Dielectric Studies of Schiff Based Benzothiazole Core Liquid Crystals at Radio Frequency Region

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Abstract— **The phase transition temperatures and textural changes in homologous series of 6-methoxy-2-(4- n-alkanoyloxybenzylidenamino) benzothiazoles mesogens (n MBABTH) for n=14 and 16) were studied using polarizing optical microscope. The temperature and frequency dependence of dielectric constant and dielectric loss were carried out in the frequency range from 1Hz to 1MHz. A few anomalies in dielectric properties were observed at near phase transitions when dielectric constant and dielectric loss had been examined as a function of frequency and temperature. Changes in dielectric constant and loss are observed at low frequencies, whereas at high frequencies they are nearly constant. Temperature dependence of activation energy and relaxation frequency studies was made for smectic and nematic phases.**

Keywords- Liquid crystals; benzothiozoles; phase transitions; dielectric constant; dielectric loss; Relaxation frequencies; Activation energy.

1. INTRODUCTION

Liquid crystals in the nematic group are most commonly used in production of liquid crystal displays (LCD) due to their unique physical properties and wide temperature range. A great number liquid crystalline compounds containing heterocyclic units have been synthesized and Interest in such structures is constantly growing [1–3], because of the greater possibilities with heterocyclics in the design of new liquid crystal molecules, but also because the insertion of heteroatoms strongly influences the formation of mesomorphic phases. The effect of heteroatoms (S, O and N) are able to change considerably the polarity, polarizability and sometimes the geometric shape of the molecule, thereby influencing the type of mesophase, the phase transition temperatures, and the dielectric and other properties of the mesogens [4]. The incorporation of heterocyclic rings such as pyridine [5], thiophene [3, 6] and 1,3,4-thiadiazole [7] as the core in liquid-crystalline materials has been widely reported. However, very little information on the incorporation of benzothiazole as a core in liquid-crystalline compounds is available [8–15]. Benzothiazole derivatives have been studied as photoconductive materials [16–18]. A benzothiazole core is found in fluorescent compounds, which is useful in applications as a result of its high fluorescence quantum yields in the presence of the rigid core structure [19-20]. Lately, benzothiazole derivatives have been continuously investigated for application in thin-film and organic field-effect transistors [21]. In the nematic phase, liquid crystal molecules are usually oriented on average along a particular direction. By applying an electric or magnetic field the orientation of the molecules are to be manipulated in a predictable manner. This mechanism provides the basis for LCDs. The dielectric parameters of liquid crystals play an important role in the development of electro-optical devices. Frequency and temperature dependent dielectric studies of different phases give information not only about bulk properties but also about molecular parameters and their mutual association and rotation under an applied electric field. Substances with high dielectric constants are widely used in the electronics industry [22]. The dielectric materials that are used as inter layers in electronic chips they significantly increase the speed of propagation of electric impulses and reduce dielectric losses. The effect of frequency on dielectric properties offers valuable information about the localized charge carrier that helps to explain the mechanism responsible for charge transport phenomena and dielectric behavior.

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The aim of present work is to report the dielectric properties as a frequency and temperature dependence for compounds of homologus series of 6-methoxy-2-(4-*n*- alkanoyloxy benzylidenamino)benzo thiazoles mesogens (*n* MBABTH) [23] where *n*=14 and 16, to understand the phase transitions undergoing with temperature.

II. EXPERIMENTAL DETAILS

2.1. Materials

Textural and phase transition temperatures were measured using Meopta Polarising Optical Microscope with hot-stage as described by Gray [24]. These compounds were filled in LC1 homogenously aligned ITO coated liquid crystal cells, (5mm X 5 mm X 6 μm) obtained from M/s Instec. USA. The temperature and frequency dependence of dielectric constant and dielectric loss were measured in the frequency range 1Hz to 1MHz of using Newton's 4th Ltd., LCR meter model PSM1700. In this study the cells filled with samples were placed in the Instec hot and cold stage (HCS 302). The temperature was monitored and controlled through a computer by a software program. The sample was heated to isotropic state and kept until to attain thermal equilibrium.

The data was taken during heating and cooling cycles but the results are shown in cooling process. The measuring signal was the square form with 2V amplitude. The accuracy for dielectric constant and loss were maintained to the error of 1% and 2% respectively and the temperature accuracy to ± 0.1°C.

The selected LCs for present studies are 6-methoxy-2-(4-*n*-alkanoyloxybenzylidenamino)benzothiazoles mesogens (*n* MBABTH for *n*=14 and 16) while their molecular structure is presented below.
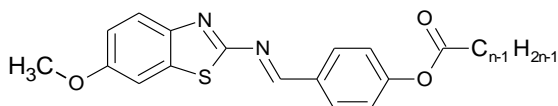
Structure of 6-methoxy-2-(4- *n*-alkanoyloxybenzylidenamino) benzothiazoles

2.2. Computational Details

The dielectric constant of a material is the ratio of the capacitance of a capacitor containing the material to the capacitance of the same electrode system with vacuum. Using the following equation the dielectric constant, (ε') was calculated.

$$\varepsilon^1 = \frac{(C_p - C_o)\,d}{\varepsilon_O \, A} + 1 \tag{1}$$

where A = area of the cell, d = thickness of the cell, ε_o = permittivity of free space 8.85×10^{-12} Fm^{-1}, C_p = capacitance with sample and C_o = capacitance without sample. The temperature coefficient of dielectric constant τ_ε was calculated using equation (2).

$$\tau_\varepsilon = \frac{\dfrac{\varepsilon(T_{final})}{\varepsilon(T_{ref})} - \dfrac{\varepsilon(T_{initial})}{\varepsilon(T_{ref})}}{T_{final} - T_{initial}} *10^6 \left[\frac{ppm}{^oC}\right] \tag{2}$$

where T $_{initial}$ = starting LC phase temperature value, T $_{final}$ = ending LC phase temperature value, ε (T $_{initial}$); ε (T $_{final}$) are the corresponding dielectric constant respectively and ε (T $_{ref}$) = dielectric constant at some reference temperature (50°C). The τ_ε value has units of parts per million per degree Celsius [ppm/°C].

The simplest model for a capacitor with a lossy dielectric is as a capacitor with a perfect dielectric in parallel with a resistor giving the power dissipation. The dielectric loss angle ($\tan\delta$) values were directly measured from experimental technique, and the imaginary part of permittivity (dielectric loss ε´´) was calculated using the equation (3) for the series of compounds studied.

$$\varepsilon^{11} = \varepsilon^1 \tan\delta \tag{3}$$

With the ε´´ data the sample conductivity σ (Siemens per meter) was estimated using equation (4). The changes in the electrical conductivity and charge transferring at different temperatures and isotropic phase, the ac conductivity at 1 KHz to 1MHz frequencies, in the LC region is measured from equation (4)

$$\sigma_{ac} = 2\pi\varepsilon_o\,\varepsilon^{11} f \tag{4}$$

where ε_o= permittivity of free space 8.85×10^{-12} Fm^{-1}, f = corresponding frequency in Hz and ε´´ = dielectric loss.

The widely adopted form of the Arrhenius equation [25] to study the effect of temperature on conductivity is shown in equation (5). The activation energy is viewed as an energetic threshold for a fruitful electric field production generated by the LC molecules orientation It is possible to calculate activation energy by Arrhenius equation by just using the conductivity at two temperatures. It would be more realistic and reliable if more data of conductivity is taken at deferent temperatures. Hence, by using the ac conductivity values measured from equation (4) in the LC temperature region at 1KHz to 1MHz, the activation energy (W) was calculated by using equation (5).

$$\sigma_{ac} = \sigma_o \exp\left(\frac{-W}{KT}\right) \tag{5}$$

where W = activation energy KJ/mol, K = Boltzmann constant in eV/K, T = temperature relative to the conductivity value calculated using a reference temperature and as well considering temperature values of corresponding phases, σ_{ac} = conductivity in LC phase and σ_o = conductivity in the isotropic phase at different frequencies.

III. RESULTS AND DISCUSSION

3.1 Textures and phase transition temperatures

The phases and their transition temperatures obtained from POM are shown in Table 1. The textural observation of 6-methoxy-2-(4- *n*alkanoyloxybenzylidenamino) benzothiazoles mesogen (for *n*=14 and 16) made through POM have shown enantiotropic smectic C and nematic phase as shown in plate 1 and plate 2. The data for phase transition temperatures measured from both POM and DSC [23] are in good agreement.

Table 1. Phase transition temperatures of *n* MBABTH

S.no	Compound	Textures	Transition Temperatures (°C)
1	*n*=14	I - N	109.6
		N - SmC	79.7
		SmC - Cr$_2$	78.8
		Cr$_2$ - Cr$_1$	65.6
2	*n* =16	I - N	107.2
		N - SmC	88.3
		SmC - Cr	83.7

Note: Iso = Isotropic,SmC = Smectic C. N=Nematic Cr= crystal
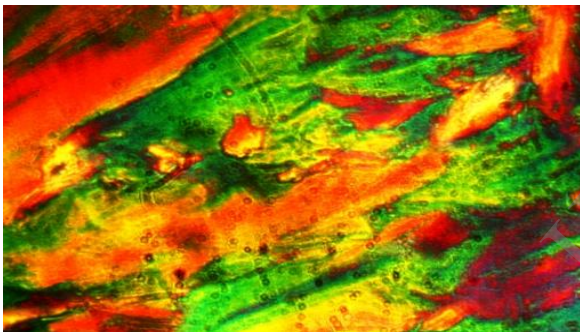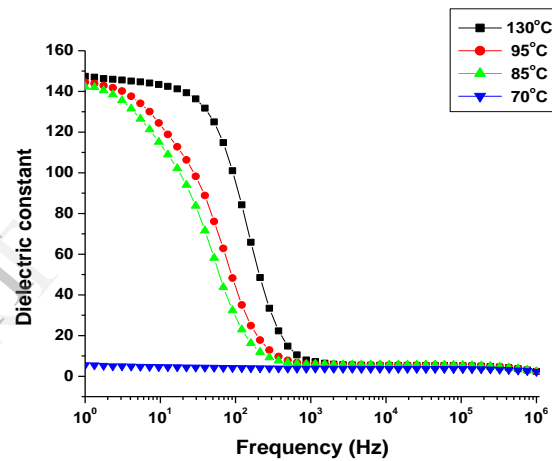

Plate1. Nematic phase in 14 MBABTH

Plate 2: Smectic C phase in 16 MBABTH

3.2 Dielectric studies

The frequency dependence of dielectric constant, temperature coefficient of dielectric constant, dielectric loss is shown in figures 1 to 3.
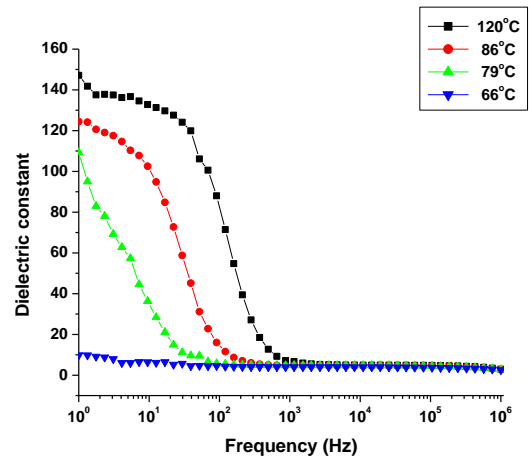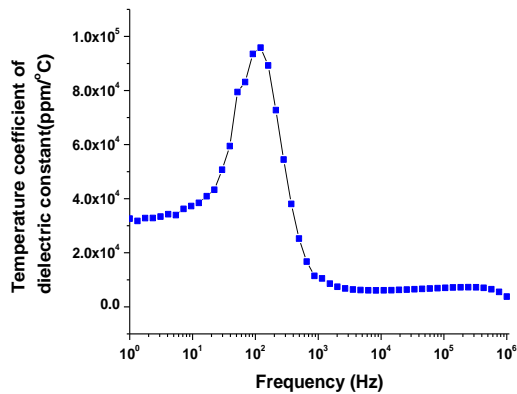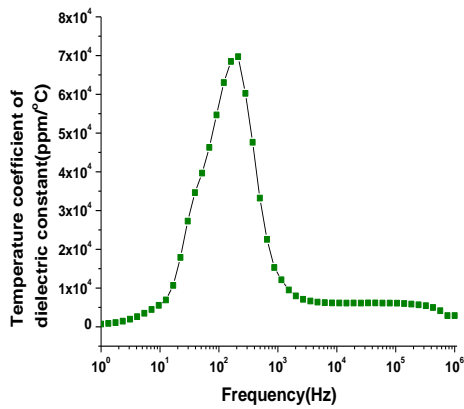

(a)

(b)

Figure 1. Frequency dependence of dielectric constant ε^{1} for
(a)   14 MBABTH and (b) 16 MBABTH at different Temperatures

The dielectric constant for both samples as a function of frequency at different temperatures is shown in figure 1. It is observed that the dielectric constant value is high at low frequencies and decreasing gradually with increased frequency and increasing with increased temperature. The observed higher value of dielectric constant at low frequencies is due to effect of space charge polarization. Figure 2 depicts the information about the frequency dependence of temperature coefficient of dielectric constant at higher frequencies. The temperature coefficient of dielectric constant stability is noticed rather to low frequencies in both compounds which are shown in figure 2. As the τ_ε is the combination of thermal and dielectric constant values the results produced by τ_ε as a function of frequency are corresponding to variations in dielectric constant and change in structural properties. It is observed that τ_ε is maximum around 100 Hz for these samples which

represents the existence of orientational polarization of liquid crystal molecule with temperature.
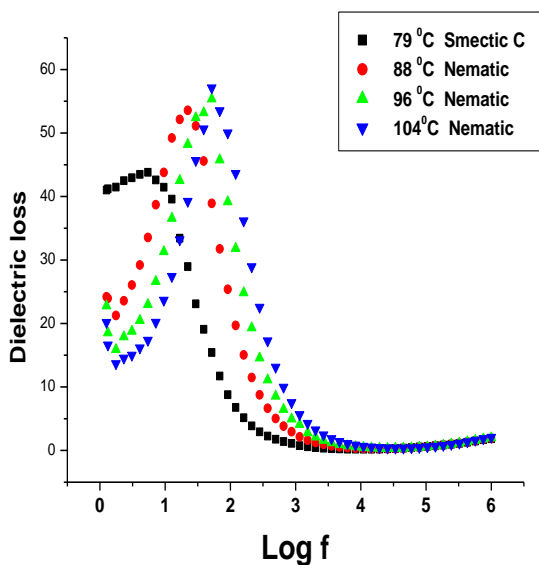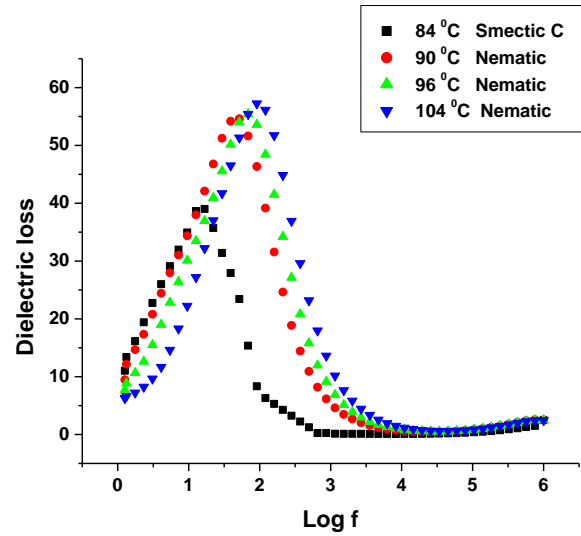

(a)

(b)

Figure2.Frequency dependence of thermal coefficient of dielectric constant τ_ε for (a) 14 MBABTH and (b) 16 MBABTH


(a)

(b)

Figure3. Frequency dependence of dielectric loss for (a)14 MBABTH and (b) 16 MBABTH at different temperatures

Figure 3 indicates the dielectric loss for 14 MBABTH and 16 MBABTH mesogens, the reported low dielectric loss at high frequencies is showing similarity with that of the variation of dielectric constant (figure 1) on owing to smaller angle of rotation. It is clear from this figure that the relaxation is shifted towards the higher frequency side as the temperature increased in both the samples. Molecules forming a nematic mesophase are rod like structures in their orientation, tending with long axes towards mutual parallelism and each molecule remaining free to rotate about its long axis and free to translate in an isotropic liquid. That the intermolecular forces are responsible for the mutual parallelism in the molecular long axes resulted in a long-range order, has been the subject of a large number of studies [26-31]. One particularly illuminating experiment [32] has been the dielectric relaxation of nematic liquid crystals for an external electric field directed either parallel or perpendicular to the local optic axis. Maier and Meier [32] reported that the dielectric loss associated with dipolar reorientation about the molecular long axis has occurred at frequencies comparable to isotropic liquids at the same temperature. The loss associated with reorientation about the short axis, however, occurred at frequencies nearly three orders of magnitude lower. This unusually low loss frequency reflects the cooperative nature of the molecular orientation. The static dielectric behavior of liquid crystals has also been of significant interest because of the importance of the dielectric anisotropy in describing the reorientation of liquid crystals in the presence of electric fields. This description has been particularly useful for applications involving electro optic devices [33,34].
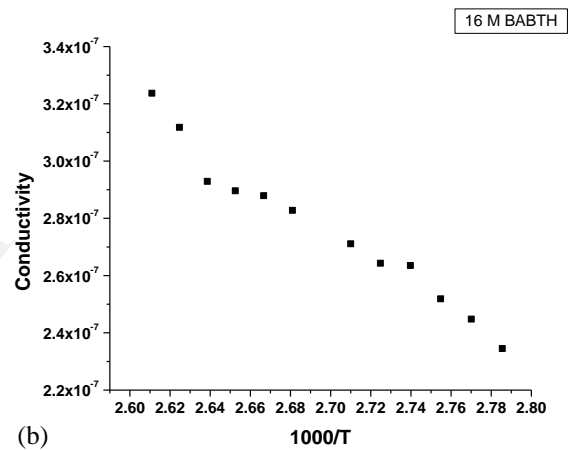
(a)

(a)
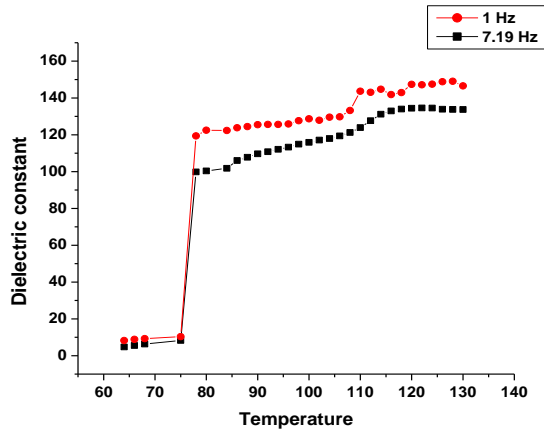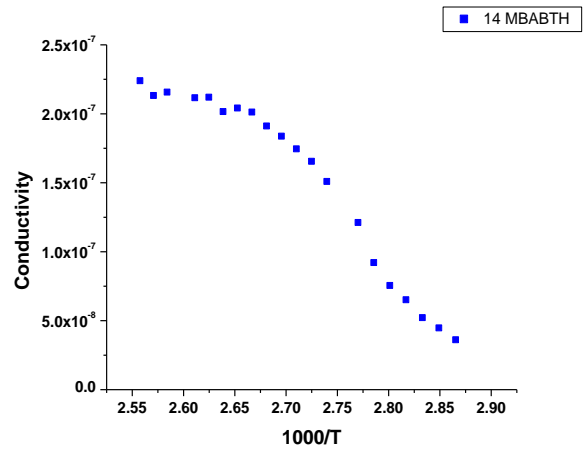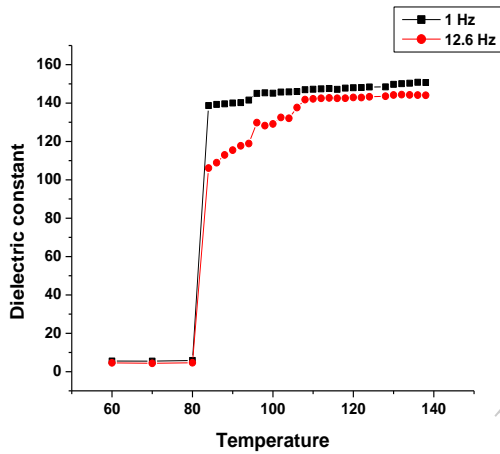
(b)

Figure 4.Temperature dependence of dielectric constant for (a) 14MBABTH and (b) 16 MBABTH at different Frequencies
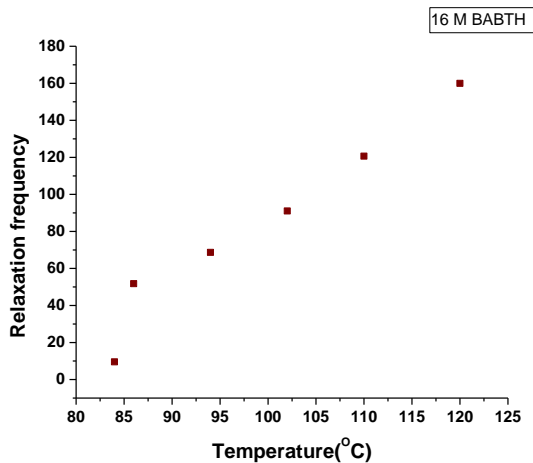

Figure 5. Temperature dependence of conductivity for (a) 14 MBABTH and (b) 16MBABTH at different temperatures

From the figure 4 it is observed that the values of dielectric constant remain almost constant up to solid phase and thereafter there is a sharp increase when the transition from solid to Smectic C. It shows a small dip at smectic C to nematic transition. So, the transition temperatures mentioned above are 78.8 ^{0}C for phase (Cr→SmA),79.7 ^{0}C for phase (SmA→SmC) and 109.6^{0}C for phase (N→I) for 14 MBABTH and 83.7^{0}C for phase (Cr→SmA),88.3^{0}C for phase (SmA→SmC, 107.2^{0}C for phase (N→I) for 16 MBABTH which are confirmed significantly through dielectric constant curves.

The temperature dependence of conductivity, relaxation frequency and activation energies are shown in figures from 5 to 7.
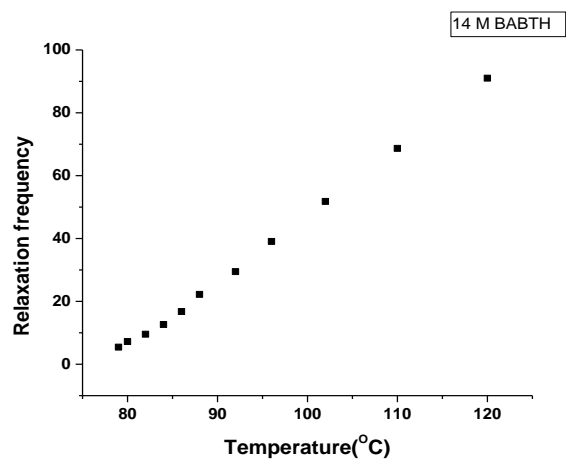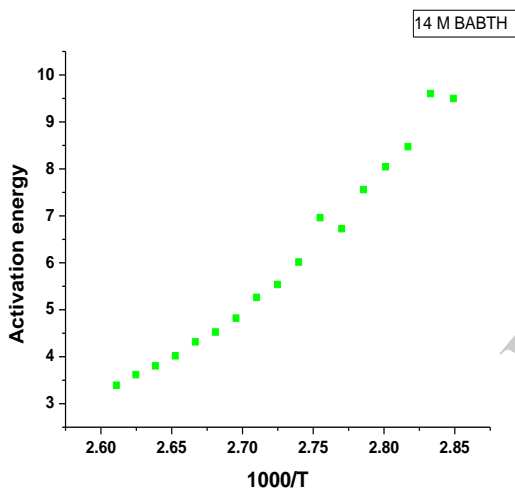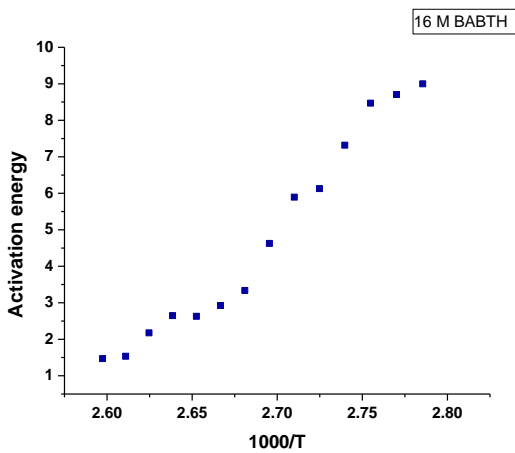

(a)

(b)

Figure 6.Temperature dependence of relaxation frequency for (a) 14 MBABTH and (b) 16 MBABTH

The conductivity as shown in figure5 has increased with increasing temperature in both samples. This is due to the restriction of charge carrier at low temperatures, as the temperature increased the mobility of charge carriers are increased so that the conductivity increases up to isotropic phase in both samples. Temperature dependence of relaxation frequency is shown in Figures 6. It shows that the relaxation frequency has increased with the increase of temperature up to isotropic phase. From Table2, it is observed that the relaxation times were decreased with increasing temperature in both the samples so that from this result we say that because of the easy orientation of the molecules are tend to align to original direction within a short period of time. The activation energy is the energy required to make reorientation of molecule and necessary to cause for dissociation. The relatively higher value of the activation energy is suggested to the higher potential barrier witnessed by the molecular dipole moment to orient to the field. At high frequencies the activation energy decreases so that it will have a relatively high dielectric strength. From figure 7, it is evident that the activation energy is increased with increased temperature. The activation energy has showed similar tendencies for both samples, it is increased with increasing temperature. This effect is due to role of the surface activity of dispersed particles on local order of the liquid crystal as a result of elastic distortions associated with the liquid crystal molecules.

(a)

(a)

(b)

Figure 7.Temperature dependence of Activation energy for (a) 14 MBABTH and (b) 16 MBABTH
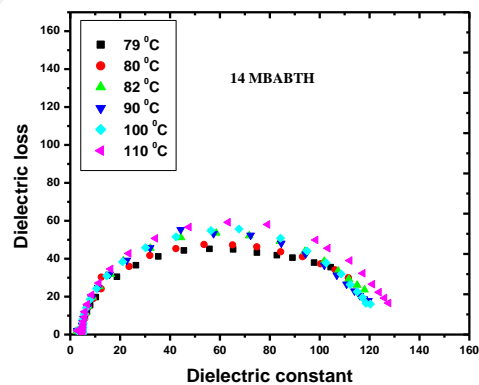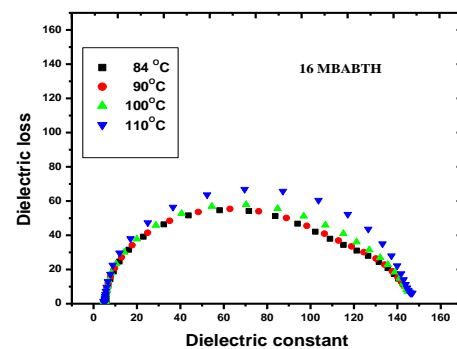
(b)

Figure 8. Cole-Cole plots at different temperature of (a)14MBABTH (b) 16 MBABTH

The variations between dielectric constant and dielectric loss plotted at different temperatures for both samples are shown in Figures 8. From these Figures, the relaxation frequency (f_R) corresponding to the peak value of the curve is determined and then, the relaxation time is calculated with the equation $\tau = 1/\omega$ where $\omega = 2\pi f_R$. These cole-cole plots showed Debye relaxation. The observed relaxation times from the cole cole plots and relaxation curves are in good agreement. Because of the chain length increasing in 16 MBABTH compound shows relatively high relaxation times when compared with 14 MBABTH.

Table 2. Ralaxation times at different temperature for 14MBABTH and 16 MBABTH

14 MBABTH		16 MBABTH	
Temperature	Relaxation time	Temperature	Relaxation time
(^{0}C)	(m sec)	(^{0}C)	(m sec)
78	78.11	74	184.50
80	59.66	80	138.88
84	44.98	82	104.82
88	33.93	84	79.11
90	19.36	90	59.63
102	14.56	100	19.30
108	10.98	108	14.56
116	8.28	112	10.98
124	6.25	124	8.28

IV. CONCLUSIONs

The phases and phase transition temperatures of homologous series of *(*6-methoxy-2-(4-*n*-alkanoyloxybenzylidenamino) benzothiazoles mesogens (*n* MBABTH for *n*=14 and 16 mesogens) are shown enantiotropic smectic C and nematic phases. The phase transition temperatures measured from both POM and dielectric studies are in good agreement. From dielectric studies space charge polarization is observed at low frequencies. τ_ε is maximum around 100 Hz for these samples which represents the existence of orientational polarization. Molecules forming nematic mesophase the intermolecular forces are responsible for the mutual parallelism in the molecular long axes resulted in a long-range order. The low loss frequency reflects the cooperative nature of the molecular orientation. The dielectric study reveals that these compounds are useful for applications involving electro optic devices.

V. ACKNOWLEDGEMENTS

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