CHAPTER - 1
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INTRODUCTION

Today's innovation in technology demands high performance new materials and spurs its research and development race. Especially in the plastics field, numerous new engineering plastics have been developed. Liquid Crystal Polyesters (LCPs) are a new class of engineering plastics which has attracted significant interest.

1.1 HISTORY

The liquid crystal phase (mesomorphism) occurs on the phase diagram between the crystal and the liquid phase. It is an unusually fascinating state because it combines properties of both the above phases. Liquid crystals behave mechanically as liquids yet exhibit many of the optical properties of crystals. The molecular organisation pattern is such that orientational ordering is dominant while long range positional ordering characteristic of a crystal is absent.

Lehmann\textsuperscript{1} confirmed Reinitzer's\textsuperscript{2} observation of liquid crystal phase in cholesteryl benzoate by polarising microscope and coined the term "liquid crystal" to denote the partially ordered fluid phase that forms upon melting the crystalline state. Much credit for the early work that extended the number of known liquid crystal systems belongs to Gattermann\textsuperscript{3,4}, Lehmann and Vorlander\textsuperscript{5}.

Coming to macromolecules, there are reports way from 1937 regarding mesomorphism in bio-polymers\textsuperscript{6}. Formation of polymeric liquid crystals was predicted in 1956 by Flory\textsuperscript{7}. But the subject received real recognition due to pioneering work by Kwolek and her coworkers in DuPont de Nemours Inc., which led to lyotropic LCP\textsuperscript{8-10}. Synthetic polyamides, with all linear -1,4- (para) disubstituted structures, were found to show mesomorphism above a critical concentration in solution. Fibres formed from this solution had remarkably high
tensile strength and bending modulus. This development gave impetus to the search in many fibre producing companies for the fibre spun from liquid crystalline melts (thermotropic LCPs) which could have extraordinary mechanical properties.

The research in thermotropic LCPs was initiated from a desire to increase the mechanical properties, heat resistance and fire retardance of poly(ethylene terephthalate) [PET] fibres and plastics by increasing the aromatic character through copolymerisation. The first observations of thermotropic liquid crystalline behaviour in polymers were made independently by Kuhfuss and Jackson\textsuperscript{11-13} as well as Roviello and Sirigu.\textsuperscript{14} The former group described a series of copolymers generated through the reaction between PET and 4-acetoxy benzoic acid which exhibited the phenomenon of opaque melts, low melt viscosities and anisotropic properties. This triggered considerable research interest in this class of polymers.

1.2 CAUSE OF LIQUID CRYSTALLINITY

It is interesting to know what is the cause for this intermediate state to ensue between an anisotropic solid and truly isotropic liquid. This is due to the existence of rigid anisotropic structural elements known as mesogens.\textsuperscript{15,16} Most mesogenic molecules conform to the generic type

\[
\begin{align*}
R_1 & \quad \bigcirc \quad X \quad \bigcirc \quad R_2 \\
& \quad \text{Mesogens do not conform to a specific chemical structure but comprise of } para \text{ disubstituted aromatics (1,4-phenylene; 4,4'-biphenylene; 1,4- and 2,6-naphthalene) coupled to rigid groups (X) such as ester, azoxy, azomethine, nitrone, ethene and ethyne. The condition for a structural element to be a mesogen is that the length to diameter ratio i.e. axial/aspect ratio must exceed 3.}
\end{align*}
\]
At present our understanding of polymeric liquid crystals is largely derived from studies of monomeric liquid crystals. The intrinsic differences between the two arise from the chain character present in polymeric materials. It can be assumed, akin to low molecular mass liquid crystals, that even in polymeric liquid crystals the rigid elongated shape of molecules and the anisotropic intermolecular forces associated with that shape are the key parameters responsible for the formation of stable liquid crystalline state.

1.3 CLASSIFICATION

Liquid crystallinity can be induced either by thermal effects or by solvation. Accordingly, the polymers are classified as in Figure 1.1.

1.3.1 Lyotropic Liquid Crystal Polymers

In these systems the mesomorphism is observable within definite range of concentration in solution. These are the first generation liquid crystalline polymeric systems, of which KEVLAR is well known.

1.3.2 Thermotropic Liquid Crystal Polymers

These are the second generation high performance systems. In this the mesomorphic transitions are sensitive to temperature. Based on linking of mesogenic moiety in the polymer the liquid crystal polymers are divided into two types (Figure 1.2): main chain and side chain systems.

1.3.2.1 Main chain liquid crystal polymers

Here mesogen is jointed together as part of backbone of the polymer. Commercialised main chain LCPs are classified into three types, from their structures, as follows:

Type I: Flow Temperature > 320°C
FIGURE 1.1 CLASSIFICATION OF LIQUID CRYSTALLINE POLYMERS
FIGURE 1.2 THERMOTROPIC POLYMERS WITH EITHER MAIN CHAIN OR SIDE CHAIN MESOGENIC UNITS
1.3.2.2 Side chain liquid crystal polymers

As the name indicates, these have the rod like moiety secured to the polymer backbone in the form of a pendant or as a constituent of the side chain. Side chain polymers essentially consist of three interrelated components: back-bone, spacer and mesogen. Mesogen unit needs to be rod like. Ultimate properties of the polymer originate from a synergistic fusion of all the three structural moieties.\textsuperscript{19-22}

1.3.3 Classification Based On Molecular Order

Liquid crystalline structures can be organised into several classes, in a manner akin to the organisation of crystalline materials into cubic, triclinic, monoclinic etc. The major liquid crystalline topologies are shown in Figure 1.3.
FIGURE 1.3 MAJOR LIQUID CRYSTALLINE TOPOLOGIES.
1.4 POLYMORPHISM IN THERMOTROPIC MATERIALS

Most thermotropic liquid crystalline materials are known to be polymorphous. i.e. they show more than one type of phase between a true solid and a liquid. An increase in temperature results in progressive destruction of order. Thus mesophase with increasing order are observable closer to the solid phase. The order of occurrence of mesophase with increase in temperature may be represented as:

Solid ----> Smectic B ----> Smectic C ----> Smectic A ----> Nematic ----> Isotropic

1.5 THEORY

Two classical approaches known are: (i) Lars Onsager's Virial model concerning isolated rigid rods and (ii) Flory's Lattice model regarding concentrated solution of connected rigid rods.

1.5.1 Virial Model

Onsager's theory based on virial expansion showed that a solution of hard asymmetric particles, such as long rods, should separate into two phases above a critical concentration. This is related to the axial ratio of particles. Such a phase separation is only due to shape asymmetry and is independent of intermolecular attractive forces. However, the drawback of this approach is that it can not be extended to highly asymmetric particles.

1.5.2 Lattice Model

Lattice theory has been successfully applied to polymeric materials. It is applicable to polydisperse systems, to mixtures of rod like polymers with random coils and to some semi-rigid chains.

\[ V_p^* = \frac{8}{x} \]  \hspace{1cm} (1.1)
This relation is widely used to represent the threshold volume fraction for the appearance of a stable anisotropic phase. \( V_p^{(*)} \) is the volume fraction of polymer solution of hard rods (no intermolecular attraction) of axial ratio \( x \).

**Figure 1.4** represents variation of volume fraction of isotropic \( V_p \) and anisotropic phases \( V_p^{*} \) with \( x \). These curves merge at \( x = 6.42 \). This is the calculated minimum value of \( x \) for stable nematic order in a melt of hard rods. In monodisperse polymers \( V_p/V_p^{*} \) is in the range 1.3 to 1.6. The ratio will be higher for polydisperse polymers.

DiMarzio\(^2\) discussed the spontaneous ordering of linear polymer molecules having a rigid rod shape in solution as well as in the melt and concluded that orientational ordering would occur as a consequence of asymmetry of the particles, without an additional requirement of any attractive interactions among the particles being involved. Both these theories also yield a critical order parameter given by:

\[
S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle
\]

where \( S \) is a measure of degree of ordering with respect to the principal direction (director). This parameter varies from 0 to 1. \( S = 1 \) for perfect alignment; for completely random isotropic phase \( S = 0 \) and for perpendicular arrangement it is 1/2.

### 1.6 STRUCTURE-PROPERTY RELATIONSHIP

It is sensible and productive to prepare different types of polymers with mesogenic units in order to understand the interdependence of structure and properties observable in LCPs. Experimentation can generate innumerable liquid crystal systems (Figure 1.5).

The rigid rod of the chain can be accommodated by at least two "para" linked aromatic rings like 1,4-phenylene, 2,6-naphthalene or "trans" 1,4-cyclohexylene rings. The rings can be connected by rigid links such as azomethine (-CH=N-) , azo (-N=N-) , azoxy (-N=O-) , ester (-C=O-) in addition to the biphenylene type linking.\(^2\) These links help to maintain
FIGURE 1.4  VARIATION OF VOLUME FRACTION OF ISOTROPIC AND ANISOTROPIC PHASES WITH THE AXIAL RATIO
FIGURE 1.5  STRUCTURE - PROPERTY RELATIONSHIP OBSERVABLE IN LIQUID CRYSTAL POLYMERS.
linearity and planarity of the aromatic rings. The mesogen can be asymmetrically substituted by replacing hydrogen with groups like F, Cl, Br, CH$_3$, OCH$_3$, phenyl etc. Ester and ether groups are normally observed connecting units to bridge mesogen and the disrupter. Recent investigations also show the presence of amide, imine, carbonates as the bridging groups. Disrupter or spacer is frequently polymethylene. In this approach, a rigid element is formed with an overall length that is substantially greater than the diameter of aromatic rings.

1.7 MESOPHASE STABILITY

The nature and thermal stability of mesophase is a function of all the structural units present in the main chain. It is expressed in equation (1.3) and can be represented as follows.

\[
\begin{array}{c|c|c}
\text{SOLID} & \text{LIQUID-CRYSTAL} & \text{LIQUID} \\
\hline
T_{m} & T_{i} & \\
\end{array}
\]

\[\Delta T = T_i - T_m\]  \hspace{1cm} (1.3)

where, $T_i$ is clearing temperature and $T_m$ is melting temperature.

1.7.1 Effect of mesogenic links on mesophase stability

Mesogenic polymers with ester mesogenic links have been studied extensively. Mesophase stability is affected by number of ester links, direction of linking and arrangement of ester links e.g.

\[
\text{SMECTIC ; } \Delta T = 23
\]

\[
\text{NEMATIC ; } \Delta T = 72
\]
On changing the direction of linking the extent of conjugation is altered and therefore the stability is affected.

### 1.7.1.1 Azo and azoxy links

Diad mesogens with azo and azoxy links have been found to show stable liquid crystal phase. However, when such mesogens are terminated with carboxyl group, the mesophase stability is limited and either monotropic or non-LC polymers are formed.

\[
\begin{align*}
\text{NON L.C.} & \quad \Delta T = 0 \\
\text{NEMATIC} & \quad \Delta T = 49
\end{align*}
\]

However, mesophase is formed if the direction of linking of carboxyl group is changed as in case of following systems:

### 1.7.1.2 Trans vinylene links

The behaviour of trans vinylenes are similar to that of azo and azoxy compounds due to the similarities in size and geometry. Mesogens of same length with the same spacer group but having azo and azoxy linking unit in one and stilbene type linking in the other differ in their stability. The stability in the former is enhanced by the presence of polar linking groups.
1.7.2 Effect of central group

Polarity, planarity and rigidity of the central group influence mesophase stability.\(^4\)

![Chemical structure I](image)

\[
\begin{align*}
T_m &= 209°C \\
T_l &= 285°C
\end{align*}
\]

When central phenyl ring is replaced by A, \(T_{N-I}\) reduces by 16°C while replacement by B reduces \(T_{N-I}\) by 40°C.

![Chemical structures A and B](image)

\[
\begin{align*}
T_m &= 152°C \\
T_l &= 269°C \\
T_{N-I} &= 273°C \\
T_m &= 142°C \\
T_l &= 245°C \\
T_{N-I} &= 251°C
\end{align*}
\]

This indicates that rigidity is more effective than the presence of \(\pi\) electrons in the central group. If the cyclohexane moiety is replaced by 1,4-cyclohexadiene and 1,3-cyclohexadiene, then the polyesters

\[
\begin{align*}
T_{N-I} &= 273°C \\
T_{N-I} &= 251°C
\end{align*}
\]
show higher $T_{N-}$ than the polyester containing cyclohexane, but the nematic phase of C is stable relative to D. The reason probably lies in the non-planarity of double bonds in 1,3-cyclohexadiene.

Effect of bent monomer is extensively studied. Erdemir et al. discovered that the isophthalic acid/hydroquinone/4-hydroxy benzoic acid (IA/HQ/4-HBA) copolyester formed only isotropic melt if IA exceeded 67 percent. Jin et al. observed that terephthalic acid/resorcinol/4-hydroxy benzoic acid (TA/RE/4-HBA) polyester loses LC character if TA/RE units exceed 33 percent. Jackson reported that hydroquinone/terephthalic acid/3-hydroxy benzoic acid (HQ/TA/3-HBA) does not form a mesophase when 3-HBA content exceeds 50 percent. Cai and Samulski observed that increased concentration of 1,4-phenylene unit in the form of 4-HBA in IA/HQ polyester expands the mesophase range. Samulski reported that 2-chloro hydroquinone/terephthalic acid (Cl-HQ/TA) and 2-methyl hydroquinone (Me-HQ/TA) polyesters are not liquid crystalline but the corresponding polyesters with 2,5-thiophene dicarboxylic acid unit exhibited liquid crystallinity over a wide range.

1.7.3 Effect of substitution on the mesogen

Substitution on the mesogen reduces coplanarity and the aspect ratio of the mesogen. Steric factors associated with such groups may hinder the interactions required for better packing between the chains. However, polar substitution helps to increase intermolecular interactions.

Effect of $t$-butyl substitution on Poly(hydroquinone-terephthalate) is seen in Table 1.1.

<table>
<thead>
<tr>
<th>$t$-Butyl Substitution, mole%</th>
<th>Temperature Range, °C</th>
<th>Transition Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>300-460</td>
<td>Solid-solid</td>
</tr>
<tr>
<td>10</td>
<td>368-460</td>
<td>Solid-solid</td>
</tr>
<tr>
<td>40</td>
<td>326-405</td>
<td>Crystal-nematic</td>
</tr>
<tr>
<td>60</td>
<td>325-391</td>
<td>Crystal-nematic</td>
</tr>
</tbody>
</table>
Effect of type and composition of substituted comonomer on temperature range of nematic state in random copolyester of PET is presented in Table 1.2.

<table>
<thead>
<tr>
<th>Comonomer m-substituent</th>
<th>Amount mole %</th>
<th>Thermal property</th>
<th>Temperature range of nematic state</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.19</td>
<td></td>
<td>Non LC</td>
</tr>
<tr>
<td>H</td>
<td>0.46</td>
<td></td>
<td>220 -&gt; 350</td>
</tr>
<tr>
<td>H</td>
<td>0.65</td>
<td></td>
<td>310 -&gt; 350</td>
</tr>
<tr>
<td>Cl</td>
<td>0.35</td>
<td></td>
<td>180 - 240</td>
</tr>
<tr>
<td>Cl</td>
<td>0.50</td>
<td></td>
<td>190 - 240</td>
</tr>
<tr>
<td>Cl</td>
<td>0.53</td>
<td></td>
<td>190 - 260</td>
</tr>
</tbody>
</table>

1.7.4 Effect of flexible spacer

All structural moieties of the repeat unit excepting the mesogenic unit may be termed as a spacer. Flexible spacers based on poly(methylene) chains are very common.31-34 Recently, spacers of poly(siloxane)50-52 and poly(ethylene oxide)53 segments have been studied. Flexible spacers decouple the mesogenic unit, which decreases both melting and clearing temperatures. There is a typical odd-even relationship between transition temperature and the number of carbon atoms in the spacer chain, as shown in Figure 1.6.

1.8 DEPRESSING MELTING TEMPERATURE

Melting temperature ($T_m$) is thermodynamically defined as,

$$T_m = \frac{\Delta H_f}{\Delta S_f}$$  (1.4)

where, $\Delta H_f$ = Heat of fusion; $\Delta S_f$ = Entropy of fusion

This has important implications in the design of LCPs. Based on theoretical prediction and the structural features so far discussed, it can be said that homopolymerisation of rigid units present in the mesogen would generate liquid crystalline polymers. Many aromatic polyesters with rigid backbones have been synthesised and examined to verify this.56-58
FIGURE 1.6  DEPENDENCE OF TRANSITION TEMPERATURE ON SPACER LENGTH
However, such rod-like moieties tend to be infusible, largely intractable crystalline solids. Liquid crystalline properties were observed for oligomers of poly (1,4-phenylene) with $n = 7$ while decomposition occurred prior to melting for $n > 7$. Melting temperatures of $610^\circ C$ and $600^\circ C$ were noted for poly(1,4-oxy benzoate) and poly(1,4-phenylene terephthalate) respectively. Hence, the problem of polymer design is to reduce the melting temperature to obtain liquid crystalline phase below decomposition temperature and preferably in the temperature range suitable for most processing equipments. The nature of crystallites in solidified LCPs was examined by Blundell. He proposed that there is little change in general configuration of LCP after $T_m$ as against vast disorder experienced during the melting of conventional polymer. This will be clear from Figure 1.7.

Lower $\Delta H_f$ and $\Delta S_f$ were noted for LCPs as compared to a conventional thermoplastic polymer such as PET. Low $\Delta H_f$ is directly related to low level of molecular cohesion within crystallites; whereas low $\Delta S_f$ is a direct consequence of chain stiffness. Given that $\Delta S_f$ is low, the $\Delta H_f$ must also be low. Otherwise, $T_m$ would be too high and the system will be intractable. Thus, chain irregularity and chain stiffness are two distinct properties that can be separately designed into the LCPs. This can be achievable in the following ways:

(Figure 1.8)

1. Use, in relatively small mole fraction, of nonlinear structural units (kinks) such as resorcinol, isophthalic acid, 3-hydroxy benzoic acid in combination with their linear counterparts seems to be the general approach. Presence of 1,3-disubstituted rings destroys linearity. Regular packing of chains is sterically hindered. This drops down the melt transition temperature. Control of composition is very critical in such cases.

2. Use of flexible bonds and sequences increases the entropy of the melt.

3. Frustrated chain packing.
FIGURE 1.7  BLUNDELL'S SCHEMATIC DIAGRAM OF THE MORPHOLOGIES ABOVE AND BELOW THE CRYSTAL MELTING POINT FOR (A) RIGID CHAIN NEMATIC POLYMER, AND (B) CONVENTIONAL POLYMER WITH CHAIN FOLDED LAMELLAR CRYSTALS
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic structure</td>
<td>600</td>
</tr>
<tr>
<td>Introduction of disruptors</td>
<td></td>
</tr>
<tr>
<td>Flexible spacers</td>
<td></td>
</tr>
<tr>
<td>R = H</td>
<td></td>
</tr>
<tr>
<td>R = CH₃</td>
<td>435</td>
</tr>
<tr>
<td>m=2, R=H</td>
<td></td>
</tr>
<tr>
<td>m=2, R=CH₃</td>
<td></td>
</tr>
<tr>
<td>m=1, R=CH₃</td>
<td></td>
</tr>
<tr>
<td>R~20 mol %</td>
<td>&lt;400</td>
</tr>
<tr>
<td>Substitution of the aromatic rings</td>
<td></td>
</tr>
<tr>
<td>R=CH₃</td>
<td>&gt;400</td>
</tr>
<tr>
<td>R=</td>
<td>~340</td>
</tr>
<tr>
<td>Copolymerization</td>
<td></td>
</tr>
<tr>
<td></td>
<td>31.5</td>
</tr>
<tr>
<td>Introduction of Crank-shaft units</td>
<td>~400</td>
</tr>
</tbody>
</table>

**FIGURE 1.8** STRATEGIES FOR LOWERING Tₘ IN MAIN CHAIN LCPs
4. **Copolymerisation**: Copolymerisation leads to either an isotropic or an LC melt, depending on the copolymer composition. This is a key difference between LCPs and low molecular mass LCs.

5. **Use of substituents**: Asymmetric substitution of mesogen decreases the melting temperature by way of decreasing the aspect ratio and crystallisability.

### 1.9 SYNTHESIS

Main Chain Liquid Crystal polyesters are condensation polymers. Condensation proceeds by step polymerisation mechanism. All step polymerisations fall into two groups depending on the type of monomer employed.

1. Two different bifunctional monomers are used:

   \[ n \text{A-A} + n \text{B-B} \longrightarrow -(\text{A-AB-B})_n^- \]

2. Both functional groups are present in a single monomer:

   \[ n \text{A-B} \longrightarrow -(\text{A-B})_n^- \]

   The synthesis could be conducted either at low or at high temperatures.

#### 1.9.1 Low temperature methods

1.9.1.1 **Schautten-Baumann reaction**

This is a well known condensation reaction between an organic acid halide and compounds having active hydrogen such as phenols, thiols, amines etc. This reaction can be conducted in the melt, solution or by interfacial methods.

1.9.1.2 **Interfacial polymerisation**

This method consists of reaction between a fast reacting intermediate and a normal reactant at the interface of two immiscible liquid phases, one of which is preferably water. The second phase consists of diacid halide dissolved in an organic solvent such as dichloromethane, carbon tetrachloride, hexane and xylene. Reaction can be carried out both in stirred and unstirred systems.
1.9.1.3 Solution polymerisation

This is carried out in a single liquid which is inert to both the reactants. The liquid can be any organic solvent without reactive functional groups. A tertiary amine is necessary as an acid acceptor. The product polymer remains either in solution or precipitates out. This method can be used to prepare many classes of polymers such as polyamides, polyureas, polyphenyl esters etc.

1.9.2 High temperature melt method

When appropriate bifunctional compounds such as diacids and diols are condensed, a linear polyester is formed with the loss of small molecule as a bi-product. Sufficiently high molecular weight polymers can be synthesised if stoichiometrically equivalent amounts of extremely pure intermediates are condensed and proper care is taken to remove non-polymeric bi-product. High temperature and reduced pressure form an integral part of these polycondensation methods. Ester interchange method has the greatest commercial application. These methods are summarised in Figure 1.9.

High temperature polycondensation of polyesters faces drawbacks such as low reaction rate, incomplete removal of bi-product and thermal instability. These are equilibrium reactions. In order to reach high conversion, bi-product removal is achieved by heat, stirring and reduced pressure. Also, side reactions should be absent and exact stoichiometric equivalence has to be assured.

1.10 CHEMICAL KINETICS AND KINETIC ANALYSIS

1.10.1 Basic Concepts of Kinetics

Chemical kinetics deals with chemical transformations and may be defined as the study of chemical systems whose composition changes with time. These changes may take place in the gas, liquid or solid phase of a substance. A reaction occurring in a single
A. DIRECT ESTERIFICATION

\[
\text{nHO-C-OC-CH}_2\text{-CH}_2\text{-OH} + \text{nHO-CH}_2\text{-CH}_2\text{-OH} \xrightleftharpoons[\Delta]{.} \text{n\text{H}_2\text{O}} \\
\text{[C-OC-CH}_2\text{-CH}_2\text{-O]}_n + \text{n\text{H}_2\text{O}}
\]

B. SELF CONDENSATION OF HYDROXY ACIDS

\[
\text{n\text{HO-R-C-OH}} \xrightleftharpoons[\Delta]{.} \text{[O-R-C]}_n + \text{n\text{H}_2\text{O}}
\]

C. DOUBLE ESTER INTERCHANGE

\[
\text{R}_1\text{-C-OR}_2 + \text{R}_3\text{-C-OR}_4 \xrightleftharpoons[\Delta]{.} \text{R}_1\text{-C-OR}_4 + \text{R}_3\text{-C-OR}_2
\]

FIGURE 1.9 SCHEMES FOR THE SYNTHESIS OF POLYESTERS

...Continued on the next page
D. ESTER INTERCHANGE:

**ACIDOLYSIS**

\[
\text{nHO-C-0-C-OH + nR-C-O-CH}_2-\text{CH}_2-O-C-R \xrightarrow{\Delta} \]

\[
\left[ \text{C-O-C-O-CH}_2-\text{CH}_2-O \right]_n + (2n-1) \text{R-C-OH}
\]

**ALCOHOLYSIS**

\[
\text{nRO-C-0-C-OR + nHO-CH}_2-\text{CH}_2-OH \xrightarrow{\Delta} \]

\[
\left[ \text{C-O-C-O-CH}_2-\text{CH}_2-O \right]_n + (2n-1) \text{R-OH}
\]

**ESTEROLYSIS**

\[
\text{nRO-C-0-C-OR + nR'-C-O-CH}_2-\text{CH}_2-O-C-R' \xrightarrow{\Delta} \]

\[
\left[ \text{C-O-C-O-CH}_2-\text{CH}_2-O \right]_n + (2n-1) \text{R-C-OR'}
\]
phase is usually referred to as a homogeneous reaction, while a reaction which takes place at an interface between two phases is known as a heterogeneous reaction. Chemical change that takes place in any reaction may be represented by a stoichiometric equation such as:

$$aA + bB \rightarrow cC + dD$$  \hspace{1cm} (1.5)

where \(a\) and \(b\) denote the moles of reactants \(A\) and \(B\) that react to form \(c\) and \(d\) moles of product \(C\) and \(D\).

1.10.2 **Rate Equation**

The change in composition of reaction mixture with time is the rate of reaction. The rate of consumption of reactants represented by equation (1.5) is

$$R = -\left(\frac{1}{a}\right)\frac{d[A]}{dt} = -\left(\frac{1}{b}\right)\frac{d[B]}{dt}$$  \hspace{1cm} (1.6)

or the rate of formation of products is

$$R = \left(\frac{1}{c}\right)\frac{d[C]}{dt} = \left(\frac{1}{d}\right)\frac{d[D]}{dt}$$  \hspace{1cm} (1.6a)

where \(R\) = rate of formation of products; \(t\) = reaction time etc.

Thus, the rate of overall reaction depends on the concentration of reactants. Therefore, in general, \(R\) may be expressed as a function of concentration of reactants as

$$R = k[A]^a[B]^b$$  \hspace{1cm} (1.7)
This equation is rate equation or a rate expression wherein, a and b denote the order of reaction with respect to A and B respectively. The overall order of a reaction is given by \( n = a + b \). The constant \( k \) is the rate constant and has the units of \((\text{concentration})^{n-1}\text{time}^{-1}\).

**Zero order reaction**

\[
R = k[A]^0 = k
\]  

(1.8)

**First order reaction of the type**

\[
A \rightarrow P
\]  

(1.9)

\[
R = k[A]^1
\]  

(1.10)

\[
[A]_t = [A]_0 e^{-kt}
\]  

(1.11)

**Second order reaction**

\[
A + A \rightarrow P
\]  

(1.12)

\[
R = k[A][A] = k[A]^2
\]  

(1.13)

\[
\frac{1}{[A]_t} = \frac{1}{[A]_0} - 2kt
\]  

(1.14)

\[
A + B \rightarrow P
\]  

(1.15)

\[
R = k[A][B]
\]  

(1.16)

\[
\frac{1}{([A]_0 - [B]_0)} \ln \left( \frac{[B]_0[A]_t}{[A]_0[B]_t} \right) = kt
\]  

(1.17)
The rate equation for an nth order reaction is

\[ R = k[A]^n \]  \hspace{1cm} (1.18)

integrated form of this is

\[ \frac{1}{n-1} \left( \frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right) = kt \]  \hspace{1cm} (1.19)

### 1.10.3 Order and Molecularity

Order is an experimentally determined quantity and can take non-integer values. The values between -2 and 3 are usually noted. Negative orders imply the contribution of inhibitor in the rate equation while the complexity of a reaction is implied by fractional orders. Molecularity of a reaction specifies the number of reactants that are involved in the reaction step. Reaction is classified as uni, bi, ter-molecular etc. depending on its molecularity. A number of methods used to determine reaction order are:

#### 1.10.3.1 Van't Hoff Method

When the order ‘n’ is unknown, a Van’t Hoff plot can be constructed to deduce the reaction order. If,

\[ \frac{d[A]}{dt} = k[A]^n \]  \hspace{1cm} (1.20)

Then,

\[ \text{then,} - \log \frac{d[A]}{dt} = \log k + n \log [A] \]  \hspace{1cm} (1.21)
In this method, the logarithm of rate is plotted against the logarithm of concentration of reactant. The slope of the graph gives the order of a reaction. Figure 1.10 shows a typical Van't Hoff plot.

1.10.3.2 Reaction Half Life Method

Reaction Half Life \( t_{1/2} \) is defined as the time required for the concentration of a reactant to reach one half of its initial concentration.

\[
  t_{(1/2)} \propto \frac{1}{[A]_0^{n-1}} \tag{1.22}
\]

where \( n = \) order of reaction; \([A]_0 = \) initial concentration

1.10.3.3 Experimental method

Experimental data is fitted in different rate law plots corresponding to different orders. The proper choice of order is that for which rate constant is constant at different times.

1.10.3.4 Initial Rates

Order can be determined from initial rates i.e. rate for different initial concentration of reactant. A plot of logarithm of initial rate against logarithm of corresponding initial concentration gives reaction order from the slope.

1.10.3.5 Ostwald's Isolation Method

This depends on the approximation that when a reactant is taken in large excess, there is no perceptible change in its concentration during the course of the reaction. If the rate law is

\[
  -\frac{d[A]}{dt} = k_2[A][B] \tag{1.23}
\]

and if \([B] \) is in excess then \([B] = [B]_0 \) and rate equation simplifies to
FIGURE 1.10  VAN'T HOFF PLOT OF LOG (-d[A]/dt) VERSUS LOG [A] FOR VARIOUS REACTION ORDERS
This technique of isolating in turn the contributions of various components can be used in unravelling a complex reaction mechanism.

1.10.4 Complex reactions

A series of elementary reactions constitute a mechanism of a complex reaction. Complex reactions can be divided into several classes: (i) Opposing or reversible reactions [equation (1.25)]; (ii) Consecutive reactions [equation (1.26)]; (iii) Parallel reactions [equation (1.27)] and (iv) Mixed reactions.

\[
\frac{d[A]}{dt} = k_1[A] \quad (1.24)
\]

It is difficult to obtain exact solution for many complex reactions. It may therefore become necessary to use approximate treatments such as steady state, Laplace transform, determinant method etc. However, when analytical solutions are impossible to obtain either directly or by using approximation methods, a numerical solution is generally possible.

1.10.5 Steady state approximation

This method is commonly applied to solve some cumbersome reactions. It was originally proposed by Bodenstein\textsuperscript{81} and further developed by Semenov.\textsuperscript{82} Complex analytical treatment is simplified by assuming the rate of change of some reaction intermediate to be equal to zero. Mathematically,
\[
\frac{d[A]}{dt} = 0
\] (1.28)

If \( A \longrightarrow B \longrightarrow C \) (1.29)

then, under steady state condition

\[
\frac{d[B]}{dt} = -k_2[B] + k_1[A] = 0
\] (1.30)

### 1.10.6 Temperature dependence of rate constants

Rate expressions are simple functions of reactant concentrations with a characteristic rate constant ‘\( k \)’. If rate equation is correctly formulated, the rate constant should be independent of concentration of species appearing in the rate law. It should also be independent of time. It does, however, depend strongly on temperature. This behaviour was described by Arrheniuses\(^8\) in 1889 on the basis of numerous experimental rate measurements. This dependence is given by Arrhenius equation as follows:

\[
k(T) = A e^{-\frac{E_{(act)}}{RT}}
\] (1.31)

### 1.11 KINETICS OF STEP POLYMERISATION

Many of the principle features of polycondensation reaction have unresolved despite their great technological importance. There are uncertainties regarding the order of reaction and whether it is markedly dependent on the medium, incidence of equilibrium in condensation and influence of the rate of by-product removal etc. These uncertainties arise because the studies have been conducted primarily in complicated bulk medium provided by pure reactants.
Kinetics of polyesterification have been reported by Lenz\textsuperscript{84}, Davies and Hill\textsuperscript{85-87}, Rolfe and Hinshelwood\textsuperscript{88}, Dostal and Raff\textsuperscript{89,90}, Flory\textsuperscript{91} and others but exceedingly varied results have been noted. Few researchers are of the view that polyesterification should be a second order reaction since these are essentially bimolecular; or second order in the early stages and third order in the later stages of reaction. Tang Au-Chin and Yao Kuo-Sui\textsuperscript{92} proposed a mechanism for the catalysis of polyesterification by hydrogen ion which leads to an intermediate order of 2.5. Makay-Bodi\textsuperscript{93} grouped diacids into two different groups on the basis of the dissociation constants ($pK_1$ and $pK_2$).

Quantitative theoretical basis of kinetics and mechanism of polycondensation reaction between dicarboxylic acid and dibasic alcohol are attributable to Flory\textsuperscript{94}. He suggested that polycondensation proceeds under the catalytic activity of carbonyl groups and postulated trimolecularity for reaction in the absence of an external catalyst. A review of existing kinetics literature leads to the following conclusions: (1) The similarities between simple esterification and polyesterification are accepted unequivocally; (2) The reactivity of functional groups is independent of chain length; (3) Monomers are the most prevalent species at every instant during polycondensation reaction; (4) Condensation kinetics of aromatic diacids and diols have not been investigated; (5) There are very few published reports on kinetics of acidolysis of all aromatic LCPs\textsuperscript{95-98}.

1.11.1 Analysis of polymerisation kinetics

The primary aim of kinetic analysis is the determination of mechanism by which system changes its composition. This involves determination of order and rate coefficients and provides Arrhenius parameters which should be rationalised in terms of thermodynamics of the process. Step polymerisation proceeds by a relatively slow increase in molecular weight of polymer. The first step is the reaction of diol and diacid monomers to form a dimer,

$$\text{HO-}R\text{-OH} + \text{HOOC-}R'\text{-COOH} \rightarrow \text{HO-}R\text{-OCO-}R'\text{-COOH} + \text{H}_2\text{O}$$  \hspace{1cm} (1.32)
dimer then forms trimer by reaction with diol monomer,

\[
\text{HO-R-OCO-R'-COO} + \text{HO-R-OH} \rightarrow \text{HO-R-OCO-R'-COO-R-OH} + \text{H}_2\text{O} \quad (1.33)
\]

and also with diacid monomer,

\[
\text{HO-R-OCO-R'-COO} + \text{HOOC-R'-COOH} \rightarrow \text{HOOC-R'-COO-R-OCO-R'-COOH} + \text{H}_2\text{O} \quad (1.34)
\]

dimer reacts with itself to form a tetramer,

\[
2\text{HO-R-OCO-R'-COO} \rightarrow \text{HO-R-OCO-R'-COO-R-O-CO-R'-COOH} + \text{H}_2\text{O} \quad (1.35)
\]

Trimer and tetramer react further. The reaction can be expressed as a general reaction:

\[
n-\text{mer} + m-\text{mer} \rightarrow (n+m)-\text{mer} \quad (1.36)
\]

Reaction mixture consists of diols, diacids and hydroxy acid molecules of varied lengths and any molecule with hydroxyl group can and will react with any molecule having carboxylic acid group. Thus, the rate of step polymerisation is the sum of the rates of all these intermediate reactions between molecules of various sizes.\(^9\)^,\(^10\) Kinetic analysis of such a difficult system is simplified by assuming that reactivities of both functional groups of a bifunctional monomer are the same and that each functional group reacts independent of the other irrespective of the chain length. These assumptions allows the treatment of polyesterification in a manner similar to esterifications.

1.11.2 Kinetic Expressions

The diacid monomer doubles up as the catalyst for the reaction. The rate is therefore

\[
\frac{-d[\text{COOH}]}{dt} = K[\text{COOH}][\text{OH}] \quad (1.37)
\]

for stoichiometrically equivalent amounts of diacid and diol,
\[- \frac{d[M]}{dt} = k[M]^3 \quad (1.38)\]

\[ [M] = \text{concentration of hydroxyl and carbonyl groups at time } t \]

\[- \frac{d[M]}{[M]^3} = K dt \quad (1.39) \]

integration of this yields

\[ 2Kt = \frac{1}{[M]^2} - \frac{1}{[M_0]^2} \quad (1.40) \]

\[ [M_0] = \text{initial concentration of hydroxyl and carbonyl groups}. \text{If } "p" \text{ is fractional conversion, concentration of functional group reacted at time } t \text{ is } M_0 p; \text{ concentration of unreacted functional group } M, \text{ is } (M_0 - M_0 p). \]

\[ [M] = [M_0](1 - p) \quad (1.40a) \]

combining equations (1.40) and (1.40a), we get

\[ \frac{1}{(1 - p)^2} = 2[M_0]^2 kt + 1 \quad (1.41) \]

when catalyst is added, rate expression changes to,

\[ [M_0]kt = \frac{1}{(1 - p)} - 1 \quad (1.42) \]

This is a rate expression for second order reaction. The plot of 1/(1-p) against time is a straight line slope of which gives the rate of reaction.
1.12 THERMODYNAMIC FORMULATION OF RATE EQUATIONS

The treatment of reaction rates described here is based on the concept that there exists a 'Transition state' or an 'Activated complex' between the initial and the final state. It exists at the highest point of potential energy surface in the reaction path from initial state to the final state through the lowest energy barrier (Figure 1.11). In the theoretical treatment of rate processes by Arrhenius, Eyring, Evans and Polanyi, the activated complex was regarded as being in equilibrium with the reactants. Modern development of the theory of reaction rates have come from Arrhenius equation,

\[ \ln k = \ln A - \frac{E}{RT} \]  

where \( k \) = rate constant; \( T \) = reaction temperature; \( E \) = activation energy and \( A \) = frequency factor. \( A \) and \( E \) are independent of temperature provided the temperature range under consideration is small.

Two theories were put forth as a consequence of this relation between rate constant and temperature are: (1) Collision theory and (2) Theory of absolute reaction rates.

1.12.1 Collision Theory

Rate constant is given by the following expression:

\[ k = Z e^{-\frac{E}{RT}} \]  

where the exponential term represents concentration of activated molecules and

\[ Z = n \left( \frac{1}{2} \sigma_A + \frac{1}{2} \sigma_B \right)^2 n_{relative} n_A n_B \]  

\( n \) and \( n_{relative} \) are the number of molecules of reaction A and reaction B respectively.
FIGURE 1.11 ENTHALPY DIAGRAM FOR A CHEMICAL REACTION

$E_{\text{act}}(\text{forward})$ Activation energy of forward reaction
$E_{\text{act}}(\text{reverse})$ Activation energy of reverse reaction

$E_{\text{act}}(\text{forward}) - E_{\text{act}}(\text{reverse}) = \Delta H^0$
This gives the number of molecules colliding per unit volume per unit time (collision frequency). \( \sigma_A \) and \( \sigma_B \) are reactive cross sections of colliding molecules, \( n_A \) and \( n_B \) are moles of A and B respectively and \( v_{\text{relative}} \) is relative velocity of colliding molecules.

Collision theory agrees well only in reactions between simple molecules in gaseous state. There are many so called 'slow' reactions in solution which have rates much slower than that predicted by the equation (1.44). Collision theory also fails in case of reversible reactions.

\[
\begin{align*}
A + B & \rightarrow AB \quad (1.46) \\

k_1 &= \frac{Z_1 e^{-\frac{E_1}{RT}}}{k_2} \quad (1.47) \\
K_2 &= Z_2 e^{-\frac{E_2}{RT}} \quad (1.48) \\
K^* &= \frac{k_1}{k_2} = e^{-\frac{E_1 - E_2}{RT}} \quad (1.49)
\end{align*}
\]

\( E_1 - E_2 \), the difference in activation energies of forward and backward reactions, is therefore the difference in the heat content of products and reactants. Collision theory then leads to the following expression,

\[
\begin{align*}
\text{k} &= Z e^{\frac{\Delta H}{RT}} \quad (1.50)
\end{align*}
\]

where \( \Delta H \) is heat of activation. This can be true only at absolute zero or when change in entropy during the reaction is negligible. Equation (1.44) thus is:

\[
\begin{align*}
k &= P Z e^{-\frac{E}{RT}} \quad (1.51)
\end{align*}
\]
where \( P \) is the steric/probability factor. Equation (1.49) takes the form:

\[
K^* = \frac{k_1}{k_2} = \frac{P_1 e^{-\frac{\Delta H^*}{RT}}}{P_2}
\]

(1.52)

since \( Z_1/Z_2 = 1 \). This equation indicates that in addition to the number of collision (\( Z \)), orientation during collision (\( P \)) too governs the rate of reaction. Change in free energy is related to equilibrium constant\(^{105,106}\) of a reaction by:

\[
\Delta G^* = -RT \ln K^*
\]

(1.53)

\[
K^* = e^{-\frac{\Delta G^*}{RT}}
\]

(1.54)

\[
\Delta G^* = \Delta H^* - T \Delta S^*
\]

(1.55)

where \( \Delta G^* \) is free energy of activation, \( \Delta H^* \) is enthalpy of activation and \( \Delta S^* \) is entropy of activation.

\[
K^* = e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}}
\]

(1.56)

On comparing equation (1.52) and (1.56) it bears out that the term \( P_1/P_2 \) accounts for the entropy of activation. Therefore, the free energy too is an important factor in the reaction and not just the enthalpy of activation alone as implied in equation (1.49). A case in point is the denaturation of proteins where in the energy of activation is exceptionally high,\(^{107}\) in excess of 100 kCal/mole, but the reaction proceeds favourably even at ambient temperatures because the reaction is accompanied by a large increase in entropy. On the other hand, condensation of vapour is relatively slow despite a small or zero heat of activation. Here, the
change is accompanied by marked decrease in entropy.

1.12.2 Theory of Absolute Reaction Rates

Collision theory fails in many cases because it treats the molecules as hard spheres and does not allow them any kind of freedom. This theory takes into consideration the degrees of freedom associated with a molecule by way of partition functions. Consider the following reaction,

$$ A + B \rightarrow (AB)^* \rightarrow P $$

where \((AB)^*\) represents the activated complex. It differs from the ordinary molecules in that it has no stable equilibrium state and exists only momentarily at some potential energy maximum. The theory assumes that the activated complex is in equilibrium with the reactant molecules A and B. Hence, equilibrium constant can be related to the energy of activation by the following equation,

$$ K^* = \frac{[AB^*]}{[A][B]} = \frac{Q_{AB}^*}{Q_A Q_B} \frac{e^{-\frac{E_0}{RT}}}{Q} $$

where \(K^*\) = equilibrium constant; \(Q\) = partition function; \(E_0\) = activation energy.

Partition function can be factorised into contributions corresponding to translational, rotational and vibrational modes. Activated complex \((AB^*)\) has \([3 (N_A + N_B) - 6]\) modes of vibration if it is nonlinear. One of these vibrations is of different character from the rest, since it corresponds to a loose vibration which allows the complex to dissociate into products. Normal mode of vibrational partition function is \(q_v\)

$$ q_v = \frac{1}{1 - e^{-\frac{\omega_v}{kT}}} $$

The above relation changes for loose vibration \((v = 0)\) to
Substituting this value in equation (1.58), we get

\[
\lim_{n \to \infty} \frac{1}{1 - e^{-\frac{kT}{h\nu}}} = \frac{1}{1 - \left(1 - \frac{h\nu}{kT}\right)} = \frac{kT}{h\nu}
\]  

(1.60)

Substituting this value in equation (1.58), we get

\[
\frac{[AB^\star]}{AB} = \frac{Q \star_{AB}}{Q_A Q_B} \frac{kT}{h\nu} e^{-\frac{\epsilon_0}{kT}}
\]

(1.61)

\(Q \star_{AB}/Q_A Q_B\) corresponds to \([3 (N_A + N_B) - 7]\) modes of vibration and \(kT/h\nu\) corresponds to loose vibration; where, \(k = \) Boltzmann constant, \(T = \) temperature, \(h = \) Planck constant and \(\nu = \) vibration frequency. Rearranging equation (1.61) gives:

\[
\nu \frac{[AB^\star]}{[A][B]} = k = \frac{Q \star_{AB}}{Q_A Q_B} \frac{kT}{h\nu} e^{-\frac{\epsilon_0}{kT}}
\]

(1.62)

Comparing equation (1.58) with equation (1.62) gives,

\[
k = \frac{kT}{h} K^\star
\]

(1.63)

Thermodynamically, free energy is related to equilibrium constant as follows,

\[
\Delta G^\star = -RT \ln K^\star
\]

(1.64)

Taking antilogarithm of equation (1.64), we get:

\[
K^\star = e^{-\frac{\Delta G^\star}{RT}}
\]

(1.65)

Equation (1.63) therefore, changes to
Above equation can also be written as

\[
k = \frac{kT}{h} e^{-\frac{\Delta H^*}{RT}}
\]  \hspace{1cm} (1.67)

Experimental activation energy obtained from Arrhenius plot is not exactly the heat of activation mentioned in the above equation. Actual relation between the two is as follows,

\[
E_{\text{exp}} = \Delta H^* + RT
\]  \hspace{1cm} (1.68)

Substituting this value for \((\Delta H^*)\) leads to the following equation

\[
k = e^{\frac{kT}{h}} e^{-\frac{\Delta S^*}{R}} e^{-\frac{E_{\text{exp}}}{RT}}
\]  \hspace{1cm} (1.69)

where, \(k\) = rate constant; \(T\) = absolute reaction temperature; \(k\) = Boltzmann constant; \(h\) = Planck's constant; \(R\) = gas constant; \(E_{\text{exp}}\) = experimental activation energy and \(\Delta S^*\) = Entropy of activation. Frequency factor "A" can be calculated if the above equation is compared with Arrhenius equation,

\[
A = e^{\frac{kT}{h}} \frac{\Delta S^*}{R}
\]  \hspace{1cm} (1.70)
In terms of relation of frequency factor and entropy of activation ($\Delta S$) the rate of reaction is lower than that given by collision theory if $\Delta S$ is negative, since probability of formation of the activated complex is low. The probability of formation of activated complex is high when $\Delta S$ is positive and therefore the rate is greater than that given by collision theory.

1.13 CHARACTERISATION

Combination of various analytical techniques is intrinsic to complete characterisation of liquid crystal polymers.

1.13.1 Differential Scanning Calorimetry

Differential Scanning Calorimeter (DSC) is widely used for thermal characterisation of polymeric materials. In this technique sample and the reference are heated/cooled simultaneously at a predetermined rate. The differential power supplied to the sample, to annul any temperature difference which might arise between the two during a thermal transition, is monitored against temperature in power compensation device (Perkin Elmer). In heat flux type DSC (Mettler), a temperature difference between sample and reference is measured as a differential voltage which is later converted to the actual heat flow. A typical thermogram so obtained shows peaks corresponding to glass transition, melting, crystallisation, solid-liquid crystal and liquid crystal-liquid crystal etc. During the transformation of a material from solid to liquid crystal or liquid crystal to isotropic liquid state, there are characteristic changes in physical and mechanical properties, morphology and also thermodynamic variables.¹⁰⁹

The instrument can measure heat of fusion, heat of crystallisation, percent crystallinity, time of crystallisation (isothermal technique) etc. It has been observed that liquid crystal polymeric structures produce a melt which tends to be cloudy instead of being clear. On further heating, a temperature is reached at which the cloudy melt changes to a clear melt. This corresponds to the transition temperature at which the molecular orientation of the
liquid crystal phase breaks up and anisotropic melt transforms into the transparent isotropic melt. In liquid crystalline materials the transitions are independent of thermal history of the material. Liquid crystal-isotropic transition and liquid crystal-liquid crystal transition are almost reversibly observed on cooling the isotropic liquid while supercooling is observed for solid-liquid crystal and solid-solid transitions.

A typical odd-even relationship between number of carbon atoms in the flexible spacer and the transition temperature is observed in polymeric materials as in low molecular liquid crystals. The enthalpy changes associated with melting of polymers are lower than those observed for small molecules of similar chemical structure.

1.13.2 Optical Microscopy

The liquid crystalline phases can be identified from the textures characteristic of different types of phases. When viewed under crossed polariser in polarising microscope nematic phase shows typical threaded or Schlieren texture. Cholesteric polymers show planar texture with oily streaks. Focal conic or fan shaped texture are characteristic of smectic phases. Pretreatment is often necessary to see textures easily in polymeric materials. It may take several days to develop textures due to high viscosity of polymeric materials.

1.13.3 X-Ray Analysis

A system for identification of type of mesophases from the diffraction pattern is developed by DeVries. Diffraction pattern of a powder sample can be divided into inner rings at small diffraction angle which are indicative of longer layer spacings. The outer rings at large angles correspond to shorter spacing in the lateral packing arrangement of molecules. Appearance of a broad halo or a sharp ring is a measure of order present in the structure.

Studies of thermotropic polymers by Wide Angle X-ray Diffraction, WAXD, in the liquid crystalline state are useful in the identification of the structure of the liquid crystalline melt.
In WAX diffraction patterns, nematic structures produce a diffuse broad ring which corresponds to average intermolecular spacing of approximately 4 to 6 Å on a flat film diffractogram. Similar diffuse halo is seen for isotropic liquid phase. Therefore, it is assumed that there is lack of lateral periodic order. At small angles, nematic patterns may present a diffuse ring corresponding to distances which are very close or equal to the length of repeat unit. This shows that there is no order along molecular long axes. Nematic phases are characterised by one broad halo in the wide angle scattering region which could imply short range positional order. Cholesteric mesophases in general resemble the nematic mesophases when observed by both small angle X-ray diffraction and WAXD.

Smectic structure is characterised by one more reflection in the small angle scattering region (15-50 Å) which is sharp and a broad halo in the wide angle region (4-5 Å). The pattern in the small angle region is due to smectic layers. The wide angle halo is due to two dimensional fluid state within the smectic layers. Detailed structural information is possible if the sample is in well oriented monodomain form.
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