Chapter 2

Ferroelectric Liquid Crystal Devices

2.1 Spontaneous Polarization

Spontaneous polarization (Ps) is an important parameter of FLCs, which is related to the response time, bistabity an so on. Ps is deduced from asymmetry considerations that all chiral tilted smectic phases exhibit a local spontaneous polarization, and thus show pyroelectricity [8]. The polarization in chiral smectic C mesophase is primarily dependent on a coupling between the local dipoles at the proximal asymmetric centers of the molecules. The Ps of FLC also affects their applications and physical properties. FLC devices are switched by electric filed, and the driving torque is provided by a combination between applied electric field and Ps. Generally, a ferroelectric liquid crystal material with large Ps leads the fast response time and bistable capability [3].

2.1.1 Thickness and Temperature Dependent Spontaneous Polarization

The unit of spontaneous polarization is in coulombs per square centimeter (liquid crystal over ITO region), base on the unit, spontaneous polarization is independent with the separation of the glass plates (cell gap). However, the spontaneous polarization is indeed cell gap dependent as the experimental results by Patel and Goodby [9], and the cell gap dependent result was shown in Fig2.1. The FLC material S-3,7-dimethyloctyl-4-n-hexadecyloxybenzoyloxybenzoate was used in the experiment at 40 $^{\circ}$C. As the result,

the Ps value was increased with increasing cell gap. For most materials, the value of spontaneous polarization saturated at 18μm cell, the gap thickness dependent Ps has been provisionally attributed to the screening effect by space charges existing at the surfaces in the cell. At small cell gap sample, space charges easily move from one surface the other during electric field reversal and affect the value of Ps. As the increase of cell gap, the effectiveness of the space charges are reduced that the transit timescale is less than Ps reversal.
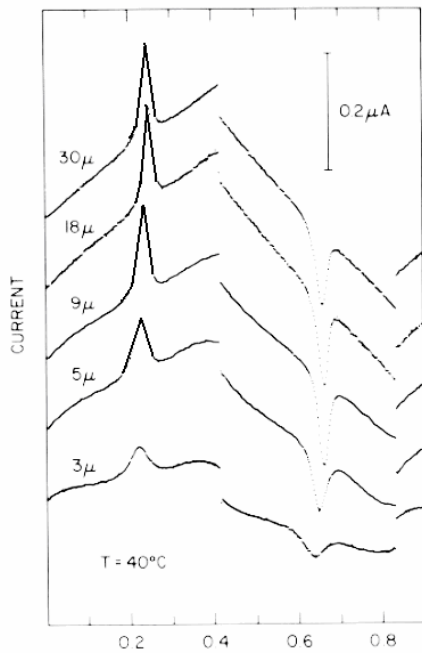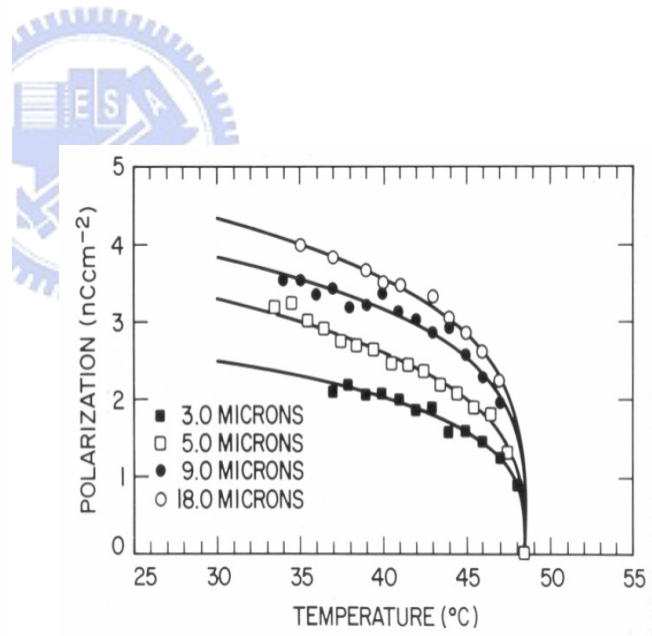

Fig. 2.1 cell gap dependent Ps [9].

Fig. 2.2 The magnitude of Ps determined as a function of temperature and cell thickness [9].

Local dipoles at the asymmetry centers of FLC molecules attribute to polarization in the tilt structure of chiral SmC phase. Generally, the optical tilt angle (cone angle) is

decreased with increasing temperature, the temperature dependent optical tilt angle can be written as,

$$\theta(T) = \theta^0 (T_C - T)^\beta \qquad (2.1)$$

Where $\theta(T)$ is the optical tilt angle at T ℃,

θ^0 is a constant,

T_c is the SmA – SmC* phase transition temperature,

T is the measured temperature,

β is supposed to be 0.5

For the material exhibit the SmA – SmC* phase transition, the temperature dependent Ps follows a law similar to the temperature dependent optical tilt angle. For ideal single molecular species, temperature dependent Ps can be written as,

$$P_S(T) = P_S^0 (T_C - T)^\alpha \qquad (2.2)$$

Where $P_s(T)$ is the polarization at temperature T (℃),

P_s^0 is constant,

T_c is the SmA – SmC* phase transition temperature,

T is the temperature at which the spontaneous polarization is characterized.

α is supposed to be 0.5

The magnitude of Ps determined as a function of temperature and cell thickness was shown in Fig. 2.2, the Ps value was reduced with increasing temperature, also the cell thickness dependent result was proposed.

2.2 Display Operation Principle

SSFLCs can be utilized to create black and white states as the description of Clark and Lagerwall [5]. FLC material creates a half wave plate, and the operation principle of the SSFLC device under crossed polarizers is shown in Fig. 2.3 [10]. FLC molecules are reoriented, where the Ps director follows the electric field. A FLC cell is put between crossed polarizers, by applying downward electric field, the long axis of molecules are oriented parallel to the polarizer and exhibits the non-transmissive dark state as shown in Fig. 2.3 (a). And light transmit through analyzer as bright state is shown in Fig. 2.3 (b), FLC molecules are reoriented by upward electric field, and the polarization of light is changed. The intensity of the passed light is depended on the cone angle and Δn of FLC, cell thickness, and wavelength of the light.
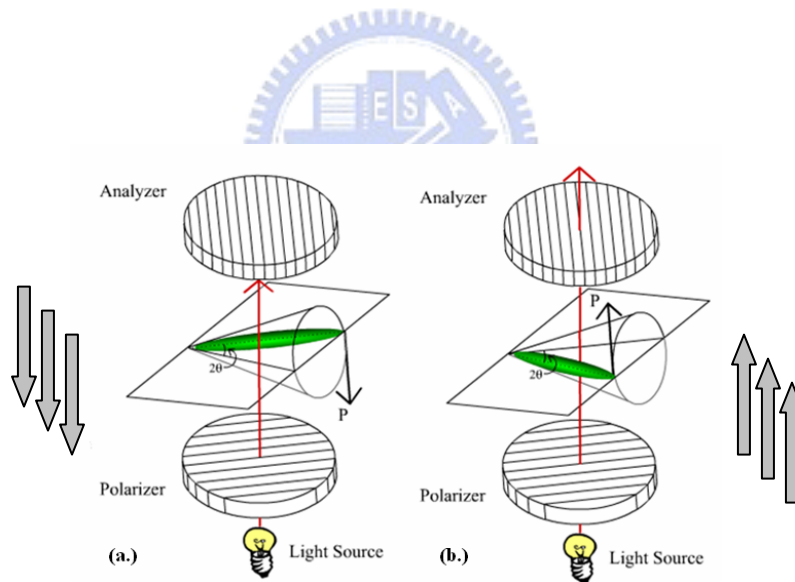

Fig. 2.3 (a) black and (b) white display states of SSFLC under crossed polarizers [10].

2.2.1 Advantage of SSFLC Devices

a. Fast response governed by the strong torque.

LC molecules are switched with the induced torque. Due to the dielectric anisotropy in LC molecules, dielectric torque is produced by the coupling with dielectric anisotropy and electric field, the dielectric torque can be written as,

$$\Gamma_d = \Delta\varepsilon(n \cdot E)(n \times E) \qquad\qquad (2.3)$$

Where Γ_d is the induced dielectric torque,

$\Delta\varepsilon$ is the dielectric anisotropy of LC material,

n   is the long axis direct.

E   is the applied electric field.

The sub-millisecond fast response time of FLC is governed by the strong driving torque. In ferroelectric liquid crystals, electric fields affect not only dielectric anisotropy but also spontaneous polarization, the torque can be written as,

$$\Gamma_f = P_S \times E \qquad\qquad (2.4)$$

Where, Γ_f is the induced torque,

P_S is the spontaneous polarization of FLC,

E   is the electric field

And the ferroelectric torque is much stronger than the dielectric torque.


b. Switching under both directions of field reversal. (V mode switching)

Depend on FLC materials, surface stabilized ferroelectric liquid crystal devices have two kinds of switching modes, half-V and V modes as shown in Fig.2.4 [4]. The half-V mode

switching is the same to the V-T characteristic of twist nematic LC device, which is only switched with positive voltage since AC driving scheme is usually adopted to prevent ion effects. And the V mode switching FLC device can be switched under both positive and negative voltage, which provides a novel driving scheme for display application.

c.Bistability

The bistablity in FLC device is the result of spontaneous polarization, and surface anchoring effect with alignment layer. SSFLCs are stabilized at both bright and dark states even there are no applied electric fields, which also means that the last switched state is maintained infinitely long, the property allows other applications of static displays with low power consumption, such as E-Books and E-papers, and the optical storage devices can be obtained.
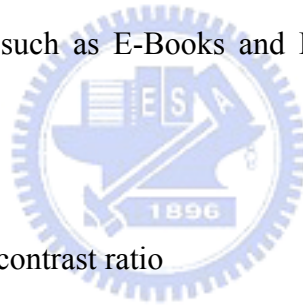
d.Wide viewing angle and high contrast ratio

The wide viewing angle SSFLC device is derived with its in-plane reoriented molecules, where the director at both dark and bright states lies in the plane parallel to the glass substrates. Ideally, a well-aligned FLC device follows a related high contrast ratio.
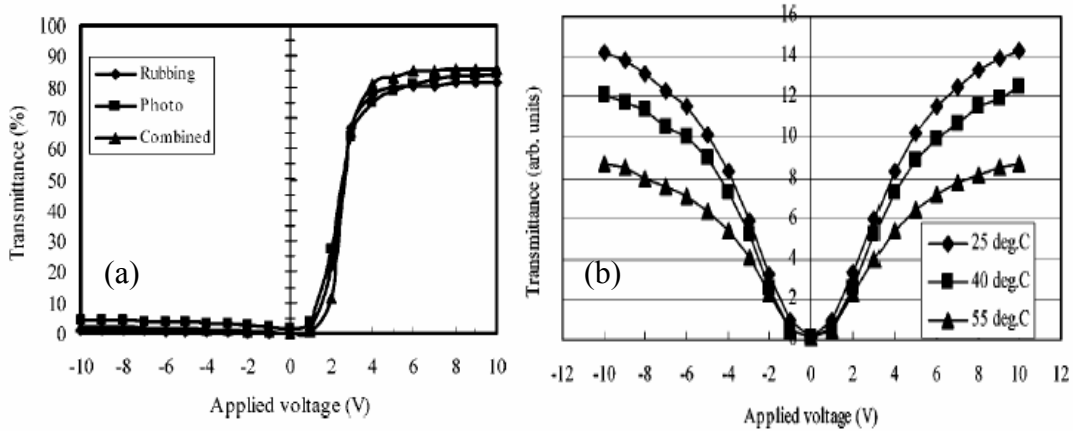
Fig. 2.4 FLC switching modes (a) half-V mode (b) V-mode [4].

2.2.2 Disadvantage of SSFLC Devices

a. Difficult to generate gray levels.

Due to the bistability and hysteresis loop, the voltage-controlled gray levels are difficult to achieve. FLC molecules tend to reorient to both bistable states and the intermediate states are not available. And the hysteresis effect leads to different transmittances with reversal electric field. Therefore, gray levels capable FLC device are difficult to approach.
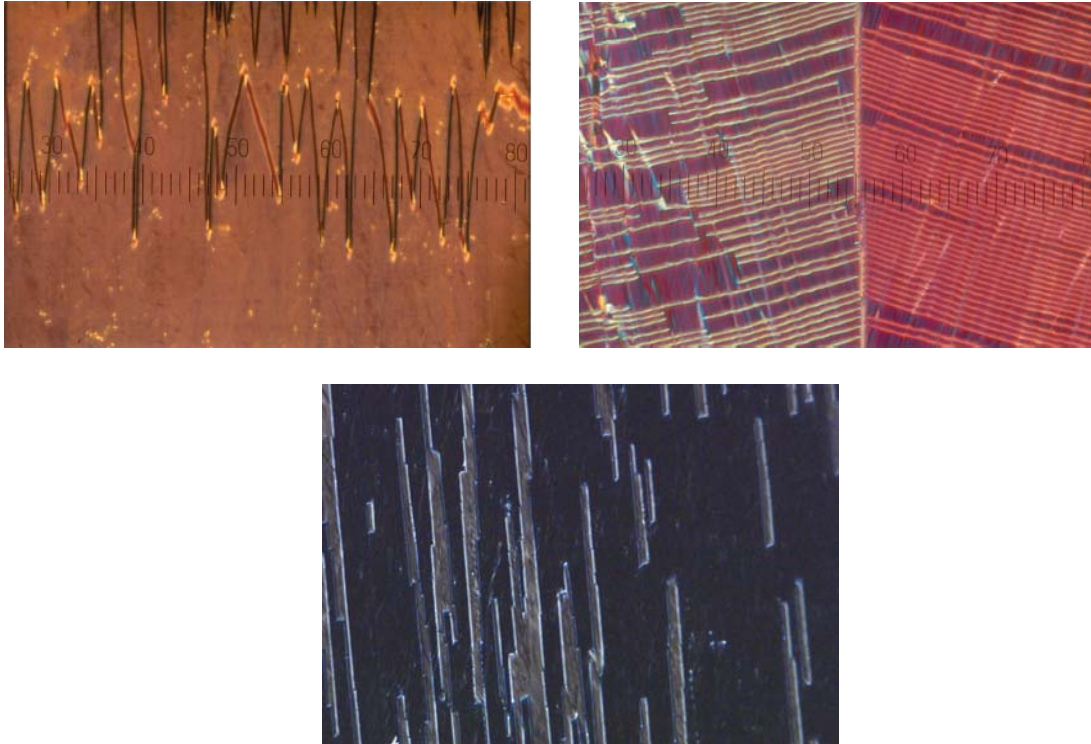
Fig. 2.5 (a) Zigzag defects of a surface stabilized ferroelectric liquid crystal in the chevron geometry. **(b)** Texture of a field induced horizontal chevron structure. (c) double domains with opposite polarization [11].

b.   Difficult to obtain large homogeneous aligned area.

Alignment defects of SSFLC devices such as zigzag defects, stripes domains usually appear with different chevron layer structures or opposite polarization directions. Zigzag defects will be appeared when domains of opposite chevron structures meet, and the un-switched zigzag lines appear in the border between two chevron structures as shown in Fig. 2.5 (a). The stripe domains will be appeared in the region where two domains of opposite layer tilt meet, a vertical chevron defect forms the domain boundary [11] as shown in Fig. 2.5.(b), and double domains with opposite polarization causing the obvious light leakage as shown in Fig. 2.5.(c). To obtain a homogeneous aligned cell, some methods [6, 12, 13] have been reported base on the pre-treatment of alignment layer, or by applying external magnetic or electric field during annealing process.

c. Sensitivity to shocks and vibrations.

A well-aligned mono-domain FLC cell is ideally formed with ordered bookshelf structure smectic layers, however, the smectic layers are sensitive with shocking and vibrating. The ideal bookshelf structure will be destroyed under the force and alignment defects will be appeared.

2.3 Ionic Effects in FLC Display

Ions always affect liquid crystal displays, since they are switched by electric field. Ions are usually produced in the chemical synthesis process of LC material or produced by charges which migrate from alignment layer during LC filling process, and also be generated in the LC mixture with the dissociation of molecules. Thus, it is difficult to eliminate ions for its multi-source.

Free ions usually move under the applied electric field, if the DC voltage is applied across the cell, ions will move to the opposite electrode and induce charge separation. Separated charges form an inner field againsting the applied DC voltage [14], this is also the reason why AC driving scheme is utilized in displays.

Ions are more impressive in FLC materials [15], in SSFLC device the spontaneous polarization is always presented and an internal polarization field exists even there is no additional applied electric field. Ionic effects becomes very important since SSFLC device keeps in its stable state with spontaneous polarization, the opposite field formed with ions will depolarize the internal polarization, and the stable state is destroyed.

2.4 Gray Scale

The continuous gray scales are important requirement for display applications, they can be achieved with twist nematic LC devices according to the amplitude of driving voltage. However, for SSFLC device, due to its bistability and hysteresis loop, the voltage-controlled gray scales are difficult to attain. The bistability implies that the molecules prefer to orient at both states and the intermediate states are not available, which leads to the lack of gray scales. The last switched state is maintained with a bistable device, in order to induce the switching process, the applied voltage leads the electric optical characteristics, such as threshold voltage and hysteretic behavior.

Due to the lack of intrinsic gray scales, several methods have been suggested to obtain gray scales based on the averaging properties of the human eye.

2.4.1 Spatial dither technique

Spatial dither technique [16] is the method to divide each pixel into sub-pixels, which are independently controlled as shown in Fig. 2.6 [17], three gray scales are achieved with two divided sub-pixels. To get more gray scales, more sub-pixels are required, and sub-pixels can be designed into different area. However, to control the divided sub-pixels, the number of data lines and electrodes must be doubled, which may slow down the signal writing speed, and the resolution is reduced with increasing the number of sub-pixels.

Data pulse	Region A	Region B	Pixel	Gray level
D0	nonswitched	nonswitched	■	0
D1	nonswitched	switched	◨	1
D2	switched	switched	□	2

Fig. 2.6 Schematic diagram of spatial dither method [17].

2.4.2 Temporal dither technique

Another technique to generate gray levels is using the time temporal dither method [16]. This approach dependents on time integration of human eyes, as shown in Fig. 2.7, the intermediate gray level is generated when the pixels is switched between dark and bright states rapidly. If the switching speed is fast enough, human eyes will perceive a constant gray level. This method has the advantage that the resolution won't be reduced. But it follows the disadvantage of higher power consumption when rapidly switch the LC device, most important of all, a fast response material is required.

Driving Scheme	Gray Levels
No signal	0
	1
	2

Fig. 2.7 Schematic diagram of temporal dither method.

2.4.3 Polymer Stabilized Method

Polymer Stabilized FLC (PSFLC) device is other method to generate gray levels. By doping photo curable monomer in FLC, and polymer networks will be formed after UV curing. FLC molecules bound with cured monomer have higher threshold voltage than normal molecules, with the different threshold voltage, the voltage-controlled gray scales can be achieved as shown in Fig.2.8 [18]. The intermediate gray level is generated by controlling the voltage between the saturated voltage of normal FLC molecules and the threshold voltage of molecules bound with cured monomer. Gray scales are obtained as shown in Fig. 2.9 [19], three gray scales with 0V, 3V and 5V are applied, respectively, the intermediate state and the texture under POM is shown in Fig. 2.9 (b). PSFLC has the potential for flexible display application, high response time and zigzag defects free, however, obviously light leakage happens at dark state due to different retardation of monomers and FLCs.
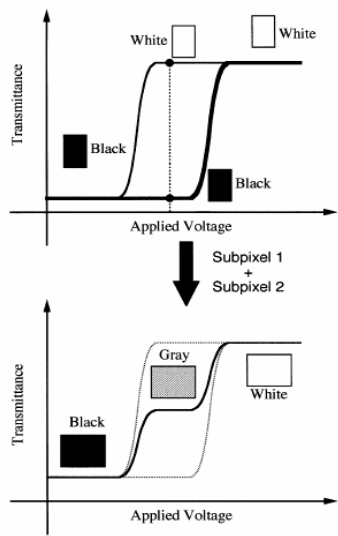
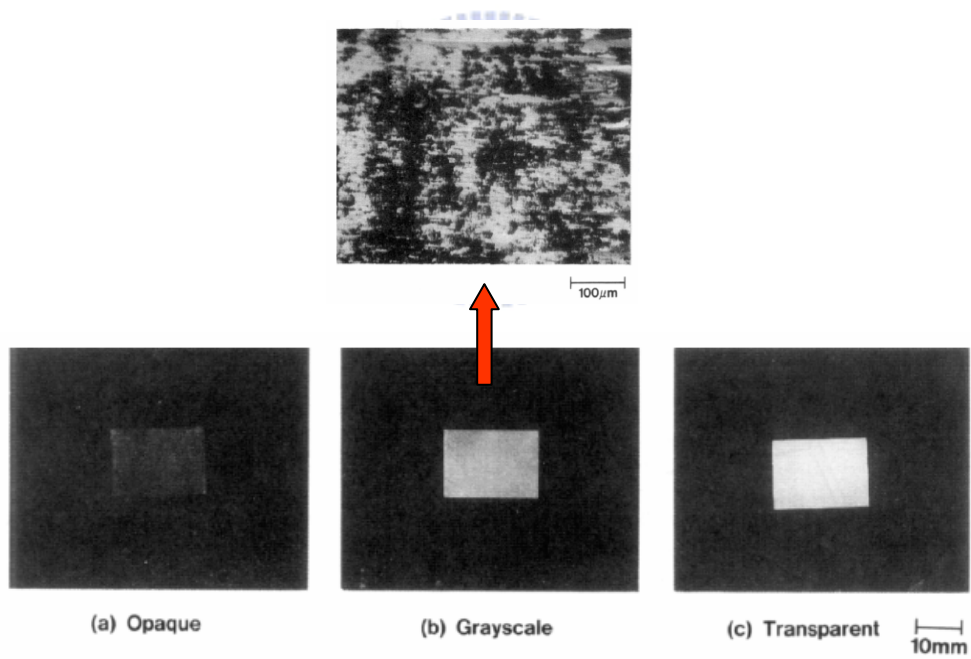Fig. 2.8 Schematic diagram of gray scales PSFLC [18].

Fig. 2.9 Photographs of PSFLC device driven by (a) 0V, (b) 3V and (c) 5V respectively, and the texture of Fig. 2.9 (b) is captured under POM [19].

2.5 Field Sequential Color LCDs

Field sequential technique has been utilized in CRT. A field sequential color LCD was first demonstrated in 1985 [20]. The continuous video is produced by time integration of human eyes, and 60 frames per second is at least required. If more than 180 frames can be achieved by a fast response material, the alternative back light, thee colors (R, G, B) LEDs can be utilized instead of the conventional CCFL. In this way, it follows the advantages of large color gamut due to LED back light, and high luminance, high resolution and low cost for production due to color filterless. The driving scheme of field sequential color FLCD of half-V and V modes switching FLC devices are shown in Fig. 2.10[4]. In half-V mode FLC device, the dark state is generated with the off state of FLC, as to V mode FLC device, the dark state can be achieved by turning of the LED back light ,which leads to the absolute dark state and improve the contrast ratio.
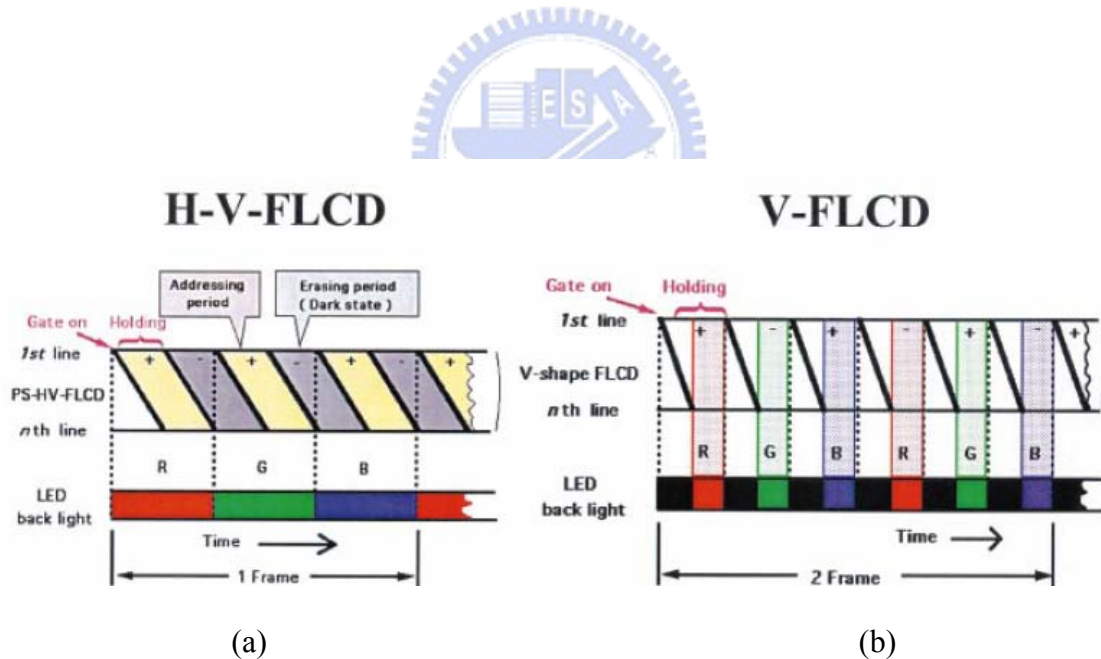

(a)   (b)

Fig. 2.10 Driving schemes of field sequential color FLCD. (a) Half-V and (b) V modes switching FLC devices [4].

2.6 Case Study

A series of side-chain liquid crystalline polysiloxanes and polymethacrylates containing oligooxyethylene spacers and 4-(S)-2-methyl-l-butyl [[(4-hydroxybiphenyl-4'-yl)-carbonyl]oxy]benzoate mesogenic side groups is synthesized by C. S. Hsu in 1993 [21], the results seem to demonstrate that "the tendency toward a chiral smectic C phase increases with increasing the flexibility of the polymer backbone and the oligooxyethylene spacer can increase dramatically the thermal stability of the chiral smectic C phase". The chemical structures and phase transitions temperature for polymers IP-IIIP is shown in Tab. 2.1, a flexible polymer backbone here has a tendency of lower glass transition temperature and a wider mesomorphic temperature range and also leads to a wider temperature range of SmC* phase.

Tab. 2.1. Chemical Structure and Phase Transitions and Phase Transition Enthalpies for Polymers IP-IIIP [21].

n = 1,2,3   IP-IIIP
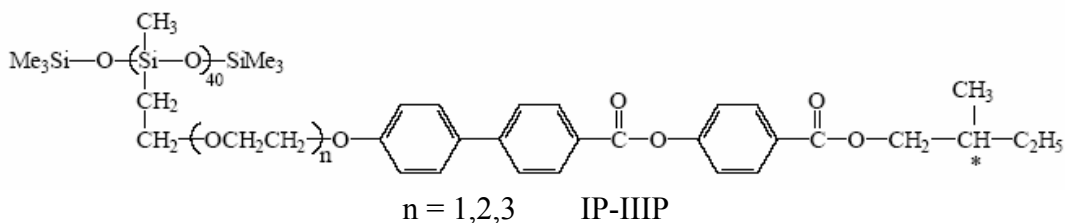
polymer	n^{α}		phase transitions, ℃ (corresponding enthalpy changes, kcal/mru)
IP	1	heating	G 9.8 SmC* 215.2 (0.07) SmA 234.6 (0.80) I
		cooling	I 229.2 (0.73) SmA 211.7 (0.03) SmC* 4.1 G
IIP	2	heating	G -11.2 SmC* 208 (-) SmA 211.8 (0.85) I
		cooling	I 212.0 (0.49) SmA 206 (-) SmC* -15.0 G
IIIP	3	heating	G -25.1 SmC* 168 (-) 190.3 (0.94) I
		cooling	I 184.2 (0.98) SmA 161 (-) SmC* -20.8 G

mru: mole repeating unit
G: glass, SmA = smectic A, SmC*= chiral smectic C, I= isotropic

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Series Ⅰ   MD*n*2NA   (*n*= 0,1, 2, 3)

Series Ⅱ   MD*n*2NB   (*n*= 0,1, 2, 3)

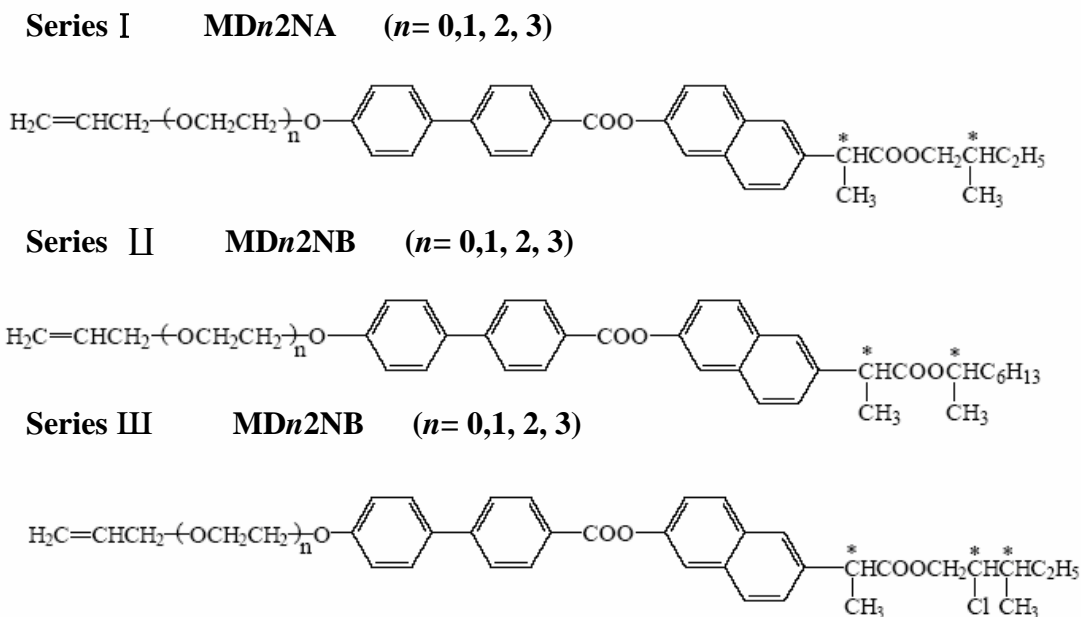**Series Ⅲ   MD*n*2NB   (*n*= 0,1, 2, 3)**

Fig. 2.11 Chemical structures of MD*n*2NA, MD*n*2NB and MD*n*2NB [22].

Three series of FLCs containing a (2S)-2-(6-(4-hydroxybipheny1-4'-carbonyloxy)-2'-naphthyl)propiobate mesogenic group and oligo(oxyethylene) spacers were synthesized and characterized by G. H. Hsiue [22], the chemical structures are shown in Fig. 2.11 and the phase transitions temperature are shown in Tab.2.2. The results present that oxyethylene unit as the spacer chain significantly depressed the phase transition temperatures. And the SmC* temperature range of series MD*n*2NB are larger than others, the SmC* temperature range of series MD*n*2NB was increased with the increase of the unit of oxyethylene chain.

Tab. 2.2. Transitions temperatures for the series MDn2NA, MDn2NB, MDn2NC [22].

Name	n	$\dfrac{Heating}{Cooling}$ Phase transitions, ℃ (corresponding enthalpy changes, kcal/mru)
MD02NA	0	$\dfrac{Cr\ 105(-)\ CrE\ 113.2(45.7)\ S_A\ 168.3(8.5)\ I}{I\ 166.8(7.3)\ S_A\ 98.6(11)\ CrE\ 83.8(31.7)\ Cr}$
MD12NA	1	$\dfrac{Cr\ 98.6(1.2)\ CrE\ 120.1(48.5)\ S_A\ 126.3(3.6)\ I}{I\ 124.8(6.2)\ S_A\ 81.3(-)\ S_C^*\ 77.1(46.1)^a\ Cr}$
MD22NA	2	$\dfrac{Cr\ 90.6(-)\ S_A\ 93.2(77.3)^b\ I}{I\ 91.7(4.9)\ S_A\ 84.7(1.1)\ S_C^*\ 68.6(62.2)\ Cr}$
MD32NA	3	$\dfrac{Cr\ 74.11(36.8)\ I}{I\ 63.5(4.5)\ S_A\ 60.0(-)\ S_C^*\ 53.4(24.7)^a\ Cr}$
MD02NB	0	$\dfrac{Cr\ 26.2(3.8)\ S_X\ 76.3(4.8)\ CrE\ 97.6(37.4)\ S_A\ 167.3(7.7)\ I}{I\ 165.9(6.1)\ S_A\ 93.7(11.6)\ CrE\ 74.5(26.4)\ S_X\ 23.2(4.5)\ Cr}$
MD12NB	1	$\dfrac{Cr\ 80.9(64.1)\ S_A\ 136.2(-)\ TGB_A\ 136.3(-)\ Ch\ 137.9(2.0)^c\ BP\ 141.1(0.4)\ I}{I\ 139.6(0.8)\ BP\ 136.3\ Ch\ 136(-)\ TGB_A\ 135.9(2.3)^c\ S_A\ 70.8(11.1)\ CrE\ 36.1(2.6)\ Cr}$
MD22NB	2	$\dfrac{Cr\ 65.3(31.4)\ S_A\ 97.5(-)\ TGB_A\ 97.7(-)\ Ch\ 102.2(0.8)^c\ BP\ 103.4(0.5)\ I}{I\ 102.4(0.4)\ BP\ 101(-)\ Ch\ 97.4(-)\ TGB_A\ 97(1.0)^c\ S_A\ 59.2(-)^d\ S_C^*\ 25.1(11.2)\ Cr}$
MD32NB	3	$\dfrac{Cr\ 20.5(15.2)\ S_X\ 39(18.7)\ S_C^*\ 52(-)^d\ S_A\ 70(-)\ TGB_A\ 72.6(-)\ Ch\ 74.2(0.4)^c\ BP\ 79.6(0.5)\ I}{I\ 78(0.6)\ BP\ 74(-)\ Ch\ 72.4(-)\ TGB_A\ 69.8(0.6)^c\ S_A\ 50(-)^d\ S_C^*\ 6.2(17.2)\ Cr}$
MD02NC	0	$\dfrac{Cr\ 120.5(54.1)\ S_A\ 164.2(11.0)\ I}{I\ 163.1(11.1)\ S_A\ 101.1(52.5)\ Cr}$
MD12NC	1	$\dfrac{Cr\ 106.4(71.8)\ S_A\ 127.3(7.8)\ I}{I\ 125.8(7.8)\ S_A\ 83.8(0.1)\ S_C^*\ 72.7(54.9)\ Cr}$
MD22NC	2	$\dfrac{Cr\ 92.0(-)\ S_A\ 94.5(72.8)^b\ I}{I\ 90.9(5.0)\ S_A\ 79.7(0.7)\ S_C^*\ 66.8(55.5)\ Cr}$
MD32NC	3	$\dfrac{Cr\ 57.2(22.9)\ S_A\ 63.3(18.1)\ I}{I\ 58.9(-)\ S_A\ 57.4(5.8)^e\ S_C^*\ 43.8(38.8)\ Cr}$

I= isotropic; CrE= crystal E; Sc*= chiral smectic C; S$_A$= smectic A; TGB$_A$= twist grain boundary A; Ch= cholesteric; BP= blue phase; Cr= crystalline phase.

In this thesis, we synthesized a series of novel ferroelectric glassy liquid crystals (FGLCs) targeting at wide chiral smectic C mesophase, fast switching, and easy alignment for the potential of display applications. Both pure FGLCs and FGLC as chiral dopant were examined. FGLC-3 possesses the widest chiral smectic C temperature range for 99.7℃, including room temperature, and SmA* mesophase was completely suppressed when FGLC-3 is used as chiral dopant. Not only the thermal properties but also the alignment and EO characteristics of FGLCs are presented in Chapter 4.