CHAPTER - 1

INTRODUCTION

Liquid crystalline materials are organic compounds with a state of order intermediate between those of solid crystals and isotropic liquids. The discovery of liquid crystals is dated back to the year 1888 when the botanist F. Reinitzer [1] observed the cloudy melting of cholesteryl benzoate and cholesteryl acetate. He donated these compounds to the physicist O. Lehmann [2] who described liquid crystals as a novel state of matter possessing anisotropic viscous, electrical, optical and mechanical properties. Friedel [3,4] suggested the term "mesomorphic phase" or "mesophase" to this state of matter. There are thousands of organic chemicals which are known to form mesophases [5,6]. In addition to this, few organo-metallic [7,8] and inorganic chemicals [9] also show liquid crystalline properties as well.

One of the most important properties of liquid crystals is the combination of long-range orientational ordering of the particles constituting the substance with a total or partial absence of long-range order in the positioning of their centres. The former is the characteristic of solids while the later is the characteristic behaviour of liquids where the short-range order is observed in the positioning of molecules, but long-range order is absent. The molecules of the compounds showing mesophases are generally non-spherical in shape —— rod like (in the form of spherocylinders or ellipsoid of revolution) or disc like. Anisotropic dispersive forces between the molecules play a major role in the stabilization of the liquid crystal phases. There are many books and review articles on liquid crystals which give details regarding molecular structure and physical properties of the compounds exhibiting mesophases, of which a few [5,6,8,13-21] are listed here. Recent developments in the field of liquid crystals and applications are also available [22-26].

1. Classification of Liquid Crystals

On a broad basis, liquid crystals are classified into two types, viz. 'lyotropic' and 'thermotropic'.

1.1 Lyotropic mesophase

Lyotropic liquid crystals are solutions of anisotropic molecules in an isotropic solvent [27-30]. The amount of solvent is the controlling parameter for forming such mesophases. Solutions of soap and water are typical examples of lyotropics and their mesomorphic properties appear both as functions of concentration and temperature. Lyotropic liquid crystals play an important role in living systems and are particularly important for the present day understanding of the structure and properties of biomembranes [23]. Since this dissertation is not concerned with lyotropic liquid crystals it will not be discussed any further.

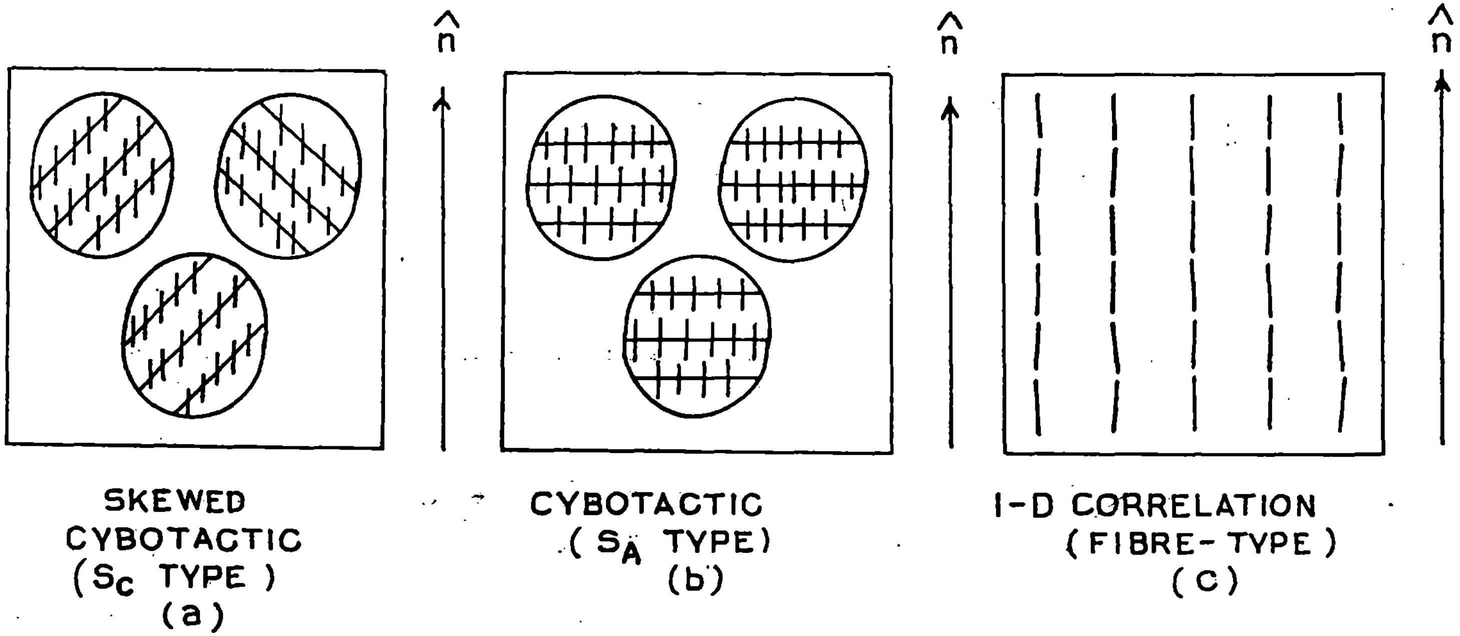
1.2 Thermotropic mesophase

In thermotropic liquid crystals mesomorphic behaviour is induced due to changes in temperature. Thermotropic liquid crystals which show reversibility of phase transitions are called enantiotropic. In certaion cases, mesomorphism is depicted only during cooling of the compound and phases of this kind are called monotropic. Friedel [31a] from his detailed optical and x-ray studies have classified thermotropic liquid crystals into three types: nematic, cholesteric and smectic.

Classification of smectic liquid crystals are based mainly on the optical and miscibility studies of Sackmann and Demus [31b]. A brief description of different thermotropic mesophases are given below.

1.2.1 Nematic mesophase

The term "nematic" coined by Friedel from a Greek word thread, describes the thread like lines seen in nematic liquid crystals under a polarising microscope. In nematics, there is no correlation between the molecular centres of gravity, but the direction of molecular long axes do statistically have a preferred direction called "director", denoted by $\hat{n}$. Since there is no restriction regarding the positions of the centre of mass, the molecules in the phase have a high degree of mobility and the nematic phase is markedly affected by external fields. In addition, the preferential orientations $\hat{n}$ and $-\hat{n}$ are not distinguishable (all orientations of the ends of the molecules are equally probable). The nematic phase is an optically uniaxial medium. Another characteristic property of this phase is that the right-and left-handed forms are indistinguishable (achirality), indicating the system to be a racemic mixture of right and left-handed molecules. X-ray studies indicate that fluctuations of smectic like order parameter manifests itself in certain nematic phases, the so-called "cybotactic nematic" phases, first observed and classified by de Vries [32]. In nematics of this kind there exist domains wherein the centres of molecules lie in a well defined plane, the molecules itself being either perpendicular to the plane (normal cybotactic nematic phase) or tilted with respect to the plane (skewed cybotactic nematic phase). Generally, these domains extend only



SKEWED CYBOTACTIC (S_C TYPE) (a)

CYBOTACTIC (S_A TYPE) (b)

1-D CORRELATION (FIBRE-TYPE) (c)

Figure 1.1. Schematic diagram showing molecular arrangements in nematics having three types of short range order.

upto limited distances. Another type of nematic phase is encountered in certain liquid crystalline compounds [33] which possesses one dimensional correlation of molecules along the director, $\hat{n}$, thus leading to the existence of strings of molecules or fibres in the nematics. This type of nematic is called fibre-type nematic. Figure 1.1 shows the schematic diagram of molecular arrangement in nematics having three different types of short range order. In addition to this, biaxial nematic liquid crystals have also been reported in certain polymeric liquid crystals [34a] and lyotropic systems [34b].

1.2.1a Cholesteric or chiral nematic phase

Cholesteric liquid crystals have a two dimensional nematic structure comprising of optically active molecules. There is no long range order in the centre of mass of the molecules and the molecules are parallel to a preferred direction $\hat{n}$, which has a helical symmetry. The pitch of the helix is temperature and concentration dependent. No substance has been found to exhibit both nematic and cholesteric phases, though cholesteric can undergo transition to nematic phase under the action of external electric and magnetic fields. Addition of a small amount of cholesteric compound to a nematic substance causes it to exhibit cholesteric phase. The cholesteric phase is thus a variation of the nematic phase and may be called chiral nematic (N^*) phase [35-37].

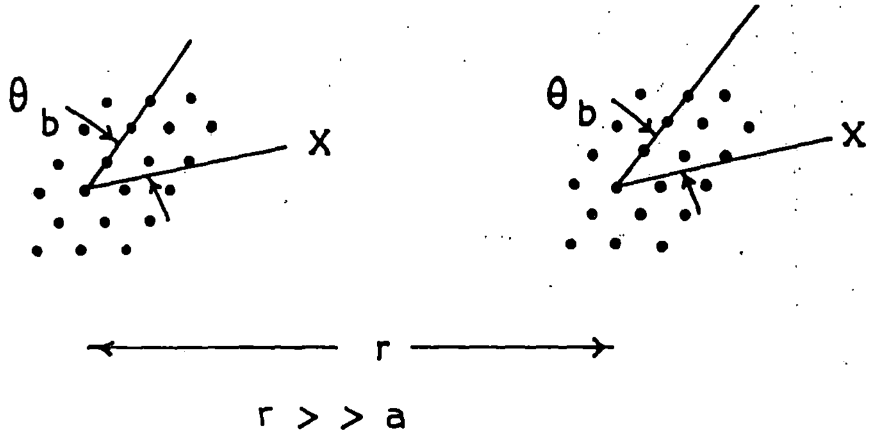
1.2.2 Smectic mesophases

Smectic liquid crystals characteristically exhibit the presence of equidistant molecular layers. Within the layers the molecular centres lie in a single plane, while their long axes are either perpendicular or tilted relative to this plane. In both cases the arrangement of the centres of the molecules within each layer correspond to a two dimensional liquid (the presence of short range order and absence of long range order). The smectic liquid crystals are generally more viscous than nematics. The interlayer attractions are weaker than the lateral forces between the molecules and the layers can slide over each other, thus showing fluid behaviour. In some smectic phases, a periodicity characteristic of a two - dimensional solid is observed in the positioning of the centres of the molecules within each layer, while the molecular long axes remain either perpendicular or inclined to the plane of the layer. Different types of thermotropic smectic phases have been identified [38-47], which are designated as follows [48]

$$S_A, S_B, S_C, S_F, S_G, S_H, S_I, S_J, S_L, \ldots\ldots$$

In addition to orientational and translational order, smectic liquid crystals also exhibit another type of order known as "bond orientational order" which can be seen in the following way. Let there be a fictitious bond between a molecule and its nearest neighbour. Then, if the orientation of this bond (i.e. the bond angle θ_b, as shown in Figure 1.2) with respect to some axis, X, chosen within the smectic layer, remains constant over distances, r, very much greater than the inter moleculer distance, a, as well as the in-plane positional correlation length ξ, then the phase is said to posses long range bond orientational order (BOO). Smectic liquid crystals having long range BOO in addition to long range moleculer orientational

Figure 1·2 BOND ORIENTATIONAL ORDER



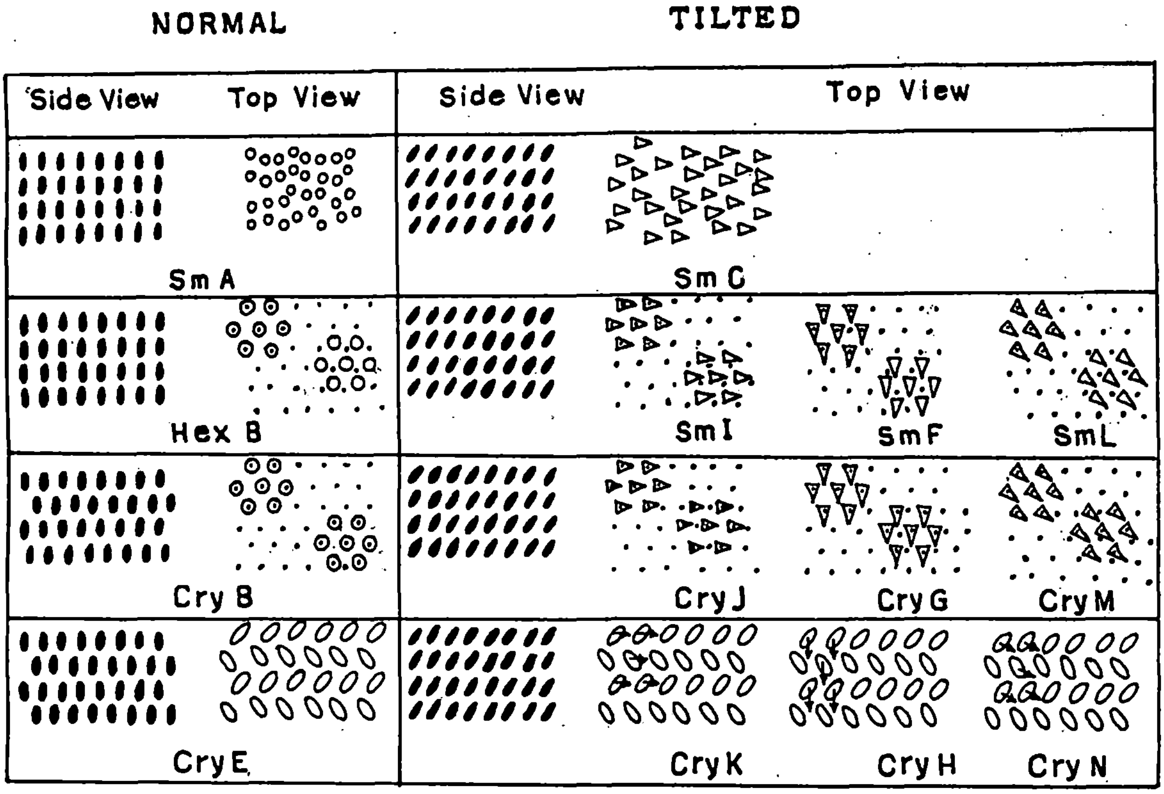


Figure 1.3. Schematic illustration of the moleculer order in various liquid crystal phases with a layer structure. The triangles represent molecular tilt direction and small dots represent two dimensional hexagonal lattices.

order within the layer, and long range positional order within as well as normal to the layer are reclassified as the so called "crystal" phases viz. Cry B, Cry G, Cry J, Cry E, Cry H etc. [19]. The so called "true" smectics on the other hand are charectarised by different degrees of ordering ranging from short range order (SRO), quasi long range order (QLRO) to long range order (LRO). A schematic illustration of molecular order in various smectic liquid crystals is shown in Figure 1.3 [48a]. Since the present work is mostly concerned with S_A, S_B and S_C phases only these phases will be discussed in more detail.

1.2.2a Smectic A phase

In smectic A phase, the preferred direction of the long molecular axes is perpendicular to the plane in which the centres of mass of the molecules are principally situated. There is a long-range translational order in the positioning of the smectic layers, but within each layer the distribution of the molecular centres is random [41,49,50], with only a short range order typical of liquids. The smectic A molecules can rotate about the long axis sweeping out a volume which is cylindrical in shape. Due to this infinite fold rotational symmetry about an axis parallel to the direction normal to the layer, smectic A liquid crystals at thermal equilibrium are uniaxial systems [51] with the optic axis perpendicular to the plane of the layer. Recent studies [52-58] have shown that the smectic A phase can be further subdivided into several distinct phases such as monolayer smectic A_1, bilayer smectic A_2, partially bilayer smectic A_d, and smectic antiphase $\tilde{A}$. Details regarding this polymorphism can be found in many recent publications [59-67].

1.2.2b Smectic C phase

The smectic C phase is very similar to the smectic A phase with one dimentional density wave of orientationally ordered molecules. However, the average orientation direction, $\hat{n}$, of the molecules which form the liquid crystal is tilted at an angle θ_t(say), with respect to the layer normal (Figure 1.4a). The layer spacing of the smectic C phase is less than that of the corresponding A phase due to this tilt. The tilt angle in the smectic C phase may be constant or temperature dependent [59]. The medium is biaxial since the director fluctuations in the n-z plane are different in magnitude from those in an orthogonal plane containing $\hat{n}$. A quadrupolar charge distribution in the molecules helps in formation of smectic C phase. A two dimensional model to demonstrate this effect is shown in Figure 1.4b where it is seen that the intermolecular electrostatic interaction is repulsive when the molecules are oriented in the direction of the layer normal (lower part of Figure 1.4b) and can be reduced by a tilted arrangement (upper part of Figure 1.4b). Again, packing considerations of the hydrocarbon chains of the molecules exhibiting this mesophase is such that, a tilted arrangement of the molecules within the layer is energetically more favourable.

1.2.2c Smectic B phase

Smectic B liquid crystals also have layered structure with the molecular long axes arranged perpendicular to the layer normal. However, the constituent molecules of the phase are packed in a hexagonal array in the plane of the layers, representing two - dimensional crystals. On the basis of x-ray

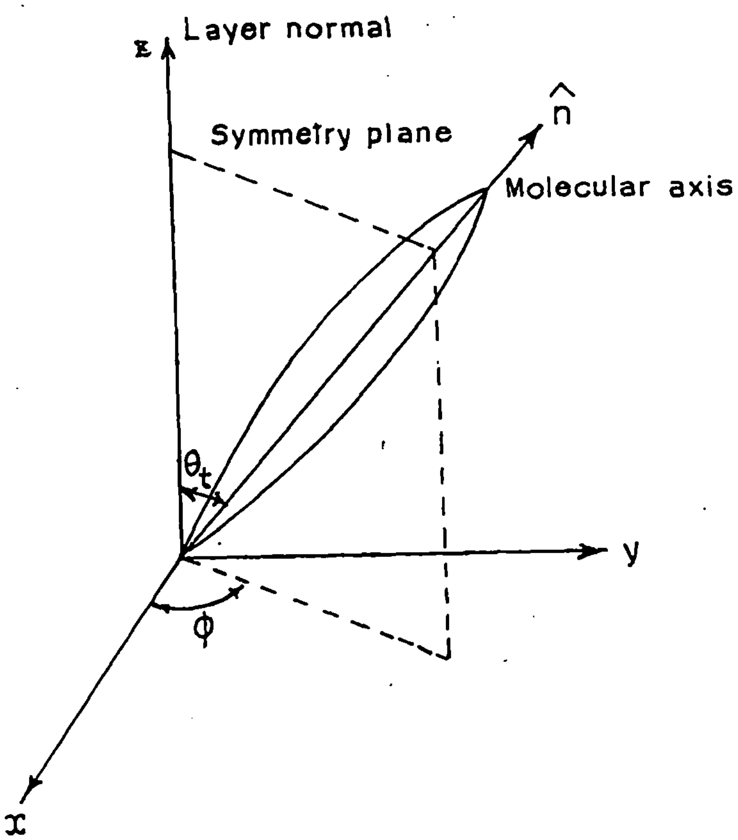


Figure 1.4a. Orientation of a molecule within the smectic C layer, showing the tilt angle θ_t with respect to the layer normal.

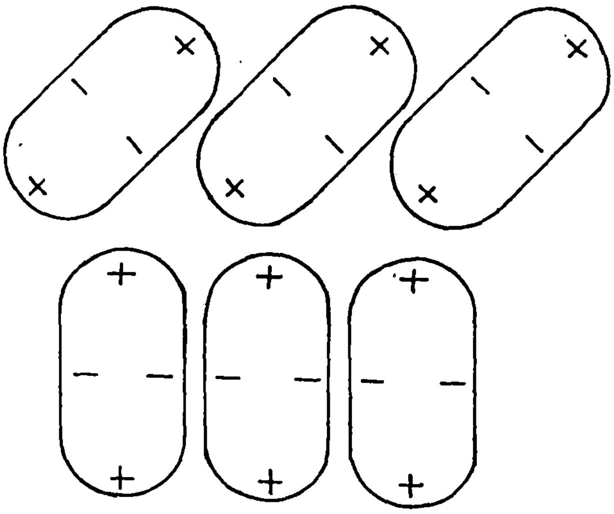


Figure 1.4b. A two dimensional model to demonstrate the quadrupolar origin of tilt in the smectic C phase[23].

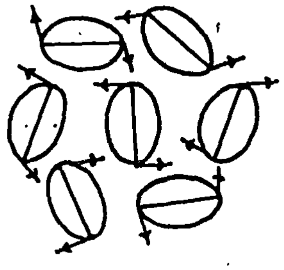


Figure 1.5. Schematic diagram of a cluster of smectic B molecules leading to a co-ordinated rotational motion within the hexagonal net.

[60] and electron diffraction [61] experiments done on bulk aligned samples as well as on thin films, the traditional smectic B phase has been further reclassified into crystal B phase and hexatic B phase [48b]. The hexatic B phase has also a layer structure with the long axis of molecule (molecular director) parallel to the layer normal. The centre of mass of the molecules exhibit a three - dimensional long range bond orientational order but only a short-range translational order. The crystal B phase, however, has long range inter- and intra layer translational order and long range bond orientational order as well. The Crystal B phase is still considered liquid crystal because of the weak coupling between the smectic layers. Hence, they exhibit shear and flow properties under stress. The Mössbauer spectra of this phase is also inconsistent with that of solid.

Due to the hexagonal arrangement of the molecules within the layers of the smectic B phase, a highly co-ordinated or synchronised rotational motion of the molecules exists [62-64], such that the edge of one molecule is presented to the side of a neighbouring molecule (Figure 1.5). Due to this hindered rotation, the smectic B phase may show optical biaxiality. In the present dissertation an attempt has been made to study the effect of this biaxiality in the smectic B phase of a liquid crystalline compound [65].

The layers of the hexagonal smectic B phase are so stacked so as to give a number of possible variations in packing arrangement between correlated layers, e.g., bilayer (ABAB.... packing), trilayer (ABCABC.... packing), random (ABCBCA....) or (rarely) correlated monolayer (AA....) structures. The stacking may change with temperature in the smectic B phase for the same compound. No change in enthalpy or texture accompany the changes in the staking type.

1.3 New liquid crystalline phases

1.3a Discotic phases

A fundamentally new mesophase, unlike the previously mentioned ones was reported in 1977 by Chandrasekhar et al [66]. The molecules of the phase are disc-like in appearance and are stacked like coins to form a new class of liquid crystals, known as discotic liquid crystals. The structure of the mesophase may be classified broadly into three types, the columnar (of which several variants have been identified) the nematic and the lamellar. Previously, very similar disc-like mesogens have been identified in petrolium and coal tar [67,68]. In recent years, significant amount of research have been performed with discotic liquid crystals [69-73].

1.3b Blue phase

The existence of this phase has been observed in a very small temperature range ($\approx 0.1^{\circ}C$) between the cholesteric and isotropic phase. Compounds exhibiting "blue" phase have a short pitch (< 7000 Å) and can display upto the 3 different variety of blue phases [74]. The structures of these blue phases are not very clear, they exhibit cubic symmetry and have a structure closely related to the cholesteric phase. The structures are explained in terms of defects in the cubic array. Blue phases do not possess double refraction, but show optical activity and selective reflection of circularly polarised light.

1.3c Chiral tilted smectic phases

Chiral smectic liquid crystals represent a class of materials which exhibit phases with a dipolar ordering i.e. they can form ferroelectric (FE), ferrielectric (FI) and antiferroelectric (AF) phases [75]. In these phases the molecules are tilted from the smectic layer normal. Due to the tilt the rotation of molecules about their long axes is not isotropic, resulting in a non-compensated macroscopic component of the molecular dipole-moment. This component lies in the smectic layer oriented perpendicularly to the tilt direction, parallel to a local polar two fold axes [76]. The ferroelectric smectic C^* phase is analogous in structure to the smectic C phase except that the molecules possesses chirality, resulting in a spontaneous "ferroelectric polarization". The chiral interactions lead to a twisted structure and consequently the polarization also has a helical arrangement too. In fact, all tilted smectic phases have equivalent ferroelectric smectic phases (smectic F^*, smectic I^*, smectic J^*, smectic G^*, smectic K^*, smectic H^*) where the constituent molecules are chiral. While the FI phase has the local dipole moments partially compensated, it is supposed that in AF phase the molecules in the neighbouring smectic layers are tilted to the opposite direction, as a result of which the opposite dipole-moments in the next layers cancels to zero. Recently, both antiferroelectric [75a] and ferrielectric [75b] smectic phases have been observed in a substance MHPOBC. Ferroelectric liquid crystals are very important for fast switching electrooptical display devices.

1.3d Polymer dispersed liquid crystals

This new class of liquid crystals generally consists of micron size droplets of low molecular weight nematic liquid crystals dispersed in a polymer binder. The nematic droplets scatter light causing a white opaque appearence in PDLC films. Application of appropriate voltage causes the nematic droplets to align in such a way that their refractive indices nearly matches that of the polymer causing transparency. They are widely used in displays, switchable windows and other light shutter devices [77-79].

1.3e Injected smectic phase

Injected smectic phases are formed in binary mixtures whose components show only nematic phases in their pure states [80-81]. One of components of the mixture characteristically have a strong terminal polar group while the other have non-polar terminal group [82-97]. Dipole-induced dipole interactions evidently play a major part in this phase stabilization. Injected smectic phase has also been observed in mixtures of other types of molecules [98-100]. Quantitative understanding of the formation of this phase is difficult as it would require potential dependent attractive and repulsive interactions for both the components. However, a model for the induced smectic phase has been discussed by de Jeu et al [101].

1.3f Re-entrant phase

Normally liquid crystals on heating give rise to a series of mesophases charecterised by increasing disorder with respect to orientational, positional and translational ordering. However, in contrary to this, in certain cases the less ordered phase reappears at a lower temperature than the more ordered phase. This phenomenon is known as re - entrant polymorphism, first discovered by Cladis etal [102] in 1975. This phase has been observed in mixtures [102-103] as well as in single compounds at high pressure [104-105] or at atmospheric pressure [106-113]. Re-entrant smectic phase have also been reported in terminal polar compounds. The mechanism of the formation of the re-entrant nematic phase at lower temperature has been explained by Cladis [114-116]. Based on the molecular point of view, Chandrasekhar [117] has reviewed and discussed qualitatively the re-entrant phenomenon.

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