International Journal of Physical Sciences Vol. 1 (3), pp. 147-153, November, 2006
Available online at http://www.academicjournals.org/IJPS
ISSN 1992 - 1950 © 2006 Academic Journals

Full Length Research Paper

Dielectric, optical and thermodynamical properties of liquid crystal sample exhibiting SmA phase

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Accepted 20 November, 2006

The dielectric constant and dielectric loss with dielectric anisotropy have been measured as a function of temperature in the frequency range of 1 kHz to 10 MHz for a newly synthesized liquid crystal sample-exhibiting SmA phase. The measurement in SmA phase indicates dielectric relaxation at frequency 4.778 kHz for 80 ^{0}C. The Enthalpy of activation was found to be 14.57 Kcal/mole. The results have been explained on the basis of Maier and Meier theory. The optical anisotropy study, white light transmittance study has also been carried out on the sample. Phase transition temperature matches very well as obtained from all the above mentioned measurement techniques. Optical anisotropy data has been used to determine order parameter by Vuks approach and its variation with temperature has been discussed.

Key words: Liquid Crystals, Dielectric Properties, Refractive Indices, Optical Transmittance.

INTRODUCTION

The importance of liquid crystals lies in their extensive use in display devises, as well as many other scientific applications (Brown, 1975). However the use of liquid crystals in different devises depends upon various properties owned by them like order parameter, dielectric constant, dielectric anisotropy, birefringent behavior, optical transmittance, elastic constants etc. A particular application of liquid crystals requires a particular set of parameters of the liquid crystal in required range. Therefore characterization of any liquid crystal sample is very important and a number of researchers are studying properties of different classes of liquid crystals (Li et al. 2004, Srivastava et al., 2002)

The liquid crystals samples are characterized by their phase transition behaviour, which can be studied both by dielectric as well as optical methods. The dielectric and optical studies have been very useful as they provide impotent information regarding molecular structure, molecular dynamics, and type of molecular interactions in the sample and hence the probable phases that could be shown by the molecules of sample (Garg et al., 1985 and Smyth, 1955). There are various tools for studying phase transition in liquid crystal. Optical polarizing microscopy (OPM) is a standard tool for determining phase transitions in the liquid crystal samples (Manohar et al., 2006). Along with this method dielectric anisotropy ($\Delta\varepsilon$) and birefringence (Δn) provide useful information about the order parameter (S) and activation energies of liquid crystal sample (Chandrasekhar, 1979). Most of the physical properties of the liquid crystal emerge from the order that exist in the sample and thus followed by the order parameter (S) (Gennes, 1974), which makes order parameter so important while studying liquid crystals. Various methods have been adopted by different workers to calculate the order parameter, like Neugebaar's anisotropic field model (Srivastava et al., 2006), Vuks isotropic internal field model (Saran et al., 1982) and Saupe and Maier anisotropic model (Singh et al., 1990) etc.

The properties described above depends upon the molecular arrangement in liquid crystal sample, which

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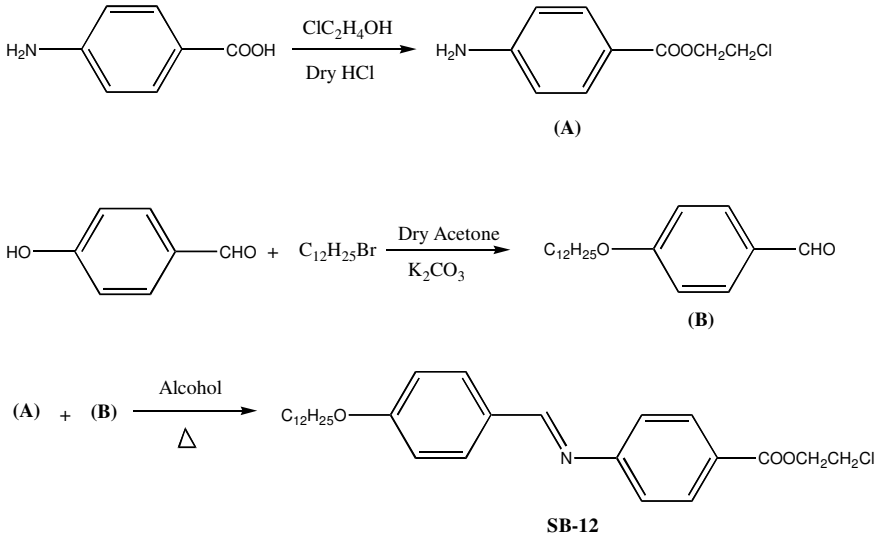

changes according to temperature. In the present paper we report studies on a newly synthesized smectic sample (**SB-12**), a thermotropic liquid crystal for its electrical and optical properties. The refractive indices and birefringence data have been used to calculate order-parameter (S), here Vuks direct extrapolation method has been used to calculate the microscopic order parameter. We have also reported the phase transition scheme for the sample **SB-12**. The components of dielectric permittivity tensor ($\varepsilon_{ll},\varepsilon_{\perp}$) measured parallel and perpendicular to the director respectively have also been reported. The data obtained from dielectric relaxation study has been used to evaluate activation energies associated with the process. The phase transition scheme has also been verified using optical transmit-tance measurement technique.

EXPERIMENTAL

Material

The synthetic route to mesogenic Schiff's base (**SB-12)**; β-chloroethyl 4(4'-n-dodecyloxybenzylidene) aminobenzoate for present investigation is illustrated in scheme 1.

The **SB-12** was prepared by condensing equimolar quantities of β-chloroethyl 4-aminobenzoate **(A)** with 4-n-dodecyloxy benzaldehyde **(B)** in boiling ethanol. The crude **SB-12** was purified by repeated crystallization using ethanol till constant transition temperatures; Cr 66°C Sm A 104°C Iso., were obtained. The structure was confirmed by elemental analysis and Infrared spectroscopy. Elemental analysis: found C 71.21, H 8.13, N 2.94; $C_{28}H_{38}NO_3Cl$ require C 71.26, H 8.06 and N 2.97 %. IR (KBr, Cm^{-1}) spectra: 2920, 2850, 1712(-COO-), 1593, 1512, 1461, 1385, 840, 771(C-Cl).

Refractive Index Measurement

Refractive index has been measured using Abbe's refractometer having an accuracy of 0.0001 in the range of 1.3 to 1.7. A polarizer has been introduced in Abbe's refractometer to block the extra-ordinary ray, which clears the contrast of the boundary line at view of refractometer. To calculate birefringence Δn following relation has been used $\Delta n = n_e - n_o$

The temperature of Abbe's refractometer is controlled by circulating heated oil using JULABO F-25, refrigerated circulator. The temperature was measured by placing a thermocouple in close vicinity of the sample with an accuracy of $\pm 0.1^0$C.

Optical Transmittance Measurement

For the optical transmittance measurement sample was filled into the standard sample holder pre-treated for planar alignment having 5μm spacer, by heating it 10^0C above the clearing point of the sample and then introducing the sample at one end of the holder it was filled in the sample holder by the capillary action and sample holder was slowly cooled up to the room temperature. Now sample holder is placed between two-crossed polarizer of polarizing microscope model CENSICO (7626) fitted with a hot stage and light intensity coming through eyepiece has been measured by light dependent resistance (LDR). The resistance value of LDR corresponding to varying light intensity due to temperature variation of the sample is proportional to the inverse of optical transmittance and has been directly measured by attached digital multimeter. The 0% and 100% optical transmittance have also been measured for empty and black ink filled sample holder to calculate the percentage optical impedance.

Dielectric Measurement

The dielectric measurements have been performed by Impedance /gain phase analyzer Hewlett-Packard (4194A). The sand-witched type of capacitor sample holder with a layer of aligner is used for dielectric measurements as described above. The dielectric measurements have been done both in perpendicular and parallel direction. The values of capacitance and dissipation factor of the sample holder with and without sample were determined. The change in capacitance value of sample holder will directly give the value of real part of permittivity of the sample, using following equa-

tion.

$$\varepsilon = \frac{\Delta C}{C_G} + 1$$

Where ΔC is the change in capacitance of the sample holder due to the presence of the sample.

ΔC = Cp –Co

Where Cp is the capacitance with sample and Co is the capacitance without sample. C_G is the geometrical capacitance of the sample holder.
The loss tangent and the dissipation factor (D) of the sample were derived from the dissipation factor and capacitance, measured for the sample holder with and without sample and is given by.

$$\tan\delta = \frac{C_p D_p - C_o D_o}{C_p - C_o}$$

Where Dp is the dissipation with sample and Do is the dissipation without sample. The loss factor is given by the following equation

$\varepsilon'' = \varepsilon' \tan\delta$

Capacitance values were read up to three places of decimal while the dissipation factors were recorded up to fourth place in the frequency range of 1 kHz to 10MHz.

THEORY

Refractive index

Vuks made a bold assumption that the internal field in a liquid crystal is the same in all directions and gave a semi-empirical equation correlating the refractive indices with the molecular polarizabilities for anisotropic materials. (Singh et al., 1990)

$$\frac{n_{e,o}^2 - 1}{\langle n^2 \rangle + 2} = \frac{4\pi}{3} N \alpha_{e,o} \quad \cdots\cdots\cdots (1)$$

Where n_e and n_o are the refractive indices for the extra ordinary and ordinary ray respectively $\alpha_{e,o}$ are the corresponding molecular polarizabilities and N is the number of molecules per unit volume, and $\langle n^2 \rangle$ is given by

$$\langle n^2 \rangle = \frac{n_e^2 + 2 n_o^2}{3} \quad \cdots\cdots\cdots (2)$$

In Eq. 1, n_e and n_o are coupled together so that the relationship between the refractive indices and the corresponding molecular polarizabilities is not clear. To reveal this relationship, we should decouple n_e from n_o by solving Eq.1. Substituting Eq. 2 to Eq. 1 and separating n_e and n_o, we obtain (Singh et al., 1990)

$$n_e = \left(1 + \frac{4\pi N \alpha_e}{1 - \frac{4\pi}{3} N\langle\alpha\rangle}\right)^{1/2} \cdots\cdots\cdots 3$$

$$n_o = \left(1 + \frac{4\pi N \alpha_o}{1 - \frac{4\pi}{3} N\langle\alpha\rangle}\right)^{1/2} \cdots\cdots\cdots 4$$

Where $\langle\alpha\rangle$ is average polarisability of the liquid crystal molecules and given by (Li et al., 2004).

$$\langle\alpha\rangle = \frac{\alpha_e + 2\alpha_o}{3}$$

When $N\langle\alpha\rangle$ is small, we can expand Eq. 2&3 into a power series. Retaining the first two terms, we get

$$n_e \cong \frac{3\sqrt{2}}{4} + \frac{\sqrt{2}\pi N\langle\alpha\rangle}{1 - \frac{4}{3}\pi N\langle\alpha\rangle} + \frac{\frac{2\sqrt{2}}{3}\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4}{3}\pi N\langle\alpha\rangle} \quad \cdots\cdots\cdots 5$$

$$n_o \cong \frac{3\sqrt{2}}{4} + \frac{\sqrt{2}\pi N\langle\alpha\rangle}{1 - \frac{4}{3}\pi N\langle\alpha\rangle} - \frac{\frac{\sqrt{2}}{3}\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4}{3}\pi N\langle\alpha\rangle} \quad \cdots\cdots\cdots 6$$

And birefringence of the LC sample is given by $\Delta n = n_e - n_o$. Now on using above equation's we have

$$\Delta n \approx \frac{\sqrt{2}\pi NS(\gamma_e - \gamma_o)}{1 - \frac{4}{3}\pi N\langle\alpha\rangle} \quad \cdots\cdots\cdots 7$$

However the average refractive index $\langle n \rangle$ of liquid crystal is defined as

$$\langle n \rangle = \frac{n_e + 2 n_o}{3} \quad \cdots\cdots\cdots 8$$

on putting the values of the n_e & n_o in above equation, we drive

$$\langle n \rangle \approx \frac{3\sqrt{2}}{4} + \frac{\sqrt{2}\pi N\langle\alpha\rangle}{1 - \frac{4}{3}\pi N\langle\alpha\rangle} \quad \cdots\cdots\cdots 9$$

On substituting Eq .7 and 8 back to eq.3 & 4 the refractive indices have the fallowing simple expression.

$$n_e = \langle n \rangle + \frac{2}{3}\Delta n \quad \cdots\cdots\cdots 10$$

$$n_o = \langle n \rangle - \frac{1}{3}\Delta n \quad \cdots\cdots\cdots 11$$

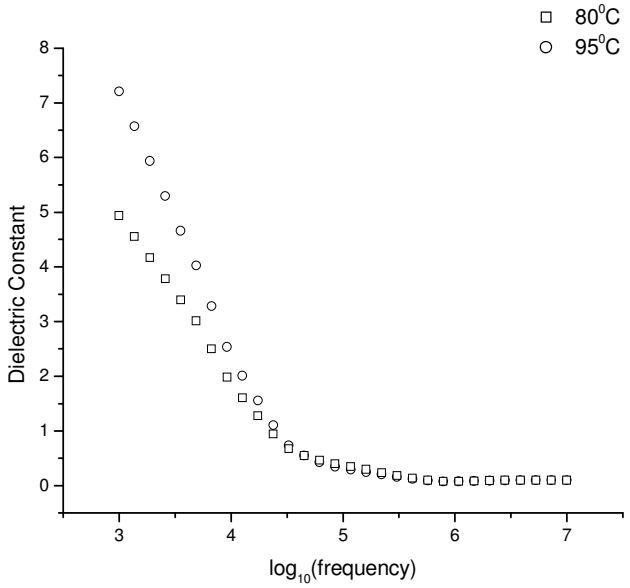

Figure 1. Variation of dielectric constant with $\log_{10}$ (frequency)

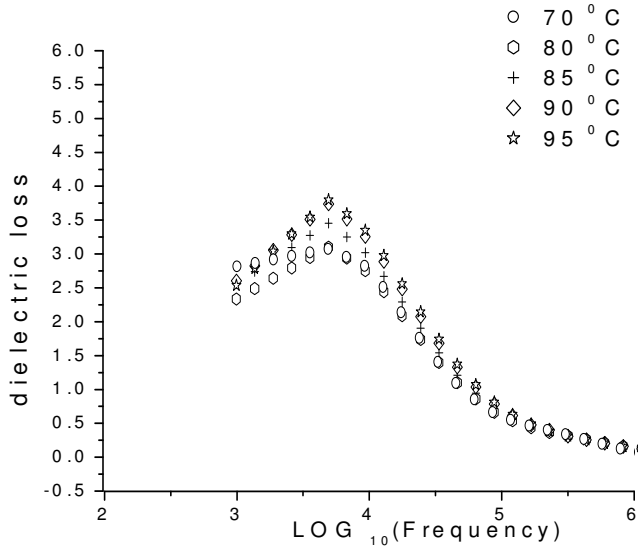

Figure 2. Variation of dielectric loss with $\log_{10}$ (frequency) at different temperatures i.e. 70°, 80°, 85°,90°& 95° C.

Order parameter (DIRECT EXTRAPOLATION METHOD)

Calculation of microscopic order parameter in the liquid crystal sample by optical birefringence is based on Vuks direct extrapolation method (Singh et al., 1990). The refractive indices n_e and n_o have been analyzed by the method of Haller and Horn.this method uses Vuks relation (Saran et al., 1982)

$$S\left(\frac{\delta\alpha}{\alpha}\right) = \frac{3(n_e^2 - n_o^2)}{(n_e^2 + 2n_o^2 - 3)} \quad \cdots\cdots\cdots\cdots \quad (6)$$

Here $\delta\alpha$ (= $\alpha_{\parallel} - \alpha_{\perp}$) is the anisotropy of polarizability and α is mean molecular polarizability.

The logarithmic of the R.H.S of above equation was plotted against log (1-T/Tc) and the straight line so obtained is extrapolated to T= 0^0K. The intercept at T= 0^0K where S= 1 led to the scaling factor $\delta\alpha/\alpha$.assuming that $\delta\alpha/\alpha$ remains fixed for all temperature. Now substituting the value of $\delta\alpha/\alpha$ in equation (6), we can obtain the value of order parameter at various temperatures.

RESULTS AND DISCUSSION

The dielectric parameters ε' & ε'' have been measured for the sample in the relaxation frequency range of 1 kHz to 10MHz for the temperature range of 38^0C to 115^0C for both parallel and perpendicular to the field. However the Figure 1-3 shows dielectric parameters in perpendicular direction only. Figure 1 and 2 represents a typical frequency dependence spectra of real and imaginary part of the dielectric permittivity measured for SB-12 in SmA phase. The dielectric permittivity is either constant or decreases as frequency increases (Urban et al., 2000 and Dhar et al., 2004)

From Figure 2 we can see that the relaxation phenomenon is taking place within the frequency range covered. The relaxation of the liquid crystal molecules has been indicated by peak of the curves, which shows that the maximum absorption of applied electromagnetic field takes place around this frequency value, which is 4.778 kHz for 80^0C.The figure shows five curves of similar nature plotted for five different temperatures in smectic phase. The only difference for these five curves is that they show peak at slightly different frequency. The peak shifts towards the higher frequency side as we increases the temperature as expected and also been reported by several workers (Dhar et al., 2004, Nagbhushan et al., 1986), the curve is also symmetrical on both the sides of the peak.

Using these plots the relaxation time and thermodynamical parameters have been determined.

Relaxation time $\tau = 1/\omega$

Where, $\omega = 2\pi f$

Thermodynamical parameters ΔF_ε, ΔG_ε and ΔS_ε are related with τ by the following equation (Schacht et al., 2000).

$$\tau = \frac{h}{kt} \exp\{\Delta F_\varepsilon / Rt\}$$

Table 1. Relaxation time (τ) and Eyring activation parameters of SB-12

Temp (^{o}k)	τ x10^5 (s)	ΔG (KJ/mol)	Δs (J/mol deg)	Δh (KJ/mole)
353	3.80	57.07		
363	3.72	58.71		
365	3.59	58.94		
367	3.49	59.19	- 0.4685	14.57
369	3.38	59.43		
371	3.28	59.68		
373	3.19	59.94		
377	2.98	60.40		
379	2.64	60.35		
381	2.55	60.58		

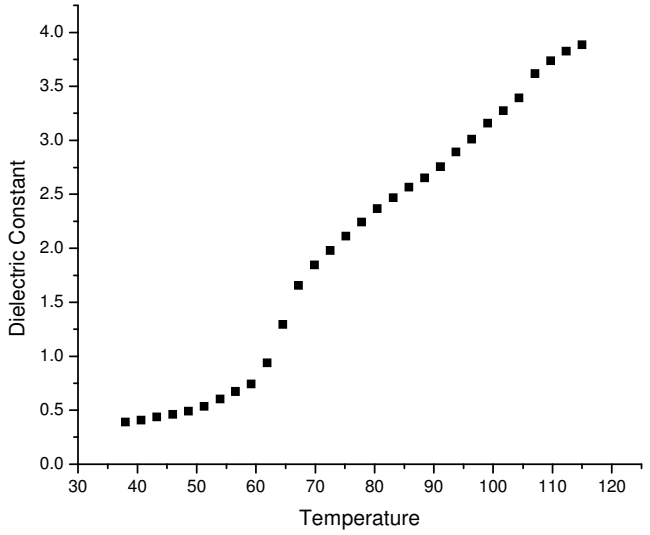

Figure 3. Variation of dielectric constant with temperature.

The value of relaxation time, ΔF_ε, ΔG_ε and ΔS_ε are given in Table.1. The value of enthalpy of activation has been found to be 14.57Kcal/mol for SmA phase.

Figure 3 shows the variation of dielectric constant with temperature at 5kHz . The two-phase transition points at 66^{0}C and104^{0}C are clear by the discontinuous change of ε′ with temperature.

In the present work we have also calculated dielectric anisotropy by using two components of ε′ i.e.$\varepsilon_\parallel$ & $\varepsilon_\perp$and variation of Δε (dielectric anisotropy) with the temperature have been shown in Figure 4. As we increase the temperature the dielectric anisotropy decreases and becomes zero at SmA to Isotropic transition temperature. This type of dielectric anisotropy with respect to temperature can be explained on the basis of Maier and Maier theory (Maier and Saupe, 1960), which gives

$$\Delta\varepsilon = \left(\frac{NFh}{\varepsilon_o}\right)\left[\Delta\alpha + \frac{F\mu^2}{2kT}\left(3\cos^2\beta - 1\right)\right]s$$

Where symbols have their usual meaning .the positive anisotropy of the sample suggested that the angle β is lesser than the 54.7^0. The Maier –Meier theory also predicts that the temperature dependence of Δε roughly follow order parameter S and the temperature factor contributes only to a limited temperature range, this is also clear from the comparison of these figures (Figures 4-6). The perpendicular component of dielectric constant increases as we increase the temperature suggesting that the molecular dipolar contribute more towards perpendicular to the director at high temperatures (Figure 3). The above natures of dielectric anisotropy also conclude that the transverse component of the dipole moment μ_t is less efficient than the longitudinal component of dipole moment μ_l.

The phase transition is indicated by discontinuities in these curves indicating that the transitions are of first order. Such type of discontinuous change has also been reported by other workers using different parameters (Arodz et al., 1989, Druon, C. and. Wacrenier J.M, 1984). It is also evident from the Figure 4 that dielectric anisotropy is high in SmA phase indicating high order parameter in the smectic phase. This fact is also supported by the high value of order parameter in SmA phase as calculated using refractometeric data.

Refractive index

The temperature variation of ordinary and extra-ordinary refractive indices (n_e, no) and the birefringence is shown in Figures 5 and 6 respectively after clearing point the birefringence becomes zero. The ordinary refractive indices (n_o) increases slightly while the extra ordinary refractive index decreases sharply with increase in temperature

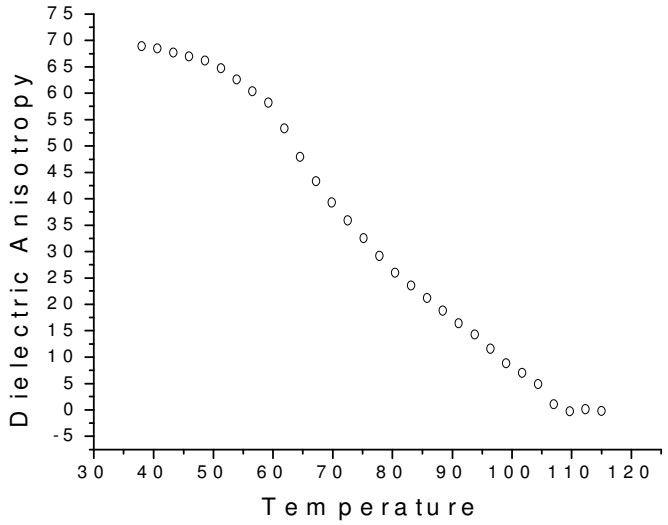

Figure 4. Variation of dielectric anisotropy with temperature.

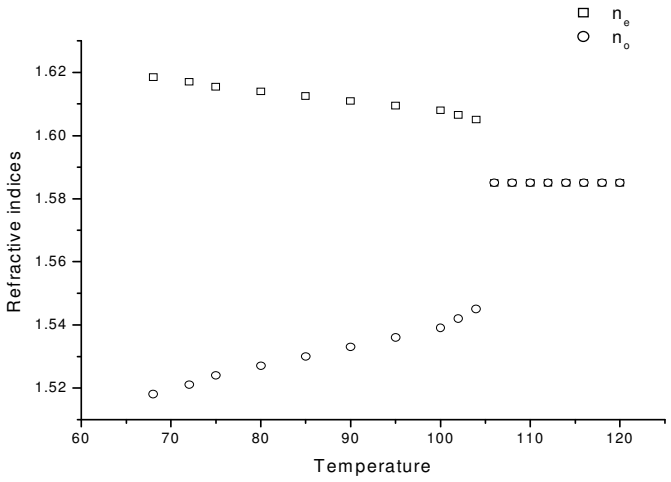

Figure 5. Variation of Refractive indices with temperature.

at the SmA to isotropic point i.e. at 104^0C refractive index values changes and becomes almost constant. It is in accordance with the results obtained by others on different samples (Rao et al., 1986 and Manohar et al., 2000). The reason for this kind of behaviour is due to birefringent nature of liquid crystal phase. As we increase the temperature, the molecular ordering decreases and this birefringent nature becomes less significant and after the isotropic temperature, the Δn vanished and the sample behave like any ordinary organic liquid. (Manohar et al., 2000).

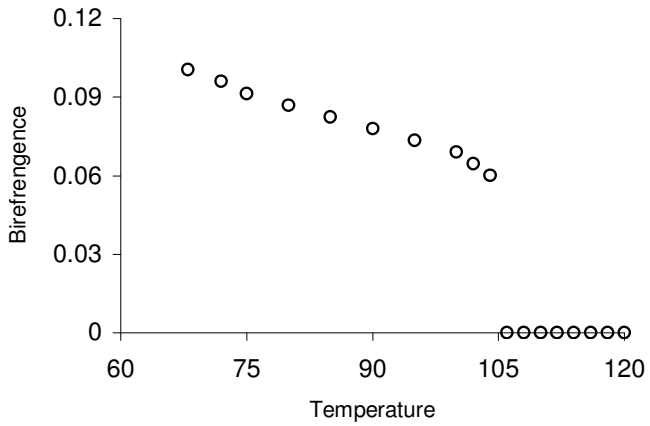

Figure 6. Variation of Birefringence with temperature.

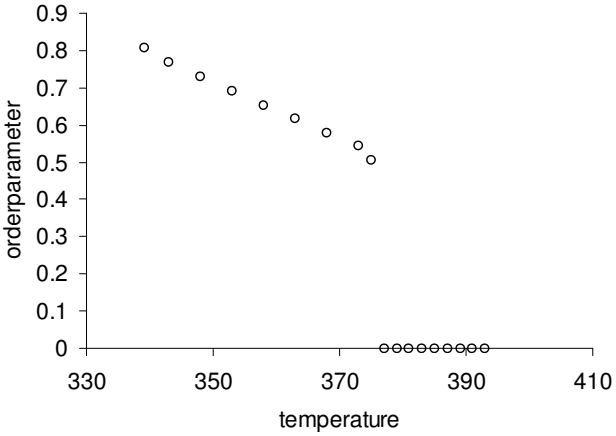

Figure 7. Variation of order parameter with Temperature.

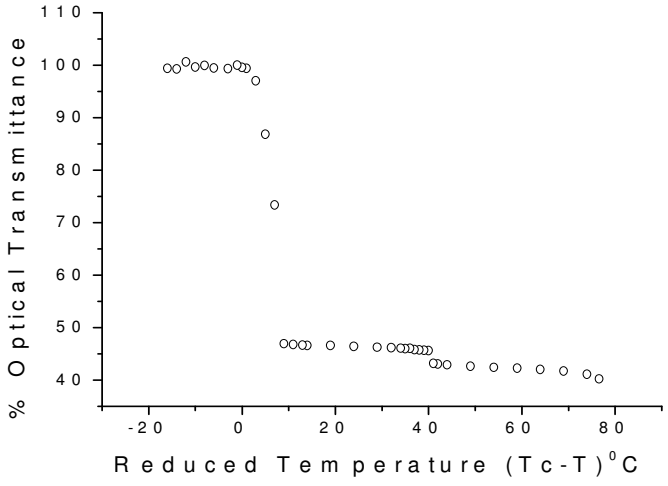

Figure 8. Variation of % Optical Transmittance with reduced temperature

To calculate the order parameter we have used birefringence values of the sample and Vuks approach (equation (6))

The variation of microscopic order parameter with temperature is shown in Figure.7 It is maximum in crystalline phase and as we increase the temperature the order parameter (S) decreases and becomes zero after the SmA to Isotropic phase transition temperature i.e. the molecular order in the sample gets extinguished.

Figure 8 shows variation of percentage optical transmittance with reduced temperature (Tc–T), The value of optical transmittance increases first slowly with increase in temperature and then it increases near the SmA to Isotropic phase transition temperature and as soon as the sample goes into isotropic phase the optical transmittance achieves its maximum value i.e. nearly 92% and after that it becomes constant with respect to increment in temperature. This type of behaviour has been reported by our group (Manohar et al., 2004) for different mixtures of liquid crystals.

CONCLUSION

The dielectric study of the sample shows dielectric relaxation in the frequency range 1 kHz to 10 MHz covered in the present work.

The dielectric anisotropy is positive and is high in SmA phase showing that the angle between dipole moment and long molecular axis is less than 54.7^0 .

The birefringence values shows ideal type of behaviour and the birefringence value is nearly constant in SmA phase i.e. 0.085.

The order parameter decreases as we move from crystalline to SmA and SmA to Isotropic phase by increasing temperature. The variation of order parameter is 0.8 to 0.45 in smectic phase while its value is zero in isotropic phase.

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