

**Master Thesis
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**Study on High- Performance PDLC
Optical Devices**

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Chapter 1 : Introduction

1-1 Research background

The liquid crystalline state has been discovered about 100 years ago when in 1888 Reinitzer and Lehmann investigated some esters of cholestrols [1]. The field of liquid crystals developed increasingly in the following decades. Due to the many discoveries, the field of liquid crystals has been more enlarged in the last 20 years. Since then, liquid crystals play an important role in material science and mainly applied in displays.

Liquid crystals displays have been developed in order to provide a display of relatively large amount of data, in devices which power consumption must be held to the lowest possible level. Liquid crystal displays (LCDs) have evolved rapidly as a result of fierce competition among the various LCD technologies, and now occupy the largest proportion of the entire display market. The evolution of LCDs continues, with new technologies and new materials in development to replace current devices.

With the advent of the internet and the increase in portable electronics, the importance of information displays has increased tremendously, due to the need for fast transfer of large amounts of information for both business and entertainment purposes. Modern displays require a high accuracy, high resolution and high speed due to the rapid flow of information.

In recent years, with the growth of broadband communication, internet usage has been increased remarkably. Thus, high performance optical device has been gaining a lot of demands in the market. Optical device is a device that use light wave to keep and transmit data in large quantity. Low power consumption with large capacity optical device is getting serious attention.

In these years, a big deal of attention has been given to a new kind of liquid crystalline materials where liquid crystal domains of micron or sub-micron size are dispersed in a polymer matrix. These materials are called Polymer Dispersed Liquid Crystals (PDLC). The interest has been initially pushed by a wide range of possible applications; new, simple and cost effective to fabricate. These applications go from large-scale flexible displays to windows with controlled transparency to thermal sensor and devices for optical processing.

In this research, a mixture of liquid crystals and polymer called polymer dispersed liquid crystal (PDLC) is being studied. We aimed on the realization of a high performance optical device.

1-2 Research objective

The evolution of PDLC does not only focus on communication device, but also getting attention from architectural industry such as smart glass. Based on electrically controlled light in PDLCs, big number of electro-optical devices is developed. LC materials occupy a small portion in an LC device, but it plays important role in determining the device performance. Since LCs has numerous application in optical devices, PDLC has advantage in its flexibility and controllability thus application field of these materials expand in nonlinear optics.

There are classification of PDLCs by the structural variety of the LCs in the substrate like a network-type PDLCs with networked bindings or a droplet-type PDLCs with a dispersive LC distributions in the substrate. In this study, we use both droplet type and network type PDLC for the research.

Many factors, including the surface effect, LC concentration, UV irradiation time, the size and morphologies of LC droplets and the LC director configuration inside them play roles to determine the properties of PDLC. The phenomena of PDLC might be enhanced by these factors.

To investigate the effect of surface condition in optical property of PDLC film, surface rubbing treatment was first introduced for more structured alignment and more efficient light scattering.

Aside from surface treatment, we also intend to control the LC droplet size by manipulating the LC concentration and UV irradiation time. We use droplet type PDLC to investigate the LC droplet growth and formation.

1-3 Thesis structure

Chapter 1 Briefing about background

Chapter 2 Explaining PDLC Theory

Chapter 3 Describing on how we prepare PDLC in the lab

Chapter 4 Evaluating surface treatment on PDLC

Chapter 5 Evaluating LC droplet size with varieties factors.

Chapter 6 Summary

Chapter 2 : Polymer Dispersed Liquid Crystal Theory

2-1 Prologue

As in other areas concerning liquid crystals, the field of liquid crystal dispersions is quite interdisciplinary [2]. The optimization of PDLC devices can be sped by understanding the physical phenomena behind the electrically switched mechanism. It is important to understand the materials that build up a PDLC which are LC and polymer for a better PDLC improvement.

2-2 Liquid Crystal

Liquid crystalline materials have been observed for over a century but were not recognized as such until 1880s. In 1888, Friedrich Reinitzer is credited for the first systematic description of the liquid crystal phase and reported his observations when he prepared cholesteryl benzoate, the first liquid crystal. In 1888, the Austrian chemist Friedrich Reinitzer, working in the Institute of Plant Physiology at the University of Prague, discovered a strange phenomenon. Reinitzer was conducting experiments on a cholesterol based substance trying to figure out the correct formula and molecular weight of cholesterol. When he tried to precisely determine the melting point, which is an important indicator of the purity of a substance, he was struck by the fact that this substance seemed to have two melting points. At 145.5°C the solid crystal melted into a cloudy liquid which existed until 178.5°C where the cloudiness suddenly disappeared, giving way to a clear transparent liquid. Puzzled by his discovery, Reinitzer turned for help to the German physicist Otto Lehmann, who was an expert in crystal optics. Lehmann became convinced that the cloudy liquid had a unique kind of order. Eventually he realized that the cloudy liquid was a new state of matter and coined the name "liquid crystal," illustrating that it was something between a liquid and a solid, sharing important properties of both[1].

Materials in nature can be divided into different phases, also called states of matter, depending on the mobility of the individual atoms or molecules. Under normal temperature and normal pressure, material is generally present in any of the three states, crystal (solid), liquid or gas (Figure 2.1). The state of the material changes depending on the temperature and pressure. In the solid state, intermolecular forces keep the molecules close together at a fixed position and orientation, so the material remains in a definite shape. In the fluid state, the molecules are still packed closely together, but they are able to move around. Hence a fluid does not have a rigid shape, but adapts to the contours of the container that holds it. Like a liquid, a gas has no fixed shape, but it has little resistance to compression because there is enough empty space for the molecules to move closer. Whereas a liquid placed in a container will form a puddle at the bottom of the container, a gas will expand to fill the container.

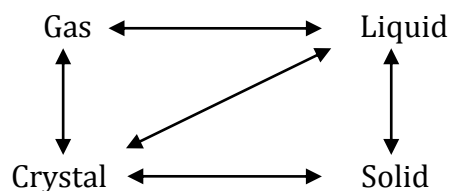


Figure 2.1 Materials condition

Apart from the three familiar states, there exist a large number of other intermediate phases. Liquid crystals are another important intermediate phase which exhibits features from both the solid and the fluid state. LCs have the ordering properties of solids but they flow like liquids [2].

The LC state (mesophase) exists within some temperature range, $T_m < T < T_c$ (Figure 2.2), where T_m is temperature of melting from solid state into a mesophase, and T_c is clearing temperature, when the LC transforms into an isotropic liquid. In the solid state, the centers of gravity of molecules possess long-range positional order, and, also, the molecules orientation points in the same direction providing the long-range orientational order[3]. When solid melts into a LC at T_m , the positional order is lost although some orientational order of the molecular long axes remains. At still higher temperature T_c , mesophase melts into an isotropic liquid with no positional and orientational order[3].

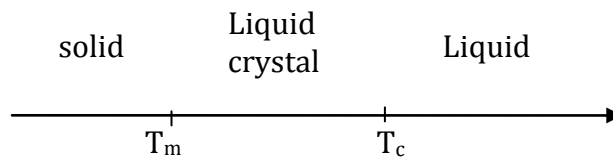


Figure 2.2 Temperature range for LC

LCs come in two basic classifications : thermotropic and lyotropic[3]. The phase transitions of thermotropic LCs depend on temperature. Thermotropic LC phases are formed by organic molecules in a certain temperature range and hence the prefix thermo-, referring to phase transitions caused by temperature change. Lyotropic LCs depend on both temperature and concentration. The molecules that make up lyotropic LCs are surfactants consisting of two distinct parts: a polar, often ionic, head and a nonpolar, often hydrocarbon tail. Lyotropic LCs are found in countless everyday situations. Soaps and detergents form lyotropic LCs when they combine with water[3].

2-3 Nematic Liquid Crystal and Electro-optic Effects

2-3-1 Nematic Liquid Crystal

LCs are composed of moderate size organic molecules which tend to be elongated. At high temperatures, the molecules will be oriented arbitrarily, as shown in the Figure 2.3, forming an isotropic liquid. Because of their elongated shape, under appropriate conditions, the molecules exhibit orientational order such that all the axes line up and form a so-called nematic liquid crystal. The molecules are still able to move around in the fluid, but their orientation remains the same. Not only orientational order can appear, but also a positional order is possible. Liquid crystals exhibiting some positional order are called smectic liquid crystals.

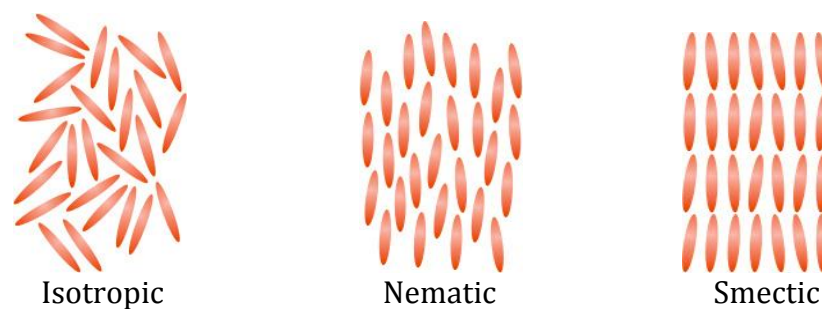


Figure 2.3 Orientation of LC phase

In smectics, the molecular centers of mass are arranged in layers and the movement is mainly limited inside the layers (Figure 2.4). In smectic phases, on average, the molecules are parallel to one another and are arranged in layers, with the long axes perpendicular to the layer plane. Within the layers, the centers of gravity of the molecules are ordered at random. Thus, smectics possess the one-dimensional quasi long-range positional order and within the layers molecules show a relatively high mobility. The layer thickness is equal to the molecule length. Smectic LCs are optically positive and uniaxial with the optic axis parallel to the molecular long axes.

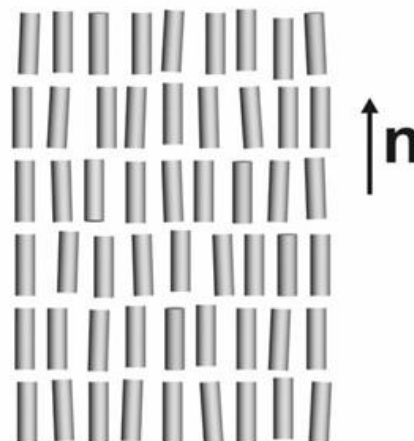


Figure 2.4 Structure of smectic liquid crystal

The simplest mesophase is a nematic LC. Most LCs used in PDLC are nematic LC. In nematics, the long molecular axes are preferably oriented in one direction, defined as the director \mathbf{n} (Figure 2.5), and molecular dipoles are compensated, so in equilibrium this mesophase is electrically neutral. Both directions of director, $+\mathbf{n}$ and $-\mathbf{n}$ are equivalent. The ordinary nematic structure shows an optically positive uniaxial behavior with the optical axis parallel to the director \mathbf{n} .

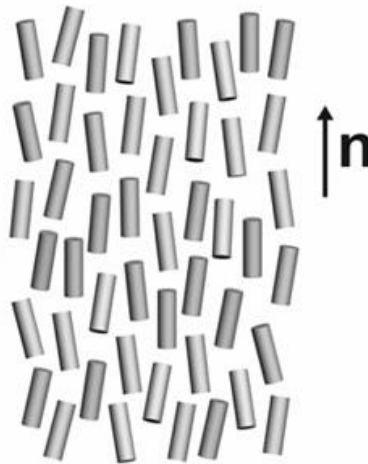


Figure 2.5 Structure of nematic liquid crystal : vibration of molecules represents thermal fluctuations of the director \mathbf{n}

Nematic LCs possess a relatively low viscosity; they can be deformed by even small external forces. Considering only weak distortions, the nematic phase formally acts as an elastic medium, and the deformations can be treated by the continuum theory of nematics.

The average direction of the molecular long axes in the LC phase defines the director \mathbf{n} , which gives the direction of the preferred orientation of LC molecules. In most LCs both direction of the vector \mathbf{n} , $+\mathbf{n}$ and \mathbf{n} are equivalent. However, for molecules with permanent dipole moments this may not be the case, and the sign of \mathbf{n} becomes important.

To specify quantitatively the amount of the orientational order in the LC phase, the scalar order parameter S is commonly used ($0 < S < 1$)

$$S = \frac{1}{2} \langle 3\cos^2\theta - 1 \rangle \quad (2.1)$$

where θ is an angle between the individual molecular long axis and the director \mathbf{n} and the brackets indicate the average value. In a perfectly system $S=1$, and in an isotropic liquid state, with no orientational order, $S=0$.

The order parameter of the LC decreases as the temperature increases and typical values are in the range 0.3 – 0.9 (Figure 2.6).

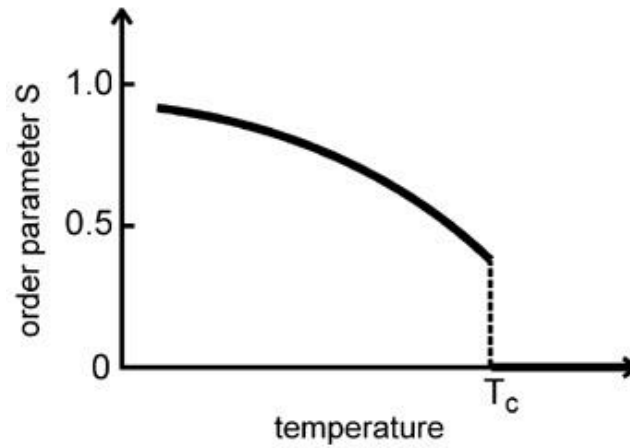


Figure 2.6 Scalar order parameter S versus temperature

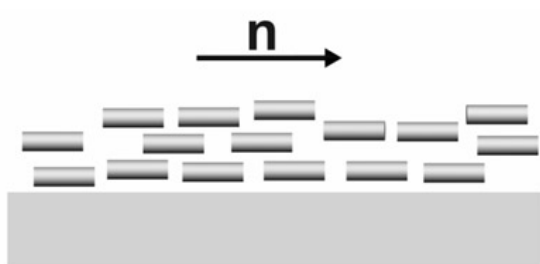
The uniaxial symmetry around the director in the LC phase leads to an anisotropy in many physical properties. For example, the refractive index, the dielectric permittivity, the magnetic susceptibility, viscosity and conductivity have a different value parallel to the director \mathbf{n} and perpendicular to it.

2-3-2 Orientation of Liquid Crystals

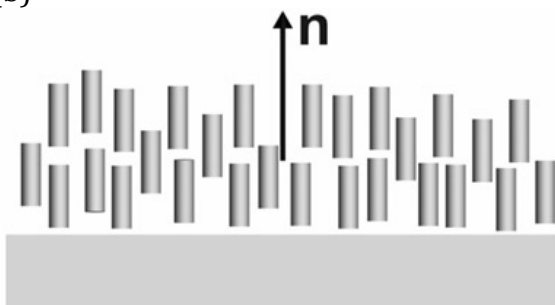
Almost any surface causes the director n orient in a specific direction near the surface. The molecules alignment at surfaces propagates over macroscopic distances.

There are three main types of the LC director n alignment near solid wall or at the free surface. These are homeotropic, planar, and tilted orientations (Figure 2.7). The surface, which is in a contact with mesophase is usually considered to be flat on the microscopic scale, and the position of the director near it is determined by polar θ and azimuthal φ angles.

(a)



(b)



(c)

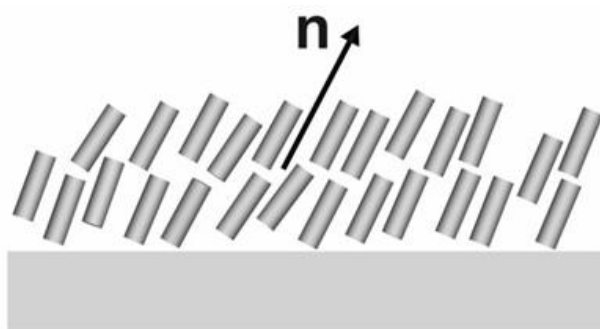


Figure 2.7 Types of liquid crystal orientation near surface : (a)planar, (b)homeotropic, (c)tilted

When the director \mathbf{n} is oriented homeotropically, the polar angle $\theta = 90^\circ$. The director with planar orientation lies in the plane of the surface or phase separation border. In this case two possible orientations exist: one, homogeneous planar orientation, when the director is oriented uniformly over the surface and φ is fixed. Another, heterogeneous planar orientation, when the orientation of the director is not uniform over the surface and φ has different fixed values in different points of the surface. In case of tilted orientation θ is fixed and φ is arbitrary. The preferred direction of the director \mathbf{n} at the surfaces set by alignment is called easy axis.

Due to the deformations of LCs there are deviations of the director from the easy axis in the areas adjacent to surfaces. Thus, to the distortion free energy should be added term related to the excess surface energy. The surface anchoring term is given by

$$F_s = \frac{1}{2} W_{\theta_0} \sin^2(\theta - \theta_0) + 1/2 W_{\varphi_0} \sin^2(\varphi - \varphi_0) \quad (2.2)$$

where θ_0 and φ_0 are fixed polar and azimuthal angles of easy axis ; W_{θ_0} and W_{φ_0} are polar and azimuthal anchoring potentials defining the energy needed for the maximal deviation of the director from the easy axis position. The surface anchoring is considered to be strong in the range $\sim 10^{-4}$ J/m² and weak in the range $\sim 10^{-6}$ J/m². The important parameter characterizing the surface anchoring strength is the extrapolation length given by $L \sim KW$, where K is an elastic constant and W is a surface anchoring coefficient.

2-3-3 Optical Anisotropy of Liquid Crystals

The optical performance of liquid crystal displays is largely determined by the birefringence of the liquid crystal. When light is shone onto a uniaxial crystal (i.e., an aligned nematic phase), it is split into two beams: an ordinary (n_o) ray and extraordinary (n_e) ray. The anisotropy of LCs causes light polarized along the director n to propagate at a different velocity than light polarized perpendicular to it (Figure 2.8). Therefore, LCs are birefringent. A uniaxial LC has two principal refractive indices, ordinary refractive index n_o and extraordinary refractive index n_e . The first one, n_o , is measured for the light wave where the electric vector vibrates perpendicular to the optical axis (ordinary wave). The index n_e is measured for the light wave where the electric vector vibrates along the optical axis (extraordinary wave). Then, the birefringent is given by,

$$\Delta n = n_e - n_o. \quad (2.3)$$

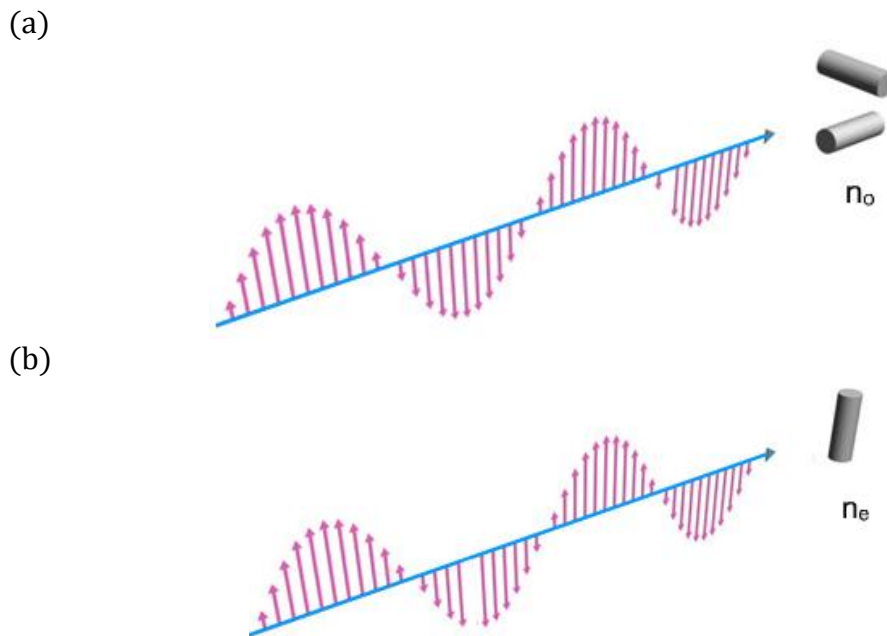


Figure 2.8 Light propagation in LCs along and normal to optical axis : (a)ordinary beam, (b) extraordinary beam.

Usually, for a nematic liquid crystal $n_e > n_o$, and the birefringence ($\Delta n = n_e - n_o$) is therefore positive. A greater degree of conjugation (caused by aromatic rings or terminal and linking groups rich in electrons) leads to higher Δn values. The range Δn for most liquid crystals is between 0.04 and 0.3; low birefringence materials have low n_o values and higher birefringence materials have higher n_o values.

2-3-4 Dielectric Anisotropy of Liquid Crystals

Dielectric properties of LCs are related to the response of LC molecules to the application of an electric field. Permittivity is a physical quantity that describes how an electric field affects and is affected by a dielectric medium and is determined by the ability of a material to polarize in response to an electric field, and thereby to cancel, partially, the field inside the material.

In the LC materials consisting of non-polar molecules, there is only an induced polarization, which consists of two parts: the electronic polarization and the ionic polarization. A molecule can be considered to consist of a series of electric dipole moments which leads to the two contributions of a permanent dipole term (μ) at some angle β and an induced dipole or polarizability term (α). A simplified version is given in below equation,

$$\Delta\varepsilon = \left[A \cdot \Delta\alpha - \frac{B\mu^2}{T} (1 - 3\cos^2\beta) \right] S \quad (2.4)$$

where A and B are material-dependent constants, S is the order parameter, and T is the temperature. The dipole contribution to $\Delta\varepsilon$ is positive for $\beta < 54.7^\circ$ and negative for $\beta > 54.7^\circ$. The larger the anisotropy the smaller electric field is needed to make the LC respond to it [3].

2-3-5 Liquid Crystals in Electric Field

LC materials may consist of polar and non-polar molecules. The polar molecules possess the permanent dipole moments caused by slight charge separation in the molecule. In the case of non-polar molecules, the induced electric dipoles are created by an applied electric field causing the slight separation of positive and negative charges in the molecule. However, they experience the same forces in an electric field.

The LC molecules can possess the permanent or induced dipole along or across the long molecular axis (Figure 2.9). If the dipole moment is parallel (or nearly parallel) to the long molecular axis then $\Delta\epsilon > 0$ and the molecules tend to orient along the electric field direction. If the molecules carry dipole moments that are more or less normal to the long molecular axis then $\Delta\epsilon < 0$ and molecules tend to orient perpendicular to the electric field direction.

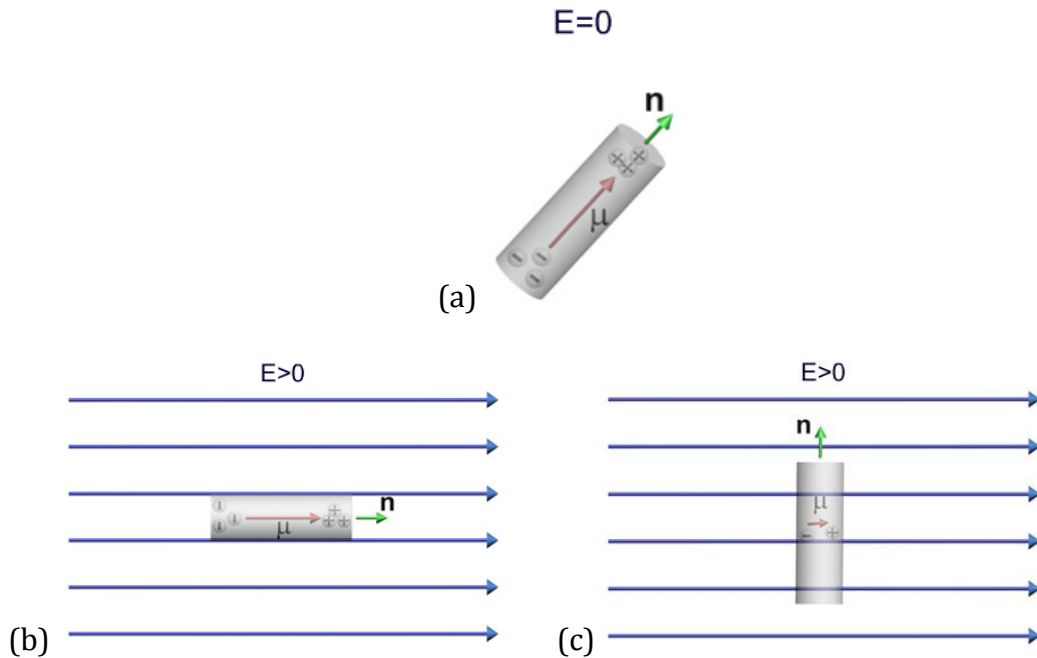


Figure 2.9 Liquid crystal molecules (a) with positive $\Delta\epsilon$ (b) and negative (c) in electric field

The orientation order of LC molecules does not change in an applied electric field. The electric field causes the director \mathbf{n} reorientation. The LC molecules respond to the applied electric field \mathbf{E} collectively that causes the distortions of the director \mathbf{n} . The electric contribution should be added to the free energy density,

$$F_e = -1/2\epsilon_0\Delta\epsilon(\mathbf{E} \cdot \mathbf{n})^2 \quad (2.5)$$

where ϵ_0 is the electric permittivity of vacuum. The larger the dielectric anisotropy the smaller electric field is needed to reorient the LC molecules.

2-3-4 Polymer

Polymers are formed by the connection of numerous repeat units called monomers. To form a polymer each monomer must be able to connect to at least two other species to form a link in a continuous chain [4].

The polymer chain can be relatively simple, with a linear structure and no variation in type of monomer (homopolymer). Alternatively, different types of monomers can be used to form a chain where the monomer type is mixed. The polymer chains can be linear, branched, or crosslinked, where different linear chains are connected to each other. Polymers containing crystalline regions can exhibit a melting transition at a temperature T_m . All polymers also exhibit a glass transition temperature T_g , which marks a second-order phase transition. The glass transition temperature is always below melting temperature. A polymer can exist in several physical forms, such as semicrystalline solid, a glass, a rubber or a viscous fluid [4].

Both T_m and T_g for polymers can be lowered by plasticization, where an absorbed low molecular weight species solvates the polymer chains. Most of the polymers used in PDLC systems will absorb liquid crystal. This is an important phenomenon in PDLC films, as liquid crystal absorbed into a polymer will both lose its mesogenic properties and alter the properties of polymer. It is likely that the polymers in most PDLC devices have strongly suppressed glass transition and melting transition.

2-4 Polymer Dispersed Liquid Crystal

2-4-1 Polymer Dispersed Liquid Crystal Theory

The first patent for a device that contains a dispersion of liquid crystals and controls light scattering by an electric field was issued to Hilsum in 1976. Progress was made in 1980`s to disperse the liquid crystal in a polymer.

In the absence of an external electric field, the orientation of LC is random. The LC director axis of each LC domain varies randomly (Figure 2.10), causing the refractive index to change from domain to domain[6]. The refractive index of the LC droplets does not match with that of the polymer matrix. Therefore, the incident light is scattered and the film becomes opaque. When the driving voltage is applied and increased, the LC is gradually oriented to the direction of the electric field and the ordinary refractive index of LC matches well with that of the polymer matrix, so that light passes through the PDLC and it becomes transparent (Figure 2.11)[6].

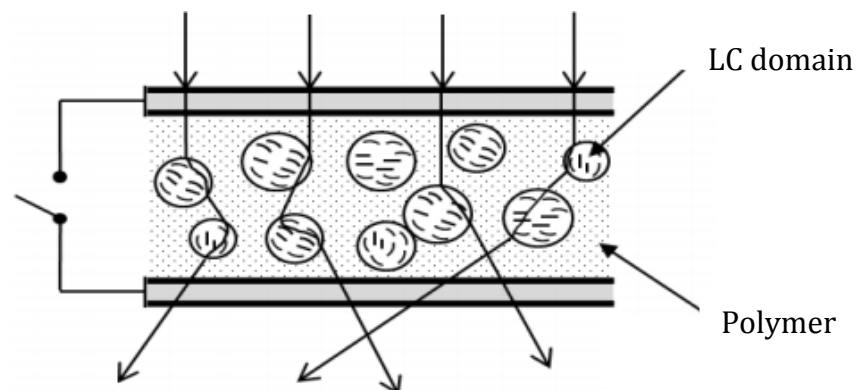


Figure 2.10 Averaged molecular orientation of the LC within the microdroplets without electric field

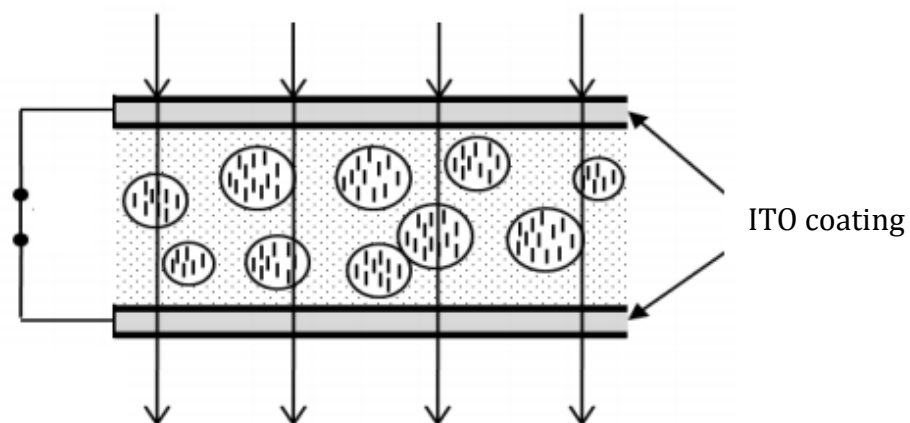


Figure 2.11 Averaged molecular orientation of the LC within the microdroplets with electric field

2-4-2 Structure of PDLC

PDLCs have two main morphologies. The observation of the microstructure of the polymer matrix is carried out by scanning electron microscopy (SEM). The Swiss cheese morphology type or also called droplet type (Figure 2.12), is characterised by liquid crystal randomly dispersed in a polymer matrix, as microdroplets. The size and shape of the LC microdroplets are in strong dependence on the parameters of preparation and the type of polymeric matrix [9].

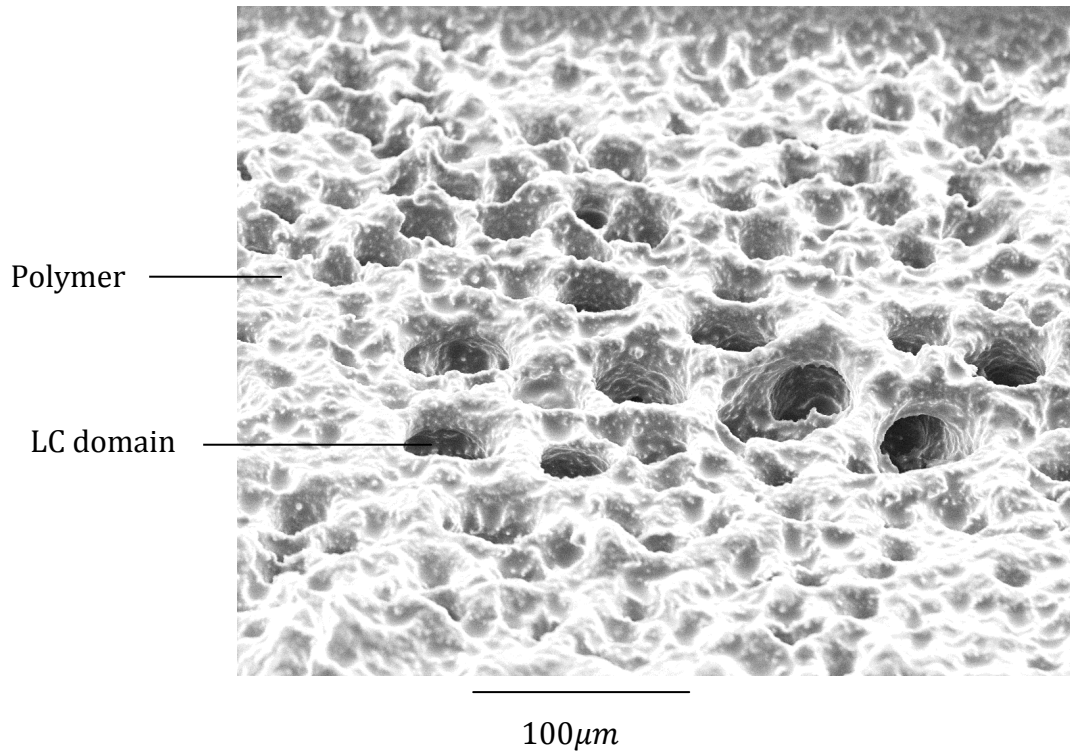


Figure 2.12 Droplet type PDLC

In the polymer ball morphology type (Figure 2.13), the polymerisable monomers are phase separated from the continuous liquid crystals and form micro-sized polymer balls. These micro-sized polymer balls merge and form a large polymer network structure with irregularly shaped voids in which LC exists. LC fills the irregular shaped voids of the polymer network, which are more or less interconnected [9].

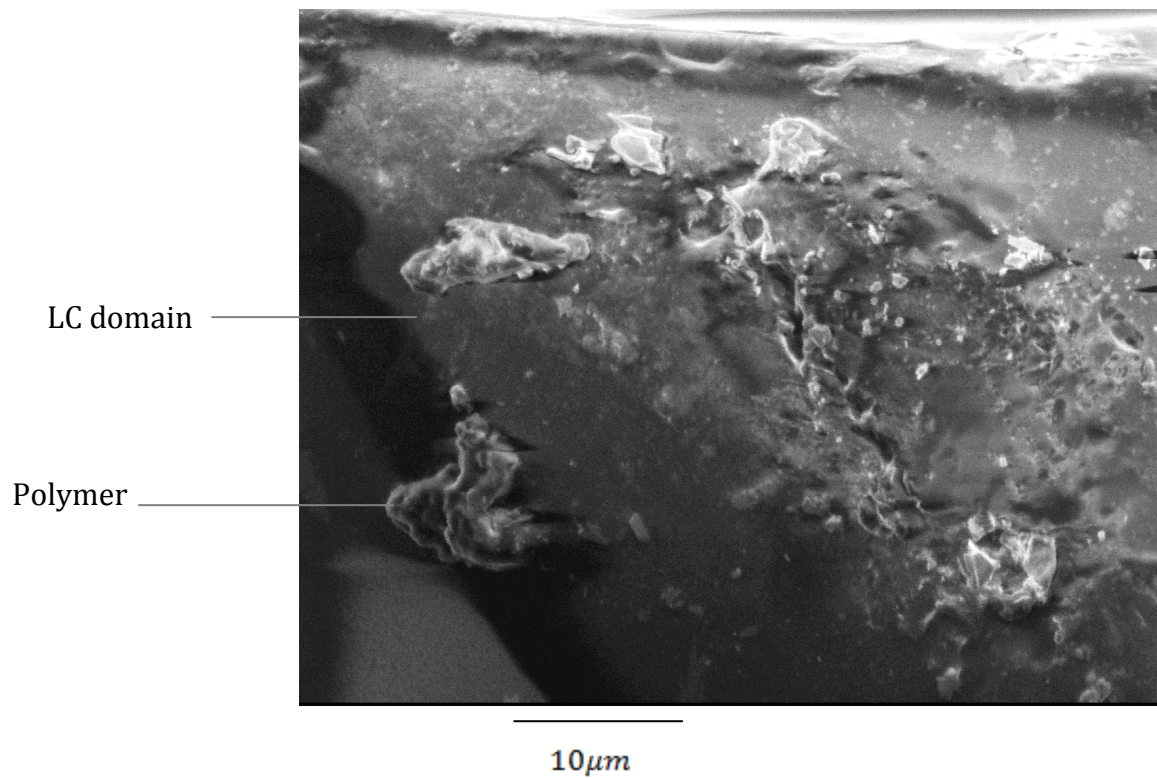


Figure 2.13 Network Type PDLC

2-4-3 Optical Transmittivity

It is well-known that the optical properties of PDLC are dominated by light scattering. In fact, the droplets dispersion in the isotropic binder gives rise to strong light scattering because of the droplet size which may be close to the light wavelength. It is also well-known that the interest for these materials was born because it is possible to control the light scattering through the application of a low frequency voltage, thus switching the PDLC cell from an opaque to transparent state. The principle of operation of such a display can be understood in the following way. The scattering coefficient α_s due to equal particles dispersed in a homogeneous medium, in the high scattering regime may be set proportional to the square of the index mismatch

$$\alpha_s = \kappa(\Delta n)^2, \quad (2.6)$$

Where $\Delta n = n_p - n_d$, n_p being the refractive index of the matrix and n_d the one of the particle[8]. As a consequence, the optical field attenuation in travelling through such a medium is described by a differential equation

$$\frac{dE}{dz} = -\frac{\alpha_s}{2}E \quad (2.7)$$

Thus after crossing a thickness d , we get

$$E(d) = E(0)e^{-\frac{\alpha_s d}{2}} \quad (2.8)$$

And the transmitted intensity

$$I(d) = I(0)e^{-\kappa(\Delta n)^2 d}. \quad (2.9)$$

When no electric field is applied, the droplets are randomly oriented, then the index mismatch changes from droplet to droplet depending on their orientation. Because the LC droplets are anisotropic, the average value of the index mismatch may be as large as 0.1 or more. As such, the transmitted light intensity is very low due to the scattering losses. As the droplets are oriented by an electric field, they present the same effective refractive index to the radiation which can be very close to the one of the polymeric binder. In this case, the scattering losses decrease because the index mismatch approaches zero and one gets high light transmission.

The two principle indexes n_{\parallel} and n_{\perp} of LC in nematic droplet in PDLC differ no more than 15% from the one of the polymeric matrix n_p . This condition is generally written as

$$\left| \left(\frac{n_{LC}}{n_p} - 1 \right) \right| \ll 1 \quad (2.10) [8]$$

2-4-4 Scattering Pattern

Figure 2.14 shows scattering pattern of PDLC. The scattering pattern is given by,

$$I_0 = I_t + I_r + I_{fs} + I_{bs} \quad (2.11)$$

where I_0 , I_t , I_r , I_{fs} , and I_{bs} are incident light, transmitted light, reflection light, pre-scattering light and post-scattering light.

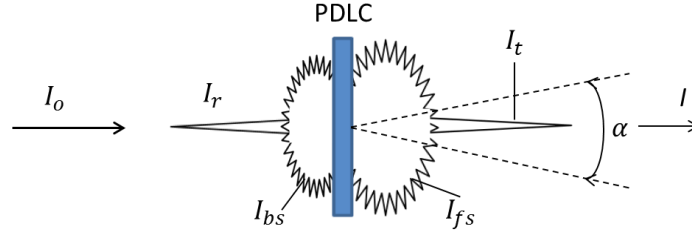


Figure 2.14 Scattering pattern of PDLC

From Lambert Law, I_t is exponential function defined as,

$$I_t = I_0 \exp(-\tau) = I_0 \exp(-\mu d) \quad (2.12)$$

where τ and μ are optical depth and extinction coefficient exponential function. In general, because PDLC is made up of transparent polymer and LC, the absorption coefficient can be ignored, and μ becomes scattering coefficient. With this, optical depth τ , is defined as,

$$\tau = \mu d = -\ln(T) \quad (2.13)$$

where T is transmittance[7].

2-4-5 The Effective Refractive Index of a Droplet

Index matching between the polymer matrix and the LC droplets is responsible for the switching to the transmission state of PDLC. The extraordinary index of the whole droplet can be defined as the average index experienced by a light wave travelling in a direction normal to N_d with dielectric induction parallel to it.

The droplet extraordinary refractive angle is obtained by averaging over all the possible director orientations in the droplet volume

$$n = \langle n_e(r) \rangle \mathcal{V}_d = \int n_e(r) f(r, \psi, \alpha) r^2 \sin\psi dr d\psi d\alpha, \quad (2.14)$$

where $f(r, \psi, \alpha)$ is the distribution of the LC director in the droplet, which in general will depend on the droplet's shape, on the anchoring at the boundaries and on external applied field [8].

2-4-3 Effects of Electric Field

The application of an electric field to a PDLC cell changes the director configuration in the droplets. Due to the interaction with the electric field, the free energy density is defined as,

$$F_E = - (1/8 \pi) \Delta \varepsilon (\mathbf{E} \cdot \mathbf{n})^2, \quad (2.15)$$

where \mathbf{E} is the local field inside the droplet.

The local field into the droplet can be related to the external one by using the electrostatic boundary conditions,

$$\mathbf{E} = \mathbf{E}_p \frac{3\varepsilon_p}{2\varepsilon_p + \varepsilon_d}, \quad (2.16)$$

where the index ' p ' stands for the polymer binder and ' d ' for the droplet. Taking into account the complex definition of the dielectric permittivity $\varepsilon = \varepsilon' + i\sigma/\omega$, at low frequency ($\omega \rightarrow 0$) we have

$$\mathbf{E} = \frac{3\mathbf{E}_p}{\frac{\sigma_d}{\sigma_p} + 2}. \quad (2.17)$$

Since the conductivity of the LC (therefore of the droplet) is generally much bigger than the polymer ($\sigma_d \gg \sigma_p$), it is clear that the local field in the droplet is much weaker than the external one. This is one of the problems met in obtaining droplets reorientation with low applied voltages.

When an electric field is applied to a PDLC cell, the droplets director tends to align along the field director and the elastic forces oppose to this alignment. In

order to describe the degree of alignment of a PDLC film subjected to an electric field, it is possible to define a sample order parameter as,

$$S_E = \langle P_2[N_d \cdot E] \rangle \mathcal{V}_f, \quad (2.18)$$

\mathbf{E} being the electric field direction and \mathcal{V}_f the cell volume [8].

Chapter 3 Procedure of Fabrication

3-1 Prologue

PDLs have been prepared by two general methods: one in which the system remains heterogeneous during the process, and another one in which the system becomes heterogeneous. Polymerization induced phase separation (PIPS) is in the second case [6]. In this study, PIPS method was performed by optically induced phase separation by UV curing. The phase separation phenomenon between LC and polymeric matrix in PDLs is a kinetic process where the transport parameters can play important role in determining the domain size and amount of LC separated from the polymer matrix.

3-2 Preparation of Polymer Dispersed Liquid Crystal

3-2-1 Materials

As mention before, PDLC is a mixture of liquid crystal and polymer. To prepare the PDLC cells, two different types of low molecular nematic LC were used, 5CB and PCH5 (Wako).

For 5CB, the chemical name is 4-cyano-4'-pentylbiphenyl. The molecular structure is shown in Figure 3.1.

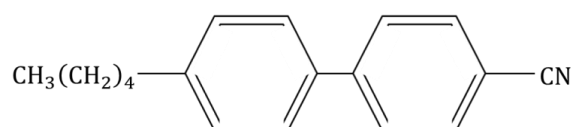


Figure 3.1 Molecular structure of 5CB

For PCH5, the chemical name is 4-trans-pentacyclohexylcyanobenzene. The molecular structure is shown in Figure 3.2.

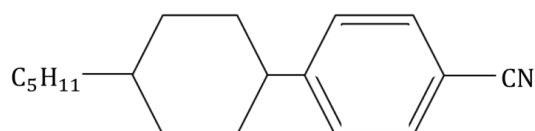


Figure 3.2 Molecular structure of PCH5.

Both 5CB and PCH5 belong to cyano group, consists of a carbon atom triple-bonded to a nitrogen atom.

Table 3.1 Characteristic of 5CB and PCH-5

	5CB	PCH5
Chemical Name	4-cyano-4'-pentylbiphenyl	4-trans-pentacyclohexylcyanobenzene
Molecular structure	$C_{18}H_{19}N$	$C_{18}H_{25}N$
Phase Transition Temperature	Cryst. 24°C N 35°C Iso.	Cryst. 30°C N 55°C Iso.
Ordinary Refractive Index, n_o	1.53	1.49
Extraordinary Refractive Index, n_e	1.71	1.60
Birefringent Index, Δn	0.18	0.11

NOA65 (Norland Products Incorporated) was used as prepolymer, which consists of a mixture of trimethylolpropane trithiol, a tetrafunctional allyl ether formed from the reaction of trimethylolpropane diallyl ether, isophorone diisocyanate, and benzophenone (BP) as a photoinitiator [] The refractive index of NOA65 is 1.52.

Table 3.2 NOA65 Characteristic

Crystalline	100%
Viscosity (cps)	1200
Refractive index	1.52
Elongation (%)	80
Elasticity (psi)	20,000

3-2-2 Procedure in Fabrication of Polymer Dispersed Liquid Crystal Cell

I. Preparation of liquid crystal and polymer mixture

LC is taken out from its container using pipette and slowly transfer into the bottle that contain NOA65 until required amount is obtained. LC and prepolymer mentioned in 3-2-1 are mixed using Hot Plate Stirrer (As One Co. Ltd) for 4 hours to form homogeneous mixture.

II. Glass substrate cut and cleaning



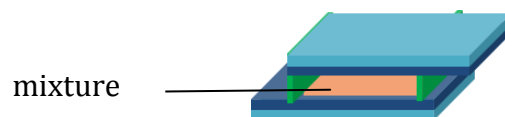
ITO (Indium tin oxide) glass (Luminescence Technology Corp : 15Ω , 25 x 25 x 0.7mm) is used as substrate. In order to obtain defined active cell area, ITO glass is cut into half and cleaned using Ultrasonic cleaner for 10 minutes. The ITO glass substrate is then baked in the oven for 1 hour.

III. Gap Making



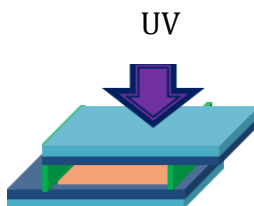
Gap is prepared by mixing spacer (Sumita New Glass & Fibre Optic) with adhesive (Cemedine Co. Ltd). 2 pieces of ITO glass that has gone through process I and II, were sandwiched with the mixture of spacer and adhesive. Then, the pair of ITO glass are clipped and left to dry for more than 3 hours.

IV. Mixture of liquid crystal and prepolymer Injection



When the hardening process is complete, the mixture prepared in I was injected into the ITO glass using pipette by capillary action.

V. UV Irradiation



In this study, PDLC cell is prepared using optically induced phase separation. In this process, mixture of NOA65 and LC is irradiated by UV. Thus, the phase separation occurs. ELC-500 (Electro Lite Corporation) is used for UV irradiation. The light intensity is 120 mW/cm^2 .

3-2-3 Polymerization Induced Phase Separation

During polymerization of what is initially a homogeneous solution of monomers and LC molecules, the polymeric components grow in molecular weight, and when the two components become sufficiently incompatible, there is a decrease of LC solubility which induces formation of separate phases.

The mixture of NOA65 and LC are dissolved homogeneously as mentioned in 3-2-2 I. At this moment, the solution is in isotropic phase. The mixture is exposed under UV light irradiation using ELC-500 (Figure 3.3) light exposure system shown in Figure. This system uses an array of custom designed lamps emitting a peak wavelength 365nm. The ELC-500 features a digital countdown programmable timer to assure repeatable results, power-down mode, safety interrupt switch, viewing panel and exposure completion audible signal. The internal chamber is lined with highly reflective material, assuring even light distribution, and also includes a clear rotating table for uniform curing.

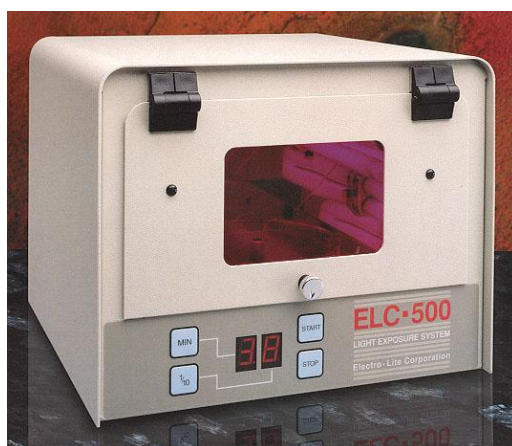


Figure 3.3 ELC-500 light exposure system

When the mixture is UV irradiated, monomers in NOA65 undergo phase transform from liquid to solid phase and become polymer (Figure 3.4). As the process continues, LC molecules become phase separated, come out from the solution and begin to form LC domain (Figure 3.5).

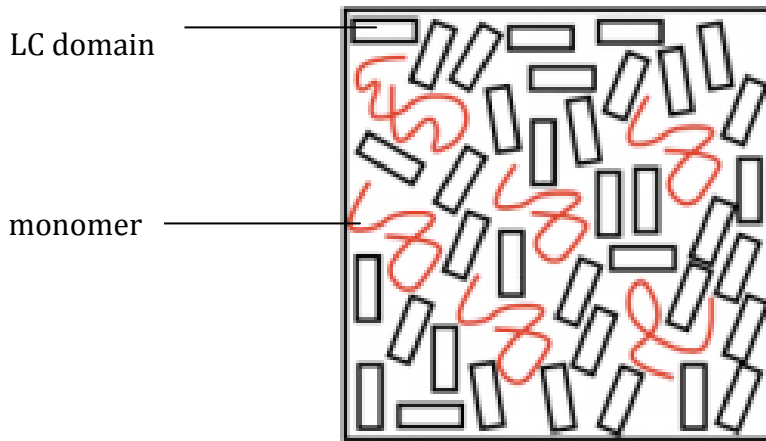


Figure 3.4 Mixture of NOA65 and LC before phase separation [10]

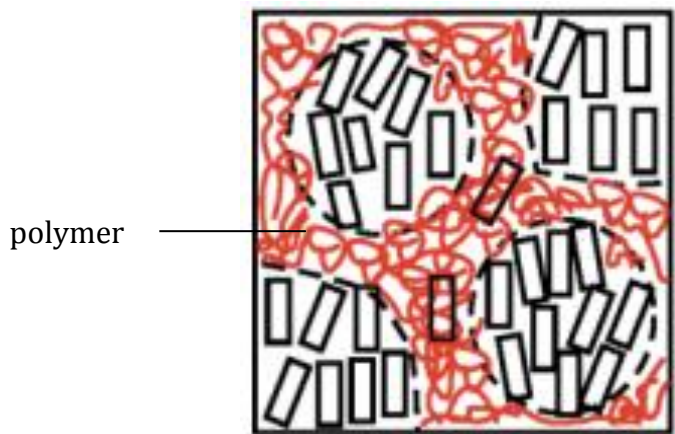


Figure 3.5 Mixture of NOA65 and LC after phase separation [10]

The reaction of optical polymerization begins by UV absorption. In the UV curing process, liquid monomers transform into solid polymer. Figure 3.6 shows the optical polymerization process.

M : monomer

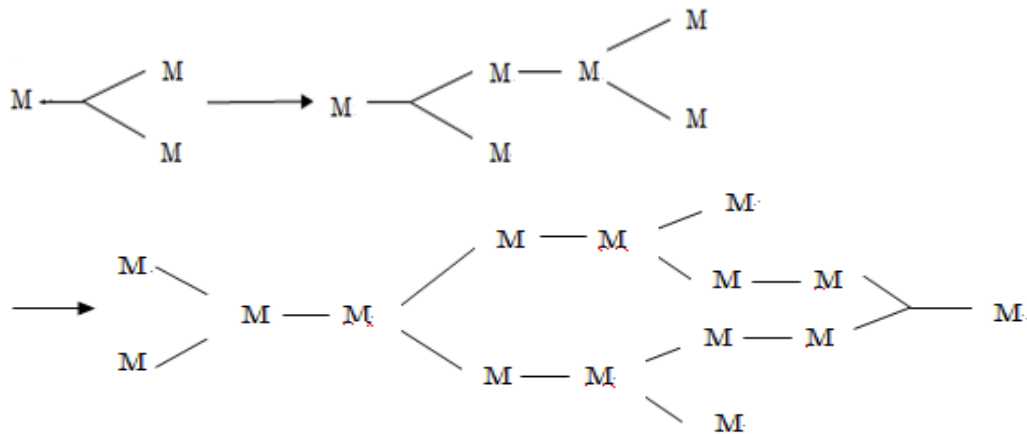


Figure 3.6 Optical Polymerization

Chapter 4 Surface Treatment on PDLC

4-1 Prologue

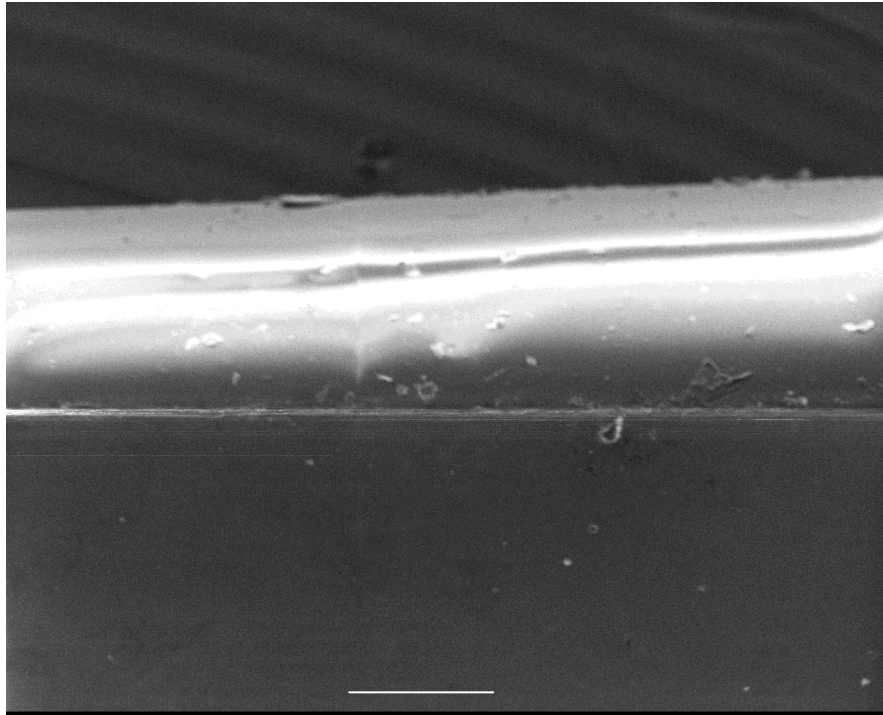
The alignment of LC molecules on rubbed polymer surfaces was discovered in 1911. In recent years, this phenomenon has been studied extensively not only because of the basic interest in understanding the underlying mechanism, but also because of its relevance to LC display technology. To orient the LC, it is necessary to treat the surface in some way. All procedures of solid substrate can be roughly divided into two major groups: mechanical treatment and chemical treatment [11]. In this study, we use mechanical treatment by rubbing the surface substrate with clean velvet cloth. By rubbing the polyimide film, microgrooves are formed. LC deposited on the rubbed polymer surface will exhibit a surface director parallel to the direction of rubbing.

The alignment with the surface is not perfect, there is small angle of 1 or 2 degrees between the surface and the molecule director which is called the pretilt. The pretilt depends on the strength of the rubbing.

One of the important parameters of LC alignment is the pretilt angle. The pretilt angle is a critical parameter to control the optical properties of liquid crystal display.

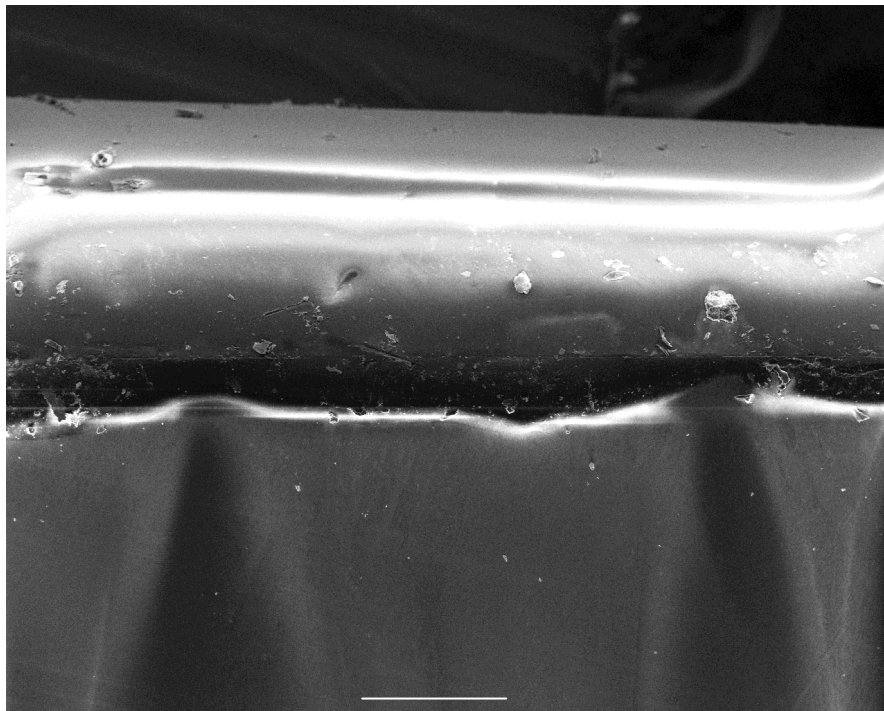
4-2 Structure of PDLC

Figure 4.1 and 4.2 show images of PDLC cells using 5CB, which constitutes a network type PDLC, were observed using a SEM .



200 μ m

Figure 4.1 Rubbing cell SEM image



200 μ m

Figure 4.2 Non rubbing cell SEM image

Figure 4.3 shows images of optical transmission through the PDLC cells using 5CB, which constitutes a network type PDLC, were observed using a polarizing optical microscope (Nikon : ECLIPSE E200).

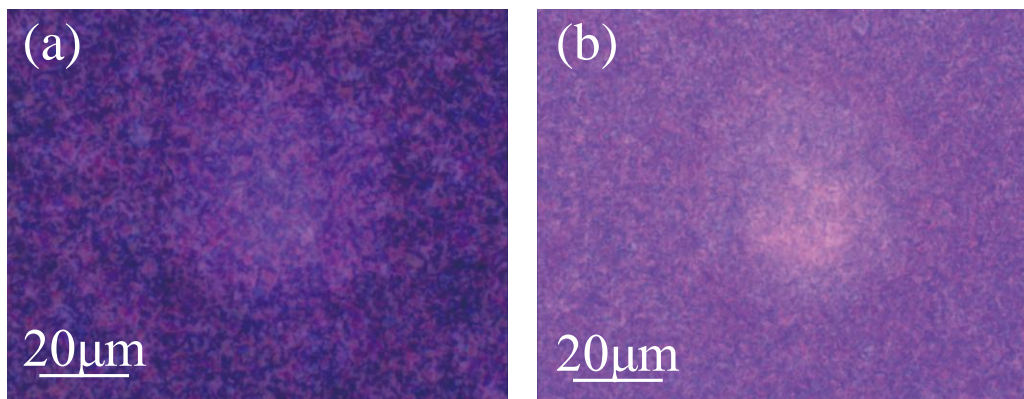


Figure 4.3 POM images of PDLC cells with (a) rubbing (b) non-rubbing treatment.

The polarizing optical microscope is equipped with both a polarizer, positioned in the light path at some position before the specimen, and analyzer (a second polarizer), placed in the optical pathway between the objective rear aperture and the observation tubes or camera port. Image contrast arises from the interaction of plane-polarized light with a birefringent (or doubly refracting) specimen to produce two individual wave components that are polarized in mutually perpendicular planes. The velocities of these components are different and vary with the propagation direction through the specimen. After exiting the specimen, the light components become out of phase with each other, but are recombined with constructive and destructive interference when they pass through the analyzer.

Anisotropic minerals show different colors when viewed under crossed polarizers. The colors seen are called interference colors. On the other hand, Light polarized perpendicular to the director in a LC travels at a different speed than that polarized parallel to the director. The result is that the light waves emerging from the material have a phase difference. A random droplet is near to isotropic phase where the birefringent is low. When the LCs in the droplet are mostly oriented, the droplet has high birefringence. Thus, leads to higher contrast.

Images in Fig 4.3 is taken under cross nicol. Results indicated that the structure of PDLC in cells with rubbing treatments had higher contrast in image than that with non-rubbing one. The optical anisotropy of both surface treatment were also observed.

4-3 Optical Transmittance of PDLC

Optical transmittance were measured using a measurement setup with a He-Ne laser (Figure 4.4). The He-Ne laser light with a wavelength of 632.8 nm was focused onto the PDLC cells. The intensity of the transmitted light was detected by a photodiode power-meter. Half wave plate was used to retard one polarization by half a wavelength, or 180 degrees.

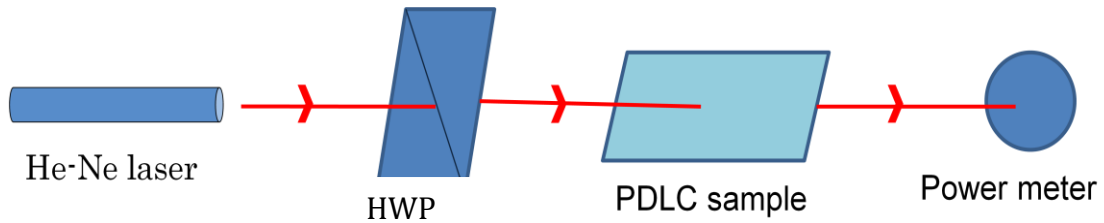


Figure 4.4 Measurement equipment

The optical transmittance of the cells were also measured for different polarization angle as shown in Fig. 4.5.

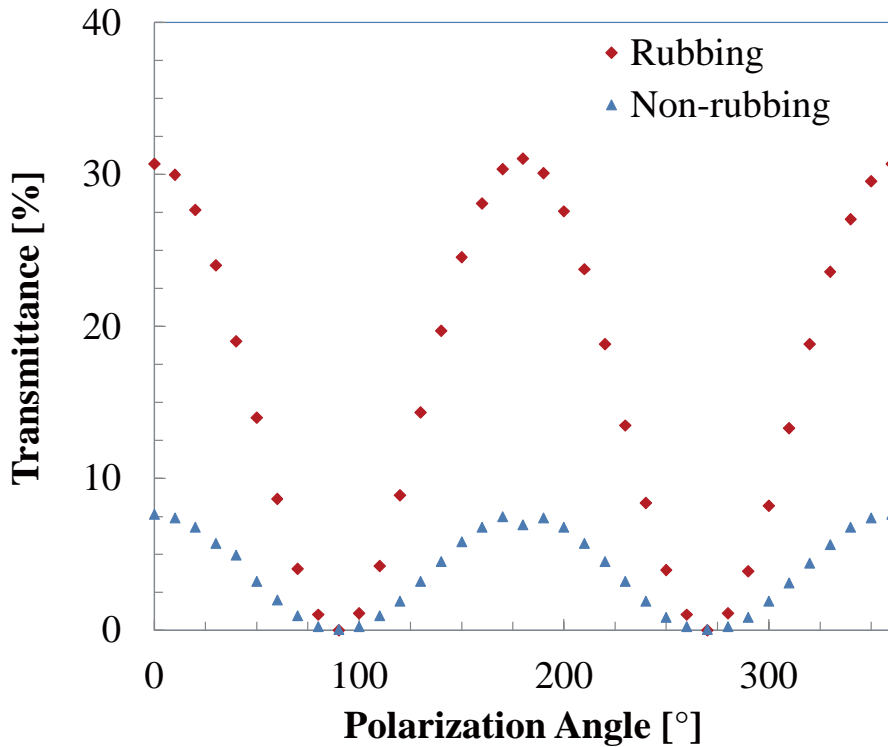


Figure 4.5 Optical transmittance for polarization angle dependency.

Polarization angle in Figure 4.5 is defined as the angle of linearly polarized light exiting from the He-Ne laser. This result also show that PDLC is depends towards polarization angle. Transmittance difference during cross nicol and open nicol condition was shown in Table 4.1.

Table 4.1 The difference of cross and open nicol for two different surface treatment.

	Difference [%]
Rubbing	30.54
Non-rubbing	7.59

External electric field is applied into PDLC by function generator, and the transmittance is measured. Figure 4.6 indicates the He-Ne laser equipment used to optical measured the optical transmittance of the applied voltage.

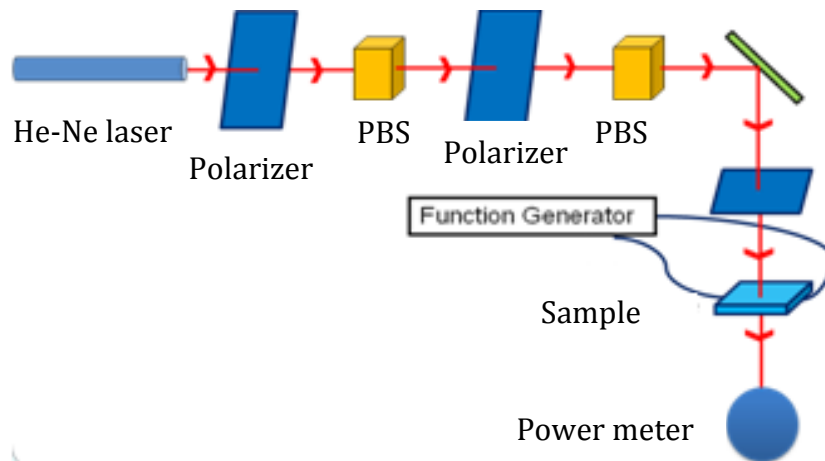


Figure 4.6 Measurement equipment

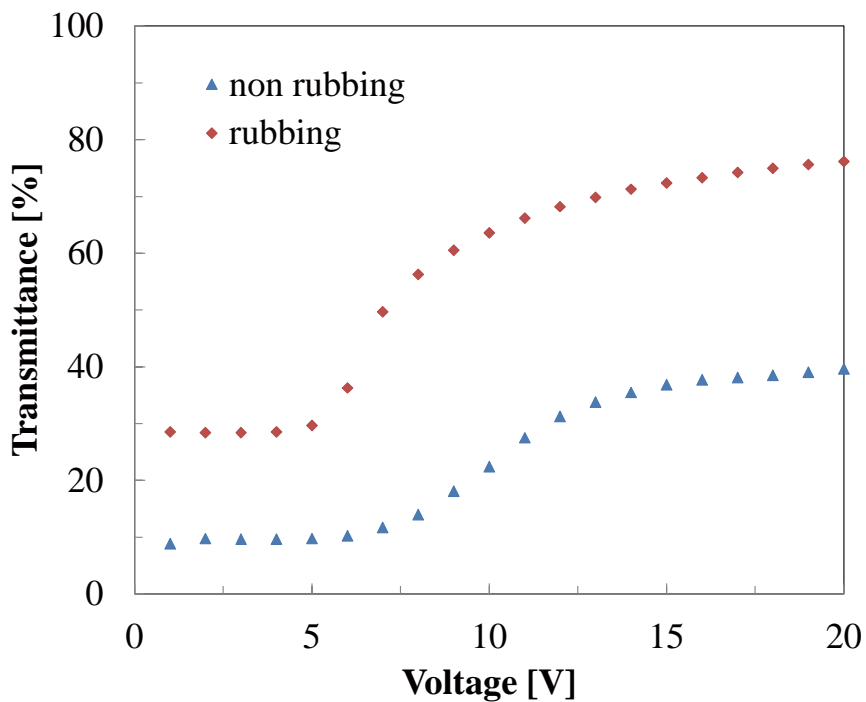


Figure 4.7 Comparison of the bias dependency of the optical transmittance of both PDLC cells with different surface treatment

Figure 4.7 indicates the comparison of the bias dependency of the optical transmittance of both PDLC cells with different surface treatment. It is shown that rubbing PDLC cells had 20% higher light throughput than that of non-rubbing.

4-4 Conclusion

The network-type PDLC was prepared through optically PIPS. 5CB is used as nematic LC, while NOA65 is used as polymer. Network-type morphologies are observed through POM microscope. We prepared two different surface treatment ; rubbing and non-rubbing. Images of rubbing and non-rubbing treatment cell observed by POM give different optical transmission. Rubbing treatment cell show stronger optical anisotropy than non-rubbing treatment cell. It is assumed that molecules of LC are more oriented that more light can pass through LC molecules during open-nicol. Thus, LC order parameter, S is assumed near to 1. In this experiment, rubbing-treated PDLC cells showed stronger optical anisotropy than non-rubbing treated cells. The relationship between voltage and transmitted light for rubbing surface treatment was investigated. We verify that PDLC is voltage dependents. The rubbing cell has higher optical transmittance by 20% than non-rubbing cell when external field is applied. We conclude that rubbing surface treatment plays role in enhancement of PDLC.

Chapter 5 Droplet Size

5-1 Prologue

One of parameter that effects the dynamic of PDLC is droplet size. In this study, we investigate the relationship between UV irradiation time, LC concentration and droplet size. During polymerization, the solubility of liquid crystal decreases until a complete separation occurs with consequent droplets formation. These droplets grow until gelation of the polymer fix the droplets size and shape. These characteristics are determined during the time from droplets nucleation to polymers` s gelation.

5-2 Droplet Size

PDLC cells using PCH5 constitutes a droplet type PDLC. To examine the droplet size of LCs in PDLC cells, weight percentage of the PCH5 was precisely controlled as 50wt%, 60wt%, 70wt% and 80wt%. These PDLC cells were irradiated with UV light accordingly for 1, 5, 10, 15, 20 and 25 minutes.

5-2-1 POM Images of PCH5 50wt%

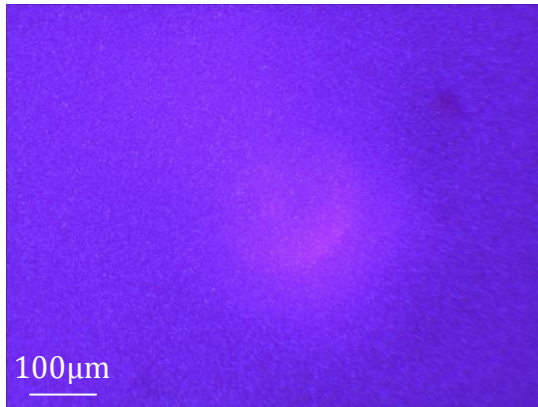


Figure 5.1 UV Irradiation 1 minute

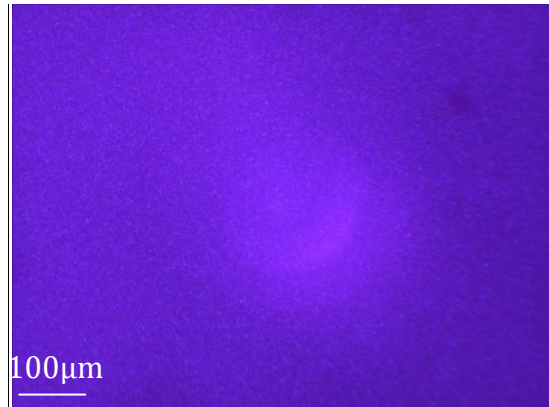


Figure 5.2 UV Irradiation 5 minutes

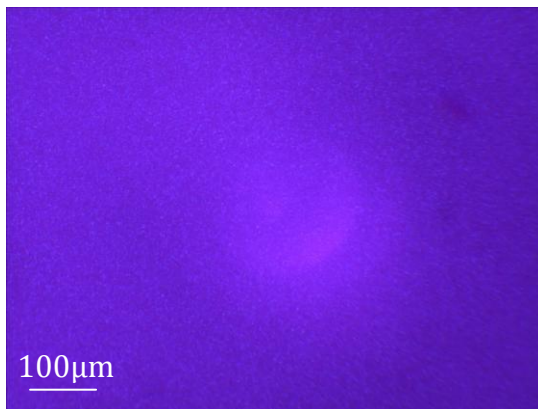


Figure 5.3 UV Irradiation 10 minutes

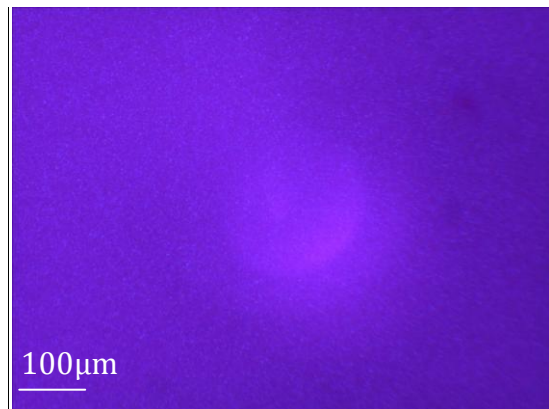


Figure 5.4 UV Irradiation 15 minutes

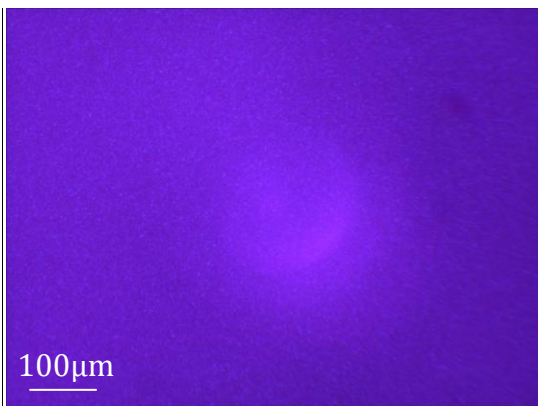


Figure 5.5 UV Irradiation 20 minutes

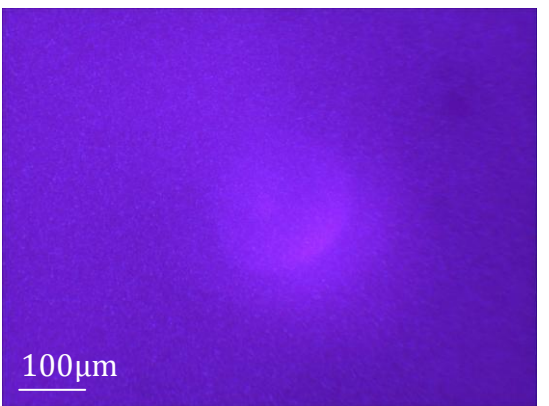


Figure 5.6 UV Irradiation 25 minutes

5-2-2 POM images of PCH5 60wt%

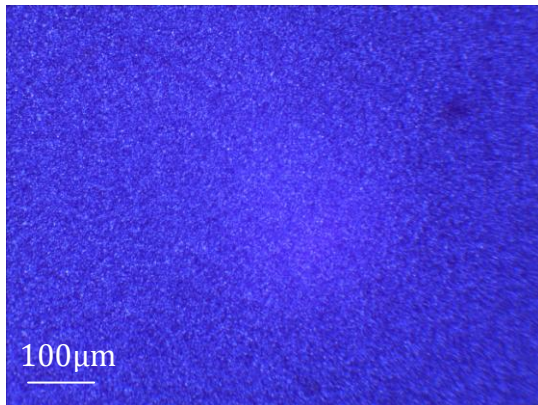


Figure 5.7 UV Irradiation 1 minute

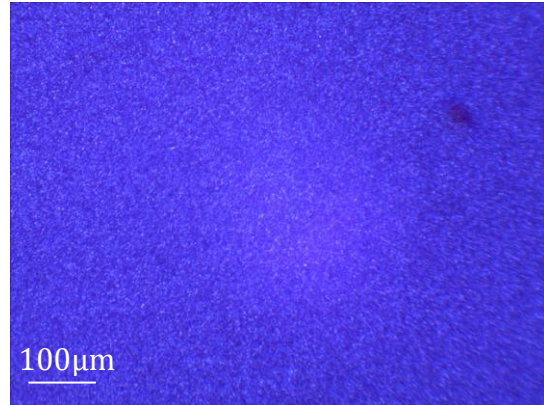


Figure 5.8 UV Irradiation 5 minutes

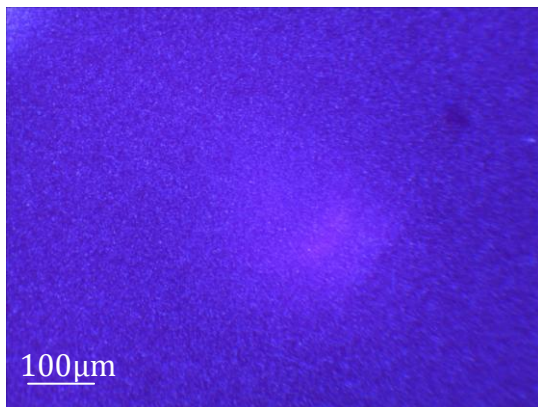


Figure 5.9 UV Irradiation 10 minutes

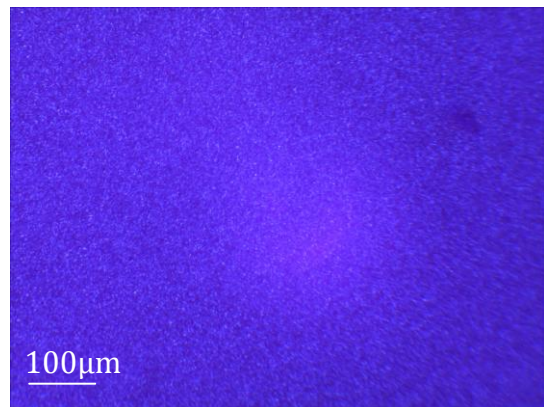


Figure 5.10 UV Irradiation 15 minutes

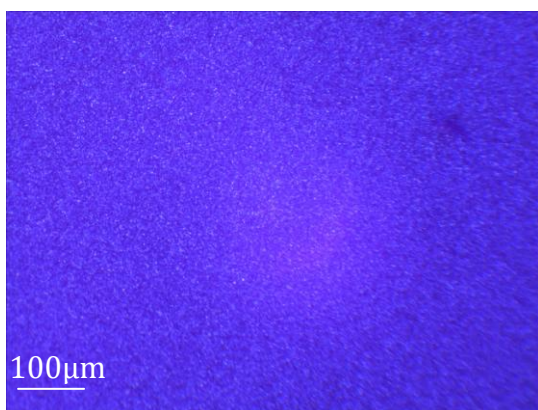


Figure 5.11 UV Irradiation 20 minutes

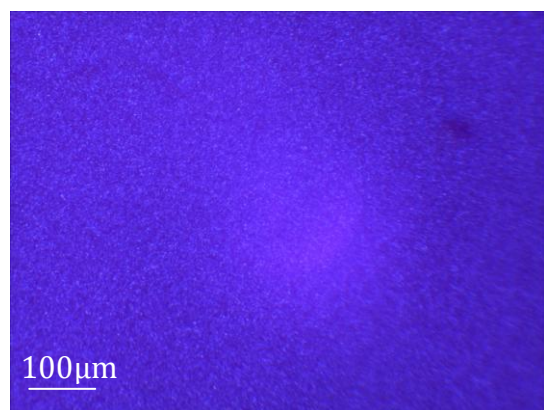


Figure 5.12 UV Irradiation 25 minutes

5-2-3 POM Images of 70wt%

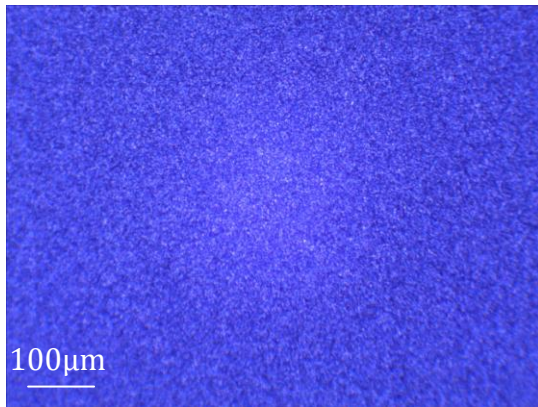


Figure 5.13 UV Irradiation 1 minute

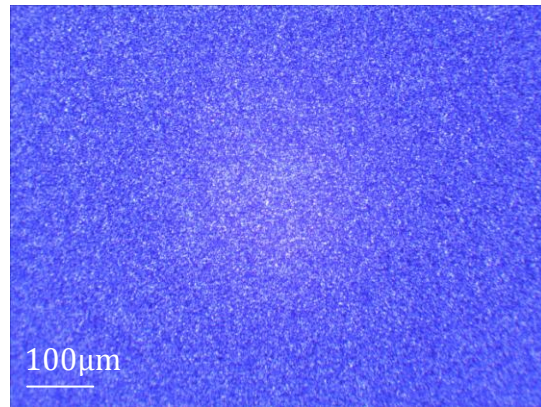


Figure 5.14 UV Irradiation 5 minutes

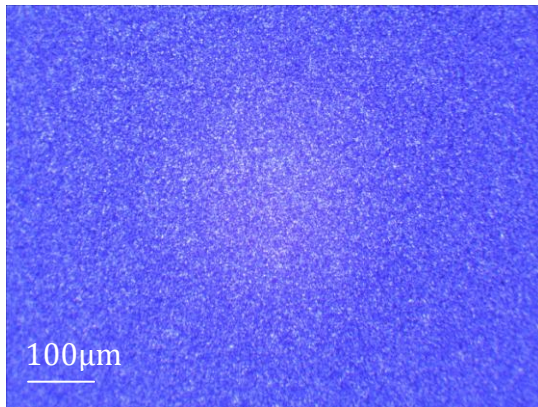


Figure 5.15 UV Irradiation 10 minutes

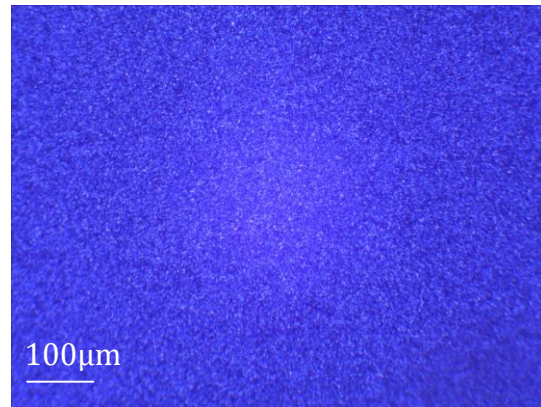


Figure 5.16 UV Irradiation 15 minutes

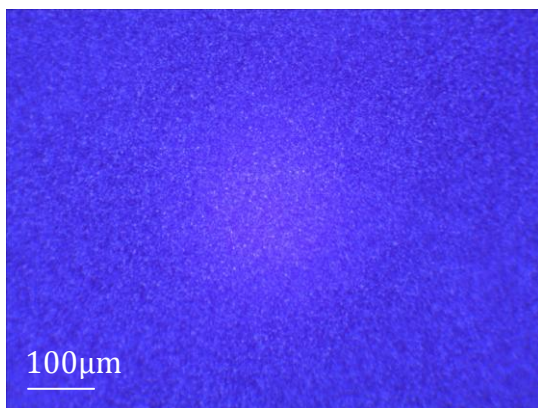


Figure 5.17 UV Irradiation 20 minutes

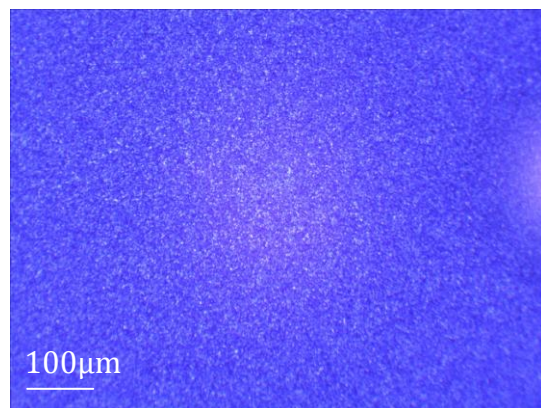


Figure 5.18 UV Irradiation 25 minutes

5-2-4 POM Images of 80wt%

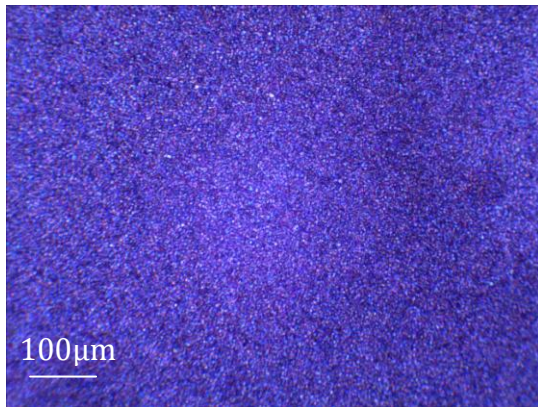


Figure 5.19 UV Irradiation 1 minute

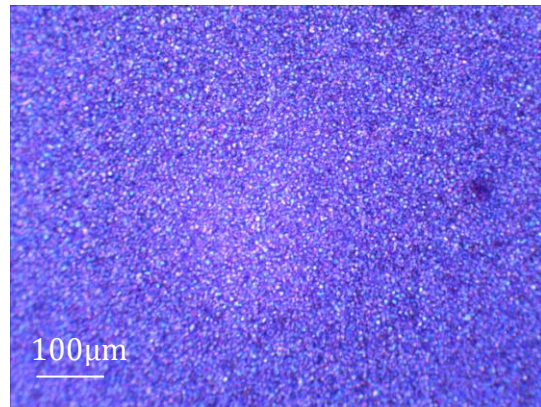


Figure 5.20 UV Irradiation 5 minutes

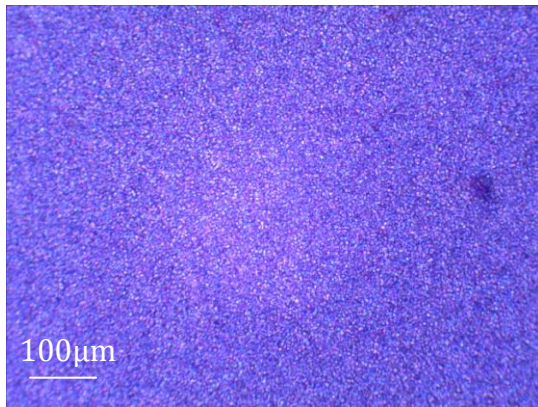


Figure 5.21 UV Irradiation 10 minutes

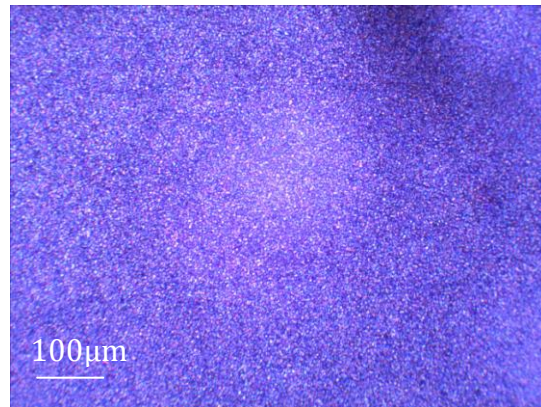


Figure 5.22 UV Irradiation 15 minutes

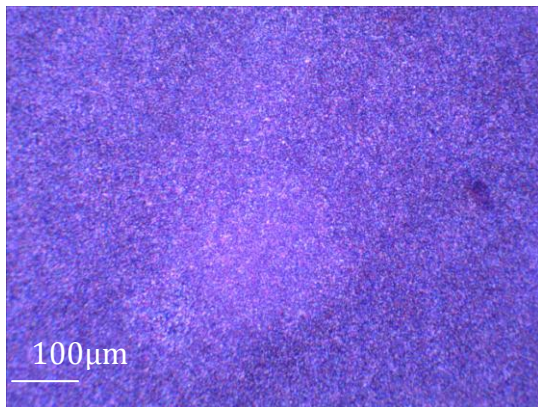


Figure 5.23 UV Irradiation 20 minutes

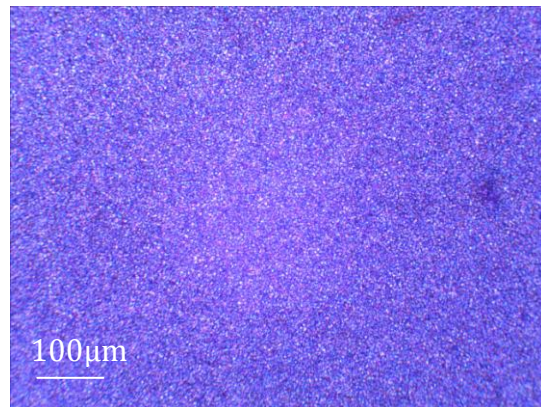


Figure 5.24 UV Irradiation 25 minutes

Figure 5.25 until Figure 5.29 shows the relation between UV irradiation time and droplet size for different PCH5 concentration. The size of the droplet was measured using Image J software.

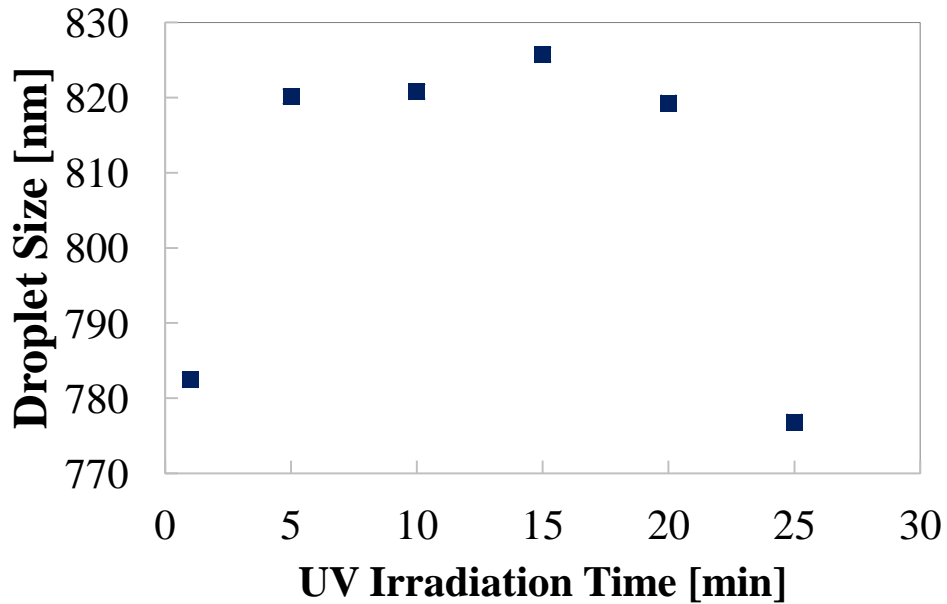


Figure 5.25 Relationship between droplet size and UV irradiation time for PCH-5 50wt%

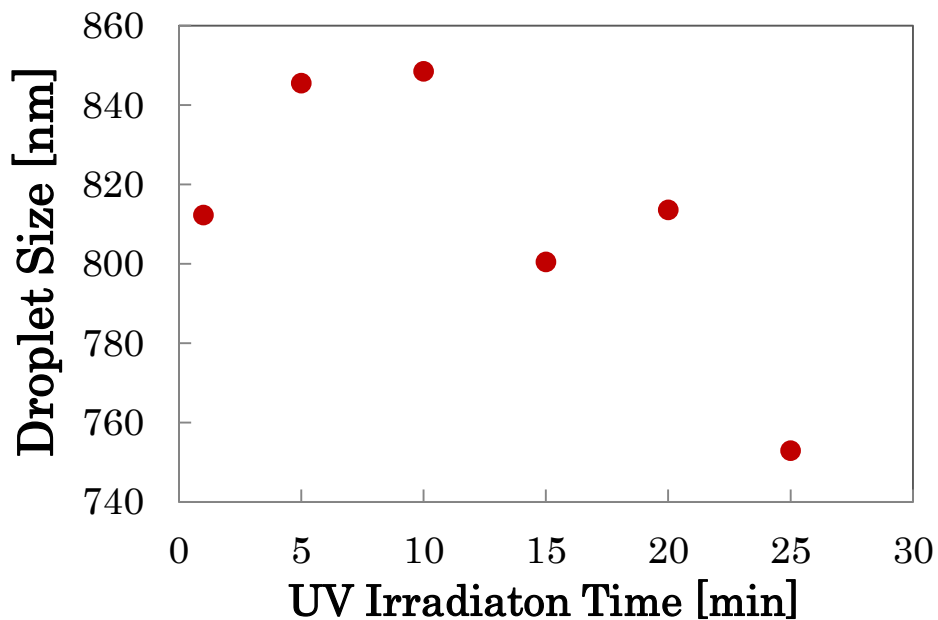


Figure 5.26 Relationship between droplet size and UV irradiation time for PCH-5 60wt%

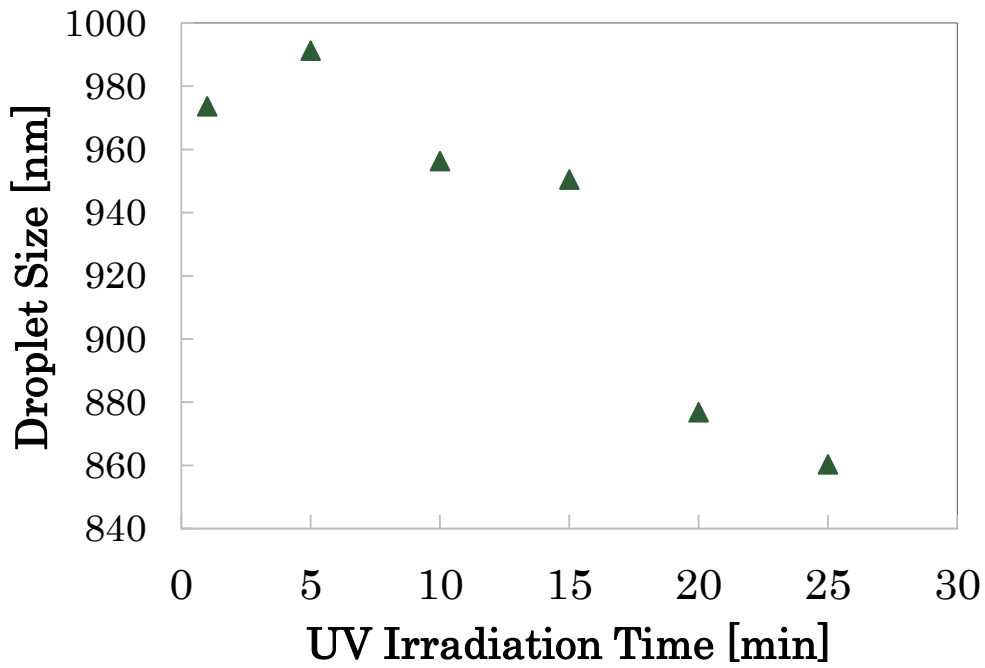


Figure 5.27 Relationship between droplet size and UV irradiation time for PCH-5 70wt%

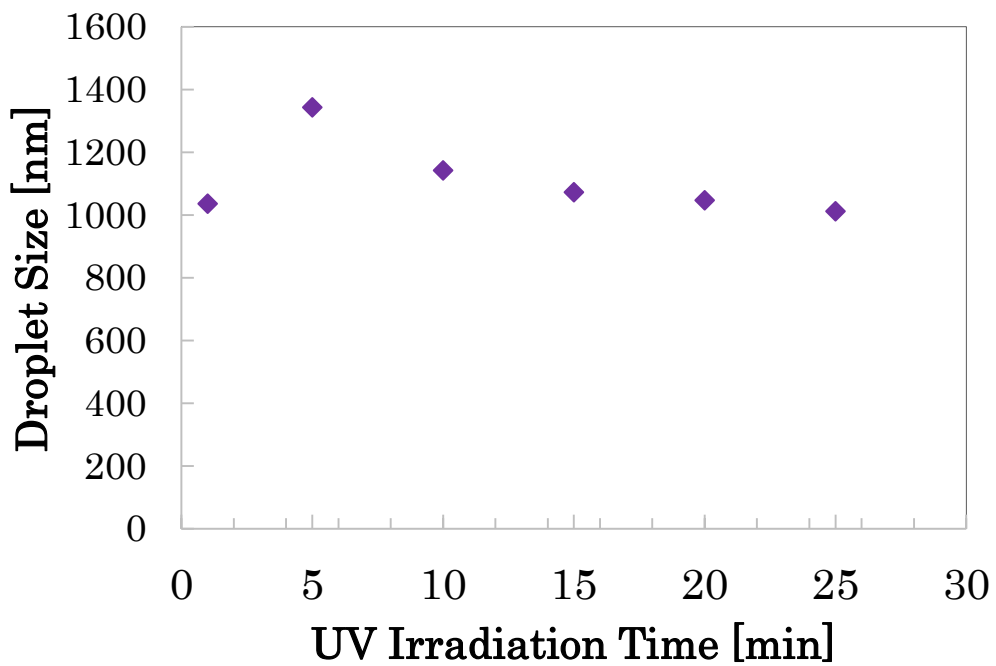


Figure 5.28 Relationship between droplet size and UV irradiation time for PCH-5 70wt%

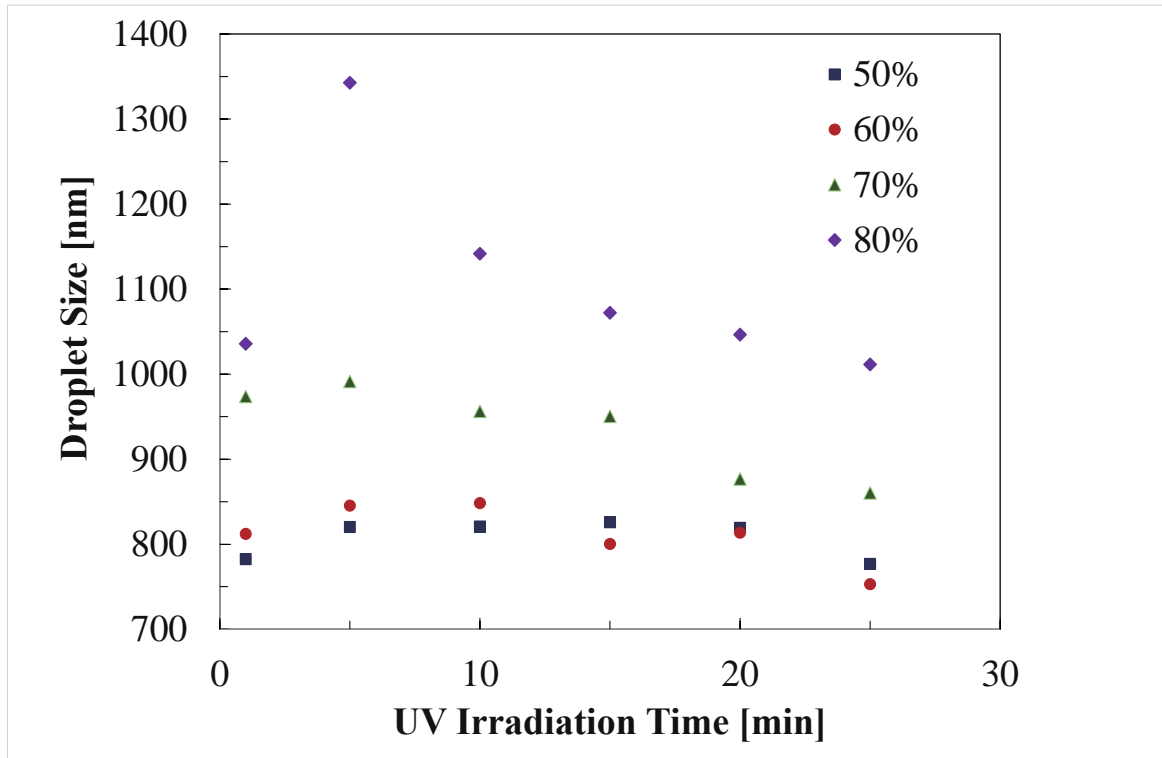


Figure 5.29 Relationship between UV irradiation time and droplet size for different PCH-5 concentration

We found that the droplet size of LC becomes larger as the LC concentration increases. The largest droplet size formed in PCH-5 80wt% is 1342 nm, in 70wt% is 991nm, in 60wt% is 848 nm and in 50wt% is 826 nm. Irradiation time of UV also effected the droplet size of LC. For PCH-5 80wt% and 70wt%, the largest droplets were formed at UV irradiation time 5minutes. For PCH-5 60wt% and 50wt% largest droplet size were formed at 10 minutes and 15 minutes each. With this result, it is assumed that higher LC concentration takes less time to produce the largest droplet, while lower LC concentration takes more time to produce the largest droplet. After the largest droplet is formed in each PCH-5 concentration, the droplet size tend to gradually grow smaller when it is irradiated longer. We observed these gradually growth phenomena on PCH-5 50wt%, 70wt% and 80%. However, we did not observe this phenomenon in PCH-5 60wt%. The droplets did not grow gradually smaller after the largest droplet formed.

In addition, we intend to certify the PDLC characterization for one of droplet-type PDLC cell. Figure 5.30 shows the waveform of 20 minutes UV irradiated PDLC cell. In CH1, the applied voltage scale is 5V/div. In CH2, the voltage scale is 10 mV/div. The time scale is 50 μ s/div. The square wave frequency is 500mHz. We verify that a PCH-5 80wt% PDLC cell under droplet-type morphology show switching response towards applied voltage.

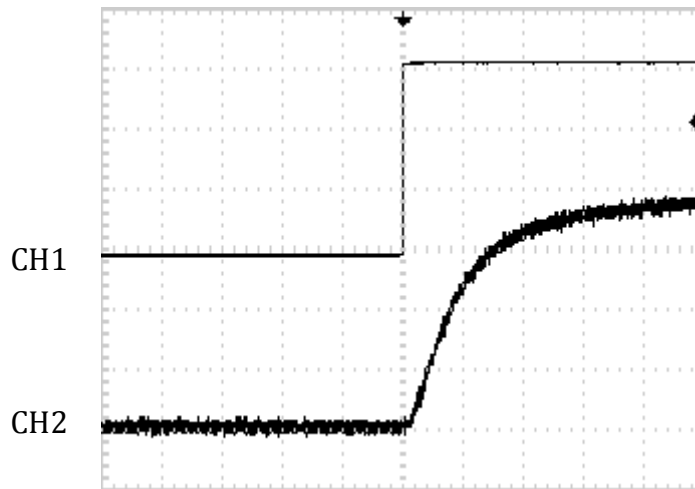


Figure 5.30 A waveform of PCH-5 80wt% PDLC cell

5-3 Conclusion

The droplet-type PDLC was prepared through optically PIPS. PCH-5 is used as nematic LC, while NOA65 is used as polymer. The PDLC fabrications of PCH-5 50wt%, 60wt%, 70wt% and 80wt% have accomplished. Droplet type morphologies are observed through POM microscope. The UV irradiation time during PIPS and the PCH-5 concentration do effect the growth of LC droplet. For LC 80wt% and 70wt%, the largest droplet were formed at UV irradiation time 5minutes, while for LC 60wt% and 50wt% largest droplet size were formed at 10 minutes and 15 minutes each. We conclude that higher LC concentration takes less time to produce the largest droplet, while lower LC concentration takes more time to produce the largest droplet. The droplets tend to grow the largest at certain UV irradiation time, and reversely turn to grow smaller when is UV irradiated in longer time. We found a gradually growth after the largest droplet is formed, except for PCH-5 60%.

We need to revise back the PCH-5 60% PDLC cell. One reason to be think here is that maybe there are utterly unformed droplets that coalesce with the neighboring or become continuous droplets. Therefore, Image J had accidentally recognize two or more different droplets as one droplet. In this study, we manage to control the formation and growth of LC droplet especially for 50wt%, 70wt% and 80% by controlling UV irradiation time and LC concentration.

Chapter 6 Summary

In chapter one, we have introduced about the background and the objective of our research. The main objective was to investigate the parameters that effect PDLC properties.

In chapter two, we explained the theoretical description of PDLC mechanism. Also, we explained about the characteristic of LC and polymer that are used to fabricate PDLC.

In chapter three, we described the steps to fabricate PDLC. We also point out the method of preparing PDLC in this study which is by optically PIPS.

In chapter four, we have investigated the surface effect condition on network type PDLC. Anisotropy characteristic was observed on both surface treatment. Rubbing cell exhibit stronger anisotropy than non rubbing cell. We found that surface effect by rubbing action does enhance the optical performance of PDLC. In optical transmittance, rubbing cell had light throughput 20% higher than non rubbing. Therefore, it is assumed that rubbing treatment play a role in the enhancement of PDLC.

In chapter 5, we investigated the droplet formation and growth. We manage to control the droplet size by manipulating LC concentration or UV irradiation time. From the experiment result we get, it is considered that higher LC concentration takes less time to produce the largest droplet, while lower LC concentration takes more time to produce the largest droplet.

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6-2 References

- [1] http://www.nobelprize.org/educational/physics/liquid_crystals/history/
- [2] Birendra bahadur *Liquid Crystals Applications and Uses* Vol. 1 World Scientific
- [3] W.H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, (London,1980)
- [4] Tokyo Kagaku Dojin *Foundation of Polymer Science* Society of Polymer Science Edition
- [5] Drazaic, P.S., *Liquid Crystals Dispersions* World Scientific publishing: Singapore, 1995
- [6] Ana Isabel Mouquinho *New Polymer Networks for PDLC Films Application* Chapter 5
- [7] H.Kikuchi, H.Fujikake, M.Kawakita, and K.Takizawa, *Light Extinction Characteristics of Polymer Dispersed Liquid Crystal films*, IEIC Technical Report, 99, 663 (2000)
- [8] Francesco Simoni *Nonlinear Optical Properties of Liquid Crystals and Polymer Dispersed Liquid Crystal* Vol. 2 World Scientific
- [9] Han, W. J., *Morphological Studies of Polymer Dispersed Liquid Crystal Materials*. Korean J.Phys.Soc. 2006,49, pg 563-568
- [8] C.E. Hoyle, T.Y.Lee, T. Roper, J. polym. Sci. Part A 42 (21) (2004) 5301-5338
- [10] *Phase Separation of Polymer and Liquid Crystal* 2010 The Society of Polymer Science, Japan
- [11] Lin Y H, Ren H W, Wu Y H, Liang X, Wu S T. *Surface anchoring effect on the morphology and performance of polymer-dispersed liquid crystal*. Proc. SPIE Int Soc opt Eng, 2005, 5741:74-82