國立交通大學

光電工程研究所

碩士論文

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鐵電式液晶顯示器之設計與應用

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Fabrication Method of Polymer Walls in FLCD

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碩士論文

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摘要

傳統液晶顯示器因其輕薄短小的特性非常適合於攜帶型顯示器的應用，近年來更邁入大尺寸家用型電視市場。但是其動態顯示品質受限於液晶的反應速度而降低其應用性。為了有效提升其動態品質，擁有高速反應的鐵電式液晶技術受到顯示業界的高度矚目，若關鍵性的鐵電式液晶配向問題能夠被解決，便能為顯示產業帶來一波革命性的進步。以高分子材料建構成的液晶顯示器被証實能夠解決其配向問題的方法之一，而有鑑於傳統高分子牆的製程方法仍有許多缺點，在此我們提出一種新型的高分子牆製程技術應用於鐵電式液晶顯示器，可以有效地提升高分子牆的品質及縮短製程的時間及複雜度，使得高分子牆能夠更實際地被應用於顯示器產業。

此新型製程技術是利用外加電場來達到液晶與高分子單體的有效分離，再利用紫外光照射使單體產生高分子光聚合反應進而固化高分子牆結構。相較於傳統製程，本研究方法不但可以減少高分子單體殘留在顯示畫素之中的比例，更能提升顯示器的對比度及亮度，而更完整的高分子牆結構可以加強顯示元件的機械性質，使之應用於可撓式顯示器的潛能大幅提升。

Design and Fabrication of the Novel Fabrication Method of Polymer Walls in FLCD

Student: Yi-Chih Wang **Advisor: Dr. Han-Ping D Shieh**

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Abstract

Fast switching liquid crystal technique is essential for achieving high dynamic display quality in current LCDs. Ferroelectric liquid crystal (FLC) is a well known material which has fast response time, but suffers an alignment problem. Recently, the polymer wall and network structures were studied in order to eliminate the alignment problem in FLC device. Besides, polymer walls can be applied to a flexible display. In this thesis, a novel process was studied to fabricate polymer walls in FLC devices by applying an electric field.

In the proposed fabrication process, the phase separation between FLC and acrylate-based monomers was induced in the specific electric field. With this process, phase separation can be induced and polymer walls can be fabricated without a photomask. Besides, shorter process time and simpler steps of this method will promote the possibility of applications in display industry.

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在碩士班兩年的研究生活中，首先要感謝指導教授謝漢萍在研究，報告及口語英語能力的細心指導，，也使我能在此設備完善的研究室學習到團體研究的精神，在專業方面更是對液晶及平面顯示器技術有深入的研究與了解，並且順利完成本篇論文與碩士學位。

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Chapter 1

Introduction

1.1 Display Technology

Display technology has been progressing promptly, since the last few yours of the 21st century. With the popularization of computer and wireless communication, multimedia application displays and mass information interchange become important parts of people, and the demand of technologies of display mass information in contents and pictures are getting more imperative. Nevertheless, electronic display is the key element for information display. Based on different applications, there are several types of electric display technologies, such as field emission displays (FEDs), plasma display panels (PDPs), cathode ray tubes (CRTs), and liquid crystal displays (LCDs)[1]. Among all devices, LCDs can provide many desired features of thin format, compact size, light weight, and high image quality. As a result, LCDs have become the most important information display devices.

1.2 Liquid Crystal Displays

LCD can fulfill the requirements of the applications including notebook, desktop monitor, television, etc. With the developments of various applications, LCDs have become the most important information displays nowadays.

LCD does not emit light by itself; even so, a “transmissive type" LCD was demonstrated by Sharp Corporation in 1989 [2]. The transmissive LCD is composed

of a backlight system which is disposed at the rear surface. Therefore, the amount of the light from the backlight which transmits through the LC panel is controlled by the liquid crystal in order to display images. The components of the LCDs compose of backlight, polarizer, circuit plate, liquid crystal, and color filter, as shown in Fig 1.1.

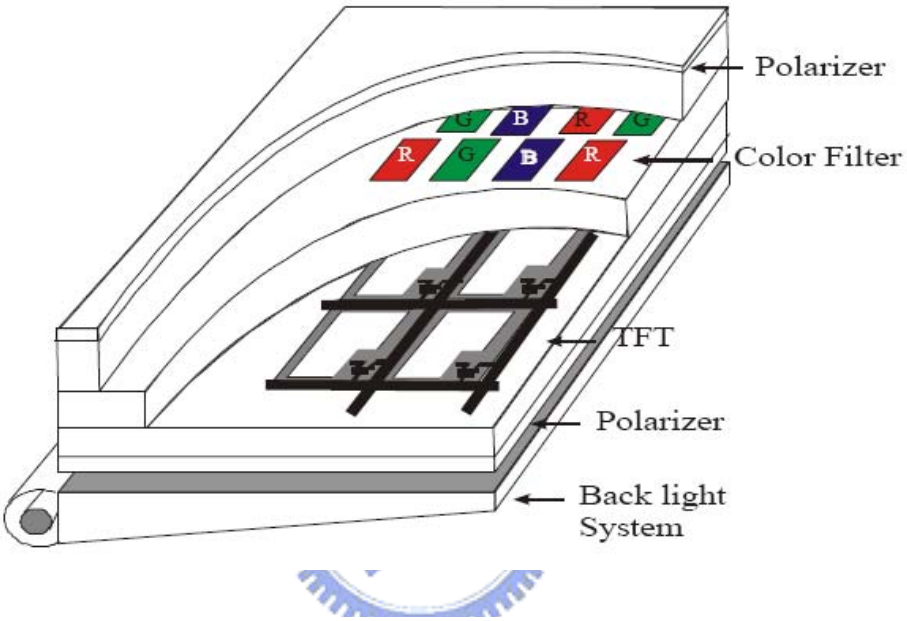


Fig. 1.1 Sketch of liquid crystal display.

Nowadays, several types of LCDs were researched in order to support different kinds of applications, such as reflective LCD [3] and transflective LCD [4]. The typical structures are shown in Fig 1.2. Cholesteric liquid crystal materials which can reflect specific wavelength of light [5] were popular in the research of reflective LCDs. A reflector was also utilized to reflect light recently, especially the transflective LCD used an inner reflector to reflect ambient light in reflect area, while light was displayed by backlight system in transmissive area. Reflective and Transflective types still have some critical issues such as achievement of full-color and simplifying the

fabrication process. Compared to these types of LCDs, transmissive one is the most popular application in multimedia display industry.

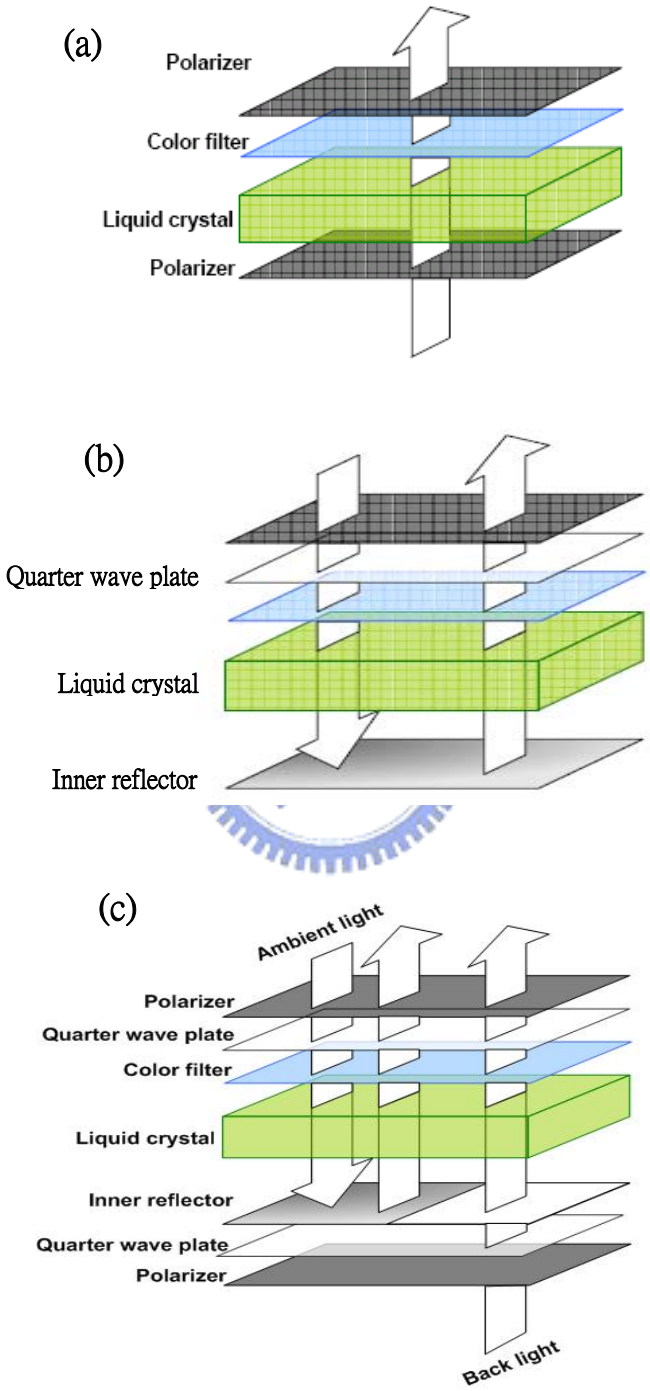


Fig. 1.2 Sketch of (a) Transmissive LCD, (b) Reflective LCD, and (c) Transflective LCD.

The common LC application in transmissive LCDs is twisted nematic (TN) type. It has the advantages such as high contrast ratio and low driving voltage, however, its slower response time will cause other display problems or restrain the application of LCDs. Based these issues, ferroelectric liquid crystal (FLC) displays were researched in order to achieve faster response time than that of TN display. In general, the response time of FLC devices is of less than 1 ms. As we know, the alignment problem of FLC devices will bring about the zigzag defect and limit the contrast ratio of it. In recent research, polymer stabilized ferroelectric liquid crystal (PSFLC) which contains polymer wall and polymer network structures can solve the alignment problem and improve mechanical property of FLC devices [6-7].

1.3 Polymer Walls in FLC Devices

Polymer structure was widely used in display applications due to its special mechanical characteristics. For example, polymer film was used in polymer dispersed liquid crystal (PDLC) display [8-9], polymer wall was utilized to improve the constructional strength in flexible display, and both of polymer wall and network structures were applied to PSFLC display.

The architecture of polymer walls in FLC devices are shown in Fig 1.3. In display application, polymer walls which are in the gaps between the display areas can well define the pixel areas in LCD panels. Besides, polymer walls greatly increase the mechanical stability of displays, adheres the top and bottom substrates, and ever provides a self-sustaining polymer structure making possible flexible devices of large area with relatively uniform thickness.

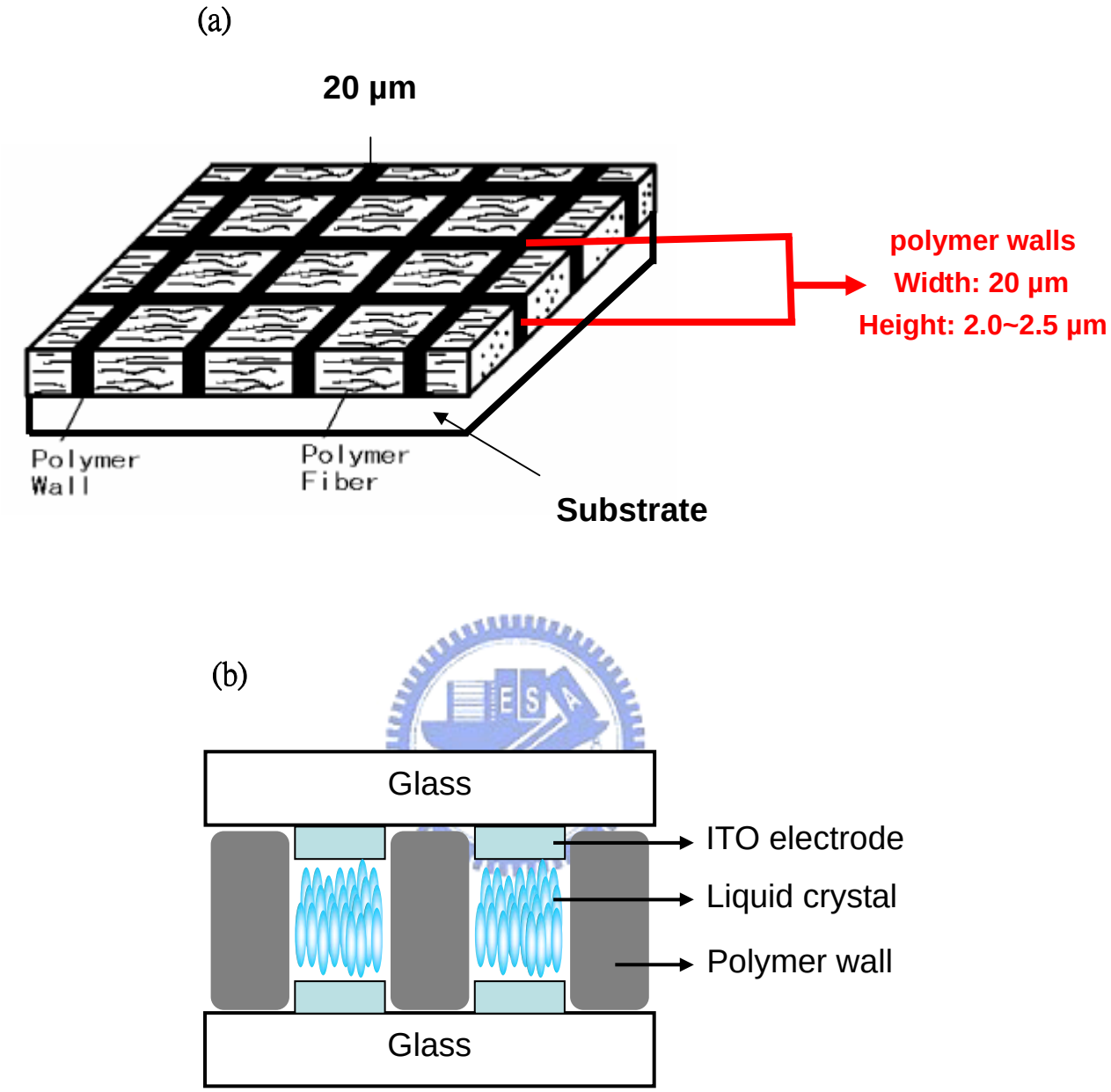


Fig. 1.3 (a) Typical polymer wall structure and (b) Cross-section of polymer walls.

The current method to fabricate polymer walls in FLC devices is photo-polymerization process. A FLC mixture was mixed with the monofunctional liquid crystalline acrylate monomers and was filled into a cell. A laminated FLC cell

was then irradiated with UV light through a photomask to form the polymer walls by polymerizing the monomers floating in UV exposed areas. There will be some sufficient amount of unreacted monomers must remain in the masked area. The unreacted monomers will decrease the contrast ratio of the FLC device. In addition, a photomask is also required in the photo-polymerization process of this traditional method. This requirement will cause the alignment problem between the pixels and photomask.

1.4 Motivation and objective

The traditional process of polymer walls in FLC device is a complex, and inefficient fabrication process as mentioned above. To pursue for more complete polymer walls and avoid the unreacted monomers which reduce the contrast ratio in FLC device as discussed above, a method of fabricating polymer walls in FLC device is required in display industry.

As a result, the main objective of this thesis is to propose a novel fabrication method of polymer wall structures based on FLC devices. This novel process has the benefits of shorter process time, higher separation quality and no photomask-alignment issue. The main concept of this design is to fabricate the polymer walls in FLC device by applying an electric field, respectively. Besides, the discussion of the results of phase separation will also be given in this thesis.

1.5 Organization of This Thesis

The thesis is organized as following: The principle of the phase separation, classification of liquid crystal, and fabrication method is presented in **Chapter 2**.After that, in **Chapter 3**, the novel fabrication process of the polymer walls in FLC device will be introduced in detail, and the major instruments used to measure the polymer walls, such as scanning electron microscope (SEM), will also be described. The experimental results, including the phase separation, polymer walls, and discussions, will be in **Chapter 4**. Finally, the conclusions of this thesis will be presented in **Chapter 5.**

Chapter 2

Principle

2.1 Liquid Crystal

Solid phase, liquid phase, and gaseous phase can express all the things in the world. The phase of matters can be changed upon different temperature and pressure of the matters. The LC phase is a distinct state of matter observed between the solid and liquid states. Therefore, LC phase is called mesophase, and the liquid crystal is also described as mesogen. There are several types of LC states, depending upon the amount of order in the material. From low temperature, the material begins in the crystalline (solid) state, it undergoes a phase change. The first LC phase is smectic phase, where there is layer-like arrangement as well as translational and rotational motion of the molecules. A further increase in temperature leads to the nematic phase, where the molecules rapidly diffuse out of the initial lattice structure and from the layer-like arrangement as well. At the highest temperatures, the material becomes an isotropic liquid where the motion of the molecules changes yet again. This section will explain the classifications of LC materials [10].

2.1.1 Nematic Phase

The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction, means the LC molecules will align along one direction. The molecules point vertically but are arranged with no

particular order, as shown in Fig 2.1. Nevertheless, if the nematic LC molecules are functioned by applying an electric field, the molecules will be aligned along the direction of the electric field due to the dipole effect, as shown in Fig 2.2. Nematic liquid crystal phase is the first one to be applied to LCD industry, such as twisted nematic (TN) type and super twisted nematic (STN) LCDs.

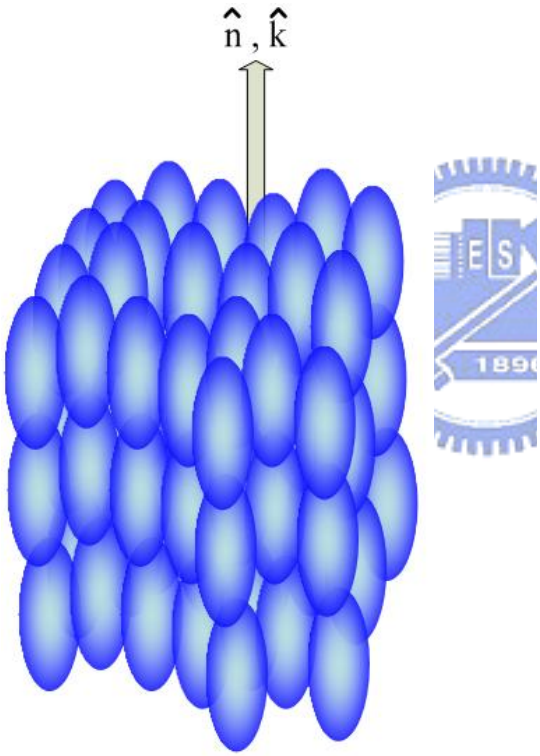


Fig. 2.1 Schematic diagram of the structure of nematic phase.

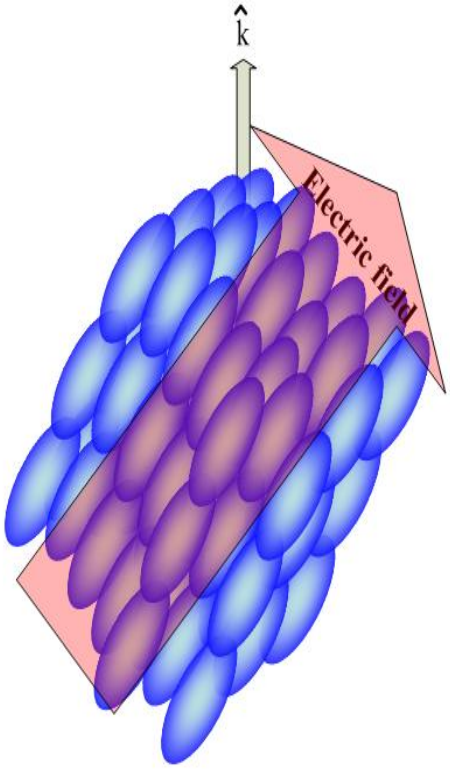


Fig. 2.2 The structure of nematic phase in the directional electric field.

2.1.2 Smectic Phase

The smectic state is another distinct mesophase of LC substances. In the smectic state, as shown in Fig 2.3, the molecules maintain the general orientation order of nematic phase, but also tend to align themselves in laminated layers or planes.

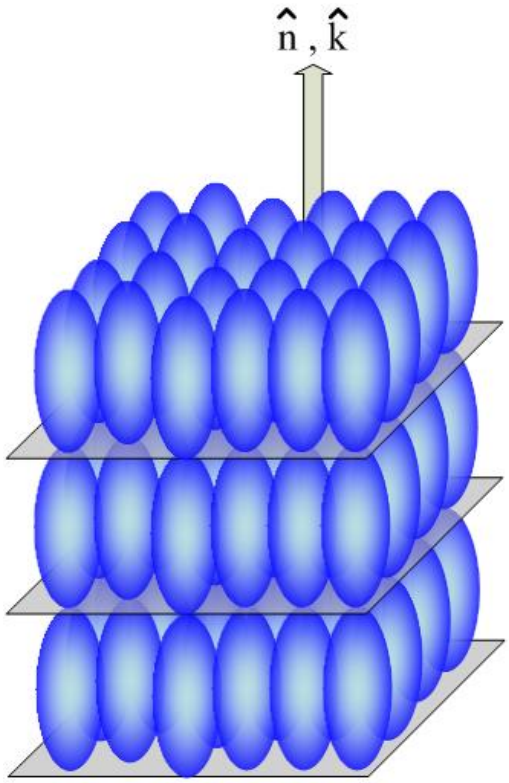


Fig. 2.3 The diagram of layer-like arrangement of smectic phase.

Smectic phase can be divided into several classifications by slight distinctions. For example, the direction of the molecule is perpendicular to the smectic plane in the

smectic-A mesophase. However, in the smectic-C mesophase, molecules are arranged as in the smectic-A mesophase, but the director is at a constant tilt angle measured normally to the smectic plane, the comparison between smectic-A mesophase and smectic-C mesophase is shown in Fig 2.4.

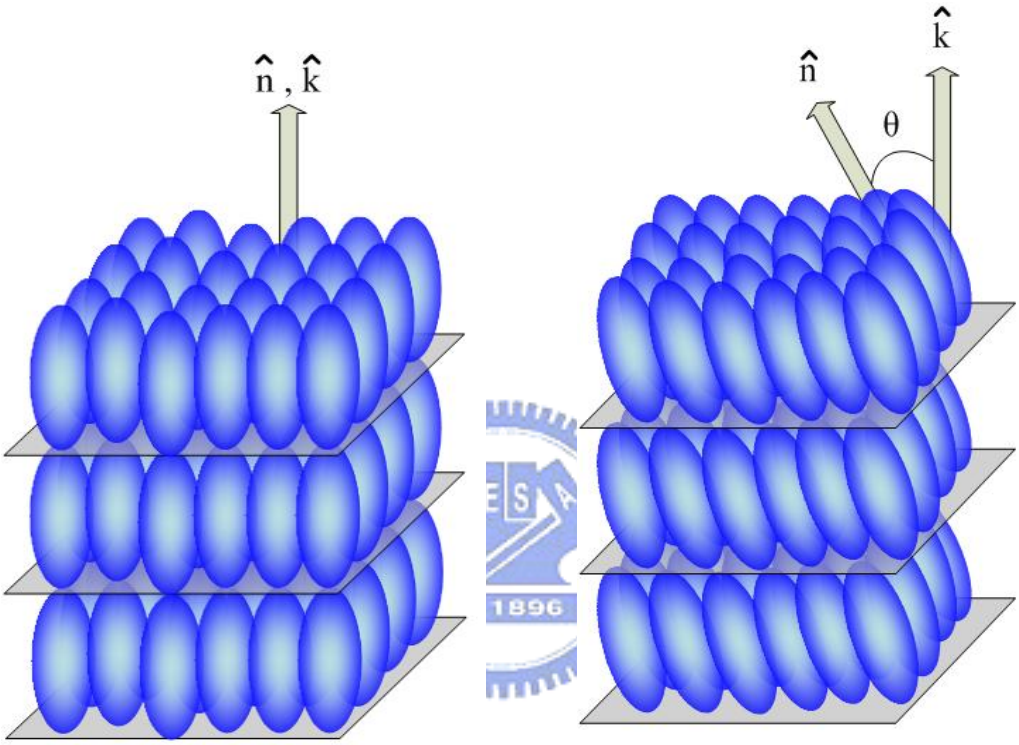


Fig. 2.4 (a) the directions of molecules in smectic-A phase are normal to the layer, and (b) the molecules in smectic-C phase have a tilt angle θ from the axis.

2.1.3 Chiral Smectic-C Phase (Smectic-C*)

The smectic-C mesophase has a chiral state designated C* [11]. Consistent with the smectic-C, the director makes a tilt angle with respect to the smectic layer. The

difference is that this angle rotates from layer to layer forming a helical structure in the chiral smectic-C (Smectic-C*). In other words, the director of the smectic-C* mesophase is not parallel or perpendicular to the layers, and it rotates from one layer to the next, as shown in Fig 2.5. Due to its ferroelectricity, this phase is also called FLC phase.

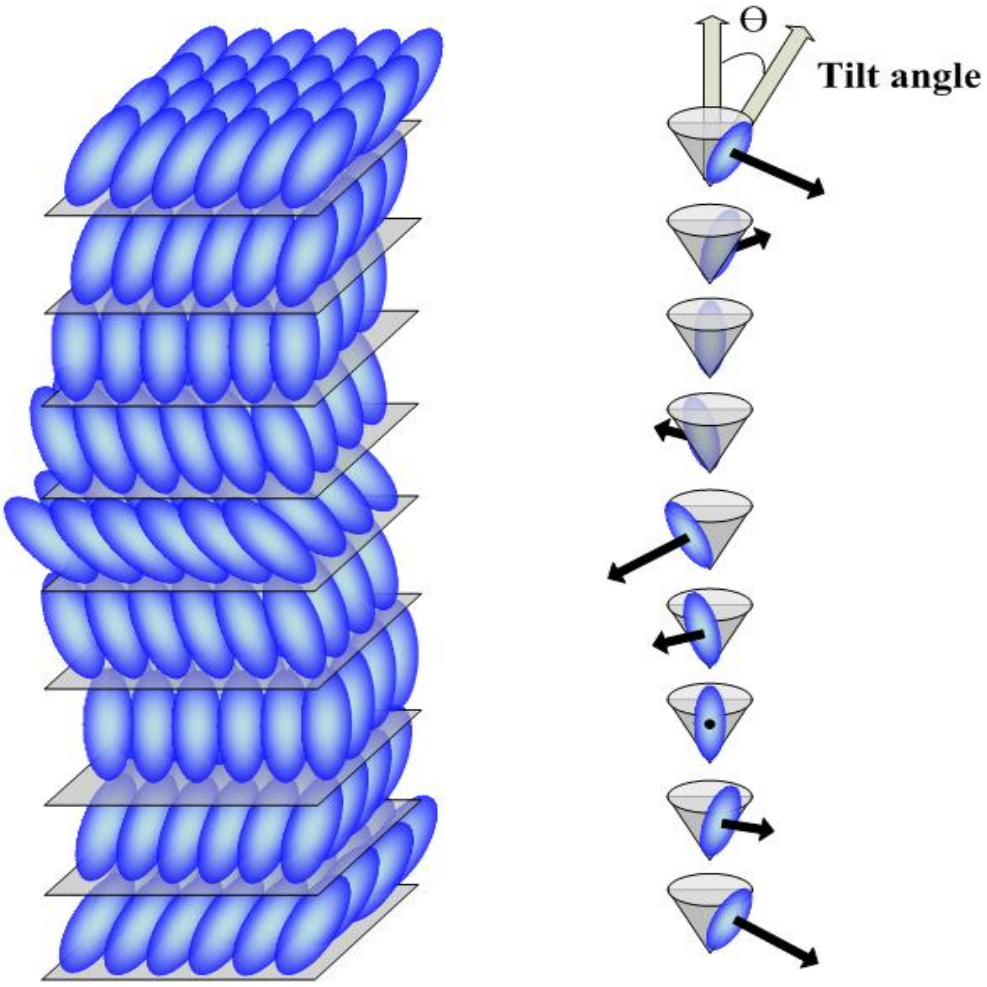


Fig. 2.5 Sketch of chiral smectic-C phase, molecule will align and switch as a cone structure. Black vectors are the polarization vectors of the molecules.

2.1.4 Chiral Nematic Phase (Cholesteric Phase)

The chiral nematic phase (N* phase) is also called Cholesteric phase [12]. This phase is typically composed of nematic mesogenic molecules containing a chiral center. The chiral center produces intermolecular forces that favor alignment between molecules at a slight angle to one another. This leads to the formation of a structure which can be visualized as a stack of very thin 2-D nematic-like layers with the director in each layer twisted with respect to those above and below. In this structure, the directors actually form in a continuous helical pattern about the layer normal as illustrated in Figure 2.6.

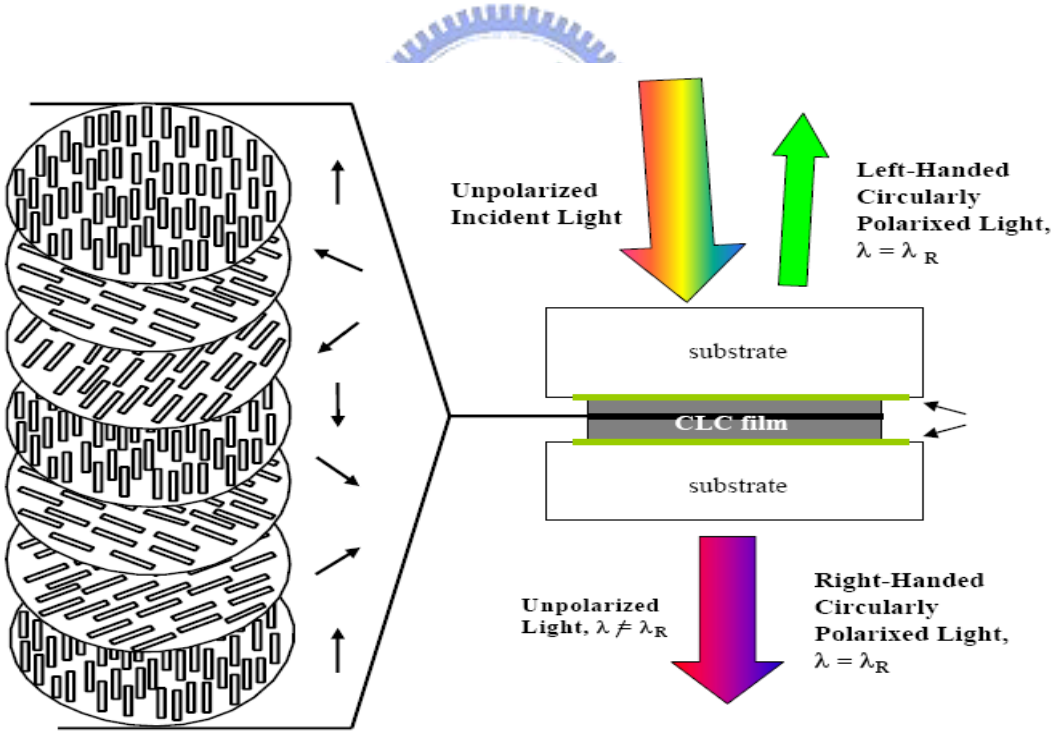


Fig. 2.6 Diagram of chiral nematic phase. Light with specific wavelength can be reflected by the liquid crystal film.

One of the important characteristic of the cholesteric mesophase is the pitch. The pitch, p, is defined as the distance it takes for the director to rotate one full turn in the helix. A byproduct of the helical structure of the chiral nematic phase is its ability to selectively reflect light of wavelengths equal to the pitch length, so that the light will be reflected when the pitch is equal to the corresponding wavelength of light in the visible spectrum [13].

2.1.5 Isotropic Phase

The isotropic phase has properties that the liquid crystal molecules align disorderly. In the isotropic state, all directions are indistinguishable from each other. In conclusion, this phase is more similar to liquid phase.

2.1.6 Ferroelectric Liquid Crystal (FLC)

When the LC molecule is chiraling, successive smectic C layers show a gradual change in the direction of tilt. As results, the director processes about the z axis from layer to layer, always lying on the surface of a hypothetical cone of angle 2θ as illustrated in Fig 2.7. The angle around the circle of precession is known as the azimuthal angle. Thus, a helical structure is created in the chiral smectic-C mesophase with the pitch being the distance along the z axis needed to reach the same molecular orientation [14].

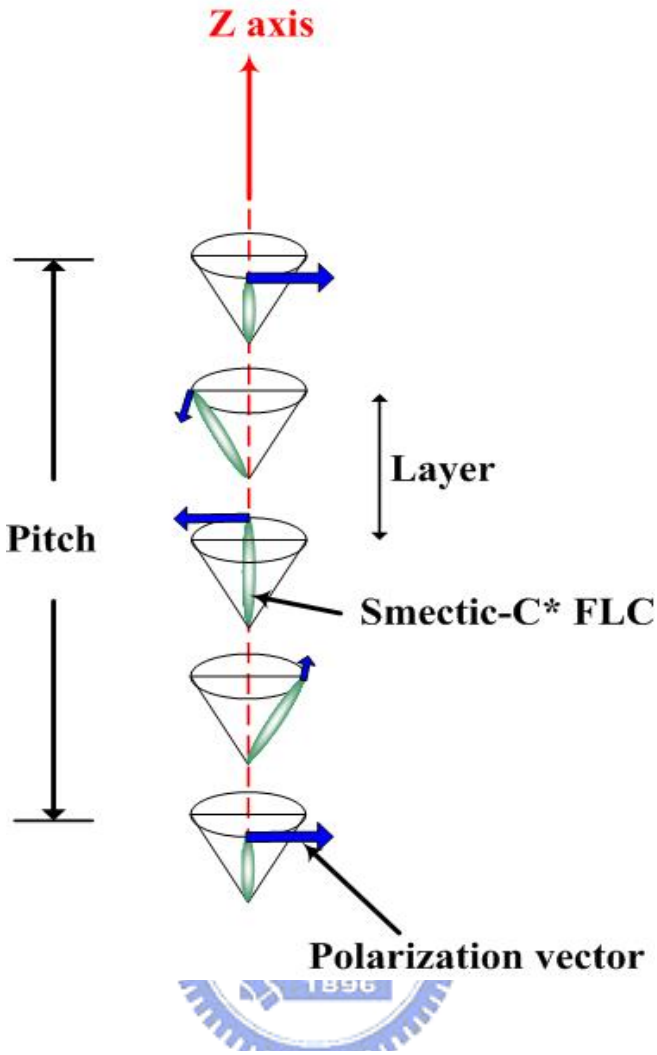


Fig. 2.7 Helical structure of ferroelectric liquid crystal.

Smectic-C* LC has a property about optical rotation. According to the asymmetry of the composition of the LC molecule, there are permanent dipole moments in smectic-C* liquid crystal. For a single layer of the smectic-C* phase, LC molecules point towards the same direction, and the director is at a constant tilt angle measured normally to the smectic plane. The dipole moments will not be canceled in smectic-C* liquid crystal phase. The dipole moments will result in a self-spontaneous molecular polarization, and the polarization vector is perpendicular to the molecule

and contained in the smectic layer plane. Therefore, all possible directions for the vector are tangent to the circle of intersection of the cone with the plane. The polarization vector is the blue vector, as shown in Fig 2.7.

The phase of FLC will be changed by varying temperature. For example, R2301 FLC has the phase sequence chiral smectic C-64.7^{o}C-chiral nematic-85^{o}C- isotropic. We can choose chiral smectic-C or chiral nematic phase in the FLC devices by controlling the temperature.

2.2 Phase Separation

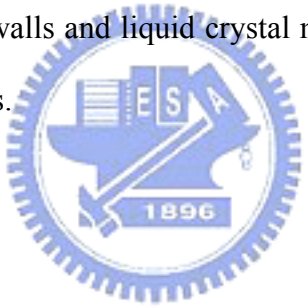
In LCD technology, some applications require for combining the polymer structure in liquid crystal. For example, flexible display technique, polymer-dispersed liquid crystals (PDLC), and polymer stabilized ferroelectric liquid crystal (PSFLC) applications. As we know, in PDLC application, the liquid crystal molecules must be well mixed with the polymer materials. Besides, the monomers should be perfectly separated from LC material in order to generate polymer wall structures in flexible display technique and PSFLC application. In order to achieve these objectives, the phase separation method between the monomers and LC molecules was studied. This section will introduce the temperature induced phase separation method which liquid crystal molecules can be spread with the monomers spontaneously.

The temperature induced phase separation method was firstly proposed in 1988. The mixture which is mixed by LC materials and monomers must be heated above the melting point of the monomers. The phase separation phenomenon will be induced during the cooling process [15-16]. LC materials can be separated out as a drop and scattered with the monomers at phase separation temperature. Recently, this method is

widely used in the fabrication process of polymer network and polymer wall structures.

2.3 Polymerization of Monomers

The current polymerization methods include step-growth polymerization, free radical polymerization, and photo-initiated polymerization. Step-growth method will have the defect about incomplete hardening of monomers. Therefore, the photo-initiated polymerization was utilized in our experiment. In order to initiate the polymerization by UV exposure, an additional photo-initiator is required in this proposed method. The concentrations of photo-initiator and exposure time will greatly affect the quality of polymer walls and liquid crystal molecules, this situation will be discussed in following sections.



2.4 Process of Polymer Walls

Polymer walls can improve the mechanical strength of the device, and were utilized in flexible devices and PSFLC displays recently. The fabrication processes of polymer walls in a FLC cell will be introduced in following sections. The current process requires a photomask to complete the polymer wall structures. Nevertheless, it suffered by the alignment and other problems, and the quality of the polymer walls is reduced. Consequently, we proposed an electric field induced method to settle these problems.

2.4.1 Process with a Photo-mask

The traditional fabrication process of polymer walls was proposed by NHK Corporation in last few years [7]. In this method, two substrates which were coated ITO electrodes and polyimide layer were used to compose a cell. The crisscross sections between upper and lower ITO patterns are pixels while the blank areas between pixels will expectantly be fabricated the polymer walls. The space between two substrates was controlled about 2 μm by spacers. The FLC mixture which was mixed with a monofunctional liquid crystalline acrylate monomer was filled into the space; the cell was heated and cooled down until the phase separation temperature very tardily. FLC molecules will be separated at this temperature from the mixture.

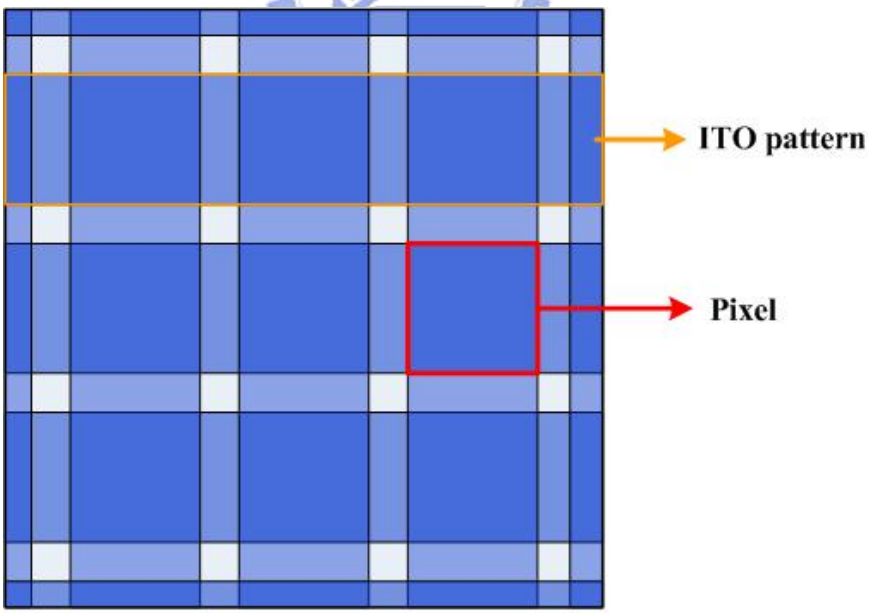


Fig. 2.8 Top view of the FLC device.

Significantly, a photomask was utilized to be an anti-dazzling screen which has the same patterns of the ITO pixels, as shown in Fig 2.8 and Fig 2.9. Perfectly overlapping the patterns of the cell and the photomask, light will be blocked by the opaque areas of the photomask. Finally, a laminated FLC cell was then irradiated with UV light through a photomask to form the polymer walls by polymerizing the monomers floating in UV exposed areas. Fig 2.10 is the flowing sketch of this fabrication process.

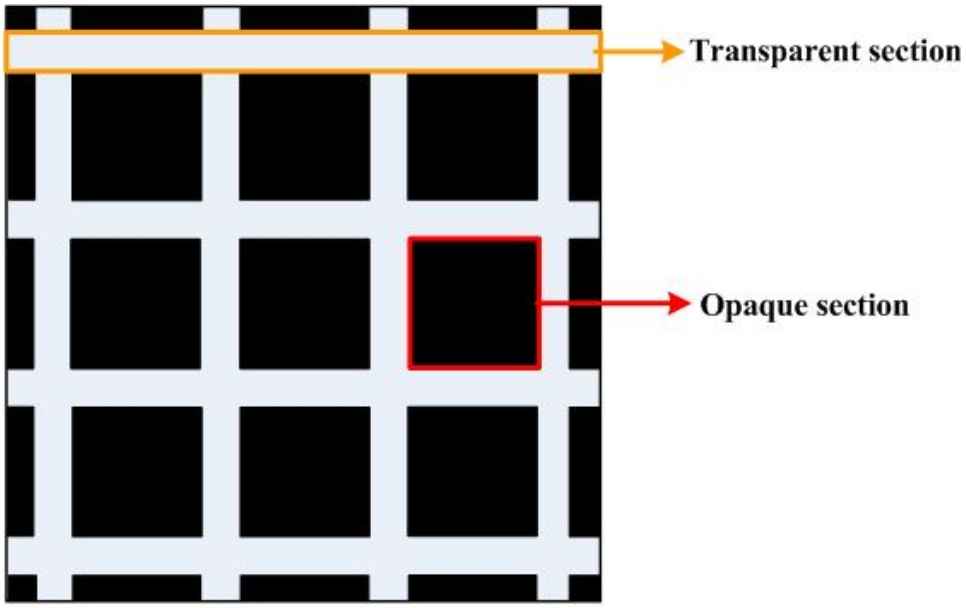


Fig. 2.9 Sketch of the photomask. Black parts are the opaque sections which can block UV light from irradiating.

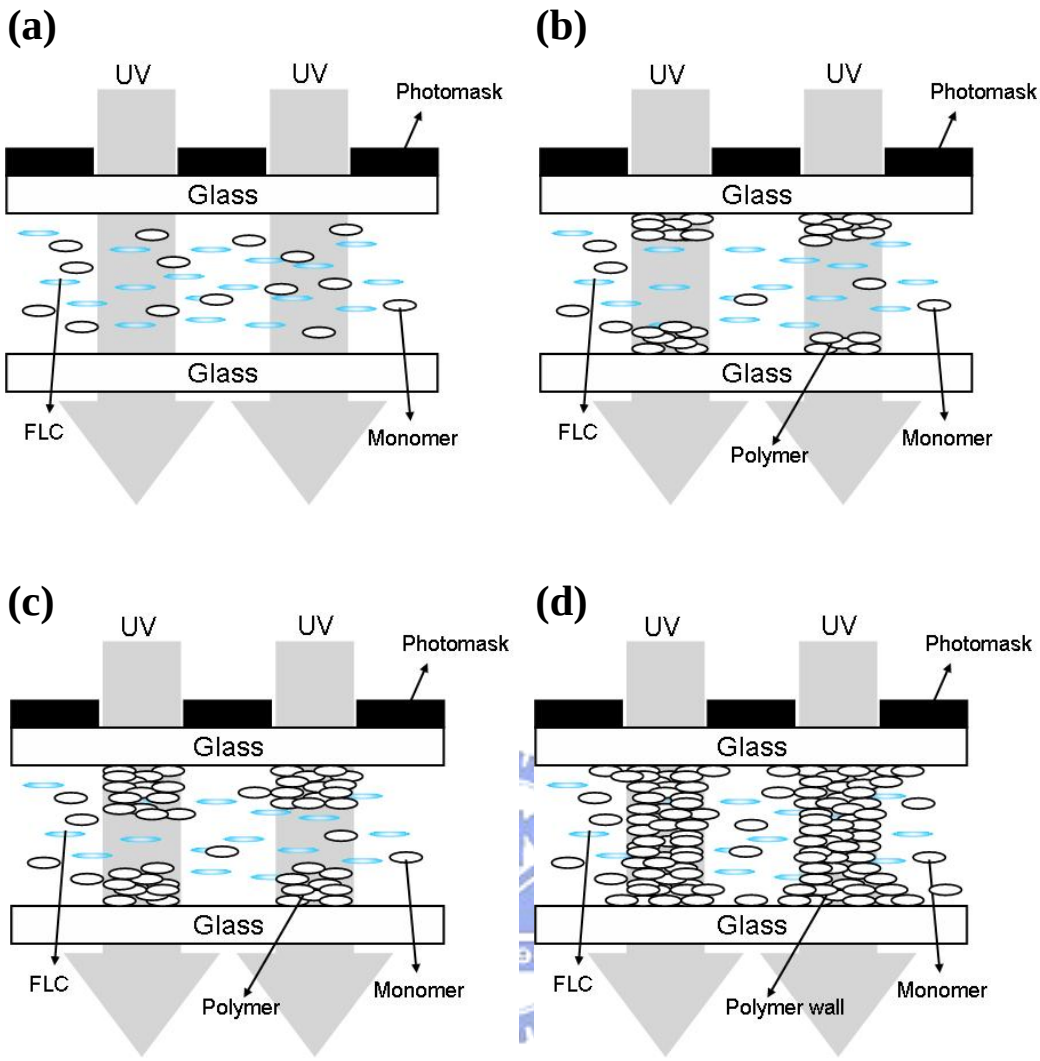


Fig. 2.10 Sketches of traditional temperature induced phase separation method under UV exposure, (a) initial condition (b) migration (c) aggregation, and (d) polymer wall formation.

Based on this temperature induced method, there will be some sufficient unreacted monomers must remain in the masked area. This situation results the poor separation quality of polymer molecules. Besides, the polymerization process will also take much time in forming polymer wall structures. Following, the novel

separation method will be introduced. Some drawbacks of temperature induced method can be successfully improved.

2.4.2 Proposed Process with an Electric Field

The electric field induced method is that an electric field is applied to separate the monomers from ferroelectric liquid crystal [17-18], as shown in Fig 2.11. The electric field between upper and lower electrodes was generated by applying an AC voltage to the electrodes. The AC signal which is shown in Fig 2.12 should be square wave, high frequency, and high amplitude. As we mentioned before, the major axis of nematic liquid crystal molecule will follow the direction of the electric field. Therefore, the direction of liquid crystal molecule can be switched up and down by turns in high frequency by controlling the waveform of the AC signal. The monomers which were mixed in the LC materials can be squeezed out of the areas where the LC molecules were being affected by an electric field. Compared to temperature induced phase separation method, the process time of this method can be shortened.

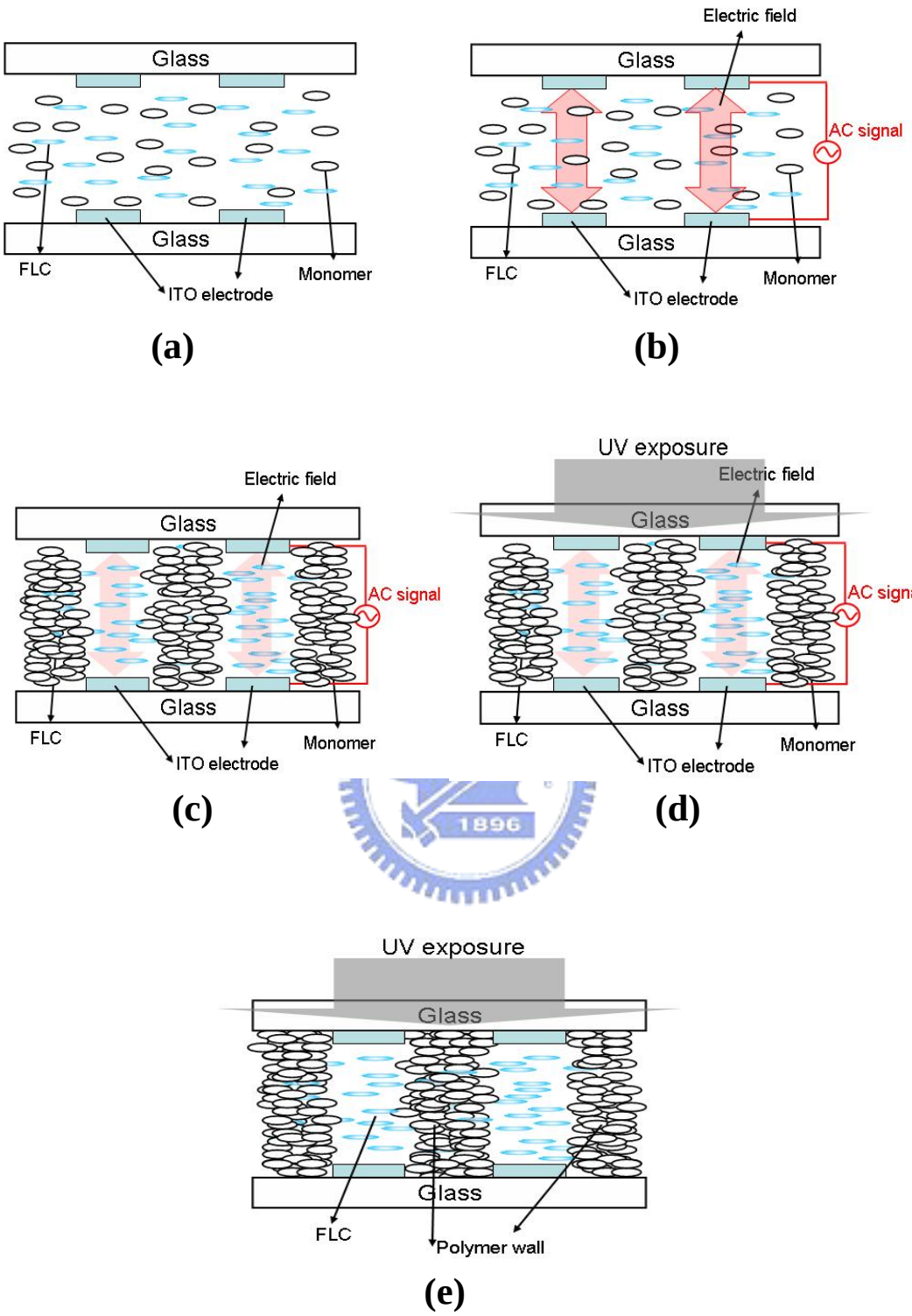


Fig. 2.11 The flow chart of the novel electric field induced phase separation method. (a) before progressing, (b) applied AC electric field, (c) phase separation, (d) photo-polymerization, and (e) formation of FLC cell with polymer walls.

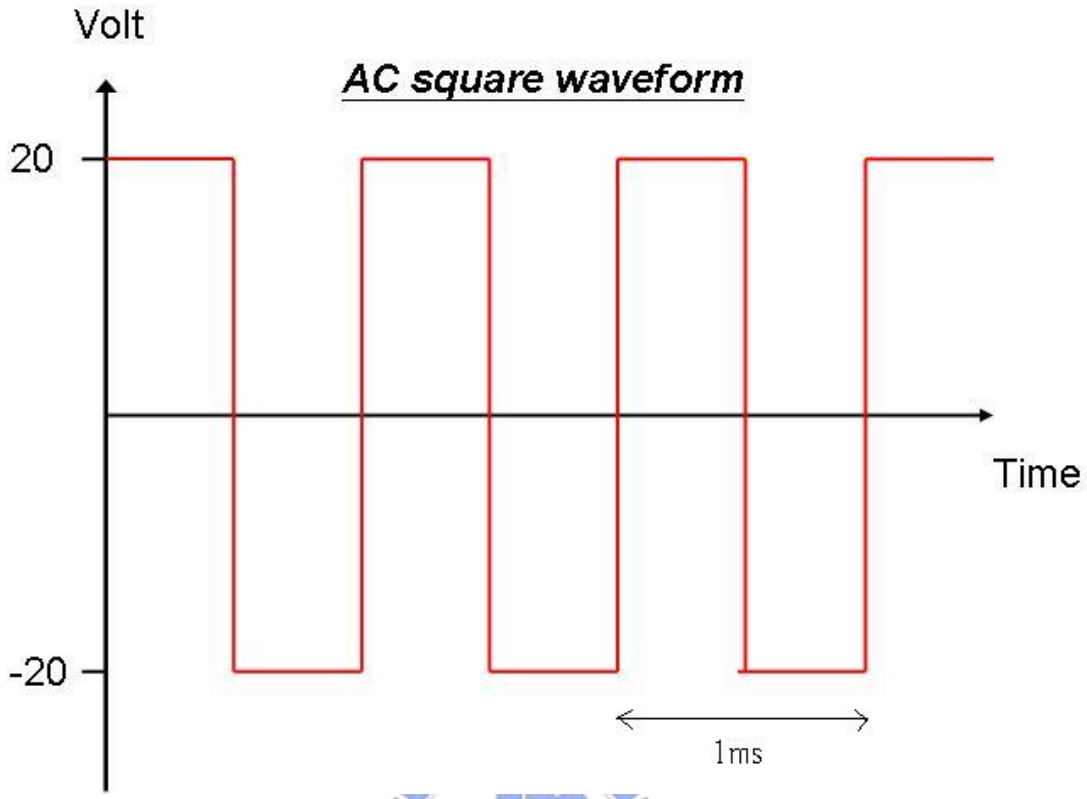


Fig. 2.12 Waveform of the applied signal for driving the FLC devices.

Initially, both of the frequency and amplitude of the AC supplier were chosen as 1 kHz and 20 Volt. However, the preliminary experimental results of phase separation revealed that the separation quality and separation speed were not good. Thus, the comparisons of phase separation results were made by applying the AC voltage with different frequency and amplitude.

The key issue of the electric field induced method is that the temperature of separation process should be in the period of chiral nematic phase. Thus, ferroelectric liquid crystal will switch as our expectation and monomers can be squeezed to assigned areas. However, the polymerization process which was induced by UV exposure after the phase separation process can not be simply defined. Polymerization process of the polymer walls in TN devices can be done at the temperature which

liquid crystal is nematic phase. Generally speaking, the polymerized temperature was chosen as room temperature. Nevertheless, the polymerized temperature in FLC devices can not be room temperature due to that FLC is smectic phase at room temperature. The phase separation results can not be maintained at this temperature. Thus, the polymerized temperature of FLC devices in our experiment will be shown and discussed in chapter4. With the electric field induced method, a high quality and rapid fabrication process of polymer walls can be attained.

2.4.3 Comparisons of these Processes

The conventional temperature induced phase separation is suffered some obvious defects, such as the quality of phase separation, longer process time, and alignment problem between the photomask and pixels. Tab. 2.1 lists their comparisons according to the separation quality, process time, and other properties. The major drawback of temperature induced method is the phase separation quality between monomers and ferroelectric liquid crystal. On the other hand, the electric field induced one can not compatible with the process of polymer network structures. Among these comparisons, the electric field induced method is the better choice of polymer wall structures than temperature induced one.

2.5 Summary

Polymer walls and polymer networks were utilized in PSFLC devices. In general, the conventional process of polymer walls required a photomask to be utilized as an anti-dazzling screen. However, poor separation quality and long process time were the drawbacks of this method. Therefore, a novel fabrication method which

used an electric field to induce phase separation between FLC and monomers was developed in this thesis. Via this electric field induced phase separation method, a high quality and rapid fabrication process of polymer walls can be attained.

Tab. 2.1 Comparisons of temperature induced and electric field induced methods.

Process	Temperature induced	Electric field induced
Alignment photomask	O	X
Additional ac voltage	X	O
Shorten process time	X	O
Better phase separation quality	X	O
Easier process	X	O
Compatibility with the process of polymer network	O	X

O : Yes X : No

Chapter 3

Fabrication and Measurement Instruments

3.1 Introduction

A novel method to fabricate polymer walls in FLC devices was proposed in this thesis. The fabrication process will be also described in this chapter.

The fabrication sequences of the proposed method included the process of the substrate and the cell formulation. The commercial available indium-tin oxide (ITO) glass was cleaned by standard process in advance. After that, the semiconductor process including spin coating, lithography and etching was utilizing in order to obtain the desired pattern. The ITO pattern upon the glass was taken for the transparent electrode. Then the spin coating and rubbing techniques will be used to make the alignment layer.

The cell process joins the ITO substrates with accurate alignment. The cell gap was controlled about 2 um by spacers and the space between the two substrates was filled with the mixture of FLC and monomers. After cell process, an electric field between upper and lower ITO patterns which was applied by the function generator and a hot stage which was used to control the temperature of the device can induce the phase separation phenomena. Finally, a UV light was required in polymerization process.

Besides, the process of phase separation between FLC and monomers was observed by the polarized optical microscope and the performance of the polymer structures was measured by SEM. The major features of the above mentioned

instruments will be illustrated in this chapter.

3.2 Fabrication Process

The features of the novel fabrication process of polymer walls have been introduced in previous chapter. This part will describe the cell fabrication process which includes spin coating, lithography, and wet etching. Moreover, the phase separation process will also be explained.

3.2.1 Cell Fabrication

The detailed fabrication steps are listed below, and the substrate pretreatment is shown schematically in Fig 3.1.

(a) Substrate pretreatment:

(1) Substrate preparation: For the display application, the glass is widely used as a substrate. In the fabrication, the glass of about 1.1 mm thick was chosen. And ITO was uniformly sputtered on the glass. Before the lithography process, ITO glass was cleaned by acetone and isopropyl alcohol.

(2) Lithography: First of all, positive photoresist was applied and coated on substrate. After soft baking, the ITO glass was exposed under ultra-violet (UV) light source through a mask. Consequently, the pattern on the mask was transformed to the positive photoresist after developing.

(3) Wet etching: After exposure and development, the substrate was etched. Removing the photoresist, the patterned ITO substrate was obtained.

(4) Polyimide coating: Polyimide thin film was spin-coated upon the ITO layer

and baked by heating. Thereafter, the solid thin film was treated by rubbing technique to perform the substrate preparation.

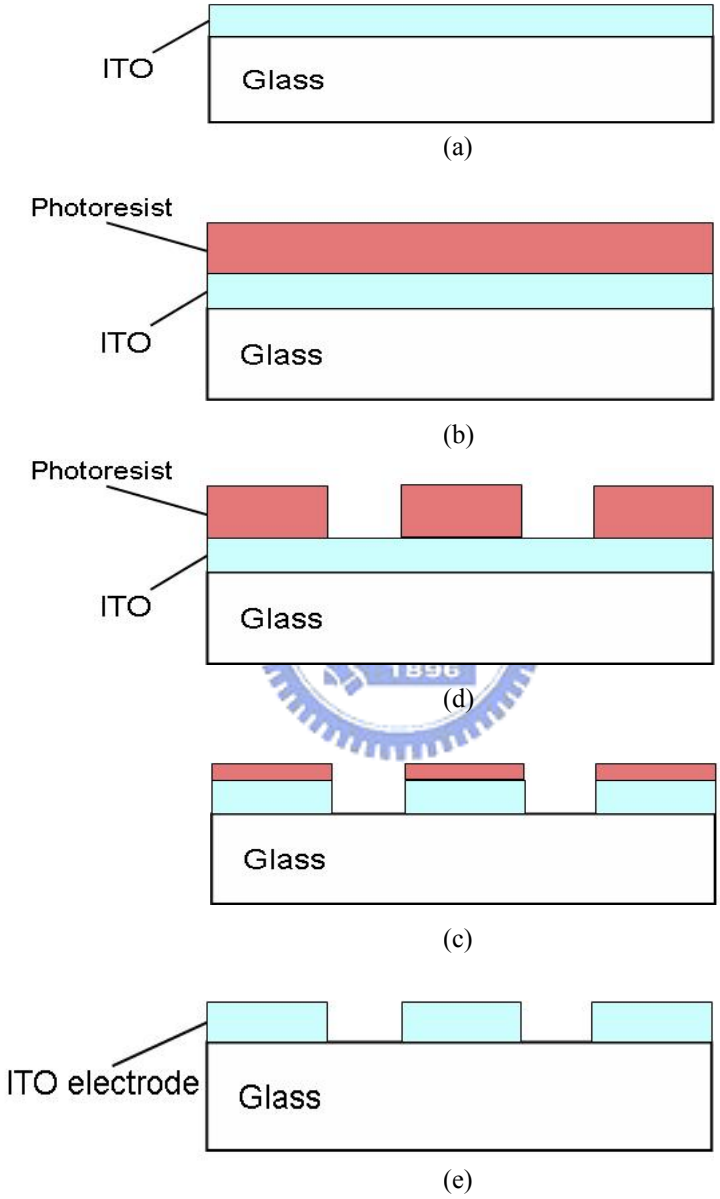
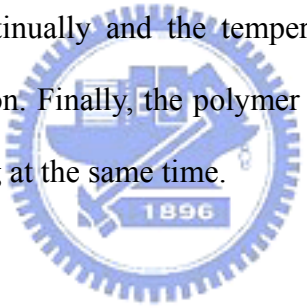


Fig. 3.1 Flow of fabricating ITO electrodes. (a) Sputtering ITO material on the surface of the glass, (b) spin-coating Positive photoresist upon the ITO surface, (c) using lithography technique to obtain the latent image, (d) etching to produce the desired ITO pattern, and (e) eliminating the remaining photomask by acetone.

(b) Cell process: Two crossed ITO glasses were glued with sealing gel containing spacers. The diameter of spacer with 2 um is required for maintaining the cell gap. Finally, the space between two substrates was filled with the mixture of FLC and monomers.

3.2.2 Polymer Walls Process

One function generator is needed to apply the AC voltage between upper and lower ITO electrodes in polymer walls process, and one hot stage is used to accurately control the temperature of the cell. After cell fabrication, the temperature of the cell was risen to higher enough, which can keep FLC in isotropic phase. Thereafter, the AC voltage was applied continually and the temperature of the cell was reduced gradually until phase separation. Finally, the polymer wall structure was produced in desired area after UV exposing at the same time.



3.3 Measurement System

After the fabrication of the polymer wall structure, the inspection will be performed to make sure that the polymer structures were conformed to the expectancy. Thus, polarized optical microscope is required for observing the polymer walls.

Optical microscope with the combination of an ocular and an object lens is the most popular instrument of observing a structure. A transmissive or reflective light can be chosen to observe the micro structure. Besides, a computer-controlled display (CCD) and a computer are usually equipped with the microscope and the picture of observation can be taken from the CCD. In display research, a polarized optical microscope is used to study the behavior of liquid crystal through a pair of polarizer,

especially. Although the magnifying power of general optical microscope has a limitation, a simple operating system still popularizes its application.

A desired angle of the polarized direction between two polarizers can be adjusted manually. In our experiment, a polarized optical microscope was utilized to observe the phase variation between FLC and monomers in encapsulation cells.

Chapter 4

Experimental Results and Discussions

4.1 Introduction

The electric field induced fabrication method of polymer wall structures was introduced in previous chapter. As mentioned before, fast process time and perfect separation quality are the main advantages of electric field induced method. This novel method can be utilized to form polymer walls in not only TNLC device but also FLC species. Therefore, electric field induced method was attempted to form polymer walls in TNLC devices. A polarized optical microscope was utilized to observe the phase separation and experimental results. The results will be shown in this chapter. After fabricating polymer walls in TNLC device, the proposed process will also be evaluated in R2301 and R3206 FLC devices. The experimental results and comparisons between different materials will then be further discussed.

4.2 Experimental Results in TNLC devices

Polymer wall structure in TNLC device was fabricated by electric field induced method. The specification of AC voltage which was applied to induce phase separation of NOA65 and TNLC was shown in Tab. 4.1. According to the electric field induced process which discussed before, the temperature of polymerization was the most important in this method, and the temperature will greatly affect the result of polymer walls. In order to observe the phase separation temperature in TNLC devices,

a hot stage and polarized optical microscope was required. The temperature of the devices can be exactly controlled by the hot stage. As the observation by the microscope shown, the phase separation temperature of TNLC devices is 46^{o}C

Tab. 4.1 Specification of applied AC voltage in TNLC device.

Parameter	**Condition**
Waveform	Square wave
Frequency	1k Hz
Amplitude	100 V (pk-pk)

The phase of TNLC material is nematic at 46 ^{o}C. After injecting the mixture of TNLC and NOA65 at 90^{o}C, the temperature of the device was decreased to 46^{o}C and AC voltage was applied to induce electric field between upper and lower ITO substrates. The electric filed can separate TNLC and NOA65 about 5 minutes. The polymer walls can be formed after polymerization by UV exposure at 46 ^{o}C. The experimental result of fabricating polymer walls in TNLC device is shown in Fig. 4.1. The width of polymer walls is about 20 μm and the pixel area is about 200 by 200 μ m. In pixel area, the nematic phase of liquid crystal can be clearly observed. The wall structure was formed in the gaps between pixels, and there are no monomers residual in pixel areas. Thus, the contrast ratio of the TNLC device can be maintained and will not be decreased by the residual of monomers in pixels. Fig. 4.2 shows another picture of TNLC device which was taken by an optical microscope with 45 degree polarization. The dark and bright states of the TNLC device driven by AC voltage can be observed in Fig. 4.3.

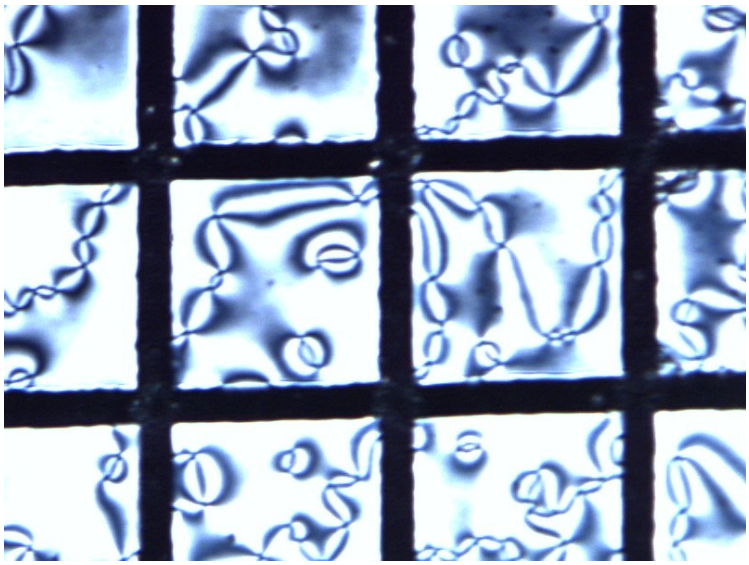


Fig. 4.1 The structure of polymer walls in TNLC device.

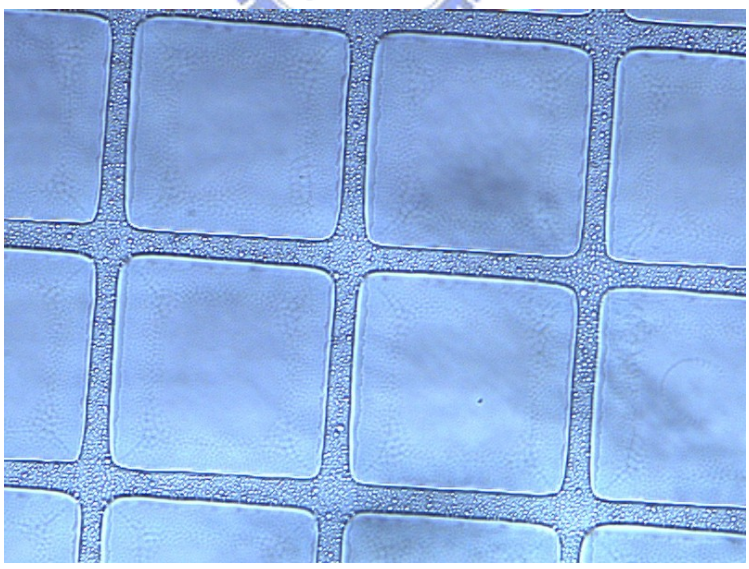


Fig. 4.2 The structure of polymer walls in TNLC device at 45 degree polarization.

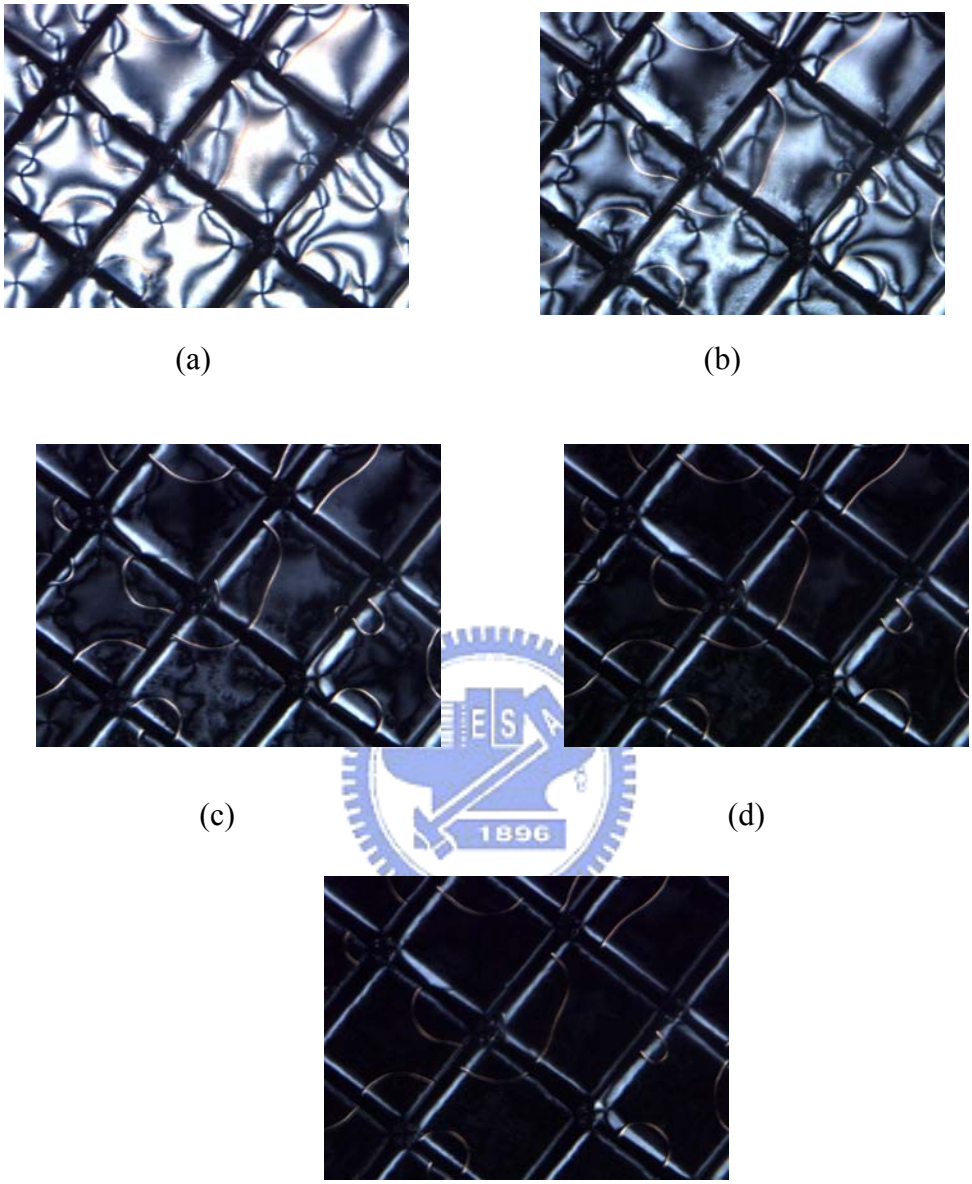


Fig. 4.3 The TNLC device which contains polymer walls is driven by an AC voltage of (a) 0V, (b) 1V, (c) 2V, (d) 3V, and (e) 4V.

The temperature of polymerization is quite important, and it will greatly affect the quality of polymer walls. Fig. 4.4 shows the experimental result of the device which was polymerized at 50^{o}C. The polymer walls are incomplete in this case, and there is no liquid crystal phase in pixel areas due to the residual of monomers in pixels. The temperature of phase separation is 46^{o}C, therefore, phase separation of TNLC and NOA65 is still incomplete at 60^{o}C. If the device is exposed by UV light at this temperature, the formulation of polymer walls will be incomplete.

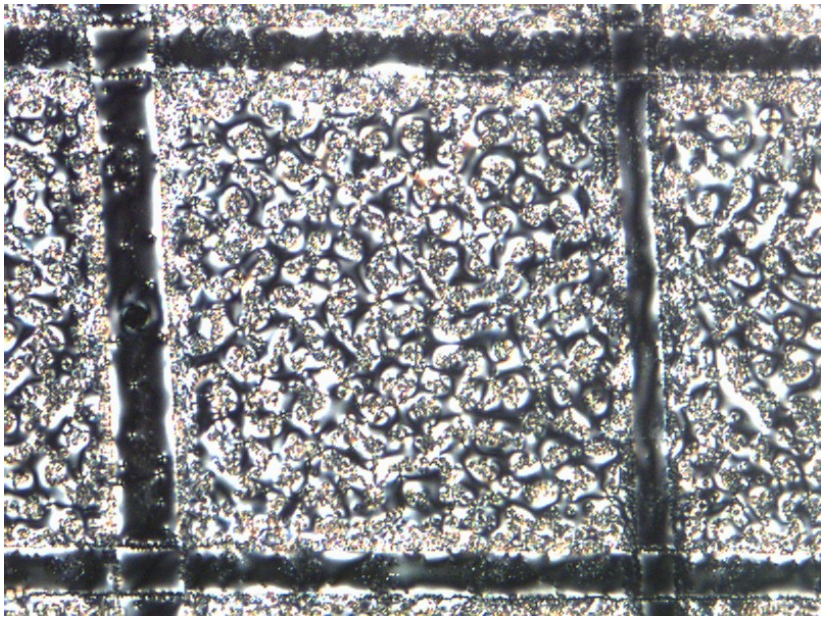
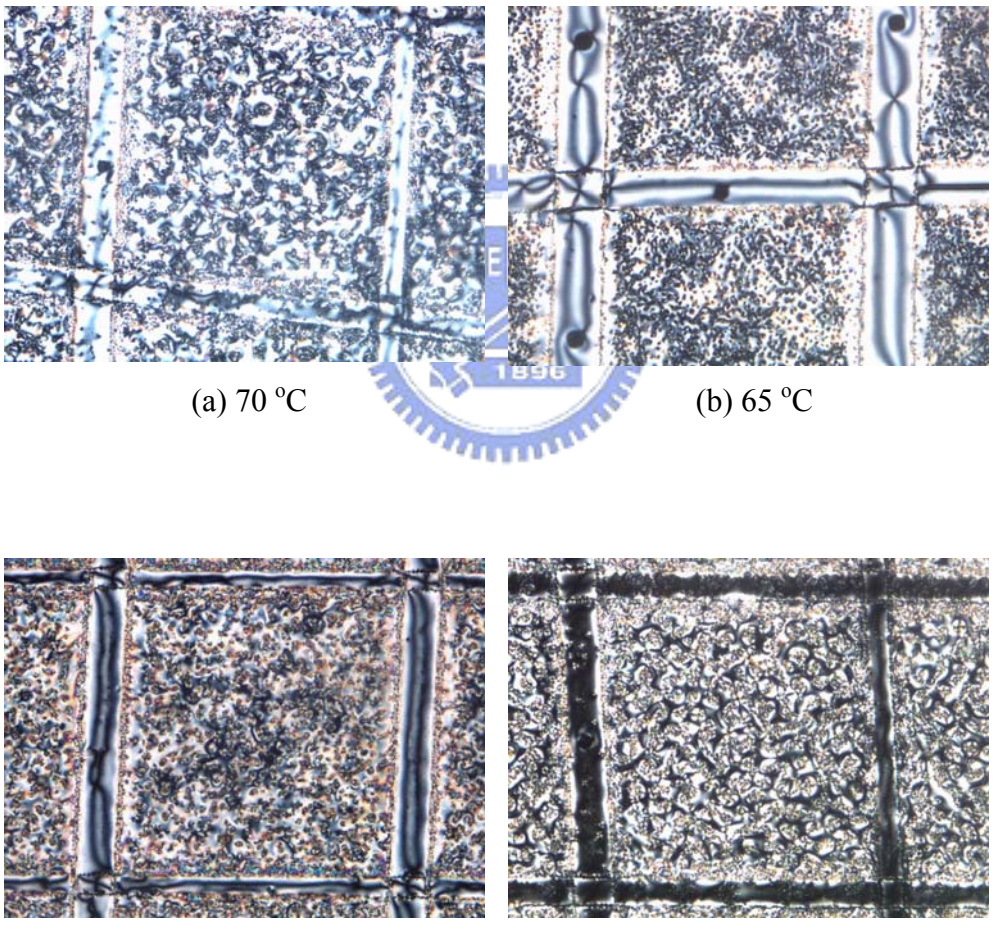


Fig. 4.4 The structure of imperfect polymer walls in TNLC device.

The final results will be affected by different polarization temperature. If the device is photo-polymerized at the temperature higher than phase separation temperature, polymer walls will not be formed in the gaps between pixels. However, monomers will be solidified in pixel areas and the liquid crystal phase of TNLC will also be destroyed, as shown in Fig. 4.5. The dark and bright states of these imperfect devices can not be observed easily. The contrast ratio of these devices is very poor.



(a) 70 °C (b) 65 °C

(c) 60 °C (d) 50 °C

Fig. 4.5 The photographs of TNLC device polymerized at (a) 70°C, (b) 65 °C, (c) 60 °C, and (d) 50 °C.

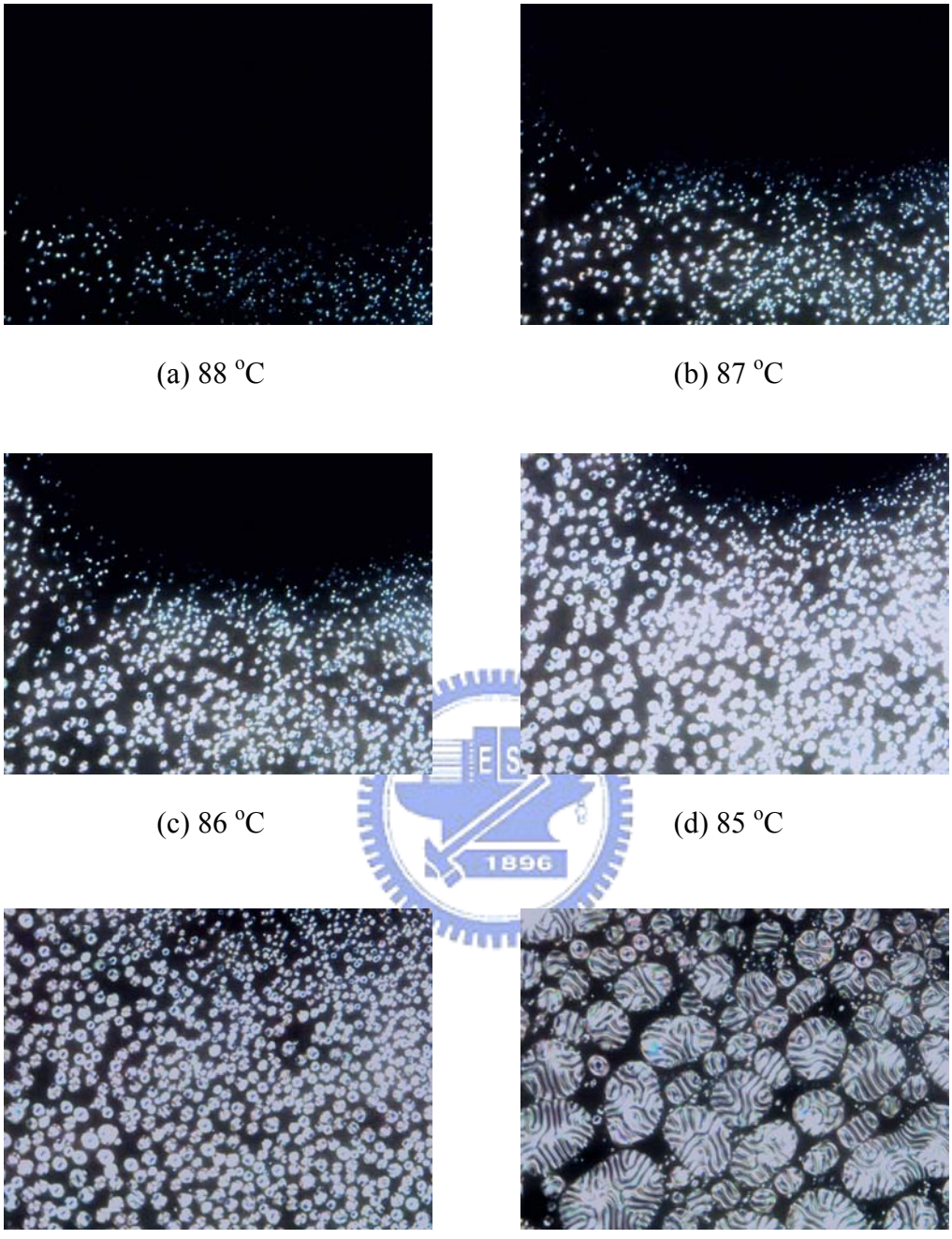
The process time of fabricating polymer walls in TNLC devices is about 30 minutes, and the quality of polymer walls in TNLC device is quite complete if the device was exposed by UV light at phase separation temperature. As the results, the electric field induced method can achieve a fabrication process of polymer walls with faster process time and better separation quality.

4.3 Experimental Results in FLC devices

The proposed process was firstly examined to form polymer walls in TNCL device by applying electric field, as shown before. After that, instead of TNLC material, FLC material was mixed with NOA65. The electric field induced process was utilized to form polymer walls in FLC devices. The result of polymer walls in FLC device will be shown in this section.

4.3.1 Polymer Structures in R2301 FLC devices

The FLC material used in this experiment was R2301 FLC. The phase transition of R2301 FLC was isotropic 86.8 ^{o}C – 84.8 ^{o}C chiral nematic 64.7 ^{o}C chiral smectic. R2301 was firstly mixed with NOA65 as 20 % concentrations. In the beginning, a hot stage and a polarized optical microscope were utilized to observe the phase separation temperature of the mixture of R2301 and NOA65. The phase separation temperature was about 84 ^{o}C to 88 ^{o}C, as shown in Fig. 4.6. When the temperature of the FLC device is higher than 88 ^{o}C, R2301 FLC is in isotropic phase. As the temperature of the device decreased to 88 ^{o}C, the phase of R2301 FLC started transferring to chiral nematic phase, as shown in Fig. 4.6.



(a) 88 °C (b) 87 °C

(c) 86 °C (d) 85 °C

(e) 84 °C (f) 83 °C

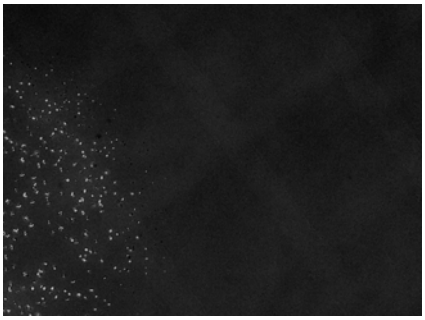
Fig. 4.6 The phase separation process of the mixture of R2301 FLC and NOA65. The temperature of the device is (a) 88 °C, (b) 87 °C, (c) 86 °C, (d) 85 °C, (e) 84 °C, and (f) 83°C.

The observation of phase separation temperature can help us finding the photo-polymerization temperature more easily. After that, an AC voltage was applied to the FLC device in order to separate R2301 FLC and NOA65 as our expectation. The specification of the AC voltage is shown in Tab. 4.2.

Tab. 4.2 Specification of applied AC voltage in R2301 FLC device.

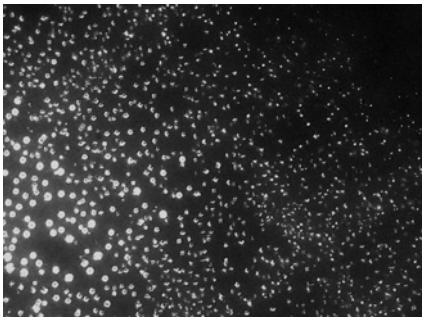
Parameter	**Condition**
Waveform	Square wave
Frequency	2 kHz
Amplitude	120 V (pk-pk)

The viscosity of R2301 FLC is higher than that of TNLC at the same temperature. Thus, the separation quality of R2301 FLC and NOA65 is not easy to be controlled, and the separation rate is slower than that of the TNLC device. In order to speed up the process of phase separation, the frequency of the AC voltage applied to induce phase separation was raised to 2k Hz. Besides, the amplitude of the AC voltage was also increased to 120 volt. Phase separation of R2301 and NOA65 can be successfully induced by applying AC voltage to the device. The photographs of separation process were shown in Fig. 4.7. The photographs in Fig. 4.7 were taken by a polarized optical microscope with different temperature.



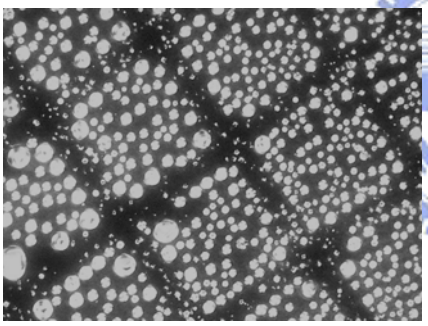
(a1) Cross-polarized mode

(a2) Non-polarized mode

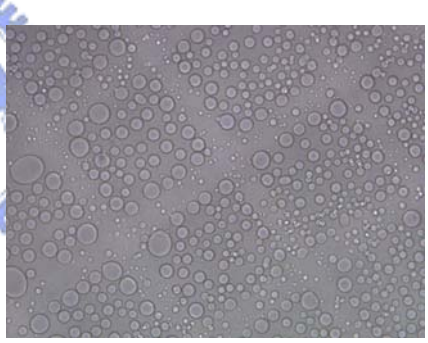


(b1) Cross-polarized mode

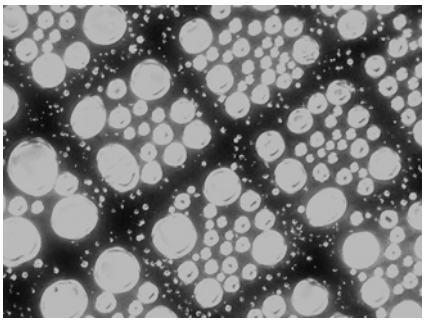
(b2) Non-polarized mode



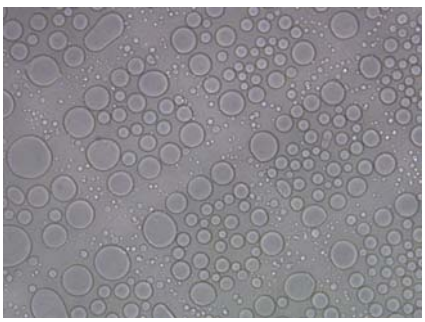
(c1) Cross-polarized mode



(c2) Non-polarized mode

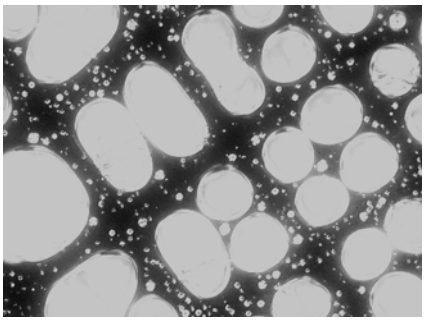


(d1) Cross-polarized mode

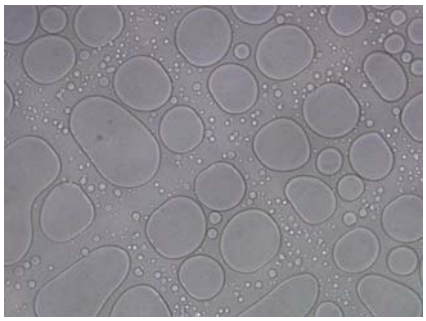


(d2) Non-polarized mode

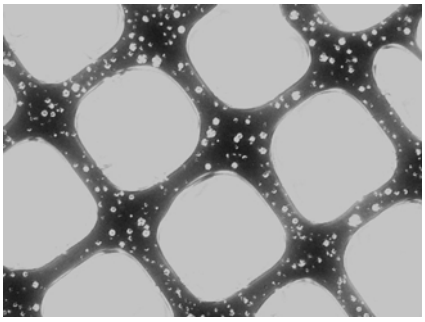
Fig. 4.7 The phase separation process of the mixture of R2301 FLC and NOA65 with an AC voltage. The temperature of the device is (a) 89 ^{o}C, (b) 88 ^{o}C, (c) 87 ^{o}C, and (d) 86 ^{o}C.



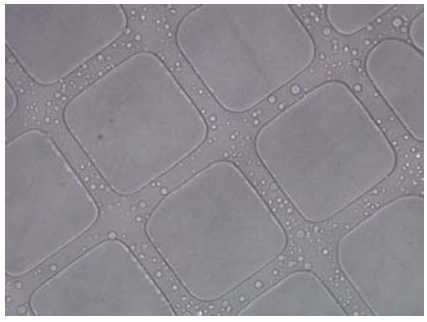
(e1) Cross-polarized mode



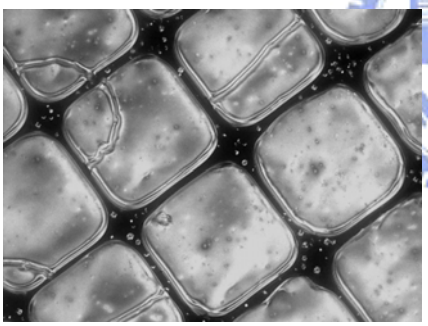
(e2) Non-polarized mode



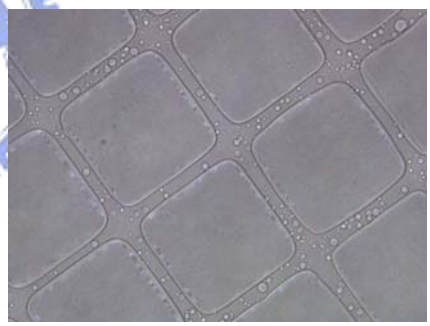
(f1) Cross-polarized mode



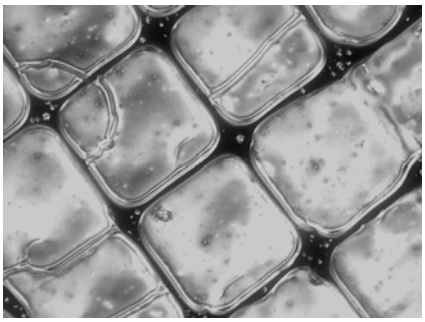
(f2) Non-polarized mode



(g1) Cross-polarized mode



(g2) Non-polarized mode



(h1) Cross-polarized mode

(h2) Non-polarized mode

Fig. 4.7 The phase separation process of the mixture of R2301 FLC and NOA65 with an AC voltage. The temperature of the device is (e) 85 ^{o}C, (f) 84 ^{o}C, (g) 83 ^{o}C, and (h) 82 ^{o}C.

The phase separation of FLC and NOA65 induced by electric field is shown in Fig. 4.7. When the temperature of the FLC device was lower than 90 ^{o}C, the phase of FLC is transferring to chiral nematic phase. As decreasing of the temperature, more FLC molecules transfer to chiral nematic phase. This phase separation process is similar to the process shown in Fig. 4.6 which was applied with no AC voltage. The difference between the separation processes in Fig. 4.6 and Fig. 4.7 is AC voltage. FLC device was applied with no AC voltage in Fig. 4.6 so that the phase separation of FLC and NOA65 was uniform in the device. Nevertheless, the process which NOA65 was separated to the gap between pixels as a network structure was due to the function of AC voltage. According to the principle of electric field induced phase separation method introduced before, FLC molecules were switched up and down by applying AC electric field and NOA65 were squeezed to the gap of pixels as polymer wall structures.

The best quality of the phase separation process was in 84 ^{o}C. However, while the temperature of the device was lower than 84 ^{o}C, the separation quality became incomplete, as shown in Fig 4.7(h). The reason is that the viscosity of FLC is larger than TNLC. Besides, the viscosity of FLC will be decreased in high temperature, so that phase separation will be induced more completely in high temperature.

Although NOA65 can be induced and separated to the gaps between pixels by applying an electric field, the polymer wall structures still can not be formed in R2301 FLC device. A UV light was utilized in photo-polymerization process in order to solidify NOA65. During the phase separation process, the R2301 FLC device must be avoided from UV exposure, or NOA65 will be polymerized before phase separation. The structure of polymer wall in R2301 FLC device was shown in Fig. 4.8. This incomplete polymer structures resulted in lower transmittance of light source in the FLC device.

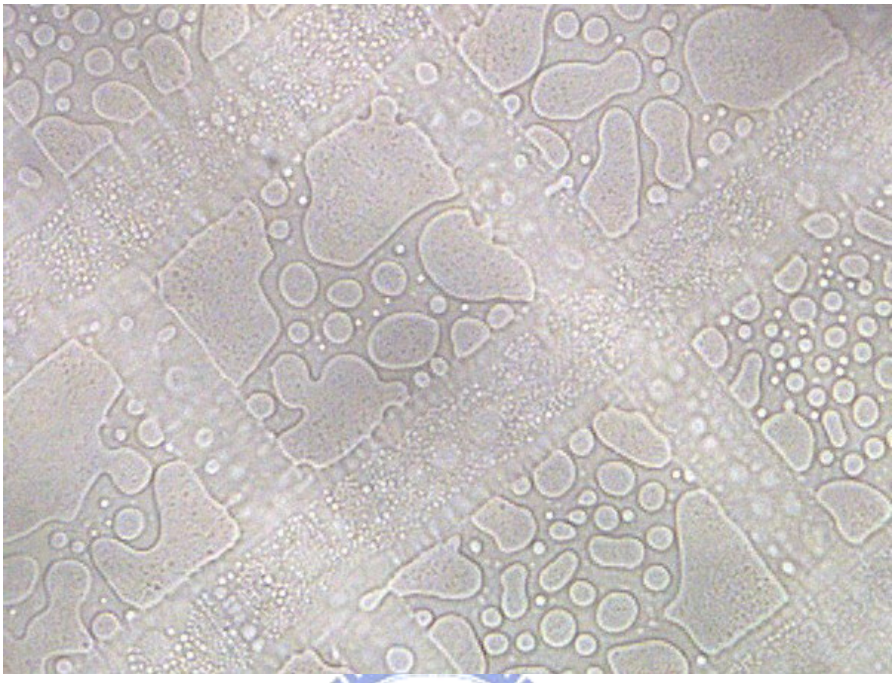
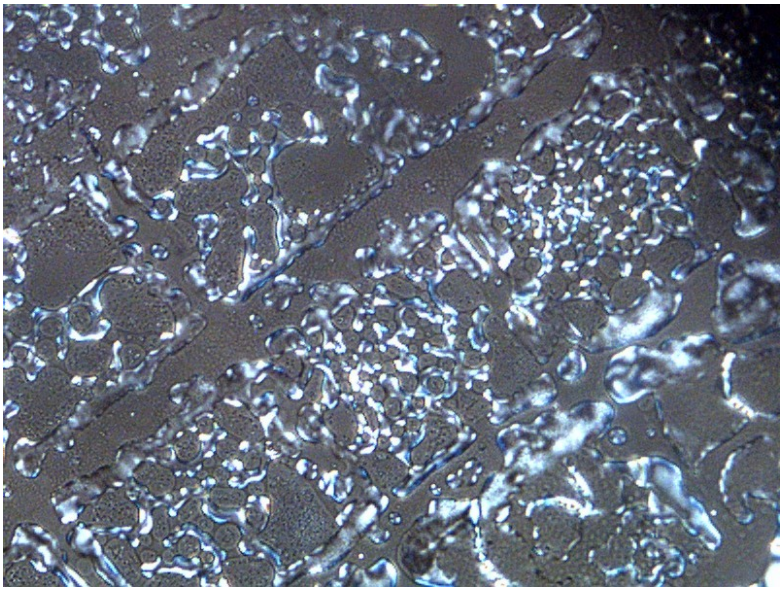
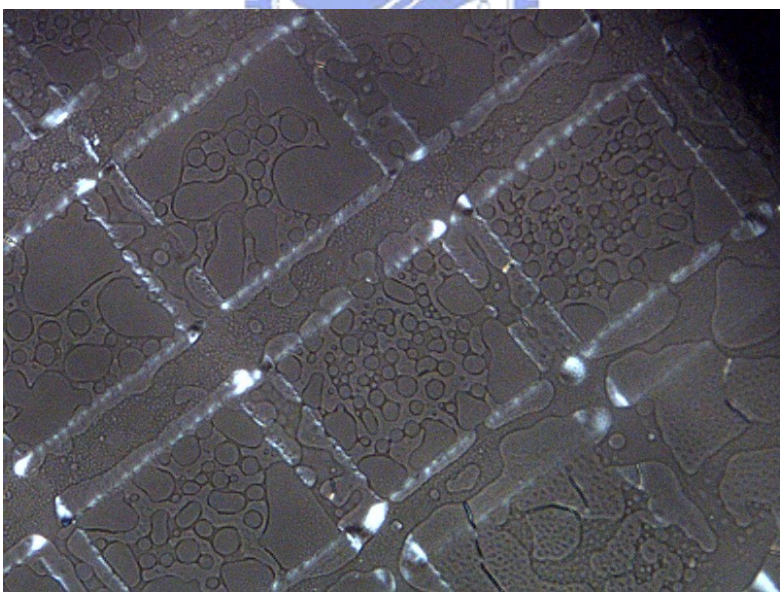


Fig. 4.8 The incomplete polymer structures in R2301 FLC device.

The switching property of R2301 FLC was affected by the polymer structure in pixel areas. Black and Bright states of the FLC device can not be clearly distinguished. Fig. 4.9(a) is the bright state of the FLC device which contains incomplete polymer structures. Chiral nematic FLC is confined in small sections, while the dark area is the polymer structures in the device, as shown in Fig. 4.9. Although R2301 FLC and NOA65 can be separated in our device by the electric field induced method, nevertheless, the polymer wall structure still can not be formed successfully. After the phase separation process, the FLC device was then exposed by UV light. However, NOA65 was not photo-polymerized in R2301 FLC device after UV exposure.



(a)



(b)

Fig. 4.9 The state of incomplete polymer structures in R2301 FLC device. (a) Cross-polarized mode and (b) 30^{o} polarized mode.

The neat NOA65 generally can be photo-polymerized by UV exposure in 5 minutes. However, after mixing NOA65 with R2301 FLC material, NOA65 can not be photo-polymerized by UV exposure in R2301 FLC device. Although the device was exposed by UV light in more than 1 hour, NOA65 was still in liquid phase.

Several experiments were performed in order to solve the photo-polymerization issue in R2301 FLC device. The issues of this photo-polymerization are:

(1) Temperature effect: Photo-polymerization of NOA65 can not be induced in the temperature higher than 60 ^{o}C due to the side reaction between NOA65 and FLC.
(2) Electric field effect: Photo-polymerization of NOA65 was restrained by the electric field.
(3) Chemical reaction effect: R2301 FLC reacted with NOA65 or photo-initiators while blending.

In order to figure out the photo-polymerization issue, NOA65 was exposed by UV light at 90 ^{o}C without applying an electric field. As a result, NOA65 can be solidified by the UV exposure in 5 minutes, as shown in Fig. 4.10. Thus, the temperature effect was not the key issue in photo-polymerization problem. Concerning the electric field effect, NOA65 was exposed by the UV light with the effect of an electric field, as shown in Fig. 4.11. NOA65 can be solidified even though it was functioned by an electric field.

According to these tests, chemical reaction between R2301 FLC and NOA65 was the most probable reason of the photo-polymerization issue. Base on this study, R2301 FLC was replaced by R3206 FLC to fabricate polymer walls in our device.

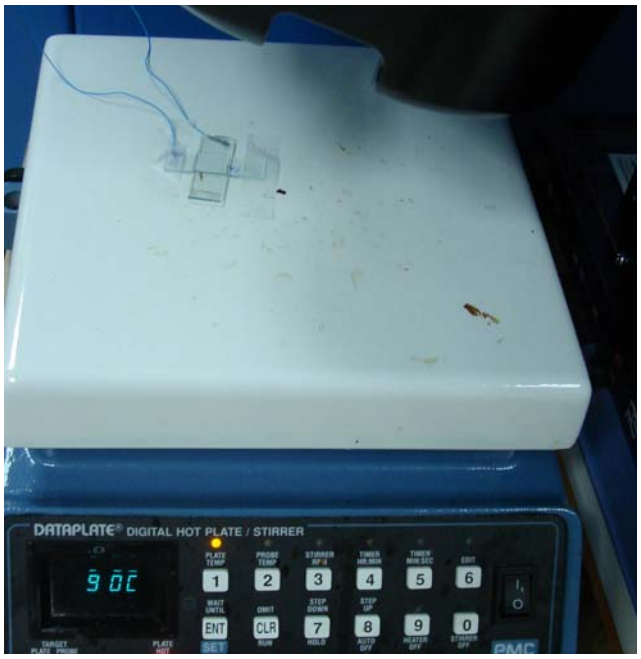


Fig. 4.10 Exposing NOA65 by UV light at 90 ^{o}C without applying an electric field.

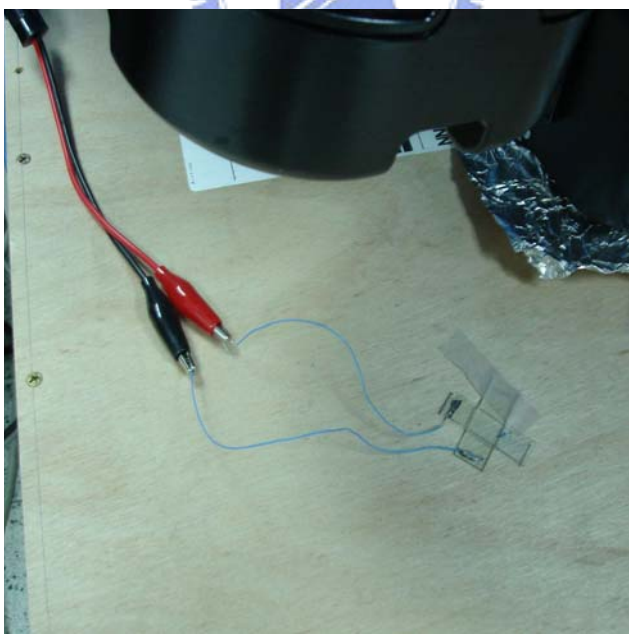


Fig. 4.11 Exposing NOA65 by the UV light with the effect of an electric field.

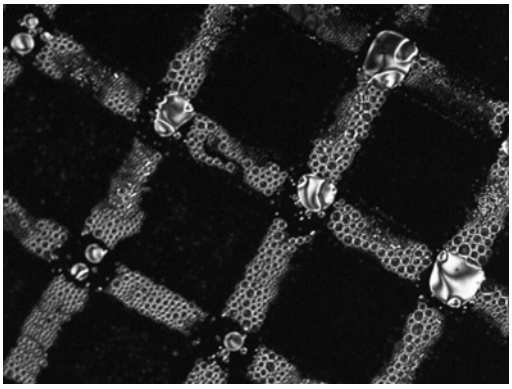
4.3.2 Polymer Structures in R3206 FLC devices

R2301 FLC was estimated that it may react with NOA series monomers, so that R3206 was utilized to replace R2301 FLC material. R2301 was mixed with monomers as 20 % concentrations and blended at 100 ^{o}C. The phase transition of R3206 FLC was isotropic 107.0 ^{o}C – 105.4 ^{o}C chiral nematic78.4 ^{o}C chiral smectic. The separation process of R3206 and monomers was the same with that in R2301 device. The specification of the AC voltag applied to induce phase separation of NOA65 and R3206 FLC is shown in Tab. 4.3.

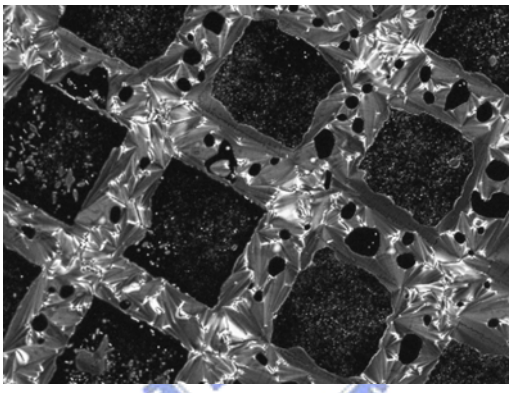
NOA65 was firstly utilized to be blended with R3206 FLC. The process of phase separation between R3206 FLC and NOA65 was shown in Fig. 4.12. Black areas are NOA65 material, and the others are R3206 FLC. Unfortunately, NOA65 can not be concentrated in the gaps under applied AC voltage.

Tab. 4.3 Specification of applied AC voltage in R3206 FLC device.

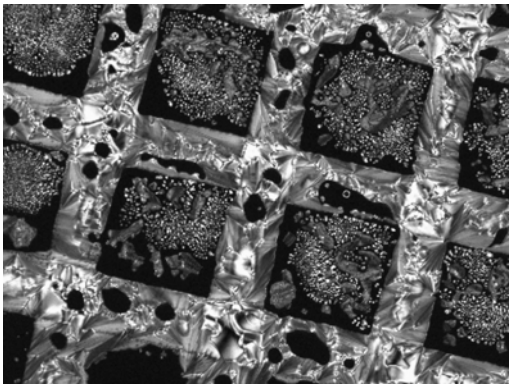
Parameter	Condition
Waveform	Square wave
Frequency	500 Hz
Amplitude	120 volt (pk-pk)



(a) 80 °C



(b) 70 °C



(c) 60 °C

Fig. 4.12 The phase separation process between R3206 FLC and NOA65 at (a) 80 °C, (b) 70 °C, and (c) 60 °C.

Although NOA65 can not be separated to the gaps between pixels by switching R3206 FLC molecules in high frequency, photo-polymerization of NOA65 can be successfully induced in R3206 FLC device. Compared with R2301 FLC device, NOA65 can be solidified by UV exposure, as shown in Fig. 4.13. Black areas are polymer structures, and the others are R3206 FLC structures. This photograph showed that NOA65 can not be utilized to form polymer walls in R3206 FLC device.

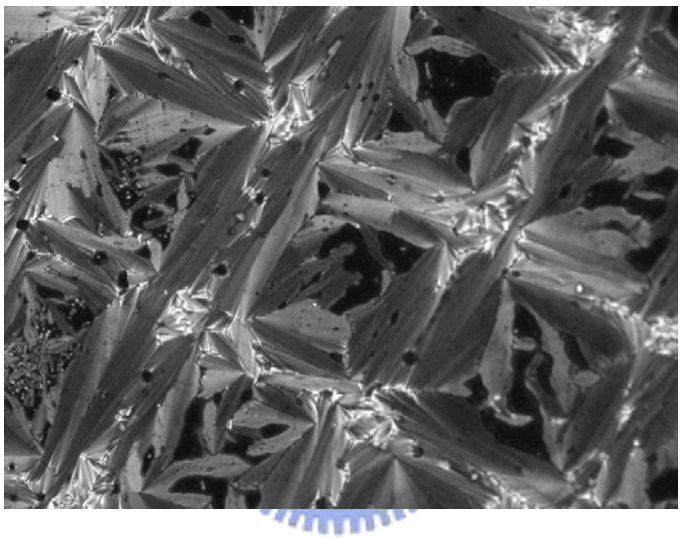
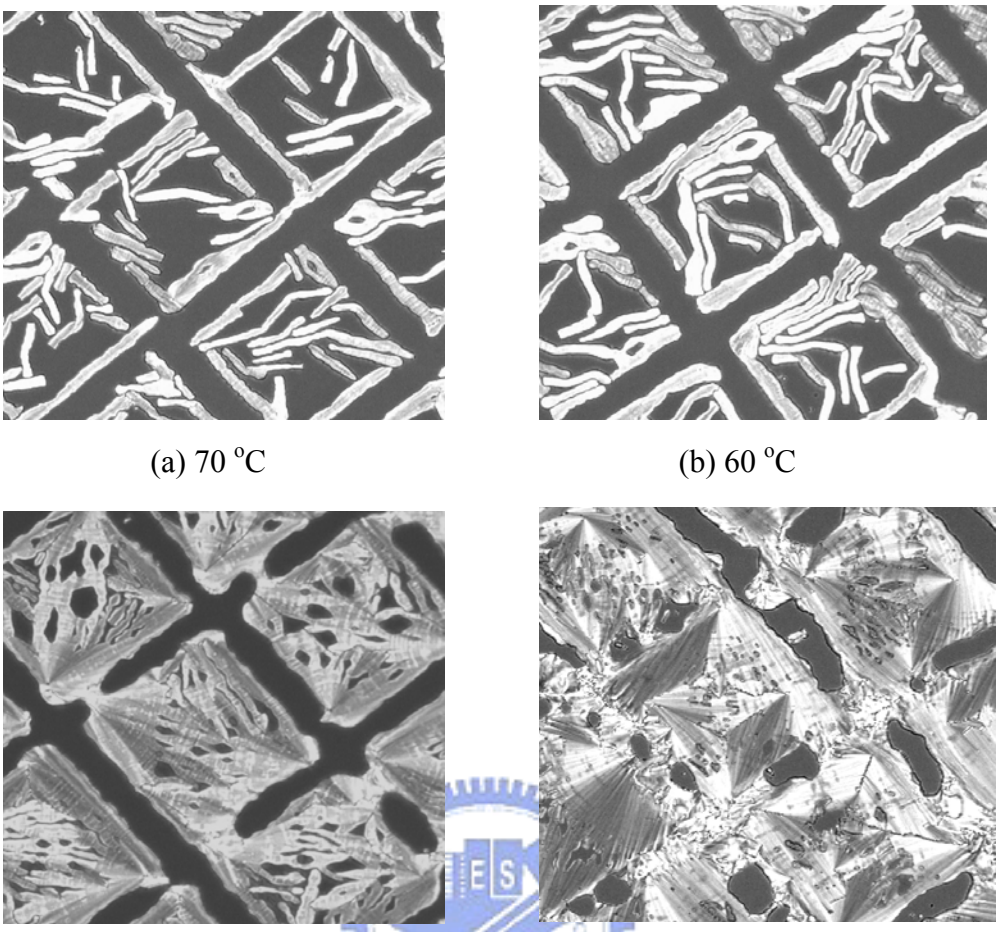


Fig. 4.13 The polymer wall structures with NOA65 monomers in R3206 FLC device.

Chemical reaction of R2301 FLC and NOA series monomers was estimated to be the major reason of photo-polymerization issue. However, after altering FLC material, the photo-polymerization insensitivity in R2301 FLC device was eliminated in R3206 FLC device. NOA65 can be solidified by UV exposure in R3206 FLC device. Unfortunately, the phase separation quality can not be as sharp as that in R2301 FLC device, as shown in Fig. 4.7. In order to improve the separation quality of R3206 FLC and monomers, NOA74 monomers were utilized to replace NOA65. The separation process of R3206 FLC and NOA74 is shown in Fig. 4.14.

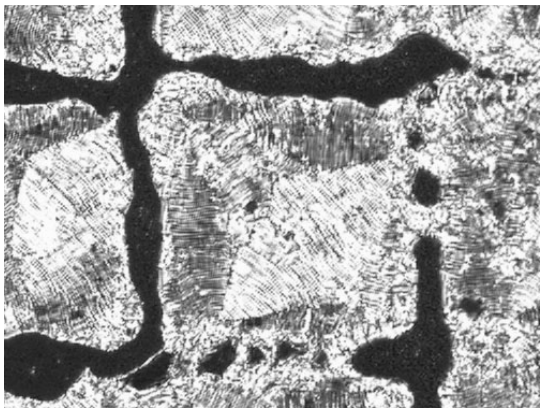


(a) 70 °C (b) 60 °C

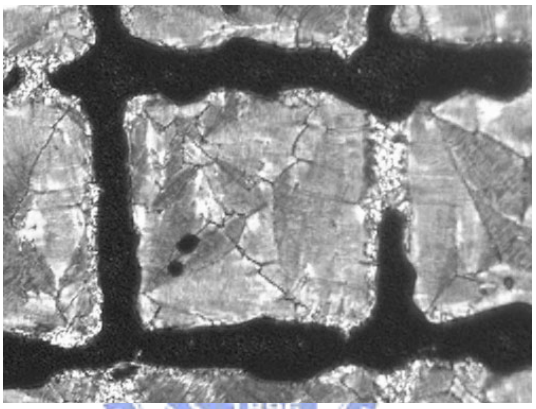
(c) 50 °C (d) 30 °C

Fig. 4.14 The phase separation process of the mixture of R3206 FLC and NOA74 with an AC voltage. The temperature of the device is (a) 70 °C, (b) 60 °C, (c) 50 °C, and (d) 30 °C.

Compared with NOA65, NOA74 can be separated to the gaps between pixels by R3206 FLC material when the temperature of the device is between 50 °C to 60 °C, as shown in Figs. 4.14 (b) and (c). When the temperature of the device decreases to room temperature, the separation quality becomes poor, as shown in Fig. 4.14 (d). Fig. 4.15 shows the polymer wall structures in R3206 FLC device exposed by UV light at room temperature. The polymer wall structures were not sharp enough compared with the polymer walls in TNLC device, as shown in Fig. 4.1. After that, the temperature of UV exposure was chosen as 55 °C, and the result is showed in Fig. 4.16.



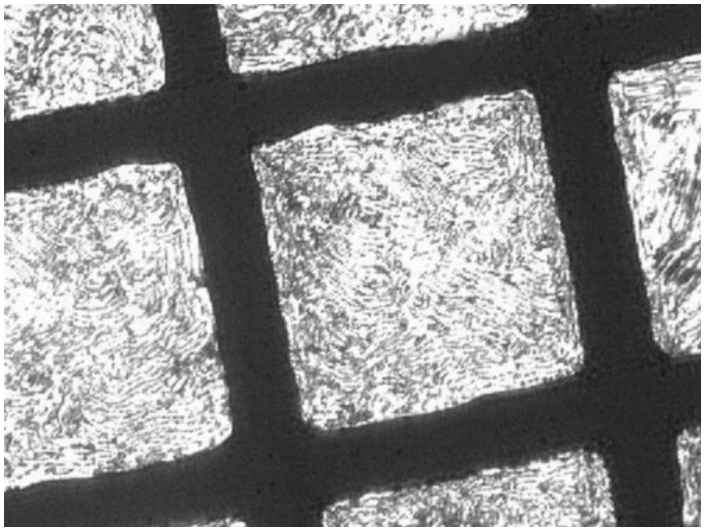
(a)



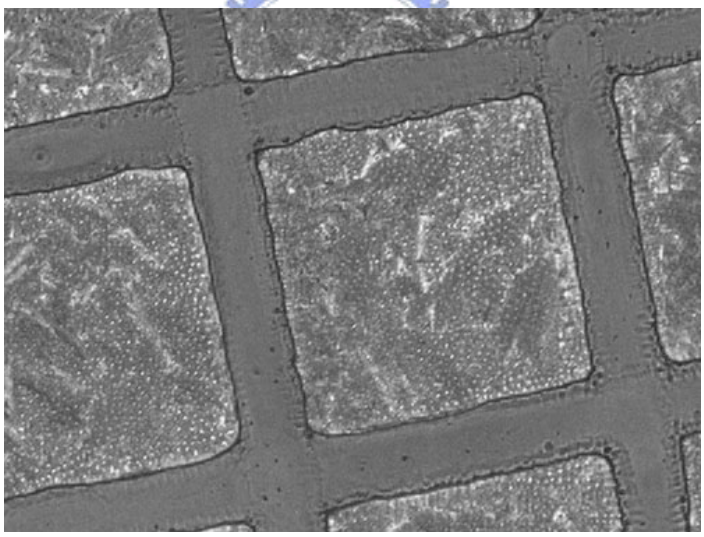
(b)

Fig. 4.15 The incomplete polymer walls in R3206 FLC device exposed by the UV light at room temperature.

The polymer wall structures in R3206 FLC device can be formed sharply by using NOA74 monomers when the device was exposed by UV light at 55 ^{o}C, as shown in Fig. 4.16. Polymer structures were solidified in the gaps between pixels while R3206 FLC was confined in the pixel areas.



(a) Cross-polarized mode



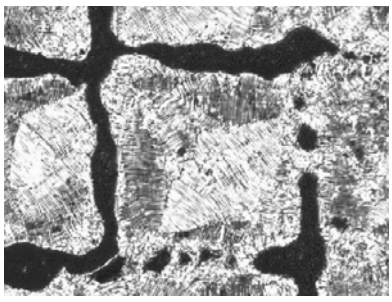
(b) 30^{o} polarized mode

Fig. 4.16 The polymer structures in R3206 FLC device exposed by the UV light at 55 ^{o}C. (a) cross-polarized mode and (b) 30^{o} polarized mode.

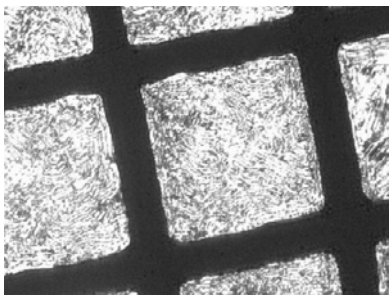
4.4 Discussion

The polymer walls were widely utilized in display technique, especially flexible and PSFLC display. The most popular method to fabricate polymer walls is to use a photo-mask to confine the exposing area. Nevertheless, the electric field induced phase separation method has not been applied in fabricating polymer walls in FLC device due to several issues which will be discussed in his section.

Compared with TNLC material, the viscosity of FLC is very high, so that the phase separation between FLC and monomers will not maintain the same quality at different temperature in FLC device. As a result, the photo-polymerization temperature in FLC device becomes important, and the temperature will greatly affect the structures of polymer walls. In our experiment, the photo-polymerization temperature in TNLC device is 46 ^{o}C, while that in R2301 FLC device is 84^{o}C, and 55 ^{o}C is that in R3206 FLC device. This photo-polymerization temperature must be narrowly figured out in order to fabricate complete polymer walls in different FLC material. Different photo-polymerization temperature will result in different quality of polymer wall structures, as shown in Fig. 4.17.



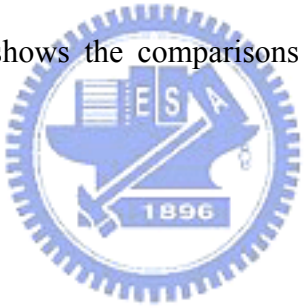
(a) room temperature



(a) 55^{o}C

Fig. 4.17 Polymer walls in R3206 FLC device exposed by the UV light at (a) room temperature and (b) 55 ^{o}C.

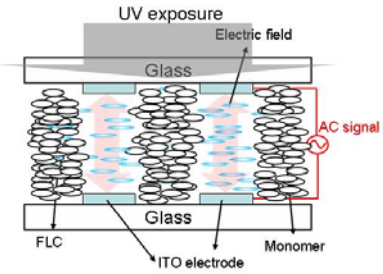
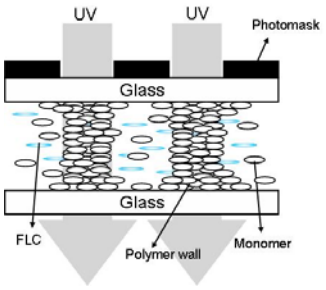
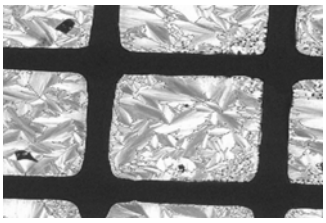
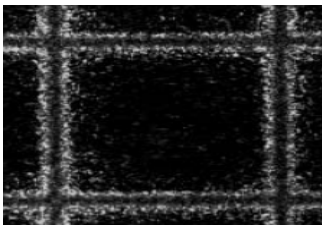
Besides, some monomers may be reacted with FLC material, and this chemical reaction will result in photo-polymerization issues. For example, R2301 FLC material will react with NOA series monomers, and NOA65 will not be photo-polymerized in R2301 FLC device even after UV exposure. On the other hand, although the photo-polymerization issue in R3206 FLC device is eliminated, the phase separation between R3206 FLC and NOA65 can not be induced due to its high viscosity of NOA65 in R3206 FLC device. As a result, NOA74 is a better choice in R3206 FLC device due to its lower in viscosity. Thus, the polymer walls can be successfully formed in R3206 FLC device by using NOA74 material. In summary, the choice of FLC and monomers is very important in the fabrication process of polymer walls. Tab. 4.4 is the comparisons of experimental results with different monomers and FLC materials. Besides, Tab. 4.5 shows the comparisons of proposed and conventional processes.



Tab. 4.4 Comparisons of different monomers and FLC materials.

FLC / Monomer	R2301 FLC	R3206 FLC
NOA65 (1000 CPS)	Complete separation of R2301 FLC and NOA65 can be induced but polymerization issue can not be solved	NOA65 can be polymerized by UV light in R3206 FLC device but can not be separated as a wall.
NOA74 (175 CPS)	Complete separation of R2301 FLC and NOA74 can be induced but polymerization issue can not also be solved	NOA74 can be successfully separated and polymerized in R3206 FLC.
NOA83H (250 CPS)	R2301 FLC and NOA83H can be separated as a wall structure faster than that of NOA65 and R2301 FLC. However, curing issue is still there.	NOA83H has a characteristic of heating polymerization. As a result, NOA83H is not suit for our experiment.

Tab. 4.5 Comparisons of proposed and conventional processes.

	NCTU Proposed Process	NHK Proposed Process
Design		
	Without photo-mask	Photo-mask
Quality of phase separation	○	△
Shorten process time	○	X
Results of polymer walls		

○: good △: fair X: bad

4.5 Summary

Polymer wall structures can be successfully fabricated in TNLC and R3206 FLC devices by applying an electric field. The photo-polymerization temperature in TNLC and R3206 FLC devices are 46 ^{o}C and 55 ^{o}C, respectively. In addition, NOA65 can not be separated to the gaps between pixels due to its high viscosity. Moreover, R2301 FLC will react with NOA series monomers, and this will result in the photo-polymerization problem even though the phase separation of R2301 FLC and NOA series monomers can be induced by the electric field. Generally speaking, electric field induced method can be utilized of fabricating polymer walls in FLC devices.

Chapter 5

Conclusions

5.1 Conclusions

A novel fabrication process of forming polymer walls in FLC device without the photomask has been demonstrated in this thesis. The principle of the proposed process is that monomers can be separated to the gaps between pixels by applying an electric field. Polymer walls can be formed after UV exposure. In recent year, polymer walls in FLC device was studied by NHK Corporation, a photomask was required in this conventional fabrication method. However, this method suffered from several drawbacks such as poor separation quality, long process time, and alignment problem between the photomask and substrates. Compared with the conventional process, a high separation quality, rapid fabrication process can be achieved by our proposed novel process. Nevertheless, some issues of this proposed process were discussed in Chapter4. In our experiment, the issues were solved and the polymer walls were successfully fabricated in FLC device by proposed process.

5.2 Future Works

With the improvement of the quality of life, multimedia application displays become an important part of people. Light weight, high dynamic display quality, and good color saturation are the major concerns in newly display technique. Moreover, portable display also attracts people due to the convenient feature. In order to achieve

these demands, PSFLC display which contains polymer wall and network structures was studied.

Polymer walls can be successfully fabricated in FLC device by the proposed process. In order to achieve polymer stabilization FLC (PSFLC), the fabrication process of polymer network will be further studied in the future. Besides, polymer walls can enhance the mechanical property of the display device. Thus, polymer wall structures can be applied in flexible displays.

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