

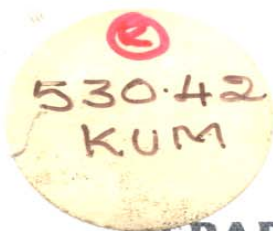
**STUDIES ON OPTICAL AND DIELECTRIC  
PROPERTIES OF SOME LIQUID CRYSTALLINE  
AND POLYMERIC MATERIALS**

*Thesis submitted to the University of Mysore  
for the degree of*

**Doctor of Philosophy**  
in  
Physics

*By*

**S.R. KUMARASWAMY**



**DEPARTMENT OF STUDIES IN PHYSICS**  
UNIVERSITY OF MYSORE  
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*Dedicated to my  
Parents and teachers*

***Declaration***

*I hereby declare that the thesis was composed by me independently and that it has not previously formed the basis for the award of any degree, diploma, associate ship, fellowship or other similar title.*

Date: 25-04-1996

Place: Mysore

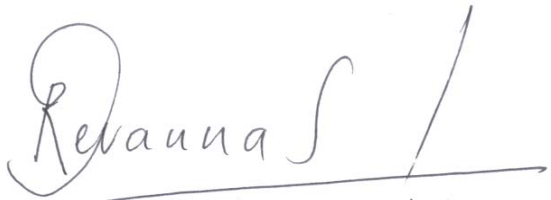
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### ***Certificate***

*I certify that this thesis entitled "Studies on Optical and Dielectric Properties of some Liquid crystalline and Polymeric Materials" has been composed by Mr.S.R.Kumaraswamy Based on investigations carried out by him in the development of Studies in Physics, University of Mysore, Manasagangotri, Mysore, under my supervision. The subject matter of this thesis has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or other similar title.*

Date: 25.04.1996

Place: Mysore



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## Preface

It is well known that compounds which exhibit liquid crystalline phases are generally organic in nature. In such compounds the molecules are arranged more or less parallel to one another in the liquid crystalline phase and their long range orientational order is the cause of their anisotropic physical properties which are strongly temperature dependent. Depending on the arrangement of molecules liquid crystalline materials are broadly classified as: (a) nematic (b) cholesteric and (c) smectic. The nematic liquid crystals are characterised by a statistical order in the molecular orientation such that the long axes of the molecules are aligned approximately about a preferred direction referred to as the 'director' denoted by a unit vector  $n^{\wedge}$ , (Figure P1). In the cholesteric liquid crystals the molecules are arranged in layers with the long axes of the molecules being oriented about a particular preferred direction in the plane of each layer, but this preferred direction rotates smoothly as one progresses from layer to layer along the normal to the layers, (Figure P2). The measured distance along the twist axis (normal to the layer) over which the direction of the alignment of the molecules rotates through a full cycle is called the pitch  $p$  of the cholesteric medium. The pitch of the cholesteric is highly sensitive to temperature. In the smectic liquid crystals the molecules are arranged in layers with their long axes parallel to one another. All smectic liquid crystals have stratified structure and also the different types of molecular arrangements are possible within each stratification. These smectic phases are divided into smectic A, smectic B, smectic C, smectic D etc. In smectic A, the molecules are perpendicular to the layer plane while in smectic C they are tilted (Figures P3 and P4). In both these cases the centres of the molecules within each layer are arranged in a liquid-like manner. Some of the smectic modifications have ordering within a layer also, e.g., smectic B, smectic H, etc.

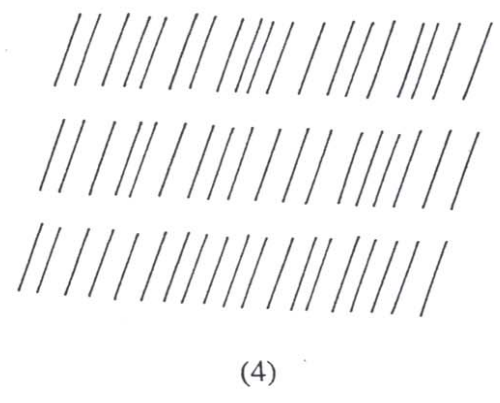
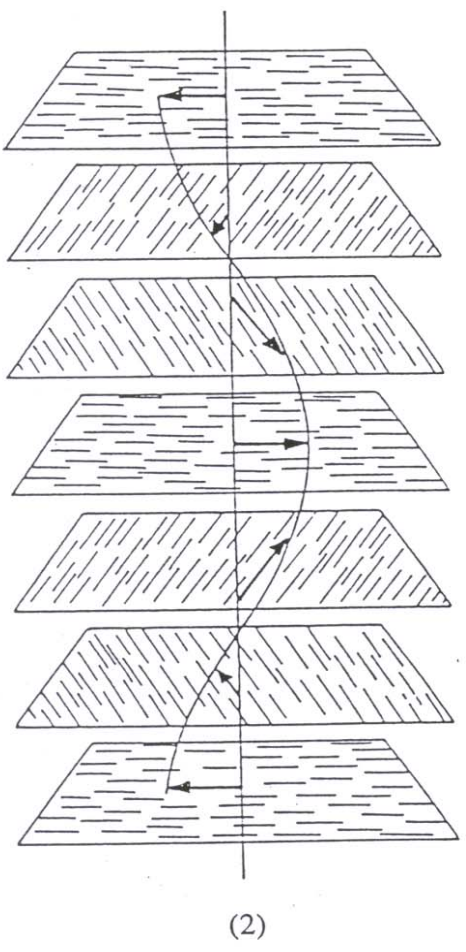
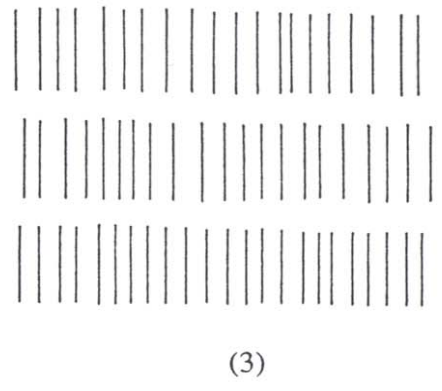
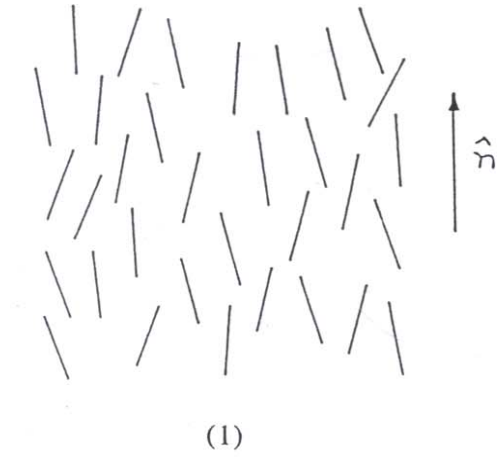


Figure P: Molecular arrangement in (1) nematic (2) cholesteric (3) smectic A, and (4) smectic C mesophases.  $\hat{n}$  denotes the director of the nematic medium.

Liquid crystal materials have been widely used in a variety of optical display devices. The operation of such devices depends upon the modulation of ambient light by a liquid crystal layer defonned by an electric field. For the theoretical understanding of this electrooptic effect and its applications it is necessary to have a detailed knowledge on the optical properties such as birefringence, orientational order, molecular polarizability etc., and also on the dielectric properties of liquid crystals. The dielectric constant measurements also give an insight into the interactions responsible for the anisotropic alignment about the preferred direction, and local molecular structure in the liquid crystalline phase. Further, nematic, cholesteric and the mixtures of nematic and cholesteric liquid crystals are generally used in optical display devices. In view of these, the author has carried out studies on :

1. The birefringence, polarizabilities, orientational order parameters, Lorentz field factors, static dielectric constants, dielectric dispersion and electrical conductivities of some nematogenic compounds.
2. The optical textures, helical pitch, light scattering, optical diffraction, birefringence and local order parameter in the case of cholesteryl do-decyl carbonate.
3. Effect of dc electric field on the optical textures exhibited by the mixtures of cholesteryl do-decyl carbonate and EBBA, a nematic compound.

Some polymer samples exhibit ringed spherulite texture similar to that of cholesteric liquid crystals. With a view to understand the molecular ordering in the spherulites of polymers the author has also carried out optical studies on spherulites exhibited by polyethylene.

Determination of molecular polarizabilities, orientational order parameter and the anisotropy of Lorentz field factors require a knowledge of the local electric field. It is in this context an introduction to the topics of local electric field and the anisotropic polarization in birefringent media is given in Chapter 1.

Chapter 2 deals with the experimental determination of refractive indices and densities of the following four nematogenic compounds:

- (i) 4'-(hexyloxy)-4-biphenylcarbonitrile (6 OCB).
- (ii) 4'-(heptyloxy)-4-biphenylcarbonitrile (7 OCB).
- (iii) 4-isothiocyanatophenyl - 4 - pentylbicyclo (2,2,2) octane - 1- carboxylate (IPBOC).
- (iv) 1-(trans-4-hexylcyclohexyl)-4-isothiocyanatobenzene (6 CHBT).

The hollow prism and the capillary tube techniques are respectively being used in determining the refractive indices and densities. Refractive indices are measured for various wavelengths and at different temperatures in the nematic and isotropic phases of these compounds.

Using the experimentally obtained data on refractive index and density, and employing Neugebauer's anisotropic local field model [1] the effective molecular polarizabilities, anisotropy of Lorentz field factors and orientational order parameters have been determined at various temperatures in the nematic phase of all the four compounds. It is well noticed from the calculations that if the alkyloxy group is substituted by alkyl group, and a phenyl group is replaced by a cyclohexyl ring the net molecular polarizability is lowered by about  $10 \text{ \AA}^3$ . All the compounds possess more or less the same temperature co-efficient of the orientational order parameter and the anisotropy of Lorentz field factors. The details of all the calculations and the results obtained are discussed in Chapter 3.

Chapter 4 deals with the calculation of the anisotropy of Lorentz field factors in the following two symmetric homologous series of compounds which exhibit nematic phase:

- Series I :      p, p' - di-n-alkyl azoxybenzenes  
 $C_mH_{2m+1}C_6H_4N:N(O)C_6H_4C_mH_{2m+1}$       (m = 3-7)
- Series II:      p, p' - di-n-alkyloxy azoxybenzenes  
 $C_{m-1}H_{2m-1}OC_6H_4N:N(O)C_6H_4OC_{m-1}H_{2m-1}$       (m = 4-9)

These two series of compounds are of interest (i) to study the effect of change in the length of the molecule on the observed anisotropy of Lorentz field factors, and (ii) to examine the change in anisotropy of Lorentz field factors when an alkyl group is replaced by alkyloxy group. Using the data on index and density reported by de Jeu et al., [2,3] and employing Neugebauer relations the author has estimated the Lorentz field factors of all the compounds of series I and series II. Following are the conclusions which emerge from the calculations. (i) The trend in the variation of anisotropy of Lorentz field factors with the relative temperature for all the members of the series I and series II is similar. (ii) The value of the anisotropy of Lorentz field factors increases linearly with increase of the orientational order parameter, and at any given relative temperature it alternates as the number of methylene groups in the end chain is increased. (iii) The presence of C-O group on either side of the central rigid portion in series II does not affect appreciably the values of the Lorentz field factors as was observed in series I.

In Chapter 5 we present our experimental investigations on the static dielectric constants of some nematogenic compounds whose birefringence and orientational order parameters are reported in Chapters 2 and 3. The nematic liquid crystals are uniaxial and exhibit two dielectric constants, namely,  $\epsilon_{11}$  parallel to the nematic director and  $\epsilon_1$  perpendicular to the nematic director. All the nematic compounds studied here show large positive dielectric anisotropy ( $\epsilon_{11} > \epsilon_1$ ). Further, the average value of the dielectric constant in the nematic phase is less than its extrapolated isotropic value. It is evident from the dipolar theory proposed by Madhusudana and Chandrasekhar [4] that in such cases the dipole moments associated with the molecules are arranged antiparallel to one another. Using the measured values of the dielectric constants and refractive indices the effective parallel and perpendicular components of dipole moment of the nematic molecules are estimated. In each case the parallel component of the dipole moment is found to be much larger than the

perpendicular component, which agrees broadly with the present experimental observations on the dielectric anisotropy.

It is well known that the dielectric constants are frequency dependent. The dielectric constant  $\epsilon_1$  exhibits a relaxation in the microwave frequency region only, while  $\epsilon_{11}$  shows a relaxation in the lower frequency region also. The author has measured the dispersion (in the frequency range 1kHz to 10 MHz) of  $\epsilon_{11}$  of three nematogenic compounds listed in Chapter 2. The relaxation frequencies  $f_R$  are determined for all the compounds at different temperatures in their nematic phase from Cole-Cole plots and also from loss curves [5,6]. The value of  $f_R$  increases with temperature. The activation energy is estimated from the values of  $f_R$  and employing Arrhenius plot [7] of  $\ln f_R$  against  $1/T$ . Using the data on the relaxation frequencies we have also estimated the nematic potentials [8] of the molecules of the above nematic systems, based on Maier and Saupe mean field theory [9]. The variation of estimated nematic potential with reduced temperature follows a curve which is similar to that of orientational order parameter. All these results are reported in Chapter 6.

In the nematic phase the electrical conductivity (arises due to ionic impurities) is usually greater in a direction parallel to the director ( $\sigma_{11}$ ) than in the direction perpendicular [10] to the director ( $\sigma_{\perp}$ ). The values of these two components increase with the increase of temperature in a nematic liquid crystal without any cybotactic structure. In other words the ratio  $\sigma_R (= \sigma_{11} / \sigma_{\perp})$  is always greater than unity and is known to depend only on the orientational order parameter, decreasing monotonically with temperature, the rate of decrease increasing as nematic-isotropic transition is approached [11,12]. The author has examined all these features by carrying out measurements on the principal conductivities of all the nematogenic compounds whose dielectric relaxation is reported in the previous Chapter and the results are presented in Chapter 7.

Studies on the optical birefringence and the characteristic optical textures exhibited by cholesteryl do-decyl carbonate are discussed in Chapter 8. One of the interesting textures observed in this sample is the ringed spherulite texture. The observed ring spacing in the spherulites is found to increase with the increase of crystallization temperature. Light scattering and optical diffraction studies have been carried out using the optical textures exhibited by the sample. The local order parameter corresponding to the untwisted nematic structure in the cholesteric layer [13] has been estimated at various temperatures in the cholesteric phase using the measured data on refractive index and density. The author has also carried out investigations on the optical textures exhibited by the mixtures of cholesteryl do-decyl carbonate and nematic EBBA. Some of the mixtures studied here are found to exhibit very interesting optical textures viz., focal conic, striped pattern etc. The striped pattern acts as a diffraction grating giving rise to several orders of optical diffraction. The spacing of the striped pattern is found to decrease with the increase of concentration of the cholesteryl compound which is in conformity with the theory given by Arnould and Rondelez [14]. Further, when the sample exhibiting the striped pattern is subjected to a dc electric field an interesting texture consisting of spiral pattern is observed. This arises as a consequence of the gradient flexo electric splay twist-bend deformation of point irregularities formed in the electrode region [16]. All these results are also presented in Chapter 8.

Chapter 9 deals with the optical effects from spherulites of low, medium and high density polyethylene samples. As in the case of cholesteric samples some polymeric materials [16-19] also exhibit ringed spherulite textures. The orientation of the polymer molecular chain in these spherulites is perpendicular to the spherulitic radii. Using the interference experiments, the author has shown that there is a continuous and periodic variation of the refractive index of the spherulites for light polarized transverse to the radial direction. This result is in conformity with that obtained by Stein and Rhodes using low angle light scattering experiments [17]. The author has also estimated the birefringence associated with spherulites

Crystallized at room temperature. The estimated values are of the same order of magnitude as what one would expect from considerations of the anisotropy of the bond polarizabilities associated with the C-C bonds in polyethylene chain.

Some of the results presented in this thesis are reported in the following publications:

1. Anisotropy of Lorentz field factors in two symmetric homologous series: Kumaraswamy S R, Krishnegowda D, Somashekar R and Revannasiddaiah D, *Ind. J. Phys.*, **66A**, 695 (1992).
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