ORIGINAL PAPER

COMPARATIVE DIELECTRIC AND OPTICAL STUDY OF A PURE AND POLYMER DOPED LIQUID CRYSTAL SHOWING SMECTIC A PHASE

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Abstract. *The dielectric measurements have been done for the determination of real and imaginary part of permittivity of a monotropic Smectic sample alongwith its polymer doped sample. The samples have been investigated in the frequency range from 1 kHz to 1 MHz and temperature range 315 K to 340 K. The dielectric measurements in smectic phase indicate Debye-type dispersion with relaxation peak at 357.72 kHz and 354 .83 kHz for pure and polymer doped samples respectively at 333 K. Measurements have also been made for refractive indices, birefringence, optical transmittance in the above mentioned temperature range and order parameter have been calculated using birefringence data. The temperature dependence of these parameters has been discussed in detail.*

Keywords: *Dielectric constant, dielectric loss, polymer doped, smectic A.*

1. INTRODUCTION

Polymer doped liquid crystals are very important class of materials as they are used in many devices [1-3]. These materials have applications in displays and light shutters. As polarisers are not required in these materials, light loss is less and brightness is high. These materials have one more advantages as they can be coated on flexible plastic sheets and also special treatment for alignment is not required. The addition of polymer in a liquid crystal not only increases the mechanical strength of the composite but also enhances many parameters.

P.G. de Gennes in 1979, proposed that a polymer liquid crystal composite can show better electro optical properties[4], The work on polymer doped liquid crystal was carried by Craighead et al. [5], followed by Fergason et al. [6]. Further many researchers worked and working on polymer doped liquid crystals including our group, because of its unique properties [7-12]. Hence in view of the above applications of polymer doped liquid crystals it is worthwhile to study the dielectric and optical properties of a polymer doped smectic A liquid crystal.

The dielectric specroscopy provides useful information about the molecular structure, dynamics, phase transition and display performance of liquid crystals [13-17] but the dielectric studies on smectic phases have been performed less than nematics and ferroelectric liquid crystals [16]. Similarly from application point of view the knowledge of optical

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anisotropy and refractive indices of liquid crystals and their temperature dependence is also of much importance [18, 19].

In the present paper results of the measurement of dielectric constant (ε′) and dielectric loss (ε″) with the variation of frequency and temperature for pure and polymer doped sample have been reported. Cole-Cole plots have been drawn to investigate relaxation. Refractive index and its anisotropy have been measured and reported and macroscopic order parameters have been evaluated for both the samples by anisotropy data. Optical transmittance values have been measured with the variation of temperature to study the phase transition behavior.

Dielectric and optical studies along with chemical structure of pure smectic sample (4-n-decyloxybenzylidene 4′-isopropylaniline) have already been published elsewhere [20].

2. MATERIALS AND METHODS

The real and imaginary parts of the permittivity of the sample have been calculated by the value of capacitance and dissipation factor, which are determined with the help of impedance/gain phase analyzer of HP-4194A. The detailed process is explained in our earlier paper [21]. Refractive indices values have been measured with the help of Abbe's refractometer (MITTAL 1245) whereas optical transmittance measurements have been done on polarizing microscope (CENSICO 7626). The constant temperature has been maintained by microprocessor based temperature controller Julabo F-25 (Germany) in all studies.

The Polymer doped with the liquid crystal is PMMA (Poly Methyl Methacrylate). The structure of the polymer is given in figure 1. The method of preparation of doped sample has also been published in our earlier paper [8].

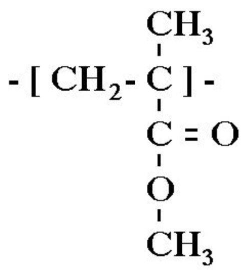

Fig. 1. Polymer used in present investigation.

The relationship between refractive index parallel ($n_{\parallel}$) and perpendicular ($n_{\perp}$) to the direction of molecular axis and macroscopic order parameter can be obtained by modifying the equations [22] as

$$n_{II} = \bar{n} + \frac{2}{3} Q \cdot \Delta n \tag{1}$$

$$n_{\perp} = \bar{n} - \frac{1}{3} Q \cdot \Delta n \tag{2}$$

where $\bar{n}$ is the average refractive index and Δn is the birefringence corresponding to complete alignment $n_{II} = n_e$, $n_{\perp} = n_o$ [23,24]. From both the equations (1) and (2), we get

$$Q = \frac{n_{II} - n_{\perp}}{\Delta n} = \frac{n_e - n_o}{\Delta n} = \frac{\delta n}{\Delta n} \tag{3}$$

where $\delta n = n_e - n_o$

The value of macroscopic order parameter equal to1 represents complete order at absolute temperature that is at 0 K δn = Δn. So the macroscopic order parameter (Q) has been obtained by extrapolating δn for T = 0K. This extrapolation is done on the linear portion of the graph drawn between birefringence δn against ln (1- T/T_c) as evaluated by others [22, 25] here T_c is the smectic to isotropic phase transition temperature.

3. RESULTS AND DISCUSSION

Fig. 2 shows the variation of dielectric constant (ε′) and dielectric loss (ε″) with log of frequency in smectic A phase at temperature 330 K for pure and polymer doped sample. In smectic A phase dielectric constant and dielectric loss are not changing upto very high frequency (60 kHz). The temperature dependence of dielectric constant and dielectric loss in smectic A phase is also almost negligible. The nature of variation of dielectric constant and dielectric loss for both the samples with frequency and temperature is same, but the dielectric constant for doped sample is slightly higher than the pure sample which is probably because the dopant enhances the effective polarization of the composite. This type of variation has been published by many researchers [8, 11, 18]. The dielectric loss curves at temperature 333 K initially increase with the frequency. Then they decrease steadily upto the measured frequency i.e. 1 MHz. The peak of dielectric loss curve corresponds to maximum loss and relaxation frequency. The relaxation observed at high frequency is may be due to rotation of terminal group present in the molecule.

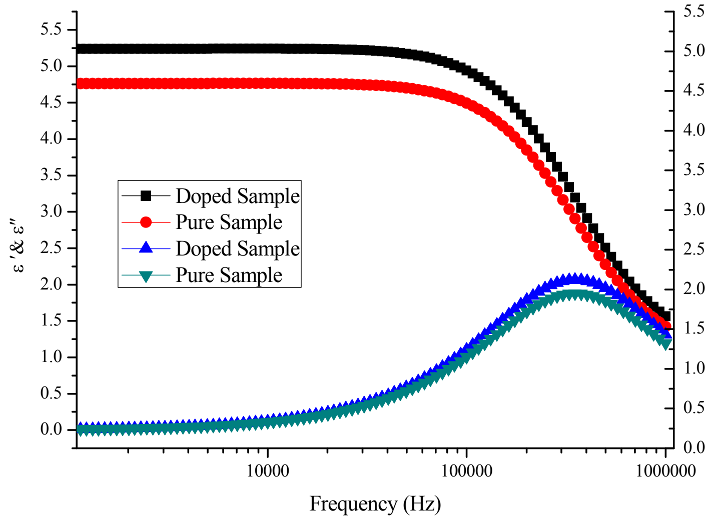

Fig. 2. Variation of dielectric constant and dielectric loss of pure and polymer doped samples in Smectic A phase at 330 K with frequency.

The Cole-Cole plost for the samples in smectic A phase have been presented in Fig. 2. The points lie on semicircle with its centre on the ε″ axis [8, 11]. The Debye’s type Cole-Cole plots found here are almost temperature independent, for the quantitative analysis of dielectric spectra, the Cole-Cole equation has been used [26].

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 - (i\omega\tau)^{1-\alpha}} \quad (4)$$

Here ε_∞ is the high frequency limit of the permittivity, $\varepsilon_0 - \varepsilon_\infty$ is dielectric strength, τ is the mean relaxation time and α represents the distribution of relaxation time.

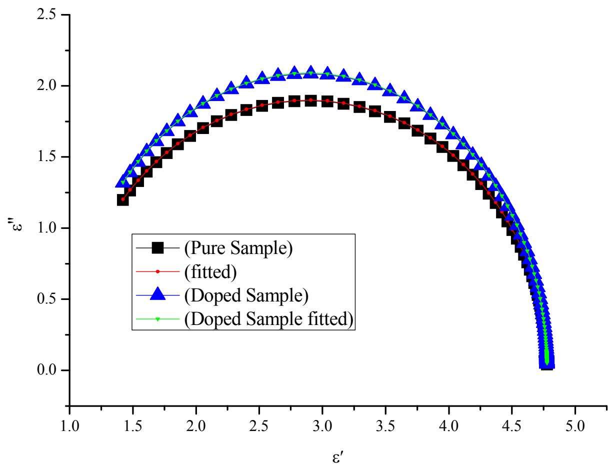

Fig. 2. Cole-Cole plot for pure and polymer doped samples in Smectic A phase.

The temperature variations of refractive indices and optical birefringence for pure and doped samples have been plotted in Fig. 3 in temperature range 326K to 338K. From the figure it can be seen that the value of ordinary refractive index increases where as the extraordinary refractive index decreases for both the samples. Then the value of ordinary as well as extraordinary refractive index approaches sharply to isotropic refractive index and becomes same at smectic A - Isotropic transition after that the refractive index decreases almost linearly with the temperature like any liquid for both the samples. The optical birefringence value for pure and doped samples decreases slowly with increase in temperature. Then its value decreases sharply with increase in temperature and becomes zero at smectic A - Isotropic transition for both the samples [18, 27].

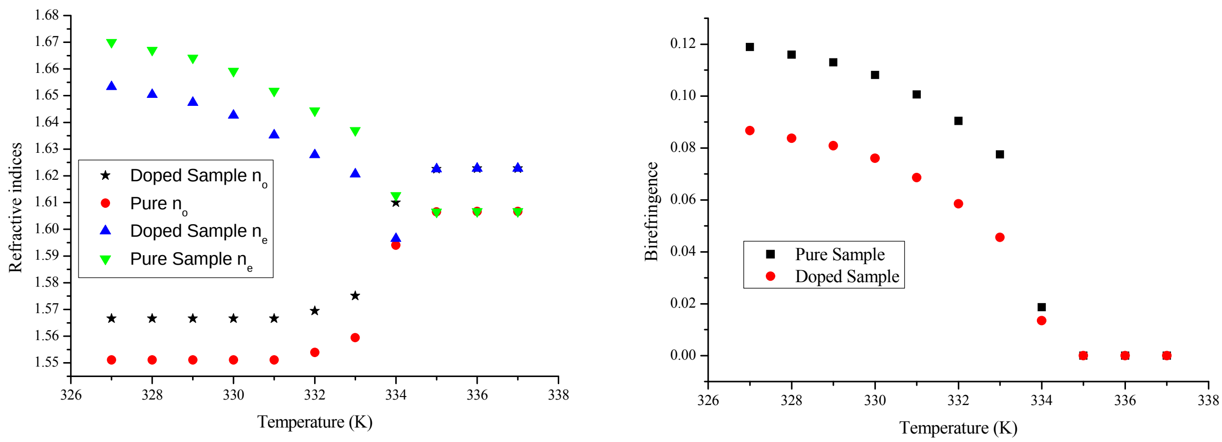

Fig. 3. Variation of refractive indices and birefringence of pure and polymer doped samples in Smectic A phase.

The variation of macroscopic order parameter Q with temperature is presented in Fig. 4. The value of order parameter indicates the degree of orderness of the molecule. Therefore, the decrease in value of order parameter indicates the increase in randomness of the molecules finally at smectic A - Isotropic transition. The order parameter value reaches to zero shows highest degree of randomness i.e. isotropic behaviour of the sample but in case of polymer doped sample the order parameter is high at all temperatures with respect to pure sample as polymer is providing more ordering to liquid crystal [18].

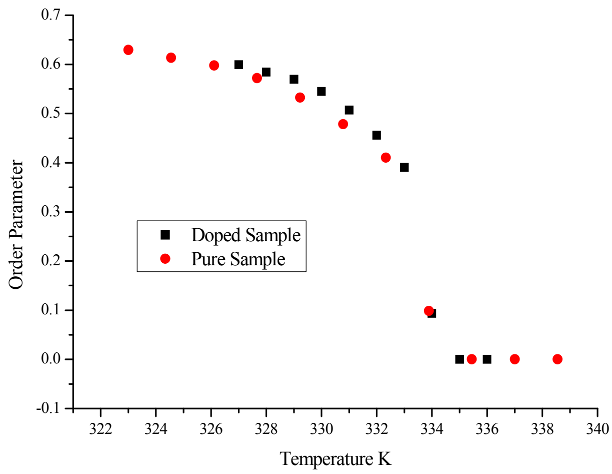

Fig. 4. Variation of order parameter of pure and polymer doped samples in Smectic A phase.

Fig. 5 shows the variation of optical transmittance. The values of optical transmittance presented in this graph are taken in arbitrary unit. The lower optical transmittance value is almost constant in isotropic phase till 333 K. Then its value increases abruptly by lowering the temperature indicates isotropic - smectic A phase transition. The higher value of optical transmittance is almost unaffected with decrease in temperature upto 321K and after that its value decreases sharply again indicating smectic A - Isotropic phase transition [18].

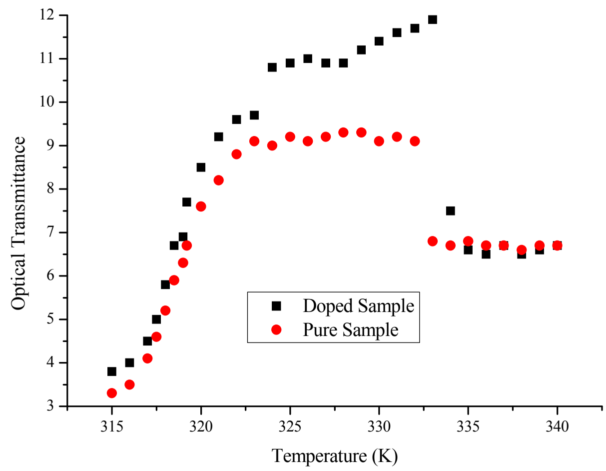

Fig. 5. Variation of optical transmittance of pure and polymer doped samples in Smectic A phase.

CONCLUSIONS

The various conclusions can be drawn from the results obtained by the experimental investigations:

- The transition temperatures obtained by optical transmittance technique and refractive index measurement are well matched with the value obtained by dielectric study.
- The refractive index values for pure and polymer doped samples have been measured and so the optical birefringence and macroscopic order parameter have been calculated.
- The dispersion in the value of dielectric constant and dielectric loss has been found and single relaxation is obtained and Cole -Cole plot is drawn for pure and polymer doped samples.
- The temperature dependence of the relaxation frequency gives the value of activation energy.

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