</td>
<td>102.7</td>
<td>99.5</td>
<td>0.61</td>
<td>498</td>
<td>3463, 1390 1723, 1244 1710 1174</td>
</tr>
<tr>
<td>25 h</td>
<td>10</td>
<td>86</td>
<td>1.4</td>
<td>122.5</td>
<td>124.0</td>
<td>0.82</td>
<td>479</td>
<td>3465, 1393 1730, 1240 1712 1171</td>
</tr>
<tr>
<td>25 i</td>
<td>11</td>
<td>90</td>
<td>2.7</td>
<td>103.8</td>
<td>105.5</td>
<td>0.76</td>
<td>486</td>
<td>3464, 1390 1717, 1244 1703 1174</td>
</tr>
<tr>
<td>25 j</td>
<td>12</td>
<td>92</td>
<td>1.4</td>
<td>122.3</td>
<td>123.5</td>
<td>0.71</td>
<td>480</td>
<td>3457, 1397 1723, 1240 1717 1178</td>
</tr>
</tbody>
</table>
indicated that the poly(ester-imide)s prepared have moderately high molecular mass. Poly(ester-imide) 25 e didn’t dissolve completely in m-cresol, instead formed a fine suspension of swelled polymer. The low solubility and the apparent high viscosity are indications of a comparatively high molecular mass.

A correlational study between molecular weight and $\eta_{inh}$ for this class of polymers were made by determining the molecular weight averages $M_n$, $M_w$ and $M_v$ of three selected polymers 25 c, 25 d and 25 f by GPC studies. The data obtained are given in Table V. The GPC chromatograms are given in fig. 49 - 51. As can be seen in the table there is a trend in the molecular weight with the $\eta_{inh}$ values.

Table V. Molecular weight averages and the inherent viscosity values of PEIM(s) 25 c, 25 d and 25 f.

<table>
<thead>
<tr>
<th># name</th>
<th>n</th>
<th>$\eta_{inh}$ dL/g</th>
<th>Number average $M_n$</th>
<th>Weight average $M_w$</th>
<th>Viscosity Average $M_v$ A.M. of $M_n$ &amp; $M_w$</th>
<th>Polydispersity $M_n/M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 c</td>
<td>5</td>
<td>0.75</td>
<td>17,700</td>
<td>78,400</td>
<td>48,050</td>
<td>4.43</td>
</tr>
<tr>
<td>25 d</td>
<td>6</td>
<td>0.62</td>
<td>16,500</td>
<td>48,500</td>
<td>32,500</td>
<td>2.94</td>
</tr>
<tr>
<td>25 f</td>
<td>8</td>
<td>0.53</td>
<td>15,900</td>
<td>36,300</td>
<td>26,100</td>
<td>2.28</td>
</tr>
</tbody>
</table>

Roughly, a viscosity average molecular weight (which is taken as the arithmetic mean of $M_n$ & $M_w$) of 26,100 g/mol was observed for polymers with an inherent viscosity value of 0.53 dL/g. The GPC chromatogram of 25 c (fig. 49) showed a small peak at large values of log M which indicated the presence of small fraction of very high molecular
weight chains. This unexpected product may be the result of side reactions at elevated temperature as shown in Scheme III leading to

$$\text{HO - (CH}_2\text{n)} \left[ \text{O - C-(CH}_2\text{)}_{10} \cdot \text{N}^{-} \text{(CH}_2\text{)}_{10} \cdot \text{O - (CH}_2\text{n)} \right] \text{OH}$$

$$\text{HO - (CH}_2\text{n)} \cdot \text{O - C-(CH}_2\text{)}_{10} \cdot \text{N}^{-} \text{(CH}_2\text{)}_{10}$$

$$\text{HO - (CH}_2\text{n)} \left[ \text{O - C-(CH}_2\text{)}_{10} \cdot \text{N}^{-} \text{(CH}_2\text{)}_{10} \cdot \text{O - (CH}_2\text{n)} \right] \text{OH}$$

$$\text{HO - (CH}_2\text{n)} \cdot \text{O - C-(CH}_2\text{)}_{10} \cdot \text{N}^{-} \text{(CH}_2\text{)}_{10} \cdot \text{O - (CH}_2\text{n)}$$

Scheme III

cross-linking or chain branching. For 25 d and 25 f only one broad peak was observed. A broad distribution of molecular weight which is typical of step growth polymerization was evident from the polydispersity values. Thermal studies showed that these molecular weight averages are reasonably high enough to show all major thermal transitions.

The infrared spectra of the polymers showed absorptions characteristic of aliphatic C-H stretch, aromatic C-H stretch, the symmetric (1744 - 1775 cm\(^{-1}\)) and asymmetric (1685 - 1720 cm\(^{-1}\)) vibrational coupling of the imide C=O group apart from the expected
absorptions due to the ester, acid and alcohol functionalities. The specific peak positions observed in the IR spectrum of each polymer are listed in Table IV. The IR spectra of the aliphatic PEIM(s) are given in figs. 52 - 61.

These poly(ester-imide)s were found to be highly thermally stable from thermogravimetric analyses. In an inert atmosphere (nitrogen), at a heating rate of 20 °C/min, the loss of mass due to the onset of degradation was noticed at a temperature around 450 °C. The decomposition temperature (Td °C) which is taken as the mid-point of the TG/DTA curve at heating rate of 20 °C/min. Td for polymer 25 a - j are listed in Table IV. See figs. 62 -71 for TG/DTA thermograms. The oxidative stability of the polymers were determined by running the TGA scans for two poly(ester-imide)s 25 b and 25 c in air at a heating rate of 20 °C/min. The Td’s were found to be 20 °C less than that in nitrogen. The TGA thermograms of PEIM(s) 25 b & c in air are given figs. 72 & 73.

DSC analyses were conducted on both virgin (unannealed) samples and samples after annealing at the crystal ordering temperature for 8 - 10 hours. In the case of unannealed samples, three heating-cooling cycles were performed. In the first cycle, samples were heated to about 50 °C above Tm at a rate of 20 °C/min, hold for 10 minutes and then quench cooled to -25 °C. The second and third heating-cooling cycles were carried out at a rate of 10 and 5 °C/min respectively. Data from the second and third cycles were taken to interpret the observed properties of the polymers. The results obtained are summarized in Tables VI and VII.

For annealed samples, two heating-cooling scans were performed at a rate of 5 and 10 °C/min respectively. The 5 °C/min cycle was done after annealing the samples in the vacuum oven for 8 hours. The second
heating-cooling cycle (10 °C/min) was performed after annealing the samples in the DSC for 3 hours after the first run. The transition temperatures along with the corresponding enthalpies for the annealed PEIM(s) at 5 °C/min heating and 10 °C/min heating are given Table VIII.

The DSC thermograms of all the virgin samples showed a change in base line corresponding to glass transition temperature, (Tg °C) followed by crystal ordering exotherm(s) and melting transition endotherm(s). The Tg of the poly(ester-imide)s 25 (a - j) ranged from 16.0 to 1.4 °C. The Tg of the polymers decreased with increase in the number of methylene units in the diols. See Table IV. A plot showing the variation of Tg with the number of methylene units is shown in fig. 33. Poly(ester-imide)s containing even number of methylene units in the diol are considered as 'even' polymers. Those containing odd number of methylene units in the alkoxy part are taken as "odd" polymers. Polymer 25 e (n = 7), showed an unexpectedly high value of (19 °C)Tg which can be attributed to the presence of cross-linked or chain branched polymers as explained in scheme III.

The 10 °C/min heating thermogram of the virgin (unannealed) even polymer 25 d (n = 6), (fig. 34) showed two distinct crystal ordering exothermers (whose peak values were taken as the crystal ordering temperatures Tco1 and Tco2) at 37.7 °C and 57.6 °C between Tg and Tm separated by plateaus. Similar results were obtained for other evens 25 b (n = 4), 25 f (n = 8), 25 h (n = 10) and 25 j (n = 12). Even though two distinct peaks were not observed for 25 j, a shoulder was visible after the
Fig. 33. Variation of glass transition temperature (Tg) of Poly(ester-imide)s 25 a-j with the number of methylene units in the diol. The Tg of polymer 25e (16.98 °C) is not included in the plot.

first crystal ordering exotherm. See figs. 74 - 77. The multiple crystal ordering transitions may be due to true 'solid state mesophase transitions' or due to the formation of crystals with different perfections. The first exotherm corresponds to the thermal crystallization of the polymer from the amorphous state to a less ordered crystalline form which undergo further ordering at elevated temperature to form a more ordered crystalline polymer. The presence of multiple peaks may also be explained as due to the formation of crystals with different size and perfection. The enthalpies of thermal crystallization (ΔHo) of the 'even' PEIM(s) ranged from -8.0 - - 20.0 J/g. The onset crystal ordering temperature decreased with increase in the number of methylene units.
Fig. 34. DSC thermogram of virgin PEIM 25 d at a heating rate of 10 °C/min in nitrogen.
which indicates that as chains become more flexible, less time and energy are needed to cause local motion and straightening or alignment of the polymer chains. Only one melting endotherm was observed in the DSC's of the virgin 'even' PEIMs. All the 'even' polymers showed a low isotropic transition temperature (below 140 °C). The melting point decreased from 135.5 °C (for 25 b, n = 4) to 122.3 °C (for 25 j, n = 12) with increase in the number of methylene units. The enthalpy of melting (ΔHm), for 'even' polymers were found to be in the range of 30 - 40 J/g. See Tables VI and VII.

Table VI. Transition temperatures and the corresponding enthalpies of virgin poly(ester-imide)s 25 a - j at a heating rate of 10 °C/min.

<table>
<thead>
<tr>
<th># name</th>
<th>n</th>
<th>Crystal Ordering °C</th>
<th>L. C. transition °C</th>
<th>ΔH crystal Ordering J/g</th>
<th>ΔH L. C. Transition J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T1</td>
<td>T2</td>
<td>Tm1</td>
<td>Tm2</td>
</tr>
<tr>
<td>25 a</td>
<td>3</td>
<td>51.9</td>
<td>_</td>
<td>63.0</td>
<td>73.0</td>
</tr>
<tr>
<td>25 b</td>
<td>4</td>
<td>40.8</td>
<td>66.9</td>
<td>135.5</td>
<td>_</td>
</tr>
<tr>
<td>25 c</td>
<td>5</td>
<td>47.3</td>
<td>81.9</td>
<td>70.0</td>
<td>108.4</td>
</tr>
<tr>
<td>25 d</td>
<td>6</td>
<td>37.7</td>
<td>57.6</td>
<td>131.6</td>
<td>_</td>
</tr>
<tr>
<td>25 e</td>
<td>7</td>
<td>99.0</td>
<td>_</td>
<td>119.9</td>
<td>_</td>
</tr>
<tr>
<td>25 f</td>
<td>8</td>
<td>32.7</td>
<td>50.6</td>
<td>125.0</td>
<td>_</td>
</tr>
<tr>
<td>25 g</td>
<td>9</td>
<td>38.6</td>
<td>53.5</td>
<td>102.7</td>
<td>108.9</td>
</tr>
<tr>
<td>25 h</td>
<td>10</td>
<td>29.6</td>
<td>46.2</td>
<td>122.5</td>
<td>_</td>
</tr>
<tr>
<td>25 i</td>
<td>11</td>
<td>26.9</td>
<td>_</td>
<td>103.8</td>
<td>_</td>
</tr>
<tr>
<td>25 j</td>
<td>12</td>
<td>17.9</td>
<td>_</td>
<td>122.3</td>
<td>_</td>
</tr>
</tbody>
</table>
The transitions were found to be reproducible in the 5 °C/min heating (Table VII). Thermograms of the 'even' polymers obtained at a heating rate of 5 °C/min are given in fig. 78 - 82.

Table VII. Transition temperatures and the corresponding enthalpies of virgin Poly(ester-imide)s 25 a - j at a heating rate of 5 °C/min.

<table>
<thead>
<tr>
<th># name</th>
<th>n</th>
<th>Crystal Ordering</th>
<th>L. C. transition</th>
<th>ΔH crystal Ordering</th>
<th>ΔH L. C. Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Tco1 Tco2</td>
<td>Tm1 Tm2 Tm3</td>
<td>ΔHo1 ΔHo2</td>
<td>ΔHm1 ΔHm2 ΔHm3</td>
</tr>
<tr>
<td>25a</td>
<td>3</td>
<td>44.4 -</td>
<td>62.3 88.5 103.9</td>
<td>-14.5 -</td>
<td>16.3 4.1 4.7</td>
</tr>
<tr>
<td>25b</td>
<td>4</td>
<td>32.9 64.6</td>
<td>134.9 - -</td>
<td>-16.0 -16.5</td>
<td>31.5 - -</td>
</tr>
<tr>
<td>25c</td>
<td>5</td>
<td>39.9 75.7</td>
<td>59.3 69.6 107.0</td>
<td>-10.2 -13.3</td>
<td>3.95 3.3 17.4</td>
</tr>
<tr>
<td>25d</td>
<td>6</td>
<td>29.0 54.7</td>
<td>131.8 - -</td>
<td>-8.3 -8.4</td>
<td>31.3 - -</td>
</tr>
<tr>
<td>25e</td>
<td>7</td>
<td>87.0 -</td>
<td>116.1 - -</td>
<td>-1.62 -</td>
<td>5.2 - -</td>
</tr>
<tr>
<td>25f</td>
<td>8</td>
<td>23.4 47.4</td>
<td>125.1 - -</td>
<td>7.0 -5.1</td>
<td>30.4 - -</td>
</tr>
<tr>
<td>25g</td>
<td>9</td>
<td>25.1 50.4</td>
<td>101.3 109.2 -</td>
<td>-11.0 -7.3</td>
<td>23.2 14.1 -</td>
</tr>
<tr>
<td>25 h</td>
<td>10</td>
<td>20.7 42.1</td>
<td>122.6 - -</td>
<td>-124 -6.0</td>
<td>37.5 - -</td>
</tr>
<tr>
<td>25 i</td>
<td>11</td>
<td>20.1 -</td>
<td>102.8 - -</td>
<td>-22.7 -</td>
<td>34.7 - -</td>
</tr>
<tr>
<td>25 j</td>
<td>12</td>
<td>- -</td>
<td>122.2 - -</td>
<td>- -</td>
<td>34.7 - -</td>
</tr>
</tbody>
</table>

The DSC curves obtained after annealing the samples were encouraging. A drastic decrease in the width of the glass transition, disappeareance of the crystal ordering exotherms and appearence of an additional melting endotherm were noticeable in the DSC traces of annealed PEIM(s) 25 b, 25 d, 25 f, 25 h and 25 j. The heating DSC thermograms of the annealed even sample 25 d at a rate of 5 °C/min showed two endothermic peaks. See fig. 35. The first transition was
Fig. 35. DSC thermogram of annealed PEIM 25 d at a heating rate of 5 °C/min in nitrogen.
observed at 88.8°C which is below the isotropic transition temperature (132.6 °C) and a few degrees above the upper crystal ordering transition of unannealed samples. Similar transitions were observed for other 'even' polymers after annealing at 5 °C/min heating (fig. 83 - 86). This is an indication of a highly ordered mesophase transition or a crystal-crystal transition. The enthalpy of this transition ($\Delta H_1$) was comparatively smaller (1 - 4 J/g) than the enthalpy of the 'high temperature' isotropic transition ($\Delta H_2$) which is common for liquid crystalline polymers. See table VII. Almost identical results were obtained for the evens in the 10 °C/min heating scans after annealing. There was no remarkable change in the position of isotropic transition after annealing. It is interesting to note that the sum of the melting enthalpies after annealing was almost equal to the enthalpy of melting before annealing, which indicates the slow heating rate of 10 °C/min and 5 °C/min were sufficient to induce maximum crystallization in the even polymers. See figs. 87 - 91 and Table VIII for details.

The odd poly(ester-imiide)s 25 (a, c, e, g and i) showed interestingly different thermal behavior. The heating thermogram of the 'odd' virgin poly(ester-imide) 25 c, at a heating rate of 10 °C/min is shown in fig. 36. Thermograms of the remaining 'odd' samples at 10 °C/min heating are given in figures 92 - 94. The thermal behavior of 25 e was totally different from the remaining 'odd' polymers and so will be discussed separately. Results obtained at a heating rate of 10 °C/min are summarized in Table VI.

The 'odd' polymers showed multiple crystal ordering exotherms and multiple melting endotherms in the DSC heating curves. The
Table VIII. Transition temperatures and the corresponding enthalpies of annealed poly(ester-imide)s 25a-j at 10 and 5 °C/min heating rates.

<table>
<thead>
<tr>
<th>Annealed Sample</th>
<th>5 °C/min heating</th>
<th>10 °C/min heating</th>
</tr>
</thead>
<tbody>
<tr>
<td># name</td>
<td>n</td>
<td>L. C. transition °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tm1</td>
</tr>
<tr>
<td>25a</td>
<td>3</td>
<td>62.6</td>
</tr>
<tr>
<td>25b</td>
<td>4</td>
<td>88.0</td>
</tr>
<tr>
<td>25c</td>
<td>5</td>
<td>81.6</td>
</tr>
<tr>
<td>25d</td>
<td>6</td>
<td>88.8</td>
</tr>
<tr>
<td>25e</td>
<td>7</td>
<td>75.7</td>
</tr>
<tr>
<td>25f</td>
<td>8</td>
<td>72.8</td>
</tr>
<tr>
<td>25g</td>
<td>9</td>
<td>76.3</td>
</tr>
<tr>
<td>25h</td>
<td>10</td>
<td>53.3</td>
</tr>
<tr>
<td>25i</td>
<td>11</td>
<td>50.0</td>
</tr>
<tr>
<td>25j</td>
<td>12</td>
<td>60.9</td>
</tr>
</tbody>
</table>

Thermograms of 25a and 25c did not show a well defined rubbery plateau whereas for 25g and 25i it was clearly noticeable. The crystal ordering temperature (44 °C for n = 3 and 20 °C for n = 11) decreased with increase in the number of methylene units. It is interesting to note that the crystal ordering temperature of the 'odd' PEIM(s) were higher than that of the 'even' PEIM(s). This indicates that 'odd' polymers needed more time to cause local motion and (or) straightening of the chains. A plot of difference between crystal ordering temperature (Tco) and glass transition temperature (Tg) with the number of methylene units is shown in fig. 37.
Fig. 36. DSC thermogram of virgin PEIM 25 c at a heating rate of 10 °C/min in nitrogen.
Here $T_g$ is taken as the reference point from which the chain motion begins. The 'odd' and the 'even' polymers gave a constant value for $T_{co} - T_g$ till $n$ equals 10. The values obtained for 'odd' polymers were higher than that of 'even' ones.

![Graph showing the variation of $T_{co} - T_g$ (°C) of poly(ester-imide)s 25a-j with the number of methylene units in the diol. The data point of 25e (81.98 °C) is not included in the plot.]

In contrast to the 'even' polymers the melting point of the 'odd' polymers increased (63.03 °C for $n = 3$ and 103.8 °C for $n = 11$) with increase in the number of methylene units. Figure 38 shows the variation of $T_m$ with the number of methylene units in the diol. These polymers showed a definite odd-even effect in the melting transition temperatures. The $T_m$ of the 'odd' PEIM(s) were lower than that of the 'even' PEIM(s). Poly(ester-imide) 25 a $(n = 3)$ showed three endotherms ranging from 63.0 to 90°C with low values of enthalpy. For 25 c $(n = 5)$ two melting
melting peaks at 70 and 108.4 °C were observed in the 10 °C/min heating trace. Two peaks at 104 and 109 °C were observed for 25 g (n = 9). Only one melting endotherm was observed for 25 i (n = 11). The enthalpies of melting for 25 g and 25 i were comparatively larger than the other odd polymers. See Table VI. This data suggests that as the length of methylene unit increased the ‘odd effect’in Tm diminished. All transitions were reproducible in the 5 °C/min heating (figs. 95 - 98) with an acceptable variation of 1 - 2 °C difference in the transition temperatures. Results are summarized in Table VII.

![Graph](image-url)

**Fig. 38.** Variation of melting point of poly(ester-imide)s 25a-j with the number of methylene units in the diols.

The heating curves of the 'odd' polymers after annealing showed no crystal ordering but there was a clear change in base line (Tg) followed by multiple melting transitions with small increase in the values
of enthalpy. See Table VIII for specific values. After annealing, 25 a and 25 c showed well defined rubbery plateaus after Tg and well resolved melting endotherms. A sample thermogram at a heating rate of 5 °C/min is given in fig. 39. Remaining thermograms of the odd samples after annealing are given in figs. 99 - 101. Poly(ester-imide) 25a showed four melting peaks at 62.5, 91.9, 103.5 and 109.6 °C respectively. For polymer 25 c, two endotherms at 81.5 and 107.2 °C were observed in the 5 °C/min heating run. Polymer 25 g showed three melting peaks at 76.26, 102.4 and 109.4 °C respectively. Polymer 25 i showed a low temperature melting endotherm at 49.9 °C in addition to the isotropic transition at 102.9 °C. All these transitions were reproducible in the second heating scan (10 °C/min) after annealing. See Table VIII. The thermograms at 10 °C/min heating are given in figs. 102 - 105. To emphasize the need for annealing the samples to get a better picture about the mesomorphic nature of these polymers, second heating scan of 25 a was done without annealing. As in the case of virgin samples, the peaks were cluttered together and only one major melting peak was observed. See fig. 102.

Analysis of cooling curves of the virgin even samples gave some information about the crystallization processes involved in these polymers. Poly(ester-imide)s 25 d and 25 f showed a single crystallization peak in the range of 70 - 80 °C, whereas 25 h and 25 j showed crystallization exotherms in the 50 - 60 °C range in the cooling curves recorded at rates of 10 and 5 °C/min. The enthalpy of crystallization for the 5 °C/min cooling was found to be appreciably larger than the value observed for 10 °C/min cooling which is indicative
Fig. 39. DSC thermogram of annealed PEIM 25 c at a heating rate of 5 °C/min in nitrogen.
of the slow kinetics involved in crystallization. In the case of 25 b, crystallization was observed only in 5 °C/min cooling. In general, thermograms at 10 °C/min cooling showed more super cooling than the 5 °C/min cooling thermograms. All showed a high degree of super cooling (~65 °C) before crystallization. The cooling curves recorded at both rates are given in figs. 106 - 115. Table IX lists specific values of crystallization temperatures ($T_c$) and enthalpies of crystallization ($\Delta H_c$). These observations support the slow kinetics of crystallization and the semi-crystalline nature of these polymers.

Table IX. Comparison of crystallization temperatures and enthalpies of virgin poly(ester-imide)s 25 a - j at 10 and 5 °C/min cooling rates.

<table>
<thead>
<tr>
<th>Virgin Sample</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td># name</td>
<td>name</td>
<td>$10^0 \text{C}/\text{min}$ cooling</td>
<td>$5^0 \text{C}/\text{min}$ cooling</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>L. C. transition $^0 \text{C}$</td>
<td>$\Delta H_c$</td>
<td>L. C. transition $^0 \text{C}$</td>
<td>$\Delta H_c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$T_c_1$</td>
<td>$T_c_2$</td>
<td>$\Delta H_{c1}$</td>
<td>$\Delta H_{c2}$</td>
</tr>
<tr>
<td>25 a</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25 b</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25 c</td>
<td>5</td>
<td>19.6</td>
<td>-</td>
<td>-2.9</td>
<td>-</td>
</tr>
<tr>
<td>25 d</td>
<td>6</td>
<td>78.5</td>
<td>-</td>
<td>-8.7</td>
<td>-</td>
</tr>
<tr>
<td>25 e</td>
<td>7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25 f</td>
<td>8</td>
<td>73.2</td>
<td>-</td>
<td>-8.1</td>
<td>-</td>
</tr>
<tr>
<td>25 g</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>25 h</td>
<td>10</td>
<td>59.9</td>
<td>-</td>
<td>-3.9</td>
<td>-</td>
</tr>
<tr>
<td>25 i</td>
<td>11</td>
<td>48.6</td>
<td>11.0</td>
<td>-2.8</td>
<td>-1.6</td>
</tr>
<tr>
<td>25 j</td>
<td>12</td>
<td>51.2</td>
<td>-</td>
<td>-28.8</td>
<td>-</td>
</tr>
</tbody>
</table>
No sharp crystallization peaks were observed in the cooling curves of the virgin 'odd' polymers. The 'high melting' 'odd' PEIM(s) 25 g and 25 h showed crystallization exotherms with low enthalpy values, but reproducibility was observed only with 25 h. PEIM 25 g crystallized only at a cooling rate of 5 °C/min. See Table IX. The cooling curves of virgin 'odd' polymers are given in figures 116 - 123. This indicates that the 'odd' PEIM(s) are more amorphous than the even PEIM(s). The absence of crystallization peaks in the cooling curves of low melting odds can be better explained based on figure 40, which is an overlay of fig. 34 and fig. 38. Due to supercooling, the transition temperature of the sample may fall close to the glass transition temperature at which the crystallization kinetics become reasonably slow due to reduction in chain mobility. No crystallization will be observed when the rate of cooling is faster than the rate of crystallization.

Poly(ester-imide) 25 e showed an unusual thermal behavior. The transition temperatures of the unannealed sample were much higher than the values expected from the graph (crystal ordering = 98.9 °C, Tg = 16.98 °C, Tm = 120 °C and ΔHm = 1.0 J/g). Table VI and VII shows results obtained at the two heating rates. It is important to note that the heating DSC heating thermograms of polymer 25 e showed a wide glass transition, broad rubbery region (figs. 124 & 125) and low enthalpy of melting. Cooling curves (figs. 126 & 127) didn’t show any crystallization peaks even though the Tm was higher. These observations, together with the low solubility of 25 e in m-cresol and high inherent viscosity, lead to the conclusion that unexpected side reactions as suggested in Scheme III
might have occurred resulting in the formation of cross-linked or branched chain polymers. In fact multiple transitions were observed in the heating curves after annealing (fig.128 & 129).

From the DSC results it can be concluded that these polymers are semi-crystalline in nature and the degree of crystallinity can be increased by annealing. Further, the complete disappearance of the crystal ordering and the dramatic decrease in the width of Tg transition in the case of ‘evens’ as opposed to the presence of Tg in ‘odd’ PEIMs after annealing indicates that the ‘evens’ PEIMs are almost completely thermally crystallizable. The presence of multiple melting endotherms and
crystallization exotherms indicated the possibility of mesomorphism in this series of polymers.

Optical studies on the polymers were made by examining a thin film of the polymer between crossed polarizers in a Polarizing Light Microscope. Thin films of the polymers were made by pressing the polymers in between a glass plate and a cover glass plate on a hot stage about 50 °C above the melting point. Polymer melts were cooled slowly (2-10 °C/min) to the desired temperature and observed textures were photographed on Polaroid films. The clearing temperatures observed on the PLM were 3 - 4 °C higher than the isotropic transition temperatures obtained by DSC analyses. This is not surprising since the peak values on the DSC curves are not the true clearing points. A more consistent value would have been obtained if the temperature corresponding to the shoulder after isotropic transition were taken as the transition temperatures. Detailed optical studies were made with polymer 25 d. The clearing temperature for this poly(ester-imide) was found to be 135 °C where as the DSC data showed the isotropic transition at 132 °C. Rapid cooling to any temperature below 115 °C resulted in the formation of birefringent textures with crystal morphology. Crystals with different perfection were observed in the optical micrographs taken at 110 °C and 115 °C. See fig. 41 a. The optical micrograph observed at 126 °C is given in fig. 41 b. It is comparable to the textures observed for twisted smectic C phase. At 128 °C (fig.41 c) a texture comparable to the focal conical one characteristic of smectic LC phase was observed. From 129 to 135 °C a granulated texture ( figs. 41 d) common for smectic phase was observed. At 90 °C, which is close to the first endothermic transition in the DSC, birefringent textures with crystal morphology was observed.
This indicates that first transition may be a crystal-crystal transition. The formation of multiple textures at different temperature close to the melting point lead to the conclusion that the polymer showed LC behavior in a narrow temperature range and those transitions were not resolved by the DSC. Similar results were observed for 25 b and 25 f. At 100°C, polymer 25 h formed a texture (fig. 130 a) which closely resembles the fan-shaped texture of smectic LCP's. The optical micrographs obtained at 115 °C and 120 °C (figs. 130 c & d) were similar to the textures observed for smectic polymers. Almost similar optical micrographs (fig. 131) were obtained for 25 j. These studies revealed that the polymer exhibited a smectic liquid crystalline phase within a very narrow temperature range. Samples had to anneal for a long time (6 - 8 hours) to completely form the textures above 115 °C. The 'even' PEIM(s) formed more ordered smectic phase (focal conic or twisted smectic C) 8-10 °C below the clearing temperature and a less ordered smectic phase near the isotropic transition temperature.

The photomicrographs of the odd poly(ester-imide) 25 a taken between the crossed polarizers showed the formation of droplet (fig. 42 a) characteristic of nematic at 73 °C. Further cooling resulted in the formation of a coarse granulated texture as shown in fig. 42 b and was the only birefringent texture observed below the clearing temperature. Similar textures were obtained for other 'odd' PEIM(s). See fig. 132. For polymers 25 a and 25 c anisotropic textures were not obtained on cooling from the melt. These samples were quench cooled to room temperature from the melt and heated up slowly at rate of 0.2 - 1 °C/min to the desired temperatures and annealed for 6 - 8 hours to get the observed birefringent texture. Long time annealing was required to form the observed texture
Fig. 41: Photomicrographs of Poly(ester-imide) 25d between crossed polarizers: (a) at 115°C on cooling from the isotropic melt; (b) after annealing at 126°C for 5 hours; (c) after annealing at 128°C for 7 hours; (d) after annealing at 132°C for 10 hours.
Fig. 42: Photomicrographs of Poly(ester-imide) 25a between crossed polarizers: (a) at 73°C on heating; (b) after annealing at 70°C for 8 hours.
confirming a slow crystallization process and a semi-crystalline nature of these poly(ester-imide)s. Polymer 25 e didn’t show any anisotropic properties under polarized light. This may be due to the high viscosity of the polymer melt, which prevent chain movement.

It is interesting to note that most of the poly(ester-imide)s prepared have a long chain of methylene units (more than 12) separated by an ester group in between the mesogens and still they showed indications of liquid crystalline properties. This may be explained as due to the rigidity of the ester group, the high persistence ratio of the mesogenic biphenyl diimide and the trans conformation of the methylene groups in the evens which promoted the co-operative alignment of the chains in the melt.

3. 3 Polycondensation of Aromatic Poly(ester-imide)s

Aromatic poly(ester-imide)s 26 a and 26 b were prepared by the transesterification of methyl esters of hydroquinone and 4,4’-biphenol with the diacid 28. The high sublimability of hydroquinone and the higher melting point of biphenol urged to convert the diphenols into their dimethyl esters for easy polymerization. The general properties of the methyl esters are given in Table III. Even the methyl ester of hydroquinone was reasonably sublimable. To avoid the loss of diacetoxyhydroquinone before the complete formation of the imide ester oligomers, the polymerization was carried out very slowly. The reaction mixture was allowed to reflux for 4 hours and kept under house vacuum for 2 more hours than the normal procedure before applying the vacuum pump. It took a total of 14 hours to get a satisfactory increase in viscosity for the melt. Polycondensation with diacetoxybiphenol was carried out according to the general procedure using one equivalent of the diester. In
both cases polymerization resulted in dark brown colored viscous melts which on cooling formed brittle polymers. Purification by reprecipitation was not attempted due to the low solubility in methylene chloride. The percentage yields and the general properties of the PEIM(s) are listed in Table X.

The yield for PEIM 26 a was 49% and 26 b was 51.5%. The infrared spectra of the polymers showed absorptions characteristic of aliphatic C-H stretch, aromatic C-H stretch, the symmetric (1744 - 1775 cm\(^{-1}\)) and asymmetric (1685 - 1720 cm\(^{-1}\)) vibrational coupling of the imide C=O group apart from the expected absorptions due to the ester, acid and alcohol functionalities. The specific peak positions observed in the IR spectrum of each polymer are listed in Table X. The IR spectra of the polymers are given in figs. 133 - 134. The inherent viscosity of the polymers in m-cresol were calculated as 0.65 and 0.68 dL/g, respectively. The decomposition temperature of PEIM 26 a and 26 b in nitrogen was found to be 489 °C. The TG/DTA thermograms are given in figs. 135 & 136. Both polymers showed close values for Tg (43.4 °C & 43.7 °C). These values were much higher than the Tg values obtained for aliphatic PEIM’s. The increase in Tg can be attributed to the increased chain stiffness and decreased conformational freedom of the polymer chains.

As in the case of aliphatic PEIM’s, DSC studies were made on both virgin and annealed. samples. Similar sample treatments, temperature programming and same heating-cooling rates were used. Data obtained from 10 and 5 °C/min cycles were taken to interpret the properties of the polymers. The heating curves of the poly(ester-imide)s 26 a and 26 b containing diphenols showed crystal ordering, Tg and Tm
Table X. Percentage yields and general properties of poly(ester-imide)s 26 a - b.

a = peak value of the first endotherm at a heating rate of 10 °C/min; b = melting point obtained from a Fisher Melttemp apparatus; c = viscosity of a 0.5 dL/g solution of the polymers in m-cresol.

<table>
<thead>
<tr>
<th># name</th>
<th>n</th>
<th>Yield %</th>
<th>Tg °C</th>
<th>Tm a °C</th>
<th>Tm b °C</th>
<th>η inh dL/g</th>
<th>Td °C</th>
<th>Major IR Peaks cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Acid/Imide/Ester</td>
</tr>
<tr>
<td>26 a</td>
<td>HyDAC</td>
<td>49</td>
<td>43.4</td>
<td>140.6</td>
<td>144.5</td>
<td>0.65</td>
<td>489</td>
<td>3443, 1397 1765 1765</td>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1717, 1185 1710 1136</td>
</tr>
<tr>
<td>26 b</td>
<td>BPDAC</td>
<td>51</td>
<td>43.7</td>
<td>154.0</td>
<td>155.5</td>
<td>0.68</td>
<td>489</td>
<td>3457, 1393 1769 1769</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1720, 1198 1713 1171</td>
</tr>
</tbody>
</table>
transitions (figs. 137 - 140). As expected the transition temperatures were much higher than the one containing aliphatic diols. The heating curves of virgin 26 a and 26 b showed only one melting endotherm at 141 and 154 °C, respectively. Transition temperatures and the corresponding enthalpies of PEIM(s) 26 a and 26 b are summarized in Table XI.

Table XI. Transition temperatures and the corresponding enthalpies of virgin poly(ester-imide)s 26 a - b at a heating rate of 10 and 5 °C/min.

<table>
<thead>
<tr>
<th>Virgin sample</th>
<th>10 °C/min heating</th>
<th>5 °C/min heating</th>
</tr>
</thead>
<tbody>
<tr>
<td># name</td>
<td>n</td>
<td>Crystal Ordering °C</td>
</tr>
<tr>
<td>26a</td>
<td>HyD Ac</td>
<td>68.5</td>
</tr>
<tr>
<td>26b</td>
<td>BP DAc</td>
<td>74.8</td>
</tr>
</tbody>
</table>

The thermograms (figs. 141 - 144) obtained after annealing at the crystal ordering temperature showed an additional peak around 100 °C. The DSC data of the annealed samples are given in Table XII.

Table XII. Transition temperatures and the corresponding enthalpies of annealed poly(ester-imide)s 26 a - b at 10 and 5 °C/min heating rates.

<table>
<thead>
<tr>
<th>Annealed sample</th>
<th>10 °C/min heating</th>
<th>5 °C/min heating</th>
</tr>
</thead>
<tbody>
<tr>
<td># name</td>
<td>n</td>
<td>L.C. transition °C</td>
</tr>
<tr>
<td>26a</td>
<td>HyD Ac</td>
<td>100.6</td>
</tr>
<tr>
<td>26b</td>
<td>BP DAc</td>
<td>98.9</td>
</tr>
</tbody>
</table>
Multiple crystallization peaks were observed in the 5 °C/min cooling thermograms of both unannealed polymers. These transitions were reproducible in the 10 °C/min cooling scan. The data obtained are summarized in Table XIII. The relevant cooling curves are given in figures 145 - 148.

Table XIII. Comparison of crystallization temperatures and enthalpies of virgin poly(ester-imide)s 26 a - b at 10 and 5 °C/min cooling rates.

<table>
<thead>
<tr>
<th># name</th>
<th>n</th>
<th>Virgin Sample</th>
<th>5 °C/min cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10 °C/min cooling</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>L. C. transition °C</td>
<td>ΔH L. C. transition J/g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tc₁</td>
<td>Tc₂</td>
</tr>
<tr>
<td>26 a</td>
<td>HyD</td>
<td>91.5</td>
<td>64.2</td>
</tr>
<tr>
<td>26 b</td>
<td>BpD</td>
<td>105.7</td>
<td>88.3</td>
</tr>
</tbody>
</table>

Poly(ester-imide)s containing aromatic diols 26 a and 26 b formed birefringent textures. Cooling the melt to temperatures below Tm resulted in the instantaneous formation of birefringent textures (figs. 149 a, b & 150 a, b) indicative of crystalline morphology. Annealing the melt for about an hour at a temperature close to the melting point resulted in the formation of undefined optical texture (figs. 149 c & 150 c) comparable to the fine scale versions of the schlieren texture. The points of singularities were not obvious and may be due to the lack of sufficient resolution of our PLM instrument.
4.0 FUTURE WORK AND CONCLUSIONS

In this thesis study, two dicarboxylic acid monomers containing preformed imides 27 and 28 were successfully prepared. Monomer 28 was used to prepare a series of ten new poly(ester-imide)s by melt polymerization. Ten aliphatic PEIM(s) were prepared by the polycondensation of the diacid 28 with α,ω-dihydroxy alkanes. Two aromatic poly(ester-imide)s were prepared by the polymerization of 28 with methyl esters of hydroquinone and 4,4'-biphenol. Inherent viscosity determinations indicated that these poly(ester-imide)s possess moderately high molecular weight. GPC studies showed a trend in the molecular weight averages consistent with the inherent viscosity values. For the polymer (25 f) with an inherent viscosity of 0.52 dL/g, the calculated value of viscosity average molecular mass corresponded roughly to 36,300 g/mol. High thermal stability in both inert (nitrogen) and oxidizing (air) conditions were observed. IR spectra supported the formation of ester-imides. The synthesized pol(ester-imide)s showed all major thermal transition. DSC and PLM studies indicated that these poly(ester-imide)s are semi-crystalline and the degree of crystallinity can be increased by annealing above glass transition. These polymers showed a definite odd-even effect. Poly(ester-imide)s containing aromatic diols showed higher transition temperatures than those containing aliphatic diols. Annealing of the polymers at the crystal ordering temperature resulted in the appearance of an additional melting endotherm in the low temperature region and better resolution of the existing ones. The title polymers exhibited an enantiotropic liquid
crystalline behavior. DSC results of the annealed 'even' PEIM(s) and the texture observed between crossed polarizers after annealing indicated the presence of an ordered smectic phase below Tm$_2$ and a less ordered smectic phase around Tm$_2$. The presence of multiple endotherms in the DSC’s and the formation of droplets near the clearing temperature followed by the formation of a coarse texture at a low temperature, which are typical of the nematic phase, led to the conclusion that 'odds' exhibited a less ordered nematic phase below the isotropic transition temperature. Multiple endotherms were evident in the DSC thermograms of poly(ester-imide)s containing aromatic diols. The optical micrographs of these polymers taken at temperatures around Tm were comparable to the fine scale versions of the Schlieren texture. PLM studies and analysis of the cooling traces revealed that poly(ester-imide)s containing aliphatic diols have a slow crystallization kinetics and it is much slower in the case of 'odd' polymers. The 'odd' PEIM(s) can be quench cooled from the isotropic melt to the isotropic glass. The rate of crystallization was found to be much faster in the case of polymers containing aromatic diols. The even and the aromatic poly(ester-imide)s were found to be more crystalline than the 'odd' ones. The poly(ester-imide) derived from aliphatic diol where n = 7 showed unusual results in the DSC and PLM studies and is explained as the result of cross-linking or branching due to side reactions. A more specific identification of the mesophases may be possible by X-ray and (or) miscibility studies on these poly(ester-imide)s. The poly(ester-imide)s containing aliphatic diols formed fibers and films with reasonable strength. Fibers spun or films made after annealing will
have better tensile strength and can be used in low temperature applications.

As the true nature of the mesophase is still uncertain, it is instructive to do X-ray diffraction studies on these polymers in the future to correctly identify their molecular ordering. The LC properties of these type of mesogens when present in the main chain are well known. It is now understood that the side chain LC polymers possess some interestingly different properties than the main chain LCP’s, so it would be worthwhile to design a method which can incorporate these mesogens into the side chain of some flexible or rigid polymers.
5.0 EXPERIMENTAL

5.1 Materials

3,3',4,4'-Biphenyl tetra carboxylic acid dianhydride was purchased from Chriskev Company Inc., Leawood, KS. 66211. 6-Amino caproic acid, 11-amino undecanoic acid, 4-aminobenzoic acid and α,ω-diols were purchased from Aldrich Chemical Company. 4,4'-Biphenol was obtained from Eastman Kodak. All solvents/reagents (methylene chloride, methanol, acetone, DMSO, acetic anhydride, dioxane and m-cresol) other than DMF and ethanol were purchased from J. T. Baker Inc. DMF was purchased from Sigma-Aldrich corporation. Ethanol was purchased from the Midwest Grain Products of Illinois. All chemicals were used without further purification.

5.2 Measurements

The required chemicals were weighed out using Sartorius Basic electronic balance. Monomers and polymers were dried under vacuum in a VWR 1410 vacuum oven. Samples for elemental analysis were further dried in a drying pistol apparatus for 24 hours. The melting points of the monomers were measured using a UNI-MELT™ capillary melting point apparatus. Infrared spectra of the monomers were recorded with KBr pellets on a Perkin-Elmer 1760 FT-IR spectrometer. Elemental analysis were done by the Baron Consultant Company, Orange, CT.

The infrared spectra of the polymers were recorded on a Perkin-Elmer 1760 FT-IR by casting film from a dilute methylene chloride solution on a NaCl plate. The inherent viscosities were measured using a
Ubbelohde Viscometer No.1B A278 at 25 °C. Polymer solutions were made in m-cresol at a concentration of 0.5 g/dL. Molecular weight determination of the polymers were done by the Eastman Kodak Co., Rochester, NY. Molecular weights were determined by gel permeation chromatography (GPC) with a Waters Pump # 590 equipped with three 10 micron PL GEL mixed bed columns and a Viscotek integrator data station. The measurements were made using spectra flow UV detector # 757. A 1.5 mg/ml solution of the polymer in THF at a solvent (THF) flow rate of 1 mL/min was used. The instrument was calibrated with narrow molecular weight polystyrene standards (500 to 2,750,000 daltons) to determine the molecular weights. Thermogravimetric analysis were conducted using a Seiko TG/DTA 220 thermogravimetric analyzer at a heating rate of 20 °C/min. The decomposition temperatures (Td) were taken at the mid-point of the decomposition (see appendix). The DSC measurements were conducted using a Seiko DSC 220 Differential Scanning Calorimeter in aluminum pans. Four heating-cooling scans were performed on unannealed samples and data obtained from the 10 °C/min. and 5 °C/min. cycles were taken to interpret the properties of the polymers. The glass transition temperatures (Tg) were read at the middle of the change in heat capacity (see appendix) of the virgin sample at a heating rate of 10 °C/min. The peak values were taken as the transition temperatures. The area under the peaks after base-line correction were taken as a measure of the enthalpy change of transitions at the respective peak temperatures. Effect of annealing on the transition temperatures were analyzed using separate samples. These samples were annealed at the crystal ordering temperature for about 8-10 hours under vacuum
before the first (5 °C/min.) cycle. The second cycle (10 °C/min.) was completed after annealing the sample in the DSC for three hours.

Optical microscopy studies were done using a Reichert Microstar Polarizing Light Microscope equipped with a Mettler FP 52 hot stage and connected to a JVC TM-9060 system monitor screen. Thin films of the polymers were made by pressing the polymer in between a glass plate and a cover glass plate on a hotstage about 50 °C above the melting point. The birefringent textures observed at different temperature were photographed on Polaroid films.

5.3 Preparation of Monomers

5.3.1 Preparation of 6,6'-(3,3',4,4'-Biphenyltetra-carboxy-diimido)-bis-Hexanoic acid 27.

3,3',4,4'-Biphenyltetra-carboxylic dianhydride (29.4 g, 0.1 moles) was dissolved in 500 ml of hot DMF in a clean dry 1000 ml round bottom flask. 6-Aminocaproic acid (26.23 g, 0.2 moles) was added to the solution and refluxed for 2 hours. To the reaction mixture 0.4 moles of acetic anhydride was added and refluxed for two more hours. The cooled reaction mixture was then poured into ice water. The diimide diacid precipitated out as a white fluffy solid. The precipitated product was separated by suction filtration, washed with water and methanol, dried in vacuo at 100 °C overnight to give 48.5 g, 93% yield. The crude dicarboxylic acid was recrystallized from 1,4-dioxane and water, filtered and dried in vacuo at 100 °C for 10 h, mp 217 - 220 °C.
IR: 3300-2500 (-OH stretch), 1769 and 1706 (symmetric and asymmetric imide =C=O stretch) and 1710( =C=O stretch of acid) cm\(^{-1}\). The infrared spectrum (fig. 43) was consistent with the structure 27.

Elemental Analysis: Molecular Formula - C\(_{28}\)H\(_{20}\)O\(_8\)N\(_2\)

Molecular weight - 520.33 g/mol

Calculated(%): C, 64.61; H, 5.42; N, 5.38

Found(%): C, 64.69; H, 5.45; N, 5.60

### 5. 3.2 Preparation of 11.11'-(3,3',4,4'-Biphenyltetracarboxydiimido)-bis-Undecanoic acid 28.

3,3',4,4'-Biphenyltetracarboxylic dianhydride (29.4 g, 0.1 moles) was dissolved in 500 ml of hot DMF in a clean dry 1000 ml round bottom flask. 11-Aminoundecanoic acid (40.2 g, 0.2 moles) was added to the solution and refluxed for 2 hours. To the reaction mixture 0.4 moles of acetic anhydride was added and refluxed for two more hours. The cooled reaction mixture was then poured into ice water. The diimide diacid precipitated as a white powdery solid. The precipitated product was separated by suction filtration, washed with water and methanol, dried in vacuo at 100 °C overnight to give 63.4 g, 96 % yield. The crude dicarboxylic acid was recrystallized from 1,4-dioxane and water, filtered and dried in vacuo at 100 °C for 10h, mp 170-172 °C.
IR: 3300-2300 (-OH stretch), 1770 and 1698 (symmetric and asymmetric imide =C=O stretch) and 1712 ( =C=O stretch of acid) cm⁻¹. The infrared spectrum (fig. 44) was consistent with the structure 28.

Elemental Analysis: Molecular Formula - C$_{38}$H$_{48}$O$_8$N$_2$
Molecular weight - 660.79 g/mol
Calculated(%):
C, 69.07 ; H, 7.32 ; N, 4.24
Found(%):
C, 68.86 ; H, 7.44 ; N, 4.53

5. 3.3 Preparation of 4,4'-(3,3',4,4'-Biphenyltetracarboxydiimido)-bis-Benzoic acid 29.

3,3',4,4'-Biphenyltetracarboxylic dianhydride (29.4 g, 0.1 moles) was dissolved in 500 ml of hot DMF in a clean dry 1000 ml round bottom flask. 4-Aminobenzoic acid (27.43 g, 0.2 moles) was added to the solution and refluxed for 2 hours. After about one hour reflux a pale yellow powdery solid precipitated out from the solution. At the end of two hours reflux, 0.4 moles of acetic anhydride was added and was refluxed for two more hours. The reaction mixture was cooled to room temperature and the precipitated solid was separated by suction filtration, washed with water and methanol, dried in vacuo at 100 °C overnight to give 32.1 g, 60 % yield. The crude products was recrystallized from DMSO, washed and dried in vacuo at 100 °C for 10h, no melting, Td = 471 °C (from TG/DTA - fig. 45).
IR: 3250-2500 (-OH stretch), 1777 and 1683 (symmetric and asymmetric imide =C=O stretch) and 1721( =C=O stretch of acid) cm⁻¹. The IR spectrum is given in fig. 46.

Elemental Analysis:  Molecular Formula - C₃₀H₁₆O₈N₂  
Molecular weight - 532.8 g/mol  
Calculated(%):  C, 67.68 ; H, 3.03 ; N, 5.26  
Found(%):  C, 65.77 ; H, 3.18 ; N, 4.96

5.3.4 Preparation of 4,4'-diacetoxybiphenyl  
Acetylation of 4,4'-biphenol was carried out in the cold by digesting biphenol (0.2 moles, 37.2 g) with excess of acetic anhydride ( 0.336 moles, 31.66 ml) and concentrated sulfuric acid (1 ml) in a clean dry 500 ml round bottom flask for two hours. The white crystalline solid precipitated out was separated by suction filtration, washed with water, dried in vacuo at 80 °C for 4h to give 45.94 g, 85% yield. The crude diacetate was recrystallized from ethanol, filtered and dried in vacuo for 4h, mp 158 - 159 °C. Lit. mp 160 - 161 °C.134

IR: 1755 (-C=O stretch), 1245 and 1200 (-C-O- stretch) cm⁻¹. The IR spectrum (fig. 47) is consistent with the structure.

5.3.5 Preparation of 1,4-diacetoxyhydroquinone  
Acetylation of 1,4-hydroquinone was carried out in the cold by digesting hydrrquinone (0.2 moles, 22.0 g) with excess of acetic anhydride (0.336 moles, 31.66 ml) and concentrated sulfuric acid (1 ml) for two hours. The white crystalline solid precipitated out was separated by
suction filtration, washed with water, dried in vacuo at 80 °C for 4 h to give 33.79 g, 87 % yield. The crude diacetate was recrystallized from ethanol, filtered, dried in vacuo at 80 °C for 4h, mp 121 - 122 °C. Lit. mp 123 - 124 °C.134
IR: 1760 (-C=O stretch), 1230 and 1175 (-C-O- stretch) cm⁻¹. The IR spectrum (fig. 48) and melting point was consistent with the structure.

5.4 Polycondensations

The diimide diacid 28 and the selected diols and diacetates were polymerized by a melt polymerization technique. The set-up used for polymerization consists of a reaction flask, (a long neck round bottom flask with a side arm) placed in salt bath (a mixture of KNO₃ and NaNO₂ in the ratio 10:8.5) as the heat source. The temperature of the bath is controlled by a heating mantle through a rheostat. The mouth of the reactor can be connected to an attachable/detachable assembly, which serves as an inlet for N₂ gas and measure the amount of distillate distilled out at the first phase of the reaction during which the side arm can be closed by a cork or to the mechanical stirrer equipped with a set up to measure the rotations per minute of the stirrer and the torque of the reaction in the second phase of the reaction. The side arm is then connected to a condenser through a dry ice - isopropanol freeze trap which in turn is connected to two more similar freeze traps in series and a vacuum pump. The condenser has valves that can be connected to a house vacuum or vacuum pump to adjust the required vacuum. It is also equipped with a meter that can read the pressure inside the reactor and a pressure release valve.
5.4.1 **General procedure for melt polymerization.**

Almost all polymerization were carried out in the same manner described below. In a dry 100 ml reaction flask placed diimide dicarboxylic acid 28 (0.03 moles, 19.82 g) and 80 -100 % excess of diol (1,3-propane diol- 0.06 moles, 4.57 g). Tetraisopropyl titanate (10 drops) was added as the catalyst. The first assembly described above was attached to the reactor and slow stream of nitrogen gas was passed through the reactor. The mixture was heated initially at 190 °C and was gradually raised to 215 °C within two hours. A few ml of the distillate was collected in the receiver. At the end of the two hours reflux, mechanical stirrer and house vacuum were applied. The stirrer speed was set at 200 rpm, the torque at this point ranged from 30 - 50 millivolts. The temperature was gradually raised to 240 °C. After about two hours the house vacuum was replaced by vacuum pump and the temperature was gradually raised to 250 °C. The temperature was kept at 250 °C for 2 hours, in the course of which the torque gradually increased to 150 millivolts. The stirrer speed was then reduced to 100 rpm and within 30 - 45 minutes the torque read off scale, upon which the stirrer speed was reduced to 50 rpm. After about 30 - 40 minutes the torque reached 120 millivolts and the reaction was stopped. With the exception of 26 a and 26 b, yellow to brown colored stirrable melts which can be drawn into long fibers were obtained at the end of polycondensations. The polymers were removed from the reactors mechanically by breaking the glass reaction flask after cooling in liquid nitrogen. They were dissolved in hot methylene chloride (some needed hours of shaking to go into solution) and were precipitated from cold methanol. The precipitated polymers had a dirty white fibrous appearance, filtered and were dried in vacuo at 80
°C for 10 hours. Polymers 26 a and 26 b were very sparingly soluble in methylene chloride and so they were used as such for characterization. The polymers were then characterized by IR, dilute solution viscosity, gel permeation chromatography, thermogravimetric analysis, differential scanning calorimetry and polarizing light microscopy with the results summarized in Tables IV - XIII.

5.4.2 Preparation of Aliphatic Poly(ester-imide)s

Polycondensation of 28 with 1,3-propanediol to give PEIM 25 a.

Diacid 28, (0.03 moles, 19.82 g) was mixed with 1,3-propanediol (0.06 moles, 4.57 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 18.08 g, 83% yield, of poly(ester-imide) 25 a with \( \eta_{inh} = 0.51 \text{ dL/g} \) and \( T_d = 487 \text{ °C} \). DSC heating scan of the virgin sample at 10 °C/min gave \( T_g = 15.9 \text{ °C} \) and \( T_m = 62.0 \text{ °C} \). DSC heating scan of the sample at 5 °C/min after annealing at 52 °C for 8 hours gave \( T_{m1} = 62.6 \text{ °C} \), \( T_{m2} = 91.8 \text{ °C} \) and \( T_{m3} = 103.5 \text{ °C} \). The infrared spectrum (fig. 52) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.

Polycondensation of 28 with 1,4-butanediol to give PEIM 25 b.

Diacid 28, (0.03 moles, 19.82 g) was mixed with 1,4-butanediol (0.06 moles, 5.41 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 18.16 g, 81 % yield, of poly(ester-imide) 25 b with \( \eta_{inh} = 0.56 \text{ dL/g} \) and \( T_d = 485 \text{ °C} \). DSC heating scan of the
virgin sample at 10 ºC/min gave \( T_g = 11.7 \) ºC and \( T_m = 135.5 \) ºC. DSC heating scan of the sample at 10 ºC/min after annealing at 65 ºC for 8 hours gave \( T_{m1} = 84.2 \) ºC and \( T_{m2} = 135.9 \) ºC. The infrared spectrum (fig. 53) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI, & VIII.

**Polycondensation of 28 with 1,5-pentanediol to give PEIM 25 c.**

Diacid 28 (0.05 moles, 33.04 g) was mixed with 1,5-pentanediol (0.08 moles, 8.332 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 31.98 g, 83 % yield, of poly(ester-imide) 25 c with \( \eta_{inh} = 0.75 \) dL/g and \( T_d = 485 \) ºC. DSC heating scan of the virgin sample at 10 ºC/min gave \( T_g = 10.2 \) ºC and \( T_m = 69.9 \) ºC. DSC heating scan of the sample at 10 ºC/min after annealing at 80 ºC for 8 hours gave \( T_{m1} = 88.5 \) ºC and \( T_{m2} = 108.1 \) ºC. The infrared spectrum (fig. 54) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.

**Polycondensation of 28 with 1,6-hexanediol to give PEIM 25 d.**

Diacid 28, (0.05 moles, 33.04 g) was mixed with 1,6-hexanediol (0.08 moles, 10.0 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 33.44 g, 90 % yield, of poly(ester-imide) 25 d with \( \eta_{inh} = 0.62 \) dL/g and \( T_d = 481 \) ºC. DSC heating scan of the virgin sample at 10 ºC/min gave \( T_g = 4.9 \) ºC and \( T_m = 131.5 \) ºC. DSC heating scan of the sample at 10 ºC/min after annealing at 60 ºC for 8 hours gave
Tm_1 = 72.0 °C and Tm_2 = 133.2 °C. The infrared spectrum (fig. 55) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.

**Polycondensation of 28 with 1,7-heptanediol to give PEIM 25 e.**

Diacid 28, (0.05 moles, 33.04 g) was mixed with 1,7-heptanediol (0.06 moles, 10.576 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 22.61 g, 67 % yield, of poly(ester-imide) 25 e with \( \eta_{inh} = 1.65 \text{ dL/g and } Td = 488 \text{ °C}. \) DSC heating scan of the virgin sample at 10 °C/min gave \( Tg = 16.9 \text{ °C and } Tm = 58.6 \text{ °C}. \) DSC heating scan of the sample at 10 °C/min after annealing at 98 °C for 8 hours gave \( Tm_1 = 73.4 \text{ °C, } Tm_2 = 88.4 \text{ °C and } Tm_3 = 113.1 \text{ °C}. \) The infrared spectrum (fig. 56) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.

**Polycondensation of 28 with 1,8-octanediol to give PEIM 25 f.**

Diacid 28, (0.03 moles, 33.04 g) was mixed with 1,8-octanediol (0.06 moles, 11.6 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 34.54 g, 89 % yield, of poly(ester-imide) 25 f with \( \eta_{inh} = 0.53 \text{ dL/g and } Td = 482.0 \text{ °C}. \) DSC heating scan of the virgin sample at 10 °C/min gave \( Tg = 2.6 \text{ °C and } Tm = 125.0 \text{ °C}. \) DSC heating scan of the sample at 10 °C/min after annealing at 51 °C for 8 hours gave \( Tm_1 = 72.2 \text{ °C and } Tm_2 = 127.7 \text{ °C}. \) The infrared spectrum
(fig. 57) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.

**Polycondensation of 28 with 1,9-nonanediol to give PEIM 25 g.**

Diacid 28, (0.03 moles, 19.82 g) was mixed with 1,9-nonanediol (0.06 moles, 9.61 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 20.28 g, 86 % yield, of poly(ester-imide) 25 g with $\eta_{inh} = 0.61$ dL/g and $T_d = 497$ °C. DSC heating scan of the virgin sample at 10 °C/min gave $T_g = 2.4$ °C and $T_m = 102.6$ °C. DSC heating scan of the sample at 10 °C/min after annealing at 54 °C for 8 hours gave $T_{m1} = 70.9$ °C and $T_{m2} = 103.8$ °C. The infrared spectrum (fig. 58) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.

**Polycondensation of 28 with 1,10-octanediol to give PEIM 25 h.**

Diacid 28, (0.025 moles, 16.52 g) was mixed with 1,10-octanediol (0.05 moles, 8.714 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 17.12 g, 86 % yield, of poly(ester-imide) 25 h with $\eta_{inh} = 0.82$ dL/g and $T_d = 479$ °C. DSC heating scan of the virgin sample at 10 °C/min gave $T_g = 1.4$ °C and $T_m = 122.5$ °C. DSC heating scan of the sample at 10 °C/min after annealing at 45. °C for 8 hours gave $T_{m1} = 61.9$ °C and $T_{m2} = 122.8$ °C. The infrared spectrum (fig. 59) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.
Polycondensation of 28 with 1,11-undecanediol to give PEIM 25 i.

Diacid 28, (0.03 moles, 19.82 g) was mixed with 1,11-undecanediol (0.06 moles, 11.29 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 21.88 g, 89% yield, of poly(ester-imide) 25 i with η_inh = 0.77 dL/g and Td = 486 °C. DSC heating scan of the virgin sample at 10 °C/min gave Tg = 2.7 °C and Tm = 103.8 °C. DSC heating scan of the sample at 10 °C/min after annealing at 30 °C for 8 hours gave Tm₁ = 52.7 °C and Tm₂ = 103.8 °C. The infrared spectrum (fig. 60) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.

Polycondensation of 28 with 1,12-dodecanediol to give PEIM 25 j.

Diacid 28, (0.025 moles, 16.52 g) was mixed with 1,10-octanediol (0.05 moles, 10.17 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 19.05 g, 92% yield, of poly(ester-imide) 25 j with η_inh = 0.71 dL/g and Td = 480 °C. DSC heating scan of the virgin sample at 10 °C/min gave Tg = 1.4 °C and Tm = 122.3 °C. DSC heating scan of the sample at 10 °C/min after annealing at 45 °C for 8 hours gave Tm₁ = 56.0 °C and Tm₂ = 123.2 °C. The infrared spectrum (fig. 61) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables IV, VI & VIII.
5.4.3 Preparation of Aromatic Poly(ester-imide)s

Polycondensation of 28 with 1,4-diacetoxybenzene to give PEIM 26a.

Diacid 28, (0.03 moles, 19.82g) was mixed with 1,4-diacetoxybenzene (0.04 moles, 7.77 g) in a dry 100 ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 12.02 g, 49 % yield, of poly(ester-imide) 26a with \( \eta_{\text{inh}} = 0.65 \text{ dL/g} \) and \( T_d = 488 \text{ °C} \). DSC heating scan of the virgin sample at 10 °C/min gave \( T_g = 43.4 \text{ °C} \) and \( T_m = 140.6 \text{ °C} \). DSC heating scan of the sample at 10 °C/min after annealing at 69 °C for 8 hours gave \( T_{m1} = 100.6 \text{ °C} \) and \( T_{m2} = 136.9 \text{ °C} \). The infrared spectrum (fig. 133) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables X - XII.

Polycondensation of 28 with 4,4′-diacetoxybiphenyl to give PEIM 26b.

Diacid 28, (0.03 moles, 19.82 g) was mixed with (4,4′-diacetoxybiphenyl (0.03 moles, 8.1063 g) in a dry 100ml reaction flask and polymerized by the procedure described above in presence of tetraisopropyl titanate (10 drops) as the catalyst to give 13.82 g, 51 % yield, of poly(ester-imide) 26b with \( \eta_{\text{inh}} = 0.68 \text{ dL/g} \) and \( T_d = 489 \text{ °C} \). DSC heating scan of the virgin sample at 10 °C/min gave \( T_g = 43.7 \text{ °C} \) and \( T_m = 154.0 \text{ °C} \). DSC heating scan of the sample at 10 °C/min after annealing at 75 °C for 8 hours gave \( T_{m1} = 98.9 \text{ °C} \) and \( T_{m2} = 157.3 \text{ °C} \). The infrared spectrum (fig. 134) is consistent with poly(ester-imide) structure. The IR peaks and enthalpy of transitions are shown in tables X - XII.
6.0 REFERENCES

84. Noel, C.; Billard, J.; Fayolle, B. J. de Physique. 1979, 40, C3-485.
Fig. 43. Infrared spectrum of monomer 27.
Fig. 44. Infrared spectrum of monomer 28.
**Fig. 45.** TG/DTA thermogram of monomer 29 at a heating rate of 20 °C/min in nitrogen.
Fig. 47. Infrared spectrum of 1,4-diacetoxyhydroquinone.
Fig. 48. Infrared spectrum of 4,4'-diacetoxybiphenol.
Fig. 49. GPC chromatogram of PEIM 25 c.
Fig. 50. GPC chromatogram of PEIM 25 d.
Fig. 51. GPC chromatogram of PEIM 25 f.
Fig. 53. Infrared spectrum of PEIM 25 b.
Fig. 54. Infrared spectrum of PEIM 25 c.
Fig. 55. Infrared spectrum of PEIM 25 d.
Fig. 56. Infrared spectrum of PEIM 25 e.
Fig. 59. Infrared spectrum of PEIM 25 h.
Fig. 61. Infrared spectrum of PEIM 25 J.
Fig. 62. TG/DTA thermogram of PEIM 25a at a heating rate of 20 °C/min in nitrogen.
Fig. 63. TG/DTA thermogram of PEIM 25 b at a heating rate of 20 °C/min in nitrogen.
Fig. 64. TG/DTA thermogram of PEIM 25c at a heating rate of 20 °C/min in nitrogen.
Fig. 65. TG/DTA thermogram of PEIM 25 d at a heating rate of 20 °C/min in nitrogen.
**Fig. 66.** TG/DTA thermogram of PEIM 25 e at a heating rate of 20 °C/min in nitrogen.
Fig. 67. TG/DTA thermogram of PEIM 25 f at a heating rate of 20 °C/min in nitrogen.
Fig. 68. TG/DTA thermogram of PEIM 25 g at a heating rate of 20 °C/min in nitrogen.
Fig. 69. TG/DTA thermogram of PEIM 25 h at a heating rate of 20 °C/min in nitrogen.
Fig. 70. TG/DTA thermogram of PEIM 25 at a heating rate of 20 °C/min in nitrogen.
Fig. 71. TG/DTA thermogram of PEIM 25 j at a heating rate of 20 °C/min in nitrogen.
Fig. 72. TG/DTA thermogram of PEIM 25 b at a heating rate of 20 °C/min in air.
### TG/DTA Data

- **Sample**: BPDA115dial1
- **Comment**: 20 °C/min
- **Temp program**: 1 × 25.0 - 550.0 °C/min
- **Gas**: Air
- **Flow**: 0.0 ml/min
- **Date**: 94/02/03 12:02
- **Reference**: Al
- **Sample mass**: 0.000 mg
- **Sampling**: 0.5 sec

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**Figure 73.** TG/DTA thermogram of PEIM 25 c at a heating rate of 20 °C/min in air.
Fig. 74. DSC thermogram of virgin PEIM 25 b at a heating rate of 10 °C/min in nitrogen.
Fig. 75. DSC thermogram of virgin PEIM 25 f at a heating rate of 10 °C/min in nitrogen.
Fig. 76. DSC thermogram of virgin PEIM 25 h at a heating rate of 10 °C/min in nitrogen.
**Fig. 77.** DSC thermogram of virgin PEIM 25 J at a heating rate of 10 °C/min in nitrogen.
Fig. 78. DSC thermogram of virgin PEIM 25 b at a heating rate of 5 °C/min in nitrogen.
Fig. 79. DSC thermogram of annealed PEIM 25 d at a heating rate of 5 °C/min in nitrogen.
Fig. 80. DSC thermogram of annealed PEIM 25 f at a heating rate of 5 °C/min in nitrogen.
Fig. 81. DSC thermogram of virgin PEIM 25 h at a heating rate of 5 °C/min in nitrogen.
Fig. 82. DSC thermogram of virgin PEIM 25 j at a heating rate of 5 °C/min in nitrogen.
Fig. 83. DSC thermogram of annealed PEIM 25 b at a heating rate of 5 °C/min in nitrogen.
Fig. 84. DSC thermogram of annealed PEIM 25 f at a heating rate of 5 °C/min in nitrogen.
Fig. 85. DSC thermogram of annealed PEIM 25 h at a heating rate of 5 °C/min in nitrogen.
Fig. 86. DSC thermogram of annealed PEIM 25 J at a heating rate of 5 °C/min in nitrogen.
Fig. 87. DSC thermogram of annealed PEIM 25 b at a heating rate of 10 °C/min in nitrogen.
Fig. 88. DSC thermogram of annealed PEIM 25 d at a heating rate of 10 °C/min in nitrogen.
Fig. 89. DSC thermogram of annealed PEIM 25 f at a heating rate of 10 °C/min in nitrogen.
Fig. 90. DSC thermogram of annealed PEIM 25 h at a heating rate of 10 °C/min in nitrogen.
Fig. 91. DSC thermogram of annealed PEIM 25 j at a heating rate of 10 °C/min in nitrogen.
Fig. 92. DSC thermogram of virgin PEIM 25a at a heating rate of 10 °C/min in nitrogen.
Fig. 93. DSC thermogram of virgin PEIM 25 g at a heating rate of 10 °C/min in nitrogen.
Fig. 94. DSC thermogram of virgin PEIM 251 at a heating rate of 10 °C/min in nitrogen.
Fig. 95. DSC thermogram of virgin PEIM 25a at a heating rate of 5 °C/min in nitrogen.
Fig. 96. DSC thermogram of virgin PEIM 25 e at a heating rate of 5 °C/min in nitrogen.
Fig. 97. DSC thermogram of virgin PEIM 25 g at a heating rate of 5 °C/min in nitrogen.
Fig. 98. DSC thermogram of virgin PEIM 25 i at a heating rate of 5 °C/min in nitrogen.
Fig. 99. DSC thermogram of annealed PEIM 25 a at a heating rate of 5 °C/min in nitrogen.
Fig. 100. DSC thermogram of annealed PEIM 25 g at a heating rate of 5 °C/min in nitrogen.
Fig. 101. DSC thermogram of annealed PEIM 25 i at a heating rate of 5 °C/min in nitrogen.
Fig. 102. DSC thermogram of annealed PEIM 25 a at a heating rate of 10 °C/min in nitrogen.
Fig. 103. DSC thermogram of annealed PEIM 25 c at a heating rate of 10 °C/min in nitrogen.
Fig. 104. DSC thermogram of annealed PEIM 25 g at a heating rate of 10 °C/min in nitrogen.
Fig. 105. DSC thermogram of annealed PEIM 25 i at a heating rate of 10 °C/min in nitrogen.
Fig. 106. DSC cooling curve of virgin PEIM 25 b at 10 °C/min in nitrogen.
Fig. 107. DSC cooling curve of virgin PEIM 25 d at 10 °C/min in nitrogen.
Fig. 108. DSC cooling curve of virgin PEIM 25 f at 10 °C/min in nitrogen.
Fig. 109. DSC cooling curve of virgin PEIM 25 h at 10 °C/min in nitrogen.
**Fig. 110.** DSC cooling curve of virgin PEIM 25 j at 10 °C/min in nitrogen.
Fig. 111. DSC cooling curve of virgin PEIM 25 b at 5 °C/min in nitrogen.
Fig. 112. DSC cooling curve of virgin PEIM 25 d at 5 °C/min in nitrogen.
Fig. 113. DSC cooling curve of virgin PEIM 25 f at 5 °C/min in nitrogen.
Fig. 114. DSC cooling curve of virgin PEIM 25 h at 5 °C/min in nitrogen.
Fig. 115. DSC cooling curve of virgin PEIM 25J at 5 °C/min in nitrogen.
Fig. 116. DSC cooling curve of virgin PEIM 25a at 10 °C/min in nitrogen.
Fig. 117. DSC cooling curve of virgin PEIM 25 c at 10 °C/min in nitrogen.
Fig. 118. DSC cooling curve of virgin PEIM 25 g at 10 °C/min in nitrogen.
Fig. 119. DSC cooling curve of virgin PEIM 25 I at 10 °C/min in nitrogen.
Fig. 121. DSC cooling curve of virgin PEIM 25 e at 5 °C/min in nitrogen.
Fig. 122. DSC cooling curve of virgin PEIM 25 g at 5 °C/min in nitrogen.
Fig. 123. DSC cooling curve of virgin PEIM 25 I at 5 °C/min in nitrogen.
Fig. 124. DSC thermogram of virgin PEIM 25 e at a heating rate of 10 °C/min in nitrogen.
Fig. 125. DSC thermogram of virgin PEIM 25 e at a heating rate of 5 °C/min in nitrogen.
Fig. 126. DSC cooling curve of virgin PEIM 25 e at 10 °C/min in nitrogen.
Fig. 127. DSC cooling curve of virgin PEIM 25 e at 5 °C/min in nitrogen.
Fig. 128. DSC thermogram of annealed PEIM 25 e at a heating rate of 5 °C/min in nitrogen.
Fig. 129. DSC thermogram of annealed PEIM 25 e at a heating rate of 10 °C/min in nitrogen.
Fig. 130: Photomicrographs of Poly(ester-imide) 25h between crossed polarizers: (a) after annealing at 100°C for 1 hour; (b) at 118°C on heating; (c) after annealing at 115°C for 8 hours; (d) after annealing at 120°C for 12 hours.
Fig. 131: Photomicrographs of Poly(ester-imide) 25j between crossed polarizers: (a) at 100°C on cooling from the isotropic melt; (b) after annealing at 120°C for 12 hours.
Fig. 132: Photomicrographs of Poly(ester-imide) 25i between crossed polarizers: (a) at 81°C on cooling from the isotropic melt; (b) at 105°C on heating; (c) after annealing at 100°C for 8 hours.
Fig. 134. Infrared spectrum of PEIM 26 b.
Fig. 135. TG/DTA thermogram of PEIM 26 a at a heating rate of 20 °C/min in nitrogen.
Fig. 136. TG/DTA thermogram of PEIM 26 b at a heating rate of 20 °C/min in nitrogen.
Fig. 137. DSC thermogram of virgin PEIM 26a at a heating rate of 10 °C/min in nitrogen.
Fig. 138. DSC thermogram of virgin PEIM 26 at a heating rate of 5°C/min in nitrogen.
Fig. 139. DSC thermogram of virgin PEIM 26 b at a heating rate of 10 °C/min in nitrogen.
Fig. 140. DSC thermogram of virgin PEIM 26 b at a heating rate of 5 °C/min in nitrogen.
Fig. 141. DSC thermogram of annealed PEIM 26a at a heating rate of 5 °C/min in nitrogen.
DSC thermogram of annealed PEIM 26a at a heating rate of 10°C/min in nitrogen.
Fig. 144. DSC thermogram of annealed PEIM 26 b at a heating rate of 10 °C/min in nitrogen.
Fig. 145. DSC cooling curve of virgin PEIM 26a at 10 °C/min in nitrogen.
Fig. 146.  DSC cooling curve of virgin PEIM 26a at 5 °C/min in nitrogen.
Fig. 147. DSC cooling curve of virgin PEIM 26 at 10 °C/min in nitrogen.
Fig. 148. DSC cooling curve of virgin PEIM 26 b at 5 °C/min in nitrogen.
Fig. 149: Photomicrographs of Poly(ester-imide) 26a between crossed polarizers: (a) at 110°C on cooling from the isotropic melt; (b) after annealing at 145°C for 6 hours; (c) after annealing at 147°C for 8 hours.
Fig. 150: Photomicrographs of Poly(ester-imide) 26b between crossed polarizers: (a) at 100°C on cooling from the isotropic melt; (b) after annealing at 145°C for 2 hours; (c) after annealing at 159°C for 8 hours.