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Dielectric and Phase Transition Studies of 1MC1EPOPB Ferroelectric Liquid Crystal

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An experimental study for R – 4′-(1 methoxycarbonyl –1 – ethoxy) phenyl 4 – (4 – octyloxyphenyl) benzoate (1MC1EPOPB) ferroelectric liquid crystal (FLC) using impedance analyzer and differential scanning calorimetric (DSC) technique is reported. The measurements have been done for permittivity, dielectric loss at different frequencies and temperatures. The data have been analyzed for distribution parameters involved in Havriliak-Negami's equation. The relaxation time measured for different relaxation processes is listed. The measurements for static dielectric constants in the parallel($\varepsilon_{\parallel}$) and perpendicular($\varepsilon_{\perp}$) directions at different temperatures have also been taken. The transition temperatures are identified for cooling and heating conditions using DSC technique as well as dielectric measurements. The interesting results have been found and some unknown phases have been monitored, the reason for which needs theoretical interpretation.

Keywords: Ferroelectric Liquid Crystal; Dielectrics; Phase Transition; Liquid Crystal; Electro-optic Devices

INTRODUCTION

The ferroelectric liquid crystals (FLCs) are of current interest as they are useful for electro-optic properties of display devices [1-3] and their applications as high speed switching devices. Yoshino et al. [4] have synthesized FLCs with a large spontaneous polarization to establish a fast response for electro-optic devices. He has also evaluated refractive index [5] at different temperatures for R – 4'-(1 methoxycarbonyl –1 – ethoxy) phenyl 4 – (4 – octyloxyphenyl) benzoate (1MC1EPOPB) a smectic material. We have chosen this system for the purpose to study dielectric response and thermodynamical properties. Measurements are conducted for static dielectric constants in parallel($\varepsilon_{\|}$) and perpendicular directions($\varepsilon_{\perp}$) at different temperatures using impedance analyzer (model HP-4194A) The measurements for permittivity(ε') and dielectric loss(ε'') at different frequencies and temperatures have been done also using impedance analyzer (model Solartron 1260). The data will be analyzed using Havriliak Negami equation. Differential Scanning Calorimeter(DSC) (model DSC-7) has been used for the measurement of heat flow at different temperatures to study thermodynamical parameters.

The results reported are new and they are fruitful for the study of switching time in display devices and to understand the physical basis of relaxation mechanism for the phase transitions identified in the FLC chosen.

EXPERIMENTAL DETAILS:

Fabrication of Cell

We have prepared capacitor cells from two indium tin oxide(ITO) coated glass plates. The conducting surface of the glass plate is cleaned well with $CHCl_3$ and dried. The parallel alignment of the sample molecules is obtained by coating of the silane solution (0.2% solution of phenyl trichlorosilane in toluene) while to get the planar alignment of the sample molecules, the BEL polymide solution (solute 2%) is used. We kept the plate, covered with aluminium foil, in the oven at 300^0C for 1 hr. for the purpose to polymerize this coating.The glass plate is taken out of the oven after the plate comes at ambient temperature and it is rubbed unidirectionally by tissue paper to obtain desired orientation of the molecules. This glass plate is cut into two

pieces which are separated by mylar spacers of desired thickness (12μm or 50μm) kept along the length of the plates so that length sides of the plates are closed while both breadth sides are open. The plates are placed one above the other such that their ends shifted on both sides to leave place for solder two wires for connection purpose. Now it is placed in the hot stage model METTLER FP82HT (temperature ranges from room temperature to 375°C with uncertainty in temperature of about less than 0.5°C) at 255°C and pressed by a wooden block to join them together. Material concerned is filled in the cell in isotropic phase using the principle of capillary action.

Static Measurements

The static dielectric constants($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) for these materials have been measured on a Hewlett-Packard impedance analyzer model HP-4194A (frequency range 100Hz to 15MHz), connected with a computer. The resolution and accuracy are 1mHz and ± 20ppm at 23°C respectively. The cell filled with material is kept in the hot stage model METTLER FP82HT. The computer program for the measurement of capacitance in parallel to the conductance has been developed to run at frequency 100Hz with the temperature variation from isotropic to crystal phase at the decreasing rate of 2°C/min with the record of small changes within this rate. Oscillator signal of the impedance analyzer is adjustable in the range 10mV to 1V rms value but it has been kept at 500mV in different runs. The temperature is controlled by a central processor unit model METTLER FP90 and it is measured using thermocouple connected with a digital multimeter with an uncertainty estimated to the 4th decimal place by the computer.

Dispersion Measurements

The dielectric permittivity and dielectric loss for these materials are measured on an impedance analyzer model Solartron 1260(frequency range 10μHz to 32MHz), connected with a computer. The uncertainty is ± 100ppm with stability of ± 10ppm in 24hrs within 1°C. The resolution varies from 10μHz to 1Hz depending upon the range of frequency from 10μHz to 32MHz. The planar oriented cell filled with material is kept in the hot stage model METTLER FP82HT. The computer program for the measurement of capacitance in parallel to the conductance has been developed to run at different points of equal intervals in the log frequency scale. We have set the range of the frequency measurement from 2Hz to 2MHz but in the present work we

are reporting the measurement from 100Hz to 2MHz with the temperature variation in steps of 0.2 to 5^0C near the phase transition and away from it. Oscillator signal of the impedance analyzer is adjustable but it has been kept at 1V in different runs in this work. The temperature is controlled by a central processor unit model METTLER FP90.

The data of permittivity and dielectric loss are analyzed using distribution of relaxation time(DRT) mechanism [6]. A generalized expression for complex permittivity(ε^*)given by Havriliak Negami [6] is given here below:

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 + (|\omega\tau)^{1-\alpha}]^\beta} \qquad (1)$$

Where α and β are distribution parameters. For $\alpha = 0$ and $\beta = 1$, we get Debye relaxation mechanism [7] while $\alpha \neq 0$, $\alpha \neq 1$ and $\beta = 1$ gives Cole-Cole [8] distribution, $\alpha = 0$ and $\beta \neq 0$, $\beta \neq 1$ gives Cole-Davidson [9] relaxation mechanism and for $\alpha \neq 0$, $\alpha \neq 1$ and $\beta \neq 0$, $\beta \neq 1$ the generalized expression given here above is valid. α and β have been computed by simulating the data of ε', ε'', ε_∞ and ε_s at different frequencies.

Differential Scanning Calorimeter Technique

The thermodynamical measurement of ferroelectric liquid crystal chosen are done using Perkin-Elmer Differential Scanning Calorimeter(DSC) model DSC-7, connected with a computer. The mass of the sample around 2-3mg is needed which is weighed by a balance (model METTLER UMT2 FACT) having an accuracy of one microgram and it is crimped in aluminium pans. This crimped pan is kept in one of the sample holders of DSC while other one identical in size without material is kept in the another sample holder as the reference pan. Nitrogen gas is flown at pressure about 25-30 lb/inch^2 to purge any impurity around the sample in the sample holder. DSC is allowed to run at the scanning rate of 5^0C/min for the first few cycles in the temperature range of isotropic to crystal phase to stabilize the transition temperatures and the heat of the transitions. When stabilization is achieved it is run at 1.0^0C/min for heating and cooling the sample under investigation.

RESULTS AND DISCUSSIONS

We have measured dielectric constant in parallel and perpendicular directions using impedance analyzer at different temperatures to identify the phase transitions for 1MC1EPOPB in the temperature range from 40^0C to 155^0C. The variations of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ as a function of temperature are given in Figure (1) and (2) respectively.

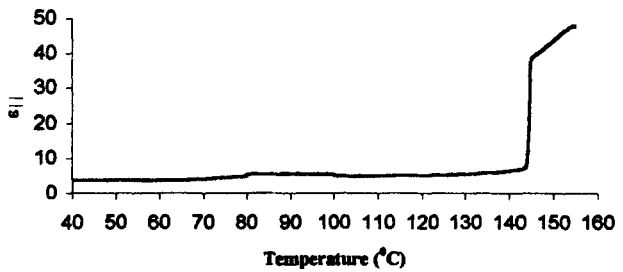

FIGURE 1 Variation of $\varepsilon_{\parallel}$ with temperature for cooling.

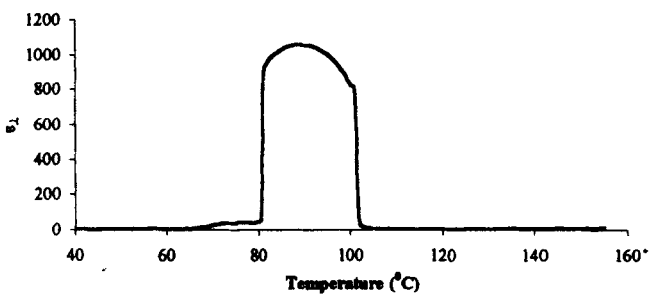

FIGURE 2 Variation of $\varepsilon_{\perp}$ with temperature for cooling.

The measurement of the dielectric permittivity and the dielectric loss have been carried out using impedance analyzer and the analysis of the observed data has been performed using eqn.(1).

The distribution parameters α and β are fitted to the data of permittivity, dielectric loss, static dielectric constant and permittivity at high frequency.The variation of distribution parameters occurring in

eqn.(1) as a function of temperature are plotted in Figure (3). The dielectric relaxation time mechanism(DRT) has been assumed for the analysis. The variation of maximum relaxation time with temperature are illustrated in Figure (4).

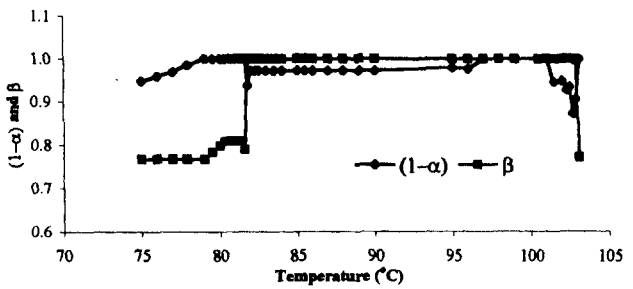

FIGURE 3 Variation of (1-α) and β with temperature for cooling.

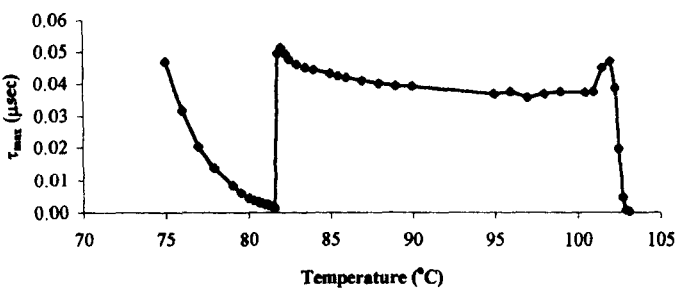

FIGURE 4 Variation of τ_{max} with temperature for cooling.

The observed data of heat flow for heating and cooling, peak transition temperature(T), width of transition(ΔT) and transition enthalpy(ΔH) are given in Table 1 for different phases of 1MC1EPOPB.

TABLE 1 Width of the transition temperature ΔT (in ^0C), peak transition temperature T_P (in ^0C) and transition enthalpy ΔH (in J/g) with scanning rate of 1^0C / min for different mesophase transitions of 1MC1EPOPB for heating and cooling.

Phase	Heating			Cooling		
Transition	ΔT	T_P	ΔH	ΔT	T_P	ΔH
I → Sm A	2.219	148.006	9.185	1.631	147.743	-9.611
SmA→SmC*	8.292	97.68	47.633			
SmC*→SmX	_	_	_	1.98	81.835	-2.979
SmX→K	_	_	_	2.036	45.893	-2.356

An examination of the Figure 1 reveals phase transition temperature for isotropic to Smectic A as 146.3^0C and that for Smectic A to Smectic C* as 102^0C. The temperature variation from Smectic C* to crystal state gives some discontinuity at temperature 80.9^0C. It may be either a new phase or some higher order transition of smectic phase. The true explanation for this phase change at 80.9^0C is not obvious at this stage but it is significant for 1MC1EPOPB FLC and it needs theoretical explanation. Figure 2 gives phase transition temperature for Smectic A to Smectic C* as 102.3^0C and Smectic C* to Smectic X as 82.4^0C.

We have analyzed the dispersion data using equ.(1) and the complex permittivity plots as a function of distribution parameters α and β. The plots of $(1-\alpha)$ and β as a function of temperature are given in Figure 3 which shows that the material in question in the temperature range 96.3 to 100.4^0C (Sm C*) behaves in a manner resembling closely the Debye behaviour i.e. there is one relaxation time. The variation of $(1-\alpha)$ and β in the range of temperatures 81.8 to 96.3^0C (Sm C*) and 100.4 to 102.7^0C (Sm C*) show departure from the Debye response and it is mathematically represented by Cole-Cole behaviour in which the complex plane is depressed by $\alpha\pi/2$. This dielectric behaviour gives more than one relaxation time like overall rotation and group rotation. The dielectic properties in the temperature region 78.8 to 81.8^0C (Sm C*) also give non Debye behaviour of

relaxation because $\alpha = 0$ and $\beta \neq 1$ which corresponds to Cole-Davidson asymmetrical dielectric behaviour. This gives asymmetrical skewed arc which is less flattened than the Havriliak-Negami mechanism. It is a pear shaped form of tilt angle $\beta\pi/2$ in equ.(1). In the temperature range 75 to 78.8^{0}C, corresponding to unknown phase Sm X generalized Havriliak-Negami equ.(1) is valid. The parameters α and β explain the dielectric interactions and distribution of relaxation time for rotation of different groups and overall orientation of the molecule. These two parameters formula given in equ.(1) is thus capable of fitting the observed permittivity (ε') and dielectric loss (ε'') for different phases of the ferroelectic liquid crystal chosen. Figure 4 gives decreasing trend of variation of relaxation time within the range of temperature 81.8 to 100.7^{0}C with a discontinuity around 96.1^{0}C as also observed in the variation of $(1 - \alpha)$ in the Sm C* phase. But it is not sharp and it may be higher order transition.

Figure 3 and 4 show that the phase transitions from Sm A to Sm C* is at 102.7^{0}C and Sm C* to Sm X is at 81.8^{0}C. The differences between transition temperatures found in Figure 1, 3 and 4 are in the range 0.7^{0}C and 0.9^{0}C respectively which is within the phase transition width.

The Table 1 for the peak transition temperature, width of transition and transition enthalpy provides thermodynamical behaviour and the transition temperatures are within the mean deviation of ±0.56 for cooling for the smectic C* to smectic X transition to that found using the technique of dielectric measurement. However DSC technique gives about 4.7^{0}C less transition temperature as compared to dielectric technique due to using heating process rather than cooling used in the dielectric measurement.

A comparison of the variations of static dielectric constant of the FLC chosen for this work and those used by Taniguchi et al. [10] is also reported. The spontaneous polarization for the liquid crystal 1MC1EPOPB is 170 nc/cm^2 and that for (R) - 1 methoxycarbonyl –1 – ethyl 4 – (4' – octyloxyphenyl) benzyloxybenzoate (1MC1EOPBB); (S) – 2- methoxycarbonyl –1 – propyl 4 – (4' – octyloxyphenyl) benzoate (2MC1POPBB); (R) – 3- methoxycarbonyl –2 – propyl 4 – (4' – octyloxyphenyl) benzyloxybenzoate (3MC2POPBB) is 51, 12 and 18 nc/cm^2 respectively. This FLC has relatively about 3 times spontaneous polarization as compared to 1MC1EOPBB, 10 times to 3MC2POPBB and 14 times to 2MC1POPBB. The peak values of the dielectric constant are about 706.8, 264.7, 135.3 and 70.6 for Sm C*

phase around their respective temperatures and they are 2.67, 5.22 and 10.0 times less than that of the value of present FLC. The FLC chosen in this work is more useful in switching devices due to its large spontaneous polarization and highest.

CONCLUSION

The work reported in this paper is new and it is reported for the first time. It is useful as it may pave the way to formulate the switching time for FLC of large spontaneous polarization as well as it may be more effective and efficient in display devices. This study when supplemented with the work of Nakayama et al. [5] about infiltration and tunability may prove to be a useful photonic material.

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