





Photopolymerization and Phase Separation Behavior of Polymer Dispersed Liquid Crystals

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Graduate School of Chosun University

Dept. of Polymer Science & Engineering

Park Sucheol



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Advisor : Prof. Hong Jin-Who

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Park Sucheol



Approved by Examining Committee:

Chairman	
Member	

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Abstract

Photopolymerization and Phase Separation Behavior of Polymer Dispersed Liquid Crystals

Park Sucheol Advisor : Prof. Hong Jin-Who Dept. of Polymer Science & Engineering Graduate School of Chosun University

Polymer dispersed liquid crystal (PDLC) films is a composite having low molecular weight liquid crystal microdroplets dispersed in a polymer matrix. Due to its attractive electro-optical characteristic, it has potential applications in switchable glass, optical and display industry. Photopolymerization-induced phase separation (PIPS) process is a preferred and versatile method to make PDLC film due to its simple manufacturing process and reliable electro-optical performances.

PIPS process is the core in PDLC technology. It is a critical factor to form a morphology of PDLC film, by which the electro-optical performances are determined. In order to achieve the optimized electro-optical performances of a PDLC film, it is essential to understand the underlying mechanisms on PIPS process.

The aim of this research is to provide fundamental knowledge on PIPS process and technical issues for enhancement of PDLC performances, which were implemented by four consecutive approaches as followings:

(1) Experimental technique to monitor PIPS process

(2) Structural factors in liquid crystal materials to PIPS process

- 1 -

(3) Structural factors in polymer components to PIPS process

(4) Correlation among chemical nature of liquid crystal and prepolymer components, PIPS process, morphology and electro-optical properties of PDLC films

(5) Construction of driving electrodes using conducting polymer thin films for improved flexibility.

Chapter 1

The background on preparation methods for PDLC films, morphology and factors to affect on the electro-optical properties were reviewed. The basic theory on PIPS process was also summarized.

Chapter 2

A novel experimental method involving simultaneous resistance and transmittance measurements was used to examine the PIPS process by simultaneous resistance and transmittance measurements of a PDLC cell. Measuring the resistance and transmittance of a PDLC cell allows the polymerization and phase separation process to be monitored during the PDLC formation process. To verify the utility of this method, resistance data were compared with conversion data obtained by photo differential scanning calorimetry (DSC) and FTIR analysis using NOA65 and NOA-65-E7 mixture. photopolymerization behavior measured by photo-DSC and FTIR analysis using NOA65 and NOA65-E7 mixture. The resistance data of NOA65 (a neat prepolymer without liquid crystal) were identical to the conversion data obtained by photo-DSC and FTIR analysis. However, the resistance data of the NOA65-E7 mixture (a prepolymer with liquid crystal) differed from the conversion data because the resistance data of the NOA65-E7 mixture was affected by the degrees of liquid crystal phase separation and monomer conversion. The

photopolymerization was slower and the degree of conversion was higher for the NOA65-E7 mixture than for the neat prepolymer due to dilution and plasticization effects, respectively.

Chapter 3

The effect of liquid crystal structures on PIPS process was investigated by simultaneous resistance and transmittance measurements. To analysis the structural effect of liquid crystals, four liquid crystal compounds having different ring structures and alkyl lengths were used. The PIPS behavior was quite different with the liquid crystal structures. Alkyl-cyclohexyl (PCHs) cyanobenzenes were much easily separated than more alkyl-cyanobiphenyls (CBs) and longer alkyl length showed slightly easier phase separation. The difference in PIPS process was also observed in the liquid crystal mixtures based on CBs and PCHs.

Chapter 4

The structural effects of prepolymer components on the PIPS process, morphology and electro-optical properties of PDLC films were investigated. Two kinds of model compounds based on thiol-allyl ether monomers with differing stoichiometric ratios and monomer functionalities were prepared. The stoichiometric ratio affects the degree of prepolymer conversion and glass transition temperature of а polymer matrix. Matching the stoichiometric balance produced a matrix with the highest degree of glass transition temperature. The average conversion and monomer functionality affected the crosslink density and glass transition temperature of the matrix, with the latter increasing as monomer functionality increased. The stoichiometric ratio and monomer functionality exerted no significant effects on photopolymerization kinetics in this

study. Due to the similar photopolymerization kinetics, the PDLC samples exhibited no significant differences in morphology and a similar level of the transmittance in the OFF state, which is strongly affected by morphology. However, the PDLC samples showed large variations in driving voltage. The structural characteristics that affect the driving voltage of the PDLC film were also examined.

Chapter 5

Conducting polymers exhibit good mechanical and interfacial compatibility with plastic substrates. We developed an optimized coating formulation based on poly(3,4-ethylenedioxythiophene) (PEDOT) and 3-(trimethoxysilyl)propyl acrylate and fabricated a flexible transparent electrode laver on poly(ethylene terephthalate) (PET) substrate. The surface resistivity and transmittance of the prepared conductive thin films were $500-900 \,\Omega/cm^2$ and 87 % at 550 nm, respectively. To evaluate the performance as a driving electrode, we fabricated a five-layer flexible polymer-dispersed liquid crystal (PDLC) device as a PET-PEDOT-PDLC-PEDOT-PET flexible film. The PDLC device exhibited low driving voltage (18VAC), high contrast ratio (60:1). and high transmittance at the ON state (60 %). which are comparable with those of the conventional PDLC device based on indium tin oxide electrodes. It has shown that the conducting polymer thin films can be used as driving electrode for PDLC devices with enhanced flexibility.

Chapter 6

PDLC films have been the most widely used variable-transparency glazing technology in the architectural and automotive industries due to its excellent optical performances, durability, and ease of processing toward large-area products. We investigated the electro-optical performance,

temperature stability, and electrical and environmental durability of commercial PDLC film and laminated glass. It can provide the understanding of current status of commercial PDLC products and further development required in PDLC technologies.

Chapter 1

Introduction

1-1 Polymer Dispersed Liquid Crystal

Polymer dispersed liquid crystal (PDLC) is a composite containing low molecular weight liquid crystal domains randomly dispersed within a continuous polymer matrix. The layer structure of PDLC film is shown in Figure 1-1. Thin (5-25µm) film between transparent conducting substrates can be switched between an intensely scattering state and a transparent state by an electric field across the film. The operating principle of a PDLC film is shown in Figure 1-2. In the field off state, the incident light is scattered due to the mismatch of refractive indices between the randomly oriented liquid crystal molecules and polymer matrix. Under an electric field, the liquid crystal directors are oriented in the direction of the electric field within the liquid crystal domains. The refractive index of the polymer matrix is matched with that of the ordinary component of liquid crystal and thus, the PDLC film appears transparent. Due to its attractive intrinsic electro-optical characteristics, the PDLC can be used as a switchable glass [1-10], an optical devices [11-16] and display devices [17-20].

Two general processes have been developed to construct PDLC films-emulsion and phase separation methods. In emulsion methods, the liquid crystal is dispersed as droplets into an aqueous polymer solution. Evaporation of water leads to formation of the PDLC film.[21-26] As opposed to emulsion methods, the phase separation methods begin with the homogeneous mixture of liquid crystal and polymer (or prepolymer)and the liquid crystal phase separates from the continuous polymer phase by polymerization (by heat or light) [27-28], cooling [29-30] or solvent evaporation [31]. Among these methods, phase separation by photopolymerization has proven to be most versatile and

useful method to achieve the PDLC film with good electro-optical properties, stability, uniformity and reproducibility. [32-33] Additionally, the wide range of starting materials for photopolymerization process can be advantageous to change the physical nature of the polymer matrix concerning that the properties of PDLC films are strongly affected by the physical properties of polymer matrix. [34-48]

The morphology of PDLC has been characterized by a number of methods such as scanning electron microscopy, transmission electron microscopy, and optical microscopy. Two distinct morphologies been observed have experimentally. The first is 'Swiss cheese' (droplet) morphology with phase-separated liquid crystal droplets dispersed in continuous polymer matrix.[39-41] The second is the 'polymer ball' morphology with small polymer particles being merged to form a larger network structure. [49-50] The liquid crystal exists in the irregularly shaped voids within the network. Examples of droplet and polymer ball morphology are shown in Figure 1-3 The droplet morphology is promoted in cases where the polymerization reaction runs via a step mechanism (thio-ene system), while the 'polymer ball' morphology is via a chain free radical mechanism (multifunctional acrylate system).

The 'Swiss cheese' morphology is preferred because it exhibits a reversible electro-optical performance, while the 'polymer ball' system shows a distinct hysteresis generally leading to a drastic deterioration of electro-optical performance.[51-52]

Besides of above two morphology, 'polymer network' morphology has also been demonstrated, which is interpenetrating networks of liquid crystal and polymer. [53-54]] The 'polymer network' morphology is formed by spinodal decomposition phase separation mechanism. The morphology is strongly dependant on the prepolymer composition, solubility between liquid crystal and prepolymer, the polymerization kinetics, and phase separation mechanism. [55-78]

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In contrary to other types of liquid crystal display devices, the electro-optical properties of PDLC films depend much more strongly on both the physical properties of polymer matrix and the phase-separated morphology rather than on the physical properties of liquid crystal. The important electro-optical properties required in the PDLC devices are opacity at OFF state, clarity at ON state, operating voltage and response times. The general relation between the electro-optical properties and the morphology of the PDLC films is summarized as below.

Opacity at OFF state

One factor that determines the opacity is the droplet size and droplet density (number of droplets per unit volume). [79-81] If the droplets are not of sufficient size or droplet density is not high enough to scatter the incident light efficiently, the opacity is reduce. The optimum droplet size to scatter visible light is 1-3 μ m. Another factor is the refractive index difference between the LC droplet (average refractive index of liquid crystal, *<n>*) and the polymer matrix (n_m). [82-86] The refractive index difference is usually enhanced by using high birefringence liquid crystal.

Clarity at ON state

The clarity at ON state is maximized by minimizing the refractive index difference between the refractive index of the polymer matrix (n_m) and the ordinary refractive index of liquid crystal (n_o). [87-88] However, some liquid crystal components do not separate and remains in polymer matrix, which changes the refractive index of liquid crystal in droplets and increases the refractive index of the polymer matrix. [82, 85]

Operating voltage

The voltage required to switch a PDLC film is dependent on the droplet size and shape, the dielectric properties, and anchoring energy. Typically,

the operating voltage is inversely proportional to the droplet size. [76-77]

Response times

Switching time are mostly determined by applied voltage, droplet size and shape, viscosity of liquid crystal and anchoring forces. Typically, the turn-on time is inversely proportional to the applied voltage, and the turn-off time is proportional to the droplet size.[76-77]

The morphology of PDLC films can be quite varied depending on the polymerization kinetics, phase separation of liquid crystals (solubility differences among liquid crystals into polymer matrix) and the polymerization conditions. То achieve the optimized electro-optical properties of the PDLC film, it is essential to understand these underlying mechanisms.

1-2 Polymerization-induced Phase Separation (PIPS)

The phase separation of liquid crystal from a polymer matrix is a crucial feature in the formation of PDLC film. Starting from a homogeneous mixture of liquid crystal and prepolymer, the prepolymer components eventually become sufficiently incompatible with the liquid crystal by increased molecular weight of polymer components (polymerization), which induces phase separation of liquid crystal fluid from polymer phase.[89–93] The details of this process determine the morphology of the PDLC film, which ultimately affects the electro-optical properties of the PDLC film.[55–62]

The morphology of PDLC films depends on the chemical nature of the liquid crystal and polymer components and on the polymerization kinetics driving the phase separation to occur. The variation in composition and temperature can lead to different morphologies.[63-67] Within each of these morphologies variation can occur in droplet size, shape, and nematic alignment.[77-78,

94-98]

The analysis of the phase separation processes is often simplified by treating the system as a simple binary mixture: that is, the liquid crystal is treated as a sing, pure species of known molecular weight. Sine many liquid crystalline materials are mixtures of several components and a range of molecular weights exist during most polymerization processes, these assumptions are quiete limiting. Nevertheless, treating the PDLC system as a binary mixture simplifies the analysis of phase separatin considerably while preserving many essential features of the process.

So far, it appears that it is not possible to predict how a given liquid crystal-prepolymer system will phase separate exactly. Still, good semiquantitative descriptions of several aspects of phase separation exist.[99-107] Moreover, once the phase separation properties of a given system are established models exist to predict how modest variations in the system will affect the phase separation process. [42, 77]

1-2-1 Phase Diagrams

In PDLC films formed by PIPS process, the initial system consists of a mixture of liquid crystal, monomers, and sometimes low molecular weight oligomers. Plotting temperature vs. liquid crystal composition, the phase diagrams typically show upper critical solution temperature (UCST) behavior (Figure 1-4). A single phase is stable at high temperatures. Miscibility decreases with decreasing temperature, and phase separation can occur in the mixture at low temperatures. The temperature at which phase separation is allowed depends on the relative concentration of the liquid crystal and monomer/polymer solution, as well as on the relative solubility of the two components of the mixture. A the extremes of concentration, the two components may be completely miscible and not separate at any temperature.

In Figure 1-4, there are two curves in the phase diagram which define the

boundary between the single and dual-phase system. The lower curve is known as the spinodal curve and marks the region where phase separation occurs spontaneously without need for activation. The upper curve is referred to as the binodal curve and defines the point at which phase separation becomes energetically possible (but not necessary). In the region between the binodal and spinodal curves the system is metastable: phase separation is thermodynamically allowed but requires a certain activation energy to proceed. Phase separation may or may not occur in this region, depending on the size of the activation barrier and whether nucleation sites are available. Whether phase separation occurs in a binodal or spinodal regime controls the kinetics of the phase separation process, which in turn can markedly affect the structure of the polymer matrix.

Once phase separation occurs the two phase do not simply separate into a pure liquid crystal into a pure monomer/polymer phase. Rather, the mixture separates into a liquid crystal-rich phase and a liquid crystal-poor phase. The concentrations of liquid crystal in each phase at a given temperature are defined by a tie line, which connects the opposite sides of the binodal or spinodal curves at a given temperature. Referring to Figure 1-4, at temperature T the liquid crystal-poor and liquid crystal-rich phases will have a liquid crystal concentrations of ϕ_1 and ϕ_2 , respectively. In a multicomponent system, this approximation can beat down, as different components of the liquid crystal or monomer/polymer solutions can segregate to different concentrations in the two phases. Also, the kinetics of polymerization can prevent each phase from achieving these equilibrium concentrations if the solid polymer limits diffusion within the system.

Besides the UCST curve, Figure 1-4 also shows the phase behavior of the liquid crystal at low monomer concentrations (exhibited in the upper right hand portion of the diagram). In a pure liquid crystal, the clearing temperature marks the temperature at which the nematic phase is converted into an isotropic phase: this temperature is found on the right hand axis of

the diagram. With increasing monomer concentration the transition temprature is depressed, leading to a curve which eventually connects to the UCST crve on the diagram. The transition between nematic and isotropic phase may be sharp. However, it is also possible that a two-phase region can be stable, with nematic and isotropic phases of slightly different composition coexisting at a given temperature. This is the case that is shown in Figure 1-4 an upper curve marks the boundary between the isotropic and two-phase regions, while the lower curve delineates the transition to the pure nematic phase.

1-2-2 Phase Separation in the Binodal and Spinodal Regimes

Phase separation is driven by the thermodynamics of the solution, but kinetic processes like nucleation and molecular diffusion often determines the nature of the process. Two distinct mechanisms are recognized in phase separation processes. If the system requires an activation energy for the initiation of a new phase then phase separation proceeds by a nucleation and growth mechanism. This process usually occurs beneath the binodal curve in the metastable portion of the phase diagram. Alternatively, under the spinodal curve phase separation occurs without an activation barrier. This lack of barrier changes the nature of the process significantly, leading to the spinodal decomposition mechanism. Which phase separation route the system chooses depends on the size of the gap separating the binodal and spinodal curve, the size of the activation barrier within the metastable region, whether nucleation sites are available, and the rapidity with which the system crosses the phase boundary lines. Such factors are often critical in PDLC systems, as the nucleation and growth and the spinodal decomposition mechanisms can lead to different types of polymer morphology in the final film.

Nucleation is the process of generating a new and more stable phase within

the initial metastable phase. The formation of nuclei requires an activation energy: once formed there is a discontinuous change in concentration in moving from the continuous phase into the nucleus. Diffusion of molecules from the surrounding fluid causes these domains to grow, which is an energetically-favorable process. The domains grow in size initially by these molecular diffusion process, but in later stages domain size increases by coalescence of neighboring domains. Growth of domains continues until two large phases with compositions ϕ_1 and ϕ_2 exist.

The spinodal decomposition process exhibits significant differences from the nucleation and growth mechanism. Within the initial single phase a second phase continuous and new phase change in a continuous fashion. becoming increasingly dissimilar over time. Small. thermally-driven fluctuations lead to a sinusoidally-varying composition within the system. The concentration profile of the system appears as the random superposition of these sinusoidal concentration gradients. Once consequence of this mechanism is that both the major and minor phases possess a high degree of connectivity and interpenetration. Over time the minor phase grows and the concentration gradient between the phases steepen until two large phases with compositions of ϕ_1 and ϕ_2 exist.

The nucleation and growth mechanism leads to isolated domains of phe phase within a continuous phase of the other phase. This structure is reminiscent of the droplet morphology and reverse (ball) morphology, in which either the liquid crystal or polymer orms nearly-discrete domains. The spinodal decomposition mechanism, on the other hand, leads to interpenetrating networks of the two phases, reminiscent of the PDLC network morphology.

1-2-3 Calculation of Phase Diagrams

The details of a phase diagram depend on the relative chemical affinities of the components, the temperature dependence of these affinities, and the

molecular weight of the components. These relationships are not unique to PDLC systems, but arise in many areas where polymer-polymer miscibility is important. For phase-separation involving polymeric components Flory-Huggins theory has proven successful in relating chemical affinity, temperature, and molecular weight, which can be used to calculate phase diagrams in mixtures of polymer and liquid crystals and model several aspects of the phase separation process in PDLC films.

The basis of the Flory-Huggins model is the determination of the free energy of mixing of a two-phase system involving a polymer. This free energy contains contributions from both enthalpic and entropic terms. The enthalpic component arises from the non-bonded interaction of the components, while the entropic term comes from the statistical mixing of the components. The entropy of mixing must take into account that the indivisual units of the polymer are connected as chain, so the statistics are performed by constraining each 'polymerization unit' to lie on a point on a lattice. This leads to an expression for the free energy of mixing ΔG_{mix}

$$\Delta G_{mix} = NRT\phi(1-\phi)\chi + NRT\left[\frac{\phi\ln\phi}{m_l} + \frac{(1-\phi)\ln(1-\phi)}{m_p}\right]$$
(1-1)

The first and second terms in equation 1-1 are the enthalpic and entropic contributions, respectively, to the free energy. ϕ is the volume fraction of the liquid crystal, and m_l and m_p as the relative molecular weights of the liquid crystal and polymer, respectively. N is the degree of polymerization (number of connected monomers in the polymer). The term χ is known as the Florry-Huggins interaction parameter and can be given by

$$\chi = \frac{1}{RT} \left[\epsilon_{pl} - \frac{1}{2} (\epsilon_{pp} - \epsilon_{ll}) \right]$$
(1-2)

where T is the temperature and R is the gas constant. The ϵ terms represent the intermolecular interaction energies for the components: ϵ_{pp} , ϵ_{ll} , and ϵ_{lp} stand for the interaction energies between polymer-polymer, liquid crystal-liquid crystal, and polymer-liquid crystal components, respectively. χ often follows the functional form

$$\chi = C + \frac{D}{T} \tag{1-3}$$

where C and D are constants. Choosing C<O and D>O provides for the UCST behavior seen in PDLC systems.

The spinodal curve of T vs. ϕ can be determined by setting the second derivative (with respective to composition) of equation 1-1 equal to zero. Using equation 1-3 to substitute for χ , the resulting equation

$$T = \left[-\frac{C}{D} + \left(\frac{1}{2D}\right) \left(\frac{1}{m_l \phi} + \frac{1}{m_p (1 - \phi)} \right) \right]^{-1}$$
(1-4)

shows analytically the relationship between phase composition and temperature for the spinodal curve. The equation can also be solved for ϕ , which leads to

$$\phi = \frac{-m_l m_p \chi + m_l - m_p \pm \sqrt{(m_l m_p \chi - m_l + m_p)^2 - 8m_l m^{2_p} \chi}}{4m_l m_p \chi}$$
(1-5)

These last two equations are equivalent, differing only in the choice of dependent and independent variables. These equations assume a monodisperse polymer size, which is unrealistic for intermediate stages of the polymerization process. It is possible to recast the model using a distribution for the polymer molecular weight.

If the system is allowed to reach equilibrium without kinetic hinderance then the composition will always follow the binodal, rather than the spinodal. The binodal curve can also be calculated from knowledge of the Flory-Huggins interaction parameter, although closed-form analytical expressions for the curve do not exist. Numerical methods must be used to solve for the binodal curve.

The ability to calculate phase diagrams allows for the development of models for the phase separation process in PDLC. The polymerization of a PIPS system usually takes place at a uniform temperature, beginning in the single-phase region of the diagram. As polymerization proceeds the area of the two-phase region broadens and moves to higher temperature. This change follows from the decreased entropy of mixing that larger molecular weight species possess, which lowers the solubility of the growing chains in the liquid crystal solvent. Phase separation occurs when this change in the position of the phase boundary line moves the system into a two-phase region, even though the temperature and overall composition of the system does not change. Such a change in the phase diagram is shown in Figure 1-6, which shows spindal lines for a hypothetical PDLC system undergoing polymerization. The curves are calculated using equation 1-4 and the values C=-0.2, D=230K, $m_l=2$, and allowing to vary. The nematic-isotropic phase boundary is left off for clarity. As the molecular weight of the polymer phase increases it is seen that the two-phase region both increases in temperature, broadens in composition, and becomes asymmetric.

1-2-4 Effect of Phase Separation Kinetics on Morphology

The size of the domains in PDLC films depends strongly on the kinetics of the phase separation process. The final size of droplets in a PDLC film is often determined by a number of factors: the rate of droplet formation, their growth through diffusion and coarsening processes, and the freezing of

the structure by the formation of a solid polymer matrix within the film. Fast polymerization processes usually result in smaller domain size, both by the rapid formation of liquid crystal domains and a swift increase in viscosity of the polymer-rich phase. Conversely, slower polymerization rates typically leads to larger droplets by giving newly phase separated liquid crystal domains time to grow and merge. The chemical makeup of the final film can also depend on the polymerization rate, as reactants can become physically separated by the polymer superstructure. [68-76, 108]

1-3 Objectives

The objective of this research in to investigate the photopolymerization and phase separation processes in the PDLC system and effect of the physical/chemical structures of liquid crystals and polymers on the photopolymerization-induced phase separation process, morphology, and properties of PDLC films. These will be implemented by three consecutive steps as followings:

Firstly, an experimental method to examine the photopolymerization and phase separation behavior by simultaneous resistance and transmittance measurements of a PDLC cell during the PDLC formation process will be introduced in chapter 2.

Secondly, the effect of liquid crystal structures on photopolymerization and phase separation processes in PDLC will be investigated in chapter 3. Thirdly, the effect of prepolymer structure on photopolymerization-induced phase separation process, morphology and properties of PDLC film will be investigated in chapter 4.

Finally, the performance of PDLC films toward switchable glass application was investigated in chapter 5.

1-4 References

[1] S. Park, J.W. Hong, Thin Solid Films, 2009, 517, 3183-3186

[2] C.M. Lampert, Proc. SPIE, 2001, 4458, 95-102

[3] C.M. Lampert, Sol. Energy. Mater. Sol. Cells, 2003, 76, 489

[4] C.M. Lampert, *Material Today*, **2004**, *28*, 28

 [5] A. Matthai, B. Sepeur-Zeits, F. Horstmann, J. Schutz, 6th International Conference on Coatings on Glass and Plastics, Dresden, Germany, June 18-22,
 2006, 39

[6] G. Macrelli, Sol. Energy. Mater. Sol. Cells, 1995, 39, 123-131

[7] J.M.S. Pena, C. Vazquez, I.Perez, I. Rodriguez, J.M. Oton, *Opt. Eng.*,
 2002, 41(7), 1608-1611

[8] D. Cupelli, F.P. Nicoletta, S. Manfredi, G.D. Filpo, G. Chidichimo, *Sol. Energy. Mater. Sol. Cells*, **2009**, *93*, 329-333

[9] L. Li, J.F. Li, S. Faris, US Patent No. 6,897,936 May 24 (2005)

[10] C.W. McLaughlin, P. Drzaic, S. Marsland, US Patent No. 4,749,261 Jun 7 (1988)

[11] L. McKenna, L.S. Miller, I.R. Peterson, *Polymer*, 2004, 45, 6977-6984
[12] H. Ramanitra, P. Chanclou, L. Dupont, B. Vinouze, *Opt. Eng.*, 2004, 43(6), 1445-1453

[13] I. Amimori, N.V. Priezjev, R.A. Pelcovits, G.P. Crawford, *J. Appl. Phys.*, **2003**, *93(6)*, 3248-3252

[14] A.Y.G. Fuh, T.H. Lin, J. Appl. Phys., 2004, 96(10), 5402-5404

[15] K.S. Jung, D.H. Jeong, K.Y. Bang, J. Kor. Soc. Prec. Eng., 2003, 20(4),
 92-102

[16] H. Ren, Y.H. Fan, S.T. Wu, Appl. Phys. Lett., 2003, 83(8), 1515-1517
[17] H. Sato, H. Fujikake, H. Kikuchi, T. Kurita, *Opt. Rev.*, 2003, 10(5), 352-356

[18] T. Schneider, F. Bicholson, A. Khan, J.W. Doane, *SID Digest*, **2005**, 1568-171

[19] C.D. Sheraw, L. Zhou, J.R. Huang, D.J. Gundlach, T.N. Jackson, M.G.

Kane, I.G. Hill, M.S. Hammond, J. Campi, B.K. Greening, J. Francl, J. West, Appl. Phys. Lett. 2002, 80(6), 1088-1090 [21] J.L. Fergason, US Patent No. 4,435,047, Mar 06 (1984) [22] J.L. Fergason, SID Digest of Technical Papers, 1985, 16, 68-70 [23] P.S. Drzaic, J. Appl. Phys., 1986, 60, 2142 [24] P.S. Drzaic., A.M. Gonzales, Mol. Cryst. Lig. Cryst., 1992, 222, 11 [25] P.V. Konynenburg, S. Marsland, J. McCoy, Solar Eergy Mater., 1989, 19, 27-41 [26] P.V. Konynenburg, R. Wipfler, J.L. Smith, Proc. SPIE, 1989, 1080, 62-69 [27] J.W. Doane, N.A. Vaz, B.G. Wu, S. Zumer, Appl. Phys. Lett. 1986, 48, 269 [28] N.A. Vaz, G.W. Smith, G.P. Montgomery, Mol. Cryst. Liq. Cryst., 1987, *146*. 17 [29] J.L. West, Mol. Cryst. Lig. Cryst., 1988, 157, 427 [30] B.G.Wu, J.L. West, J.W. Doane, J. Appl. Phys., **1987**, 62, 3925 [31] J.W. Doane, A Golemme, J.L. West, J.B. Whitehead, B.G. Wu, *Mol. Cryst.* Lig. Cryst., 1988, 165, 511 [32] N. Vaz, G.W. Smith, G.P. Montgomery, Mol. Cryst. Lig. Cryst., 1987, 146,1 [33] N.A. Vaz, G.W. Smith, US Patent No. 4,728,547 Mar 1 (1988) [34] N.A. Vaz, G.W. Smith, US Patent No. 4,728,547, Mar 01 (1988) [35] V. Rachet, P. Feneyrou, B. Loiseaux, R.L. Barny, J.P. Huignard, U. Maschke, Mol. Cryst. Lig. Cryst., 2004, 421, 165-174 [36] L.V. Natarajan, C.K. Shepherd, D.M. Brandelik, R. L. Sutherland, S. Chandra, V.P. Tondiglia, D. Tomlin, T.J. Bunning, *Chem. Mater.*, **2003**, *15*, 2477-2484 [37] A.F. Jacobine, J.G. Woods, M.A. Rakas, US Patent No. 5,516,455, May 14 (1996)[38] L.J. Miller, C.V. Ast, F.G. Yamagishi, US Patent No. 4,891,152, Jan 02 (1990)[39] J.B. Nephew, T.C. Nihei, S.A. Carter, *Phys. Rev. Lett.*, **1998**, *80(15)*,

3276-3279 [40] A.J. Lovinger, K.R. Amundson, D.D. Davis, Chem. Matter, 1994, 6, 1726 [41] D. Nwabunma, T. Kvu, *Polvmer*, **2001**, *42*, 801–806 [42] Y. Hirai, S. Niiyama, H. Kumaim, T. Gunjima, *Proc. SPIE*, **1990**, *1257*, 2-8 [43] C.H. Noh, J.E. Jung, J.Y. Kim, D.S. Sakong, K.S. Choi, Mol. Cryst. Lig. Cryst.Sci. Tec. A, 1993, 227, 229 [44] D. Coates, S. Greenfield, M. Goulding, E. Broun, P. Nolan, Proc. SPIE, **1993**, *1911*, 2-14 [45] F.G. Yamagishi, L.J. Miller, US Patent No. 5,011,624, Apr 30 (1991) [46] K.R. Amundson, M. Srinivasarai, US Patent No. 5,906,770, May 25 (1999) [47] D.B. Chung, US Patent No. 5,494,604, Feb 27 (1996) [48] N. Yamada, T. Hirai, N. Ohnishi, S. Kouzaki, F. Funada, K. Awane, *Jpn.* Display, 1992, 695-698 [49] F.G. Yamagishi, L.J. Miller, C.I. Van Ast., *in Proc. SPIE*, **1989**, *1080*, 24 [50] S.J. Chang, C.M. Lin, A.Y.G. Fuh, Jpn. J. Appl. Phys., 1996, 35, 2180-2183 [51] R. Hasegawa, M. Sakamoto, H. Sasaki, *Appl. Spectrosc.*, **1993**, *47*, 1386 [52] Y. Hirai, S. Niiyama, Y. Ooi, H. Kumai, T. Wakabayashi, T. Gunjima, *SID* Digest, 1994, 833 [53] T. Fugisawa, H. Ogawa, K. Maruyama, *Japan Display*, **1992**, 695 [54] T. Fugisawa, H. Nakata, M. Aizawa, J. Photopolym. Sci. Tech., 1998, *11(2)*, 199–204 [55] A. Golemme, S. Zumer, J.W. Doane, M.E. Neubert, *Phys. Rev.* **1988**, *A37*, 559 [56] G.P. Montgomery, N.A. Vaz, G.W. Smith, *Proc. SPIE*, **1988**, *958*, 104 [57] G.P. Montgomery, N.A. Vaz, *Liq. Cryst.*, **1988**, *3*, 543 [58] S.A. Carter, J.D. GeGrange, W. White, J. Boo, P. Wiltzius, J. Appl. *Phys.*, **1997**, *81(9)*, 5992–5999 [59] M. Wang, W. Li, Y. Zou, C. Pan, J. Phys. D: Appl. Phys., 1997, 30, 1815-1819

[60] M. Aleksander, S. Klosowicz, SPIE, 2004, 5565, 389-396 [61] H. Duran, S. Meng, N. Kim, J. Hu, T. Kyu, L.V. Natarajan, V.P. Tondiglia, T.J. Bunng, *Polymer*, **2008**, *49*, 534-545 [62] T.J. White, L.V. Natarajan, V.P. Tondiglia, T.J. Bunning, C.A. Guymon, Macromolecules, 2007, 40, 1112-1120 [63] J.D. LeGrange, S.A. Carter, M. Fuentes, J. Boo, A.E. Freeny, W. Cleveland, T.M. Miller, *J. Appl. Phys.*, **1997**, *81(9)*, 5984-5991 [64] H. Fujikake, K. Takizawa, H. Kikuchi, T. Fujii, Jpn. J. Appl. Phys., **1998**, 37, 895-899 [65] E. Nastal, E. Zuranska, M. Mucha, J. Appl. Polym. Sci., 1999, 71, 455-463 [66] W.S. Park, K.S. Choi, J. Kor. Phys. Soc., 1999, 34(3), 231-236 [67] J.W. Han, T.J. Kang, G. Park, *J. Kor. Phys. Soc.*, **2000**, *36(3)*, 156–163 [68] S.H. Kim, C.P. Heo, K.S. Park, B.K. Kim, *Polym. Inter.*, **1998**, *46*, 143 - 149[69] M. Mucha, Prog. Polym. Sci., 2003, 28, 837-873 [70] M.D. Sarkar, N.L. Gill, J.B. Whitehead, G.P. Crawford, *Macromolecules*, **2003**, *36*, 630–638 [71] B.K. Kim, S.H. Kim, J. Polym. Sci.: Part B: Polym. Phys., 1998, 36, 55-64 [72] S.H. Kim, C.P. Heo, K.S. Park, B.K. Kim, *Polymer International*, **1998**, 46, 143-149 [73] C.Y. Pan, M. Wnag, R. Bai, T. Zou, *Phys. Lett. A*, **1997**, *234*, 498-500 [74] A.F. Senyurt, G. Warren, J.B. Whitehead, C.E. Hoyle, Polymer, 2006, 47, 2741-2749 [75] W. Li, H. Cao, M. Kashima, F. Liu, Z. Cheng, Z. Yang, S. Zhu, H. Yang, J. Polym, Sci.: Part B: Polym. Phys., 2008, 46, 2090-2099 [76] W. Li, Z. Cheng, G. Pan, H. Liu, H. Gao, Z, Yang, H. Yang, Opt. Mater., **2008**, *31*, 434–439 [77] K.Amundson, A. V. Blaaderen, P. Wiltzius, *Phys. Rev. E*, **1997**, *55(2)*,

1646 - 1654[78] S.J. Klosowicz, M. Aleksander, *Opto-Electron. Rev.*, **2004**, *12(3)*, 305-312 [79] H. Nomura, S. Suzuki, Y. Atarashi, Jpn. J. Appl. Phys. 1990. 29(3), 522-528 [80] P.S. Drzaic, Proc. SPIE, 1990, 1257, 29-36 [81] N. Vaz, G.P. Montgomery, J. Appl. Phys., **1989**, 65, 5043 [82] P. Nolan, M. Tillin, D. Coates, *Lig. Cryst.*, **1993**, *14(2)*, 339-344 [83] D. Coates, S. Greenfield, I.C. Sage, G. Smith, *Proc. SPIE*, **1990**, *1257*, 37 [84] A.M. Lackner, J.D. Margerum, E. Ramos, K.C. Lim, Proc. SPIE, 1989, 1080.53 [85] S. Pane, M. Carprusso, H. Hakemi, *Lig. Cryst.*, **1997**, *23(6)*, 861–867 [86] P.S. Drzaic, A.M. Gonzales, P.V. Konynenberg, SPIE, **1994**, 2175, 148-157 [87] P.S. Drzaic, SPIE, **1993**, 1911, 153-159 [88] S.J. Klosowicz, SPIE, 1995, 2372, 258-261 [89] B. Lin, P.L. Taylor, Polymer, 1996, 37, 5099-5106 [90] J. Borrajo, C.C. Riccardi, R.J.J. Williams, H.M. Siddigi, M. Dumon, J.P. Pascault, Polymer, 1998, 39, 845-853 [91] H. Nakazawa, S. Fujinami, M. Motoyama, T. Ohta, T. Araki, H. Tanaka, T. Fugisawa, H. Nakada, M. Hayashi, M. Aizawa, Computational and Theoretical Polym. Sci., 2001, 11, 445-458 [92] M. Motoyama, H. Nakazawa, T. Ohta, T. Fugisawa, H. Nakada, M. Hayashi, A. Aizawa, Computational and Theoretical Polym. Sci., 2000, 10, 287-297 [93] T. Kyu, H.W. Chiu, *Polymer*, **2001**, *42*, 9173–9185 [94] R.O. Crawford, E.P. Boyko, B.G. Wagner, J.H. Erdmann, S. Zumer, J.W. [95] Doane, J. Appl. Phys., **1991**, 69(9), 6380-6386 [96] H. Nomura, S. Suzuki, Y. Atarashi, Jpn. J. Appl. Phys., 1991, 30(2), 327-330 [97] J. Zhou, D.M. Colard, J.O. Park, M. Srinivasarao, J. Am. Chem. Soc.

2002, *124*, 9980–9981
[98] S.S. Patnaik, R. Pachter, *Polymer*, 1999, 40, 6507-6519
[99] G.W. Smith, *Mol. Cryst. Liq. Cryst. Tec. A*, 1993, 225, 113-130
[100] M. Baullaff, *Mol. Cryst. Liq. Cryst.*, 1986, 136, 175-195
[101] J.R. Dorgan, D.S. Soane, *Mol. Cryst. Liq. Cryst.*, 1990, 188, 129-146
[102] J.C. Lin, P.L. Taylor, *Mol. Cryst. Liq. Cryst. Tec. A*, 1993, 237, 25-31
[103] Y. Hirai, S. Niiyama, H. Kumaim, T. Gunjima, *Proc. SPIE*, 1990, 1257, 2-8
[104] G.W. Smith, *Int. J. Mod. Phys. B*, 1993, *7*, 4187-4213
[105] G.W. Smith, *Phys. Rev. Lett.*, 1993, *70*, 198-201
[106] G.W. Smith, *Mol. Cryst. Liq. Cryst.*, 1994, 239, 63-85
[107] S. Meng, T. Kyu, L.V. Natarajan, V.P. Tondiglia, R.L. Sutherland, T.J. Bunning, *Macromolecules*, 2005, *38*, 4844-4854

[108] S. Park, J.W. Hong, Polym, Testing, 2008, 27, 428-433



Figure 1-1. Layer structure of PDLC film.





Field OFF : Scattering

Field ON : Transparent

Figure 1-2. Operating principle of PDLC film.





Figure 1-3. Examples of (a) polymer ball and (b) droplet morphology.



Figure 1-4. Idealized representation of a binary phase diagram between liquid crystal and an isotropic monomer or polymer.



Figure 1-5. Two-dimensional representation of the phase structure in a nucleation and growth phase separation process and in a spinodal decomposition phase separation process.



Figure 1-6. Calculation of the spinodal lines for phase separation in an idealized binary system as a function of increasing molecular weight of the polymer phase. The areas under curves represent the two-phase resion. Each curve corresponds to a different molecular weight of polymer.



Chapter 2

Monitoring the Photopolymerization Reaction and the Phase Separation Process during the PDLC Formation Procedure

2-1 Introduction

In contrary to other types of liquid crystal display devices, the electro-optical properties of PDLC films depend much more strongly on both the physical properties of polymer matrix and the phase-separated morphology than on the physical properties of the liquid crystal. Understanding the PDLC formation process first requires an understanding of the photopolymerization and phase separation processes that markedly influence morphology and electro-optical properties of the produced PDLC the films.[1-11] Many studies have investigated the photopolymerization reaction and the liquid crystal phase separation process using differential scanning calorimetry (DSC), FTIR spectroscopy, rheology, dielectric analysis, light scattering and polarized microscopy.[12-21] However, these experimental methods have systematic limitation when examining either the photopolymerization reaction or phase separation during the PDLC formation process.

In this chapter, we will introduce an experimental method to investigate the photopolymerization reaction and the liquid crystal phase separation behavior during the PDLC formation process using simultaneous resistance and turbidity measurements of a PDLC cell. The experimental method could effectively monitor the photopolymerization and phase separation processes in PDLC samples. To verify the utility of the method, resistance data are compared with conversion data obtained by photo-DSC and FTIR analysis using NOA65 and NOA65-E7 mixture.

2-2 Experimental

2-2-1 Materials

NOA65 (Norland Products Inc.) and E7 (Merck) were used as a prepolymer and a nematic liquid crystal mixtures, respectively.

The reaction of NOA65 is based on thiol-ene chemistry, which consists of a mixture of a tetrafunctinal allyl ether (4-AE) and trifunctional thiol (3-SH) monomers.[11] The synthesis of the 4-AE monomer and photopolymerization reaction are shown in Figure 2-1 and Figure 2-2, respectively. The photopolymerization reaction of NOA65 runs via a step-growth free-radical polymerization mechanism. Exposure to UV light promotes the photoinitiator (benzophenone) to an excited state that initiates polymerization through hydrogen abstraction of the thiol monomer, thus generating a thivl radical. The thivl radical adds into one of the carbon-carbon double bonds (C=C) of 4-AE producing a β -thioether carbon radical that efficiently abstracts a hydrogen atom from a thiol, thereby continuing the propagation reaction. The polymerization reaction terminates by radical coupling or by hydrogen abstraction. Termination can also occur as a result of stoichiometric imbalance, whereby no more thiol is available to react with the ene or vice versa.

E7 consists of 4-pentyl-4'-cyanobiphenyl (5CB), 4-heptyl-4'cyanobipheyl (7CB), 4-octyloxy-4'-cyanobiphenyl (M24), and 4-pentyl-4'-cyanoterphenyl (T15).[22] The chemical structure of the components are shown in Figure 2-3. The composition of E7 is 51% 5CB, 25% 7CB, 16% M24, and 8% T15. E7 has a nematic-to-isotropic transition temperature (T_{NI}) of 60.0°C

2-2-2 FTIR measurement

FTIR spectroscopy was used to examine the photopolymerization behavior. FTIR spectra were obtained using a Nicolet 7700 spectrometer at 2 cm⁻¹ resolution. The sample materials were placed between two KBr discs and the thickness was maintained using 10µm spacers. A metal halide lamp (EFOS UV System) with a fiber-optic light guide was used as a light source to induce the photopolymerization. The UV light intensity was measured with a radiometer (IL1400A, International Light Inc.) and maintained at 1.6 mW/cm² at 365 nm. The FTIR spectra were obtained every 4 seconds during continuous UV irradiation. The photopolymerization behavior was analyzed in the 2570cm⁻¹ and 929cm⁻¹ bands, which correspond to the S-H stretching vibration of thiol monomer and C=C bending vibration of 4-AE monomer, respectively. Absorbances in the bands were obtained from peak areas. The percentage conversion was calculated using

$$Conversion(\%) = \left(1 - \frac{A_o - A_t}{A_o}\right) \times 100$$
(2-1)

where, A_o and At are the absorbance before irradiation and at time t, respectively.

2-2-3 Photo-DSC measurement

Photo-differential scanning calorimetry (photo-DSC) was used to examine the photopolymerization behavior. Photo-DSC thermograms were obtained using a photocalorimeter (TA5000, Thermal Analysis) under a nitrogen atmosphere. Photopolymerization was initiated using a black light lamp (B-14N, Spectronics) whose UV intensity was maintained 1.6 mW/cm² at 365 nm. All measurements were performed at room temperature. The area of the exothermic peak is proportional to the heat released as the thiol is added across the

double bonds to form single bonds during photopolymerization. The percentage conversion can be calculated using

$$Conversion(\%) = \left(\frac{\Delta H_{\exp}}{\Delta H_o}\right) \times 100$$
 (2-2)

where, ΔH_{exp} (in J/g) is the experimental heat of reaction measured by integrating the area under the exothermic peak and ΔH_o (in J/g) is the heat of the complete reaction in which all the thiol adds across the ene monomers per gram of material.

2-2-4 DSC measurement

The thermal behaviors of the samples cured in photo-DSC measurements were examined using DSC thermograms obtained with a DSC device (N-650, Scinco).

2-2-5 Resistance and transmittance measurement of PDLC cells

An experimental setup to measure the resistance and transmittance of a sample cell for irradiation with UV light is illustrated in Figure 2-4. The sample cell was prepared by sandwiching the sample material between two ITO-glass plates (50 x 30mm²) and the cell gap was maintained at 20µm using polymer ball spacers. A resistance meter (Megaresta H0709, Shishido Electrostatic) was used to monitor the resistance of the sample cell. A halogen lamp (Avalight-HAL, Avantes) and CCD detector (Avaspec 2048, Avantes) coupled to a fiber-optic cable were used to monitor the transmittance of the sample cell. A black light lamp (B-14N, Spectronics) was used to initiate the photopolymerization. All measurements were performed at room temperature.

The photopolymerization process can be monitored by measuring the

electrical conductivity of the UV curable formulation.[23-25] The conductivity of the system is determined by dipolar and ionic components. The dipolar component arises from rotational motion of molar dipoles and the ionic component arises from the diffusion of ionic impurities that may form during synthesis. The electrical effects due to these conducting species is reduced as the photopolymerization progresses. The relation between conductivity and resin viscosity can be expressed as

$$Viscosity \propto resistance \propto \frac{1}{conductivity}$$
 (2-3)

The photopolymerization-induced phase separation and the droplet formation processes of a PDLC sample cell can be monitored by measuring the transmittance. The transmittance of the sample cell will gradually decrease as the liquid crystal droplets are formed and grow sufficiently to scatter the incident visible light.

2-3 Results and Discussions

The photopolymerization behavior of NOA65 and the NOA65-E7 mixture were investigated using photo-DSC measurement. The photo-DSC thermograms of neat NOA65 and the NOA65-E7 mixture (30/70w%) are shown in Figure 2-5. The photo-DSC thermogram of the PDLC sample was normalized by the mass of NOA65 to allow compare the photopolymerization behavior of NOA65 in each sample directly. The photo-DSC thermograms indicate that the photopolymerization behavior differs markedly between the NOA65-E7 mixture and neat NOA65. The times of the exothermic peak maximum are 8.7 seconds and 26.1 seconds for neat NOA65 and the NOA65-E7 mixture, respectively, which indicates that photopolymerization is faster for neat NOA65. The enthalpy, which is related

to the percentage conversion of NOA65, is 153.6 J/g and 170.7 J/g for neat NOA65 and the NOA65-E7 mixture, respectively, indicating that the conversion is higher for the NOA65-E7 mixture. The slower photopolymerization and higher conversion rate for the NOA65-E7 mixture can be explained as follows. The photopolymerization of NOA65 propagates by the addition of thiyl radicals to allyl ether monomers, whereas the addition reaction in the NOA65-E7 mixture is hindered by the liquid crystal molecules (a dilution effect). At the same time, the liquid crystal molecules dissolved in the cured NOA65 matrix act as a plasticizer and thereby, delay the gelation. The delayed gelation increases the degree of conversion for the NOA65-E7 mixture.

FTIR spectroscopy was also used to examine the photopolymerization reaction of NOA65. The FTIR spectra of uncured and cured NOA65 are shown in Figure 2-6, which shows that the absorption peaks for both the S-H stretching of thiol monomer (at 2570cm⁻¹) and C=C bending of allyl ether monomer (at 929cm⁻¹) were decrease by the thiol-ene reaction of NOA65. The FTIR spectra of uncured and cured NOA65-E7 mixture are shown in Figure 2-7. The characteristic band of liquid crystal is the C≡N stretching of cyanobiphenyl group (at 2227cm⁻¹). The conversion of the S-H and C=C groups for neat NOA65 are plotted as functions of irradiation time in Figure 2-8. The conversion profiles show that about 60% thiol and allyl ether groups polymerize rapidly within 50 seconds, after which the degree of conversion slowly increases with time. The conversion rate of the S-H group is same as that of the C=C group, which reflects the stoichiometric reaction of the thiol-ene system. The final degree of conversions are 78% and 73% for the S-H and the C=C groups, respectively, which is attributable to the molar concentration of the C=C group ([C=C]) being slightly higher than that of S-H group ([S-H]) in NOA65. The conversion profiles of the NOA65-E7 mixture are plotted in Figure 2-9, which shows that its overall photopolymerization is similar to that of neat NOA65. The degree of conversion initially

increases rapidly, after which it exhibits a gradually increase with time, and the conversion rates of the S-H and C=C groups are similar. To compare the photopolymerization behavior between NOA65 and the NOA65-E7 mixture, the conversion profiles of S-H group are plotted in Figure 2-10. Neat NOA65 shows a faster conversion rate and lower final degree of conversion than the NOA65-E7 mixture, which coincide with photo-DSC data.

Calculating a conversion profile from a photo-DSC thermogram using equation (2-2) requires knowledge of the enthalpy value for complete conversion (ΔH_o), whereas FTIR spectroscopy does not require this information. From the final conversion degree of 78% for neat NOA65 obtained by FTIR analysis and the enthalpy value of 153.6 J/g obtained from the photo-DSC thermogram, $\Delta H_o(J/g)$ of NOA65 can be estimated at 194.4 J/g, from which the conversion profiles of NOA65 and the NOA65-E7 mixture plotted in Figure 2-11 are obtained. The overall conversion profiles of NOA65 and the NOA65-E7 mixture by photo-DSC thermograms well match those obtained from FTIR analysis.

The resistance of neat NOA65 measured by the experimental setup (shown in Figure 2-4) is plotted as a function of irradiation time in Figure 2-12 and compared with the conversion profiles from FTIR and photo-DSC measurements. The similarity of these data shows that the resistance value is directly associated with the degree of conversion according to equation 2-3, which demonstrates that measuring the resistance represents a good experimental method for monitoring the photopolymerization reaction of UV-curable formulations. The relation between resistance and the degree of conversion for neat NOA65 can be expressed as

$$Conversion \% = 1.67 \left[\log \left(Resistance \right) - 2 \right]$$
(2-4)

Figure 2-13 compares the change in the resistance of the NOA65-E7 mixture with the conversion profiles obtained from FTIR and photo-DSC measurements.

While the resistance increases as the photopolymerization reaction progresses, its absolute value is much lower than the conversion data from FTIR and photo-DSC data. Furthermore, the resistance value of the NOA65-E7 mixture is much lower than that of neat NOA65. in contrast to the conversion data obtained from FTIR and photo-DSC measurements. This difference can be attributed to the physical meaning of resistance and the differences in physical structures between neat NOA65 and the NOA65-E7 system. The enthalpy measured by a photo-DSC thermograms and the absorbance measured by a FTIR spectrum arise from the heat released by the reaction and the concentration of a specific functional group, respectively. While these two values arise directly from the conversion of UV curable components, the resistance is related to the bulk viscosity of the system, which in turn is associated with the physical structure of the system as well as the conversion of UV-curable components. It has been reported that much of the liquid crystal remains in polymer matrix in PDLC films made by the polymerization-induced phase separation method. The liquid crystal molecules dissolved in the polymer matrix act as a plasticizer that reduces the viscosity of the polymer matrix.[26-27] The plasticization of the polymer matrix by the dissolved liquid crystal molecules results in a lower resistance value than that of neat NOA65 despite the higher degree of conversion.

To verify the above-mentioned plasticization effect, DSC thermograms of the cured NOA65, the NOA65-E7 mixture and E7 are shown in Figure 2-14. Firstly, the plasticization effect can be verified by the difference in the glass transition temperature of the polymer matrix (ΔT_{g_matrix}) between neat NOA65 and the NOA65-E7 mixture. While the glass transition of the cured NOA65 appears at -16°C, the glass transition of the NOA65-E7 mixture appears at -33.0°C. The depression of this temperature for the NOA65-E7 mixture represents the evidence of the plasticization effect. Secondly, the amount of liquid crystal molecules dissolved in the polymer matrix can be estimated by measuring the nematic-isotropic enthalpy of the pure liquid

crystal and the PDLC film. The amount of phase separation in a droplet can be calculated using

$$\neq matic fraction (\%) = \left(\frac{\Delta H_{\exists} (PDLC)}{\Delta H_{\exists} (LC) \bullet X}\right) \times 100$$
 (2-5)

where, $\Delta H_{WI}(LC)$ and $\Delta H_{WI}(PDLC)$ are the nematic-isotropic enthalpies of pure liquid crystal and PDLC film, respectively, and X is the mass fraction of liquid crystal in the prepolymer-liquid crystal mixture. According to the DSC thermograms of E7 and the PDLC film with the NOA65-E7 mixture, $\Delta H_{NL}(LC)$ and $\Delta H_{MI}(PDLC)$ are 3.12 J/g and 1.49 J/g, respectively and X is 0.7. Using these values into equation (2-5) reveals that the calculated nematic fraction is 68.2%, which means that only 68.2% of the liquid crystal is separated and has the nematic phase in droplets with 31.8% of the liquid crystal remains in the matrix as the isotropic phase. This approach involves an assumption that the liquid crystal composition of PDLC film is identical to that of pure liquid crystal. However, most liquid crystal materials used are multicomponent eutectic mixtures. E7 contains four liquid crystal components, each of which has a solubility different from that of polymer matrix, and thus the liquid crystal composition in droplets might differ from that of pure liquid crystal. Therefore, there might be some deviation in the *nematic fraction* calculated using equation (2-5). Despite this expected deviation, this represents a good experimental method for estimating the proportions of the liquid crystal in the nematic phase in droplets and the isotropic phase in the matrix.

The experimental method for monitoring the photopolymerization process using resistance measurement can be summarized as follows:

(1) The resistance value of the pure UV-curable formulation is directly related to the degree of monomer conversion in the UV-curable formulation.
(2) The resistance value of the NOA65-E7 mixture is related to the degree of

monomer conversion and liquid crystal phase separation.

Figure 2-15 shows the resistance and transmittance changes of the NOA65-E7 mixture on the UV irradiation time. The resistance increases gradually over 60 seconds and then levels off after 60 seconds. The transmittance decreases rapidly from 15 to 25 seconds, decreases slowly to 60 seconds, and then levels off. As the molecular weight of the polymer increases, the solubility of liquid crystal gradually decreases and the liquid crystal molecules are separated at a specific point. According to the transmittance data, the phase separation of liquid crystal molecule begins before 15 seconds, and droplets are formed at about 15 seconds. As the liquid crystal phase separation process continues, the size and number (i.e., density) of droplets rapidly increase during 15 ~ 25 seconds. Then, the rate of droplet growth markedly decreases after 25 seconds, but it remains nonzero at 60 seconds.

The resistance. conversion S-H of group by FTIR analysis. and transmittance changes on the UV irradiation time are plotted in Figure 2-16. When comparing the resistance and conversion data, the resistance increases similar to the conversion data at the initial stage (stages I and II), but not at the stage after significant liquid crystal phase separation (stages III and IV). The photopolymerization process continues by 120 seconds from the conversion data, whereas the resistance decrease levels off at 60 seconds. Moreover, the level-off time of resistance is very similar to the time at the termination of liquid crystal phase separation process. These results can also be explained by the resistance decrease arising from both a viscosity increase due to monomer conversion and a decreased strong dipole component (liquid crystal molecules) dissolved in matrix due to phase separation (degree of phase separation). The resistance decrease for the NOA65-E7 mixture can be summarized as follows:

(1) During stage I, where most of liquid crystal remains in polymer phase,

the resistance decrease arises mainly from the viscosity increase due to the monomer conversion because the amount of dipole component within the matrix is almost constant.

(2) During stages II and III, where the phase separation of liquid crystal starts and continues, the resistance decrease arises from both the viscosity increase due to the continued monomer conversion and decrease in the amount of dipole component within the matrix due to liquid crystal phase separation.

(3) During stage IV, where the phase separation of liquid crystal is terminated, the resistance decrease arises mainly from the viscosity increase due to the continued monomer conversion because the amount of dipole component within the matrix does not decrease any further. However, the resistance change is very small because the dipole component effect within the matrix is significantly diluted.

2-4 Summary

We have developed an experimental method for investigating the photopolymerization and phase separation processes simultaneously during the PDLC formation using simultaneous resistance and turbidity measurements of a PDLC cell. The photopolymerization behaviors of NOA65 and the NOA65-E7 mixture were investigated using resistance data and compared with conversion data obtained from FTIR spectra and photo-DSC thermograms. While the resistance of the NOA65-E7 mixture in the PDLC sample was affected by the degree of monomer conversion and liquid crystal phase separation. The phase separation behavior of liquid crystal molecules was investigated using transmittance data of PDLC samples.

The liquid crystal molecules in NOA65 hindered the photopolymerization reaction of NOA65. The delayed photopolymerization and the presence of liquid crystal molecules dissolved in the polymer matrix delayed the gelation of the photopolymerization reaction, which resulted in the monomer conversion rate being higher for the NOA65-E7 mixture than for the NOA65.

The amount of phase separated liquid crystal mixture was measured by DSC measurement. For the NOA65-E7 (30/70w%) mixture, about 68% of liquid crystal molecules were separated from the matrix to form nematic droplets, with the other 32% of liquid crystal molecules remaining in matrix and reducing its glass transition temperature of the matrix.

2-5 References

[1] N. Vaz, G.W. Smith, G.P. Montgomery, Mol. Cryst. Lig. Cryst., 1987, 146, 1 [2] J.B. Nephew, T.C. Nihei, S.A. Carter, *Phys. Rev. Lett.*, **1998**, *80(15)*, 3276-3279 [3] A.J. Lovinger, K.R. Amundson, D.D. Davis, Chem. Matter, 1994, 6, 1726 [4] D. Nwabunma, T. Kyu, *Polymer*, **2001**, *42*, 801–806 [5] V. Rachet, P. Feneyrou, B. Loiseaux, R.L. Barny, J.P. Huignard, U. Maschke, Mol. Cryst. Liq. Cryst., 2004, 421, 165-174 [6] L.V. Natarajan, C.K. Shepherd, D.M. Brandelik, R. L. Sutherland, S. Chandra, V.P. Tondiglia, D. Tomlin, T.J. Bunning, *Chem. Mater.*, **2003**, *15*, 2477-2484 [7] Y. Hirai, S. Niivama, H. Kumaim, T. Gunjima, *Proc. SPIE*, **1990**, *1257*, 2 [8] C.H. Noh, J.E. Jung, J.Y. Kim, D.S. Sakong, K.S. Choi, Mol. Cryst. Liq. Crvst.Sci. Tec. A. 1993. 227. 229 [9] D. Coates, S. Greenfield, M. Goulding, E. Broun, P. Nolan, Proc. SPIE, **1993**, *1911*, 2-14 [10] A.F. Jacobine, Thiol-Ene Polymerization. In Radiation Curing in Polymer Science and Technology, Fouassier, J.P.; J.F. Rabek, Eds.; Elsevier Applied Science: New York, 1993, 3, 219 [11] C.E. Hoyle, T.Y. Lee, T. Roper, J. Polym. Sci. Part A: Polym. Chem. **2004**, *42*, 5301-5338 [12] G.W. Smith, G.M. Ventouris, J.L. West, Mol. Cryst. Lig. Cryst., 1992, 213, 11-30 [13] G.W. Smith, Mol. Cryst. Lig. Cryst., **1990**, 180B, 201-222 [14] S.R. Challa, S.Q. Wang, J.L. Koenig, Appl. Spectrosc., 1997, 51(3), 297-303 [15] S.R. Challa, S.Q. Wang, J.L. Koenig, Appl. Spectrosc., 1997, 51(1), 10-16 [16] R. Bhargava, S.Q. Wang, J.L. Koenig, *Macromolecules*, **1999**, 32.

8982-8988

[17] R. Bhargava, S.Q. Wang, J.L. Koenig, *Macromolecules*, **1999**, *32*, 989-8995
[18] R. Bhargava, S.Q. Wang, J.L. Koenig, *Macromolecules*, **1999**, *32*, 2748-2760

[19] N.J. Crawford, M.D. Dadmun, T.J. Bunning, L.V. Natarajan, *Polymer*, 2006, 47, 6311-6321

[20] J.G. Kloosterboer, C. Serbutoviez, F.J. Touwslager. *Polymer* **1996**, *37(26)*, 5937-5942

[21] S. Park, J.W. Hong, Polym, Testing, 2008, 27, 428-433

[22] P. Nolan, D. Coates, US Patent No. 5,476,611, Dec 19 (1995)

[23] J.D. Cho, S.T. Han, J.W. Hong, Polym. Testing, 2007, 26, 71-76

[24] R.A. Pethrick, D. Hayward, *Prog. Polym. Sci.*, **2002**, *27*, 1983-2017

[25] D. Zahouily, C. Decker, E. Kaisersberger, M. Gruener, *RadTech Technical Proceedings*, 2004

[26] P. Nolan, M. Tillin, D. Coates, *Liq. Cryst.*, **1993**, *14(2)*, 339-344

[27] S. Pane, M. Carprusso, H. Hakemi, *Liq. Cryst.*, **1997**, *23(6)*, 861-867







Trimethylolpropane diallyl ether (2-AE) Isophorone diisocyanate (IPDI)





Dibutyltin dialaurate (catalyst)



4-AE

Figure 2-1. Synthesis of tetrafunctional allyl ether monomer (4-AE) in NOA65.



Figure 2-2. Photopolymerization process of NOA65.





Figure 2-3. Chemical structure of liquid crystal compounds in E7 and their phase transition temperatures. (K : crystal, N : nematic, S_A : smectic A, I : isotropic)



Figure 2-4. Schematic illustration of an experimental setup for simultaneous resistance and transmittance measurements of a PDLC cell during UV exposure.



Figure 2-5. Photo-DSC thermograms for neat NOA65 and the NOA65-E7 mixture.



Figure 2-6. FTIR spectra of cured and uncured NOA65.



Figure 2-7. FTIR spectra of cured and uncured NOA65-E7 mixture.



Figure 2-8. Conversion profiles of thiol and allyl ether groups for neat NOA65.



Figure 2-9. Conversion profiles of thiol and allyl ether groups for the NOA65-E7 mixture obtained by FTIR analysis.



Figure 2-10. Conversion profiles of thiol monomer for neat NOA65 and the NOA65-E7 mixture obtained by FTIR analysis.



Figure 2-11. Comparison of conversion profiles between FTIR spectra and photo-DSC thermograms for neat NOA65 and the NOA65-E7 mixture.



Figure 2-12. Resistance and conversion profiles obtained from FTIR spectra and photo-DSC analysis for neat NOA65.



Figure 2-13. Resistance and conversion profiles obtained from FTIR and photo-DSC analysis for the NOA65-E7 mixture.



Figure 2-14. DSC thermograms for cured NOA65, the cured NOA65-E7 mixture and E7.



Figure 2-15. Resistance and transmittance profiles for the NOA65-E7 mixture as a functions of irradiation time.


Figure 2-16. Resistance, conversion and transmittance of the NOA65-E7 mixture as functions of irradiation time.



Chapter 3

Effect of Liquid Crystal Structures on Photopolymerization and Phase Separation Behaviors in PDLC

3-1 Introduction

The polymerization-induced phase separation process in PDLC starts from the homogeneous mixture of liquid crystal and prepolymer, which makes it difficult to achieve complete phase separation between the polymer and LC in the final stage. The incomplete phase separation causes problems in the performances of PDLC film as followings.

(1) Liquid crystals remained in a polymer matrix alter the optical, dielectric properties, mechanical and thermal properties of the matrix. The dissolved liquid crystal typically increases the refractive index of the matrix. This leaves less liquid crystal behind to scatter light and makes it difficult to meet the refractive index matching condition between liquid crystal and polymer matrix. Furthermore, the dissolved liquid crystal acts as a plasticizer and degrades the mechanical and thermal properties of PDLC film.[1-2]

(2) In an industrial point, the waste of liquid crystal in polymer matrix results in high cost of PDLC products because liquid crystal materials are very expensive. The extent of liquid crystal phase separation is an critical issue to optimize the PDLC performances as well as to reduce the amount of LC available to form droplets.

Most practical liquid crystal materials are eutectic mixtures of many compounds to broaden the temperature range of nematic phase and tune the various electrical and optical properties. Invariably, the different components in a mixture will possess somewhat different solubility characteristics in the polymer matrix. The solubility difference will change

the composition of the liquid crystal remaining behind in the droplets and thus alter the physical properties of liquid crystal such as nematic temperature range, refractive indices and dielectric constant. This makes it very complicated to design and formulate liquid crystal mixtures having exact refractive index matching condition to prepolymers. It is reported that a refractive index difference of only 0.01 between the matrix and ordinary component of liquid crystal induces a significant haziness to a PDLC film in the field ON state.[3-4] Therefore, it is important aspect to elucidate the structural effect of liquid crystal on polymerization-induced phase separation behavior to optimize the performances of PDLC films.

The objectives of this chapter are as followings:

The primary objective is to investigate the structural effect of liquid crystal compounds on the rate and extent of photopolymerization and phase separation. This may provide valuable information to select and design the liquid crystal materials for improved PDLC performances.

The secondary objective is to show the versatility of an experimental method of simultaneous resistance and turbidity measurements to investigate the photopolymerization and phase separation processes PDLC durina the formation. Ιt is а simple method that provides the rate of photopolymerization, the rate of liquid crystal phase separation, the extent of liquid crystal separated in nematic droplets, and the conversion at the onset of turbidity. Moreover, it is an useful experimental method to examine the structural effect of either liquid crystals or prepolymers in PDLC systems on the polymerization-induced phase separation process.

3-2 Experimental

3-2-1 Materials

A formulated UV-curable adhesive, NOA65 (Norland Products Inc.), was used as a prepolymer. To investigate the structural effect of liquid crystal compounds, the four liquid crystal compounds were selected which have different ring structures and alkyl groups of different lengths: 4-n-pentyl-4'-cyanobiphenyl (5CB), 4-n-heptyl-4'-cyanobiphenyl (7CB), 4-trans-pentyl cyclohexyl cyanobenzene (5PCH) and 4-trans-heptyl cyclohexyl cyanobenzene (7PCH). The chemical structures of liquid crystal compounds were shown in Figure 3-1. The PDLC formulations comprised mixtures of NOA65 and each LC compound at a 50:50 weight percent.

3-2-2 Measurements

Photopolymerization and phase separation behavior during the PDLC formation process were investigated by simultaneous resistance and transmittance measurements for PDLC cells. The experimental setup and conditions are described in the experimental section of chapter 2.

Photo-DSC was used to investigate the photopolymerization process of prepolymer. The detailed was described in the experimental section of chapter 2.

The thermal behavior of the PDLC samples cured in photo-DSC measurements was examined by DSC thermograms. DSC thermograms were obtained using a DSC (N-650, Scinco).

UV spectra of the liquid crystal compounds and the photoinitiator (benzophenone) were obtained using a spectrometer (Cary5000scan, Varian) using n-hexane as a solvent.

Scanning electron Microscopy (SEM) was used to examine the PDLC morphology. The PDLC samples were freeze-fractured, soaked in n-hexane for

24h to remove the liquid crystals from the exposed surface, and then placed in a vacuum chamber for 24h to remove the solvent.

3-3 Results and Discussions

The transition enthalpy of liquid crystals between nematic state and isotropic state is related to the degree of internal order in nematic state. High value of the nematic-isotropic enthalpy indicates that strong interaction forces of the molecules in the nematic state are present. As an empirical fact, these materials also exhibit a poor solubility in liquid crvstalline mixtures or liquid crystal-prepolymer solutions. The nematic-isotropic enthalpy values of liquid crystal compounds used in this study were measured by DSC and the thermograms were shown in Figure 3-2. The nematic-isotropic enthalpy is in the order 5CB < 7CB << 5PCH < 7PCH. From the approximation above, the solubility of liquid crystal compounds into prepolymer is expected to be in the order 5CB > 7CB >> 5PCH > 7PCH.

Figure 3-3 shows the photo-DSC thermograms of the mixtures of NOA65 and each LC compound investigated in this study, which shows photopolymerization behavior differs significantly between CBs and PCHs samples. The PCHs show faster photopolymerization and earlier termination than CBs. For LC compounds having the same ring structure, a longer alkyl group causes slightly earlier and faster photopolymerization. Parameters characterizing the photo-DSC thermograms are listed in Table 3-1. The time at peak maximum, which is related to the rate of photopolymerization, is much earlier for PCHs than for CBs. The enthalpy, which is related to the conversion of NOA65, is higher for PCHs than for CBs. The slower photopolymerization and lower conversion for CBs compared with PCHs can be thought by the UV shielding and dilution effect. To investigate the UV shield effect, the irradiation spectrum of UV lamp used in this study and the absorption spectra of 5PCH, 5CB and photoinitiator (BP) were measured and shown in

Figure 3-4. UV lamp emits UV light over the range 300~400nm with a peak at 365nm. While 5CB absorbs the UV light from the lamp over the range 300~340nm, 5PCH exhibits no absorption. The UV spectra of 7PCH and 7CB are almost same as 5PCH and 5CB, respectively. Given that the CBs absorbs or shields the UV light over the range 300~340nm from the lamp, CBs reduce the photopolymerization and conversion of NOA65. However the shield effect does not seem to be the major factor when considering the amount of shielding light by CBs is only 10% to the total UV energy.

The photopolymerization of NOA65 propagates by the addition of thiyl radicals to ene monomers.[5-6] The addition reaction in a homogeneous mixture of LC and NOA65 is restricted by LC molecules (dilution effect), and hence the photopolymerization rate might be higher if LC molecules separate into droplets earlier. If PCHs separate earlier than CBs, PCHs would result in the earlier photopolymerization of NOA65 compared with CBs. This will be verified with phase separation behavior of PCHs and CBs in Figure 3-5(b).

Figure 3-5(a) shows the resistance of PDLC samples as a function of irradiation time. As the polymerization reaction of NOA65 progresses, the resistance increases in accordance with the viscosity increases. Similar to the photo-DSC thermograms, the resistance increases much faster for PCHs than for CBs. Moreover, the resistance increases faster and reaches a higher level when the alkyl group is longer. The resistance results coincide well with the photo-DSC results. However, while the enthalpy is in the order 7PCH > 5PCH > 7CB \approx 5CB, the final resistance is in the order 7PCH > 5PCH > 7CB \approx 5CB, the final resistance by considering the meaning of these two parameters. The enthalpy measured by a photo-DSC thermogram arises from the heat released by the reaction of NOA65, and is directly associated with the conversion of NOA65 regardless of the phase separation of liquid crystal molecules. However, the resistance arises from the bulk viscosity of PDLC, which is associated with the plasticization effect of liquid crystal molecules (degree of liquid crystal phase separation) as well as the

conversion of NOA65.[7-9] The liquid crystal molecules dissolved in the polymer matrix act as a plasticizer and reduce the viscosity of PDLC. According to this approach, the differences can be explained as follows:

(1) Despite the percentage conversion of NOA65 reaching the same level for the NOA65-5CB and NOA65-7CB systems, the presence of more 5CB molecules remaining in the matrix results in greater plasticization compared to 7CB. This is evident from the transmittance data in Figure 3-5(b).

(2) While the conversion of NOA65 is approximately 10% higher for the NOA65-7PCH system than for the NOA65-5PCH system, the difference in final resistance is very small. In contrast to CB, 5PCH and 7PCH can be significantly separated to form droplets, which can be crudely estimated from the transmittance data. Therefore, the 10% difference in the final conversion does not significantly affect the final resistance.

Figure 3-5 (b) shows the transmittance as a function of irradiation time. The transmittance of 5CB did not change, which indicates that 5CB molecules cannot separate sufficiently from the matix to form droplets to scatter the light, despite significant conversion of NOA65. The transmittance of 7CB decreases from 60 seconds and its final transmittance is still high, indicating that some of the 7CB molecules are separated from the matrix to form droplets. However, the amount and/or size of droplets formed are too small to markedly scatter the light. In contrast, the transmittance of PCHs changes relatively earlier and reaches a much higher level than for CBs. This behavior clearly show that the PCH molecules are easily separated during the photopolymerization process. Finally, the transmittance of 7PCH decreases earlier and reaches a higher level than that of 5PCH.

The resistance and enthalpy values at the initiation of turbidity are listed in Table 3-2. Turbidity is initiated at 15 and 18 seconds for 7PCH and 5PCH, respectively, at which times the enthalpy values are 67,0 and 56.0J/g. It is interesting that although 7PCH requires a higher conversion of NOA65 to form droplets than 5PCH, 7PCH reaches the required conversion faster than does

5PCH. On the other hand, 7CB requires a much higher conversion to form droplets compared with PCHs.

According to the photo-DSC and resistance data, the photopolymerization reactions terminate at about 60 seconds for PCHs and 120 seconds for CBs. The transmittance values do not change after these times. The results also indicate the following:

(1) The photopolymerization of NOA65 is greatly restricted by CB molecules, and the gelation is delayed due to both restricted photopolymerization and the plasticization of CB molecules dissolved in the matrix.

(2) At the gel point, phase separation of liquid crystal moleucles and droplet growth is terminated because the mobility of liquid crystal molecules is largely reduced.

In the photo-DSC thermograms, it can be seen that the slope of exothermic peak at the initial stage of photopolymerization reaction is higher for PCHs than for neat NOA65. In contrary, the slope is lower for CBs than for neat NOA65. This indicates that PCHs accelerate CBs and delav the photopolymerization reaction of NOA65. The acceleration and delay of photopolymerization can be considered with plasticization and dilution molecules effects by liquid crystal dissolved into matrix. The plasticization effect might accelerate the photopolymerization reaction by lowering the viscosity of polymer matrix and the dilution effect might delay the photopolymerization reaction by hindering the reactive species from encountering each other. With these approaches, the plasticization effect is much larger than dilution effect for PCH samples because PCH molecules easily separate in the initial stage of photopolymerization reaction and relatively smaller amount of PCH molecules are remained. In contrary, the dilution effect is much larger than plasticization effect for CB samples because CB molecules separate in later stage of photopolymerization reaction and much of CB molecules still remained in matrix.

The transmittance data provide evidence of the dilution effect discussed

with reference to the photo-DSC results. The PCH molecules separate into droplets earlier and more readily than CB, which results in the earlier photopolymerization of NOA65. This mechanism would also explain the second exothermic peaks in the photo-DSC thermograms of 7PCH, 5PCH and 7CB. The time of the second exothermic peak coincides well with the initiation of turbidity. Therefore, the second exothermic peak appears to originate from the accelerated photopolymerization due to the phase separation of liquid crystal molecules. However, the transmittance data indicate that 5CB cannot be separated sufficiently from the matrix to form droplets, resulting in no second exothermic peak in its photo-DSC thermogram.

Figure 3-6 shows SEM micrographs of the PDLC samples. As expected from the resistance and transmittance data, no droplets are evident for 5CB, while small droplets are present in 7CB. The droplets are more distinct and larger for PCHs than for CBs. The droplets are much larger for 7PCH than for 5PCH, which results from the earlier and higher level of phase separation for the former compound.

Similarly, the extent of phase-separated liquid crystal was estimated by DSC measurements of cured PDLC films. The DSC thermograms of cured PDLC samples were shown in Figure 3-7. The nematic-isotropic enthalpy values for 5CB and 5PCH are 0.19J/g and 1.09J/g, respectively. Considering the ratio of liquid crystal in the PDLC samples and the enthalpy values of pure liquid crystal compounds in Figure 3-2, the calculated nematic fraction in the PDLC samples are 19.5% and 70.6% for 5CB and 5PCH, respectively.

According to the experimental data, PCHs appear to be more advantageous in polymerization-induced phase separation process of PDLC than CBs. However, E7 is the most widely used liquid crystal mixture in PDLC, which consists of 51% 5CB, 25% 7CB, 16% M24 and 8% T15. We may expect a PDLC film with higher degree of liquid crystal phase separation than NOA65-E7 system if the CB compounds in E7 are substituted with PCH compounds. To verify the expectation, we prepared a liquid crystal mixture (P7), consisting of 51%

5PCH, 25% 7PCH, 16% M24 and 8% T15, and compared the polymerization-induced phase separation behavior of NOA65-P7 mixture with NOA65-E7 mixture. Figure 3-8 shows the resistance and transmittance for NOA65-E7 (30/70w%) and NOA65-P7 (30/70w%). The resistance decreases faster and reaches a higher level for NOA65-P7 than for NOA65-E7. And the transmittance decreases faster and reaches a lower level for NOA65-P7 than NOA65-P7 than Source for NOA65-P7 than for NOA65-P7 than for NOA65-P7 than I liquid crystal phase separation are faster for NOA65-P7 than for NOA65-E7. Considering the NOA65-P7 results in lower transmittance (higher scattering) than NOA65-E7, even though PCHs have lower birefringence than CBs, the degree of phase separation is higher for NOA65-P7 than NOA65-P7 than NOA65-P7.

3-4 Summary

The photopolymerization and phase separation behavior during the process of PDLC formation were investigated by simultaneous resistance and transmittance measurements of PDLC cells. The photopolymerization behavior as determined from resistance measurements was compared with data from photo-DSC measurements. While the photo-DSC data only reflect the reaction behavior of polymer components, the resistance provides information on rate/degree of polymerization and phase separation of liquid crystals.

The effect of the liquid crystal structure on the photopolymerization and phase separation behavior was investigated using liquid crystal compounds having different ring structures and alkyl length. The phase separation behavior was largely different with the ring structure of liquid crystal. PCHs showed phase separation much more easily than CBs and longer alkyl length showed slightly easier phase separation. These differences in phase separation characteristics resulted in very different photopolymerization behaviors, with the photopolymerization rate and conversion both being much

higher for PCHs than for CBs.

The difference in photopolymerization-induced phase separation behavior between PCH compounds and CB compounds was also observed in the liquid crystal mixtures. A liquid crystal mixture based on PCH compounds exhibited faster and higher degree of phase separation than that based on CB compounds.

3-5 References

[1] P. Nolan, M. Tillin, D. Coates, *Liq. Cryst.*, **1993**, *14(2)*, 339-344
[2] S. Pane, M. Carprusso, H. Hakemi, *Liq. Cryst.*, **1997**, *23(6)*, 861-867
[3] P.S. Drzaic, *SPIE*, **1993**, *1911*, 153-159
[4] S.J. Klosowicz, *SPIE*, **1995**, *2372*, 258-261

- [5] G.W. Smith, Mol. Cryst. Liq. Cryst., 1991, 196, 89-102
- [6] C.E. Hoyle, T.Y. Lee, T. Roper, J. Polym. Sci. Part A: Polym. Chem.
 2004, 42, 5301-5338
- [7] R.A. Pethrick, D. Hayward, Prog. Polym. Sci., 2002, 27, 1983-2017

[8] D. Zahouily, C. Decker, E. Kaisersberger, M. Gruener, *RadTech Technical Proceedings*, 2004

[9] S. Park, J.W. Hong, *Polym, Testing*, **2008**, *27*, 428-433

Table 3-1. Parameters for the PDLC samples obtained from photo-DSC thermograms.

	t _{max1} (s)	t _{max2} (s)	W1/2 (S)	ΔH (J/g)
NOA65	8.7	_	_	153.6
5CB + NOA65	12.3	-	58.4	180.3
7CB + NOA65	10.7	57.9	45.4	179.9
5PCH + NOA65	7.8	17.7	22.9	198.8
7PCH + NOA65	7.3	10.7	16.4	222.3

 t_{max1} : time at first peak maximum in photo-DSC thermogram

 t_{max2} : time at second peak maximum in photo-DSC thermogram

 $w_{1/2}$: full width at half maximum

∠H : enthalpy of exothermic peak

Table 3-2. Parameters for the PDLC samples obtained from resistance and transmittance measurements.

	t _{ini_turb} (s)	t _{ter_turb} (s)	∆H _{ini_turb} (J/g)	R _{180s} (Ω)
5CB + NOA65	_	_	_	2.0×10 ⁶
7CB + NOA65	66	120	82.0	4.3x10 ⁶
5PCH + NOA65	18	60	56.8	1.1×10 ⁷
7PCH + NOA65	15	58	67.0	1.4x10 ⁷

 t_{ini_turb} : time at the initiation of turbidity (scattering) increase t_{ter_turb} : time at the termination of turbidity increase $\Delta H_{ini_turb::}$ enthalpy to the initiation of turbidity increase R_{180s} : resistance at 180 seconds



Figure 3-1. Chemical structures of liquid crystal compounds used.



Figure 3-2. DSC thermograms of liquid crystal compounds used in this study.



Figure 3-3. Photo-DSC thermograms of neat NOA65 and NOA65-LC samples.



Figure 3-4. UV spectra of 5PCH, 5CB and BP (photoinitiator) as well as the irradiation spectra from UV lamp used.



Figure 3-5. (a) Resistance and (b) transmittance profiles for PDLC samples with different liquid crystal compounds.



Figure 3-6. SEM micrographs of PDLC samples with different liquid crystal compounds.



Figure 3-7. DSC thermograms of the cured PDLC samples.



Figure 3-8. Resistance and transmittance profiles for (a) NOA65-E7 (30/70w%) and (b) NOA65-P7 (30/70w%).

Chapter 4

Effects of Prepolymer Structures on the Photopolymerization Process, Morphology and Electro-optical Properties of PDLC Films

4-1 Introduction

A large number of researches performed since the early 1990s have addressed the phase separation process, morphology, and electro-optical properties of PDLC systems based on photopolymerization process.[1-9] Thiol-ene and acrylate systems have been the major photopolymerization processes used to produce PDLC films. Thiol-ene systems polymerize via the step-growth polymerization mechanism, whereas acrylate systems polymerize via the chain-growth radical polymerization mechanism.[10-11] The increase in molecular weight is much slower and the gelation takes place at a higher degree of monomer conversion in step-growth polymerization. These intrinsic properties of thiol-ene systems enable the PDLC films to be produced with a uniform morphology with narrow dispersity in the shape and size of liquid crystal droplets and a higher degree of liquid crystal phase separation. The thiol-ene system used most widely to construct PDLC films is commercial optical adhesive, Norland Optical Adhesive (NOA65).[2-4,11] The refractive index of the cured NOA65 is 1.50~1.52, which correspond to the normal range of the ordinary refractive indices of conventional nematic liquid crystal mixtures consisting of cyanobiphenyl molecules, which yields PDLC films with good electro-optical performance.

One of the most important factors determining the electro-optical properties of PDLC is its morphology which is strongly affected by the prepolymer composition, solubility between the liquid crystal and

prepolymer, the polymerization kinetics, and the phase separation mechanism.[12-22] For PDLC films prepared using thiol-ene systems, the droplet morphology and structural parameters such as droplet size, shape, distribution and density can be varied with the chemical characteristics of the prepolymer, monomer functionality and polymerization kinetics.[23-27] Therefore, it is an important to elucidate how the structure of prepolymer components affects their morphology and electro-optical properties.

While the morphology and electro-optical properties of PDLC films based on the thiol-ene photopolymerization reaction have been examined extensively, a systematic approaches to the prepolymer compositions have been very limited because most studies have used a formulated commercial product (NOA65) as the prepolymer. It is important to consider variations in the kinetics and network structure of thiol-ene systems according to the chemical nature of monomers, their functionality, and the molar ratio of thiol-ene monomers.

In this chapter, we investigated the structural effects of the prepolymer characteristics, such as the monomer conversion, photopolymerization kinetics and crosslink density, on the photopolymerization-induced phase separation process, morphology, and PDLC performance. Two kinds of model compounds with differing stoichiometric ratios of thiol-ene and monomer functionalities were prepared.

4-2 Experimental

4-2-1 Materials

(4-AE) Tetrafunctional allvl monomer from ether was prepared trimethylolpropane diallyl ether (2-AE) and isophorone diisocyanate. The synthesis scheme shown in Figure 2-1. Trimethylolpropane is tris-(3-mercaptopropionate) (3-SH) was used as the thiol monomer. The monomers were purchased from Aldrich Chemical and used without further purification. 2,2-Dimethoxy-2-phynylacetophonone (Irgacure 651. Ciba

Specialty Chemicals) was used as the photoinitiator.

PDLC films were prepared using a homogeneous mixture of the nematic liquid crystal material (E7, Merck) and the formulated prepolymer at a 1:1 weight ratio.

4-2-2 Measurements

Photo-DSC was used to investigate the photo-polymerization process of prepolymer. The detailed was described in the experimental section of chapter 2.

The thermal behaviors of the PDLC samples cured in photo-DSC measurements were examined using DSC thermograms. DSC thermograms obtained with a DSC device (N-650, Scinco).

Scanning electron microscopy (SEM) was used to examine the PDLC morphology. The PDLC samples were freeze-fractured, soaked in hexane for 24h to remove the liquid crystals from the exposed surface, and then placed in a vacuum chamber for 24 h to remove the solvent.

Normal-normal spectral transmittance of PDLC cells was measured using an experimental setup comprising a halogen lamp (Avalight-HAL, Avantes) and a CCD detector (Avaspec 2048, Avantes). The transmittance spectra were obtained at a collection angle of \pm 3°. The transmittance value at λ =650nm was recorded from the transmittance-voltage curve.

4-3 Results and Discussions

Two kinds of prepolymer formulations based on thiol-allyl ether chemistry were prepared to examine the structural effects of prepolymers on the polymerization-induced phase separation, morphology, and electro-optical properties of PDLC films: (1) model compounds with different stoichiometric ratios of thiol to allyl ether monomers (designed as [SH]/[AE]: UPSR

samples) and (2) model compounds with various monomer functionalities (UP2E samples).

4-3-1 Effect of the Stoichiometric Ratio

In the polymerization mechanism of the thiol-ene system, the polymerization reaction terminates by stoichiometric imbalance, and there is no more thiol available to react with the ene or vice versa.[10-11] This approach was used to prepare prepolymer formulations with different stoichiometric ratios, as listed on Table 4-1. The prepolymer formulations of UPSR samples are expected to result in different degrees of monomer conversion. The number prefixed to "UPSR" denotes the molar percentage of the thiol group in the prepolymer formulation.

The photopolymerization behaviors of the prepolymers were investigated using photo-DSC measurements. Photo-DSC thermograms of the prepolymer samples are shown in Figure 4-1(a) and parameters obtained from them-time of the exothermic peak maximum (t_{max}) and enthalpy of the photopolymerization reaction (ΔH_{cure})-are listed in Table 4-2. The results show that the degree of monomer conversion increases to a maximum as the monomer composition approaches the stoichiometric balance of [SH]:[AE] = 50:50, as expected. However, the photopolymerization rate is similar for all the prepolymer samples ($t_{max} = 4.0 \sim 5.0$ sec).

Photo-DSC thermograms of the PDLC samples are shown in Figure 4-1(b) and parameters obtained from photo-DSC thermograms were listed in Table 4-2. To compare the photopolymerization behaviors of the PDLC samples directly with those of the prepolymer samples, the photo-DSC thermograms of the PDLC samples were normalized by the weights of the prepolymers. As for the prepolymer samples, the PDLC samples exhibit a maximum conversion for [SH]:[AE] = 50:50 and no significant difference in photopolymerization rate. The photopolymerization is slightly slower for the PDLC samples than for the

prepolymer, which is due to the restricted photopolymerization reaction being restricted by the liquid crystals (a dilution effect). However, the final conversion rate is slightly higher for the PDLC samples than the prepolymer samples due to the effect of plasticization by the liquid crystals.

Figure 4-2 shows the SEM micrographs of PDLC samples, which exhibit densely dispersed submicron droplets in the polymer matrix. The morphology and droplet size do not differ significantly among the PDLC samples. The droplet size is generally determined by polymerization kinetics, with a higher polymerization rate producing smaller droplets. From the photo-DSC data, the photopolymerization rate is similar level for all the PDLC samples ($t_{max} = 7.6 \sim 9.6$ sec), which demonstrates that the morphology of the PDLC film is largely determined by the photopolymerization kinetics.

DSC thermograms of the cured polymer samples were shown in Figure 4-3(a). The parameters obtained from the DSC thermograms, the glass transition temperature of polymer matrix (T_g), were listed in Table 4-2. As the prepolymer composition approaches to the stoichiometric balance, T_g of the cured prepolymers increases and exhibits the maximum T_g . for [SH]:[AE] = 50:50.

DSC thermograms of the cured PDLC samples are shown in Figure 4-3(b). The parameters for the DSC thermograms are listed in Table 4-2. As for the prepolymer samples, T_g of the PDLC samples increases to maximum as the stoichiometric balance of [SH]:[AE] = 50:50 is approached. The nematic-isotropic enthalpy (ΔH_{NI}) remains within the range of 0.67 ~ 0.73J/g for all the PDLC samples. Considering that ΔH_{NI} of pure E7 was 3.12J/g (Figure 2-14), the nematic fraction of liquid crystal is in the range of 0.21 ~ 0.23.

The T_g value of a polymer formed by UV curing is determined by both the chemical structure of the involved monomers and the degree of monomer conversion, with a higher conversion resulting in a higher T_g . For PDLC

samples formed by UV curing, the glass transition temperature is affected by the amount of liquid crystals dissolved in the polymer matrix as well as the chemical structure of the monomer and the degree of monomer conversion. T_a values of the cured polymer and PDLC samples are plotted in Figure 4-4, which shows that T_g increases as the stoichiometric balance is approached. However, T_g of the UPSR-60 sample decreases greatly despite its relatively high degree of monomer conversion, which can be attributed to the chemical structure of monomers. In contrast to 3-SH monomer, 4-AE monomer contains ure than groups that form hydrogen bonds that acts as a physical crosslink, thus contributing to increase the T_g value of the matrix. Therefore, the amount of hydrogen bonds (in 4-AE) critically affects both T_g and the degree of monomer conversion. The \mathcal{T}_g values show similar behaviors of the cured PDLC samples and the polymer samples because the samples exhibit similar plasticization effects of liquid crystal molecules dissolved in the matrix (nematic fraction = 21 ~ 23%). The glass transition temperature (T_g), the enthalpy of photopolymerization reaction (ΔH_{cure}) and the mole fraction of urethane group in prepolymer composition (x_{H-bond}) for the PDLC samples are plotted in Figure 4-5 to show the relation between T_g and the structural factors.

The transmittance of the PDLC samples as functions of applied voltage are plotted in Figure 4-6. The transmittances in the OFF state (T_{off}) and the saturation voltage (V_{sat} , that required to reach maximum transmittance) are plotted in Figure 4-7. The scattering in the OFF state is affected mainly by the droplet size, droplet density (i.e., number of droplets per unit volume), and by the birefringence of the liquid crystal.[28-29] The birefringence effect can be eliminated because all samples were made using the same liquid crystal materials (E7 mixture), giving them similar degrees of liquid crystal phase separation. The SEM micrographs showed that the morphological characteristics, droplet size and droplet density did not differ significantly between the samples. As expected, all PDLC samples

exhibit similar level of T_{off} values, but there were large variation in the saturation voltage.

4-3-2 Effect of Matrix Crosslink Density

According to the polymerization mechanism of the thiol-ene system, the polymerization reaction propagates by a free-radical chain-transfer process. The functionality of reactive components (the thiol and ene monomer) should be at least 2 for the reaction to progress.[17-18] The polymerization reaction with difunctional monomers produces a linear polymer. Constructing the network structure requires the average functionality of each component to be greater than 2. This approach was used to prepare prepolymer formulations with different crosslink densities in the matrix. The compositions of the prepolymers are listed on Table 4-3. As the 2-AE content increases, the crosslink density in the cured matrix is expected to decrease. The matrix crosslink density (σ_{cross}) can be estimated using

$$\sigma_{cross} = \sum_{i} \frac{(f_i - 2)w_i}{M_i} \tag{4-1}$$

where f_i , w_i , M_i are the functionality, weight fraction, and molar mass of monomer I, respectively.

Photo-DSC thermograms of the prepolymer samples are shown in Figure 4-8(a) and the parameters obtained from them are listed in Table 4-4. Variations in monomer functionality resulted in no significant differences in the photopolymerization rate. Because the samples have similar [SH]/[AE] values, they show similar degrees of monomer conversion (ΔH_{cure}).

Photo-DSC thermograms of the PDLC samples are shown in Figure 4-8(b). As for the prepolymer samples, the PDLC samples show no significant differences in photopolymerization or monomer conversion rates. The photopolymerization reaction is slower for the PDLC samples than for the prepolymer samples due

to the dilution effect of the liquid crystals. Moreover, the degree of monomer conversion is slightly lower for the PDLC samples than for the prepolymer samples, which is not the case for the UPSR samples. This indicates that the dilution effect on the photopolymerization reaction is much larger than that of the plasticization effect, because the solubility of the liquid crystals is higher for 2-AE monomer than for 4-AE monomer.

SEM micrographs of the PDLC samples are shown in Figure 4-9. As for the UPSR samples, the droplet size does not differ significantly among the PDLC samples. It appears that fewer droplets are formed for the PDLC samples with a lower crosslink density. However, the morphology of the PDLC samples with lower crosslink density is thought to be destroyed by n-hexane (the solvent) during sample preparation and exposure to the electron beam during SEM measurements due to poor solvent resistance and thermal stability of the matrix due to the decreased crosslink density. The actual morphology is thought to be similar across the samples. This confirms that the droplet size and morphology are mainly determined by polymerization kinetics rather than by structural characteristics of prepolymers based on the thiol-allyl ether system.

DSC thermograms of the cured prepolymers are shown in Figure 4-10(a) and the parameters obtained from them are listed in Table 4-4. The T_g gradually decreases as the content of 2-AE increases. The photo-DSC data show that they have similar level of ΔH_{cure} values. Therefore, the monomer conversion effect is consistent with the UPSR samples. Instead, the decrease in the crosslink density and the amount of hydrogen bonds would result in T_g decreasing as the 2-AE monomer content increases.

DSC thermograms of the PDLC samples are shown in Figure 4-10(b) and the parameters obtained from the them are listed in Table 4-4. As for the prepolymer samples, both T_g and ΔH_{NI} tend to decrease as the 2-AE monomer content increases. The lower nematic fraction in the PDLC samples could be due to increased solubility of liquid crystals in the polymer matrix as the

2-AE monomer content increases. The higher amount of liquid crystal dissolved in the polymer matrix would also decrease T_g . The T_g of the prepolymer and PDLC samples are plotted versus the weight percentage of 2-AE monomer in Figure 4-11.

The transmittances of the PDLC samples as functions of the applied voltage are shown in Figure 4-12. All PDLC samples show the same transmittance in the OFF state. As discussed above, the scattering in the OFF state is determined mainly by morphological characteristics (e.g, droplet size and density), and hence all the PDLC samples exhibit similar degrees of scattering in the OFF state because they have similar morphological characteristics. However, the saturation voltage (V_{sat}) decreases markedly as the crosslink density in the polymer matrix decreases.

The driving voltage of a bipolar drolet can be expressed as [28-29]

$$V_{d} = \frac{d}{3a} \left(\frac{\rho_{p}}{\rho_{LC}} + 2 \right) \left(\frac{K(l^{2} - 1)}{\epsilon_{o} \Delta \epsilon} \right)^{1/2}$$
(4-2)

where a and b are the length of the major and minor axes of the droplet, respectively. l is the ratio of the lengths of the major and minor axes(i.e., a/b), d is the film thickness, ρ_p is the resistivity of the polymer matrix, ρ_{LC} is the resistivity of the liquid crystal, K is the elastic constant of the liquid crystal, ε_o is the free-space permittivity, and $\Delta\varepsilon$ is the dielectric anisotropy of the liquid crystal.

This equation (4-2) shows that the driving voltage is a function of the physical constants of the liquid crystal (K, $\Delta \varepsilon$), the morphology (a, b) and dielectric properties (ρ_p , ρ_{LC}) of the PDLC film. Parameters related to the liquid crystal material can be eliminated because all of the PDLC samples were constructed using the same type of liquid crystals. The morphological characteristics can also be neglected because the droplet size and shape are very similar for the PDLC samples in this study. Therefore, the resistivity

of the polymer matrix(ρ_p) is a critically influence the driving voltage of the PDLC samples.

The resistivity of the liquid crystal (ρ_{LC}) is related to the purity of the liquid crystal droplets, which is determined by unreacted monomers or photo-initiators dissolved therein. We assumed that the resistivity of the liquid crystal was the same for all the PDLC samples because it was difficult to determine these values exactly in this study.

The resistivity of the polymer matrix (ρ_p) is determined by dipolar and ionic components of the matrix. The dipolar components arises from rotational motion of molar dipoles and the ionic component arises from the diffusion of ionic impurities. The resistivity of the matrix is proportional to T_{g} , since the two physical components are determined by the mobility of polymer molecules. Therefore, the relation can be summarized as

$$V_d \propto \rho_p \propto T_q$$
 (4-3)

Figure 4-13 plots V_{sat} versus T_g for the PDLC samples (UPSR and UP2E samples), which shows that the driving voltage Is linearly proportional to T_g and hence that the experimental relationship is consistent with the mechanisms described above.

4-4 Summary

We investigated the structural effect of prepolymer components on the photopolymerization-induced phase separation behavior, morphology and electro-optical properties of PDLC films. Two kinds of model compounds were prepared based on thiol and allyl ether monomers with various stoichiometric ratios and monomer functionalities.

The stoichiometric ratio (i.e., [SH]/[AE]) affected the degree of monomer

conversion and the glass transition temperature of polymer matrix: both of these parameters were maximal at the stoichiometric balance of [SH]:[AE] = 50:50. The photopolymerization rate was not markedly affected by the stoichiometric ratio, which resulted in the PDLC samples having similar morphologies. The level of scattering in the OFF state was constant across the PDLC samples, but varied markedly with the driving voltage.

The functionality of monomers strongly affected the crosslink density and the glass transition temperature of the polymer matrix. The prepolymer and PDLC samples with different monomer functionalities exhibited no significant difference in the degree of monomer conversion, photopolymerization rate or morphology. As the crosslink density decreased, the glass transition temperature of the polymer matrix and the driving voltage of the PDLC samples were markedly decreased.

These results indicate that the following rules apply to PDLC formations based on the thiol-ene system:

(1) Slight differences in the stoichiometric ratio and the monomer functionality do not significantly affect the photopolymerization behavior in the thiol-allyl ether reaction.

(2) The morphology of a PDLC film is largely determined by polymerization and phase separation kinetics rather than by structural characteristics of the prepolymer components such as the stoichiometric ratio and crosslink density in the thiol-allyl ether reaction.

(3) The scattering in the OFF state is markedly affected by the morphological characteristics of PDLC films, such as the droplet size and density.

(4) The glass transition temperature of a PDLC matrix can be changed by varying the monomer conversion, crosslink density and chemical structure of the constituent monomers.

(5) The driving voltage is a complex function of the physical constants of the liquid crystal and the morphology and dielectric properties of the PDLC

film. The glass transition temperature of the matrix is linearly proportional to the driving voltage of the PDLC film because it is influenced by the resistivity of the polymer matrix.

4-5 References

[1] N. Vaz, G.W. Smith, G.P. Montgomery, Mol. Cryst. Lig. Cryst., 1987, 146, 1 [2] J.B. Nephew, T.C. Nihei, S.A. Carter, Phys. Rev. Lett., 1998. 80(15). 3276-3279 [3] A.J. Lovinger, K.R. Amundson, D.D. Davis, Chem. Matter, 1994, 6, 1726 [4] D. Nwabunma, T. Kyu, *Polymer*, **2001**, *42*, 801–806 [5] V. Rachet, P. Feneyrou, B. Loiseaux, R.L. Barny, J.P. Huignard, U. Maschke, Mol. Cryst. Liq. Cryst., 2004, 421, 165-174 [6] L.V. Natarajan, C.K. Shepherd, D.M. Brandelik, R. L. Sutherland, S. Chandra, V.P. Tondiglia, D. Tomlin, T.J. Bunning, *Chem. Mater.*, **2003**, *15*, 2477-2484 [7] Y. Hirai, S. Niivama, H. Kumaim, T. Gunjima, *Proc. SPIE*, **1990**, *1257*, 2 [8] C.H. Noh, J.E. Jung, J.Y. Kim, D.S. Sakong, K.S. Choi, Mol. Cryst. Liq. Crvst.Sci. Tec. A. 1993. 227. 229 [9] D. Coates, S. Greenfield, M. Goulding, E. Broun, P. Nolan, Proc. SPIE, **1993**, *1911*, 2-14 [10] A.F. Jacobine, Thiol-Ene Polymerization. In Radiation Curing in Polymer Science and Technology, Fouassier, J.P.; J.F. Rabek, Eds.; Elsevier Applied Science: New York, 1993, 3, 219 [11] C.E. Hoyle, T.Y. Lee, T. Roper, J. Polym. Sci. Part A: Polym. Chem. **2004**, *42*, 5301-5338 [12] S.J. Klosowicz, M. Aleksander, *Opto-Electron. Rev.*, 2004. 12(3). 305-312 [13] A. Golemme, S. Zumer, J.W. Doane, M.E. Neubert, Phys. Rev. 1988, A37, 559 [14] G.P. Montgomery, N.A. Vaz, G.W. Smith, Proc. SPIE, 1988, 958, 104 [15] G.P. Montgomery, N.A. Vaz, *Liq. Cryst.*, **1988**, *3*, 543 [16] S.A. Carter, J.D. GeGrange, W. White, J. Boo, P. Wiltzius, J. Appl. *Phys.*, **1997**, *81(9)*, 5992–5999

[17] M. Wang, W. Li, Y. Zou, C. Pan, *J. Phys. D: Appl. Phys.*, **1997**, *30*, 1815-1819 [18] M. Aleksander, S. Klosowicz, SPIE, 2004, 5565, 389-396 [19] J.D. LeGrange, S.A. Carter, M. Fuentes, J. Boo, A.E. Freeny, W. Cleveland, T.M. Miller, *J. Appl. Phys.*, **1997**, *81(9)*, 5984-5991 [20] H. Fujikake, K. Takizawa, H. Kikuchi, T. Fujii, Jpn. J. Appl. Phys.. **1998**. 37. 895-899 [21] E. Nastal, E. Zuranska, M. Mucha, J. Appl. Polym. Sci., 1999, 71, 455-463 [22] W. Li, Z. Cheng, G. Pan, H. Liu, H. Gao, Z, Yang, H. Yang, Opt. Mater., **2008**, *31*, 434–439 [23] K.Amundson, A. V. Blaaderen, P. Wiltzius, Phys. Rev. E, 1997, 55(2), 1646-1654 [24] A.F. Senyurt, G. Warren, J.B. Whitehead, C.E. Hoyle, *Polymer*, **2006**, *47*, 2741-2749 [25] T.J. White, L.V. Natarajan, V.P. Tondiglia, T.J. Bunning, C.A. Guymon Macromo/ecu/es, 2007, 40, 1112-1120 [26] H. Duran, S. Meng, N. Kim, J. Hu, T. Kyu, L.V. Natarajan, V.P. Tondiglia, T.J. Bunnng, *Polymer*, **2008**, *49*, 534-545 [27] M.D. Sarkar, N.L. Gill, J.B. Whitehead, G.P. Crawford, *Macromolecules*, **2003**, *36*, 630–638 [28] P.S. Drzaic, Liquid Crystal Dispersion. Vol 1, World Scientific:, Singapore, 1995 [29] J.W. Doane, Polymer Dispersed Liquid Crystal Displays. In Liquid Crystals Applications and Uses, B. Bahadur; World Scientific : Singapore, 1990

	3-SH (w%)	4-AE (w%)	[SH]/[AE]
UPSR-35	30	70	35/65
UPSR-40	35	65	40/60
UPSR-45	40	60	45/55
UPSR-50	45	55	50/50
UPSR-60	55	45	60/40

Table 4-1. Prepolymer formulations with various molar ratios of thiol t allyl ether([SH]/[AE]) monomers.
Table 4-2. Parameters from photo-DSC thermograms and thermal analysis for the prepolymer and PDLC samples (UPSR series).

	t _{max} (sec)	∆H _{cure} (J/g)	<i>T</i> g (℃)	∆H _{NI} (J/g)
UPSR-35	5.0	158.5	1.6	_
UPSR-40	4.4	190.6	4.5	-
UPSR-45	4.2	207.7	6.9	_
UPSR-50	4.2	237.6	7.4	-
UPSR-60	4.0	194.3	-8.4	-
UPSR-35 + E7	9.6	179.2	-24.8	0.71
UPSR-40 + E7	8.8	205.8	-22.9	0.67
UPSR-45 + E7	8.2	215.2	-13.4	0.72
UPSR-50 + E7	7.6	239.4	-12.3	0.69
UPSR-60 + E7	8.8	238.2	-26.5	0.73

 t_{max} : time of the peak maximum in photo-DSC thermogram ΔH_{cure} : enthalpy of the exothermic peak in photo-DSC thermogram T_g : glass transition temperature of the polymer matrix ΔH_{NI} : nematic-isotropic enthalpy of the liquid crystal for the PDLC sample

	3-SH (w%)	4-AE (w%)	2-AE (w%)	[SH]/[AE]	σ_{cross} (10 ⁻³ mol/g)
UP2E-00	30	70	0	35/65	2.90
UP2E-05	30	65	5	34/66	2.75
UP2E-10	30	60	10	33/67	2.60
UP2E-15	30	55	15	32/68	2.45
UP2E-20	30	50	20	31/69	2.30

Table 4-3. Prepolymer formulations with various crosslink densities.

 $\sigma_{{\it cross}}$: crosslink density of the matrix

Table 4-4. Parameters from photo-DSC thermograms and thermal analysis for the prepolymer and PDLC samples (UP2E series).

	t _{max} (sec)	ΔH_{cure} (J/g)	<i>T</i> g (℃)	ΔH_{NI} (J/g)
UP2E-00	5.0	158.5	1.6	_
UP2E-05	4.6	185.7	-6.4	_
UP2E-10	5.2	185.3	-10.6	_
UP2E-15	5.4	179.8	-25.1	_
UP2E-20	5.6	181.9	-30.1	-
UP2E-00 + E7	9.6	179.2	-24.8	0.71
UP2E-05 + E7	7.8	166.4	-26.1	0.73
UP2E-10 + E7	8.2	168.2	-34.1	0.59
UP2E-15 + E7	8.6	176.0	-38.5	0.48
UP2E-20 + E7	8.8	170.3	-42.3	0.58

*t*_{max}: time at peak maximum in photo-DSC thermogram

 ΔH_{cure} : enthalpy of exothermic peak in photo-DSC thermogram

 T_g : glass transition temperature of polymer matrix

 ΔH_{NI} : nematic-isotropic enthalpy of liquid crystal in PDLC film



Figure 4-1. Photo-DSC thermograms of (a) prepolymer samples and (b) PDLC samples with various [SH]/[AE] values (UPSR series).



Figure 4-2. SEM micrographs of PDLC samples with various [SH]/[AE] values (UPSR series).



Figure 4-3. DSC thermograms of (a) cured polymers and (b) PDLC samples with various [SH]/[AE] values (UPSR series).



Figure 4-4. Glass transition temperatures of the cured polymers and PDLC samples with various [SH]/[AE] values (UPSR series).



Figure 4-5. Glass transition temperature (T_g) , enthalpy of photopolymerization reaction (ΔH_{cure}) and the extent of hydrogen bond (x_{H-bond}) versus [SH]% in the polymer matrix with various [SH]/[AE] values (UPSR series).



Figure 4-6. Transmittances of PDLC samples as functions of applied voltage (UP-SR series).



Figure 4-7. Transmittance in the OFF state and saturation voltage versus he percentage thiol content for the PDLC samples (UPSR series).



Figure 4-8. Photo-DSC thermograms of (a) prepolymer samples and (b) PDLC samples with various crosslink densities in the polymer matrix (UP2AE series).



Figure 4-9. SEM micrographs of the PDLC samples with various crosslink densities in the polymer matrix (UP2E series).



Figure 4-10. DSC thermograms of (a) cured polymers and (b) PDLC samples with various crosslink densities in the polymer matrix (UP2E series).



Figure 4-11. Glass transition temperature of the cured prepolymers and PDLC samples with various crosslink densities in the polymer matrix (UP2E series).



Figure 4-12. Transmittances of PDLC samples as functions of applied voltage (UP2E series).



Figure 4-13. Transmittance in the OFF state and saturation voltage versus percentage weight of 2-AE monomer for the PDLC samples (UP2E series).



Figure 4-14. Saturation voltage (V_{sat}) versus glass transition temperature for the PDLC samples.

Chapter 5

Fabrication of Polymer Dispersed Liquid Crystal Films using Conducting Polymer Thin Films as Driving Electrodes

5-1 Introduction

Poly(3,4-ethylenedioxythiophene)(PEDOT), a polymer complex with polystyrenesulfonic acid in water, is one of the most promising conducting polymers because of its good environmental stability, high conductivity, good film-forming properties and excellent transparency.[1-3] Many studies have investigated the potential applications of PEDOT such as anti-static coatings. electrodes in photoelectronic devices, and electromagnetic shielding layers. [4-5] The latest progress in fabrication of PEDOT and its blends has attracted enormous industrial interest. Especially, conductive films derived from the combination of inherently conductive polymers and resistive polymers have considerable potential as anti-static coatings for photographic films and higher density computer chips. [6-8] Some groups have reported on investigations of transparent conducting films and coatings. Recently, conductive transparent films by UV curing based on poly(aniline)/dodecylbenzene sulfonic acid was reported by Kim et. al..[9] The UV-curable formulation containing conductive microgels had surface $10^7 - 10^8 \Omega / cm^2$. Transparent UV-curable antistatic hybrid resistance of coatings prepared by the sol-gel method was reported by Wouters et al.[10] They demonstrated that surface resistivity of the organic-inorganic hybrid coating could be reduced from 10^{16} to $10^{6} \Omega/cm^{2}$ using high concentration of PEDOT in the coating formulation.

Polymer dispersed liquid crystal (PDLC) films have been used as electro-optical devices which are constructed between two conducting

substrates. Indium tin oxide (ITO)-coated plastic substrates have most widely been used as the driving electrodes. However, ITO coated films require complicated and high-cost manufacturing process and it can be sasily cracked when the flexible substrate is bent.[11] In order to enhance the flexibility of PDLC devices, we focused on the conducting polymer, especially PEDOT. We designed coating formulations with high concentration of PEDOT to meet the surface resistance level for the PDLC devices and prepared conducting thin films with good mechanical stability.

In this study, we will demonstrate a preparation method of a conducting polymer thin film on a poly(ethylene terephthalate) (PET) substrate and constructed a PDLC device using the conductive film as driving electrodes. The electro-optical and mechanical properties of the PDLC conducting polymer thin film were investigated.

5-2 Experiments

5-2-1 Materials

PEDOT was purchased from H.C. Stark (Baytron PAG). 3-(Trimethoxysilyl) propyl acrylate (APTS) as a monomer, and n-methyl-2-pyrrolidone(NMP) and isopropyl alcohol (IPA) as solvents were obtained from Aldrich Chemical and used without further purification. Wetting agent (Dynol 604) and photo-initiator (2-hydroxy-2-methyl-1-phenyl propan-one, Darocure 1173) were purchased from Air products Co. and Ciba specialty chemicals, respectively.

5-2-2 Preparation of the Conductive Films with PEDOT

The recipe for the conductive coating formulation was listed in Table 5-1. A few coating formulations with various APTS contents were prepared keeping the content of other components constant. The prepared formulations were coated on PET films. The coated films were dried in a convection oven at 60 °C for 10min and exposed radiation of 80W/cm² using a medium-pressure mercury

lamp. The optimized coating properties were obtained by a subsequent heat treatment at 120°C up to 2 hours.

5-2-3 Characterization of the Conductive Films

The surface resistance of the cured films was measured by a 4 point technique using a resistance meter (R-CHEK 4 point meter, EDTM, USA). Curing behavior of the coating formulation was investigated using FTIR-ATR Spectroscopy. Infrared spectra were obtained on the UV irradiation. The morphology of the conductive films and the PDLC film were observed by scanning electron microscopy (SEM, JEOL model JSM-6340F). The transmission spectra of the conductive films were obtained using a UV-visible spectrometer (Varion-3-Bio).

5-2-4 Fabrication of PDLC Films using Conducting Polymer Thin Films

A formulated UV-curable adhesive, NOA65 (Norland Products Inc.), was used as a prepolymer. A eutectic mixture, E7 (Merck), was used as liquid crysatl material. The PDLC formulation comprised a mixture of NOA65 and E7 at a ratio of 1:1. A PDLC device was prepared by sandwiching the PDLC formulation between two PEDOT-coated films separated by 20µm using spacers. Photopolymerization was initiated using a UV lamp (B-14N, Spectronics) producing an intensity of 1.6mW/cm² at 365nm.

5-3 Results and Discussion

5-3-1 Preparation of the Conductive Films Containing PEDOT

The recipe for the conductive coating formulation was listed in Table 5-1. The formulation was designed to form a conducting layer by UV and heat curing and optimized to obtain low surface resistance by loading high

concentration of PEDOT. For the purpose we used ATPS as a binder material which has both an acrylate group for UV curing and 3-alkoxy groups for heat curing. The chemical structure of ATPS was shown in Figure 5-1. Because the heat curing of APTS progresses at low temperature, the coating solution can be applied to a plastic substrate such as PET or PC by conventional wet coating methods. The conducting thin films with 200nm, 365nm, 500nm and 650nm coating thickness were prepared using mayer bars.

5-3-2 Characterization of Conductive Thin Films Containing PEDOT

The surface resistance of the prepared conductive thin films was strongly influenced by the coating thickness and the concentration of PEDOT. Figure 5-2 shows the surface resistance of the conductive thin films with 500nm coating thickness as a function of APTS concentrations. It can be seen that the surface resistance increases as APTS concentration increases. When the coated film was treated by UV irradiation and heat at 120°C, APTS forms crosslink structures, which provides the film mechanical durability. However, the amount of APTS should be optimized considering the electrical resistance at the same time. The optimal surface resistance and film durability could be obtained at 0.514 w% of APTS in the coating formulation.

The dependance of surface resistance on coating thickness was investigate. The surface resistance of the conductive films with 0.514 w% of APTS was plotted as a function of the coating thickness in Figure 5-3. As coating thickness increases, the surface resistance decreases and levels off about $600 \,\Omega/\text{cm}^2$ at 500nm thickness. The film of 500nm thickness exhibited same surface resistance after UV irradiation and heat treatment at 120°C for 2 hours, which is sufficient for the conducting electrode of PDLC devices.

The polymerization behavior of APTS was investigated by real-time FTIR spectroscopy by analyzing the characteristic bands in the spectra. Fig. 4 shows the real-time FTIR spectra of the coated film on UV irradiation. The

characteristic bans for acrylate group and alkoxy silane group are 811cm⁻¹ and 980cm⁻¹, respectively. The spectra clearly show that the acrylate group reacts by UV irradiation. The conversion of acrylate group as a function of UV irradiation time was plotted in Figure 5-5. Besides the acrylate group, the absorption band of alkoxy silane group also largely decreases during the UV irradiation in the spectra. This is thought by the condensation reaction of alkoxy silane group by the heat emitted UV lamp or released by the reaction of acrylate group. No further decrease in the absorption band of alkoxy silane group was observed in the FTIR spectra after the subsequent heat treatment after UV irradiation. However, the pencil hardness was increased up to 2 grades after the subsequent heat treatment at 120°C for 2 hours.

Figure 5-6 shows the optical transmittance of the bare PC sheet and conductive coated sheets with different coating thicknesses. Because of the intrinsic blue color of PEDOT material the transparency at long wavelength region was reduced for the conductive coated samples. However, the overall transmittance of the conductive coated samples exhibits similar level at about 87% in the range of coating thickness 200~500nm, which can be acceptable for the application to the transparent electrodes for PDLC devices.

SEM micrograph of the conductive thin films was shown in Figure 5-7. It can be seen that the conductive coating layer consists of closely packed spherical PEDOT nano-particles in size of 20-40nm which are linked together by APTS polymer molecules (dark regions). The APTS polymer acts as a binder of PEDOT nano-particles and provide the conductive coating layer the mechanical stability. The mechanical properties of the conductive coating samples on PC substrates were evaluated with the following methods. The interfacial adhesion between the substrate and the coating layer was evaluated by a tape test method (DIN 58196-K2) and the hardness of the coating was measured by a pencil test (ASTM D3363-92a), which proved that

the conductive coating had acceptable interfacial strength and surface hardness (F grade) to be used in the PDLC devices.

5-3-3 Fabrication of PDLC Films using Conducting Polymer Thin Films

Figure 5-8 shows a surface SEM micrograph of the PDLC composite prepared by photopolymerization-induced phase separation in this study. Liquid crystal microdroplets with diameter of $1\sim3\mu$ m were densely dispersed in a polymer matrix. The photographs of the PDLC devices constructed by the conducting polymer thin films was shown in Figure 5-9. In the absence of an external applied voltage, liquid crystal molecules in the microdroplets are randomly orientated and scatter the incident light. When the external field is applied, the liquid crystal molecules align parallel to the electric field. Because the ordinary refractive index of liquid crystal is similar to the refractive index of polymer matrix, the PDLC film appears clear. The surface resistance and transmittance at 550nm wavelength of the conducting thin film was $600 \Omega/cm^2$ and 88%, respectively.

To evaluate the performance of the conducting polymer electrode in this study, the electro-optical behavior of the PDLC device was compared with that constructed by ITO coated films. Surface resistance of the ITO coated film was $600 \,\Omega/cm^2$. The transmittance vs. applied voltage curves for the PDLC devices were plotted in Figure 5-10. The PDLC device by conducting polymer thin films shows higher driving voltage and lower transmittance at ON state than the PDLC device by ITO coated films due to the relatively higher surface resistance of the conducting polymer thin film and the intrinsic color of the PEDOT material. However, it shows acceptable electro-optical performances and the conducting polymer thin film in this study can be used as the driving electrodes for PDLC devices, The PDLC device constructed by PEDOT thin films exhibits 18VAC of driving voltage, 60:1 of high contrast ratio, and 60% of transmittance at the ON state. The results in this study

are comparable to the previous researches on the transparent conductive coatings based on polyaniline, polypyrrole and PEDOT. [12-14]

5-4 Summary

We developed a conductive coating formulation based on PEDOT and APTS for flexible transparent electrode coating on plastic substrates. The surface resistances and transmittance of the prepared thin films were $500 -900 \,\Omega/cm^2$ and 87% at 550nm, respectively. The PDLC device was constructed using the conducting polymer thin film as driving electrode. The PDLC device had acceptable electro-optical performances, 18VAC of driving voltage, 60:1 of high contrast ratio, and 60% of transmittance at the ON state. We have demonstrated the organic conductive coating layer based on PEDOT and APST can be used as a transparent electrode on polymer substrates.

5-5 References

[1] M. Dietrich, J. Heinze, G. Heywang, F. Jonas, *J. Electro. Chem.*, 1994, **369**, 87.

[2] G. Heywang, F. Jonas, Adv. Mater., 1992, 4, 116.

[3] A.N. Aleshin, S.R. Williams, A.J. Heeger, Synth. Metal, 1998, 94, 173.

[4] H. W. Heuer, R. Wehrmann, S. Kirchmeyer, *Adv. Funct. Mater.*, 2002, 12, 89.

[5] H. C. Ko, M. Kang, B. Moon, H. Lee, Adv. Mater., 2004, 19, 1712.

[6] G. Rabiloud, High Performance Polymers, Conductive Adhesive; Technip Eds.; Paris, 1997.

[7] V.G. Kulkarni, *Synth. Metal*, 1995, **71**, 2129.

[8] V.G. Kulkarni, Transparent Conductive Coatings, Handbook of Conducting Polymers; Marcel Dekker Eds; New York, 1998, 2, 1059.

[9] Y.B. Kim, W.S. Kim, J.A. Yu, J.W. Hong, *Polym. Adv. Tech.*, 2002, **13**, 522

[10] M.E.L. Wouters, D.P. Wolfs, M.C. van der Linde, J.H.P. Hovens, A.H.A. Tinnemans, *Prog. Org. Coating*, 2004, **51**, 312.
[11] P. C. Wang, A.G. MacDiarmid, *Displays*, 2007, **28**, 101.
[12] E. Harlev, T. Gulakhmedova, I. Rubinovich, G. Aizenshtein, *Adv. Mater.*, 1996, **8**, 994.
[13] F. Roussel, R. Chan-Yu-King, J.-M. Buisine, *Eur. Phys. J. E*, 2003, **11**, 293.
[14] D. Hohnholz, H. Okuzaki, A.G. MacDiarmid, *Adv. Funct. Mater.*, 2005, **15**, 51.

Table 5-1. A recipe for the conductive coating formulation.

Ingredients	Weight %	
Baytron PAG [®]	42.92	
NMP	2.58	
APTS	0.86-0.28	
Dynol 604 ^a	0.3	
IPA	53.34	
Photoinitiator	0.04	

^a Dynol 604 is a wetting agent on plastic substrate



Figure 5-1. Chemical structure of 3-(trimethoxysilyl)propyl acrylate (APTS).



Figure 5-2. Surface resistance of the conductive thin films at 550nm coating thickness as a function of APTS content.



Figure 5-3. Surface resistance of the conductive films of 0.514w% APTS as a function of the coating thickness



Wavenumber (cm⁻¹)

Figure 5-4. Real-time FTIR-ATR spectra of the conductive coating formulation containing 0.514w% APTS on UV irradiation.



Figure 5-5. Conversion of acrylate group as a function of UV irradiation time.



Figure 5-6. Transmittance of the conductive films with various coating thickness and the bare substrate.



Figure 5-7. Cross-section SEM micrograph of the APTS/PEDOT thin film on PC substrate after UV curing and heat treatment at 120°C for 2h.



Figure 5-8. Surface SEM micrograph of the PDLC film prepared by photopolymerization-induced phase separation method.





[Scattering at OFF state]

[Clear at ON state]

Figure 5-9. PDLC device constructed by conducting polymer thin films as electrodes.



Figure 5-10. Transmittance as a function of applied voltage for the PDLC devices constructed by conducting polymer thin film and ITO as electrodes.


Chapter 6

Polymer Dispersed Liquid Crystal Film for Variable-transparency Glazing

6-1 Introduction

The market for electrically switchable glazing based on chromogenic technologies is ever-expanding, and now covers architectural, automotive, aircraft and information displays [1-17]. Common examples of electrically switchable glazing technologies are polymer-dispersed liquid crystal (PDLC), suspended-particle and electrochromic devices. Among chromogenic glazing systems, PDLC has been most widely used in architectural and automotive applications due to its relatively simple manufacturing process, good optical properties, and excellent long-term durability.

PDLC films, which are composed of liquid crystal microdroplets dispersed in a polymer matrix, have been the subject of much academic and industrial research in the past decades. These electro-optical systems can be switched by applying an electric field from a scattering OFF state to a transparent ON state. There are essentially two technologies to make PDLC films with liquid crystal microdroplet dispersions, namely emulsion and phase separation methods. The emulsion method begins with the emulsification of the liquid crystal into an aqueous solution of a film forming polymer. This emulsion is coated onto a conductive substrate and allowed to dry. As the film dries, the polymer forms a solid phase. Lamination of a second conductive substrate leads to the final PDLC film [18-19]. In the phase separation method, a homogeneous solution of liquid crystal and prepolymer is coated and laminated between two conductive substrates. The separation of liquid crystal microdroplets occurs during the curing of the prepolymer

[20-23]. On the industrial aspect, the photopolymerization-induced phase separation (PIPS) method is preferred and versatile. The PIPS method is faster and easier than the emulsion method for roll to roll processing because the emulsion method includes water evaporation and drying process, which requires much time. Another advantage of PIPS method is that it is possible to control the microdroplet morphology and the electro-optical performance of PDLC film by optimizing materials and process parameters [24-28].

The PDLC films and PDLC laminated glass have been supplied to the architectural and automotive markets since 1990s. which have been progressively developed to improve the optical performance and reduce the cost to meet market demands. The important characteristics of switchable glazing are the visible-light contrast between translucent and clear states, the corresponding modulation of thermal energy, low haze over a wide-viewing angle in clear state, and the long-term durability. Recently large-area PDLC films up to 1.25 m x 3.5m with a high uniformity have been developed and available in the market. In this paper, we will investigate the electro-optical properties, temperature stability, and durability of the commercial PDLC film and PDLC laminated glass products. It would provide the understanding of the current status of the commercial PDLC products and further development required in PDLC technologies.

6-2 Experimental

6-2-1 Sample Preparation

The investigated PDLC film and laminated glass samples were commercial products manufactured by Q-Sys. The samples had dimensions of 20 cm x 20 cm. PDLC films were manufactured based on photo-polymerization induced phase separation (PIPS) process. A homogeneous mixture of prepolymers and liquid crystals was coated between two ITO-coated polyester films by precision

coating, laminating, and UV curing. PDLC glass was made by laminating the PDLC film between two clear 3.0-mm-thick glass plates using 0.25-mm-thick EVA interlayer.

6-2-2 Optical Measurements

Parallel light transmittance at 550nm is measured by an experimental set-up comprising a halogen lamp (Avalight-HAL, Avantes), CCD detector (Avaspec 2048, Avantes) and rotating sample stage. Light transmittance in the range of ultraviolet (200~400nm), visible (400~800nm), near infra-red (800~2000nm) bands was measured by spectrometer (Cary500Scan, Varian). The total transmittance and haze values were measured in the range of wavelength 400~800nm by spectrophotometer (CM-3500d, Konica Minolta) equipped with the integrated sphere.

6-2-3 Durability

The electrical durability was evaluated by the haze value of PDLC film during 3 million cycles of switching with a switching interval of 1 sec and an applied voltage 100VAC at 60 Hz.

The durability to UV light was tested based on the color difference (ΔE) of the samples in a QUV weatherometer (Q-Panel Lab Products). The samples were subjected to UV ageing by exposure to fluorescent UV lamps (UVB-313) under wet-cycle conditions: 8h of UV irradiation at 70°C, followed by 4h of dark condensation at 50°C for up to 2000h. The UV light intensity was 0.6W/cm2 at 313nm. The color indices (L^* , a^* , b^*) were measured with a spectrophotometer (CM-3500d, Konica Minolta). The color difference (ΔE) value was calculated by equation (5-1)

$$\Delta E = \sqrt{(L^* - L_o^*)^2 + (a^* - a_o^*)^2 + (b^* - b_o^*)^2}$$
(5-1)

6-3 Results and Discussions

Figure 6-1 shows the light transmittance of PDLC film and laminated glass samples as a function of the applied voltage. The transmittance of the PDLC film sample in OFF state was 0.6% at 550nm, and gradually increases up to 73% with applied voltage, peaking at about 40V for the small samples used. Note that the operation voltage is proportional to the area of PDLC film, but is still only 100VAC for the largest commercial PDLC film (125cm x 350cm). The electro-optical behaviour of the PDLC laminated glass was the same as that for PDLC film except for the maximum transmittance being lower (67%) due to the absorption of incident light by and residual haze by EVA interlayer.

Figure 6-2 shows the haze and total transmittance of PDLC glass sample as a function of applied voltage as measured by a spectrophotometer with integrated sphere. The haze changed markedly from 90% in OFF state to 9% in ON state, whereas the total transmittance changed only from 65% to 80%, respectively. This is due to the nature of light modulation by PDLC technology: the scattering of incident light by the PDLC film results inthe total amount of light passing through the film being very similar for the scattering and cleat states.

In large-area applications, the light passing through the film is observed over a wide range of angles, with the scattering increasing with the viewing angle due to an increase in the effective refractive index of liquid crystals in the droplets. Figure 6-3 shows the transmittance of the film in the ON state at different viewing angles. Although the off-axis transmittance gradually decreased with increasing viewing angle, the PDLC film exhibited a relatively wide viewing angle (65° for half the maximum

transmittance). The off-axis haze can be reduced by using liquid crystal materials with a low birefringence, but this also reduces the scattering (haze) in the OFF state. It is therefore important to determine the optimal trade-off between the haze in the OFF state and the off-axis haze in the ON state.[29-31]

It would be useful if PDLC glass could modulate the transmittance of thermal energy as well as visible light. Figure 6-4 shows the transmittance spectra of the PDLC glass sample over UV, visible and NIR bands. The transmittance values obtained by integrating the spectra in each band are listed in Table 1. Energy in the UV band is completely blocked both in the OFF and ON states by the EVA interlayer, while the visible band is markedly modulated (change of transmittance \approx 50%) by PDLC layer, and the NIR band is affected less (change in transmittance \approx 25%). The change in the NIR band can be increased by adjusting the droplet size and using liquid crystal materials with a high birefringence. [32] However, the extent of the change is small, and the optical performance in the visible band is markedly deteriorated, which is significant given that the modulation performance in visible band is more important than that in the other bands.

Figure 6-5 shows the transmittance changes in OFF and ON states as functions of temperature. The haziness at OFF state decreased from 60°C, and the clarity transmittance in the ON state decreased rapidly from 0°C, with the film not becoming clear at temperatures below -20°C.

Finally, we investigated the durability to electrical switching and UV. The haze values in the ON and OFF states in the cycling of switching are shown in Figure 6-6, which indicates that the PDLC film exhibited excellent stability to electrical switching. The changes in color difference and haze in the OFF state of the film and glass samples during the QUV cycling test are shown in Figure 6-7. While the film sample rapidly yellowed and the haze in the OFF state was markedly decreased due to the degradation of liquid crystal molecules by UV exposure, the glass sample exhibited excellent

durability to UV exposure. These results indicatethat the complete block of the UV light by the EVA interlayer in the glass sample protected the PDLC film.

6-4 Summary

The optical properties, thermal stability, and durability of this commercial PDLC film and laminated glass were investigated. The OFF haze and ON clarity were optimized to meet the market needs of privacy and clarity, respectively. The PDLC glass blocks 98% of UV, modulates the NIR band in the range 12~38%, and exhibits good temperature stability from 0°C to 60°C. However, the temperature stability should be extended for exterior architectural and automotive applications. The PDLC film exhibits excellent durability to electrical switching up to 3 million times. While the PDLC is sensitive to UV, the PDLC glass exhibited excellent durability to UV due to the protection provided by the interlayer film, which shows the PDLC products can be used for architectural applications.

6-5. References

[1] S. Park, J.W. Hong, Thin Solid Films, 2009, 517, 3183-3186

[2] C.M. Lampert, Proc. SPIE, 2001, 4458, 95-102

[3] C.M. Lampert, Sol. Energy. Mater. Sol. Cells, 2003, 76, 489

[4] C.M. Lampert, *Material Today*, **2004**, *28*, 28

[5] A. Matthai, B. Sepeur-Zeits, F. Horstmann, J. Schutz, 6th InternationalConference on Coatings on Glass and Plastics, Dresden, Germany, June 18-22, 2006, 39

[6] G. Macrelli, Sol. Energy. Mater. Sol. Cells, 1995, 39, 123-131

[7] J.M.S. Pena, C. Vazquez, I.Perez, I. Rodriguez, J.M. Oton, Opt. Eng., 2002, 41(7), 1608-1611

[8] D. Cupelli, F.P. Nicoletta, S. Manfredi, G.D. Filpo, G. Chidichimo, Sol. Energy. Mater. Sol. Cells, 2009, 93, 329-333

[9] L. Li, J.F. Li, S. Faris, US Patent No. 6,897,936 May 24 (2005)

[10] C.W. McLaughlin, P. Drzaic, S. Marsland, US Patent No. 4,749,261 Jun 7 (1988)

[11] P.V. Konynenburg, S. Marsland, J. McCoy, Sol. Energy. Mater., 1989, 19, 27

[12] P.V. Konynenburg, R. Wipler, J.L. Smith, Proc. SPIE, 1989, 1080, 62

[13] P.S. Drzaic, A.M. Gonzales, P.V. Konynenburg, *Proc. SPIE*, **1994**, *2175*, 148

[14] J.A. Check, US Patent No. 5,463,491, Oct 31 (1995)

[15] M. Rottmann, A. Kraft, *6th International Conference on Coatings on Glass and Plastics,* Dresden, Germany, June 18-22, **2006**, 457

[16] J.H. Day, R.D. Willett, SPIE Opt. Eng. Press, Bellingham, WA, 1990, 122
[17] G.P. Cronin, T.J. Gudgel, S.R. Kennedy, A. Agrawal, D.R. Uhlmann, Mater. Res., 1999, 2, 1

[18] J.L. Fergason, US Patent No. 4,435,047, Mar 06 (1984)

[19] P.S. Drzaic, J. Appl. Phys., 1986, 60, 2142

[20] J.W. Doane, N.A. Vaz, B.G. Wu, S. Zumer, Appl. Phys. Lett. 1986, 48,

269 [21] N.A. Vaz, G.W. Smith, G.P. Montgomery, Mol. Cryst. Liq. Cryst., 1987, *146*. 17 [22] N. Vaz, G.W. Smith, G.P. Montgomery, Mol. Cryst. Lig. Cryst., 1987, *146*. 1 [23] N.A. Vaz, G.W. Smith, US Patent No. 4,728,547 Mar 1 (1988) [24] J.D. LeGrange, S.A. Carter, M. Fuentes, J. Boo, A.E. Freeny, W. Cleveland, T.M. Miller, *J. Appl. Phys.*, **1997**, *81(9)*, 5984-5991 [25] H. Fujikake, K. Takizawa, H. Kikuchi, T. Fujii, Jpn. J. Appl. Phys., **1998**, *37*, 895-899 [26] E. Nastal, E. Zuranska, M. Mucha, *J. Appl. Polym. Sci.*, **1999**, *71*, 455-463 [27] W.S. Park, K.S. Choi, J. Kor. Phys. Soc., 1999, 34(3), 231-236 [28] J.W. Han, T.J. Kang, G. Park, J. Kor. Phys. Soc., 2000, 36(3), 156-163 [29] P. Nolan, M. Tillin, D. Coates, *Lig. Cryst.*, **1993**, *14(2)*, 339-344 [30] S. Pane, M. Carprusso, H. Hakemi, *Lig. Cryst.*, **1997**, *23(6)*, 861–867 [31] P.S. Drzaic, A.M. Gonzales, P.V. Konynenberg, SPIE, **1994**, 2175, 148-157 [32] L. McKenna, L.S. Miller, I.R. Peterson, *Polymer*, **2004**, *45*, 6977



Table 6-1. Normal-normal transmittance values of the PDLC laminated glass in UV, visible and NIR portions. The values were calculated by integrating the spectra in each portions of Figure 6-4.

	UV	Visible	NIR
OFF	0.1	6.1	12.9
ON	1.8	62.0	38.4



Figure 6-1. Normal-normal spectral transmittance (at 500nm, room temperature) of PDLC film and laminated glass as a function of applied voltage.



Figure 6-2. Haze and normal-hemispherical transmittance of PDLC laminated glass as a function of applied voltage.



Figure 6-3. Normal-angular spectral transmittance of PDLC film at ON state. The applied voltage is 50AVC, 60Hz.



Figure 6-4. Normal-normal transmission spectra of PDLC laminated glass at OFF and ON state. The applied voltage at ON state is 50VAC, 60Hz.



Figure 6-5. Dependence of normal-normal transmittance (λ =550nm) of PDLC glass on temperature. The applied voltage at ON state is 50VAC, 60Hz.



Figure 6-6. The change of haze value during the electrical switching cycles. The ON state haze is measured at 50VAC, 60Hz. The switching interval of OFF and ON state is 1 sec and the applied voltage at ON state is 100VAC, 60Hz.



Figure 6-7. Durability to UV exposure of PDLC film and laminated glass. (a) color difference and (b) haze at OFF state on the cycling time in QUV. The UV cycling condition is composed of UV irradiation at 70°C for 8h, followed by dark condensation at 50°C for 4h.

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