CHAPTER 7

Electro-optical properties of a new series of fluorinated antiferroelectric orthoconic liquid crystalline esters

7.1 Introduction

The structure, intermolecular interactions and physical properties of antiferroelectric liquid crystals with a tilt angle of 45^o, known as orthoconic antiferroelectric liquid crystals (OAFLCs) [1-7] are a subject of intensive interest because of their promising applications. The rich variety of structures that are observed in these orthoconic smectic materials has initiated the process of understanding the behaviour of several mesomorphic properties that are interesting from a fundamental point of view. In the surface stabilized structure these materials behave like an optically negative uniaxial medium [1,2] with the optic axis perpendicular to the smectic layer surface. As a result, the surface-stabilized OAFLCs is optically isotropic in the surface plane *i.e.* behave as a homeotropically aligned medium for normal incidence. For this reason the orthoconic antiferroelectric liquid crystals have an excellent dark state [8] between crossed polarizers and the contrast is remarkably increased, regardless of the surface stabilized structural defects. Therefore, OAFLCs almost remove certain difficulties that arise to obtain a good planar alignment contrary to the other antiferroelectric liquid crystals (AFLCs). The other characteristic features of surface stabilized orthoconic antiferroelectric liquid crystals (SSOAFLCs) [9,10] *i.e.* tristable switching, inherent grey scale capability, video-rate performance speed, wide viewing angle, remarkable mechanical durability, faster response (a few μs), and high resolution have made them promising candidates for high speed applications in liquid crystal display (LCD) technology [11], usually for passive multiplexed driving displays with symmetric driving schemes and easy grey scale generation. The OAFLCs can also be used to achieve lossless phase modulation in three-level phase only modulator [12,13], fibre telecommunication and beam-steering applications [14] etc.

In general, surface stabilized orthoconic antiferroelectric liquid crystal materials with high spontaneous polarization are potentially attractive as the electric field couples directly to the spontaneous polarization. Apart from that, materials with high spontaneous polarization possess low switching time which is necessary to establish a fast response time on the application of low field. The V-shaped electro-optic switching [15-19], is one of the promising display mode of applications in everyday life. Extensive study of the V-shaped switching, known as threshold less or hysteresis free switching may be a useful directive to understand the molecular dynamics of ferroelectric mesophase on the application of external electric field.

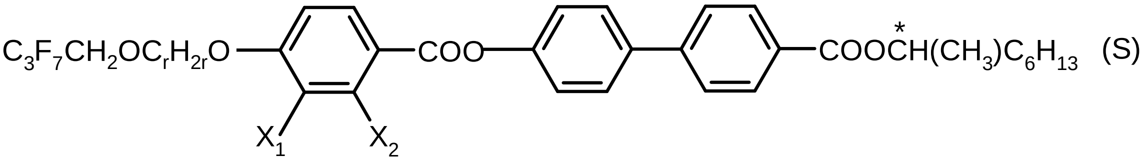
In this chapter, the mesomorphic properties of some analogues of (S)-MHPOBC (4‑(1‑methylheptyloxy)carbonylphenyl4'-octyloxy-4-biphenyl carboxy late) have been described, where the molecular structure has been varied systematically. The molecules are modified with respect to the aliphatic spacer length and lateral fluorination. Temperature dependence of the spontaneous polarization, relaxation time, viscosity and anchoring energy coefficient has been extensively studied for nine OAFLC compounds. The electro-optic behaviors have also been investigated for all the materials at various frequencies of the applied electric field in order to study their V or W shaped response. The data obtained from electro-optic measurement may guide to design and synthesize antiferroelectric liquid crystals with tilt angle around 45^o degree, possessing optimized performance in high-speed technological applications.

7.2 Materials

The antiferroelectric phase was first discovered in the well known sample MHPOBC (S‑4‑(1‑methylheptyloxy)carbonylphenyl4'-octyloxy-4-biphenylcar boxylate) [20,21] by Chandani *et al.* [22]. A homologous series of analogues of (S)-MHPOBC with perfluoroalkanoyloxyalkoxy terminal chain were synthesized earlier [23]. One or few fluorine atoms are laterally substituted to the three ring rigid core of these compounds. The variation of the terminal and lateral fluorination significantly affects the mesophase formation and physical properties of liquid crystals. All these compounds with orthoconic tilt and long helical pitch [11] have a great potential for high-end display technology.

Different families of fluorinated orthoconic anti-ferroelectrics synthesized by Dąbrowski *et al.* were reported earlier [24]. Recently, the most stable family of compounds has been synthesized [23] and nine of them have been studied in this work [25]. Full details of the synthetic procedures were reported by Żurowska *et al.* [23]. The structure, phase sequence and transition temperatures of all the compounds 1-9 are shown in Table 7.1.

Table 7.1 Molecular structure, phase sequence and transition temperatures (ºC) of nine pure orthoconic compounds. "•" the phase exists.



Comp.	r	X_1	X_2	Cr		SmC_A*		SmC*		SmA		Iso
I.3(HF)	3	H	F	•	39.1				89	•		•
I.5(HF)	5	H	F	•	28.1	•	99	•	100	•	101.4	•
I.7(HF)	7	H	F	•	25.1	•	94.7	•	99	•	100.9	•
I.6(FH)	6	F	H	•	57.3	•	80.1	•	108.5	•	112.7	•
I.7(FH)	7	F	H	•	37.4	•	103.1	•	104	•	109.1	•
I.6(FF)	6	F	F	•	62.6	•	84.8	•	110.5	•	112.8	•
I.7(FF)	7	F	F	•	50.2	•	104.6	•	107	•	109	•
I.6(HH)	6	H	H	•	60.5	•	94.7	•	125	•	126.3	•
I.7(HH)	7	H	H	•	57.8	•	116.3	•	121	•	123	•

7.3 Phase transition temperatures

Mesophases have been identified by observing the microscopic texture of the compounds using polarizing optical microscope (Motic BA300) equipped with a Mettler Toledo FP90 hot stage. It is observed that the compound **I.3(HF)** exhibit only antiferroelectric (SmC_A*) phase in the entire mesomorphic range. However, during cooling in all the other compounds, the mesophases appear with the following sequence: Iso-SmA-SmC*-SmC_A*-Cr

In SmA phase, bâtonnets-shaped texture develops which on further cooling coalesce to form a focal conic texture in the SmC* phase. On the other hand, the SmC$_A$* phases have been identified by its characteristic broken fan-shaped texture. The experimental values of the transition temperatures of all the nine OAFLC compounds are close to those reported by Żurowska *et al.* [23]. For all the investigated compounds, the antiferroelectric phase SmC$_A$* is found to dominate the phase sequence over a broad temperature range. However the SmA and SmC* phases also appear for short temperature range. From the transition temperatures of the compounds under investigation it is observed that clearing point and the SmC*-SmA phase transition temperature of compounds with even oligomethylene spacer are higher than those with odd oligomethylene spacer. However, for the SmC$_A$*-SmC* transition in these compounds an opposite trend is observed. Compounds **I.6(HH)** and **I.7(HH)** have no fluorination in the central phenyl ring and show the highest transition temperatures than mono (FH)/(HF) and diflourinated (FF) compounds. Lateral fluorination in X_1 position (Table 7.1) not only lowers the transition temperatures of the compounds but also suppresses the SmA phase in comparison to the fluorination in X_2 position [26]. Table 7.1 indicates an increase in the stability of the antiferroelectric phase with increase in the spacer length. This suggests that the interface and the packing arrangement of liquid crystalline molecules have a significant effect on the mesomorphism.

7.4 Spontaneous polarization measurement

The spontaneous polarizations, P_s, [27-37] for all the compounds as a function of reduced temperature (T/T_C) from the Curie point T_C (SmC*-SmA transition) are shown in Figure 7.1. All the nine compounds possess a high value of the saturated spontaneous polarization (~250 nC/cm^2) due to the bulky nature of the chiral unit, large dipole moment of the ester linkage and fluorinated terminal chain [38,39].

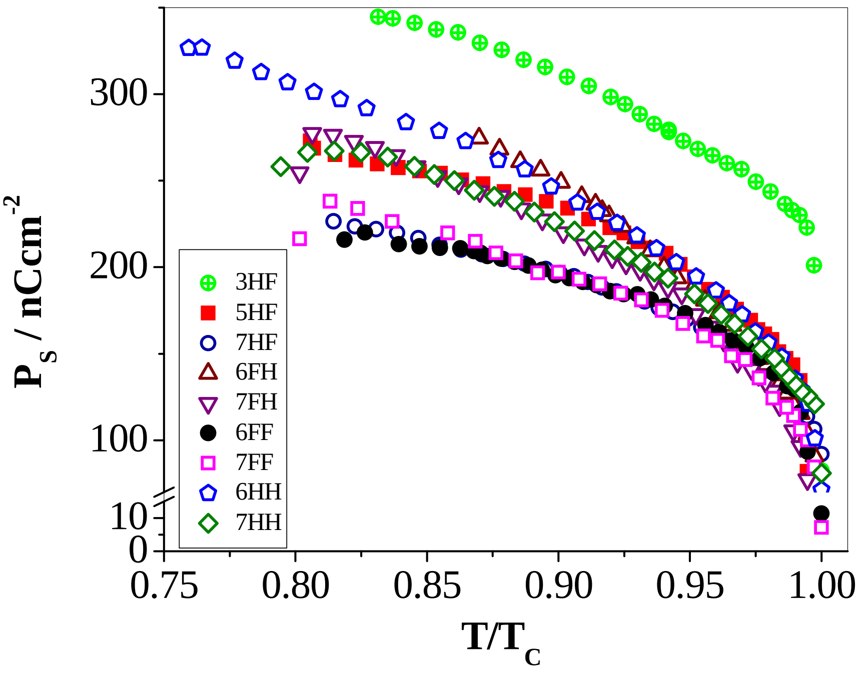


Figure 7.1 Experimental values of spontaneous polarization as a function of reduced temperature for nine OAFLC compounds.

The values of spontaneous polarization changes in the following order:

I.6 (HH) > **I.7(HH)**

I.6(FH) > **I.7(FH)**

I.3(HF) > **I.5(HF)** > **I.7(HF)**

I.6(FF) > **I.7(FF)**

Interestingly, compounds with longer aliphatic spacer length (r) in the terminal position, show lower values of the spontaneous polarization. This fact may be attributed to the volume effect *i.e.* a heptyl spacer occupies greater volume than a hexyl spacer [40] and by definition; spontaneous polarization is proportional to the volume of that compound. The behaviour of the reduced temperature dependent spontaneous polarization curve (Figure 7.1) indicates the second order nature of the SmC*–SmA phase transition. It may be mentioned that the values of the spontaneous polarization for compounds without lateral fluorines are found to be slightly higher than the laterally fluorinated liquid crystalline compounds. Addition of one or two fluorine atoms to the molecular core of similar structure leads to a decrease in the value of the spontaneous polarization. This is perhaps due to the fact that in laterally mono and difluorinated liquid crystalline compounds, the orientation of the dipole moment of highly polar lateral fluorine atoms point in an opposite direction with respect to the orientation of the core and the chiral carbon atom. Moreover, the fluorine atom traps the π electrons and pulls them away from the conjugation along the main molecular axis. Less the polar fluorine atom attached to the compound, higher is the spontaneous polarization for that compound. A comparison of mono fluorinated materials (FH)/(HF) reveals that fluorination in position X_1 ensures higher values of spontaneous polarization than substitution in position X_2. The result obtained from spontaneous polarization measurement confirms that fluoro substitutions have a significant impact on the molecular dipoles associated with the generation of the polarization in the ferroelectric and antiferroelectric mesophases. The temperature dependence of the spontaneous polarization curves (Figure 7.1) have been fitted using the following expression [22]:

$$P_s = P_0(\mathrm{T}_C - T)^{\beta} \quad \text{for } \mathrm{T} < \mathrm{T}_\mathrm{C} \qquad (7.1)$$

where, T_C is the SmC*-SmA phase transition temperature, β and P_0 are the adjustable parameters. The corresponding fitting parameters so determined are listed in Table 7.2.

The critical exponent β is in the range 0.19-0.34, which is close to the value 0.3125 (= 5/16), predicted by the three-dimensional Ising model [41], suggesting a second order nature of the SmC*-SmA phase transition. However, for the compounds with lateral fluorine substitution in position X_2, the β values are close to 0.25, indicating a tricritical mean field behaviour of the SmC*-SmA phase transition [41].

Table 7.2 Fitted parameters P_0, T_C and exponent β obtained from the fitting of the experimental values of the spontaneous polarization for nine pure compounds.

Compound	P_0 in nCcm^{-2}	T_C in K	β
I.3(HF)	105.3±0.5	374.2±0.5	0.28±0.02
I.5(HF)	90.2±0.3	374.8±0.2	0.25±0.01
I.7(HF)	76.6±0.2	374.7±0.1	0.26±0.01
I.6(FH)	71.9±3.2	384.3±0.3	0.34±0.01
I.7(FH)	71.2±1.5	376.4±0.2	0.31±0.01
I.6(FF)	98.5±1.9	385.1±0.1	0.19±0.01
I.7(FF)	80.1±1.2	380.0±0.1	0.25±0.01
I.6(HH)	76.8±2.3	400.2±0.3	0.31±0.01
I.7(HH)	76.0±3.9	396.3±0.6	0.29±0.01

7.5 Relaxation time measurement

Figure 7.2 portrays the Arrhenius behaviour of the reduced temperature dependent relaxation time. No discontinuous change is observed on passing through the SmC*-SmC$_A$* phase transition. Among all the nine investigated compounds, **I.6(FF)** and **I.7(FF)** exhibit the highest relaxation time. The presence of an extra lateral fluorine atom increases the molecular cross section and also the molecular weight. However rest of the compounds possess moderately low relaxation time (~150μs). Unsubstituted or mono fluorinated OAFLC compounds with longer aliphatic spacer demonstrate high-speed electro optic response which can be utilised to develop high definition moving pictures in LCDs. High spontaneous polarization value of these compounds probably accounts for their low relaxation time.

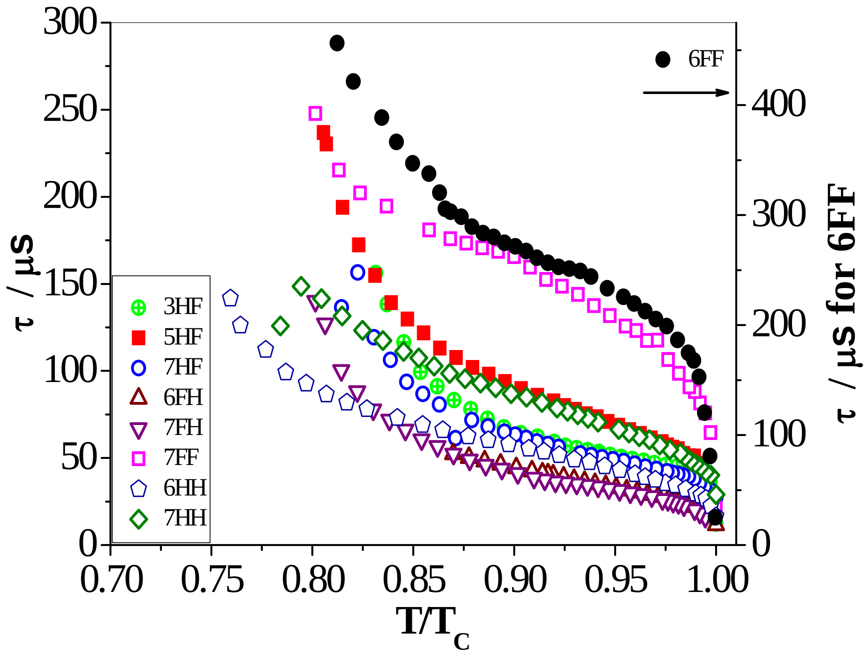


Figure 7.2 Relaxation time (τ) as a function of reduced temperature for the nine OAFLC compounds.

7.6 Effective torsional bulk viscosity measurement

The effective torsional bulk viscosity, which is related to the rotation of the molecule about the SmC* cone, is one of the most important parameters to study the dynamical behaviour of FLC and AFLC systems. As it is directly proportional to the relaxation time, the reduced temperature dependence of the effective torsional bulk viscosity as depicted in Figure 7.3 also shows almost a similar trend to that of the relaxation time.

The increase in the tilt angle leads to an increase in the rotational hindrance barrier, which contributes towards enhancement of the spontaneous polarization and viscosity [42]. Moreover the bulky nature of the chiral unit and polar fluorine atom is also responsible for hindering the molecular rotation. The Arrhenius plot of viscosity is presented in Figure 7.4.

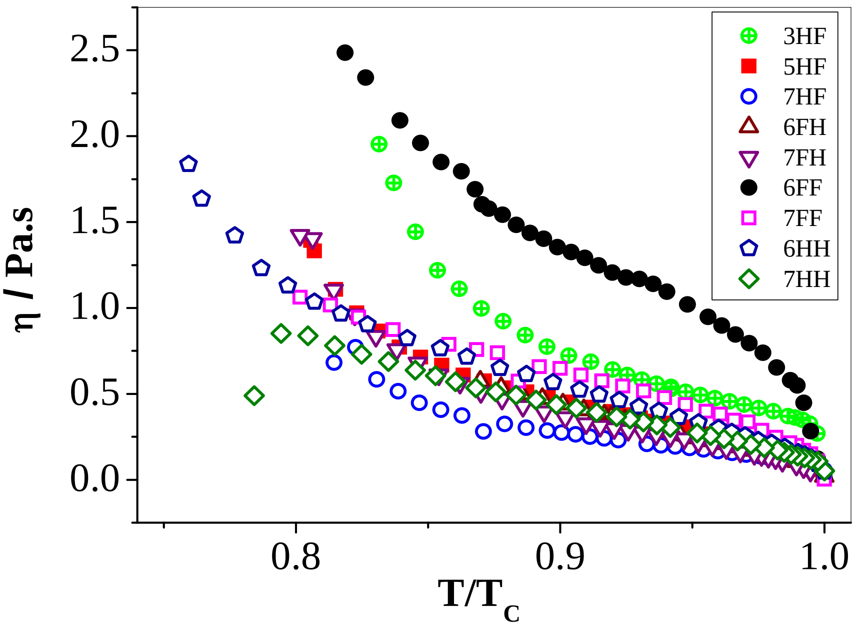


Figure 7.3 Effective torsional bulk viscosity (η) as a function of reduced temperature for the nine OAFLC compounds.

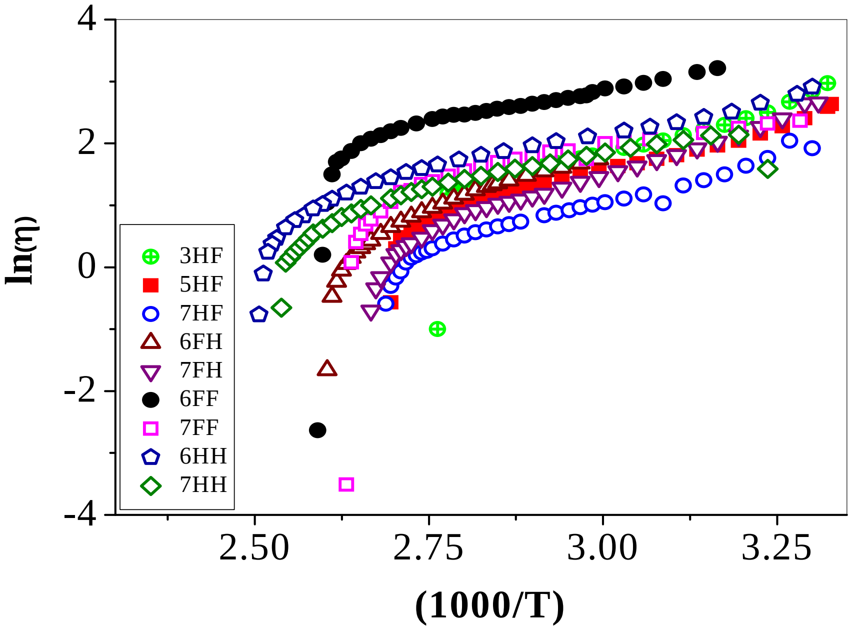


Figure 7.4 Logarithmic plot of effective torsional bulk viscosity versus (1000/T) of nine OAFLC compounds.

7.7 Anchoring energy strength co-efficient measurement

Reduced temperature dependence of both the dispersion anchoring strength coefficient (W_D) and polarization anchoring strength coefficient (W_P) are shown in Figures 7.5 and 7.6 respectively. The anchoring strength coefficient yields a quantitative characterization of the aligning liquid crystal molecules and usually two different coefficients are introduced: the dispersion anchoring strength coefficient W_D and polarization anchoring strength coefficient W_P. The knowledge of two anchoring energy coefficients helps in grasping the behaviour of the surface effect on the molecular structures.

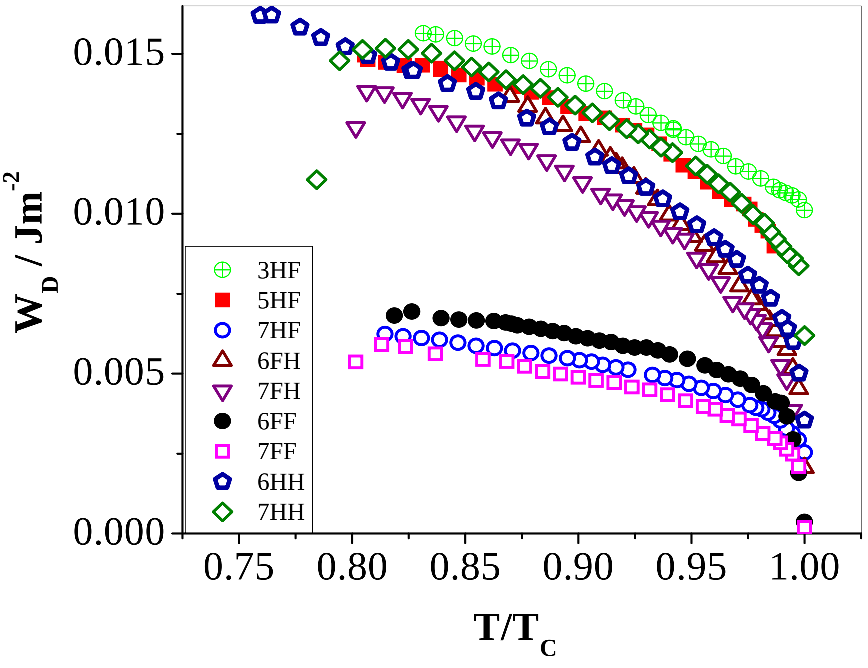


Figure 7.5 Dispersion anchoring strength co-efficient (W_D) as a function of reduced temperature for nine OAFLC compounds.

Dispersion anchoring energy arises from the non electrostatic interaction between the surface and liquid crystal molecules whereas the polarizing anchoring energy originates from the electrostatic force between the dipole moment of the surface and liquid crystal molecules [32-36]. A typical decreasing behaviour with increasing temperature on approaching the SmC* to SmA phase transition is observed in both the cases. This pattern suggests that the enthalpy of the molecule continuously increased with temperature and thus broke their interaction barrier [43]. The value of W_P is higher than that of W_D, as expected. From the comparative study of the polarization anchoring strength coefficient W_P, it may be concluded that the compounds with large spontaneous polarization perhaps contribute more to polarization anchoring and possess large value of W_P.

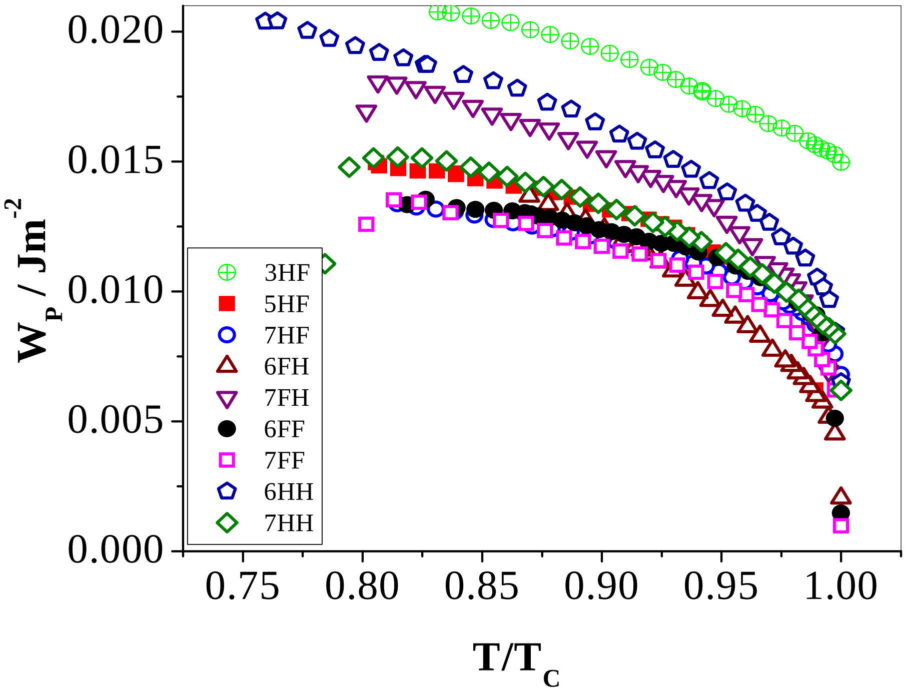


Figure 7.6 Polarization anchoring strength co-efficient (W_P) as a function of reduced temperature for nine OAFLC compounds.

7.8 Thresholdless switching

Figure 7.7 represents the electro-optic response of the transmittance versus electric field, measured in both SmC* and SmC_A* phases for compound **I.7(HH)**. The planar aligned sample has been viewed in the transmission geometry between two crossed polarizers in such a way that the optic axis of the cell in the absence of electric field is in the direction of one of the polarizers. It has been found that the transmission curves critically depend on the temperature and frequency as shown in Figure 7.7. In both the ferroelectric and anti-ferroelectric phases, the characteristic V shaped switching appears for driving frequency of 5Hz. The V shaped response [44] indicates that switching between the third zero voltage state and the uniform ferroelectric switching state has no threshold. On the contrary, at higher frequency (at 50Hz) characteristic tristable switching *i.e.* W shaped switching is observed. On lowering the temperature, the responses display slight hysteresis as a result of which the tip of the V-shape becomes distorted. This distorted response curve which apparently indicate a threshold less response may appear due to the averaging of many bistable micro domains switching at slightly different voltages and times. Probably, these domains consist of different bistable structures with spontaneous polarization essentially perpendicular to the cell plane or at an angle with respect to the cell plane [17].

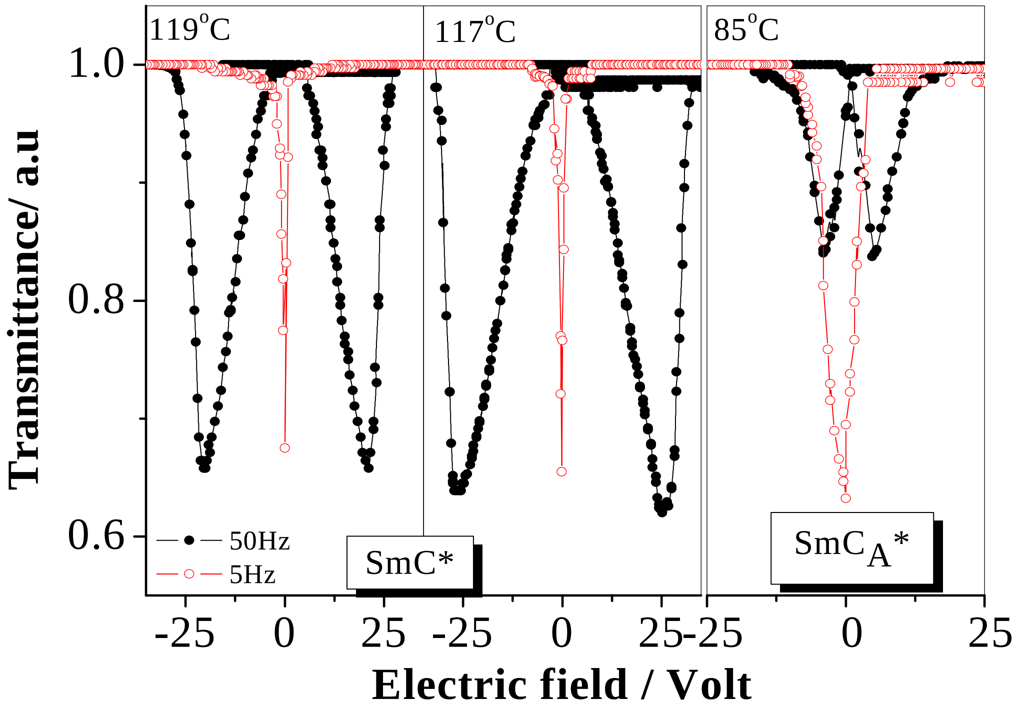


Figure 7.7 Optical transmittance as a function of applied electric field for the compound **I.7(HH)** in 5μm planar cell at various temperatures by applying a triangular waveform of different frequencies.

As the temperature decreases, the maximum transmitted intensity values increase due to the increase in tilt angle. The temperature dependence of the transmission curve can also be explained in terms of spontaneous polarization at low temperature. Such a high value of spontaneous polarization at low temperature is enough to transform a twisted structure at zero fields to a uniform polarization stabilized state. The curve is slightly asymmetric around E=0. This fact may be attributed due to the slight asymmetric nature of the molecular tilt in the positive and negative uniform polarization stabilized state.

The V-shaped switching results from the frustration between antiferroelectricity and ferro-electricity. The V- or W- shaped switching is assumed to occur due to the interaction between the liquid crystal molecules and the surface of the substrate of a planar cell [45]. For the investigated compounds having polar terminal group and aliphatic spacer units, they overlap at the interfaces between layers. As a result the terminal fluorine atoms weaken the interactions between the molecules at the interfaces of the smectic layers and the V-shaped switching is easily achieved. The phenomena of V- or W-shaped switching have been explained by several workers and many models have been suggested *viz* by Fukuda *et al.* (Langevin model) [46,47], Rudquist *et al.* (‘block model’) [48,49], Čopič *et al.* (influence of ions) [50,51] and Panarina *et al.* [52] respectively. The experimental results in this work indicate that the thresholdless V-shaped switching should occur in all SmC* and SmC$_A$* materials with sufficiently large spontaneous polarization in combination with strong polar interaction with cell surfaces which is in close agreement with the “block model” of Rudquist *et al.* [48,49].

7.9 Conclusion

The electro-optical properties of a new series of fluorinated orthoconic antiferroelectric liquid crystalline esters that form SmA, SmC* and SmC$_A$* mesophases has been described in this chapter. The investigated compounds possessing longer aliphatic chains resulted in the stabilization of the SmC* and SmC$_A$* phases. The materials reported in this chapter are of interest in the development of liquid crystals for high end display technology. Generally, mixing of various compounds to get the optimum properties for antiferroelectric liquid crystal display applications, leads to reduction of spontaneous polarization. Therefore, a compound with a large spontaneous polarization is necessary for practical applications. All the nine compounds investigated here possess a high value of the saturated spontaneous polarization (~250nC/cm^2) in the antiferroelectric phase. The most likely cause of the high spontaneous polarization is the bulky nature of the chiral unit, large dipole moment of ester linkage and fluorinated terminal chain of the mesogens. As the orientation of the dipole moment of polar substituted fluorine atoms is in the reverse direction with respect to the orientation of core and the chiral carbon, greater the number of fluoro substituent lower is the value of the spontaneous polarization. The incorporation of more aliphatic spacer length (r) to the molecular core reduces the magnitude of the spontaneous polarization. The temperature dependence of the spontaneous polarization shows normal behaviour. Experimental observation demonstrate that the nature of SmC*-SmA phase transition in these compounds is of second order. The values of the critical exponent β lie in the range 0.19 to 0.34 within the experimental error limit. All the compounds enter the SmC* phase through a second order transition from the SmA phase, where the layers already exist and the tilt develops as the temperature decreases. As a result, spontaneous polarization and viscosity are both enhanced. It is also observed that compounds with large spontaneous polarization leads to higher value of polarizing anchoring energy coefficient. Most importantly, relaxation time measurements show that unsubstituted or monofluoro substituted compounds are the fastest switching (~150μs) liquid crystals than others due to their relatively low viscosities and transverse dipole moments. The polarization stabilized V-shaped switching of these materials in planar cells has also been investigated. V-shaped switching in FLCs is not an intrinsic property of the liquid crystal material alone but is a result of the judicious combination of liquid crystal material and the architecture of the cell. This phenomenon is observed in case of liquid crystalline compounds with sufficiently large spontaneous polarization in combination with strong polar interactions with the cell surfaces. The V-shaped electro optical response is a property of the material placed in the surface stabilized geometry, wherein layer P_s exists at smectic layer boundaries, with random orientations and variable magnitudes from boundary to boundary. Hence, there is no net spontaneous polarization and the electro-optic effect is considered as threshold less switching. From the experimental results obtained in this work, it is observed that the thresholdless switching behaviour of the investigated compounds significantly depends on the temperature and applied field. The compounds **I.6(HH)** and **I.7(FH)** with large spontaneous polarization and low relaxation time seem to be interesting for mixture formulation in surface stabilized orthoconic antiferroelectric liquid crystal (SSOAFLC) display applications.

References

[1] K. D’Havé, A. Dahlgren, P. Rudquist, J.P.F Lagerwall, G. Andersson, M. Matuszczyk, S.T. Lagerwall, R. Dąbrowski, W. Drzewiński, Antiferroelectric liquid crystals with 45° tilt – a new class of promising electro-optic materials, *Ferroelectrics*, **244**, 115 (2000).

[2] P. Rudquist, Orthoconic antiferroelectric liquid crystals, *Liq. Cryst.*, **40**, 1678 (2013).

[3] W. Drzewiński, R. Dąbrowski, K. Czupryński, Orthoconic antiferroelectrics. Synthesis and mesomorphic properties of optically active (S)-(+)-4-(1-methylheptyloxycarbonyl)phenyl-4’-(fluoroalkanoyloxy alkoxy)biphenyl-4-carboxylates and 4’-(alkanoyloxyalkoxy)biphenyl-4-carboxylates, *Pol. J. Chem.*, **76**, 272 (2002).

[4] W. Piecek, R. Dąbrowski, P. Morawiak, M. Żurowska, L. Jaroszewicz, The orthoconic antiferroelectric smectic liquid crystals and their engineering by doping with homo- and heterostructural compounds, *Phase Transit.*, **85**, 910 (2012).

[5] A. Chelstowska, M. Czerwinski, A. Tykarska, N. Bennis, The influence of antiferroelectric compounds on helical pitch of orthoconic W-1000 mixture, *Liq. Cryst.*, **41**, 812 (2014).

[6] M. Czerwinski, A. Tykarska, Helix parameters in bi- and multicomponent mixtures composed of orthoconic antiferroelectric liquid crystals with three ring molecular core, *Liq. Cryst.*, **41**, 850 (2014).

[7] A. Mishra, A.S. Pandey, R. Dabrowski, R. Dhar, Dielectric and switching parameters of para-, ferro and antiferroelectric phases of (S)-(+)-4-(1-methylheptyloxycarbonyl)phenyl 4-(6-perfluorooctanoyloxyhex-1-oxy) biphenyl-4-carboxylate, *Liq. Cryst.*, **40**, 699 (2013).

[8] K. D’havé, P. Rudquist, S.T. Lagerwall, H. Pauwels, W. Drzewiński, R. Dąbrowski, Solution of the dark state problem in antiferroelectric liquid crystal displays, *Appl. Phys. Lett.*, **76**, 3528 (2000).

[9] S. Lagerwall, A. Dahlgren, P. Jägemal, P. Rudquist, K. D’have, H. Pauwels, R. Dąbrowski, W. Drzewiński, Unique electro-optical properties of liquid crystals designed for molecular optics, *Adv. Funct. Mater.*, **11**, 87 (2001).

[10] R. Dąbrowski, W. Drzewiński, J. Dziaduszek, J. Gąsowska, P.A. Henderson, P. Kula, J.M. Otón, N. Bennis, Orthoconic antiferroelectric liquid crystals containing biphenyl, terphenyl, or naphthyl mesogenic unit, *Opt. Elec. Rev.*, **15**, 32 (2007).

[11] J.M. Otón, X. Quintana, P.L. Castillo, A. Lara, V. Urruchi, A. Bennis, Antiferroelectric liquid crystal display, *Opt. Elec. Rev.*, **12**, 263 (2004).

[12] D. Engström, P. Rudquist, J. Bengtsson, K. D'havé, S. Galt, Three-level phase modulator based on orthoconic antiferroelectric liquid crystals, *Opt. Lett.*, **31**, 3158 (2006).

[13] D. Engström, P. Rudquist, J. Bengtsson, K. D'havé, S. Galt, Near-lossless continuous phase modulation using the analog switching mode (V-shaped switching) in ferroelectric liquid crystals, *Appl. Opt.*, **45**, 5258 (2006).

[14] D. Engström, M.J. O'Callaghan, C. Walker, M.A. Handschy, Fast beam steering with a ferroelectric-liquid-crystal optical phased array, *Appl. Opt.*, **48**, 1721 (2009).

[15] S.T. Lagerwall, Ferroelectric and antiferroelectric liquid crystals, Wiley-VCH, New York (1999).

[16] S. Inui, N. Iimura, T. Suzuki, H. Iwane, K. Miyachi, Y. Takanishi, A. Fukuda, Thresholdless antiferroelectricity in liquid crystals and its application to displays, *J. Mater. Chem.*, **6**, 671 (1996).

[17] Hammarquist, K. D’have, M. Matuszczyk, N.A. Clark, J.E. Maclennan, P. Rudquist, V-shaped switching ferroelectric liquid crystal structure stabilized by dielectric surface layers, *Phys. Rev. E.*, **77**, 031707 (2008).

[18] Petrenko, J.W. Goodby, V-Shaped switching and interlayer interactions in ferroelectric liquid crystals, *J. Mater. Chem.*, **17**, 766 (2007).

[19] L.M. Blinov, E.P. Pozhidaev, F.V. Podgorov, S.A. Pikin, S.P. Palto, A. Sinha, A. Yasuda, S. Hashimoto, W. Haase, Thresholdless hysteresis-free

switching as an apparent phenomenon of surface stabilized ferroelectric liquid crystal cells, *Phys. Rev. E.*, **66**, 021701 (2002).

[20] K. Nowicka, A reliable method for detecting phase transitions in liquid crystals with polar order, *Liq. Cryst.*, **41**, 197 (2014).

[21] K. Aihara, Y. Sasaki, K. Ema, High-resolution calorimetric study of critical behavior at the smectic-C*-smectic-C-alpha* phase transition, *Liq. Cryst.*, **40**, 1373 (2013).

[22] A.D.L. Chandani, T. Hagiwara, Y. Suzuki, Y. Ouchi, H. Takezoe, A. Fukuda, Tristable switching in surface stabilized ferroelectric liquid crystals with a large spontaneous polarization, *Jpn. J. Appl. Phys.*, **27**, L729 (1988).

[23] M. Żurowska, R. Dąbrowski, J. Dziaduszek, K. Garbat, M. Filipowicz, M. Tykarska, W. Rejmer, K. Czupryński, A. Spadlo, N. Bennis, J.M. Oton Influence of alkoxy chain length and fluorosubstitution on mesogenic and spectral properties of high tilted antiferroelectric esters, *J. Mater. Chem.*, **21**, 2144 (2011).

[24] R. Dąbrowski, P. Kula, Z. Raszewski, W. Piecek, J.M. Otòn, A. Spadło, New orthoconic antiferroelectrics useful for applications, *Ferroelectrics*, **395**, 116 (2010).

[25] A. Pramanik, M.K. Das, B. Das, M. Żurowska, R. Dabrowski, Electro-optical properties of a new series of fluorinated antiferroelectric orthoconic liquid crystalline esters, *Liq. Cryst.*, **42**, 412 (2015).

[26] M. Hird, Flourinated liquid crystals properties and applications, *Chem. Soc. Rev.*, **36**, 2070 (2007).

[27] K. Miyasato, S. Abe, H. Takezoe, A. Fukuda, E. Kuze, Direct method with triangular waves for measuring spontaneous polarization in ferroelectric liquid crystals, *Jpn. J. Appl. Phys.*, **22**, L661 (1983).

[28] Ph. Martinot-lagarde, Direct electrical measurement of the permanent polarization of a ferroelectric chiral smectic C liquid crystal, *J. Phys. Lett.(Paris)*, **38**, L17 (1977).

[29] S.S. Bawa, A.M. Biradar, K. Saxena, S. Chandra, Direct pulse technique for spontaneous polarization dynamics and molecular reorientation processes in ferroelectric liquid crystals, *Rev. Sci. Instrum.*, **59**, 2023 (1988).

[30] M. Glogarova, H. Sverenyak, A. Fukuda, H. Takezoe, Electrooptic properties of chiral smectic liquid crystals with a dipolar order, *Liq. Cryst.*, **14**, 463 (1993).

[31] K. Furukawa, K. Terashima, M. Ichihashi, S. Saitoh, K. Miyazawa, T. Inukai, Chiral smectic C liquid crystals having an electronegative substituent ortho to the chiral tail group - a study of a factor determining the magnitude of spontaneous polarization, *Ferroelectrics,* **85**, 451 (1988).

[32] V.M. Vaksman, Y.U.P. Panarin, Measurement of ferroelectric liquid crystal parameter, *Mol. Mats.*, **1,** 147 (1992).

[33] L.M. Blinov, V.G. Chigrinov, Electro-optical effects in liquid crystal materials, Springer-Verlag, New York (1994).

[34] A.I. Allagulov, S.A. Pikin, V.G. Chigrinov, Bistable and monostable polarized states of a liquid-crystalline ferroelectric in an electric field, *Liq. Cryst.*, **5**, 1099 (1989).

[35] A.K. Misra, A.K. Srivastava, J.P. Sukla, R. Manohar, Dielectric and electro-optical parameters of two ferroelectric liquid crystals: a comparative study, *Phys. Scr.*, **78**, 065602 (2008).

[36] J.F. Lyuu, C.C. Chen, J.Y. Lee, The anchoring energy coefficient of dye guest-host ferroelectric liquid crystals, *Mol. Cryst. Liq. Cryst.*, **329**, 99 (1999).

[37] R. Manohar, S.P. Yadav, K.K. Pandey, A.K. Srivastava, A.K. Misra, Comparative study of dielectric and electro-optical properties of pure and polymer ferroelectric liquid crystal composites. *J. Polym. Res.*, **18**, 435 (2011).

[38] J.W. Goodby, J.S. Patel, E. Chin, Rotational damping and the spontaneous polarization in ferroelectric liquid crystals, *J. Phys. Chem.*, **91**, 5151 (1987).

[39] B. Bahadur, Liquid crystals: applications and uses, World Scientific, Singapore (1990).

[40] S.J. Cowling, A.W. Hall, J.W. Goodby, Y. Wang, H.F. Gleeson, Examination of the interlayer strength of smectic liquid crystals through the study of partially fluorinated and branched fluorinated end-groups, *J. Mater. Chem.*, **16**, 2181 (2006).

[41] H. Yurtseven, D. Kavruk, Analysis of the spontaneous polarization and the dielectric constant near the ferroelectric phase transition in TSCC, *Ferroelectrics,* **367**, 190 (2008).

[42] Park, S.S. Seomun, M. Nakata, Y. Takahashi, Y. Takanishi, K. Ishikawa, H. Takezoe, Collective molecular motion during V-shaped switching in a smectic liquid crystal, *Jpn. J. Appl. Phys.*, **38**, 1474 (1999).

[43] S.S. Seomun, B. Park, A.D.L. Chandani, D.S. Herman, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, Evolution of switching characteristics from tristable to V-shaped in an apparently antiferroelectric liquid crystal, *Jpn. J. Appl. Phys.* **36**, 3586 (1997).

[44] S.S. Seomun, T. Gouda, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, Bulk optical properties in binary mixtures of antiferroelectric liquid crystal compounds showing V-shaped switching, *Liq. Cryst.*, **26**, 151 (1999).

[45] S.S. Seomun, T. Fukuda, A. Fukuda, J.G. Yoo, YuP Panarina, J.K. Vij, Alignment instability caused by anchoring of the in-plane directors to the rubbing direction in the V-shaped switching, *J. Mater. Chem.*, **10**, 2791 (2000).

[46] A. Chandani, Y. Cui, S.S. Seomun, Y. Takanishi, K. Ishikawa, H. Takezoe, A. Fukuda, Effect of alignment layer on V-shaped switching in a chiral smectic liquid crystal, *Liq. Cryst.*, **26**, 167 (1999).

[47] M. Takeuchi, K. Chao, T. Ando, T. Matsumoto, A. Fukuda, M. Yamashita, V-shaped switching due to frustoelectricity in antiferroelectric liquid crystals, *Ferroelectrics*, **246**, 1 (2000).

[48] P. Rudquist, M. Buivydas, J.P.F Lagerwall, R. Shao, T. Bellini, N.A. Clark, X.H. Chen, D.M. Walba, M. Wand, Poster session presented at: 17th Int. Liq. Cryst. Conerence (P2-063); 1998 July 19-24; Strasbourg, France; N.A. Clark cited in A. Fukuda, *Liq. Cryst. Today*, **8**, 6 (1998).

[49] P. Rudquist, J.P.F. Lagerwall, M. Buivydas, F. Gouda, S.T. Lagerwall, N.A. Clark, J.E. Maclennan, R. Shao, D.A. Coleman, S. Bardon, T. Bellini, D.R. Link, G. Natale, M.A. Glaser, D.M. Walba, M.D. Wand, X.H. Chen, The case of thresholdless antiferroelectricity: polarization-stabilized twisted SmC* liquid crystals give V-shaped electro-optic response, *J. Mater. Chem.*, **9**, 1257 (1999).

[50] M. *Čopič*, J.E. Maclennan, N.A. Clark, Structure and dynamics of ferroelectric liquid crystal cells exhibiting thresholdless switching, *Phys. Rev. E*, **65**, 021708 (2002).

[51] M. *Čopič,* J.E. Maclennan, N.A.Clark, Influence of ions on the “V-shaped” electro-optic response of ferroelectric liquid crystals, *Phys. Rev. E*, **63**, 031703 (2001).

[52] Yu.P. Panarina, V. Panov, O.E. Kalinovskaya, J.K. Vij, On the V-shaped switching in antiferroelectric liquid crystals, *Ferroelectrics*, **246**, 35 (2000).