

# CHAPTER-5

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*Dielectric and electro-optic properties of two compounds of the biphenyl benzoate cored chiral mesogenic series having only ferroelectric SmC\* phase*

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## 5.1 Introduction

In the last two chapters we have discussed about three compounds of the selected series, all having three oligomethylene spacers but different number of carbons in the fluorinated chain. The shortest member 1F3R, having only one fluorine in the chain was found to have only orthogonal phases, with two hexagonal higher order smectic phases SmE\* and SmB\* along with SmA\* phase. As a result of adding more carbon atoms in the fluorinated chain, in the next two higher members, 2F3R and 3F3R, tilted phase were introduced – SmJ\*/G\*, SmF\*, SmC\* - along with SmA\*. However in the low temperature regime the compounds retained the hexagonal phase structure. In this chapter we report properties of two higher derivatives of the series, with same number of oligomethylene spacers but having more number of carbons in the fluorinated chain, namely (*S*)-(+)-4'-[(3-undecafluoro-hexanoyloxy)prop-1-oxy]biphenyl-4-yl 4-(1-methylheptyloxy)- benzoate (5F3R) and ((*S*)-(+)-4'-[(3-tridecafluoro-heptanoyloxy) prop-1-oxy]biphenyl-4-yl 4-(1-methylheptyloxy)-benzoate (6F3R) [1]. As an effect of adding fluorine in the chains all the hexagonal or orthogonal phases are eliminated from these compounds. They are found to exhibit only the tilted SmC\* phase albeit within a wide temperature range and directly melt into isotropic phase which is not common in FLC compounds. The intermediate member of this series having 4 carbon atoms in its fluorinated chain viz., 4F3R has also been studied by us but not included in this dissertation and is also found to have similar phase behaviour [2]. For displaying only ferroelectric SmC\* phase over a wide span of temperature make them promising material to be used as dopant in the preparation of long range ferroelectric liquid crystal mixture. Besides, for having such a typical

phase behaviour, the study of the different dielectric and electro-optic properties of these compounds might be proved to be revealing. Keeping these in mind we discuss detailed dielectric and electro-optic characterisation of these two compounds in this chapter. The molecular structure of 5F3R and 6F3R are shown in **figure 5.1**.

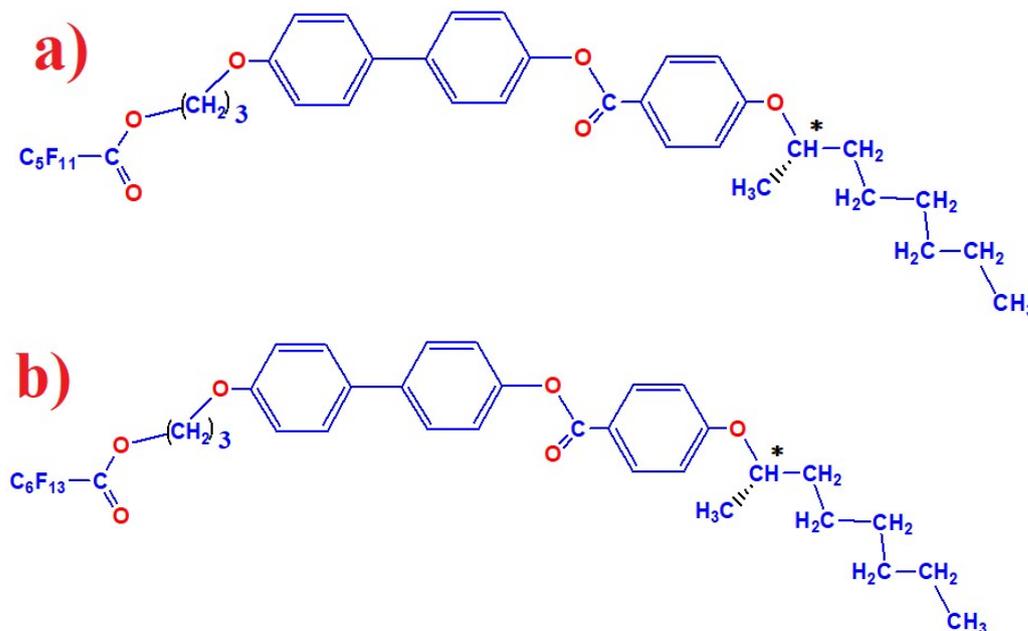


Figure 5.1: Molecular structure of a) 5F3R and b) 6F3R.

## 5.2 Experimental methods

The phase transition temperatures of the compounds were identified by polarising optical microscopy, using Olympus BX41 polarizing microscope equipped with a CCD camera. A Hioki 3532 50 impedance analyzer was used to perform the frequency dependent dielectric study in the frequency range from 40 Hz to 5 MHz. The dielectric spectra were fitted to the Cole-Cole function [3], modified for the low frequency parasitic effect. Spontaneous polarization was measured by reversal current method [4]. An Agilent 33220A function generator and a Tektronix TDS 2012B storage oscilloscope were used for electro-optic measurements. The response time was measured by measuring the time delay of the occurrence of polarization bump from the applied square

pulse (of frequency 60Hz) edge while monitoring the voltage across a resistor R in series with the cell. Optical tilt of the molecules was determined by electrically switching the sample under a low frequency (10 mHz) square wave and simultaneously observing it under polarizing microscope. The angle of rotation of the sample between two dark states was considered as a measure of double the tilt angle.

To control the temperature, in all experiments a Mettler FP90 temperature controller with FP82 hot-stage was used. The detailed procedures of each experiment have been discussed in chapter 2.

## 5.3 Results and Discussions

### 5.3.1 The phase behaviour of the compounds

Both the compounds directly melt into SmC\* phase from crystalline state and maintain that phase for a wide range of temperature and finally reach the isotropic phase. The phase sequence and the transition temperatures, as observed by POM, dielectric and electro-optic study, are summarised in **table 5.1**.

Table 5.1: Transition temperatures of the compounds. Figures within parentheses denote cooling data.

Compounds	Transition temperatures	$\Delta T_{\text{SmC}^*}$
5F3R	Crystal (75°C) 83°C SmC* 139.5°C isotropic	56.5°C
6F3R	Crystal (80°C) 83°C SmC* 146.2°C isotropic	63.2°C

Both the compounds melt from the crystalline state at the same temperature, although at much higher temperature compared to the two lower homologues. But 6F3R has a wider span of SmC\* phase than that of 5F3R. Thermal ranges of both compounds are much higher than its

lower derivatives 2F3R and 3F3R, as discussed in chapter 4. In both compounds super-cooling effect was observed. In 5F3R the SmC\* phase extended up to 75°C and in 6F3R it extended up to 80°C.

### 5.3.2 Optimised geometry

To investigate the structural-property relationship, the molecular structures of the compounds were optimised, applying Hartree-Fock method and using 3-21G basis set in a commercial package [5]. The optimised structures are shown in **figure 5.2**. The optimised length of 5F3R and 6F3R were found to be 35.19Å and 36.46 Å respectively. This is larger than the lower derivatives 1F3R, 2F3R and 3F3R as expected. Dipole moments ( $\mu$ ) of 5F3R and 6F3R are respectively found to be 6.53 D (-5.05, 0.39, 4.12) and 6.52D (-5.04, 0.65, 4.08) where the components of dipole moments along the three coordinate axes are shown within brackets.

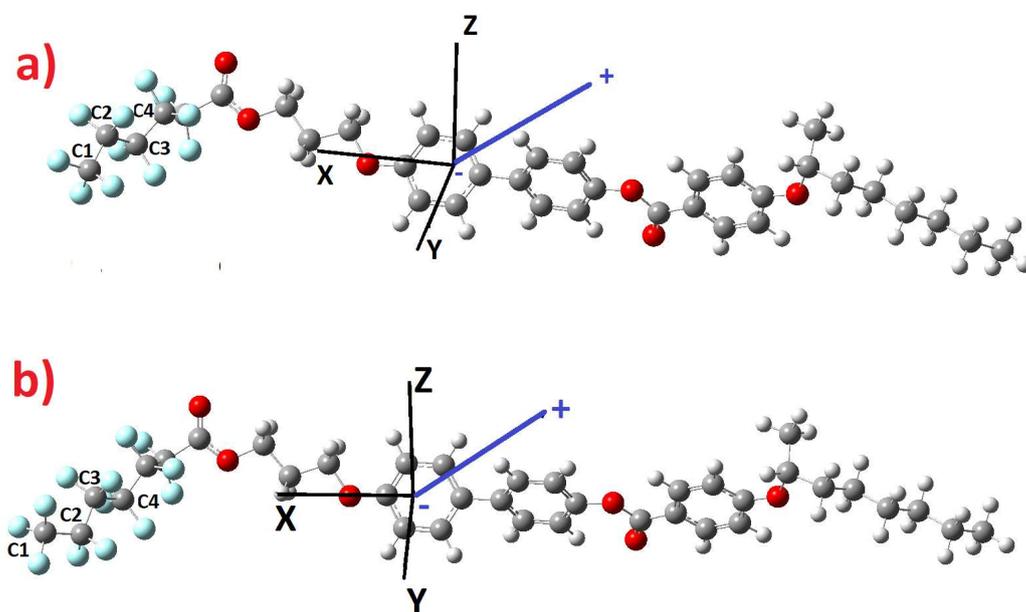


Figure 5.2: Optimised geometry of a) 5F3R and b) 6F3R.

The dipole moments of these molecules are found to be larger than 3F3R, probably for the presence of extra fluorine in the chain. However,

$\mu$  is still smaller than that of 2F3R, which may be due to the twist of the fluorinated chain at the carboxylic group by an angle  $\sim 85^\circ$  after the addition of extra fluorine. Same effect was observed in 3F3R, as discussed in chapter 4. It is worth noticing that the direction of dipole moment of 5F3R and 6F3R had rotated almost by  $90^\circ$  along Y axis, in comparison to that of 2F3R and 3F3R. The absolute values of the dipole moments remain almost same for 5F3R and 6F3R, but the component of  $\mu$  along x axis (parallel to the molecular director) is found to increase for 6F3R, most likely for the presence of extra fluorine in the chain. Conformation of the fluorinated chains of the two molecules has also changed slightly. For example the torsion angle, between the last four carbons in the chain (denoted as C1, C2, C3 and C4 in **figure 5.2**) of 6F3R is found to be larger by a fraction of a degree than that of 5F3R.

### 5.3.3 Polarized optical microscopy (POM) study

The optical textures of 5F3R are shown in **figure 5.3**, similar textures were observed in 6F3R. The parallel lines associated with the chirality of the molecules [6] are observed in the texture but more prominently in 5F3R. However no major domains can be seen in the textures of both the compounds, rather a poorly developed trace of broken fan shape texture is displayed. This type of textures were reported before in the SmC\* phase of other members of same series having direct transition from SmC\* to isotropic phase [1].

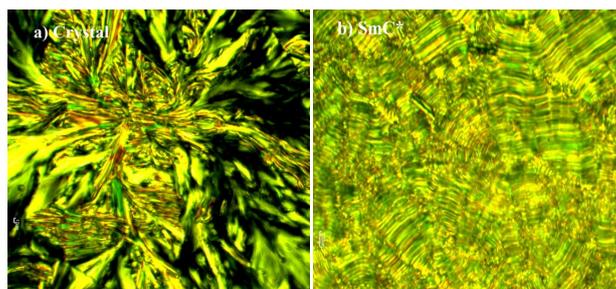


Figure 5.3: Optical texture of 5F3R at a) Crystalline state b) SmC\* phase.

### 5.3.4 Frequency dependent dielectric study

The dielectric data were taken in cooling cycle in homogeneous cells. It has already been discussed in chapter 2 that the dielectric relaxation in SmC\* phase is usually dominated by two collective modes. One is Goldstone Mode (GM) which is originated due to phase fluctuation of the azimuthal orientation of the directors and the other is soft mode (SM) which is related with the amplitude fluctuation of the tilt of the molecular directors [7,8]. But in 5F3R only one mode of relaxation was observed throughout SmC\* phase. This mode could be suppressed by applying a suitable DC bias perpendicular to the smectic layer. The critical frequency ( $f_c$ ) and dielectric increment ( $\Delta\epsilon$ ) of this relaxation was found to increase with temperature. The highest value of  $f_c$  and  $\Delta\epsilon$  was recorded to be 1600Hz and 143.5 respectively. From the bias dependency and range of critical frequency and high dielectric increment it can be inferred that this mode is due to GM relaxation. On the other hand, in 6F3R two modes of relaxations were observed throughout the SmC\* phase. The lower frequency mode, whose critical frequency and dielectric increment varied with temperature from 1.4-44 Hz and 470-570 respectively, was observed even in the crystalline and isotropic phase. This mode was also observed to be suppressed under DC bias. Thus it is related with Maxwell-Wagner (MW) relaxation. The mechanism of this relaxation has been discussed in detail in chapter 2. This mode was also observed in 1F3R, 2F3R and 3F3R (chapter 1 and 2) and also in some other compounds (2F6R, 4F6R, 6F6R) of same homologous series [9]. However, MW mode was not observed in 5F3R. As, this mode arises due to accumulation of charge in between liquid crystal layer and polymer layer inside the dielectric cell [7], hence the absence of this mode in 5F3R may be related with the purity or the conductivity of the

compound, since same type of cell was used in measurement. The critical frequency (172 Hz-1850 Hz) and dielectric increment (65-166) of the second mode of relaxation were observed to increase with temperature. It was also got suppressed by DC bias. This mode was identified as the GM mode of relaxation. Two representative fitted spectra of both the compounds are shown in **figure 5.4** and. Corresponding Cole-Cole plots are shown in **figure 5.5**. The variation of critical frequency and dielectric increment with temperature are shown in **figure 5.6** and **5.7** respectively. Values of  $\alpha$  signify that GM of both compounds deviate significantly from ideal Debye type process.

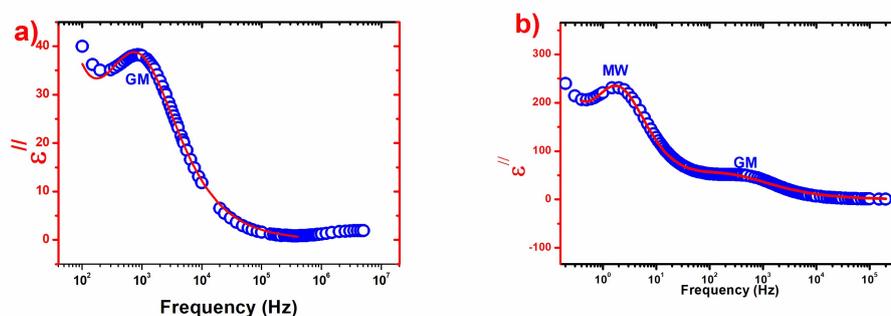


Figure 5.4: Fitted dielectric spectra showing a) GM in 5F3R (95°C) and b) both MW and GM in 6F3R (86°C). Fitted parameters for a) are  $\Delta\epsilon_{GM}$ :  $94 \pm 3.2$ ,  $f_{CGM}$ :  $870 \pm 13$ ,  $\alpha_{GM}$ :  $0.19 \pm 0.003$ ,  $\sigma_{GM}$ :  $1.2E-7 \pm 1.4E-9$  and for b) are  $\Delta\epsilon_{MW}$ :  $495 \pm 5$ ,  $f_{CMW}$ :  $1.9 \pm 0.5$ ,  $\alpha_{MW}$ :  $0.1 \pm 0.02$ ,  $\Delta\epsilon_{GM}$ :  $165 \pm 4$ ,  $f_{CGM}$ :  $230 \pm 1$ ,  $\alpha_{GM}$ :  $0.3 \pm 0.01$ ,  $\sigma_{GM}$ :  $2.2E-9 \pm 1E-10$ .

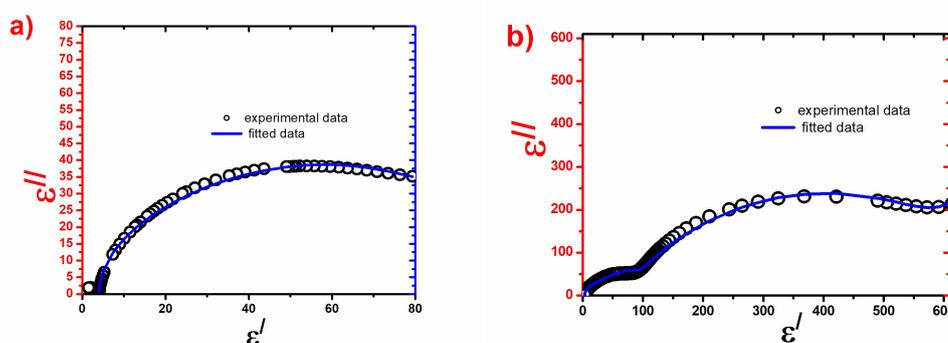


Figure 5.5: Fitted Cole-Cole plot of 5F3R (95°C) and b) 6F3R (86°C)

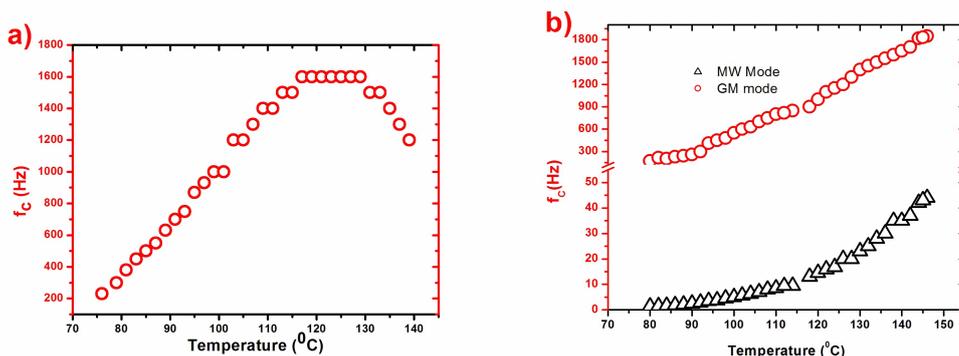


Figure 5.6: temperature dependence of critical frequency of a) 5F3R and b) 6F3R.

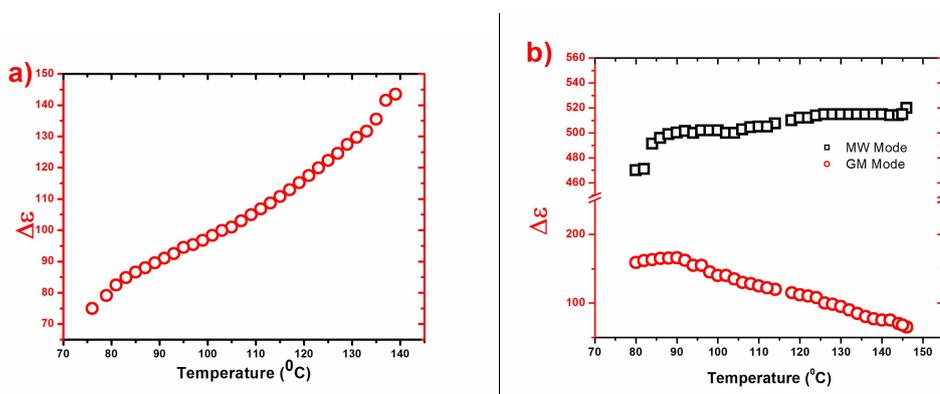


Figure 5.7: Temperature variation of dielectric increment of a) 5F3R and b) 6F3R.

In both compounds the dielectric increment of GM relaxation increased with temperature. As discussed in chapter 2 and 4, from **figure 5.7** it is evident that both compounds have strong biquadratic coupling between the tilt and the polarization in the expression of Landau free energy over the bilinear one, but for 5F3R it is stronger. Highest value of  $\Delta\epsilon$  of 5F3R ( $\sim 143.7$ ) is found to increase slightly from that of 2F3R ( $\sim 140$ ) and 3F3R ( $\sim 135$ ). For 6F3R it increases quite significantly ( $\sim 166$ ). Thus, it can be hypothesized that GM mode  $\Delta\epsilon$  of this homologous series is found to increase with number of fluorines in the chain, except for 3F3R.

The GM critical frequency of both the compounds also found to increase with temperature. It was shown in chapter 4 that the critical frequency of GM relaxation depends on the modified elastic constant, helical pitch, rotational viscosity of azimuthal motion and wave vector of the compound [2]. As these parameters are temperature dependent, so it can be deduced that  $f_C$  should also somehow depend on temperature. These type of temperature dependency of  $f_C$  was also observed in 2F3R and 3F3R as discussed in chapter 4, in some other compounds of the same homologous series [2] and also in some FLCs with different structures[10]. The highest value of GM  $f_C$  in SmC\* phase of 6F3R (1850Hz) is found to be higher than that of 5F3R (1600Hz), which is again higher than that of 2F3R (1300Hz) and 3F3R (1285 Hz). Thus GM mode  $f_C$  also found to increase with increasing number of fluorine in the chain of this homologous series, except for 3F3R.

Soft mode was not observed in any of the compounds. As discussed in chapter 3, SM was not observed previously in absence of any orthogonal to tilted phase transition and the possible reason was discussed there. The present compounds (5F3R and 6F3R) exhibit only tilted SmC\* phase and directly melt into isotropic phase, without any orthogonal phase in between. Thus absence of soft mode relaxation is in conformity with our previous results.

Using Landau model, Blinc and Zeks [11] for the first time proposed the idea of soft mode at the SmA\*–SmC\* phase transition for the case of a modulated structure. It was later modified by Carlsson et al. [12]. They described the phase transition with reference to two order parameters, namely, one primary order parameter (two-component tilt vector) and one secondary order parameter (two-component in-plane polarization). SmA\* to SmC\* transition is a second order phase transition. During this

transition the continuous symmetry group  $D_{\infty}$  of  $SmA^*$  breaks loose into  $C_2$  symmetry of  $SmC^*$ . Two characteristic modes are observed during this transition. The soft mode is a symmetry breaking mode. When the transition is attained from a higher temperature it slows down (softens). On the other hand the Goldstone mode attempts to re-establish the broken symmetry. Consequently near  $SmA^*$  to  $SmC^*$  transition the soft mode splits into the phase (GM) and amplitude (SM) modes. As shown by Clark and Lagerwall [13], in most of the cases  $SmA^*$  to  $SmC^*$  phase transition is a second order phase transition. However, during  $N^*$  to  $SmC^*$  or isotropic to  $SmC^*$  transition, the tilted smectic layers have to form directly at the transition. So, theoretically no soft mode is expected which is confirmed by experiment. These kinds of transitions in most cases are of first order. In the present compounds as well,  $SmC^*$  phase is achieved directly from isotropic phase, and it can be seen from the clearing point enthalpy [1] and temperature dependence of both the primary and secondary order parameters discussed below that the phase transition is first order.

Sometimes a residual higher frequency mode termed as domain mode can be observed under a strong bias field [14,15]. Usually compounds having  $P_s > 50 \text{ nC/cm}^2$  are found to exhibit this mode. No such mode is observed in the present compounds. This may be due to less  $P_s$  of the present compounds (see below). It is also not apparent whether presence of SM in  $SmC^*$  and  $SmA^*$  phases is a precondition for observing the domain mode, because in all the above referred compounds SM was present in both the phases.

### 5.3.5 Spontaneous polarization ( $P_S$ )

Both 5F3R and 6F3R showed moderate value of spontaneous polarization. The super-cooling effect was observed even in  $P_S$  measurement. The highest  $P_S$  value in SmC\* phase were found to be around 39 nC/cm<sup>2</sup> and 40.5 nC/cm<sup>2</sup> in 5F3R and 6F3R respectively which are higher than what was found for 2F3R (28 nC/cm<sup>2</sup>) and 3F3R (35 nC/cm<sup>2</sup>) in SmC\* phase. This is probably an effect of additional fluorine atoms in the chain which results in the increase of molecular dipole moment (only exception is 2F3R as discussed before) and hence the spontaneous polarization. The temperature variations of spontaneous polarization ( $P_S$ ) of the compounds are shown in **figure 5.8**. The observed data were fitted to mean field model equation  $P_S = P_0(1 - \frac{T}{T_C})^\beta$ , near SmC\* to isotropic transition ( $T_C$ ) [16]. In the expression  $\beta$  is the critical exponent of secondary order parameter  $P_S$ . The fitted values of  $T_C$  matched nicely with the observed values, it deviated only by 1°C. However, unlike the compounds discussed in chapter four, here  $\beta$  values are found to deviate significantly from the mean field value (0.5) for 2<sup>nd</sup> order transition for both compounds. However this nature was observed in another compound (4F3R) of the same homologous series [2]. It can be noted here that for 5F3R the fitted parameters presented here differ from the published paper, as here we have fitted the data only near  $T_C$ . It is worth noticing that the change in enthalpy values at SmC\* to isotropic transition of 5F3R and 6F3R was quoted as 7.47 and 7.92 kJ/mole respectively in the reference [1]. This also indicates that the corresponding transition is not second order rather points to first order.

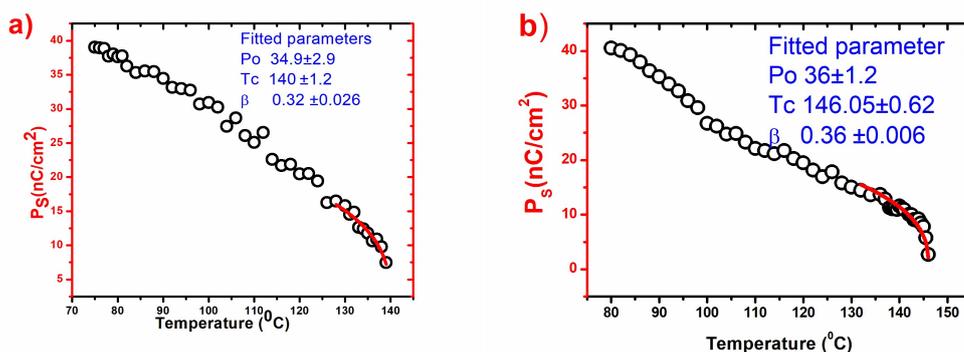


Figure 5.8: Temperature variation of spontaneous polarization of a) 5F3R and b) 6F3R. Fitted curves are also shown as discussed in text.

### 5.3.6 Electrical response time ( $\tau$ )

As discussed in the preceding chapters, the electrical response time ( $\tau$ ) is a significant parameter for FLCs. The response time of FLCs are typically found to be smaller than that of nematics by a few orders, which make FLCs more useful for high-speed display applications.

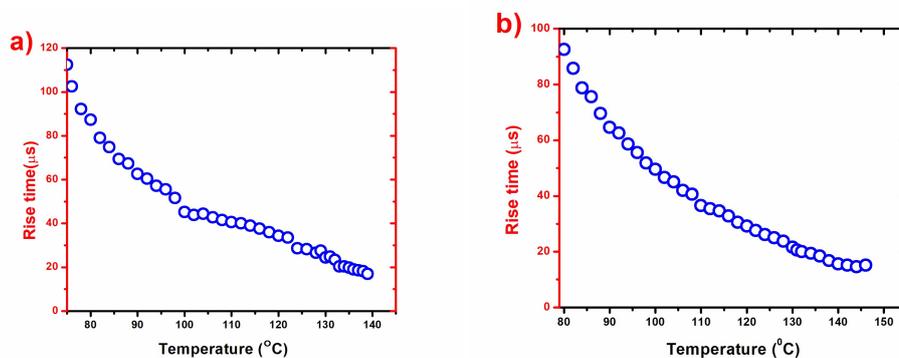


Figure 5.9: Temperature variation of response time of a) 5F3R and b) 6F3R.

The compounds show very fast switching, highest value of response time  $\tau$  under a square pulse is found to be around 112 and 93  $\mu\text{s}$  in 5F3R and 6F3R respectively. These are expected since the compounds possess

moderately large Ps and low rotational viscosity, described below. These values are marginally larger than what was observed in 2F3R (79.6  $\mu\text{s}$ ) [Chapter 4] and 4F3R (88 $\mu\text{s}$ ) [2], but smaller than that of 3F3R ( $\sim 200$   $\mu\text{s}$ ) [Chapter 4]. However,  $\tau$  value at the melting point (83 $^{\circ}\text{C}$ ) was found to be  $\sim 79$   $\mu\text{s}$  for both the compounds. Response time in lower micro second range makes the compounds promising to be used in fabrication of sharp response FLC mixtures.

Both compounds show super-cooling effect also in response time measurement which signify that SmC\* phase really extends to lower temperature region while cooling. The temperature variations of  $\tau$  are shown in **figure 5.9**. It is found to decrease monotonically with increasing temperature which is a result of faster decrease of rotational viscosity compared to spontaneous polarization which makes the rotation of the molecules easier around the tilt cone in smectic plane.

It may be of interest to see the variation of response time with molecular cores and fluorination. In a biphenyl cored non-fluorinated FLC with ester group on both sides of core response time was reported to be of the order of a few millisecond [17], response time was found to vary between 150 and 600  $\mu\text{s}$  for the compound obtained by adding of one more mono-fluorinated phenyl group in the above core structure [18], in a terphenyl based non-fluorinated compound with similar core structure as of 5F3R reported response time was around 3  $\mu\text{s}$  [19].

### **5.3.7 Optical tilt angle**

The tilt angle describes the angle between the core of the molecule and the smectic layer normal [1]. Moreover, as discussed in chapter 2, tilt angle of the molecules is the primary order parameter of the SmC\* phase while the spontaneous polarization is the secondary parameter [20–22].

Tilt angles ( $\theta$ ) of the compounds were measured optically and are represented in **figure 5.10**.

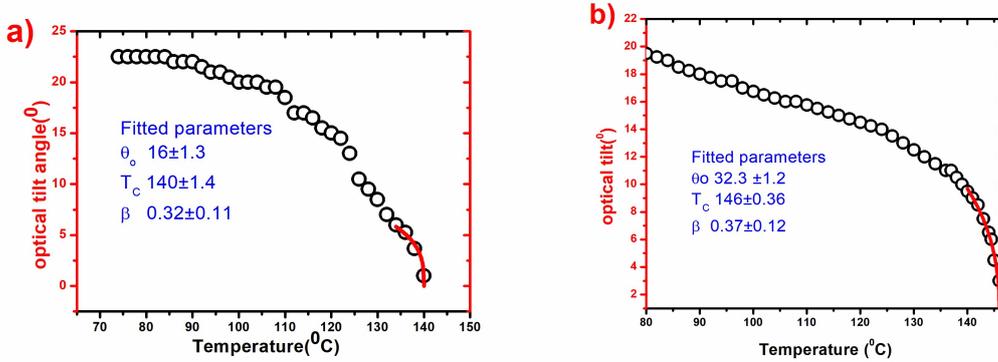


Figure 5.10: Temperature variation of optical tilt angle of a) 5F3R and b) 6F3R.

To investigate the nature of phase transition, the tilt angle data was fitted with the mean field model equation  $\theta = \theta_0(1 - \frac{T}{T_C})^\beta$ , near SmC\* to isotropic transition. Fitted  $T_C$  values are found to match with measured data. The  $\beta$  values are found to deviate again from its ideal 2<sup>nd</sup> order phase transition value and matched with the values obtained from  $P_S$  data. Highest value of the tilt angle of 5F3R is found to be exactly equal to the ideal value of tilt ( $22.5^\circ$ ) required for surface stabilised ferroelectric liquid crystal display (SSFLCD) [23–25]. Though this tilt is marginally less in 6F3R ( $19.5^\circ$ ), yet it is quite close to the ideal value.

### 5.3.8 Rotational viscosity ( $\gamma_\phi$ )

The Rotational viscosity in SmC\* phase which is associated with the rotation of the molecular director around the SmC\* cone has been calculated by the following equation obtained from generalized Landau model [12]

$$\gamma_\phi = \frac{1}{4\pi\epsilon_0} \frac{1}{\Delta\epsilon f_C} \left(\frac{P_S}{\theta}\right)^2 \quad [5.1]$$

Here,  $\Delta\epsilon$  and  $f_c$  were taken from the dielectric data;  $P_s$  and  $\theta$  were obtained from electro-optic measurements as described before.  $\gamma_\phi$  of 6F3R is found to be larger than that of 5F3R, 2F3R and 3F3R which might be because of higher spontaneous polarisation of the compound. Temperature variations of  $\gamma_\phi$  for both compounds are shown in **figure 5.11**. Rotational viscosity is found to decrease with temperature in both compounds as expected. It is observed that the rotational viscosity falls to one eighth of its value near Cr-SmC\* transition within a span of 20°C. However, in 5F3R it shows an increasing trend just before the transition to isotropic phase which may be due to pre-transitional effect. Similar diverging trend has been reported in some other members of this series such as in 4F4R, 4F5R and 7F3R described in chapter 6 and 7, and also in some other systems[26]. Further, highest values of  $\gamma_\phi$  found in these compounds are almost one-fourth the value observed in the ferroelectric phase of a partially fluorinated terphenyl based AFLC compound [27]. Thus rotational viscosity may be reduced substantially by introducing flexibility in the molecular structure. Moreover, it is found to conform the Arrhenius relationship:  $\gamma_\phi \propto \exp(E_a/k_\beta T)$ , where  $E_a$  is the activation energy for the molecular rotation on the cone under the application of the AC field on the FLC material, and  $k_\beta$  is the Boltzmann constant. Activation energy was calculated from a linear least squares fit of the plot of  $\ln \gamma_\phi$  versus inverse temperature, using only those data upto which  $\gamma_\phi$  followed the decreasing trend. Activation energy is found to be 4.71 kJ mol<sup>-1</sup> and 4.68 kJ mol<sup>-1</sup> for 5F3R and 6F3R respectively.

The rotational viscosity in SmC\* may also be measured only with the electro-optic parameters using **equation 5.1** [28].

$$\gamma_\phi = \tau P_s E \quad [5.1]$$

where,  $\tau$  is the response time  $P_S$  is spontaneous polarization and  $E$  is the applied field. To compare the value obtained both from dielectric and electro-optic data we have plotted them together in **figure 5.12**. At lowest temperature the value matched perfectly. At higher temperature,  $\gamma_\phi$  calculated by electro-optic parameters were found to be marginally larger (effect is more in 5F3R) than that calculated by dielectric parameters.

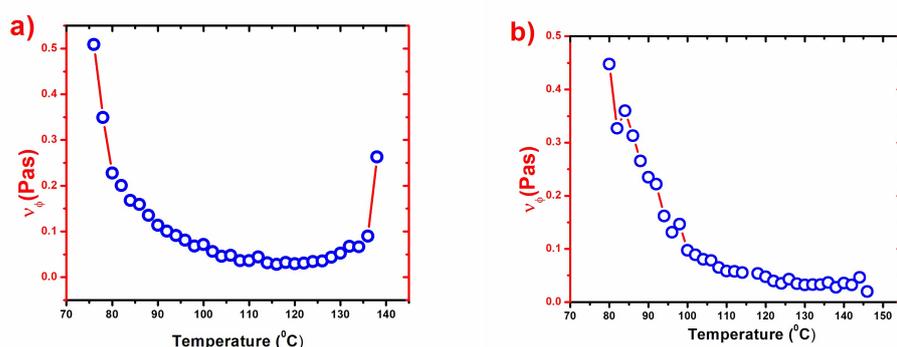


Figure 5.11: Temperature variation of rotational viscosity of a) 5F3R and b) 6F3R.

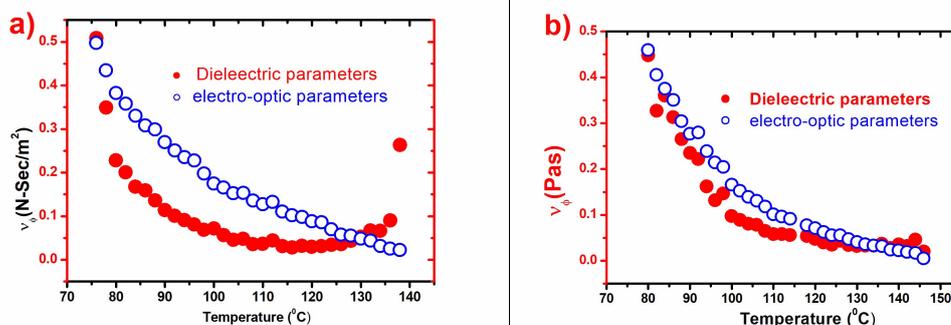


Figure 5.12: Temperature variation of rotational viscosity measured both by electro-optic and dielectric methods of a) 5F3R and b) 6F3R.

## 5.4 Conclusion

Unlike their lower derivatives, the compounds 5F3R and 6F3R are found to have only SmC\* phase over a wide range of temperature and then melt into isotropic phase without going through the orthogonal

SmA\* phase. Temperature dependences of both primary (tilt) and secondary order parameter (spontaneous polarization) near SmC\* to isotropic phase transition suggest that the transition deviate significantly from second order. Goldstone mode relaxation is observed in both the compounds with quite high dielectric increments. Maxwell Wagner mode of relaxation is observed only in 6F3R. Moreover, soft mode relaxation is not observed in any of the compounds as a consequence of the absence of any tilted to orthogonal phase transition. It is thus concluded that soft mode is possible to observe only when SmA\*-SmC\* transition is present in a compound. The compounds exhibit moderate values of spontaneous polarisation. Maximum value of the optical tilt angle of the molecules is exactly 22.5° in 5F3R and close to that in 6F3R. Response time is found to be around 100 micro second. Important display parameters of the materials are thus close to their optimum values required for SSFLC display devices. The two compounds are therefore expected to be useful for formulation of FLC mixtures suitable for display and other applications.

## Reference

- [1] Ziobro D, Dąbrowski R, Tykarska M, et al. Synthesis and properties of new ferroelectric and antiferroelectric liquid crystals with a biphenyl benzoate rigid core. *Liq. Cryst.* 2012;39:1011–1032.
- [2] Goswami D, Sinha D, Debnath A, et al. Molecular and dynamical properties of a perfluorinated liquid crystal with direct transition from ferroelectric SmC\* phase to isotropic phase. *J. Mol. Liq.* 2013;182:95–101.
- [3] Böttcher C, Belle O, Rip A, et al. *Theory of Electric Polarization, Vol II.* Amsterdam, New York: Elsevier, Scientific Publishing Co; 1973.
- [4] Miyasato K, Abe S, Takezoe H, et al. Direct Method with Triangular Waves for Measuring Spontaneous Polarization in Ferroelectric Liquid Crystals. *Jpn. J. Appl. Phys.* 1983;22:L661–L663.
- [5] Gaussian 09, Revision D.01, M. J. Frisch *et al.* Gaussian, Inc., Wallingford CT, 2013.
- [6] Dierking I. *Textures of Liquid Crystals.* wiley-vch. Weinheim: WILEY-VCH; 2003.
- [7] Hasse W, Wróbel S. *Relaxation Phenomena: Liquid Crystals, Magnetic Systems, Polymers, High-Tc Superconductors, Metallic Glasses* Berlin: Springer; 2003.
- [8] Gouda F. *Dielectric relaxation spectroscopy of chiral smectic liquid crystals.* Chalmers University of Technology, Goteberg; 1992.

- [9] Czerwiec JM, Dąbrowski R, Żurowska M, et al. Dielectric Properties of Ferroelectric Liquid Crystals with Diversified Molecular Structure - ERRATUM. *Acta Phys. Pol. A* 2010;117:553–556.
- [10] Mikułko A, Arora P, Glushchenko A, et al. Complementary studies of BaTiO<sub>3</sub> nanoparticles suspended in a ferroelectric liquid-crystalline mixture. *Europhys. Lett.* 2009;87:27009.
- [11] Blinc R, Zekes B. Dynamics of helicoidal ferroelectric smectic-C liquid crystals. *Phys. Rev. A.* 1978;18:740–745.
- [12] Carlsson T, Žekš B, Filipič C, et al. Theoretical model of the frequency and temperature dependence of the complex dielectric constant of ferroelectric liquid crystals near the smectic-C\* — smectic-A phase transition. *Phys. Rev. A* 1990;42:877–889.
- [13] Clark NA, Lagerwall S. Introduction to ferroelectric liquid crystals, *Ferroelectric Liquid Crystals Principles, Properties and Applications*. Goodby J, Blinc R, Clark NA, et al., editors. Philadelphia: Gordon and Breach; 1991.
- [14] Marzec M, Haase W, Jakob E, et al. The existence of four dielectric modes in the planar oriented S\*<sub>c</sub> phase of a fluorinated substance. *Liq. Cryst.* 1993;14:1967–1976.
- [15] Wróbel S, Cohen G, Davidov D, et al. Dielectric, electro optic and X-ray studies of a room temperature ferroelectric mixture. *Ferroelectrics* 1995;166:211–222.
- [16] Lagerwall ST. *Ferroelectric and antiferroelectric liquid crystals*. Newyork: WILEY-VCH; 1999.

- [17] Eidenschink R, Geelhaar T, Merck E, et al. Parameter characteristics of a ferroelectric liquid crystal with polarization sign reversal. *Ferroelectrics* 1988;84:167–181.
- [18] Nayek P, Ghosh S, Roy S, et al. Electro-optic and dielectric investigations of a perfluorinated compound showing orthoconic antiferroelectric liquid crystal. *J. Mol. Liq.* 2012;175:91–96.
- [19] Srivastava AK, Dhar R, Agrawal VK, et al. Switching and electrical properties of ferro- and antiferroelectric phases of MOPB(H)PBC. *Liq. Cryst.* 2008;35:1101–1108.
- [20] Collings P, Hird M. Introduction to liquid crystals Chemistry and Physics. Gray G, Goodby J, Fukuda A, editors. London: Taylor & Francis; 1997.
- [21] Priestley E., Wojtowicz PJ, Sheng P. INTRODUCTION TO LIQUID CRYSTALS. London: Plenum Press; 1974.
- [22] Demus D, Goodby J, Gray GW, et al. Handbook of Liquid Crystals. New y: WILEY-VCH; 1998.
- [23] Węglowska D, Perkowski P, Piecek W, et al. The effect of the octan-3-yloxy and the octan-2-yloxy chiral moieties on the mesomorphic properties of ferroelectric liquid crystals. *RSC Adv.* 2015;5:81003–81012.
- [24] Debnath A, Mandal PK, Węglowska D, et al. Induction of a room temperature ferroelectric SmC\* phase in binary mixtures with moderate spontaneous polarization and sub-millisecond switching time. *RSC Adv.* 2016;6:84369–84378.
- [25] Hird M. *Ferroelectricity in Liquid Crystals and Its Applications.*

- Liq. Cryst. 2011;38:1467–1493.
- [26] Pirkl S, Glogarová M. Ferroelectric liquid crystals with high spontaneous polarization. In: Lallart M, editor. *Ferroelectr. - Phys. Eff. Croatia: InTech; 2011. p. 407–428.*
- [27] Haldar S, Dey KC, Sinha D, et al. X-ray diffraction and dielectric spectroscopy studies on a partially fluorinated ferroelectric liquid crystal from the family of terphenyl esters. *Liq. Cryst.* 2012;39:1196–1203.
- [28] Pozhidaev E, Osipov M, Chigrinov V, et al. Rotational viscosity of the smectic C\* phase of ferroelectric liquid crystals. *Sov Phys JETP.* 1988;94:125–132.