Preparation of Polymer-Dispersed Liquid Crystal Films Containing a Small Amount of Liquid Crystalline Polymer and Their Properties

NO-HYUNG PARK,[1] SEONG-A CHO,[1] JU-YOUNG KIM,[2] KYUNG-DO SUH[1]

[1] Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul 1330791, Korea

[2] Department of Material Engineering, Samchok National University, Kangwon 245-711, Korea

ABSTRACT: Polymer-dispersed liquid crystal (PDLC) films were synthesized by the copolymerization of liquid crystalline polymer (LCP) precursor, urethane acrylate (UA), and mesogenic monomer (AI) at different conditions. The morphology of polymer matrix changed with the weight ratio of polymer/liquid crystal (LC) ratio and curing temperature, resulting in a large change in the droplet size of LC domains in the PDLC film. The components used in the synthesis of polymer matrix, that is, the weight ratio of LCP, AI, and UA, also strongly influenced the morphology of PDLC films. A small amount of LCP was copolymerized with UA and AI in the preparation of polymer matrix to improve the electrooptical properties such as the viewing angle. Added LCP also affected the morphology and the properties of PDLC. The hydrophobicity of LCP caused changes in the droplet size of LC domain in PDLC films and the anchoring energy between matrix polymer and LC droplets. As the hydrophobicity of the matrix increases, the droplet size of LC domain also increases; on the contrary, anchoring energy decreased, leading to the decrease of driving voltage. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3178–3188, 2000

Key words: polymer-dispersed liquid crystal (PDLC); haze-free; UV-curing; liquid crystalline polymer (LCP); diffusion

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films,[1] which consist of micron-sized droplets of liquid crystal (LC) dispersion and polymer matrix, are specialized materials for electrooptic devices. The principle of PDLC operation is based on field-controlled light scattering from nematic microdroplets. When an electric field is applied to PDLC film, refractive index[2-4] between the aligned LC along the direction of electric field and polymer matrix is matched, which causes a change to the film from the opaque state to the transparent state. Because of the dependence of PDLC on electric field, such films can be applied to projection display and privacy windows, etc.[1-4] Electrooptical properties of PDLC film depend on several factors, such as the shape and the droplet size of LC domains in PDLC, the amount of diffused liquid crystal in the matrix polymer, and so on. Therefore, selecting an optimal polymer matrix for PDLC has a large impact on its optical performance.

One of the major problems in PDLC films is haze phenomenon.[5-7] Haze phenomenon is accurately defined as the angular dependence of light scattering in on-state due to mismatching between the extraordinary refractive index of the
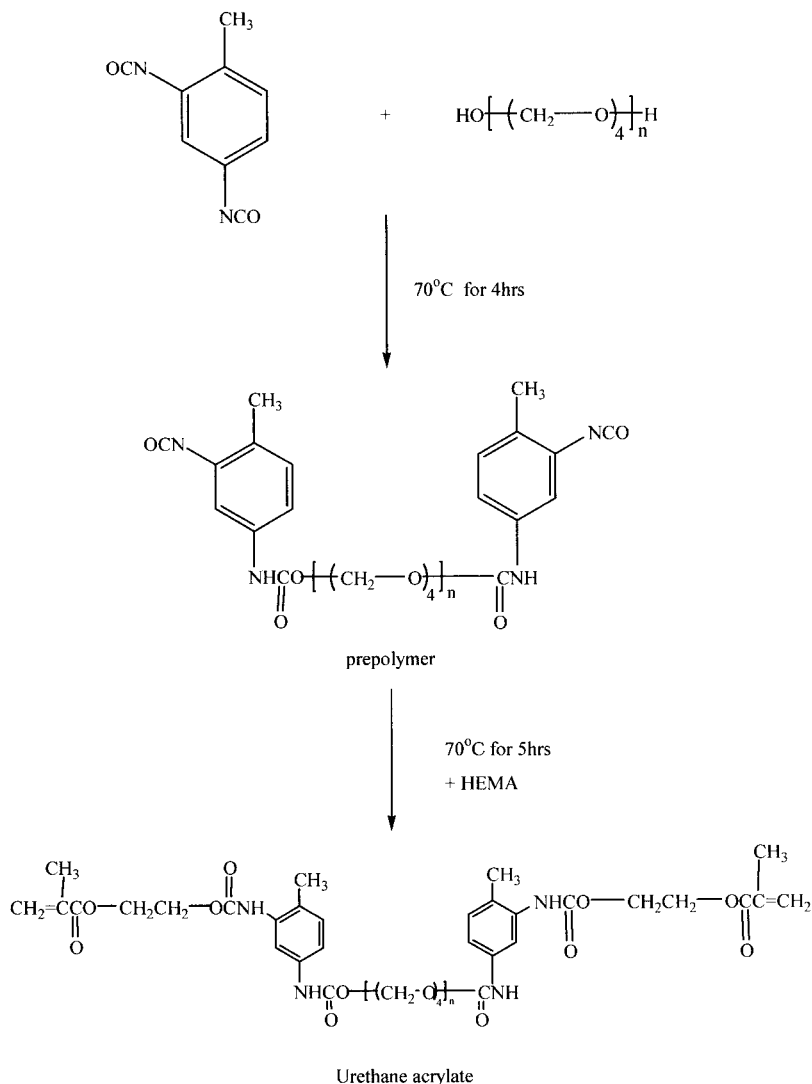
Scheme 1   Schematic representation of synthesis of urethane acrylate (UA) and its proposed molecular structure.

oriented LC molecules and the refractive index of polymer matrix. Means for overcoming haze phenomenon have been investigated and several methods have been reported.[5] In our study, conventional isotropic polymers containing small amounts of mesogenic polymer are used to overcome the haze phenomenon, instead of using an isotropic polymer matrix. It has been reported that the use of side-chain liquid crystalline polymer (LCP) as a matrix of PDLC film can improve driving voltage, switching time, haze properties, and so on.[5,6] Several research groups reported on the LCP as matrix polymer for preparation of PDLC films. Chien et al.[6] reported on the synthesis and the characterization of mesogenic amine

and epoxy liquid crystal polymer. They showed the application of liquid crystalline epoxy polymers for PDLC. However, the materials used for preparing PDLC films in this demonstration confirmed the need for improvement to get useful commercial devices. Also, Carfagna et al.[7] utilized main-chain type liquid crystalline epoxy resins as matrix polymer of PDLC film. The use of LCP as a matrix polymer improved physical properties as well as electrooptical properties of PDLC; high T_g, low driving voltage, and fast switching time were found. Generally, LCPs of matrix polymer for PDLC film must be homeotropically aligned to give the character of haze-free PDLC. Unlike the aligning process of LCP, which is a very compli-

cated and difficult process, the LC molecules within LC elastomer matrix can be aligned easily by weak shear.

In this study, we will present the synthesis of copolymers based on LCP precursor, urethane acrylate, and acrylic acid and use of the copolymers obtained as matrix polymer of PDLC. All PDLC cells used in this work were prepared by the polymerization-induced phase separation (PIPS) method using UV irradiation. Also, we shall represent the effect of LCP content used in the synthesis of matrix, curing temperature, and spacer length of LCP. We shall present the morphology of PDLC films measured by using the contact method[8] and electrooptical properties, especially angular dependence.

EXPERIMENTAL

Materials

In the synthesis of urethane acrylate, poly(tetramethylene glycol) (PTMG, M_w = 1000, Hyosung BASF, Korea) was used after drying and degassing at 80°C for 1 day. 2,4-Toluene diisocyanate (TDI, TCI Chemicals, Japan) was purified by filtration and 2-hydroxyethyl methacrylate (HEMA, Aldrich Chemicals, USA) was used as received. For the preparation of mesogenic monomers, 4-anisaldehyde (Junsei Chemicals, Japan), 4-aminophenol (Wako Pure Chemicals, Japan), potassium carbonate (K$_2$CO$_3$, Yakuri Chemicals, USA), and dichloroalkanes (Aldrich Chemicals) were used without further purification. Methanol (MeOH, Duksan Chemicals, Korea), chloroform (Samchun Chemicals, Korea), and N-methyl-2-pyrrolidone (NMP, Samchun Chemicals, Korea) were used as solvent. E7 (Merck Co., Germany) was used as the low-molecular-weight LC, which is composed of cyanobiphenyls and cyanoterphenyl mixture. Irgacure 651 was used as photo initiator to cure the PDLC cells.

Synthesis of Matrix Materials

Urethane acrylate (UA) was synthesized through a two-step process. TDI was charged into a 500-mL four-necked kettle with a reflux condenser, a thermometer, a mechanical stirrer, and an inlet system for nitrogen gas. Then, PTMG was poured into the reactor and reacted for 5 h at 70°C to synthesize the NCO isocyanate group-terminated prepolymer. Reactant was then cooled

to room temperature and HEMA was added and reacted with prepolymer for 4 h at 70°C. The proposed chemical structure is illustrated in **Scheme 1**.
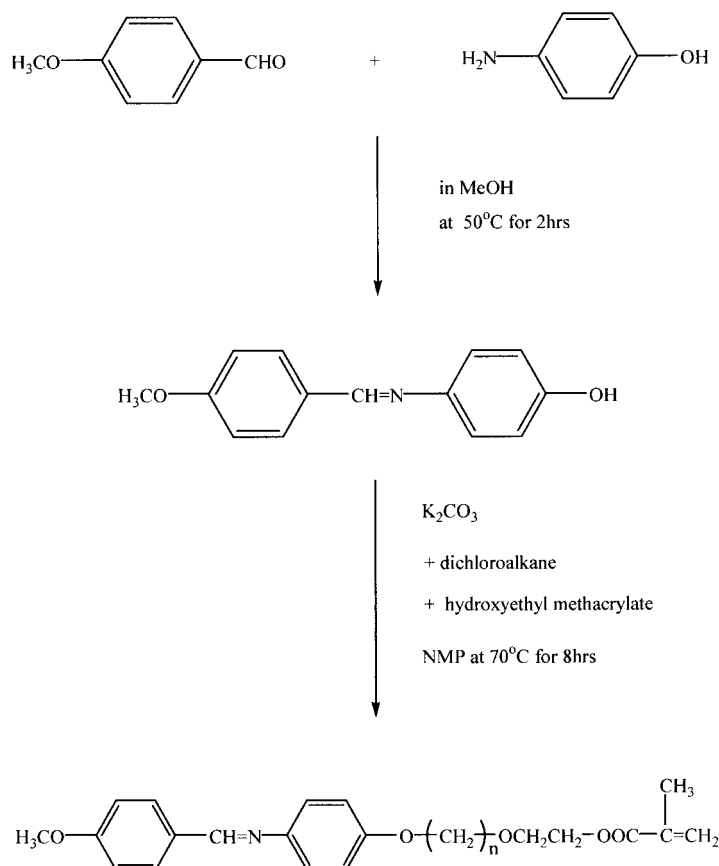
For the synthesis of the mesogenic monomer (AI) having different spacer lengths, 4-anisaldehyde and 4-aminophenol were reacted for 2 h at 50°C in MeOH. Precipitate was filtered and dried at 80°C overnight. Finally, 4-hydroxy-N-(4-methoxybenzylidene)-aniline (light-brownish powder, yield: 85%) was obtained. The product was dissolved in NMP and reacted with dichloroethane, dichloropropane, dichlorobutane, and dichloropentane for 4 h at 50°C in the presence of K$_2$CO$_3$, respectively. Successively, HEMA was added and reacted for 5 h at 70°C to introduce reactive vinyl group. The AI solution obtained was precipitated in water, and the precipitate was then filtered and dried at ambient temperature. In this process, AIs containing different spacer length are designated as AI2, AI3, AI4, and AI5, respectively. Overall reaction scheme is illustrated in **Scheme 2.**

Preparation of PDLC Films

UA, AI series, and acrylic acid were copolymerized and used as matrix polymer for PDLC film. We expect that UA in matrix polymer supports the PDLC films, AI gives functionality for improving the viewing angle and acrylic acid is used as solvent for AI and diluent of UA. Three weight percent of Irgacure 651 is added and used as a UV-curing initiator. For the preparation of PDLC films, various amounts of E7 were vigorously mixed with the mixture of UA, AI, and acrylic acid above T_{NI} of E7 (65°C) and coated onto ITO-coated glass. The cell was prepared by using a 5.3-μm PET film spacer to adjust the film thickness exactly. Finally, UV curing[9] was carried out at various temperatures for 5 min. Table I shows the recipe for the preparation of PDLC in detail.

Measurements

To investigate the affinity between LC and matrix polymers, contact angles were measured by using contact angle goniometer (Erma contact angle meter, model, G-1). The morphology of PDLC films was observed by a scanning electron microscope (SEM, Hitachi S-3200N) and Olympus BH-2 polarized optical microscope. To determine the diffused amount of LC in matrix polymer, a DSC (Perkin–Elmer DSC-7) was measured with a

Scheme 2 Schematic representation of synthesis of mesogenic monomer (AI) and its proposed molecular structure.

5°C/min heating rate. An IR spectroscope (Nicolet Magna IR 760) was used to investigate the diffusion of LC into matrix polymer. For examining the electrooptical properties of PDLC films, a 200-Hz square wave was applied for all samples. The transmitted light intensity was measured as a function of the applied rms voltage by using an EG & G model 550–2 probe with a mode 550–1 photometer. A silicon photocell was used to detect the pulsed transmitted light intensity for a transient response. The voltage pulse and optical response were monitored on a Tektronix 2430 digital scope and the results were plotted on a HP 7004B X-Y recorder.

RESULTS AND DISCUSSION

To investigate the affinity between matrix polymer and low-molecular-weight LC, the contact angle[10] was measured. UV-cured matrix polymers having different spacer length were pre-

pared to examine the effect of the spacer length of matrix polymer on affinity between LC and matrix polymer. For the preparation of matrix polymer, AI having different spacer lengths was polymerized with UA and acrylic acid. The weight ratio of AI/UA/acrylic acid was fixed at 0.01/1/0.5. A drop of E7 was placed on each film and the contact angle was measured. The results for contact angle measurement are illustrated in Figure 1.

It has been reported that the contact angles of conventional PDLC films are in general >60°.[11] However, the contact angle of our samples is <30°, indicating relatively high affinity between matrix polymer and low-molecular-weight LC. This can be interpreted as due to the hydrophilicity of acrylic acid used in the preparation of matrix polymer. Also, it can be predicted that the driving voltage applied for our PDLC film will be relatively high, because high affinity between matrix polymer and LC is detrimental to alignment of LC within PDLC matrix. As the spacer length

Table I Recipe for PDLC Preparation

Symbols	AI	UA	Acrylic Acid	E7[a]
AUA2[b]	0.01 (AI2)[c]	1	0.5	3.775
AUA3	0.01 (AI3)	1	0.5	3.775
AUA4	0.01 (AI4)	1	0.5	3.775
AUA5	0.01 (AI5)	1	0.5	3.775
AUA5-1	0 (AI5)	1	0.5	3.750
AUA5-2	0.005 (AI5)	1	0.5	3.763
AUA5-4	0.015 (AI5)	1	0.5	3.788
AUA5-5	0.020 (AI5)	1	0.5	3.800
AUAL1	0.01 (AI1)	1	0.5	1.151
AUAL2	0.01 (AI1)	1	0.5	3.620
AUAL3	0.01 (AI1)	1	0.5	4.53

[a] Unit : weight ratio.
[b] AUAx : x is chain length of AI.
[c] AIy : y is chain length of alkyl group in AI.

in AI increases, the contact angle of LC also increases, indicating that affinity between matrix polymer and LC decreases. Because E7 shows relatively high hydrophilicity, the increase of contact angle indicates that the hydrophobicity of matrix polymer increases with the increase of spacer length.

The contact angle can be related to anchoring energy at the polymer/LC interface. This relation is described by following two equations[12]

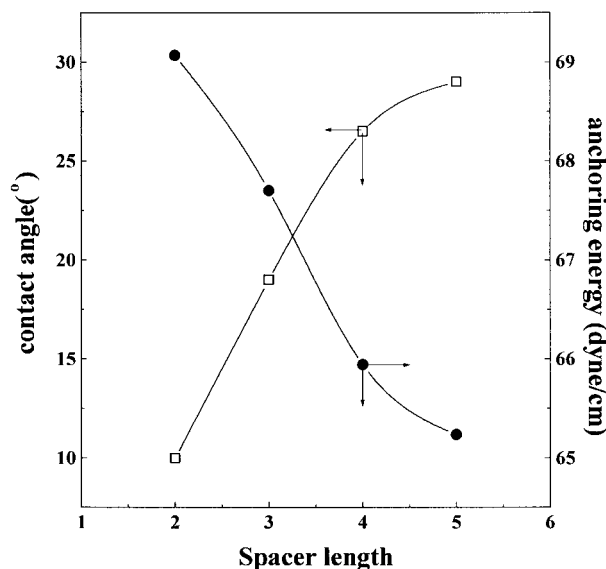$$\gamma_S - \gamma_{SL} = \gamma_L \cos \alpha$$

Figure 1 Contact angle measurement and anchoring energy versus the chain length of alkyl group in PDLC. (-■-): contact angle; (-●-): anchoring energy.
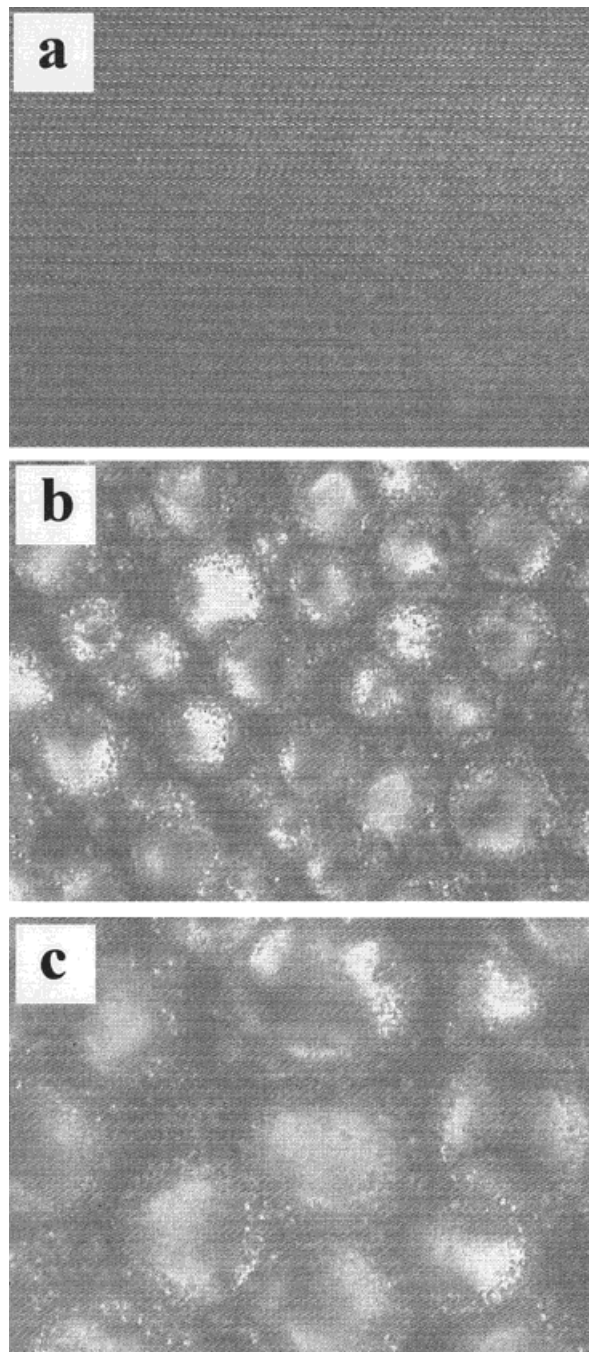

Figure 2 Polarized optical microscope photographs with the weight ratio of polymer/LC: (a) AUAL1; (b) AUA2; (c) AUAL3.

$$W_A = \gamma_S + \gamma_L - \gamma_{SL} = \gamma_L(1 + \cos \alpha)$$

Here, γ_S, γ_L, and γ_{SL} are the surface tension of solid and liquid and the interfacial tension between liquid and solid, respectively. α is the contact angle and W_A means anchoring energy be-
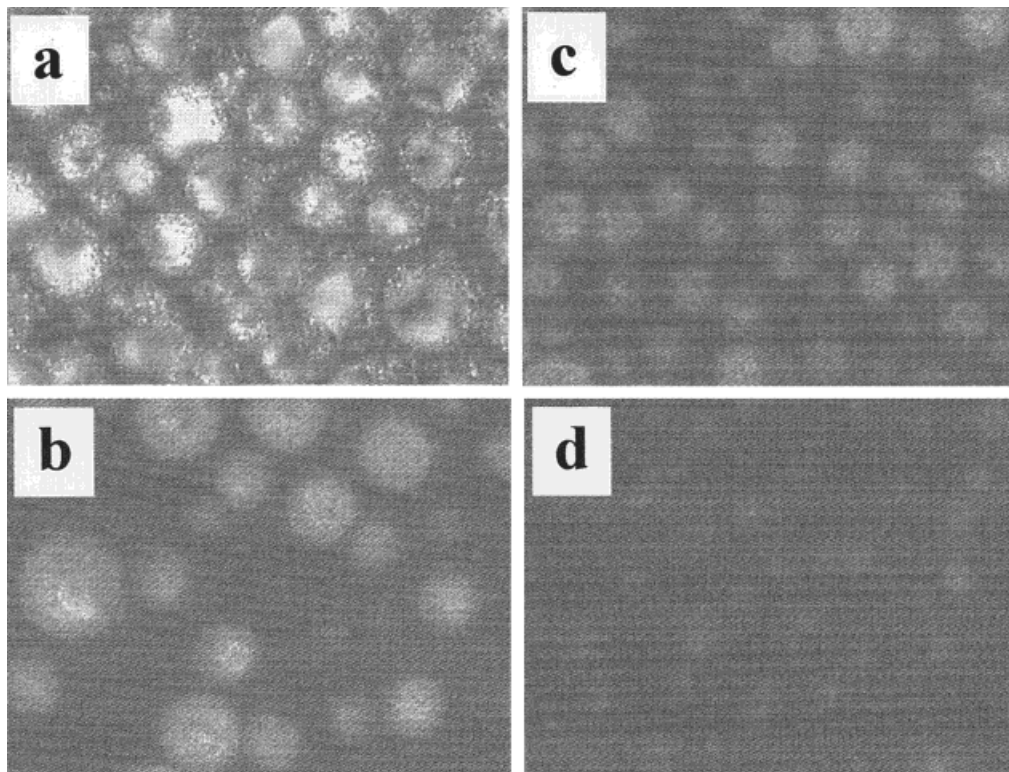
Figure 3 Polarized optical microscope photographs versus curing temperature: (a) 25°C; (b) 40°C; (c) 45°C; (d) 65°C.

tween polymer/LC. By using these equations, anchoring energy can be plotted in Figure 1. As affinity between matrix polymer and LC increases, the anchoring energy of polymer/LC interface increases as well. It is well known that anchoring energy influences the electrooptical properties such as threshold voltage. High anchoring energy makes it difficult to align low-molecular-weight LC in PDLC film when electric field is applied. That is, a larger electric field is required to align LC in the matrix, leading to the increase of threshold voltage. So, it can be expected that the threshold voltage of our samples will increase with the decrease in the spacer length of AI used in the preparation of PDLC matrix polymer.

To establish conditions for the preparation of PDLC cells, PDLC cells were manufactured at various polymer/LC ratios and curing temperatures.[13] The effects of temperature were investigated at AUA4 sample. The results are shown in Figures 2 and 3.

In Figure 2, the droplet size of LC domain in matrix increases with the increase of LC content in PDLC film. When the weight ratio of polymer

to LC is below 1/2.5, macroscopically homogeneous PDLC samples could be obtained. Figure 3 represents the change in droplet size of LC domains in PDLC films prepared at different curing temperatures. Droplet size of LC domains decreases with the increase of the curing temperature, which can be interpreted as due to the polymerization rate. In other words, the degree of PIPS and the growth of LC domains by diffusion and coalescence[14] are strongly hindered by the higher rate of polymerization at higher temperature, leading to the decrease in droplet size of LC domains dispersed in matrix. LC domains could not be observed by polarized optical microscope above T_{NI}. It is known that the range of droplet size is 2–3 μm to obtain the best electrooptical properties of PDLC films.[1–4] In our system, we can tentatively conclude that the optimal weight ratio of polymer/LC is the 1/2.5 and the optimal curing temperature is 45°C for the preparation of PDLC films. Thus, all tests were conducted at this condition.[15,16]

Figure 4 shows the morphology of PDLC having different spacer lengths, examined by SEM.
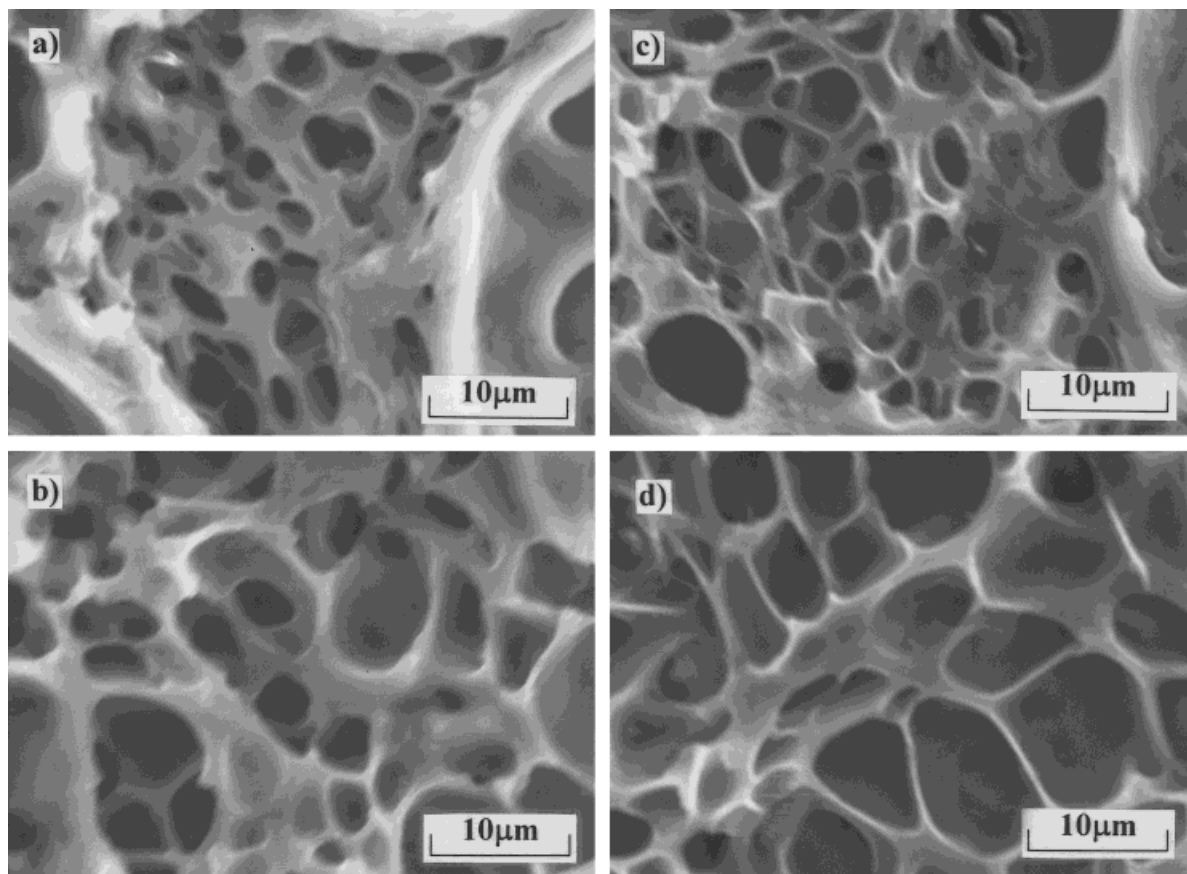

Figure 4 SEM photographs of PDLC samples prepared with different AI: (a) AUA2; (b) AUA3; (c) AUA4; (d) AUA5.

Samples for the measurement of SEM were prepared by the extraction of low-molecular-weight LC in PDLC films with chloroform for 1 h. As spacer length in AI increases (from AUA2 to AUA5), the droplet size of LC dispersed in matrix polymer increases due to the decrease of affinity between LC and matrix polymer, as shown in Figure 1. AUA2 shows the smallest size of LC domains, approximately 2 μm. It can be expected that PDLC films prepared by using AI2 show the best electrooptical properties of PDLC films in our condition.

To evaluate the effect of the added amount of AI5 on the morphology of PDLC films, the morphology of AUA5 prepared with different amounts of AI5 was examined. Results are represented in Figure 5. As the amount of AI5 content in the preparation of PDLC films increases, the droplet size of LC domains in PDLC matrix increases due to the increase of hydrophobicity of matrix polymer. The five PDLC experiments discussed above indicate that curing condition and

components of matrix polymer influence the final morphology and properties of PDLC films.

Thermal properties of PDLC films, having different spacer length, were also investigated by using DSC thermograms and are illustrated in Figure 6.

The T_{NI} of pure LC is 57.15°C and the enthalpy change at transition temperature is 1.149 J/g. However, LC in PDLC films shows different results from those observed with pure LC. T_{NI} of LC in PDLC films decreases, because anchoring the polymer/LC boundary stimulates the transition of LC from nematic to isotropic phase. In this work, as the spacer length of AI increases, the orientation of AI molecules at polymer/LC interface increases, which leads to a decrease of the T_{NI} of LC in PDLC films. However, the enthalpy change at T_{NI} increases with the increase in spacer length of AI. This can be interpreted as due to the decrease in the amount of dissolved LC in PDLC films. Generally, it is reported that a small amount of low-molecular-weight LC is dissolved in matrix
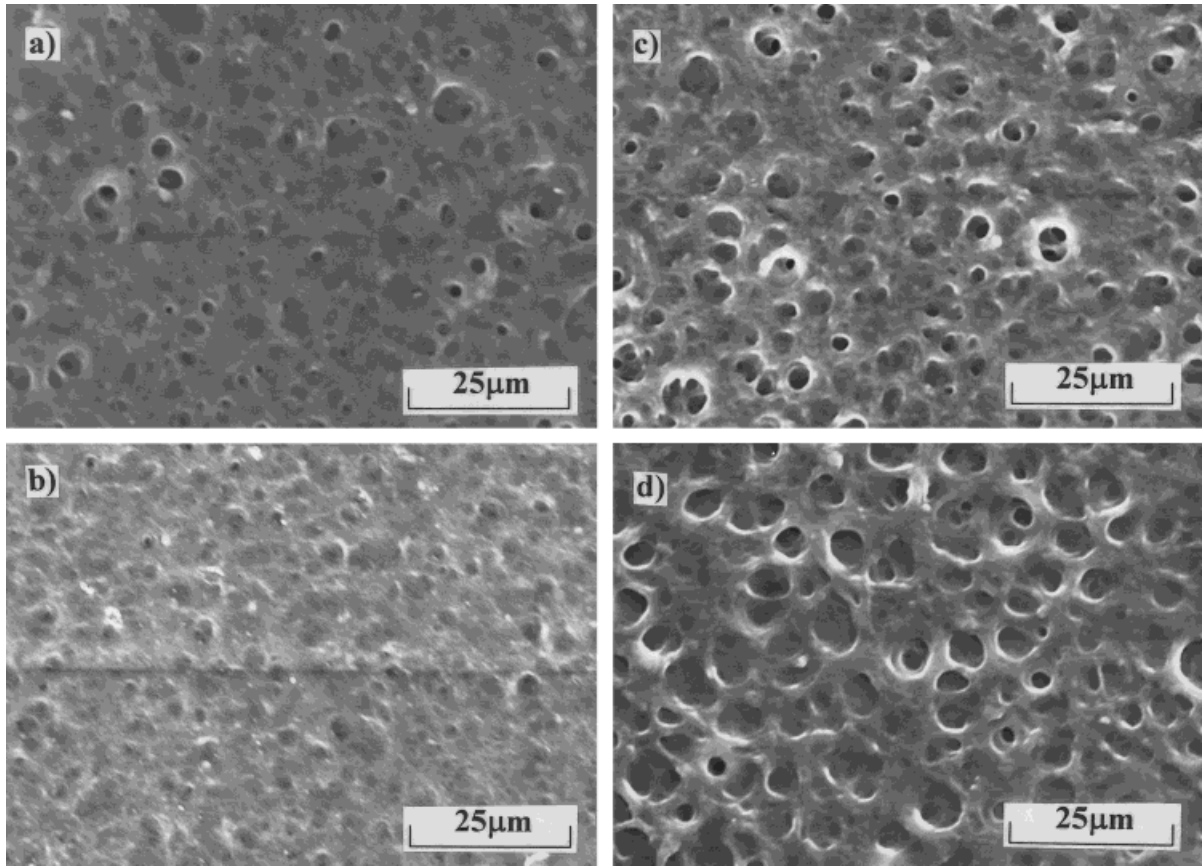
Figure 5   SEM photographs of PDLC prepared with different added amounts of AI: (a) AUA5–1; (b) AUA5–2; (c) AUA5–4; (d) AUA5–5.

polymer, and dissolved LC has an influence on the thermal properties and electrooptical properties of PDLC films. Dissolved LC also affects the local refractive index of matrix polymer, so that it will be difficult to match refractive index between matrix polymer and low-molecular-weight LC domains. The criteria for this phenomenon can be estimated by the following equations[17]

$$\alpha = \frac{\Delta H_{NI(obs)}}{\chi \Delta H_{NI(LC)}}$$

$$\chi = \frac{m_P}{m_{LC} + m_P}$$

where α is the amount of low-molecular-weight LC in LC droplet, $\Delta H_{NI(obs)}$ and $\Delta_{NI(LC)}$ are observed transition enthalpy and transition enthalpy of pure LC, respectively, m_P, m_{LC}, and χ are the weight of polymer and LC in PDLC film and weight fraction of polymer matrix in PDLC
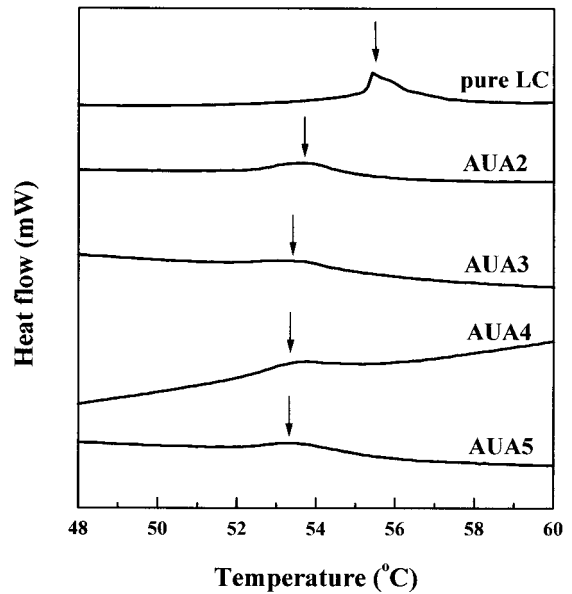

Figure 6   DSC thermograms of pure LC and PDLC samples.

Table II   Results of DSC Thermograms of Pure LC and PDLCs

Samples	T_{NI} (°C)	ΔH (J/g)	α
LC	57.15	1.149	—
AUA2	55.42	0.68	2.071
AUA3	55.35	0.698	2.126
AUA4	55.1	0.725	2.208
AUA5	55.06	0.791	2.409

film, respectively. DSC results for PDLC samples are represented in Table II.

As spacer length of AI increases in the PDLC formulation, the amount of dissolved LC in the matrix polymer decreases. That is, AUA5 prepared with the use of AI5 in the PDLC preparation exhibits a larger amount of low-molecular weight LC in LC droplet than other AUA samples. Thermal properties of PDLCs can be interpreted as due to the increase of affinity between matrix polymer and LC. So, we tentatively concluded that affinity affects the morphology of final films by controlling the diffusion and coalescence.

The diffusion of LC into polymer was tested by a contact method.[8] First, the mixtures of UA, AI series, and acrylic acid were polymerized through UV irradiation at the weight ratio of 1/0.01/0.5. Low-molecular-weight LC was brought into contact with the matrix polymer to form a polymer/LC interface. They were placed in a convection oven at 60°C for 1 day to allow LC to diffuse into the matrix polymer. As the spacer length of

AI increases, the hydrophilicity of matrix polymer decreases, leading to the decrease in the diffusion distance. FTIR spectroscopy was used to verify the diffusion distance, and FTIR charts are illustrated in Figure 7.

As the diffusion distance from LC phase to polymer phase increases, the characteristic peak of E7 around 2500 cm^{-1} (—CN peak) decreases, indicating that LC is diffused into polymer phase. The diffusion of LC into matrix polymer can be confirmed by the characteristic peaks of LC, and the relative amount of LC diffusion is determined by the ratio of intensity of a characteristic peak in PDLC to the intensity of pure LC. It is generally known that the diffusion of low-molecular components into polymer obeys the second Fick's rule.[18,19] The above results fit the following equations:

$$\frac{A}{A_0} = \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$\text{erf } x = \frac{2}{\sqrt{\pi} \displaystyle\int_0^x e^{t^2}\, dt}$$

where A and A_0 are the intensities of characteristic peaks in the diffusion region and in pure LC. D is the diffusion coefficient and t indicates diffusion time. Our system follows the second Fick's rule, and the results are shown in Figure 8.
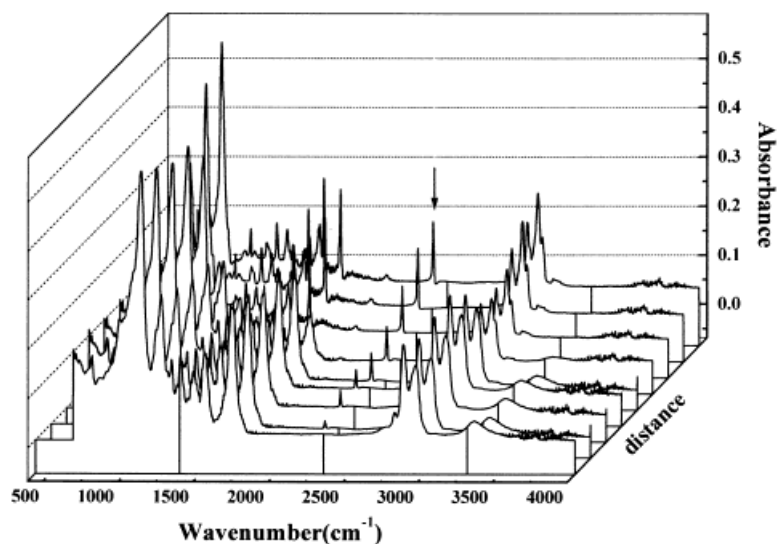
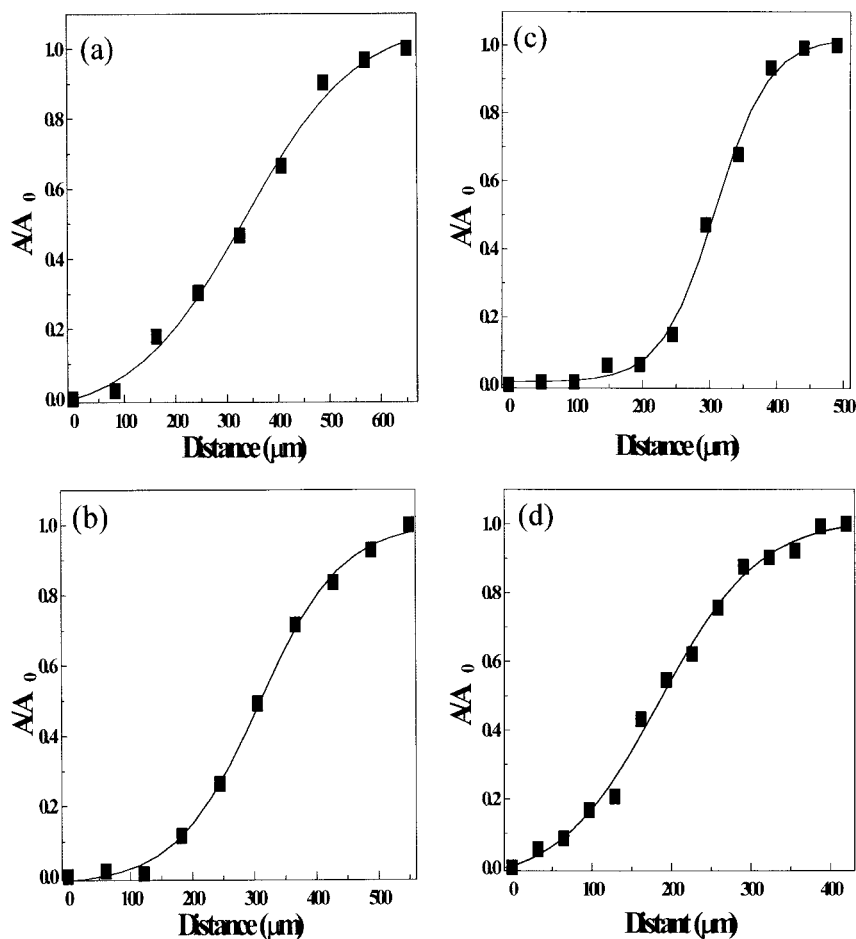**Figure 7**   FTIR charts with diffusion distance (AUA5).

Figure 8   Plot of diffusion distance versus A/A_0: (a) AUA2; (b) AUA3; (c) AUA4; (d) AUA5.

All series correspond to error function of the second Fick's rule.

We have considered that the above factors influence the morphology of PDLC. We report in this section the electrooptical properties of PDLC films, which are the most important properties of PDLC films. They have also an influence on the morphology of PDLC. The electrooptical properties of PDLC are represented in Table III and Figure 9.

In Figure 9(a), transmittance change with driving voltage is illustrated. Threshold voltage is about 8 V and maximum transmittance is 78%.[20] High-threshold voltage and low transmittance are due to the high affinity between polymer and LC. However, viewing angle is relatively satisfactory in comparison with conventional PDLC, as shown in Figure 9(b). The small amount of AI added is aligned by weak shear during cell preparation and aligned molecules improve the viewing angle.[21] As the hy-

drophobicity of the polymer matrix increases, the driving voltage decreases due to the increase of droplet size of LC domains and the lower anchoring energy. Because of decreased scattering, high transmittance could be obtained. However, the viewing angle is not dependent on the hydrophobicity of the matrix polymer.

CONCLUSION

As the LC content increased in the preparation of PDLC films, the droplet size of the LC domain

Table III   Electrooptical Properties of AUA Series

	AUA2	AUA3	AUA4	AUA5
Driving Voltage (V)	8	7	6.7	6.2
Transmittance (%)	78	80	80.6	83.5
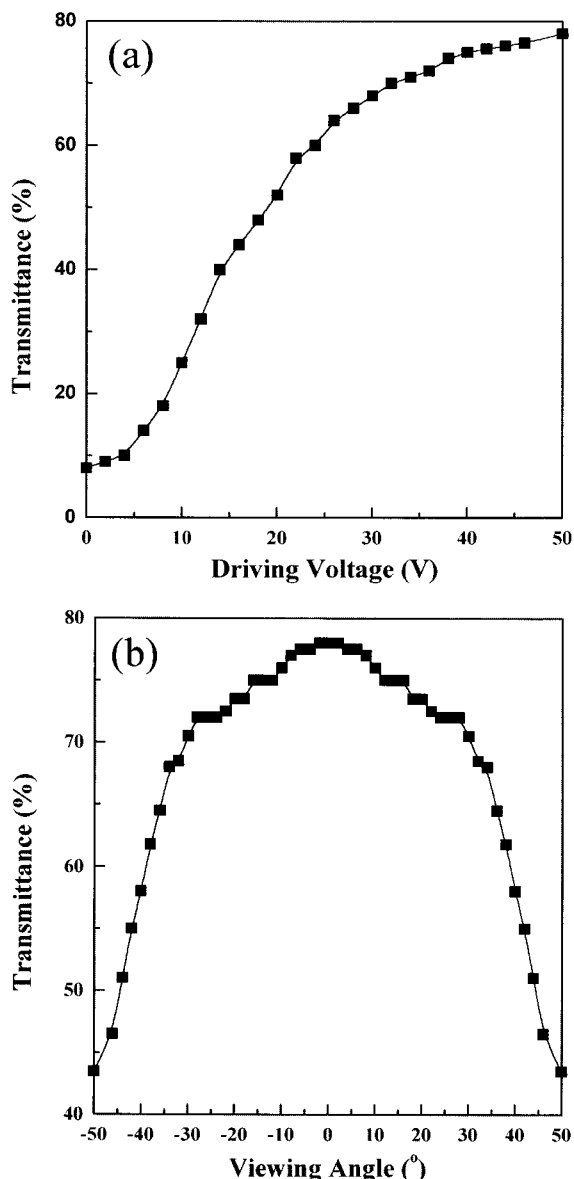
Figure 9 The electrooptical properties of AUA2: (a) T–V curve; (b) viewing angle.

rule. For electrooptical properties, PDLC films prepared with AUA2 showed 50 V of saturation voltage and about 80% of maximum transmittance. Saturation voltage is relatively high because of high affinity between matrix polymer and LC. The small amount of LCP added improves the viewing angle.

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dispersed in matrix polymer increased. The increase of curing temperature enhanced the rate of polymerization but restricted the growth of droplets. As a consequence, the size of LC domains dispersed in polymer matrix decreased. Increasing an added amount of AI in the preparation of PDLC resulted in changes in the affinity between LC and matrix polymers, leading to a change in final morphology. The diffusion of LC into polymer matrix was affected by the properties of the matrix polymer, which followed the second Fick's