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Time Domain Reflectometry Studies on a Nematic Liquid Crystal

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The complex dielectric permittivity spectra of p-pentyl phenyl-p-propylbenzoate (PPPB) ($K \xrightarrow{13^\circ C} N \xrightarrow{17^\circ C} I$)*, of a nematic liquid crystal are obtained using Time Domain Reflectometry (TDR) method over a frequency range 10 MHz–10 GHz at various temperatures covering both nematic and isotropic phases. The relaxation behavior at different temperatures was studied through cole–cole arc. The dielectric behavior in nematic (N) phase could be described by the Cole–Davidson model, while isotropic (I) phase is found to obey to a large extent Debye model. Two relaxation times,* τ_1 *and* τ_2*, are obtained for N phase which are the characteristic of Cole–Davidson model.* τ_1 *and* τ_2 *are interpreted as corresponding to different degrees of freedom in different direction in liquid crystalline state. The fact that* τ_1 *and* τ_2 *obtained for the I phase are almost equal favors Debye model. The results are presented over a temperature range, and these results are discussed to understand the phase transition involved. The work included in this article is useful as it provides information about the macroscopic structure of the liquid crystals in general and PPPB in particular. The N phase is the least ordered of liquid crystalline phases, and hence the studies even on an unaligned samples give information that is very close to aligned ones as far as those properties which are due to overall effects like dielectric behavior.*

Keywords: dielectric relaxation; isotropic; liquid crystal; nematic; time domain reflectometry

INTRODUCTION

The dielectric studies [1] and the data obtained from them are required for a large variety of materials under different physical conditions for

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many industrial, scientific, and medical applications involving microwave energy. These include data over a wide range of temperature on low loss dielectrics to asses their suitability for use in telecommunications, dielectric wave guides, lenses and microwave integrated circuits, substrates, and on lossy materials for estimating their heating response in microwave applications. Those data also help in giving insight in the molecular structure of compounds and thus is a tool for fundamental research. Liquid crystals [2] combine the material properties of solids with the flow properties of liquids. As such they have provided the foundation for a revolution in low power flat panel display technology (LCDs). Most of the dielectric measurements of liquid crystals (LCs) have been performed on the aligned samples that have either a parallel or a normal orientation against the electric field. On the other hand, for molecules having a strong dipole moment directed along the long axis of the molecule, such studies concern mainly the relaxation process connected with the molecular rotation around the short axis also make sense. Further, nematic liquid crystals are characterized by the presence of an orientation order of elongated rod-like molecules. The nematic phase is the least ordered of liquid crystalline phases, and hence the studies even on unaligned samples give information which is very close to aligned ones as far as those properties which is due to overall effects like dielectric behavior.

The dielectric study provides information about the molecular characteristics of the material and plays a key role in understanding the intermolecular interaction in the material. Among various existing dielectric techniques to measure the dielectric properties, one use microwave cavity spectrometer .in frequency domain and time domain reflectometer (TDR) in time domain. The microwave cavity spectrometer and the time domain reflectometer are good techniques, as they need very small quantity of the sample however the microwave cavity spectrometer suffers from its disadvantage of requiring form factor to determine dielectric permittivity and dielectric loss. Using TDR several dielectric studies have been reported [3–25] on different organic molecules and few of them being on liquid crystals and their mixtures [1–9,24,25] and especially on nematics. These studies are aimed at understanding dipole relaxation and short range intermolecular correlation in nematic phase as well as in isotropic phase. However, studies using TDR technique are meager both in aligned and unaligned nematic liquid crystals although TDR technique has got several advantages [17]. In the light of this the DR spectra of **p**-pentyl phenyl-p-propylbenzoate (PPPB) using TDR technique are obtained at various temperatures in the range K----13°C----N----17°C----I. The results are reported and discussed.

THEORY

There are some theories available which give insight into the different processes of dielectric relaxation involved in the case of molecules whose resultant dipole moment lies $||^{\mathrm{lel}}$ to the long molecular axis or inclined to it both in aligned and unaligned samples. For example, dielectric measurements performed on some unaligned samples show the presence of two dispersion regions, one in the range of MHz while other in GHz frequency range [12].

Using TDR technique one can obtain DR spectra at various temperatures in the temperature range required and the dielectric parameters ε_s, ε_∞, τ, and β can evaluated [12]. The Cole–Davidson and Cole–Cole models have been considered for interpretation. Using the dielectric spectrum in liquid crystalline state an attempt has been made to fit the data, which shows existence of two relaxation times τ_1 and τ_2 using the equation

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_{s1} - \varepsilon_{s2}}{(1 + j\omega\tau_1)^{\beta_1}} + \frac{\varepsilon_{s2} - \varepsilon_\infty}{(1 + j\omega\tau_2)^{\beta_2}},$$

where β_2 is assumed to be 1. The Debye theory has been applied to the dielectric spectrum in isotropic phase.

EXPERIMENTAL

PPPB was supplied by Eastman Kodak Co. Rochestar and is used without further purification. The complex permittivity spectrum was studied using Time Domain Reflectometry (TDR) method as described elsewhere in the literature [15–18]. The processing of the data was carried out as described by Cole [19,20] to get the complex permittivity at 110 frequencies ranging from 10 MHz to 10 GHz and dielectric parameters ε_s, ε_∞, τ, and β are obtained by nonlinear least squares fit method [21]. The temperature of the sample was controlled within ±0.2°C. The reliability of this experimental setup was tested by determining dielectric parameters of some standard liquids like chlorobenzene, acetone, and 1-2 dichloroethane.

RESULTS AND DISCUSSION

The Cole–Cole plots for typical two temperatures are presented in Figs. 1 and 2. Figure 1 corresponds to temperature of 15°C (nematic phase), while Fig. 2 represents for 40°C (isotropic phase).

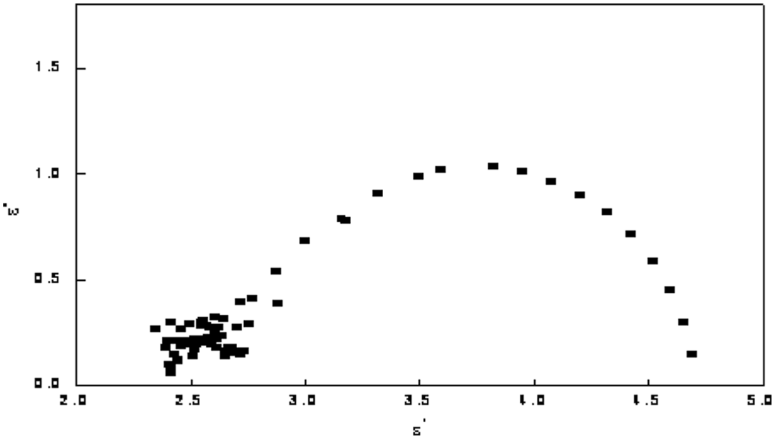

FIGURE 1 Cole–Cole arc at 15 degree of PPPB in N phase.

The various values calculated including β values at various temperatures are presented in Table 1 assuming single relaxation and Cole–Davidson model.

Theories are available in literature to explain the dielectric behavior in the nematic phase. Some of these theories are due to Martin et al. [5], Pokrovski [6], Tsvetkov [7], Norido et al. [8], and Duncan et al. [9]. All these theories are based on the modifications of Debye's model, except the last one. Further, dielectric relaxation study made on some homeotropically aligned and unaligned polymer nematic samples also yield interesting results [11,12]. In the unaligned

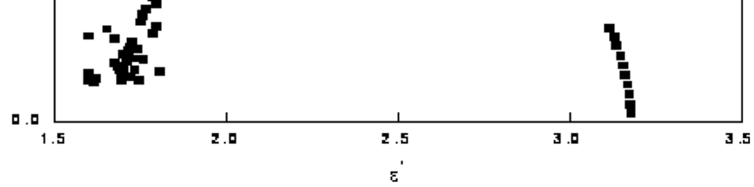

FIGURE 2 Cole–Cole arc at 40 degrees of PPPB in I phase.

TABLE 1 Variation of Dielectric Constants and Relaxation Times with Temperature in N and I Phases of PPPB Assuming Single Relaxation Process

t°C	ε_s	τ (n s)	β
13	5.06 [8]	1.356 [50]	0.892 [15]
15	4.86 [8]	1.150 [54]	0.852 [15]
17	3.80 [7]	0.778 [44]	0.762 [16]
20	2.39 [8]	0.536 [18]	1.0
25	2.87 [7]	0.482 [14]	1.0
30	3.08 [6]	0.440 [16]	1.0
40	3.20 [6]	0.355 [15]	1.0
50	3.31 [7]	0.326 [15]	1.0
60	3.81 [8]	0.272 [14]	1.0

The numbers in the brackets in Table 1 indicate the error in the values, e.g., 0.536 [18] means 0.536 ± 0.018.

nematic phase, the loss curves are broad, less intense, and asymmetric compared to the aligned one, indicating the presence of two relaxation processes δ and α in the ascending order of frequency, out of which, the δ process appearing to be more predominant. The position of 'f_{max}' for maximum absorption in case of aligned sample at a given temperature shifts towards the lower frequency in comparison with the unaligned sample. Results obtained for the liquid crystal under study in the form of unaligned sample are presented below and discussed in the light of above observations.

The variation of ε_s and τ with temperature is illustrated in Figs. 3 and 4, respectively, which indicate the N–I transition at 17°C. It is observed that the static permittivity ε_s decreases with temperature in the N-phase and shows increasing trend in the I-phase. The latter may be partly due to the decreasing antiparallel association of molecules with increase in temperature. The value of ε_s in N phase is greater than that in the I phase indicating the material to be positive dielectric anisotropic ($\Delta\varepsilon_s > 0$). The dielectric relaxation time decreases with temperature in both the N and I phases, which is in line with the above argument.

The β values, which are less than one for all observed temperatures in the N phase, indicate that the dielectric relaxation process in the N phase may be well described by the Cole–Davidson model ($\beta < 1$). The value of β is found to be one in the I phase as expected according to the Debye model. The observed longer 'τ' value in the N phase may be explained on the basis of the fact that the relaxation process is essentially an "end over end" tumbling motion of the molecules, which has to surmount the nematic potential barrier.

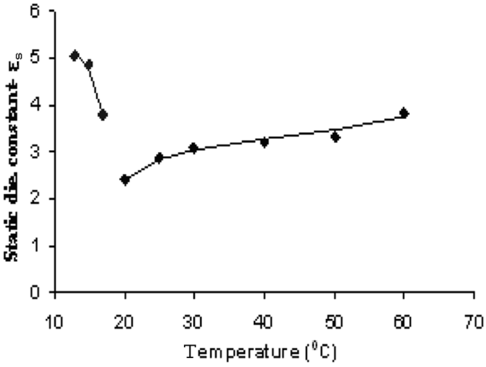

FIGURE 3 Variation of static dielectric constant ε_s with temperature for PPPB in nematic (N) and isotropic (l) phases.

The numbers in the brackets in Table 2 indicate the error in the values, e.g., 0.914 (52) means 0.914 ± 0.052. “N” and “I” indicate the nematic and isotropic phases, respectively.

However, some interesting results are observed when the data is fitted for the two relaxation times τ_1 and τ_2, and these results are given in Table 1 along with corresponding values of dielectric constants. Both the relaxation times τ_1 (low-frequency relaxation) and τ_2 (high-frequency relaxation) decrease with temperature as expected. High values of τ_1 in the N phase may be explained as due to “end over end” tumbling motion of the molecules, which has to surmount the nematic potential barrier, and smaller values of τ_2 may be explained

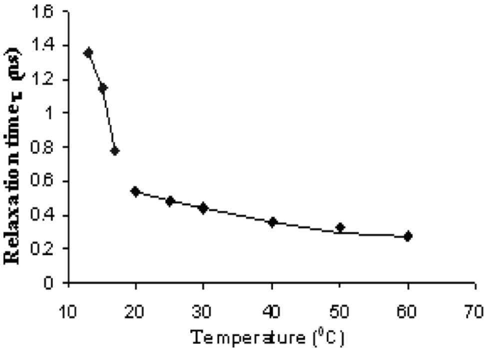

FIGURE 4 Variation of dielectric relaxiation time τ with temperature for PPPB in nematic (N) and isotropic (l) phases.

TABLE 2 Variation of Dielectric Constants and Relaxation Times with Temperature in the N and I Phases of PPPB Assuming Two Relaxation Processes

t (°C)	ε_{s1}	τ_1 (ns)	ε_{s2}	τ_2 (ns)	Phase
13	5.77 (10)	1.827 (70)	2.55 (8)	0.096 (16)	N phase
15	4.97 (8)	1.454 (68)	2.51 (7)	0.087 (140)	
17	3.70 (8)	1.200 (56)	2.50 (7)	0.070 (15)	
25	3.01 (7)	1.022 (62)	1.99 (8)	0.060 (12)	I phase
30	3.45 (9)	0.914 (52)	2.00 (7)	0.060 (16)	
40	3.29 (6)	0.580 (45)	2.00 (8)	0.034 (14)	
50	3.44	0.580 (45)	2.00 (7)	0.035 (16)	

as due to diffusional reorientation about the longer axis of the molecule [10].

By what is said in the above paragraphs, it is clear that the variations of the said parameters with respect to the temperature indicate transitional and pretransitional effects as the structure is transformed from an ordered state to disordered state, and vice versa. The various phenomena that take place near the phase transition can however be explained on the basis of Frenkel's heterophase fluctuation theory. This observation is in line wth earlier observations [24–27].

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