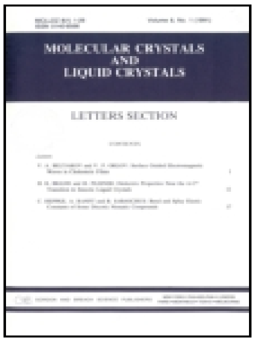

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Dielectric Relaxation Spectroscopy of Liquid Crystal in Nematogenic Mesophase

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ABSTRACT
In the present study, we report the dielectric behavior of a high temperature nematic liquid crystal (NLC) in both the planar as well as homeotropic alignments. To understand the mechanism of such high temperature NLC, we have performed dielectric spectroscopy in frequency range 100 Hz to 10 MHz. The different dielectric parameters, viz., effective dielectric permittivity and dielectric anisotropy of the sample have been determined with the variation of frequency and temperature. It is found that the dielectric parameters depend on dipole moment and rotation of side chain of molecule. The phase transition of this high temperature NLC has been confirmed by the DSC study.

KEYWORDS
Dielectric permittivity; dielectric loss; nematic liquid crystal; twist defect

1. Introduction

The dielectric spectroscopy represents a very powerful method for enlightening the molecular structure, orientational ordering, and dynamics of liquid crystals (LCs) molecules. A number of factors influence the dielectric properties of liquid crystal materials. The value of the dipole moment, the ratio of the longitudinal to transverse lengths of molecules, the end to end distance and flexibility of the terminal groups and the rigidity of molecular cores seems to be the most imperative structural factors. The study of the dielectric and electro-optical properties of liquid crystals is important from both the points of view—basic understanding as well as tailoring and optimizing materials characteristics for electro-optical applications. A particular application of liquid crystals requires a particular set of parameters of the liquid crystal in the required range. The main concerns are the improvement in electro-optical and dielectric properties such as response time, splay elastic constant, rotational viscosity, and dielectric anisotropy for liquid crystal displays, spatial light modulator, signal processing, and other applications [1–3].

In liquid crystals, two main relaxation processes are identified—one is connected with the rotations around the short axis (the low frequency process) and the second one is connected with much faster rotations around the long axis (the high frequency process). Such motions are also referred as molecular "tumbling" and "spinning", respectively.

In the present work, we have studied the dielectric behavior of a high temperature nematic liquid crystal, DoBDPMP. The dielectric study has been carried out in planar as well as

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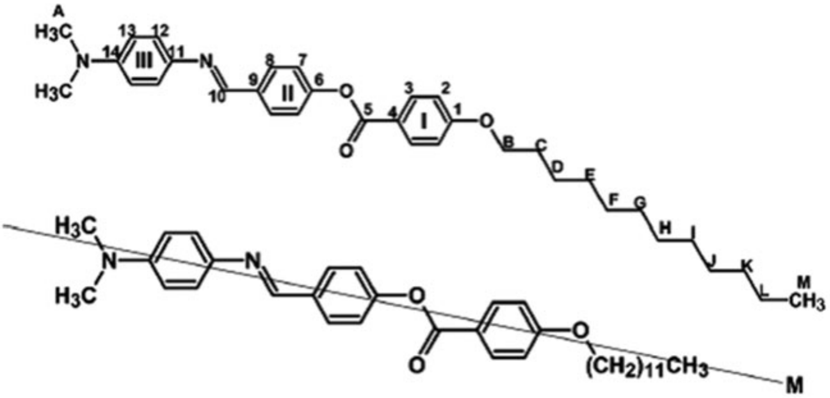


(4-(dodecyloxy) benzoic acid 4[-((4-(dimethylamino) phenyl) imino) methyl] phenyl ester)

Figure 1. Molecular structure of NLC DoBDPMP.

homeotropic alignments of the molecules. The manuscript is organized as follows. In sec. 2, the experimental details are given. Results and discussion are presented in sec. 3 and paper ends with the conclusion in last sec. 4.

2. Experimental details

2.1. *Materials*

One of the very important characteristics of the sample under investigation, nematic liquid crystal DoBDPMP (4-(dodecyloxy) benzoic acid 4[-((4-(dimethylamino) phenyl) Amino) methyl] phenyl ester), is expected to retain its mesophase behavior even in the presence of a nonmesogenic nitro- or cyano-substituted phenyl ring containing acceptor. Its molecular structure derived from CS Chem Draw Ultra 7.0 is shown below in Figure 1. It exhibits the phase sequence: Isotropic 209.3°C Nematic 146°C Crystal. Optical textures as shown in Figure 2 have been taken in crystalline state and near the nematic to isotropic (NI) phase transition by polarizing optical microscope (POM).

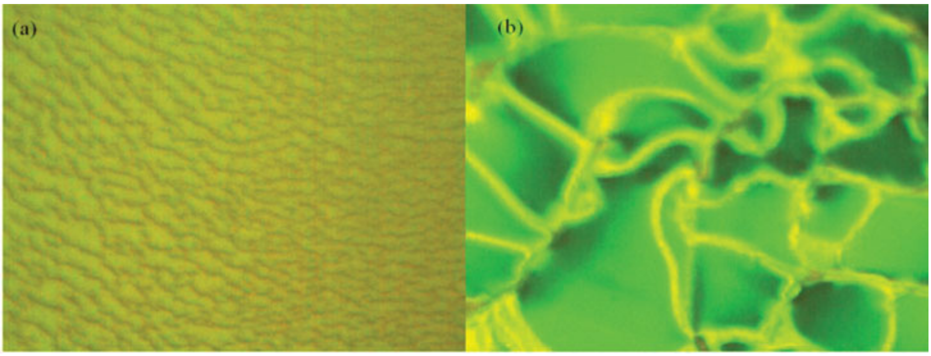


Figure 2. (a) Optical texture in crystalline state (b) nematic to isotropic (NI) phase transition.

2.2. *Preparation of the sample cell*

We have carried out the dielectric study of the nematic liquid crystal cell was conducted in planar and hometropic geometries. The sandwiched type (capacitor) cells were made using two optically flat glass substrates coated with indium tin oxide layers (ITO). To obtain planar alignment, the conducting layer was treated with the adhesion promoter and polymer nylon (6/6) (Sigma Aldrich). After drying the polymer layer, substrates were rubbed unidirectionally in an antiparallel direction [4–6]. Similarly for homeotropic alignment, the glass substrates were coated with dilute solution of Lecithin (Cetyltrimethyl ammonium Bromide). The substrates have been dried at 220°C for 4 hours before assembling the cell. The cell thickness was fixed by placing a Mylar spacer (6 μm in our case) in between glass plates and then sealed with UV sealant. The assembled cells were calibrated with CCl_4 and C_6H_6 and then filled with sample at a temperature higher than the isotropic temperature of the sample by capillary method. After filling the sample in a cell, it was cooled slowly under the applied AC electric field. The proper alignment of the sample cell was confirmed by placing the sample cell into crossed position of polarizing optical microscope (Radical RXLr-5). The correct and proper alignment of the liquid crystal molecules is extremely important for the precise measurement of electrical properties and which, in turn, influences dielectric parameters.

2.3. *Dielectric measurements*

The dielectric data have been determined by measuring the value of capacitance and the dissipation factor has been measured with the help of Impedance/Gain Phase Analyzer (HP-4194A) in the frequency range of 100 Hz to 10 MHz. These measurements have accuracy of ±0.17%. The temperature has been maintained with the help of Julabo temperature controller (F-25) with an accuracy of ±0.01°C. After reaching the required temperature, the sample holder has been left for 10 min on the same temperature before taking the measurement so that the thermal equilibrium could be maintained between the hot plate and the sample. The dielectric measurement was carried out in the heating cycle [5]. Measurements in the higher frequency range have been limited to 10 MHz because of the dominating effect of finite sheet resistance of ITO coated on glass plates and lead inductance [4–6]. The real and imaginary part of dielectric permittivity is given by the following equation.

$$\varepsilon' = \varepsilon'(\mathrm{dc}) f^{-n} + \varepsilon'(\infty) = \frac{\delta\varepsilon'[1 + (2\pi\pi f\tau)^{1-\alpha}\sin(\alpha\pi/2)]}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)}\sin(\alpha\pi/2)} \tag{1}$$

$$\varepsilon'' = \frac{\sigma(dc)}{\varepsilon_0 2\pi f^k} + \frac{\delta\varepsilon'(2\pi f\tau)^{(1-\alpha)}\cos(\alpha\pi/2)}{1 + (2\pi f\tau)^{2(1-\alpha_{GM})} + 2(2\pi f\tau)^{(1-\alpha)}\sin(\alpha\pi/2)} + Af^m \tag{2}$$

Here σ(dc) is ionic conductance and ε_o is free space permittivity, f is the frequency of relaxation, $\delta\varepsilon'$ is the relaxation strength, τ is the relaxation time, α is the distribution parameter, $\varepsilon'(\infty)$ is the high frequency limit of the dielectric permittivity, ω is the angular frequency while n, m, and k are the fitting parameter. The term $\varepsilon(\mathrm{dc})/\mathrm{f}^{-\mathrm{n}}$ and $\sigma(\mathrm{dc})/\ \varepsilon_o 2\pi \mathrm{f}^{\mathrm{k}}$ are added in the above equation for low frequency effects due to the electrode polarization, capacitance, and ionic conductance. The term Af^{m} term is added in equation (2) for high frequency effect due to the ITO resistance and lead inductance [4–6]. The low and high frequency data have been corrected from the least square fitting of experimental data.

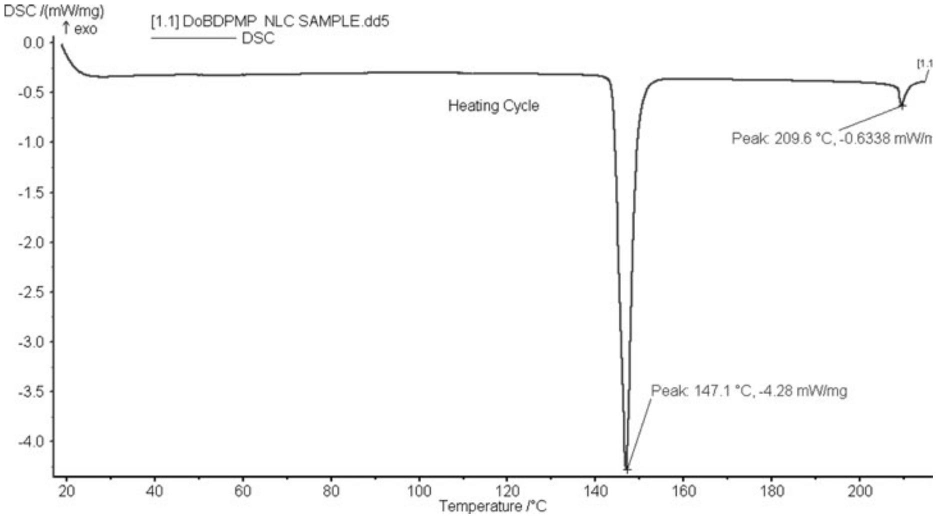


Figure 3. DSC thermograph of NLC DoBDPMP.

3. Result and discussion

The compound DoBDPMP exhibits an enantiotropic nematic phase as confirmed by a hot-stage polarizing optical microscope and differential scanning calorimeter (DSC). The DSC thermograph is shown in Figure 3 which gives the transition temperatures matching fairly well with the synthesizing group [6]. The core of the mesogen consists of three phenyl rings and azo methine and ester-linking units. The dodecyloxy unit is present in one terminal, and the other terminal consists of a dimethyl amino group. We observe that $T_{CN} \approx 147.1^\circ\text{C}$ and $T_{NI} \approx 209.6^\circ\text{C}$. The dimethyl amino group is not a good terminal functionality to observe a mesophase but a good charge-transfer donor. Very few liquid crystalline compounds containing a dimethyl amino terminal group are reported in the literature. In view of this, the core of the mesogen is designed to have three phenyl rings with azomethine and ester groups as linking units to enhance the molecular polarizability.

Information about the dynamics of a molecular ensembly can be obtained by analyzing the dielectric data. If the frequency of the applied electric field corresponds to the reorientation times of the molecular dipoles, the complex dielectric function shows a characteristic pattern. The permittivity has been studied with varying frequency (100 Hz–10 MHz) at different temperatures in the nematic phase. With increasing frequency, the dielectric permittivity also decreases for both the alignments, i.e., parallel and homeotropic of liquid crystal sample cells. The frequency of maximal loss is related to characteristics relaxation rate or relaxation times of the fluctuating dipoles. The perpendicular and parallel components of effective dielectric permittivity ($\varepsilon\perp$ & $\varepsilon_{\parallel}$) are shown in Figure 4(a, b), at different temperatures as a function of frequency. Here term effective is used for the dielectric permittivity for which we have removed contribution of sheet resistance, ITO coatings and lead inductance of the cell. By the least square fitting of experimental data, we have removed these contributions and we observed the effective dielectric permittivity [5]. Generally, the same nature of both components of effective dielectric permittivity for nematic phase has been observed, but at 168°C the parallel component of effective dielectric permittivity decreases.

The perpendicular component of the effective dielectric permittivity remains constant at all temperatures but decreases with frequency, a sharp decrement in the value of effective dielectric permittivity in the low frequency region has been observed. The high value of effective

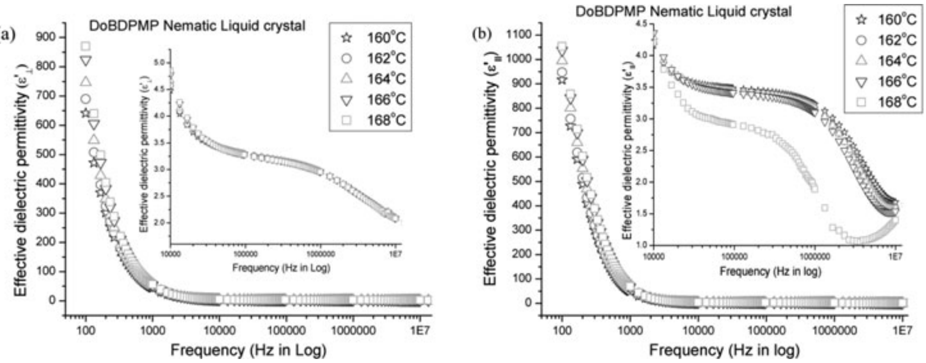


Figure 4. Effective dielectric permittivity of DoBDPMP for (a) planar (b) hometropically aligned nematic liquid crystals. Inset shows the dielectric permittivity in frequency range 10 KHz–10 MHz.

dielectric permittivity in low frequency is observed due to highly conducting ionic charges present in current NLC. The parallel component of effective dielectric permittivity shows the same trend but it decreases with the increase in temperature. The parallel component is large as compared to the perpendicular component of effective dielectric permittivity of the sample due to the greater contribution of parallel component of dipole moment than that of the perpendicular component of dipole moment in effective dielectric permittivity (see in Figure 5(a)). Inset figure shows that a high relaxation mode is appearing for both the alignments of NLC. This relaxation in high frequency region is observed due to the molecular reorientation of NLC molecules along short axis.

The temperature variation of dielectric anisotropy at two frequencies 10 KHz and 10 MHz has been shown in Figure 5(b). It can be seen that the value of dielectric anisotropy at 10 MHz is less as compared to that at 10 KHz. This type of trend is exhibited due to zigzag shape of molecule which may result in rotational freezing of the molecule. This may lead to the tumbling of the molecule at higher temperature, and this rotational freezing could be due to charge-transfer (CT) property of the NLC sample. These CT interactions play a crucial role. The value of dielectric anisotropy strongly depends upon the chemical structure of the molecules which affects the value of dipole moment. It means the dielectric anisotropy of NLC is related to the orientational order of a mesogen in the electric field which effects the carbon-hydrogen dipolar coupling and the direction of the molecular axis. Its coupling will

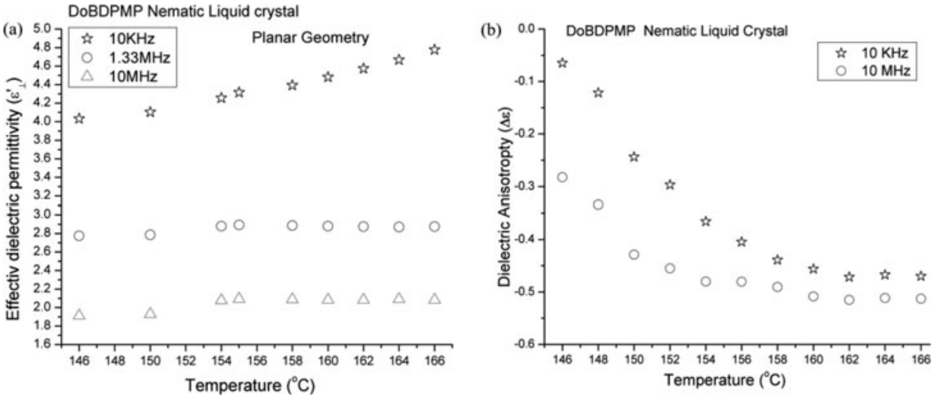


Figure 5. (a) Perpendicular component of effective dielectric permittivity of NLC with variation of temperature. (b) Behavior of dielectric anisotropy of NLC DoBDPMP with variation of temperature.

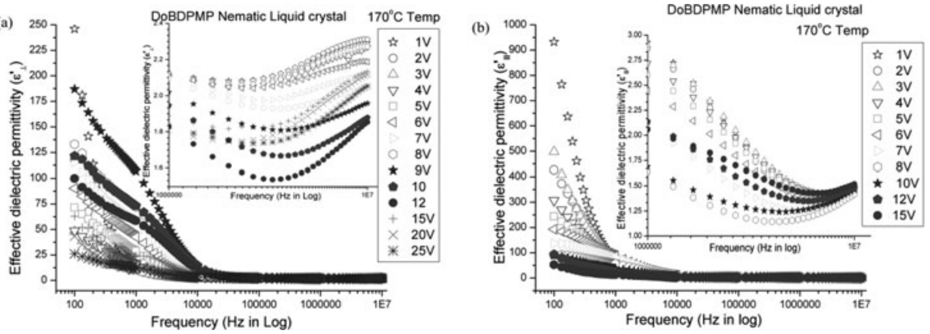


Figure 6. Effective dielectric permittivity of (a) planar (b) homeotropically aligned sample as a function of frequency at different bias voltages. Inset shows the dielectric permittivity in frequency range 1 MHz–10 MHz.

be highly valuable in determining the order parameter of different chemical groups of the molecules. However, the main effect must be attributed to the change of the direction of the long axis with respect to the net dipole moment characterized by the angle β. The influence of dielectric anisotropy on DoBDPMP can be analyzed by applying Maier and Meier theory [7, 8]. According to this theory, dielectric anisotropy is given as,

$$\varepsilon_{||} = 1 + \frac{NhF}{\varepsilon_0}\left\{\bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{F\mu^2}{3K_BT}\left[1 - \left(1 - 3\cos^2\beta\right)S\right]\right\} \tag{3}$$

$$\varepsilon_{\perp} = 1 + \frac{NhF}{\varepsilon_0}\left\{\bar{\alpha} + \frac{1}{3}\Delta\alpha S + \frac{F\mu^2}{3K_BT}\left[1 + \frac{1}{2}\left(1 - 3\cos^2\beta\right)S\right]\right\} \tag{4}$$

$$\Delta\varepsilon = \varepsilon_{||} - \varepsilon_{\perp} = \frac{NhF}{\varepsilon_0}\left[\Delta\alpha + \frac{\mu^2F}{2K_BT}\left(3\cos^2\beta - 1\right)\right]S \tag{5}$$

where $\Delta\alpha$ represents the anisotropy of molecular polarizability, μ the resultant dipole moment of the molecule, N the number density, $\Delta\varepsilon$ dielectric anisotropy, F parameter depending on reaction field factor, and β the angle between the molecular axis and the direction of the off axis. The compounds with permanent dipole at linking group have a tendency of dielectric anisotropy. The dielectric anisotropy depends upon the angle β and the order parameter [9]. The contribution of dipole moment in parallel and perpendicular directions for the NLC making an angle β with the long molecular axis is given by $\beta = \tan^{-1}(\mu_t/\mu_l)$, here μ_t and μ_l are the transverse and longitudinal components of the dipole moment of the molecule. Negative dielectric anisotropy can be achieved by introducing polar groups in the lateral positions of LC. Incorporating more polar groups in the LC sample helps to increase the negative dielectric anisotropy. According to Clausius–Mossotti relation, the molecular polarizability depends upon the frequency and temperature of the mesogen molecule. The angle of molecular axis from the para axis of the phenyl rings is attributed to the presence of linking group. Therefore, it is clear that the magnitude of dielectric anisotropy increases in negative order with the variations of temperature and frequency. A confirmation of this effect shows that in high frequency region, the parallel component of effective dielectric permittivity decreases but perpendicular component of dielectric permittivity increases with the variation of bias voltage.

Figure 6(a, b) shows the variation of perpendicular and parallel components of the effective dielectric permittivity with frequency at different bias voltages. A similar behavior has been

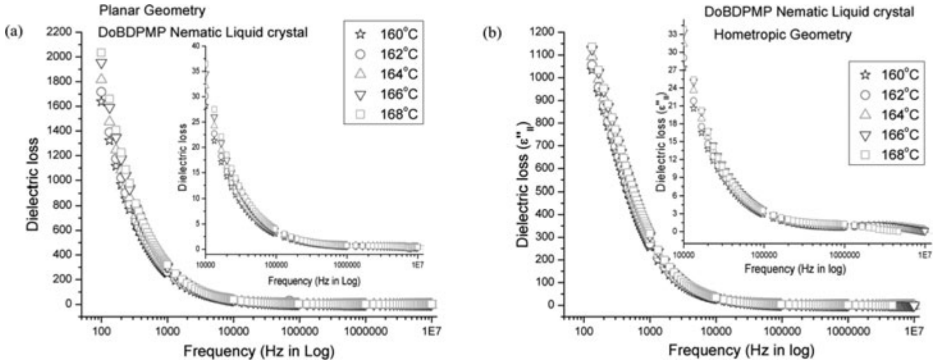
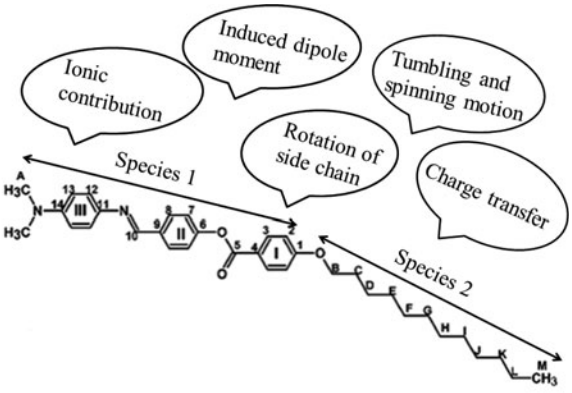


Figure 7. Behavior of dielectric loss for (a) planar (b) hometropically aligned sample as a function of temperature. Inset shows the dielectric loss in frequency range 10 KHz–10 MHz.

observed by varying the perpendicular and parallel components of effective dielectric permittivity ($\varepsilon'_{\perp}$ & $\varepsilon'_{||}$) with frequency for both types of geometry of liquid crystal sample cell at different bias voltages. The perpendicular and parallel components of the effective dielectric permittivity decreases with the frequency for each bias voltages. While in the frequency region less than 1 MHz, the perpendicular component of effective dielectric permittivity increases. This may be because the parallel alignment of liquid crystal changes to homeotropic alignment below 1 MHz. This behavior has not been observed for hometropically aligned liquid crystal. Above 1 MHz frequency, ITO sheet resistance would have been generated due to higher frequency range. So this result is not very promising above 1 MHz frequency region. At lower frequency, the nature of the effective dielectric permittivity is due to tumbling motion. It can correlate with molecular rotation around the short molecular axis. At high frequency, the effective dielectric permittivity is due to the molecular rotation along the long molecular axis, such motion is referred to as spinning. This constancy in trend has been due to molecular structure. The molecules undergo orientational change about molecular axis. The phenyl ring of such compound undergoes π flips along the para axis. Thus the core fragment interaction is attributed due to fast rotation of phenyl ring with respect to para axis. The large span of the structure of aromatic ring carbonyl and $CH = N$ carbons provides a large dispersion of the peaks in high frequency region. The specific structural property and dimensions are extremely important because a recent study reported smectic phase of a hockey stick shape mesogen that is structurally similar to DOBDPMP [3].

Figure 7(a, b) shows the variation of dielectric loss with frequency at different temperatures for planar and homeotropically aligned liquid crystal sample cell. A low frequency relaxation has been observed due to ionic contribution for both planar and homeotropically aligned liquid crystal sample. Another relaxation at high frequency is also observed due to molecular reorientation of NLC molecules along short axis. This variation in planar and homeotropic losses could be attributed due to rotation of side terminal chain of molecule, coupling between the orientational and conformational orders and is the influence of dipole moment. This also effects interlayer permeation of chain of molecules (the shorter tails and the longer tails coexist along the molecules end) causing correlation between cores in adjacent layers exhibiting such a trend.

We made an attempt to explain above-mentioned behavior with the help of topological models as shown in Figure 8. It is known that NLC exhibits several defects including twist defect [10]. In this model, it is clear that the whole molecule is divided in two species 1 and



(4-(dodecyloxy) benzoic acid 4[-((4-(dimethylamino) phenyl) imino) methyl] phenyl ester)

Figure 8. Topological model to explain the behavior of system.

2. Species 1 is already a LC molecule. The addition of species 2 may lead to a few drawbacks but it reduces the twist defect [11].

Maier–Saupe theory [7] assumes that the force between liquid crystal molecules is a dispersion force. The dispersion force is quantum mechanical in nature and represents interaction between induced dipole moments. In fact, we have observed that the average force experienced by a single molecule, due to other molecules, can be derived including more forces than just the dispersion force because in our case the molecules are not perfect rods but more of stretched rods. This has been taken into account in deriving the average force on a single molecule which is quite high. Actually, when electric field is raised with frequency then species 1 follows the field but species 2 simultaneously with LC properties tries to overcome any twist produced by the field shown in Figure 8, thus behaving as a shield and without any hindrance to the core LC molecule. In addition, the twist defect can be minimized by utilizing the specific molecule which is the subject of this study. Thus, we predict that the average force on each molecule is inversely proportional to the magnitude of the twist defect. (In our case, this average force is large as compared with other liquid crystal molecules).

4. Conclusion

We have studied the dielectric behavior of a high temperature nematic liquid crystal DoB-DPMP. The effective dielectric permittivity, dielectric loss, and dielectric anisotropy have been calculated. It has been observed that the dielectric permittivity of sample shows very high value in low frequency region due to high conductivity of ionic charges present in the system at such high temperature. We observe a relaxation mode at high frequency due to molecular reorientation of NLC molecule along short axis. The bias study of NLC shows that the NLC has high threshold value as the value of effective dielectric permittivity decreases slowly with field for planar aligned sample. As present, material has nematic phase at very high temperature, which is of less practical use, but still it can be used in applications as strong theoretical background has been given to overcome the twist defect. For this sample, the rotation of side chain, ionic contribution, charge transfer property, the interlayer permeation of tails producing a correlation between cores in adjacent layers, the stretched rod-like structure and most importantly, the relatively high average force experienced by each molecule in a bulk sample along with longer side chain of the molecule work together to reduce the twist defect.

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