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Measurement of Dielectric Response of 1MC1EPOPB and 1BC1EPOPB Ferroelectric Liquid Crystals

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ABSTRACT

Dielectric measurements have been carried out using an impedance analyzer for two ferroelectric liquid crystals R-4' (1-methoxycarbonyl-1-ethoxy) phenyl 4-(4-octyloxy phenyl) benzoate (1MC1EPOPB) and R-4' (1-butoxycarbonyl-1-ethoxy) phenyl 4-(4-octyloxy phenyl) benzoate (1BC1EPOPB). The two types have large spontaneous polarization, $+1700 \mu\text{C}/\text{m}^2$ for 1MC1EPOPB and $+2400 \mu\text{C}/\text{m}^2$ for 1BC1EPOPB. The permittivity and dielectric loss have been measured at different temperatures in the range 343.0 K to 383.0 K for 1MC1EPOPB and 318.0 K to 353.0 K for 1BC1EPOPB in the frequency range 2 Hz to 2 MHz. Both of the ferroelectric liquid crystals, 1MC1EPOPB and 1BC1EPOPB show a new phase smectic X along with smectic C* and smectic A phases. The work reported in this paper is new and is very useful in understanding their application in switching devices.

Index Terms — Dielectric properties, ferroelectric liquid crystal, dielectric permittivity, dielectric loss, phase transition, dielectric relaxation, spontaneous polarization, impedance analyzer, interaction, switching devices.

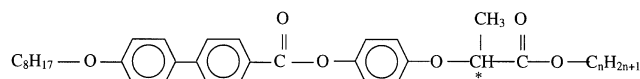
1 INTRODUCTION

THE dielectric spectroscopic technique [1–4] has been used by various workers for the study of systems in different phases. This method [5–6] has been found to be one of the best ones to make measurement of permittivity and dielectric loss with high accuracy and sensitivity. In this paper we have chosen R-4' (1-methoxycarbonyl-1-ethoxy) phenyl 4-(4-octyloxy phenyl) benzoate (1MC1EPOPB) and R-4' (1-butoxycarbonyl-1-ethoxy) phenyl 4-(4-octyloxy phenyl) benzoate (1BC1EPOPB), smectic ferroelectric liquid crystals, which are relatively of large spontaneous polarization $+1700 \mu\text{C}/\text{cm}^2$ and $+2400 \mu\text{C}/\text{cm}^2$ respectively. These ferroelectric liquid crystals were synthesized by Yoshino et al. [7–8]. The dielectric spectroscopic technique has been used to measure permittivity (ϵ'_{\perp}) and dielectric loss (ϵ''_{\perp}) at frequencies 2

Hz to 2 MHz in the temperature range 343.0 K to 383.0 K for 1MC1EPOPB and 318.0 K to 348.0 K for 1BC1EPOPB using planar aligned cells. The variations of permittivity and dielectric loss in the selected range of frequencies and temperatures are analyzed. The variations of dielectric strength ($\Delta\epsilon$) and relaxation frequencies (f_r) in the corresponding temperature ranges are also studied for the two ferroelectric liquid crystals under study.

2 EXPERIMENTAL DETAILS

The samples of 1MC1EPOPB and 1BC1EPOPB, synthesized by Yoshino et al [7–8], have the following structures



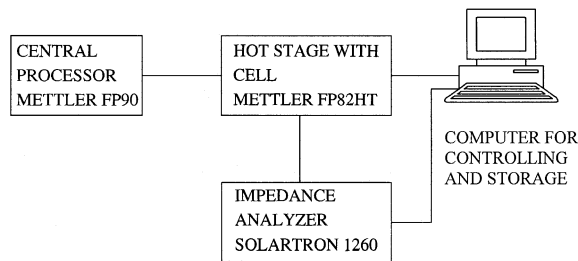
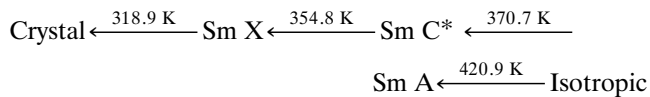


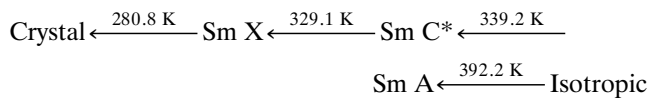
Figure 1. Block diagram of experimental arrangement with Impedance Analyzer, Hot stage, Central Processor and Computer for dielectric measurements.

$n = 1$ 1MC1EPOPB and $n = 4$ 1BC1EPOPB

The two samples have following phase sequence
1MC1EPOPB:



1BC1EPOPB:



The block diagram of the apparatus used with name of each block marked is shown in Figure 1. The experimental arrangement for dielectric technique consists of an impedance analyzer model Solartron 1260 (10 μ Hz to 32 MHz), hot stage model METTLER FP82HT and central processing unit model METTLER FP90 connected with a computer. The sample is filled in a planar oriented cell in isotropic phase using the principle of capillary action. The planar oriented cell with thickness 48 μ m is used for 1MC1EPOPB and 33 μ m for 1BC1EPOPB for dispersion studies. The uncertainty in the measurement is ± 100 ppm with stability of ± 10 ppm in 24 h within 1 K. The resolution varies from 10 μ Hz to 1 Hz. The planar oriented cell filled with material is kept in the hot stage. The computer program has been developed to run at different points of equal intervals in the log frequency scale for the measurement of capacitance in parallel to the conductance. We have set the range of the frequency measurements for the two samples under investigation with the temperature variation in the steps of 0.2 to 5 K near the phase transition and away from it. The impedance analyzer has adjustable oscillator signal but the signal is kept at 1 V in different runs in the present work. The central processing unit model METTLER FP90 is used to control the temperature of the hot stage.

3 RESULTS AND DISCUSSIONS

We have illustrated the variations of dielectric permittivity and dielectric loss as a function of frequency in 2d at middle temperature of each phase for 1MC1EPOPB and

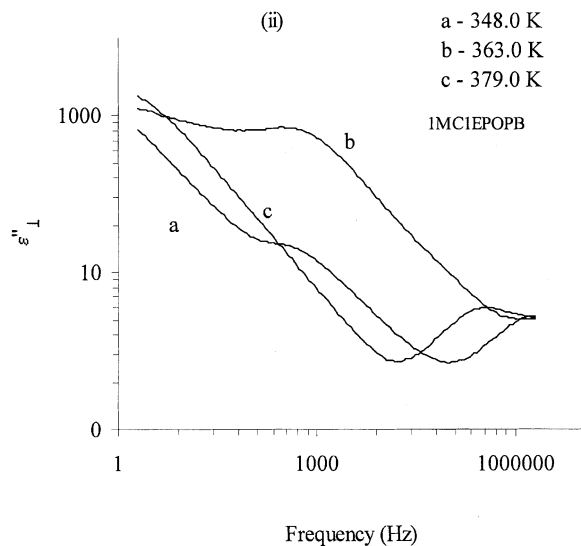
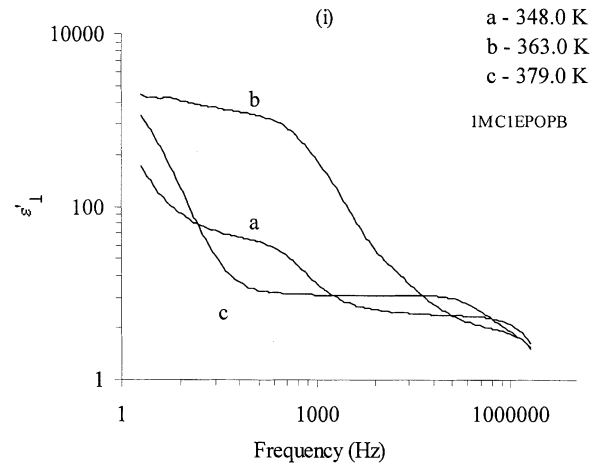


Figure 2. i, dielectric permittivity (ϵ'_{\perp}); ii, dielectric loss (ϵ''_{\perp}) for 1MC1EPOPB at (a) 348.0 K; (b) 363.0 K and (c) 379.0 K.

1BC1EPOPB in Figures 2 and 3. Although similar characteristics may be seen at all other temperatures except in the case of smectic A and smectic X where the peak shifts towards the lower frequency as the temperature decreases. The variation of relaxation frequency (f_r) and dielectric strength ($\Delta\epsilon$) with temperature for 1MC1EPOPB and 1BC1EPOPB are plotted in Figures 4 and 5, respectively.

An examination of Figures 2 and 3 gives that the Soft mode occurs for smectic A phase above 100 kHz for 1MC1EPOPB as well as for 1BC1EPOPB showing loss peak around 200 kHz for 1MC1EPOPB at 379 K and 100 kHz for 1BC1EPOPB at 344 K. Figures 2 and 3 also illustrate that the Goldstone mode originates for smectic C* phase below 1 kHz for 1MC1EPOPB and 500 kHz for 1BC1EPOPB. The loss peaks are occurring around 0.3 kHz for 1MC1EPOPB at 363 K and 0.5 kHz for 1BC1EPOPB at 333 K. The relaxation process shown in

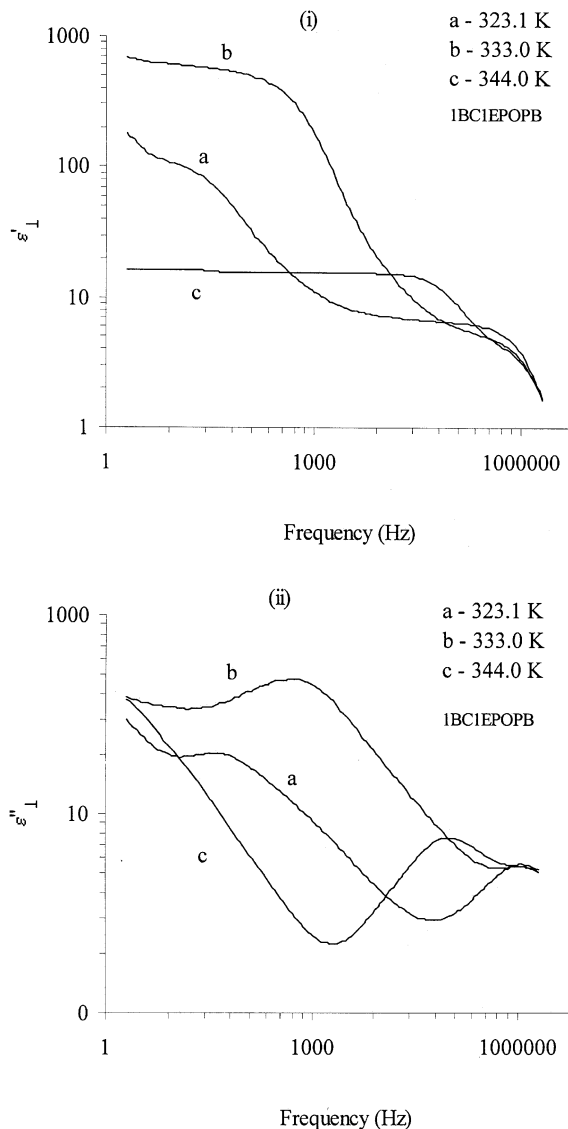


Figure 3. i, dielectric permittivity (ϵ'_{\perp}); ii, dielectric loss (ϵ''_{\perp}) for 1BC1EPOPB at (a) 323.1 K; (b) 333.0 K and (c) 344.0 K.

Figures 2 and 3 in smectic X phase is below 10 kHz for 1MC1EPOPB and 0.4 kHz for 1BC1EPOPB giving loss

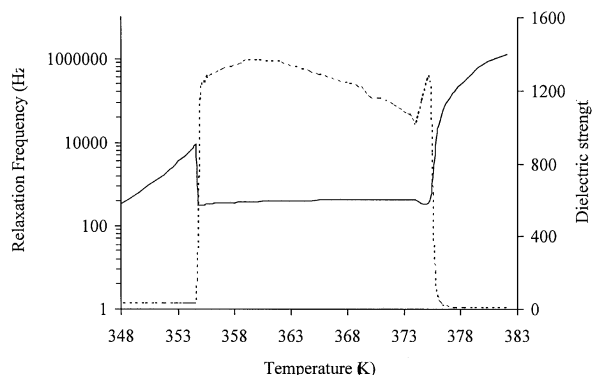


Figure 4. Variation of relaxation frequency (f_r) (—) and dielectric strength ($\Delta\epsilon$) (----) with temperature for 1MC1EPOPB.

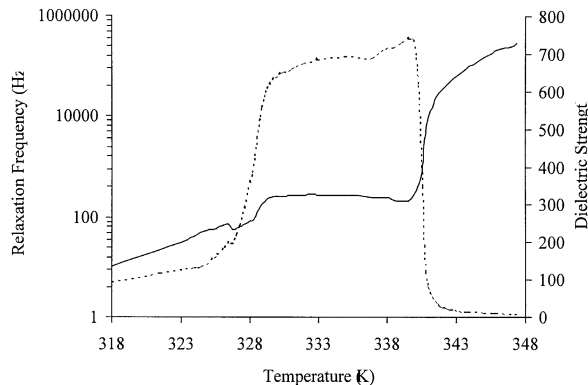


Figure 5. Variation of relaxation frequency (f_r) (—) and dielectric strength ($\Delta\epsilon$) (----) with temperature for 1BC1EPOPB.

peak at 0.3 kHz for 1MC1EPOPB at 348 K and 0.04 kHz for 1BC1EPOPB at 323.1 K. We expect Soft mode for smectic X as the characteristics of smectic A and smectic X seems to be similar in variation.

The observed data of dielectric permittivity (ϵ'_{\perp}) and dielectric loss as a function of frequency in the log-log plot in approximately the mid temperatures of smectic A (379 K), smectic C* (363 K) and smectic X (348 K) phases for 1MC1EPOPB are shown in Figures 2i and 2ii, respectively. The log-log plots of dielectric permittivity and dielectric loss at approximately the mid temperature of smectic A (344.0 K), smectic C* (333.0 K) and smectic X (323.1 K) phases for 1BC1EPOPB are given in Figures 3i and 3ii, respectively. Figure 2i makes it evident that at very large frequency of 2000 kHz the permittivity plots with frequency for 379.0 K, 363.0 K and 348.0 K coincide giving a permittivity independent of temperature. The plots of ϵ'_{\perp} for 379.0 K and 363.0 K have one point of intersection with $\epsilon'_{\perp} = 9.54$ at 42.4 kHz. The permittivity plot for smectic X at 348.0 K has 3 points of intersections with the permittivity plot for smectic A at 379.0 K around 409 kHz, 1.59 kHz and 0.0152 kHz. The variation of ϵ'_{\perp} with frequency for smectic X at 348.0 K has one common point with the same plot for smectic C* at 363.0 K at about 118 kHz. The variation of ϵ'_{\perp} with frequency for smectic A at 379.0 K shows that the decrease in the value of ϵ'_{\perp} is very sharp and almost linear from 1120 at 0.002 kHz to 16.1 at 0.047 kHz as the frequency is increased and then it is almost independent of frequency till 9.38 at 66.8 kHz. On further increase in frequency it decreases again to the value 2.3 at 2000 kHz. The plot of ϵ'_{\perp} decreases from 1960 at 0.002 kHz to 922 at 0.259 kHz and then decreases to 2.3 at 2000 kHz much faster for smectic X at 363.0 K as the frequency increases. The plot of permittivity for smectic X has the smallest value 290 of ϵ'_{\perp} out of the three phases under investigation at 0.002 kHz.

Figure 2ii shows that the plots of dielectric loss with frequency for smectic A at 379.0 K, smectic C* at 363.0 K

and smectic X at 348.0 K have a common value about 2.67 at 2000 kHz. The plot of ϵ''_{\perp} for smectic A intersects the plot for smectic C* around at 0.004 kHz and 409 kHz. It also has two points of intersection with the similar plot for smectic X at about 0.206 kHz and 33.8 kHz. The plot of dielectric loss for smectic A has the value of 1790 at 0.002 kHz, which is the largest of the three plots. As the frequency is decreased the value of dielectric loss decreases linearly till 0.741 at 17.1 kHz from there it changes the sign of the slope and starts rising to 3.56 at 365 kHz and then again starts decreasing on further increase in frequency till 2000 kHz. The similar plot for smectic X decreases from 663 at 0.002 kHz to 0.716 at 105 kHz and then the slope is reversed and the dielectric loss starts increasing with frequency till 2000 kHz.

From Figure 3i it is clear that the permittivity plots with frequency for 344.0 K, 333.0 K and 323.1 K coincide giving a permittivity independent of temperature at very large frequency of 2000 kHz. The curve for smectic C* and smectic X have one more point of intersection at about 83.7 kHz while the curves for smectic C* and smectic A intersect around 10 kHz. Also there are two points of intersection for smectic A and smectic X at about 165 kHz and 0.400 kHz. The smectic C* has largest value 680.77 of ϵ'_{\perp} out of the three phases under investigation at 0.002 kHz. As the frequency increases the value of ϵ'_{\perp} decreases from 680.77 to 365.1 at 0.363 kHz slowly and then the variation in the value of ϵ'_{\perp} is steeper. The smectic X has the value of $\epsilon'_{\perp} = 177.11$ at 0.002 kHz and decreases to 96.25 at 0.015 kHz with increase in frequency. As the frequency is further increased from 0.015 kHz, the ϵ'_{\perp} falls sharply to 7.76 at 4.4 kHz and then it is almost independent of frequency up to 260 kHz and hereafter it decreases at increasing rate. The permittivity plot with frequency for smectic A has nearly constant value $\epsilon'_{\perp} = 16.42$ up to 22.7 kHz before it has sharp decrease.

Figure 3ii reveals that at 2 MHz all the three curves for variation of ϵ''_{\perp} with frequency corresponding to smectic A, smectic C* and smectic X have nearly equal values. The plot, showing the changes in ϵ''_{\perp} with frequency for smectic A at 344.0 K, intersects the similar curves for smectic C* at 333.0 K and smectic X at 323.1 K around 85 kHz and 10 kHz respectively in log-log plot. But smectic C* and smectic X curves do not intersect each other within the frequency range from 2 Hz to 2 MHz of measurement. The smectic A curve for dielectric loss with frequency decreases with nearly a constant slope from 140 at 2 Hz to 0.65 at 880 Hz and attains a minima with $\epsilon''_{\perp} = 0.49$ at 1.9 kHz. The lowest loss amounts to least possibility of dispersion for smectic A phase at 344 K. On further increase in frequency the direction of slope reverses and dielectric loss increases with constant slope to 4.09 at 40.2 kHz and attains a peak at 104 kHz having the value $\epsilon''_{\perp} = 5.82$ after which the slope again reverses its direction. The curve for smectic C* has the value $\epsilon''_{\perp} = 149.58$ at 2 Hz and has

very slow decrease to 114.02 at 14 Hz with the increase in frequency. Now it starts increasing and after attaining a maximum value $\epsilon''_{\perp} = 229$ at 511 Hz it decreases. After 1 kHz the ϵ''_{\perp} decays with a constant slope up to 232 kHz and then it is nearly constant. The smectic X curve has value 88.2 for ϵ''_{\perp} at 2 Hz and then decreases with the increase in frequency up to 37.5 at 12 Hz and after that small variations with a constant slope are found. This slope changes sign after 59.6 kHz.

The change of relaxation frequency (f_r) and dielectric strength ($\Delta\epsilon$) when the structure is transformed from the twisted (smectic A) to helical one (smectic C*), is seen in Figures 4 and 5. On cooling, for both the samples the change of structure is manifested by a jump down in f_r and jump up in $\Delta\epsilon$. In smectic C* the molecules are tilted with respect to the smectic layer normal direction giving helical structure while in the smectic A phase they are along the layer normal direction and show twisted structure. Thus in the vicinity of smectic A to smectic C* transition, thermal fluctuations cause fluctuations in the amplitude of either long-range (smectic C*) or local (smectic A) tilt. But in both the phases, an associated elastic constant controls the magnitude of these fluctuations. This elastic constant softens on approaching the transition and therefore, the amplitude of fluctuation increases. This in turn increases the contributions to the dielectric strength and an accompanying decrease in the relaxation frequency and therefore $\Delta\epsilon$ has a maximum and f_r a minimum at the smectic A to smectic C* transition. While at the smectic C* to smectic X transition $\Delta\epsilon$ jumps down and f_r jumps up. From Figures 4 and 5 it is evident that the dielectric strength is largest in the smectic C* phase and decreases sharply in smectic X and smectic A phases for both the samples. The relaxation frequency is maximum in the smectic A phase but it is almost constant for smectic C* in both the samples under study.

4 CONCLUSION

THE Goldstone mode and Soft mode gives loss peaks around frequencies 0.3 kHz and 200 kHz for 1MC1EPOPB at 379.0 K and 363.0 K respectively while 0.5 kHz and 100 kHz for 1BC1EPOPB at 333.0 K and 344.0 K respectively. Our observations indicate that smectic X phase in the temperature range 322.9 K to 354.8 K for 1MC1EPOPB and 280.8 K to 329.1 K for 1BC1EPOPB has the same trend of variations in both the systems chosen for all the parameters (ϵ'_{\perp} , ϵ''_{\perp} , f_r and $\Delta\epsilon$). We have also observed that different phases coincide at some frequency for both the systems. Further we have concluded that disorder increases for smectic A and smectic X with the rise in temperature while more ordered state is found for smectic C* for both the systems at almost all the temperatures. The measurements reported in this paper are fruitful for understanding molecular collisions, structure

and change of the phase as a function of temperature and dielectric behaviour at different frequencies. These observations for smectic ferroelectric liquid crystals considered may help in understanding its applications in fabricating fast switching devices.

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