CHAPTER I

Introduction

Liquid crystals represent states of matter that are intermediate between the crystalline solid and the amorphous liquid.[1] A substance in this state is strongly anisotropic in some of its properties and yet exhibits a certain degree of fluidity. The transition to these mesomorphic states may be brought about by purely thermal processes (thermotropic mesomorphism) or by the action of solvents (lyotropic mesomorphism). Since the studies described in this thesis deal with only thermotropic liquid crystals, we shall give in the following a very brief description of the thermotropic liquid crystals and their broad structural characteristics.

1.1 Classification of thermotropic liquid crystals

Thermotropic liquid crystals are classified broadly into three types: nematic, cholesteric and smectic.

1.1.1 Nematic

The nematic liquid crystal has a long range orientational order of the molecules, but no long range translational order (Fig. 1.1a). The rod like molecules are oriented, on an average, along a preferred direction called director denoted by a unit vector $\vec{n}$ ($\vec{n}$ and -$\vec{n}$ are equivalent). The preferred direction usually varies continuously from point to point in the medium, but a well aligned sample is optically uniaxial (positive) and strongly birefringent. (Biaxial nematic phases have been discovered only very recently.[2])

1.1.2 Cholesteric

The cholesteric mesophase is also a nematic type of liquid crystal except that it is composed of optically active molecules. As a consequence the structure acquires a spontaneous twist axis about an axis normal to the director (Fig. 1.1b). The spiral structure imparts certain unique optical properties to this phase like selective reflection of circularly polarized light, very high optical rotatory power, etc. Certain compounds showing the cholesteric phase exhibit other mesophases called the Blue Phases[3] between the cholesteric and isotropic phases.

1.1.3 Smectic

Smectic liquid crystals have stratified (layered) structures; in addition to the orientational order there is a translational order as well. Depending on the order within the layer and the extent of interlayer correlation, smectics can be classified into different groups,[4] the simplest of which is the smectic A (SmA) phase.

Smectic A

In this phase the molecules are arranged in layers with their long molecular axis, on an average, parallel to the layer normal but there are no interlayer correlations (Fig. 1.1c). Thus the SmA phase can be looked upon as an orientationally ordered

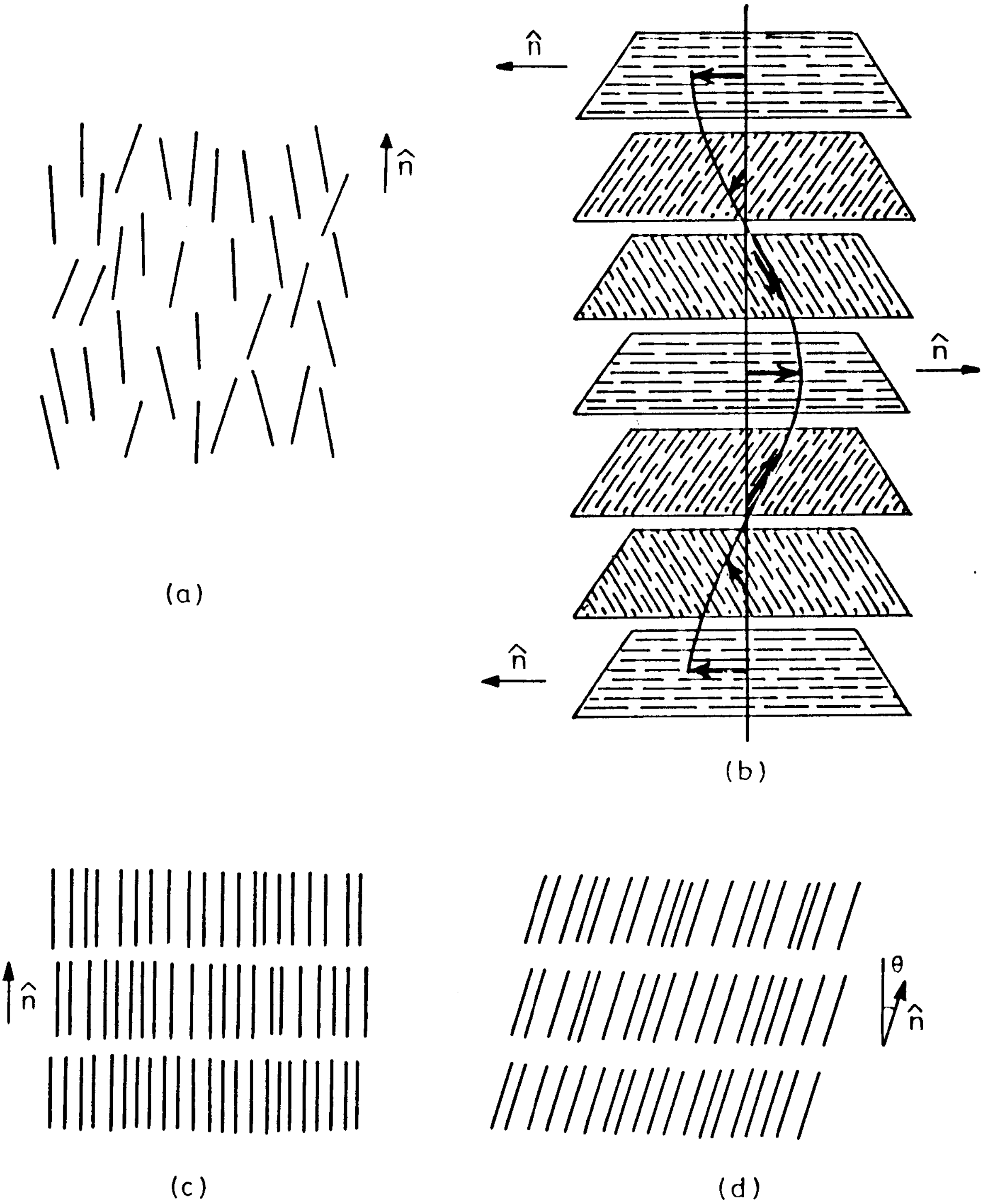

Fig.1.1. Molecular arrangement in (a) nematic, (b) cholesteric, (c) smectic A, and (d) smectic C mesophases. $\vec{n}$ denotes the director.

fluid with a one-dimensional mass density wave parallel to the director.

Smectic C

The smectic C (SmC) phase is similar to the SmA phase except that the director in each layer is tilted with respect to the layer normal (Fig. 1.1d).

There are other higher order smectic phases, some of which are discussed in Chapter V.

1.2 Ferroelectricity

Origin of Ferroelectricity in Liquid Crystals

Based on the following symmetry arguments Meyer reasoned that SmC phase of chiral liquid crystals should be ferroelectric and demonstrated the effect in a compound known, for short, as DOBAMBC.[5]

1.2.1 Symmetry reasons leading to ferroelectricity

Since the director $\vec{n}$ is apolar in liquid crystals (except under very special circumstances[6]) we need to consider only the possibility of spontaneous polarisation in a direction normal to the local director axis. Nematic and SmA phases have cylindrical symmetry about the director axis; thus ordering of the molecules in a plane perpendicular to the director does not take place, i.e., $P_x = P_y = 0$ in figure 1.2a. In the SmC phase the molecules are tilted and the elements of its monoclinic symmetry are a two fold axis (C_2) parallel to the layer (along y-axis), a mirror plane m perpendicular to the two fold axis, and a centre of inversion 'i' (see Fig.1.2b). The presence of the mirror plane destroys any spontaneous polarisation P_s along the two fold

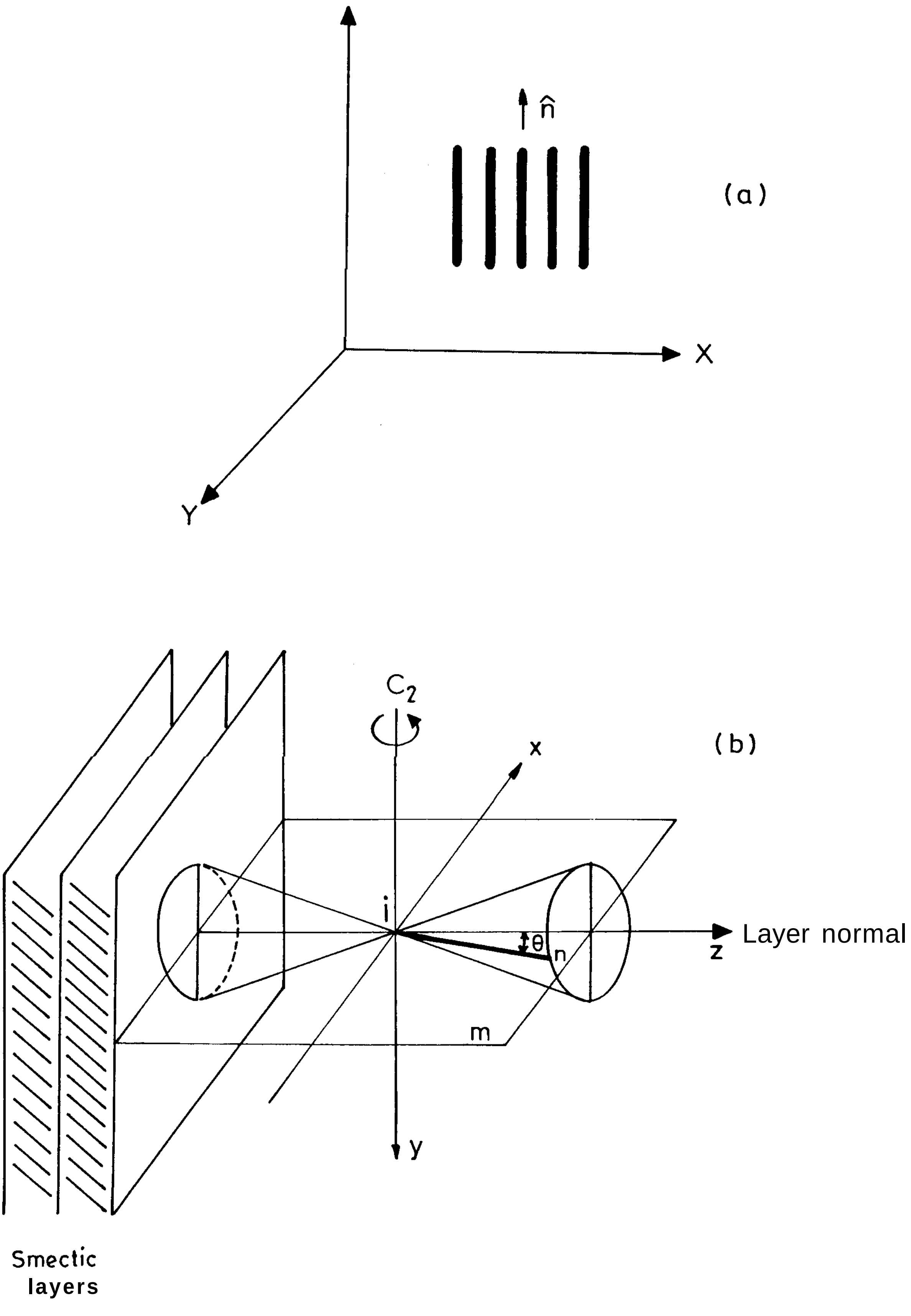

Fig.1.2. Symmetry elements in (a) smectic A and (b) smectic C phases.

axis. If the molecules are chiral, i.e., optically active, then the mirror plane and the centre of inversion are absent; and the remaining two-fold axis C_2 allows the existence of P_s parallel to it. Hence, the SmC* phase exhibited by chiral substances is ferroelectric. But the presence of chirality makes the azimuthal direction of tilt to precess around the layer normal on going from one layer to the next giving rise to a helicoidal structure of macroscopic dimensions ($\sim \mu m$).[7,8] Thus the spontaneous polarization of each layer also precesses around the layer normal averaging out to zero in the undisturbed state (see Fig. 1.3a). The helical structure can be unwound by the application of an external force, e.g., electric field. The resulting uniform state (Fig. 1.3b) shows a non-zero value of P_s, whose magnitude goes to zero in the SmA phase. Figure 1.4 is a typical plot of P_s vs. reduced temperature.

Here one should note an essential feature of ferroelectric SmC* phase. The ferroelectric-paraelectric, i.e, SmC* - SmA transition is driven by the intermolecular forces producing the tilt and not by the ferroelectric coupling,[9] i.e., tilt is the primary order parameter and P_s plays the role of the secondary order parameter. This is confirmed by the fact that the A-C* transition temperature of the chiral and racemic versions are almost the same. Thus ferroelectric liquid crystals (FLC) belong to a class of ferroelectrics known as *improper ferroelectrics.*[10]

1.2.2 Properties of FLCs

We shall first summarize some of the important properties of FLCs, since they will be helpful in understanding the new results reported in this thesis.

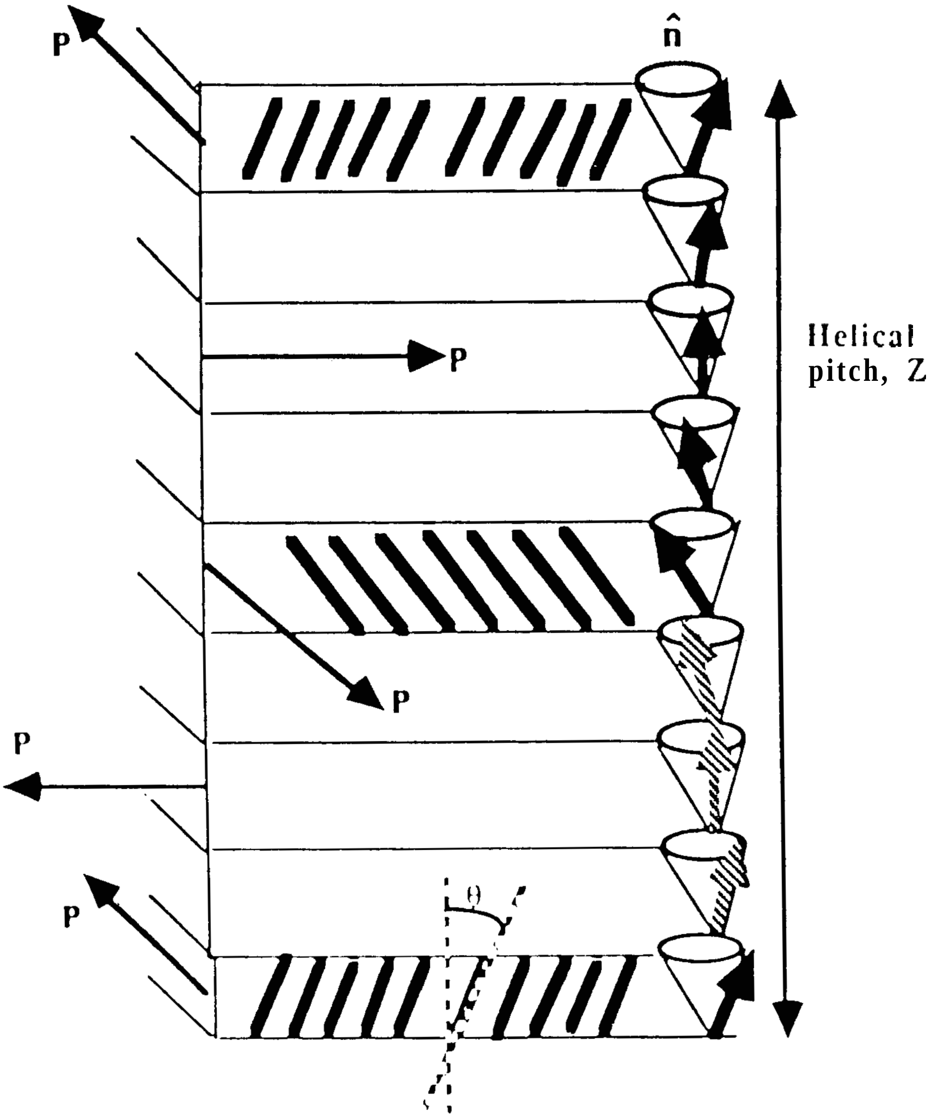

Fig.1.3a. Twisted smectic C* structure.

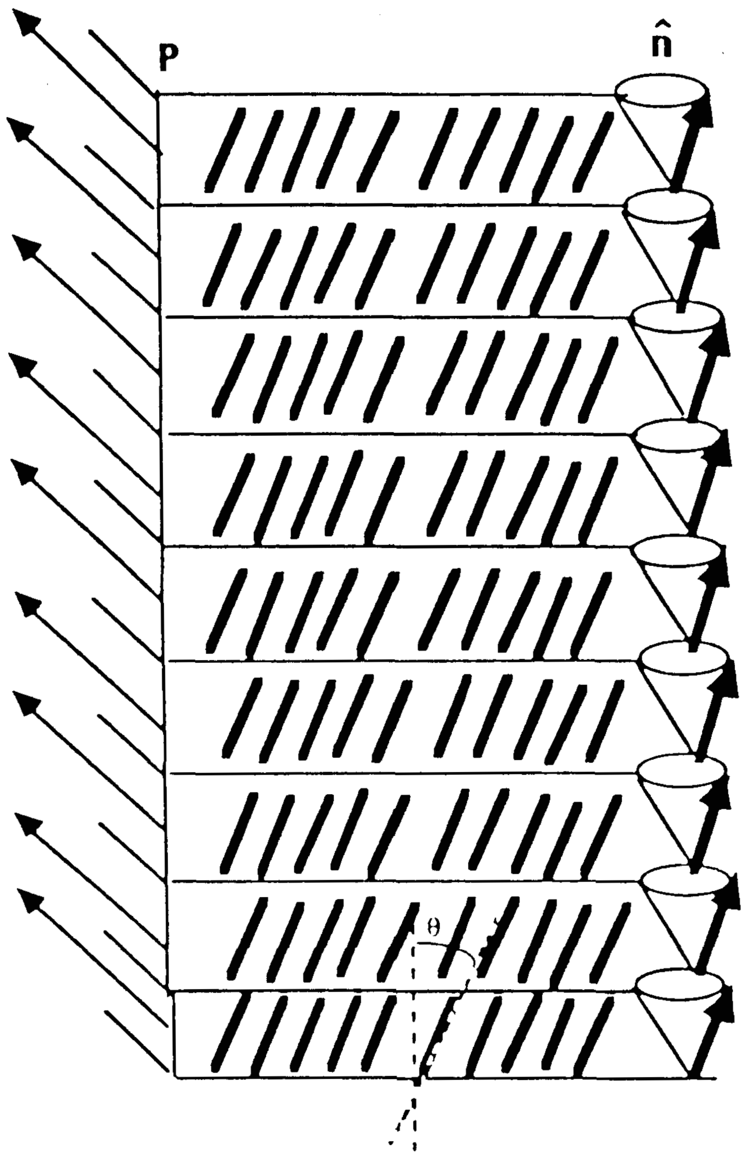

Fig.1.3b. Unwound smectic C* structure.

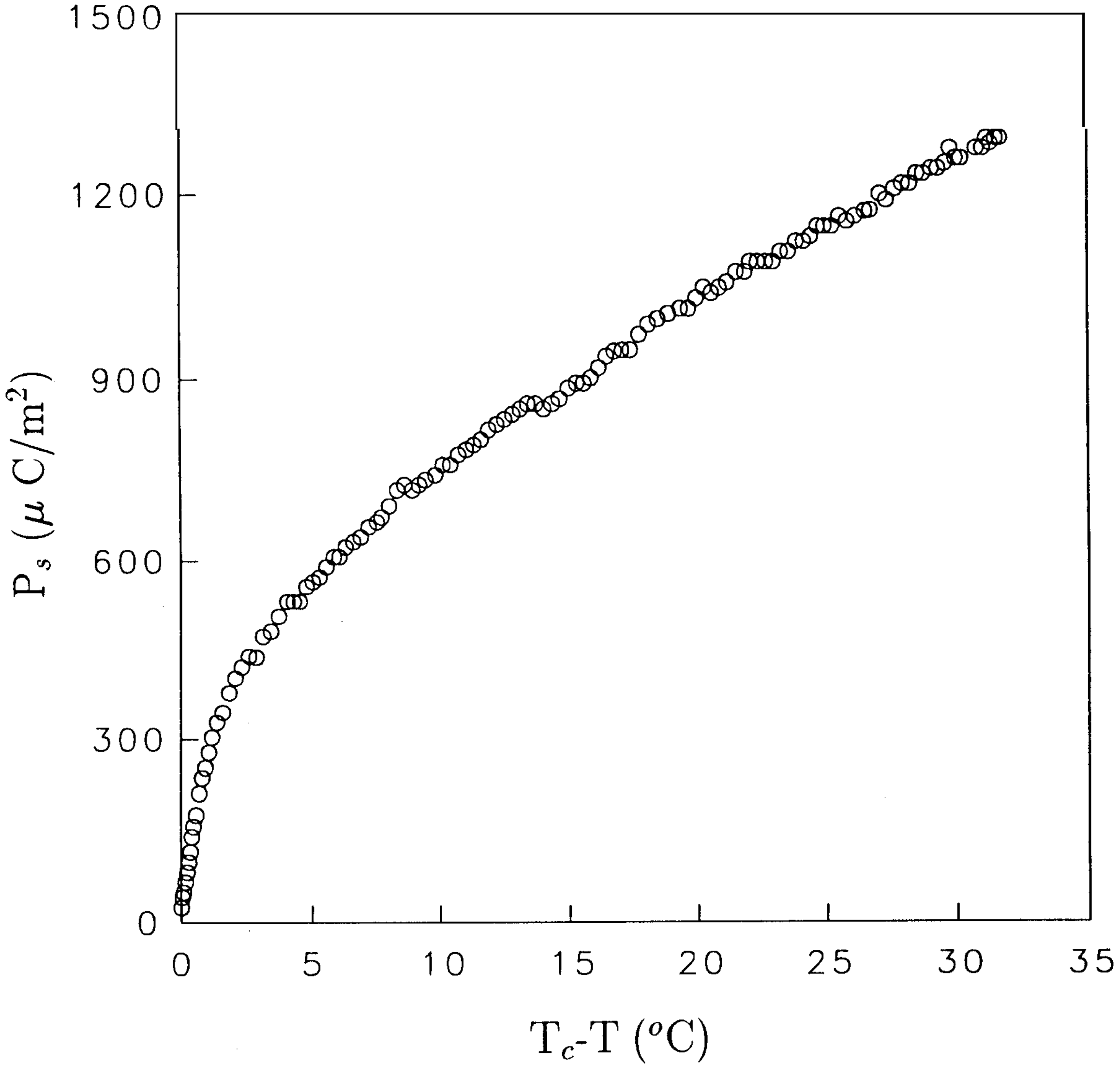

Fig.1.4. Typical plot of P_s vs. (T_c - T) for the compound D_{12} (see § *2.2)*.

Helix and the unwinding field

As mentioned earlier, in the C* phase the precession of the director around the layer normal gives rise to a helical structure. There are two kinds of molecular interactions involved in forming the helix.[9] First, as in a cholesteric, there is a spontaneous twist due to the chirality. Second, there is a spontaneous bending due to the polar symmetry of the structure (see Fig.1.5). Either of these effects by itself could create a helix as the ground state of the system. The helix can be unwound either by surface interaction or by the application of a strong electric or magnetic field. The field necessary to unwind the helix is known as the *critical* unwinding field. For obvious reasons, the magnitude of this is important while selecting materials for applications.

Electroclinic effect

This phenomenon bears a similarity to the piezoelectric effect in solid ferroelectrics, but it is called the electroclinic effect because the fluid nature of the liquid crystalline phase does not allow the static shear strain associated with piezoelectricity.

Origin of the electroclinic effect: Consider a SmA phase composed of chiral molecules. Now if an electric field is applied in a direction parallel to the layer and normal to the director, the transverse dipoles of the molecules tend to align in the direction of the field producing a non-zero average dipole moment in that direction. This in turn induces a tilt of the molecule in a plane perpendicular to the induced dipole moment. This phenomenon of inducing tilt by the application of an electric field is called the electroclinic effect.[11] In the low field limit the induced tilt is directly proportional to the applied field. A change in the orientation of the director changes the direction of the optic axis thus resulting in a linear electrooptic response. The

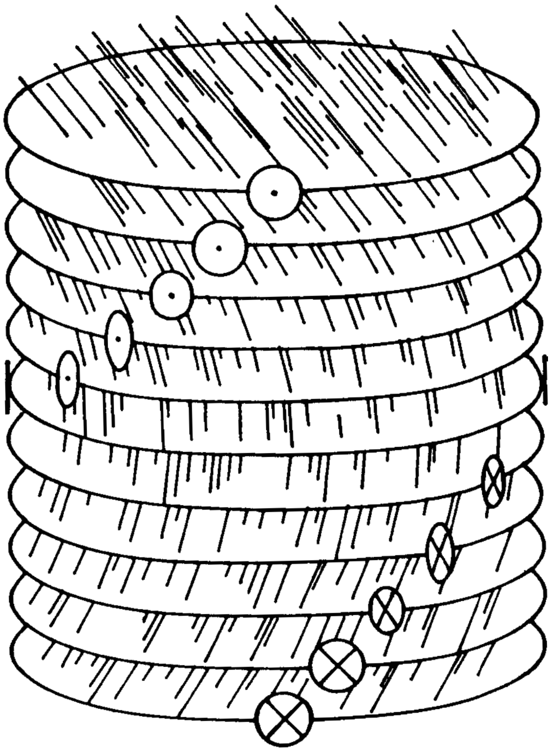

Fig.1.5. Twist and bend of the director in smectic C* phase. (After Escher, Ref. 8).

effect can be employed for making optical modulators and other devices.

Dielectric Properties

The ferroelectric nature of chiral smectics is clearly revealed in the dielectric properties. Figure 1.6 is a typical plot of the static transverse dielectric constant $\epsilon_\perp$ as a function of temperature. The frequency dependent complex dielectric constant of these substances exhibits two important relaxation modes, viz., soft mode (SM) and the Goldstone mode (GM) in the low frequency regime, besides, of course, the high frequency polarisation modes.[12-15] These two low frequency director relaxation modes are related to the two components - the amplitude and the phase - of the tilt order parameter.

Soft mode: Near the **A-C*** transition in the A phase the molecules are susceptible to tilt fluctuations whose frequency decreases (softens) on approaching the transition. In analogy with the transverse optical phonon mode in ferroelectric solids, this mode is called the soft mode.[16] This mode can be studied by dielectric measurements.

Goldstone mode: The change in the symmetry from D_∞ to C_2 across the A-C* transition can be viewed as a continuous breaking of the symmetry group. In such cases, according to the Goldstone theorem[17] a symmetry recovering mode called the Goldstone mode will appear in the low temperature phase. Since the presence of the helix in the C* phase recovers the uniaxial symmetry of the A phase, the Goldstone mode is associated with distortions of the helix and is also referred to as the phason mode. Because of the macroscopic nature of the helix the relaxation frequency of the GM is small ($\simeq 10^2 - 10^3 Hz$). For the same reason the strength of the GM is very large. Studies of GM relaxation have been made more interesting by the fact that

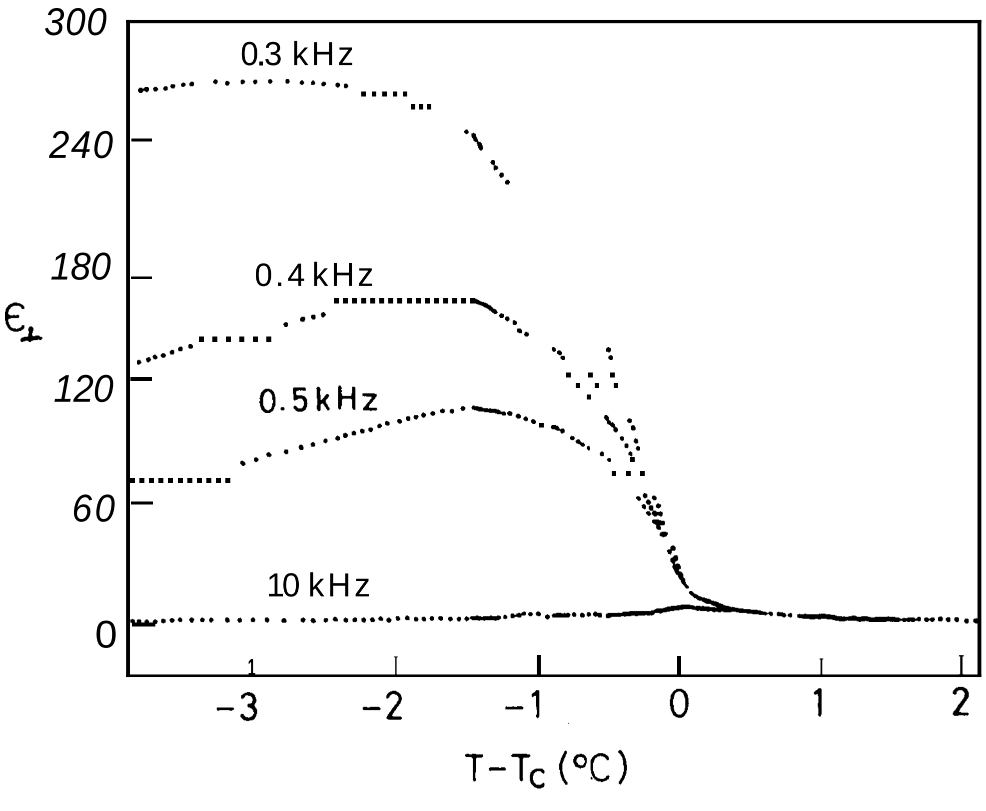

Fig.1.6. Typical plot of $\epsilon_\perp$ vs. temperature for a ferroelectric liquid crystal C_{10} (see § 2.2).

owing to the presence of the helix the C* phase is in principle an incommensurate (IC) system (the smectic layer thickness is incommensurate with the periodicity of the helix). Although the theory of IC systems[18] predicts the existence of gapless phason mode, frozen impurities and other complications had prevented observation of such a phenomena in other condensed matter systems. Light scattering study in the C* phase have demonstrated that such an effect indeed exists.[19]

Rotational viscosities in the smectic C* phase

Due to the linear coupling between P_s and the applied field E, FLCs are now finding application as a fast electrooptic switch. One of the important material properties which controls the speed of electrooptic switching is the rotational viscosity γ_ϕ associated with the motion around the smectic C cone.[20] Thus a study of the rotational viscosities in the SmC* phase is of great interest.

From classical mechanics it is known that the rotational viscosity is a **3** $\times$ **3** tensor $\bar{\gamma}$ which relates the viscous torque Γ and the angular velocity $\dot{\alpha}$ as

$$\Gamma = \bar{\gamma}\dot{\alpha} \tag{1.1}$$

The diagonal components of $\bar{\gamma}$ can be obtained in the manner elucidated by Escher et.al.[21]. One of the principal axis of $\bar{\gamma}$ lies in the layer plane and normal to the tilt direction. The corresponding viscosity is γ_θ, the viscosity associated with the tilt fluctuations. A second principal axis of $\bar{\gamma}$ is parallel to the director and the corresponding viscosity $\gamma_{||}$, is the viscosity associated with the rotation of the molecule about its long molecular axis. The remaining principal axis must lie in the layer plane and along the $\vec{c}$ director, the corresponding viscosity is denoted as γ_G as it is related to the Goldstone mode. These three viscosities are schematically shown in Fig. 1.7. It has become a common practice to use one more viscosity coefficient γ_ϕ,

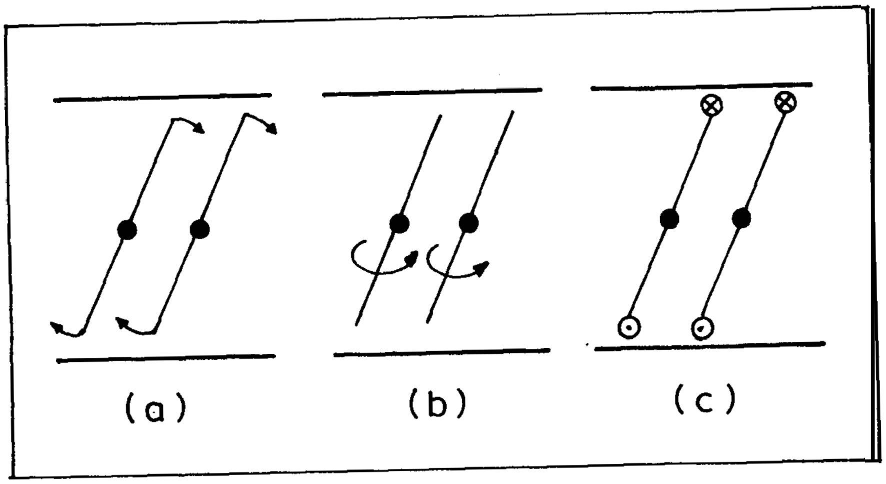
(a) (b) (c)

Fig.1.7. The three principal axes of $\bar{\gamma}$. Smectic layer normal and tilt direction lie in the paper plane. (a) γ_θ, (h) $\gamma_{||}$ and (c) γ_G from Ref.21.

which corresponds to the rotation of the $\vec{c}$ director about the layer normal (which is similar to the rotation of the molecules in the SmC cone). However, it has been shown that γ_G and γ_ϕ are related as,

$$\gamma_\phi = \gamma_G / sin^2\theta \tag{1.2}$$

It has been argued that γ_G is a more fundamental property.[22]

With this background about the properties of FLCs, we now present an overview of the contents of this thesis.

1.3 Measurement of Spontaneous Polarization

Experiments have shown that the electrooptic response of FLC depends primarily on the magnitudes of P_s and γ_ϕ.[23] Since the response time is inversely related to the magnitude of P_s, increasing P_s improves the switching speed. Furthermore, due to the linear coupling between P_s and E, an increase of P_s helps in reducing the operating voltage. Both these considerations are relevant to the design of electrooptic devices. To synthesize compounds with a large P_s it is useful to know the relationship between the magnitude of P_s and the molecular structure.[7,24–26] Although a number of studies[27–30] of P_s measurements have been reported, not much is known about the dependence of the magnitude of P_s on the structural details of the molecule. Chapter II describes results of systematic measurements of P_s on a number of compounds belonging to four structurally related, homologues series, derived from *trans-p-n*-alkoxycinnamic acid synthesised in our laboratory.[31] A detailed description of the apparatus constructed to measure P_s is given, and the procedure employed for automated data collection at close intervals of temperature is described. The studies bring out the influence of several factors such as chain length, the number of chiral centres, spacer groups between the chiral centre and the core etc., on the magnitude of P_s. Finally some of the features observed are discussed in terms of a microscopic model.[32]

1.4 Dielectric studies in the vicinity of the A-C* transition

As mentioned earlier, dielectric spectroscopy in the low frequency regime shows in the vicinity of the **A-C*** transition, two relaxation modes, viz., the soft mode (SM) and the Goldstone mode (GM), which may be related to the two components of the order parameter. The soft mode is due to the amplitude fluctuations of the tilt and is observable very close to the transition in both the SmA and SmC* phases. The symmetry recovering Goldstone mode owes its existence to the presence of the phase (azimuthal) fluctuations of the tilt and can be observed only in the SmC* phase. These modes can also be studied by light scattering method.[19] Many of the earlier experiments on these two modes were done on compounds with low value of P_s. Chapter III describes investigations of the effect of the magnitude of P_s on SM and GM. For this purpose high precision dielectric measurements near the Sm A-Sm **C*** transition have been carried out on three compounds exhibiting high, medium and low value of P_s. The capacitance and dielectric loss measurements were made using a versatile high precision impedance analyser (HP 4192A) covering a frequency range of 5Hz to 13MHz. The temperature of the sample was maintained to a constancy of ± 5mK during any dispersion measurement. The data acquisition and analysis were handled by a microcomputer. The details of the experimental set up and analysis procedure are described. Under usual circumstances it is difficult to separate out SM from GM in the Sm C* phase because the GM strength is very large compared to SM. However careful measurements have enabled us to separate out the GM and SM relaxations in the Sm C* phase, even in the absence of a bias field, over a larger temperature range than in any other previous report.[33] The results are discussed in the light of the predictions of the generalized thermodynamical model[34,35] and a good agreement has been obtained.

It is known that in liquid crystals the length of the alkyl chain plays a significant role in determining the behaviour of different physical properties. However, there are hardly any studies on the effect of alkyl chain length on the dielectric properties of FLCs. Chapter III also describes systematic measurements of soft mode and Goldstone mode carried out as a function of chain length. The results show that the Goldstone mode relaxation frequency f_G shows an odd-even kind of behaviour with changing chain length, while $\Delta\epsilon_s, \Delta\epsilon_G$ and soft mode relaxation frequency f_s vary monotonically. Analysis of the data using the equations given by the generalized mean field model[36] allows determination of two important Landau coefficients a and C. The details of this analysis procedure are also given in this chapter.

1.5 Measurement of Rotational Viscosity

It has been repeatedly mentioned that one of the basic parameters involved in determining the performance of a FLC device is the rotational viscosity γ_ϕ. Moreover, for understanding the dynamics of the ferroelectric switching, γ_ϕ is an important parameter. So far, several methods[21,37,38] have been developed to measure this parameter, but a detailed comparison of the values obtained by different techniques does not seem to have been made. Also, there are hardly any systematic studies of this viscosity as a function of chain length of the molecule.[38,39] Keeping this in view, γ_ϕ was measured by employing different techniques. Chapter IV describes in detail the different methods, along with the underlying principles, and experimental set-up adapted to measure γ_ϕ. The four different techniques employed are the transient current response to (a) an applied square wave,[40] (b) an applied triangular wave,[41] and (c) to an applied sine wave[21] fields and (d) the transient optical response to an applied square wave field.[23b] The results show that γ_ϕ values obtained from the four different techniques are in remarkably good agreement with each other over a wide range of temperatures. These studies also show that there is a systematic variation in the magnitude of γ_ϕ with chain length. Except very close to the transition, the thermal variation of γ_ϕ shows an Arrhenius type of behaviour and the activation energy appears to be the same for all the homologues.

Measurements of γ_s, the soft mode rotational viscosity associated with the tilt amplitude fluctuation, are also described in this chapter. Unlike γ_ϕ there are very few studies[12,37] of γ_s. In most of the earlier studies γ_s was determined by the pyroelectric technique. We have adopted the dielectric dispersion method for the determination of γ_s. The measurements show that γ_s also shows, except in the immediate vicinity of the transition, an arrhenius variation with temperature. The effect of chain length on the thermal variation of γ_s is also described in this chapter.

1.6 Experimental studies in the vicinity of C*-I* transition

The results described hitherto are on the least ordered of the tilted chiral smectic phases, viz., the smectic C* phase. Other tilted, but more ordered chiral smectic phases, e.g., Smectic I*. Smectic F*, etc., also exhibit ferroelectric properties. Unlike the C* phase, only a few reports[42-44] on the physical properties, in particular the electric properties, of these higher order FLCs exist. In Chapter V results of the measurements of tilt angle θ, P_s, transverse static dielectric constant $\epsilon_\perp$ and rotational viscosity γ_ϕ on two compounds exhibiting C* and SmI* phases are presented. A brief introduction to the higher order tilted smectic phases is also given in this chapter. All these higher order tilted smectic phases have, along with the lamellar order, an additional ordering called "bond orientational order" (BOO).[45] Since tilt breaks the axial symmetry, the C* phase also possesses BOO albeit of small magnitude.[46] I* and F* phases have enhanced BOO as compared to the C* phase. Owing to the symmetry being the same, the transition between C* and I* can only be first order; otherwise the I* phase evolves continuously from the C* phase without a transition.[47] The two compounds on which measurements were done are such that in one compound there is a first order C*-I* transition and in the other I* evolves continuously from C* phase. Thus these studies bring out the effect of the nature of the transition on the magnitude and thermal variation of P_s, θ and $\epsilon_\perp$. Further, these measurements allow for comparing the nature of the $P_s - \theta$ coupling in the C* and I* phases.

1.7 High Pressure Studies of Ferroelectric liquid crystals

The application of pressure on liquid crystals has led to the observation of many interesting phenomena like reentrant phases,[48] multicritical points,[49] etc., some of which can also be obtained by using binary mixtures. But the main advantage of high pressure studies is that these effects can be observed even in single component systems. Not many systematic studies of the effect of pressure on the properties of ferroelectric liquid crystals have been made.[50-53] In particular there is no report on the effect of pressure on the rotational viscosity γ_ϕ and the coercive field E_c.

A study of these effects is of interest because pressure increases the intermolecular interactions and causes an increase in the viscosity which in turn biases the free rotation of the molecule and hence affects the value of P_s.

In Chapter VI the studies of some physical properties of FLC as a function of pressure are presented. Details of the high pressure optical set-up,[54,55] previously used mainly for studying P-T diagrams, and the modifications made to it for carrying electrical measurements, are described. The measurements done on three compounds, having different values of P_s, show that the value of P_s at a constant relative temperature with reference to A-C* boundary is observed to decrease with increasing pressure. The exponent governing the temperature variation of P_s increases with increasing pressure. The coercive field E_c which is a measure of the critical unwinding field E_h increases with pressure. The results of what are probably the first experimental studies of γ_ϕ as a function of pressure are also presented. It is found that γ_ϕ increases linearly with pressure.

The nature of the A-C* transition depends on the range[56] of the A phase and/or the strength of the transverse dipole moment[57] of the constituent molecule. The P-T data show that the range of A phase increases with pressure. In order to see whether the transverse dipole moment of the molecule plays a significant role in determining the nature of the A-C* transition under pressure, we have measured the transverse dielectric constant $\epsilon_\perp$ which gives a measure of the transverse dipole moment. It is seen that $\epsilon_\perp$ decreases drastically with pressure. A reason for this may be that the GM frequency f_G decreases with pressure. The γ_ϕ measurements corroborate this view. To study the effect of pressure on GM as well as SM, $\epsilon_\perp$ was measured as a function of pressure at five selected frequencies. The results show that both f_G and f_s decrease with pressure. Analysis of the data in the A phase enable the determination of the parameters controlling SM relaxation.

Most of the results described in this thesis have been published in the following papers.

1. Spontaneous polarisation and rotational viscosity measurements on ferroelectric liquid crystals derived from trans-p-n-alkoxy-cinnamic acids (in collaboration with S.K.Prasad, S.Chandrasekhar, B.Shivkumar and B.K.Sadashiva), Mol. Cryst. Liquid. Cryst., **182B**, 313 (1990).

2. Ferroelectric liquid crystals derived from trans-p-n-alkoxy-cinnamic acids (in collaboration with B.Shivkumar, B.K.Sadashiva and S.Krishna Prasad), Ferroelectrics, 114, 273 (1991).

3. Dielectric studies of Goldstone mode and softmode in the vicinity of the A - C* transition (in collaboration with S.Krishna Prasad, B.Shivkumar and B.K.Sadashiva), J. de. Physique II, **1,** 171 (1991).

4. Dielectric studies near the A - C* transition in a homologues series (in collaboration with S.Krishna Prasad, V.N.Raja, S.Chandrasekhar and B.Shivkumar), Ferroelectrics (in Press).

5. Measurement of rotational viscosities in the Smectic C* phase (in collaboration with S.Krishna Prasad, V.N.Raja and B.Shivkumar), Ferroelectrics,**121**, 319 (1991).

6. Comparison of different techniques of determining rotational viscosity in the Smectic C* phase. Proceedings of the Solid State Physics Symposium 1991, B.H.U., Varanasi, Vol. 34C, p.359

7. Experimental studies in the vicinity of the C* - I* transition (in collaboration with V.N.Raja, S.Krishna Prasad and D.S.Shankar Rao) Ferroelectrics,

121 , 343 (1991).

8. High pressure studies on Ferroelectric liquid crystals (in collaboration with S.Krishna I'rasad, V.N.Raja, S.Chandrasekhar and B.Shivkumar) Ferroelectrics, 121, 307 (1991).

9. Rotational viscosity in the ferroelectric C* phase - A high pressure study (in collaboration with S.Krishna Prasad, V.N.Raja, S.Chandrasekhar and B.Shivkumar) Proceedings of the XIII AIRAPT International Conference on High Pressure Science and Technology, October 1991, Bangalore (Oxford and IBH Publishing House, 1992), p.526.

10. Effect of pressure on the spontaneous polarization, the critical unwinding field and the transverse dielectric constant in ferroelectric liquid crystals (in collaboration with S.Krishna Prasad, V.N.Raja, S.Chandrasekhar and B.Shivkumar) Proceedings of the XIII AIRAPT International Conference on High Pressure Science and Technology, October 1991, Bangalore (Oxford and IBI-I Publishing House, 1992), p.529.

11. Dielectric studies of ferroelectric liquid crystals at high pressure (in collaboration with S.K.Prasad and S.Chandrasekhar), Presented at the 14th Int.Liquid Crystal Conf. Pisa (June 21-26, 1992) and submitted for publication in the conference proceedings.

12. Comparative study of a ferroelectric monomer and its copolymer (in collaboration with S.Krishna I'rasad, D.S Shankar Rao, V.N.Raja, S.Chandrasekhar, J.Naciri and R.Shashidhar), Presented at the 14th Int. Liquid Crystal Conf., Pisa June 1'392. However this work has not been included in this thesis.

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