

PART I

Introduction

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1.1 Introduction

Liquid crystals can be described as belonging to a thermodynamically stable state which is intermediate between liquids and crystals. For long it was believed that matter exists only in three different states. Reinitzer, while working with esters of cholesterol, discovered that these esters showed two melting points, and, that the state of matter between these "melting points" could not be truly classified as belonging to the solids (crystals) or to the liquids, instead it displayed some characteristics of both. Hence, this new state of matter was named as *Flussige Kristalle* or Liquid crystals.^{1,2} It was soon realised that certain organic molecules could display this new state of matter under two different conditions; (i) either by action of heat (thermotropism) or (ii) by effect of solvent (lyotropism), leading to the birth of two new branches of this nascent field, the thermotropics and the lyotropics. In this thesis, the thermotropic liquid crystals have been investigated.

Liquid crystals display a wide range of sub-states. Depending upon the ordering of molecules within each of these sub-states, liquid crystals can be classified as belonging to the Nematics, the *Smectics* or to the *Discotics*. The first two classes are shown by molecules that are lath-like or rod-like in shape. In the nematic phase, molecules have long range orientational order, but no positional order. Thus, this phase is nearest to the liquid phase and has several properties (especially the flow properties) similar to that of true liquids. Smectic phase is distinguished by the molecules having positional as well as orientational order within the phase (the molecules are arranged in layers). This phase displays properties similar to crystals (especially the optical and electrical properties). The columnar phase was discovered as recently as 1977,³ and in this phase the molecules have a disc-like or plate-like shape.

These molecules are arranged one on top of other aperiodically, resulting in liquid like columns.

These are only the broad classifications. Chirality of the constituent molecules induces a new dimension to the number of sub-phases. The nematic phase gives rise to the ***Cholesteric*** phase. In this, a screw axis is superimposed perpendicular to the preferred molecular direction (***director***). The smectic phase has been classified into an array of sub-phases, depending upon the orientation of the molecules in the phase and their extent of correlation with respect to their relative position. This array is further enhanced due the chirality of the constituent molecules. Thus, at present about **twenty-four** different smectic sub-phases are known. In the following sections, we briefly describe various types of liquid crystalline phases.

I.1.1 Nematic liquid crystals

In the nematic liquid crystalline phase, the molecules exhibit an orientational order, but they do not have positional order (Fig I.1).⁴ The molecules can easily slide past one another which is characteristic of a fluid phase. The molecules obviously have a potential energy minimum when they are aligned along the direction of ***average*** orientation. This direction is represented by a unit vector called the director ($\hat{n}$). The director is apolar, *i.e.* $\hat{n}$ and $-\hat{n}$ are indistinguishable.

The order parameter is described by the equation :

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

where θ is the angle made by the molecular long axis with the director $\hat{n}$. The angular brackets denote a statistical average. Generally a nematic liquid crystal is optically uniaxial, positive and strongly birefringent.

I.1.2 Cholesteric liquid crystals

The cholesteric phase is also basically a nematic phase except that it is composed of optically active molecules. In this case the **minimum** energy configuration between two molecules occurs when there is a small angle between their long axes. The director twists about an orthogonal axis to produce a helical arrangement (Fig. I.2).⁴ This helical arrangement has a specific handedness. It can be right-handed or left-handed depending on the nature of the chiral centre. The handedness changes when the structure is reflected in a mirror, *i.e.* the reflected image of a left-handed structure looks like a right handed one and ***vice versa***. It is not possible to superimpose the given structure on its mirror image, *i.e.* the cholesteric structure lacks mirror symmetry. The pitch of the helix is often of the order of the wavelength of visible light and the medium produces selective reflection of visible light. The cholesteric is optically uniaxial, negative with the optic axis along the helical axis. When a left-handed cholesteric and a right-handed cholesteric are mixed together the pitch of the mixture becomes sensitive to temperature and composition. It is possible to have certain compositions for which the handedness of the helix changes sign at a particular temperature. At that temperature, there is an exact compensation of the right- and left-handed forms of helix and the mixture is said to be a compensated cholesteric. **Friedel** noted that, at that temperature, the mixture exhibits the properties of a nematic phase.⁵

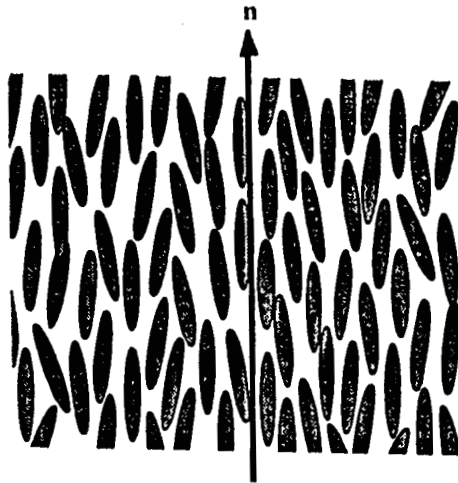


Fig. I.1 Molecular arrangement in Nematic phase (after A. M. Donald and A. H. Windle.⁴)

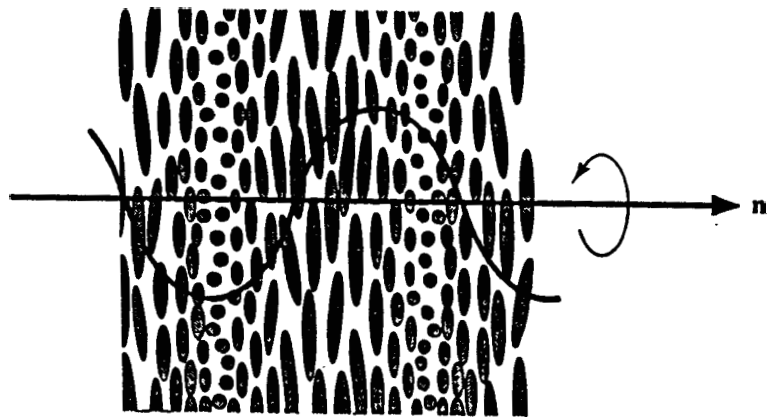


Fig. 1.2 Molecular arrangement in Cholesteric phase (after A. M. Donald and A. H. Windle.⁴)

I.1.3 Smectic liquid crystals

Smectic liquid crystals are characterised by one degree of translational order with the molecules arranged in layers. Depending upon the molecular arrangement within a layer, there are several types of smectic phases.

In the smectic **A** phase which is referred to as the S_A phase (Fig. I.3)⁴, the average orientation of the long axes of the molecules is along the layer normal whereas the centres of molecules in each layer are arranged randomly. It can be considered as a one-dimensional crystal and two-dimensional liquid. It is optically uniaxial with the optic axis lying normal to the plane of the layers.

The smectic **C** phase (Fig. I.4)⁴ is similar to smectic **A** except that the molecules are tilted with respect to the layer normal. This tilted orientation gives rise to optical biaxiality in the smectic **C** phase. In a smectic **C** phase composed of chiral molecules (chiral smectic **C** or S_{C^*} phase), the chiral interactions lead to the formation of a helical arrangement. The helix is formed by a precession of the tilt direction about an axis perpendicular to the layers with a characteristic pitch 'P' as shown in Fig. I.5.¹⁵ Depending on the chirality of the constituent molecules, the helix can be either right-handed or left-handed. This is the natural state of the structure for the S_{C^*} phase, when the influence of external fields or surface effects is absent. The helix of the S_{C^*} phase can be unwound either by surface interactions or by the application of a strong electric or magnetic field.

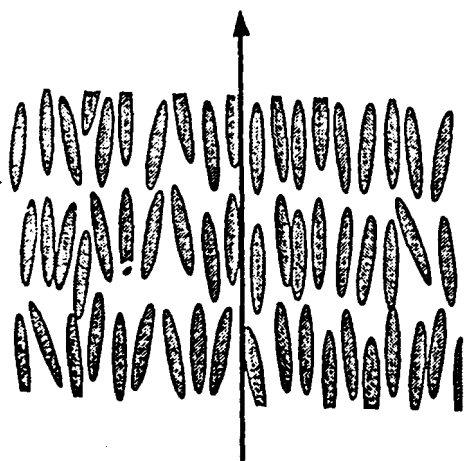


Fig. 1.3 Molecular arrangement in Smectic A phase (after A. M. Donald and A. H. Windle.⁴)

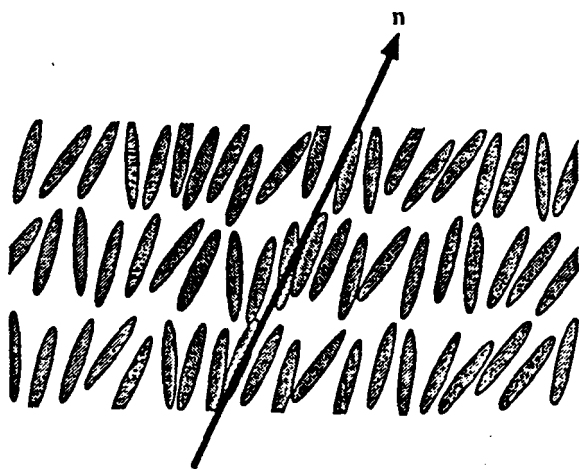


Fig. 1.4 Molecular arrangement in Smectic C phase (after A. M. Donald and A. H. Windle.⁴)

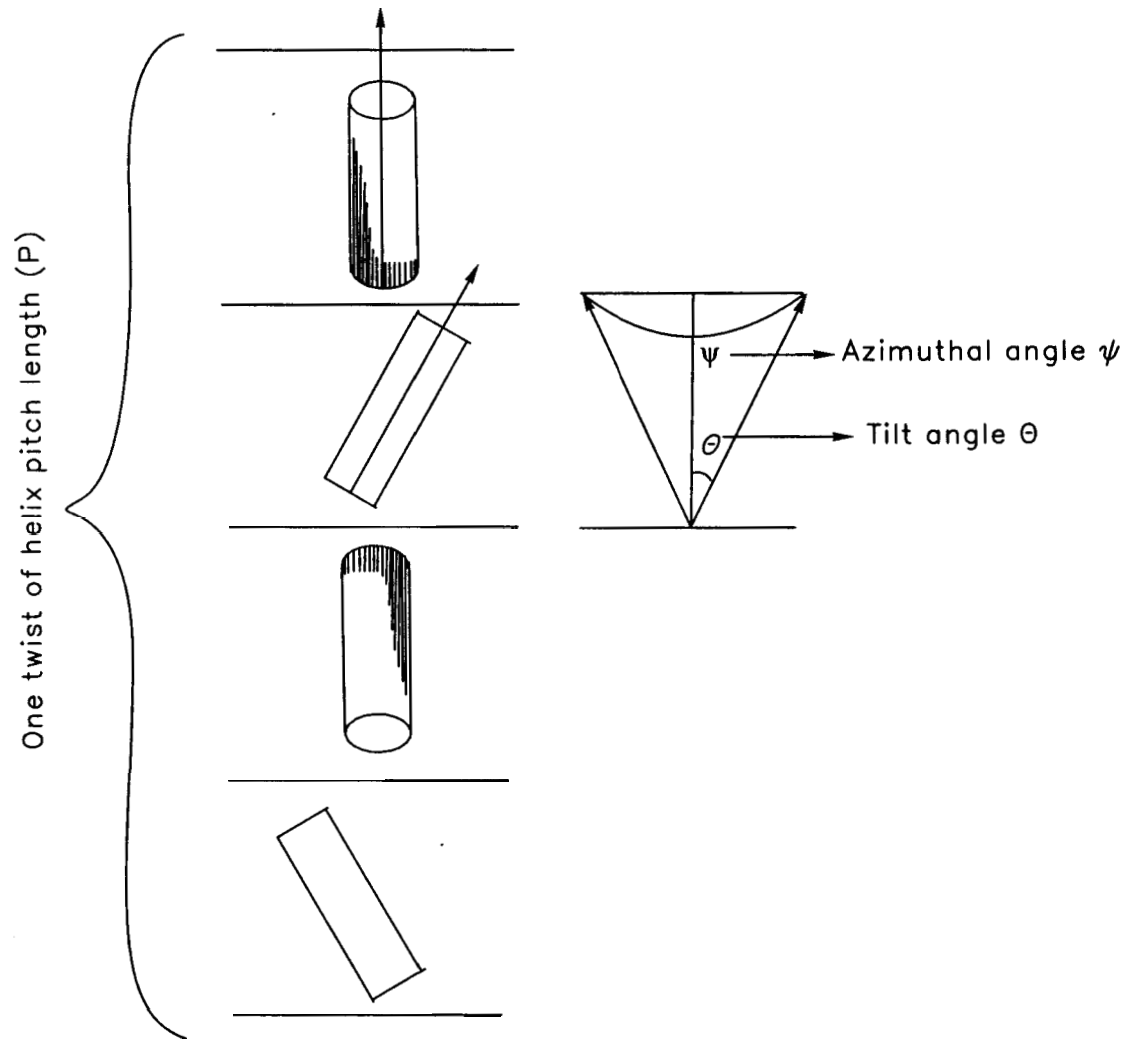


Fig.I.5 The structure of chiral smectic C phase (after J.W. Goodby.¹⁵)

I.1.4 Ferroelectric liquid crystals

Using a symmetry argument, Meyer *et al.*⁶ showed that smectic C* phase should be ferroelectric. His argument can be summarised as follows. Let us consider a vertical cross section of the smectic C structure passing through the layer normal $\vec{z}$ and the director $\hat{n}$ (Fig. I.6).⁷ This structure has the following symmetry elements:

- (i) a two-fold rotation axis about X;
- (ii) a mirror plane lying in the YZ plane.

These symmetry elements are consistent with the apolar nature of the director. If the molecules are chiral, as in the case of smectic C* phase, the YZ plane is no longer a mirror plane. So the medium is left with only a two-fold axis as the symmetry element. The two-fold axis sustains the properties described by a polar vector along that axis. When the molecules have permanent transverse dipole moments, then there can be a polarisation $\vec{P}$ along the two-fold axis, *i.e.* the medium can become ferroelectric. The dipole moment and hence the polarisation is normal to the plane containing the director and the layer normal and hence such a ferroelectric is called **transverse** ferroelectric. The first compound to be synthesised with the requisite features was 4-n-decyloxybenzylidene **4'-amino-2-methylbutylcinnamate** or DOBAMBC for short.

There have been attempts to understand the origin of polarisation in S_{C^*} phase at the molecular level.^{8,9,10} Polarisation is dipole moment per unit volume. The spontaneous polarisation (P_s) observed in the S_{C^*} phase is about two orders of magnitude less than the summation of dipole moments of individual molecules. This could be because P_s is an average of the dipoles oriented in the direction of the

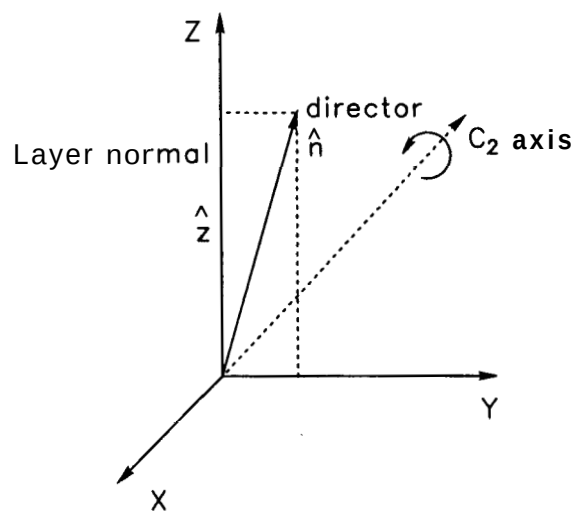


Fig.I.6 The ferroelectric liquid crystal C_2 symmetry operation (after **H.P.Padmini**.⁶⁾)

polarisation vector. The rotation about the molecular long axis, *i.e.* the director, is anisotropic in the S_C^* phase. Because of this rotational bias, a few particular molecular orientations of the chiral centre are preferred over others. Therefore, a dipolar ordering takes place. The extent of ordering is determined by the molecular structure and specifically by the rigid coupling between molecular dipoles and the chiral centre.^{9,10} However, this is only an assumption and there is not sufficient experimental data to ensure a firm relationship between molecular structure and the magnitude of polarisation.¹¹

Walba *et al.*¹² have proposed a model which suggests that polarisation originates from a novel kind of molecular recognition related to a diastereomeric host-guest complexation. They also show how the sign of the polarisation can be predicted using their model. The director here is considered as "the axis of minimum rotational inertia for each conformation," which, in turn, implies a zig-zag model where the core is more tilted than the chains.

Gray and McDonnell¹³ proposed a rule relating the molecular structure, absolute configuration and the twist sense for the cholesteric phase. Goodby *et al.*,¹⁴ in addition to the above factors consider the inductive effect at the chiral centre and relate it to the sign of polarisation. Parity of the chiral centre is determined by the number of carbon atoms it is away from the aromatic (central) core of the molecule. More than thirty examples are known which follow these rules. The twist sense of the helix and the optical rotation *i.e.* (rotation of the plane polarised light) can now be associated with the direction of polarisation as follows.

$$\mathbf{Ps} (-) = \mathbf{1} (-) = \mathbf{R.H. helix}$$

$$\mathbf{Ps} (+) = \mathbf{d} (+) = \mathbf{L.H. helix}$$

Two tilt orientations are possible in the S_C^* phase of the zig-zag structure (Fig. I.7).¹⁵ The angle made by the core is the optic angle (a) and that made by the chains is the steric angle (θ). One hypothesis for revision of initial guidelines lies in the change in the tilt orientation of the molecules. The rigid aromatic core in this case may be packed in a more upright orientation relative to the layer planes than the molecule as a whole ($a < \theta$), *i.e.* reverse of that postulated previously ($a > \theta$). There have been reports of inversion of sign of polarisation on cooling the ferroelectric phase.^{16,17,18} This behaviour has been attributed to a change in the conformation of the molecule at certain temperature. Also a change of intermolecular interaction when the molecular tilt exceeds some critical value which may induce a change of the molecular interaction (conformation) and reversal of the sign of polarisation.⁸ This change has also been brought about by doping a liquid crystal exhibiting an S_C phase.¹³ The temperature at which the polarisation changes sign is dependent upon the concentration of the chiral material in the non-chiral host.

1.1.5 The twist grain boundary phases (TGB_A and TGB_C)

de Gennes,¹⁹ predicted that twist or bend distortions can be incorporated into a layered smectic A structure by the presence of an array of screw or edge dislocations. Later, Renn and Lubensky²⁰ modelled such an array of dislocations for chiral molecules and called the phase as twist grain boundary phase (TGB_A phase). This phase was finally discovered in some propiolate derivatives synthesised by Goodby and co-workers.²¹ In the TGB_A phase small blocks of smectic A layers rotate with respect to one another, thereby forming a helical structure. The helical axis is perpendicular to

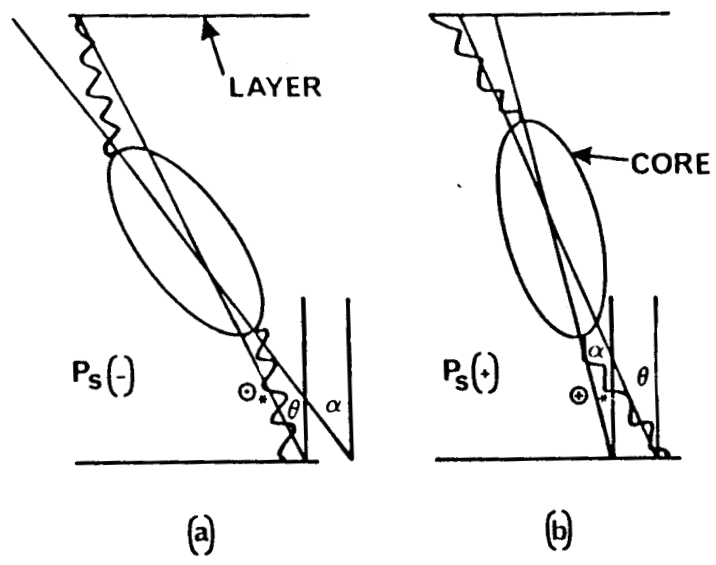


Fig.1.7

the molecular long axis. The screw dislocations separate the blocks from one another. Thus, a small angular rotation is allowed between the blocks. As a helix is formed with the aid of screw dislocations, the dislocations themselves are periodic. The rows of screw dislocation form the grain boundaries in the phase. The pitch of the helix is of the order of wavelength of visible light and hence light is reflected selectively. A schematic representation of this phase is shown in Fig I.8.¹⁵

Renn and Lubensky²² extended their theory to the **TGB_C** phase. This phase too was discovered, in some fluoro substituted **tolane derivatives**.²³

The early structural studies carried out by Goodby *et al.*²¹ on chiral 1-methylheptyl 4'-[(4''-n-alkoxyphenyl) propioloyloxy] biphenyl-4-carboxylates revealed that **TGB_A** phase formed only when certain conditions such as those described below were satisfied.^{24, 25}

- (i) The presence of a short temperature range **S_A** phase and **S_A-S_C*** transition close to the clearing point, thus allowing pretransitional fluctuations to stabilise the resulting TGB phase;
- (ii) the transition from the cholesteric or liquid phase must approach second order;
- (iii) the system must have strong chirality so as to be able to induce a twist through the smectic phase.

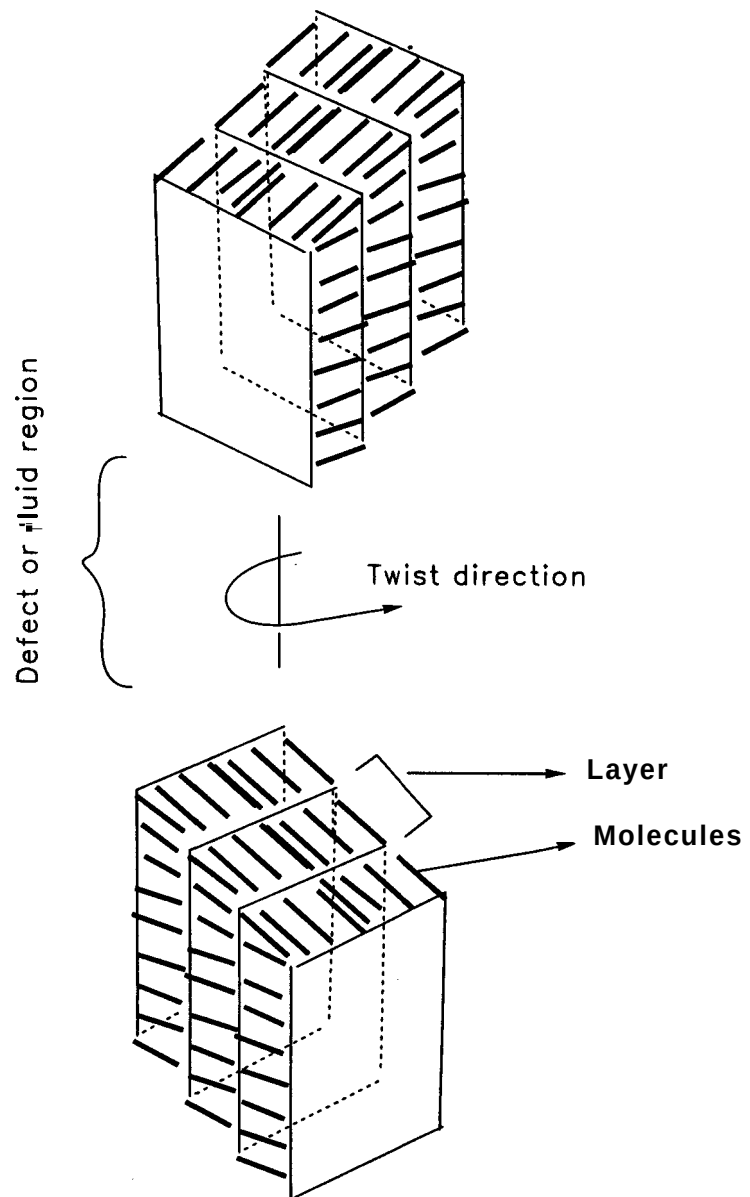


Fig.I.8 The structure of helical smectic A* phase (after J.W. Goodby.¹⁵)

1.2 Introduction to polymeric liquid crystals

Vorlander's prodigious contribution to liquid crystal research during the first quarter of this century displayed admirable chemical intuition. Working with little more than the notion that lath-like molecules are predisposed to form liquid crystalline melts, he postulated that 'infinitely long mesogens' would be compatible with supramolecular organisational constraints in liquid crystals.²⁶ In addition to this superficial reference to the plausibility of preparing a polymeric liquid crystal [PLC], Vorlander subsequently synthesised a dimeric liquid crystal [DLC], a mesogen consisting of two lath-like segments (mesogenic cores) connected together by a flexible alkyl chain (spacer).²⁷ The DLC is currently a subject of active research in model compound studies that have direct bearing on linear, semi-flexible PLC's. After Vorlander's early contributions, research in this field in the early part of the century was practically dormant. In fact, until the late 1960's, when the industrial potential of PLC's were discovered, only a few isolated discoveries relevant to PLC's were reported.

In mid 1960s low molar mass liquid crystals (LMMLC) with a single functional group (*e.g.* a vinyl group) were polymerised to form side chain PLC. Melts of such side chain PLC retained liquid crystal textures (nematic, smectic and cholesteric) over a well defined temperature range usually in excess of that exhibited by the corresponding LMMLC implying thereby that the mesophase is 'stabilised' via polymerisation.²⁸ Since those early days, technologically important end uses of side chain polymers have been identified.

- 1) Cholesteric polymers function as tunable wavelength reflectors and notch filters;²⁹
- 2) side chain copolymers solubilise dichroic dye additives for use in electro-optic displays;³⁰

- 3) they serve as non-centrosymmetric host matrix for hyperpolarisable guest molecules in non-linear optical devices;³¹
- 4) lyotropic smectic LMMLCs can be polymerised to stabilise vesicles in **drug-delivery** schemes."

Extension of lyotropic polymerisation process to smectic monolayers could stabilise thin organic dielectric layers for microelectronic device **fabrication**.³³ Lyotropic side chain PLCs having amphiphilic side chains have been prepared and their aqueous mesophases **characterised**.³⁴ There have also been successful efforts to incorporate oblate, disc-like mesogenic cores into the thermotropic side chain PLCs.

During roughly the same period that side chain PLCs were first synthesised, linear block copolymers prepared from monomers with distinctly different chemical properties were shown to form liquid crystalline phases in melt or in the presence of solvent for one of the **blocks**.³⁵ Block copolymer solids in which **microphase-separation** is well developed exhibit unique mechanical properties; while preferential swelling of a block in such copolymers yield a variety of **morphologies**.³⁶

Academic research in the main chain PLCs started in mid 1970s and has focussed on the semiflexible, alternating copolymer **PLCs**.³⁷ Exaggerated odd-even behaviour (relative to **LMMLCs**) of both thermodynamic and microscopic properties of these PLCs are associated with the parity of the alkyl spacer segment of the copolymer (*i.e.* whether or not there is an even or an odd number of chemical bond in the spacer). The influence of the parity of the spacer and more generally, the implications of connecting **mesogenic** cores **via** flexible spacers has been widely studied.

I.2.1 Classification of liquid crystalline polymers

As mentioned earlier, the necessary condition for appearance of the LC state is a rigid, anisometric molecular shape. This concept can be directly applied to the polymers, the monomer units of the polymer backbone containing the anisometric (mesogenic) units. If we restrict ourselves to the most important LC materials having a cylindrical or lath-like geometry, two basically different types of polymers are conceivable.

(a) The mesogenic units are connected head to tail, forming a main chain polymer.

Polymers having this constitution are called '**Main chain LC polymers**' (**MCLCP**).

(b) The mesogenic units are attached as side chain pendants to the polymer backbone.

These polymers are called '**Side chain LC polymers**' (**SCLPC**).

In addition to homopolymers (these have only a single type of monomer unit along the main chain), a variety of copolymers have been synthesised. These copolymers have different mesogenic moieties including monomer units of both the above types (a) and (b), or non-mesogenic moieties together with the mesogenic units. Furthermore, the linear primary structure of the main chain can be varied to yield a crosslinked or branched main chain polymer. Crosslinked polymers (e.g. elastomers) are of special interest because of their elastic properties.

I.2.2 Main chain liquid crystalline polymers

The mesogenic monomer units can be directly connected within the polymer main chain. The resulting rigid, rod-like polymer can be described by the molecular axis ratio, which is directly proportional to the degree of polymerisation (DP). If the

mesogenic groups are connected via a flexible spacer, the main chain becomes semiflexible. Assuming a sufficiently long spacer length, the backbone can be described as a chain of freely joined rods which have the axial ratio of the original mesogenic unit. These two different chemical structures for polymers yield different phase behaviour, which are a function of the DP. Following the theory that the existence of the LC state is explained only by the packing effects of the anisometric molecules, the LC phase stability is determined by the axial ratio of the rigid unit. Consequently for a rigid rod polymer the LC phase should be directly determined by the DP, whereas for the other model, shown in Fig. I.9³⁸ (semiflexible one), only the mesogenic element in the backbone should determine the phase stability.

In reality, polymers exhibit behaviour which resembles both the models. The degree of flexibility of the main chain determines the phase stability. Also, as for LMMLC, not only the axial ratio of the mesogenic groups, but also their chemical constitution and their substitution strongly affect the LC phase behaviour.

1.2.2.1 Synthetic strategy for main chain liquid crystalline polymers

The synthesis of LC main chain polymers normally follows step-growth reactions, such as polycondensation or polyaddition, where the reactants contain suitably substituted mesogenic compound or a non-mesogenic substance. These monomers form the mesogenic segment of the polymer main chain by a polymerisation reaction. To obtain high molar mass polymer, the functional groups are limited to those reactions which give high yields.³⁹ Polyesters or polyamides are preferred systems, because high molar mass polymers can be easily obtained by standard polymerisation reactions.

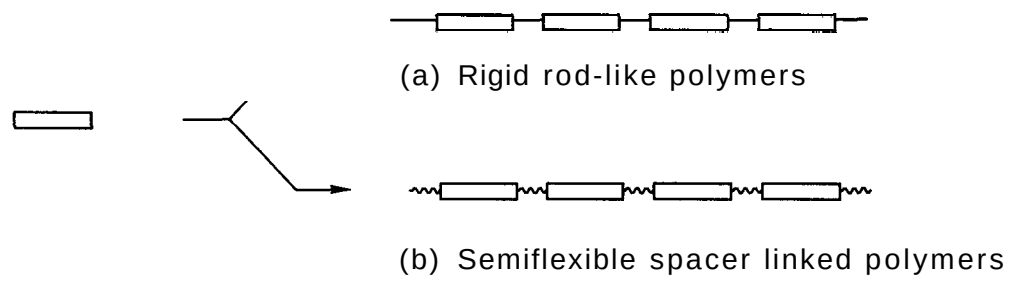


Fig.I.9 Schematic of LC main chain polymers (after H.Finkelmann.³⁸).

1.2.2.2 Rigid main chain liquid crystalline polymers

A large number of polymers having a rigid, rod-like main chain have been synthesised,⁴⁰ and many are described in the patent literature. Commercially easily available materials like 4-hydroxybenzoic acid are preferred as starting materials. Although low molar mass phenyl esters of benzoic acid form a large class of intensively investigated LC materials, the polycondensation of compound 1,4-hydroxybenzoic acid and polycondensation of terephthalic acid and hydroquinone, (Fig. 1.10)³⁸ yield polyesters which are not LC materials.^{41,42}

These polymers are insoluble and do not fuse without decomposition. They can be processed only by sintering. For example, the polyamide of terephthalic acid and 1,4-phenylenediamine (Fig. 1.11)³⁸ which is well known under the name Kevlar, is also infusible, but is soluble in concentrated sulphuric acid. In solution, a nematic phase occurs which is processable, for example, by spinnable fiber spinning.

These examples show that rigid rod-like polymers having symmetrical structures are not suitable for obtaining LC polymer melts. With increasing DP, beginning with the monomer, the melting temperature rapidly increases above the decomposition temperature. To overcome the problems posed by high temperatures required for the transformation from the crystalline to the LC phase, two modifications of the LC main chain are conceivable.

- (a) The cylindrical shape of the backbone can be reduced by introducing non-linear but rigid elements in the main chain. This helps in bringing down the temperatures of transformations and LC phases can be observed.
- (b) Lateral substitution of **alkyl** chains. These act as lubricant between the **rod**-like particles attached to the monomer units of the polymer. Also these can act

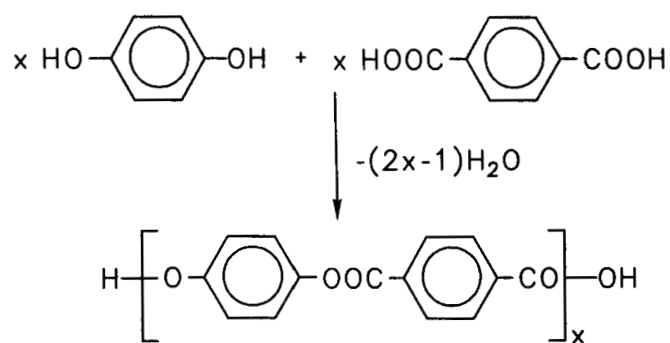
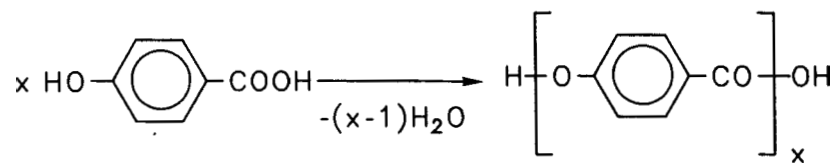


Fig.I.10 Scheme for polyester synthesis (after H.Finkelmann.³⁸).

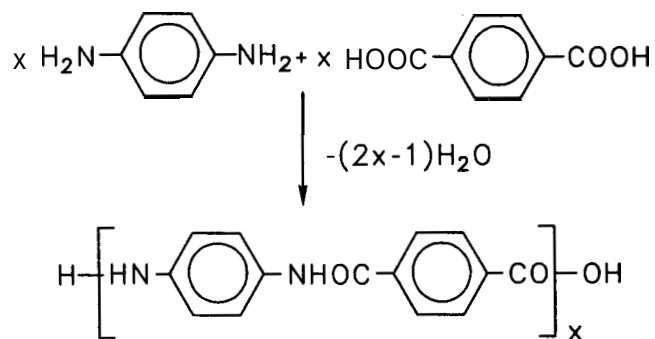


Fig.I.11 Scheme for polyamide synthesis (after H.Finkelmann.³⁸).

as solvent molecules attached to the macromolecule. This concept has been successfully applied to cellulose derivatives, which become thermotropic LC materials with long chain lateral substituents.⁴³

1.2.2.3 Semiflexible main chain liquid crystalline polymers

To overcome the problems of high melting points of polymers containing only rod-like chain segments, flexible moieties like alkylene or alkyleneoxy chains can be introduced into the polymer main chain. Again, a variety of systems is conceivable by varying the chemical structure of the mesogenic moieties, lengths of the flexible segments or the number of different monomer units in regular or statistically irregular copolymers. Although this has been extensively reviewed,^{36,44} three typical examples can be used to illustrate the main idea.

Polymerisation of α,ω -substituted polymethylene chains with functionalised mesogenic compounds provides a convenient method for making semiflexible main chain polymers. Polyesters synthesised from 4,4'-dihydroxy-2,2'-di-methylazobenzene and alkandioic acid (Fig. I.12) exemplify such systems.⁴⁵

Another approach is the polymerisation of a non-mesogenic monomer such that a rigid, but flexibly linked, mesogenic moiety is built up by a polycondensation reaction (Fig. I.13).³⁸

An interesting synthesis has been described by Jackson and Kuhfuss.⁴⁶ The starting material is the commercially well known poly(ethyleneterephthalate) (PET), which is transesterified with 4-hydroxybenzoic acid (PHB). With increasing amounts of PHB, the mesogenic moieties are statistically irregularly built up in the main chain.

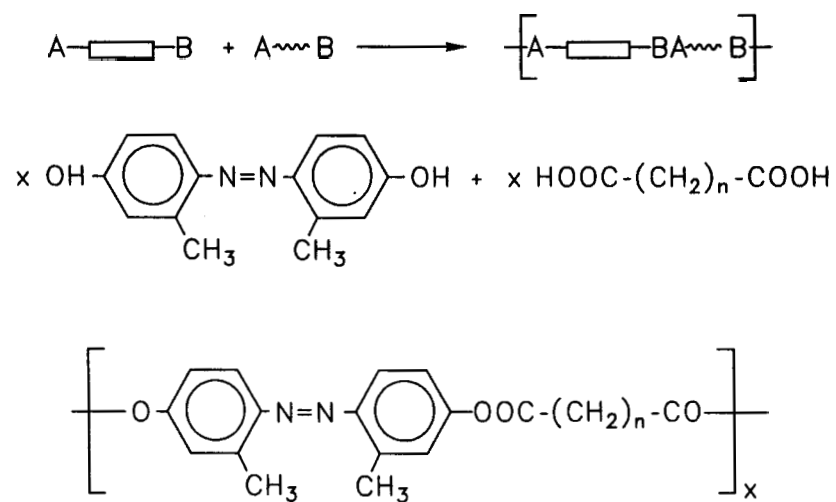


Fig.I.12 Scheme for A-BA-B type MCLCP (after H.Finkelmann.³⁸).

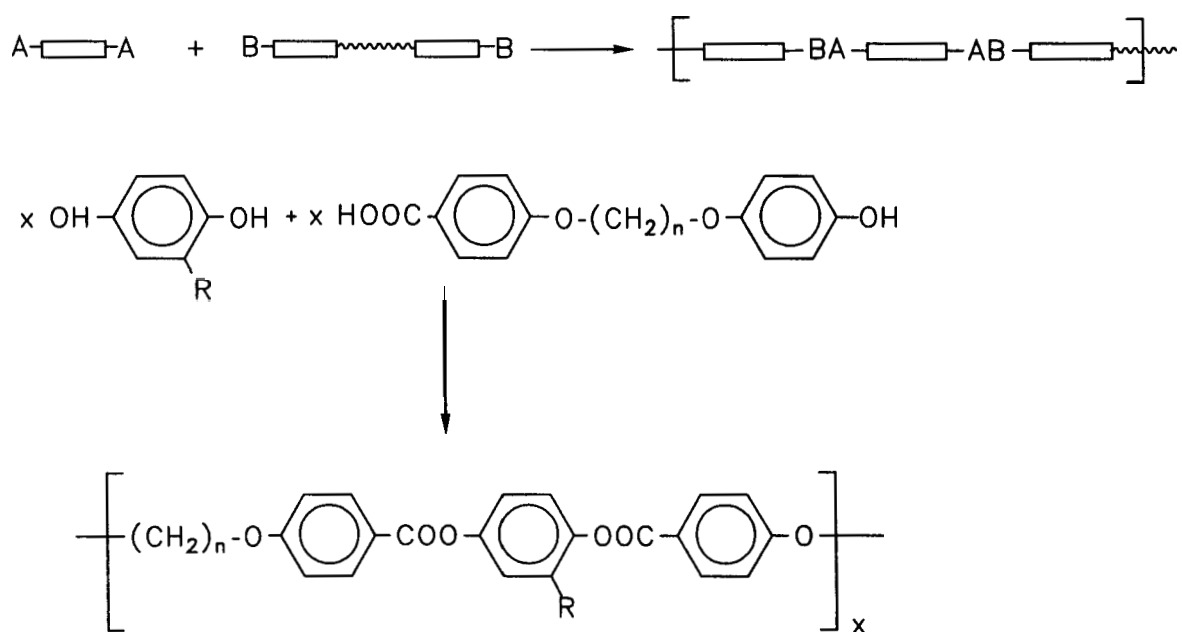


Fig.I.13 Scheme for A-B-A-B type MCLCP (after H.Finkelmann.³⁸).

Furthermore, the mesogenic groups differ in their length (Fig. I.14).³⁸ By this method, the flexibility of the main chain can be regulated by the amount of transesterified PHB.

I.2.3 Side chain liquid crystalline polymers

In 1978, the side chain, LCP was simply a hydrocarbon polymer with spaced-off simple mesogenic units. Today, a plethora of structural modifications exist for these materials, based upon numerous classes of polymers prepared by a variety of polymerisation techniques. For example, relatively simple solid-liquid phase transfer catalysed synthetic procedures have been described for specific side chain **LCPs**.⁴⁷ These techniques surely must be significant from a large scale production standpoint, should this class of electroactive polymers fulfil their promises and become commercially important materials. Cyclic side chain LCPs now exist in addition to the more conventional linear materials which can be homo- or copolymeric. In the latter types, co-monomers may be mesogenic or non-mesogenic and the non-mesogenic component can be functional (photochromic, photoconductive, hyperpolarisable) or non-functional (internal plasticiser or diluent).

The cores attached to spacers are now probably best referred to as mesogenic systems rather than mere mesogens, since disc-shaped and rod-shaped single and paired structures have been prepared and appended in different fashions. Today, it is **infact** difficult to conceive a single shape appropriate to pictorially represent the broad class of mesogenic systems that have been prepared. Indeed, the creative organic chemist appears to be able to produce the most diverse structures and incorporate them into polymers which subsequently exhibit **mesomorphism**.⁴⁸ A firm understanding of the role of the spacer in side chain LCPs is now established, and interesting

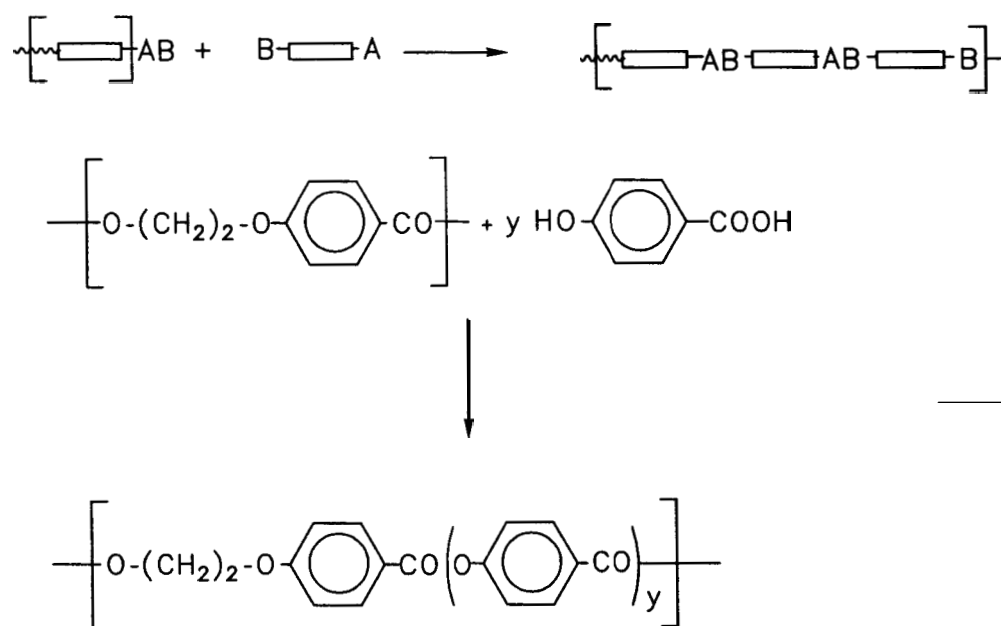


Fig.I.14 Scheme for A(B)_n type MCLCP (after H.Finkelmann.³⁸).

microphase separated LCPs have been studied,⁴⁹ which have important ramifications from a device physics point of view. The chemistry and functionality of the spacer has also been modified; perfluorinated and ethylene oxide type spacers exist, and the latter can be organised by their terminal **mesogens** and function as open crown ethers. Inorganic siloxane spacers and crosslinks are well known. Use of the latter leads to various classes of liquid crystalline elastomer and lightly cross-linked networks which can be made to exhibit the interesting ferroelectric S_C^* phase. An in-depth discussion on side chain LCP formation is given later.

1.2.3.1 Side chain siloxane polymers

Systematic investigations of the synthesis, characterisation and applications of SCLCPs began only after Ringsdorf and co-workers,^{50,51,52} proposed that a flexible spacer should be inserted between the polymeric main chain and the mesogenic side groups to decouple the motions of the main chain and side groups in the liquid crystalline state. Previous investigations concerning the synthesis of polymers with LMMLC compounds attached to their backbones did not lead to a synthetic method which could systematically produce SCLCPs, since most involved polymers with the mesogen attached directly to the backbone. The research prior to the introduction of the spacer concept have been reviewed by Wendorff.⁵³

The research performed after 1978 has been extensively reviewed.⁵⁴ Particularly helpful are the reviews by Finkelmann and Rehage,⁵⁵ and Shibaev and Plate,^{56,57} which tabulated and organised most of the SCLCPs and their phase transitions available at that time.

Based on the spacer model, a large number of side chain liquid crystalline polymers and copolymers were synthesised and details are currently available in the literature. Different smectics, chiral smectic, nematic and cholesteric mesophases are exhibited by these polymers based on different mesogenic groups and polymer backbones. Nevertheless, even the most elementary synthetic and structural principles of this field are not completely elucidated. Answering basic questions related to the influence of polymer molecular mass, polydispersity and tacticity, the nature of the spacer and its length, and the nature of the mesogenic group and polymer backbone on phase transitions, and on the nature of the mesophase or the extent of decoupling, is not a trivial job.

Essentially, three things can be varied in a SCLCP: ***The backbone, the spacer*** and ***the mesogenic unit***. We will consider these in turn, showing how variations in structures affect the properties.

1.2.3.2 The backbone

Most of the work in the literature refers to SCLCPs with acrylic, methacrylic or siloxane backbones. Studies of the temperature range over which liquid crystal phases are stable are a little contradictory, probably due to a lack of comparability of molecular mass of the polymers. The general indication is that the glass transition temperature decreases and the clearing temperature increases, with increasing chain flexibility.

1.2.3.3 The spacer

A spacer is not always necessary for LC behaviour, the mesogenic unit can be attached directly to the backbone. An example is the biphenyl ester of polyacrylic acid which shows smectic behaviour.⁵⁸ The spacer is usually a methylene unit sequence or oxyethylene or sometimes siloxane units. Spacer length has profound effect on the phase transitions.

Short spacers, usually less than six methylene units lead to nematic behaviour, while longer than six lead to smectic phases. Clearing temperatures show an odd-even behaviour for the number of spacer units. It is usually higher for the even number of units. The reason for this can be illustrated as shown in Fig. I.15.

If we consider the functional group that joins the mesogenic unit to the spacer as part of spacer, then for an odd number of spacer units, the mesogenic unit is tilted with respect to the backbone, thus destabilising the liquid crystalline phase. As a result the anisotropic phase is stable over a much narrow range of temperature. This odd-even effect tends to become less pronounced at longer spacer lengths and the clearing temperature generally increases. The glass transition temperature decreases with increasing spacer length.

1.2.3.4 The mesogenic unit

Mesogenic unit usually consists of one or more core group (mostly a phenyl, biphenyl or a naphthalene group), joined together with a suitable linkage group. Increasing the length of the mesogenic group by having more aromatic rings tends to increase the temperature range over which the liquid crystalline phase is stable.⁵⁹ The terminal group in the para-position has an effect upon the phase behaviour of the

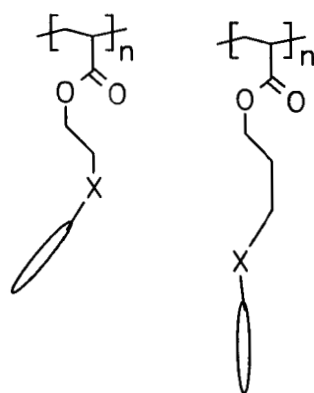


Fig.I.15 Figure showing the effect of linkage group X on the stabilisation of liquid crystalline phase.

polymer. Polar terminal groups such as -CN tend to lower the clearing temperature, whereas long chain alkoxy groups give more stable thermotropic phases with higher clearing temperatures.

Mesogenic units attached laterally to the polymer backbone have been synthesised and generally show nematic behaviour,⁶⁰ disc-like mesogens attached to polysiloxane backbone show columnar mesophase.⁶¹ Unusual SCLCPs include cyclic siloxane oligomers with pendant mesogens,⁶² and polymers in which a liquid crystalline polyester backbone has a mesogenic pendant attached to it.⁶³

1.2.4 Synthesis of side chain liquid crystalline polymers

Synthetic polymer chemists have provided a wide range of sophisticated SCLCPs, enabling physicists to establish structure-property relationships and theoreticians to test their understanding of these systems. The investigation of potential applications has been an additional spur towards synthesis in this area. Typical approaches towards synthesis of SCLCPs are summarised below.

Free radical polymerisation of mesogenic acrylic monomers, although a very convenient technique from an experimental point of view, tends to generate polymers of broad molecular mass distribution and ill-defined tacticity. This is a disadvantage when carrying out careful studies of structure-property relationships. The usual approach is to prepare an acrylic mesogen and carry out solution polymerisation.

Grafting of a mesogenic unit on a polymeric backbone can be achieved in various ways, but the most common application is the hydrosilylation reaction of polysiloxanes containing a reactive Si-H group using a platinum catalyst.⁶⁴ A disadvantage of grafting is that the backbone polymer is usually polydisperse, although

living polymerisation of monomers with protected functionalities may overcome this problem. Also, unless the extent of grafting is very high the sequence of mesogenic units along the chain will be randomised and the result will be a random co-polymer.

Production of monodisperse SCLCPs by living anionic or group transfer polymerisation of mesogenic monomers has been unsuccessful, although Percec⁶⁵ and his group have achieved some success with cationic polymerisation of vinyl ether mesogens, where reasonably narrow molecular weight distribution range was obtained. Kodaira and Mori⁶⁶ have synthesised SCLCPs with near monodisperse methacrylate backbone by using metallo-porphyrin initiated living polymerisation of a mesogen-functionalised methacrylate monomer. Kornia *et al.*⁶⁷ have used nor-bornene functionalised mesogen to generate near monodisperse methacrylate polymer by living ring-opening metathesis polymerisation. Recent developments in SCLCPs have produced novel materials that will be the basis of new physical studies and applications. A few examples to illustrate the point are described below:

1.2.4.1 Novel mesogens

Rigid-rod mesogens are not always required to form the thermotropic phases. Fluoroalkyl ether derivatives of hydroxymethyl acrylate show smectic phases at room temperature with a clearing temperature of 32°C.⁶⁸ With interest in chiral phases growing, a number of polymers with chiral groups have been reported.^{69,70} SCLCPs with crown ethers have also been reported⁷¹ and these have potential use in molecular recognition devices.

I.2.4.2 Novel methods of coupling the mesogens to the backbone

Ion complexated SCLCPs have been reported where the mesogenic units are not directly bound to the backbone but are held through ionic interactions and these displayed smectic phases with high thermal stability.⁷² Kato and Frechet⁷³ reported a polymer where the spacer was chemically bound to the backbone, while the mesogen hung onto the spacer through a hydrogen bonding.

I.2.5 Copolymers

Random copolymers of mesogens and non-mesogens give an SCLCP wherein the effect of mesogen is diluted. This rarely alters the phase seen but has a profound effect on the transition temperatures. In such cases a minimum mesogenic content is to be expected, below which the mesogenicity would be lost. In some cases it is as low as 20% mole-fraction. This minimum amount increases as the spacer length increases. Much work was done in the case of methacrylate monomers. One interesting case of copolymerisation of mesogenic methacrylate and poly(methylmethacrylate) macro-monomer was recently reported. Block co-polymers using the same two monomers have also been reported.^{74,75} Group-transfer polymerisation and living polymerisation catalysed by methylaluminium porphyrins, have been successfully used for this purpose.⁷⁶

1.3 Applications

1.3.1 Applications of low molar mass liquid crystals

The main application of low molar mass liquid crystals is in electronic displays. Nematic liquid crystals are widely used for display applications. Cholesteric liquid crystals are used as temperature sensors in the medical field,⁷⁷ in disposable thermometers, aerodynamic testing *etc.*⁷⁸ They have also been used to produce panels that exhibit an optical memory effect.⁷⁹ Chromatography is of great importance in modern chemical analysis and physico-chemical investigations. Liquid crystals are now among the materials used in chromatography. The use of liquid crystals as stationary phases in gas chromatography (GC) was described for the first time in 1963 by Kelker⁸⁰ and later by Dewar and Schroeder.⁸¹ Eversince, liquid crystal stationary phases have been applied successfully for separation of composite mixtures, chiefly isomers, including those of polycyclic hydrocarbons.

Liquid crystals are used to control or alter the chemical reactivity of dissolved solutes.^{82,83} They alter reactivity as a result of their ability to control solute diffusion, orient reactants and discriminate between stable solutes and transition states according to their sizes and shapes. This ability depends on the degree of order present in the liquid crystal and the structure of the reactants in relation to that of the mesogen.

The electric field induced antiferroelectric - ferroelectric phase transition is applicable to display devices. Two main characteristics are the sharp threshold behaviour under a dc-field between antiferroelectric and ferroelectric (AF-F) states and the hysteresis in the switching, making a bistable-switching device possible. The AFLC display (AFLCD) utilises both F states, as clearly noticed by two driving frames. The two states give the same transmittance, so that they can be used alternately. The

AFLCD is not affected by the 'ghost-effect' which is a serious problem in FLCD. Another problem in FLCD is the weakness against mechanical shock because of the smectic layer structure. AFLC cells have a remarkable feature of self alignment recovery during an operation from damage caused by mechanical and thermal shocks. Also the non-chevron structure gives rise to an additional advantage and relatively high contrast ratio.

However the AFLC may not be suited for image storage devices, since a constant voltage has to be applied to the cell in order to **memorise** addressing images. This may be applicable for real time holography. But, only a clear understanding of the complex nature of these mesophases may allow an advantageous use of these in display devices and allied applications.

1.3.2 Applications of liquid crystalline polymers

A variety of potential applications for side chain **LCPs** has been considered to date. Broadly speaking, applications fall into two classes: electro-thermo-optical effects and separation and complexation effects. Some examples from each class are given below:

1.3.2.1 Electro-thermo-optical effects

- (i) Optical data storage: Digital, holographic and analogue optical data storage have all been demonstrated using cholesteric, nematic and smectic **SCLCPs**.⁸⁴
- (ii) Optical elements and optical claddings: Selective wavelength notch and bypass filters may be made from cholesteric SCLCPs as also from **MCLCPs**.^{85,86}
- (iii) Optical non-linear effects: SCLCPs, loaded with appropriate dyes or with inherently coloured mesogenic systems are under investigation primarily for

second-order effects such as second harmonic generation (SHG) and the electrooptic effect.^{87,88}

- (iv) Photo effects: Thermotropic and lyotropic SCLCPs bearing photoconducting groups have been prepared and are currently under **investigation**.⁸⁹
- (v) Electronic effects: Today some speculation exists as to the possibility of producing conductive LCP systems *e.g.* in the spinal columnar **LCPs** of Sirlin *et al.*⁹⁰
- (vi) Electro-optical displays and Elasto-optical effects: SCLCPs have been used as dopants for electro-optic displays to advantageously modify the elastic constants.⁹¹ Bulk samples of SCLC elastomers have been prepared for use in modulators and photoelastic coatings.⁹²

1.3.2.2 Separation and complexation effects

SCLCPs with oxyethylene spacers can dissolve metal **cations**.⁹³ Interest in these and **MCLCPs** with enhanced ionic conductivity may lead to applications in novel 'solid' polymer **electrolytes**.⁹⁴ Control of permeation of gases and simple drugs has been reported recently using SCLCP membranes.⁹⁵ One very well developed application of SCLCPs is as stationary phase in GC **systems**.⁹⁶

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