

Dielectric and Optical Studies of a Mesogenic Material Showing Smectic C Phase

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Abstract: Investigations on the dielectric permittivity and the dielectric loss of a newly synthesized mesogenic material indicating monotropic smectic C phase in the frequency range of 1 KHz to 5 MHz has been reported. The optical behaviour has also been examined by measuring the refractive index, birefringence and optical transmittance in the temperature range 25°C to 110°C. The birefringence values have been used to calculate order parameter of the sample in the above mentioned temperature range. The phase transition temperature measured using different techniques are found to be in good agreement with each other. The dielectric behaviour and optical properties of sample has also been discussed in detail with variation of temperature.

Keywords: Smectic, Dielectrics, Birefringence, Order parameter.

1. Introduction

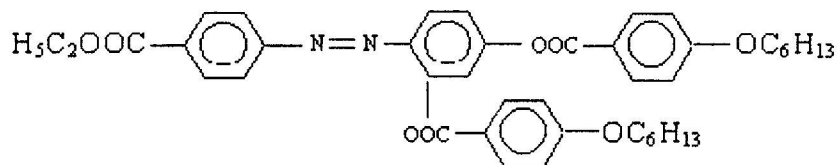
Liquid crystals are those materials which have attracted attention of a number of researchers in past years because of their unique electro-optical properties and their wide applications in display devices¹⁻⁵. It is well known that the molecular arrangement and consequently the order parameter of liquid crystal changes due to change in temperature as the liquid crystal goes from one phase to another phase. The use of liquid crystal in a particular device depends upon various properties like dielectric constant, dielectric loss, optical transmittance, viscosity and order parameter etc.⁶. The dielectric and optical studies of liquid crystal are important as they provide information about their molecular structure, intermolecular forces and molecular dynamics⁷. Various structural changes arising from transition between the meso phases of liquid crystal material are generally studied using their optical properties⁸⁻¹². The measurement of the transition temperature using temperature dependent dielectric parameter is a well established technique. Dielectric studies are important from the point of view that they provide information on the anisotropic behaviour of liquid crystals. The study of dielectric spectra may also exhibit absorption domain whose characteristic is linked to the rotational motion of molecule along its longitudinal axis or transversal axis¹³⁻¹⁵.

With this in view, we report here the dielectric study on a newly synthesized monotropic liquid crystal material showing smectic C phase. The data obtained from

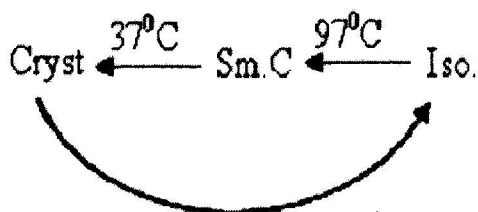
dielectric studies has also been used to evaluate activation energies associated with the process. In addition to this we have also measured refractive indices and birefringence for varying temperatures. The birefringence data has been used to calculate the order parameter of sample which is an important parameter governing nearly all the physical properties of a liquid crystal^{16,17}. The phase transition which has been measured by dielectric studies and birefringence measurement technique is further supported by data obtained from optical transmittance measurement.

2. Experimental Details and Theory Material

Material under investigation in the present work is a newly synthesized Smectic liquid Crystal (Monotropic) SND6, with the following structure.



The phase sequence is as follows



3. Dielectric Measurements

The dielectric measurements have been performed by a computer controlled Impedance/ gain-phase analyzer, Hewlett/Packard (HP 4194A). The transparent and highly conducting ITO coated optically flat glass substrate has been used as electrode, which allows one to control the alignment of the liquid crystal molecules and also to study the dielectric relaxation process. Both the electrodes of the cells have been treated with adhesion promoter and polymer (Nylon 6/6) and rubbed unidirectionally to get planar alignment. Thickness of the cell has been maintained at $5\mu\text{m}$ by using a Mylar spacer. The cell has been calibrated using standard liquids like CCl_4 and benzene. The liquid crystal material has been introduced into the cell by capillary action at a temperature slightly above its isotropic temperature. A well aligned cell has been obtained by applying an electric field in the slow cooling cycle from the isotropic to room temperature and simultaneously observing it under polarizing microscope (CENSICO 7626). Instec hot plate (HCS-302) is used for temperature stability with accuracy of $\pm 0.01^{\circ}\text{C}$.

The values of capacitance and conductance of the sample holder with and without sample has been measured. The real and imaginary part of permittivity of the sample has been obtained, using the following relations respectively

$$\varepsilon' = \frac{C_m - C_o}{C_l} + 1,$$

and

$$\varepsilon'' = \frac{(G_m - G_o)}{2\pi f C_l},$$

where C_m and G_m are the capacitance and conductance of cell filled with sample, C_o and G_o are the capacitance and conductance of cell without sample and C_l is the live capacitance.

The capacitance values has been read up to three places of decimal while conductance has been recorded up to forth place of decimal in the frequency range of 1 KHz to 5 MHz.

4. Birefringence Measurements

Refractive index has been measured using Abbe's refractometer¹⁸ having an accuracy of 0.0001 in the range of 1.3 to 1.7. For refractive index measurements small quantity of sample has been introduced between two prisms of the refractometer. The birefringent sample produces two boundaries in the view field of refractometer corresponding to n_e and n_o . An analyzer is adjusted in such a position that it makes the boundary of two fields observed in Abbes refractometer sharp and by coinciding this sharp boundary to intersection of crosswire, the reading is noted. After this the analyzer is rotated through 90°, which make the other boundary sharp. This sharp boundary is now made to coincide again with intersection of crosswire and reading is noted. These two values give the values of two refractive indices and Birefringence Δn has been calculated by using the following relation-

$$\Delta n = n_e - n_o,$$

where n_e and n_o gives the values of refractive indices for extra ordinary and ordinary rays.

5. Order Parameter

Order parameter has been calculated using Vuks direct extrapolation method¹⁹. The refractive index n_e and n_o have been analyzed by the method of Haller²⁰ and Horn²¹. This method uses vuks relation¹⁹.

$$S \left[\frac{\delta\alpha}{\alpha} \right] = \frac{3(n_e^2 - n_o^2)}{(n_e^2 + 2n_o^2 - 3)}.$$

Here $\delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$ and α is the molecular polarizability

R.H.S. of equation is plotted against $\ln [1-T/T_c]$ in order to evaluate the value of $\delta\alpha/\alpha$. Straight line so obtained is extrapolated to $T = 0K$, where the complete order occurs and the value of order parameter $S=1$ on $T=0K$. So the value of intercept gives the values of $\delta\alpha/\alpha$. directly. By substituting this value in above equation, we can obtain the values of order parameter for different temperatures.

6. Optical Transmittance Measurements

Optical transmittance measurements have been done by placing the sample holder filled with sample on rotating stage between two crossed polarizers of polarizing microscope, CENSICO (7626). A LDR has been fitted on one of the eyepieces of microscope, whose two terminals are connected to a digital multimeter to monitor the change in the resistance of LDR with the change of intensity of light. The temperature of the sample is varied using a hot plate. The variation of temperature gives rise to change in phase of the sample. This allows the light of different intensity to transmit through the sample and incident on LDR whose resistance changes accordingly and can be read by digital multimeter. The optical transmittance data has been normalized by considering 100% transmittance through empty cell and 0% transmittance through sample holder filled with black ink.

7. Results and Discussion

Fig-1 shows the variation of dielectric constant with log of frequency. The value of dielectric constant remains constant in the lower frequency range i.e. 1 KHz to 10 KHz. On further increase in temperature dielectric constant decreases slowly. This type of behaviour is normal in smectics and has been observed by other workers for smectics as well as other liquid crystals²².

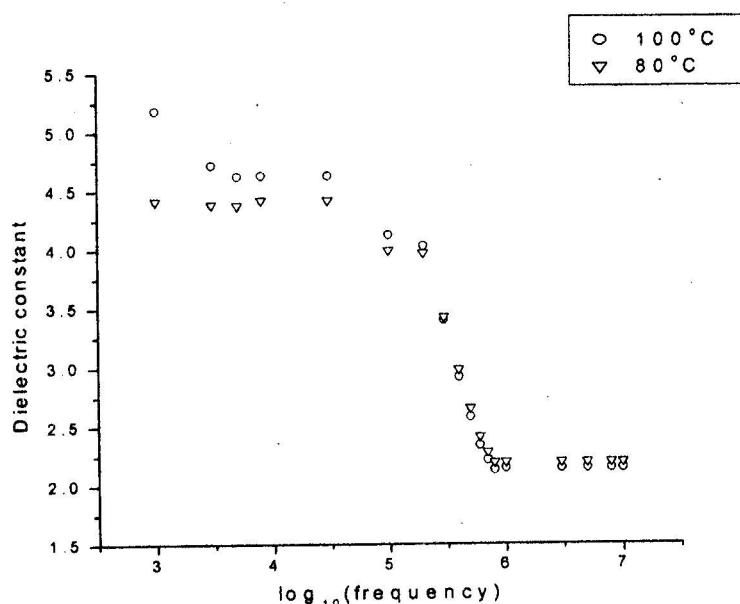


Fig-1: Variation of dielectric constant with log₁₀ frequency

The plot showing the variation of dielectric loss vs. Log₁₀ (freq.) is given in figure 2. The peak of the curve exhibits relaxation of molecules of the system at nearly 600 KHz. which shows that maximum absorption of energy takes place around this frequency. This type of low frequency relaxation is not common in smectic liquid crystals and the

relaxation for planer alignment cell is expected at much higher frequencies due to the rotation of molecule along long molecular axis.

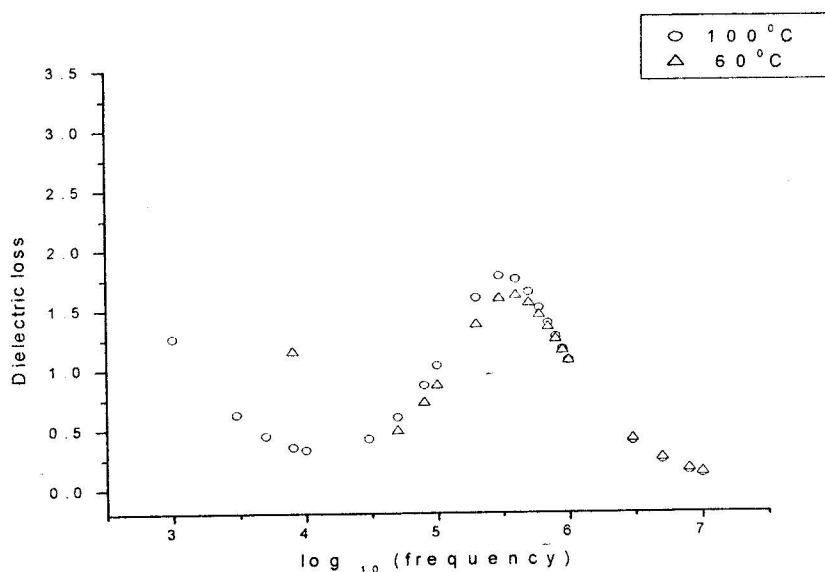


Fig-2: Variation of dielectric loss with log₁₀ frequency

This low frequency relaxation observed here can be assigned to the reorientation of long molecular axis in liquid crystal matrix^{23,24}, which is restricted by anisotropic ordering potential. Similar type of low frequency relaxation has been reported by Arora et. al.²⁵ for nematic liquid crystal. Some of the researchers have also reported such type of low frequency relaxation for other types of liquid crystals^{26,27}. The loss curve is symmetrical on both sides of the peak. This type of behaviour has also been observed by many other researchers for different nematic, cholesteric and smectic liquid crystals²².

Thermo dynamical parameters have been determined by using the dielectric relaxation data and by using the following Eyring equation²⁸

$$\tau = h/kt (\exp \Delta F/RT)$$

$$\text{and } \Delta F = \Delta H - T \Delta S$$

where $\tau = 1/\omega$ is the relaxation time and $\omega = 2\pi f$, where f is the frequency of the applied electric field.

The value of enthalpy of activation energy and entropy has been found to be 6.23k cal/mol and -60.32 cal/mol deg. The observed negative entropy value for the system indicates well ordered system, which is expected for smectic liquid crystals²⁹.

The calculated values of dielectric constant (ϵ') and dielectric loss (ϵ'') as a function of temperature at different frequencies are shown in figure 3 and 4. The values of dielectric constant remains almost constant up to 98 °C but show sharp change at 97 °C. This change shows its isotropic to smectic phase transition and it starts decreasing on further cooling and

again show a change at 37°C indicating smectic C to crystalline phase change. Almost similar type of behaviour is observed for dielectric loss but smectic to crystalline transition is not as prominent as in case of dielectric constant. Both the parameters ϵ' and ϵ'' increases with increase in temperature²².

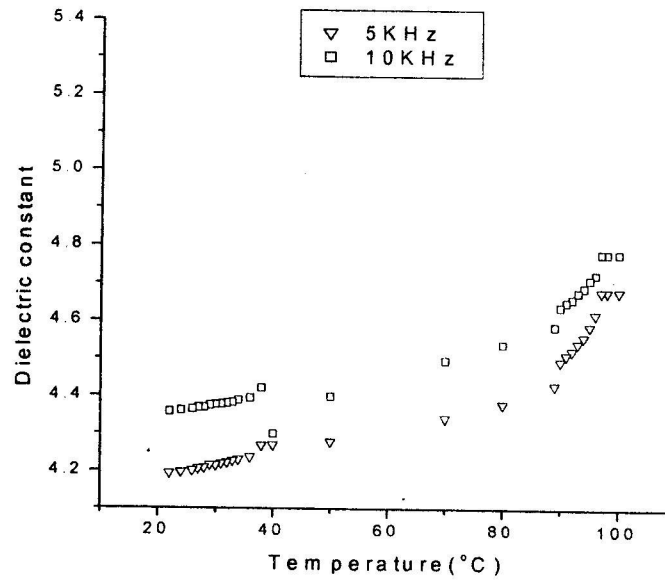


Fig-3: Variation of dielectric constant with temperature

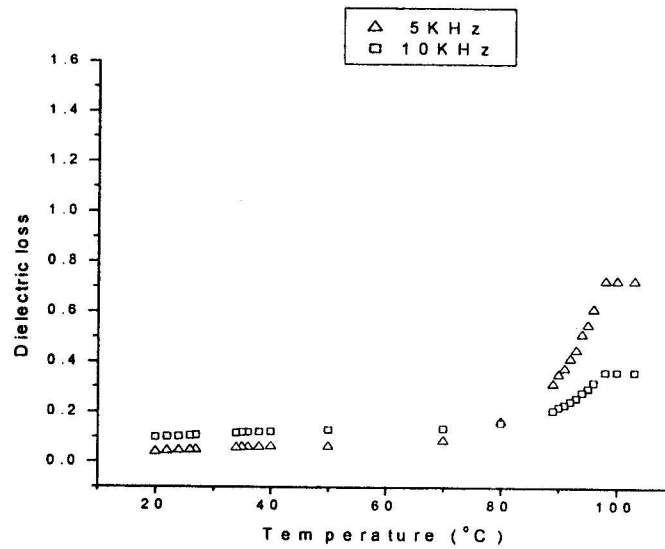


Fig-4: Variation of dielectric loss with temperature

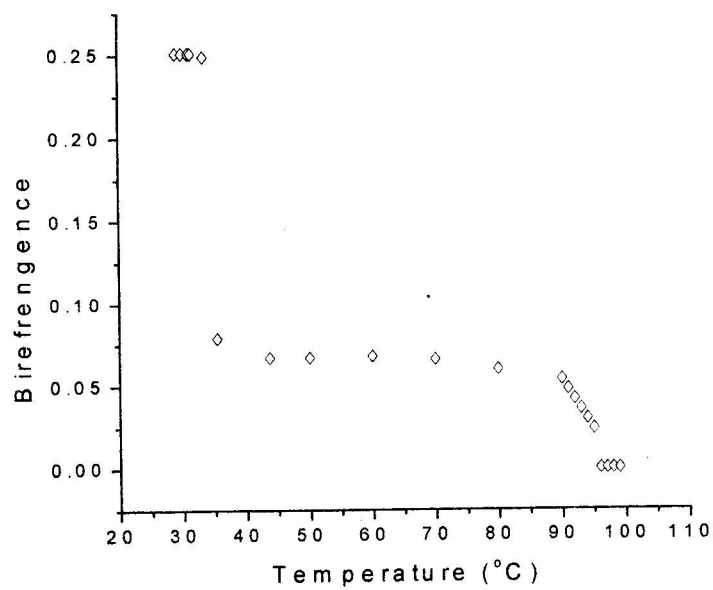


Fig-5: Variation of Birefringence with temperature

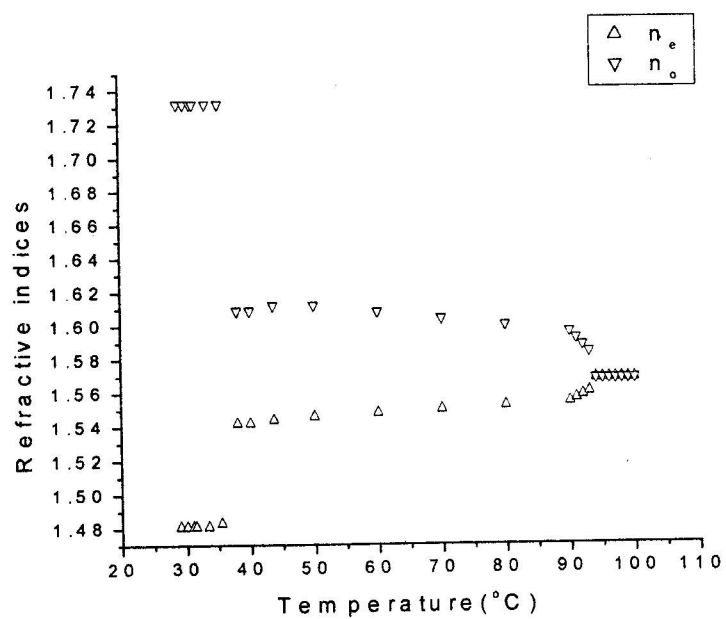


Fig-6: Variation of refractive indices with temperature

Fig. 5 shows the variation of birefringence with temperature. The isotropic to smectic C and smectic C to crystalline transitions are indicated by sharp discontinuities in the birefringence curve at 97°C and 37°C respectively. As the sample goes into smectic C phase nearly at 97°C the birefringence values starts increasing sharply as the anisotropic nature of the sample starts at this transition temperature and after reaching the value of 0.07 it remain almost constant up to 37°C i.e. smectic C to crystalline phase transition temperature. During the isotropic phase birefringence is zero as the sample behaves like an ordinary liquid³⁰.

Fig. 6 shows the plot for the variation of ordinary and extraordinary refractive indices with respect to temperature. In the cooling run the values

of n_e and n_o changes sharply at 97°C shows isotropic to smectic phase transition after that the values of n_e and n_o remain almost constant up to 38°C , another discontinuity occurs at 37°C , when sample become crystalline from Smectic C phase. This type of behaviour has also been reported for Nematic and Cholesteric mixtures by several other workers³⁰⁻³².

Behaviour of variation in the order parameter with temperature is given in fig.7. The order parameter remains almost constant up to 99°C after that the material represents the two phase transitions in the observed range of temperature. The decrease in order parameter with increase in temperature is due to the fact that increase in temperature also increases the thermal disturbance of the molecule, which leads to a decrease in order parameter.

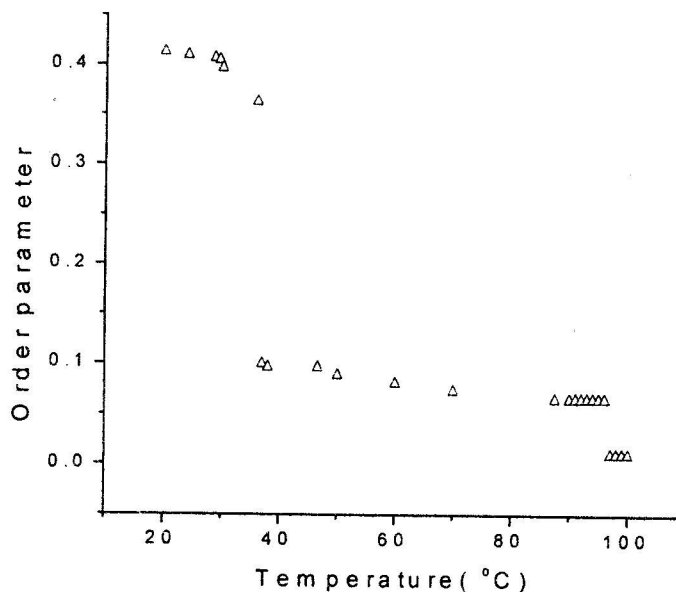


Fig-7: Variation of order parameter with temperature

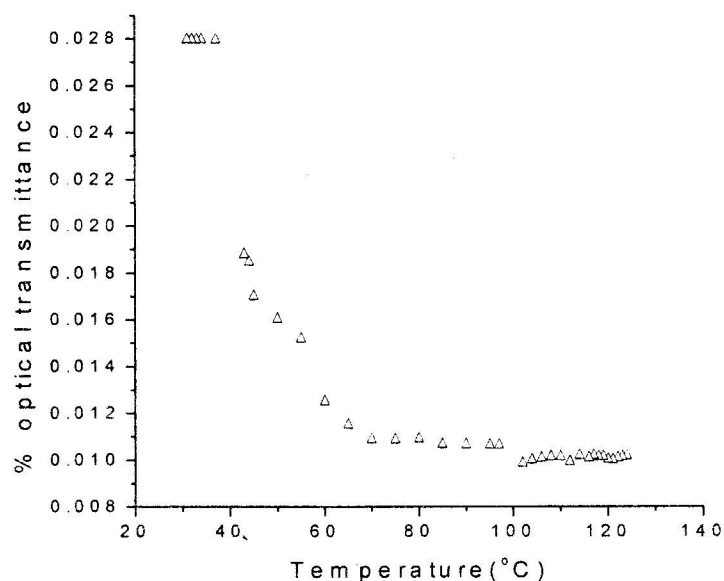


Fig-8: Variation of % optical transmittance with temperature

Fig 8 shows the variation of percentage optical transmittance with temperature. The value of optical transmittance remains constant up to 98°C but on further cooling the value of optical transmittance increases slowly and at 97°C it increases sharply. Sudden increases in the value of optical transmittance shows the phase transition of the sample. This is isotropic to smectic phase transition. The value of optical transmittance increases on further decrease in temperature and at 37°C the smectic to crystalline phase transition take place. At 37°C, optical transmittance achieves its maximum value and after that it remains almost constant with decrease in temperature. It can be observed that before going to crystalline phase it shows a pre transitional behaviour which has been observed by other workers for cholesteric as well as nematic mixtures³³. The phase transition temperature as obtained by optical transmittance study agrees fairly well with temperature obtained by dielectric and birefringence studies.

8. Conclusion

- The measurement of dielectric parameters, optical transmittance and birefringence show the Iso-SmC and SmC-Cryst phase transitions.
- In the sample slight variation in higher values of order parameter in the solid phase is due to the fact that anisotropy is considerable in this phase.
- Transition temperature obtained from different techniques i.e. optical transmittance, dielectric and birefringence measurements are found to be in good agreement.

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