

Optical Switching Behavior of Polymer-Dispersed Liquid Crystal Composite Films with Various Novel Azobenzene Derivatives

Jui-Hsiang Liu, Hung-Yu Wang

Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

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ABSTRACT: Polymer-dispersed liquid crystal (PDLC) composite films were fabricated by thermal polymerization with E7 liquid crystal, monomers, and novel azobenzene derivatives synthesized in this study. To investigate the effects of azocompounds on the optical switching of PDLC films, a series of novel azobenzene derivatives of 4-alkyloxy-4'-methoxyazobenzene with carbon numbers of 3–6, chiral compounds of amyl-4-(4-hexyloxyphenylazo)benzoate, and bornyl-4-(4-hexyloxyphenylazo)benzoate were synthesized. The compounds synthesized in this investigation were identified using FTIR, NMR, and elemental analysis. The optical texture of the composite films was analyzed under crossed

nicols with a polarizing microscope. The morphological observation of the solid polymer in the composite films was performed with a scanning electron microscope (SEM). The optical behavior of the composite films on UV irradiation and the effects of the curing time on the thermal stability of the composite films were investigated. Isomerization of the azobenzene derivatives due to UV irradiation was confirmed by a texture study and image recording method. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 789–799, 2004

Key words: chiral; composites; crosslinking

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) composite films have a considerable potential for large-area displays and light-control applications, since they can be switched electrically from a light-scattering to a transparent state and do not require polarizers and alignment layers.^{1,2} The dispersion of a small amount of a polymer in a liquid crystal matrix [polymer-stabilized liquid crystal (PSLC)] has shown considerable promise for liquid crystal display applications.^{3,4} These polymers have high surface areas and, consequently, tend to stabilize the liquid crystal order efficiently, even at low concentration. There are now several experimental studies of the effects of various factors on the morphology of the network polymers.^{5,6} Various forms of dispersion have been reported under different acronyms: dispersions from aqueous polymers (NCAP),⁷ dispersions from phase-separation processes (PDLC),⁸ and dispersions with variations in types of material and concentration (LCPC)⁹.

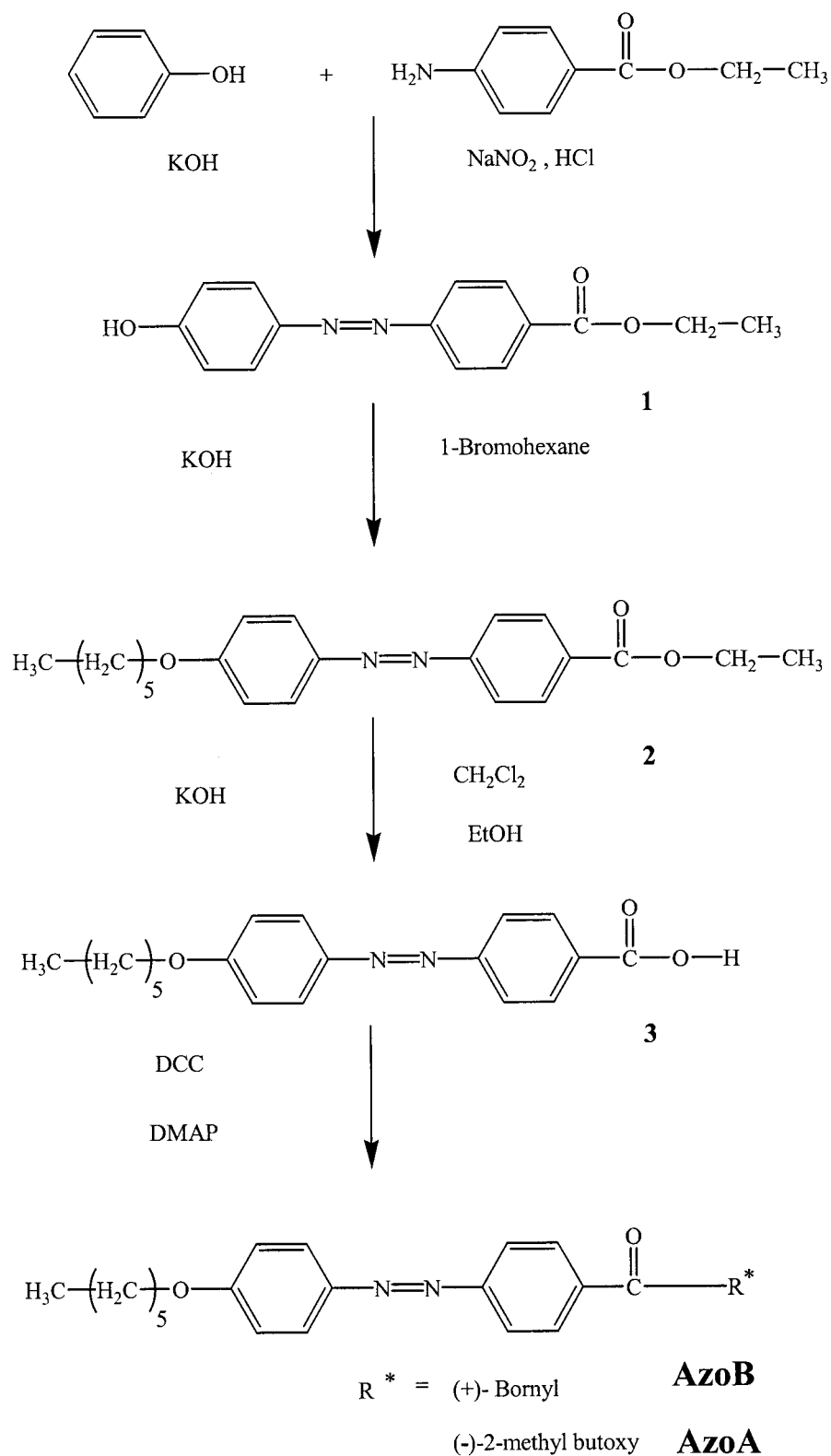
It is well known that azobenzene undergoes isomerization from *trans* to *cis* under ultraviolet light irradiation, while the *cis* form can return to the *trans* form either photochemically or thermally. Such geometrical changes could produce concomitant changes in the

physical and chemical properties, not only in the azobenzene itself but also in the surrounding matrices. When azobenzene is embedded in a nematic liquid crystal, the two isomers produce different environments, which are characterized by the two different molecular shapes. The rodlike rigid molecule of the *trans* form is favorable for the stabilization of the liquid crystal phase, while the bent *cis* isomer tends to destabilize the phase structure. Therefore, the ordered nematic phase is isothermally transformable into a disordered isotropic phase by the *trans*–*cis* photoisomerization of the guest azobenzene. The photochemical phase transition of liquid crystals has been examined by transmission and reflection mode analyses.^{10–14}

From such a viewpoint, the light-scattering mode control of light was proposed and accomplished by employing a polymer matrix combined with the liquid crystal system in lieu of the function of the polarizers similar to a PDLC.^{15–18} In general, the light-scattering state is operated through electrical control of the ordering of the liquid crystal domains as in other liquid crystal devices. PDLCs with a memory function, which have potential for image storage and laser-addressed displays, were also reported.^{19–22} In these composite films, optical information can be recorded due to a reversible change in the threshold frequency induced by the isomerization of azobenzene.

In our previous study, we reported optical control of light through a polymer/liquid crystal composite film based on the control of the electric field.²³ In the

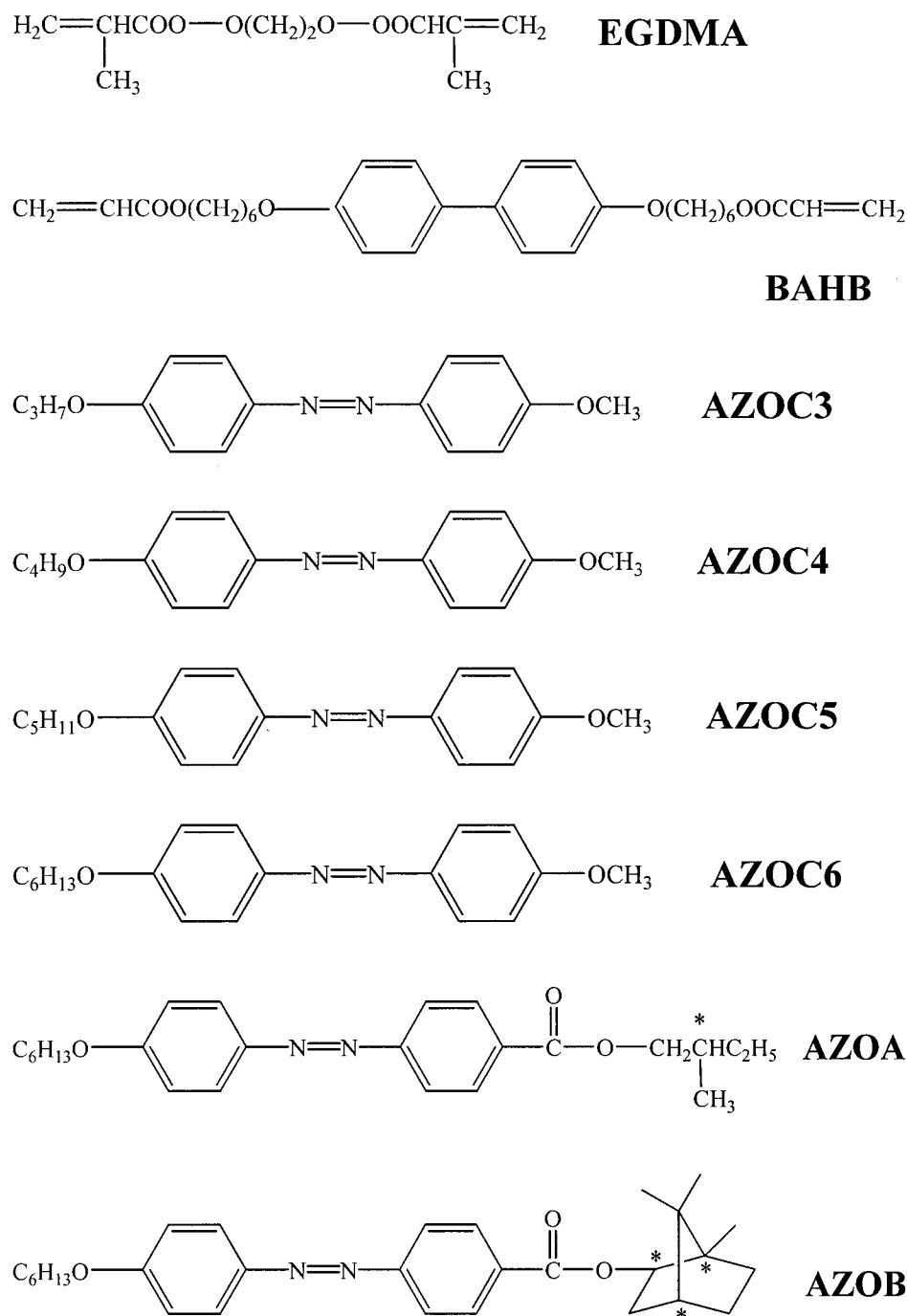
Correspondence to: J.-H. Liu (jhliu@mail.ncku.edu.tw).



Scheme 1

system, the phase separation of polymers in liquid crystal led to the formation of focal-conic texture domains. In the case of the absence of an electric field, the focal-conic structure is formed and caused by light-

scattering phenomena. When an electric field is applied to the PSCT cells, the direction of liquid crystals reorient parallel to the direction of the applied field and the PSCT cells become transparent.



Scheme 2

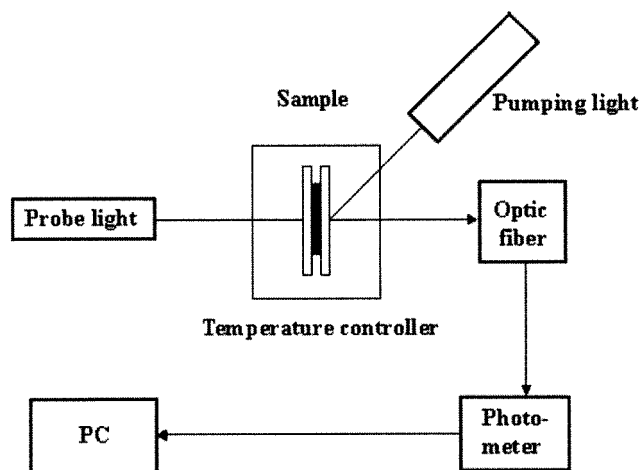
In this study, a series of azobenzene derivatives of 4-alkyloxy-4'-methoxyazobenzene with carbon numbers of 3–6, chiral compounds of amyl-4-(4-hexyloxyphenylazo)benzoate, and bornyl-4-(4-hexyloxyphenylazo)benzoate were synthesized. PDLC composite films were fabricated by thermal polymerization with E7 liquid crystal, monomers, and synthesized azocompounds. The optical switching behavior of the composite films and the isomerization of the azobenzene derivatives were all investigated. The effects of the

curing time on the clearing temperature of the composite films were also studied.

EXPERIMENTAL

Measurements

Fourier transform infrared spectra were recorded on a Jasco VALOR III FTIR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on



Scheme 3

a Bruker AMX-400, high-resolution NMR spectrometer. Optical rotations were measured at 30°C in dimethylformamide (DMF) using a Jasco DIP-360 automatic digital polarimeter with readings to $\pm 0.001^\circ$. Elemental analyses were conducted with a Heraeus CHN-O rapid elemental analyzer. Gel permeation chromatography (GPC) measurements were carried out at 40°C on a Hitachi L-4200 instrument equipped with TSK gel GMH and G2000H columns using THF as an eluent. Thermal analysis of the azobenzene compounds and PDLC films were performed by a Perkin-Elmer differential scanning calorimeter (DSC) at a heating and cooling rate of 10 K/min in a nitrogen atmosphere. The liquid crystal phases were investigated by an Olympus BH-2 polarized optical microscope (POM) equipped with Mettler hot stage (Model FP-82) and the temperature scanning rates were determined at a rate of 5 K/min.

Materials

AzoC3, AzoC4, AzoC5, and AzoC6 with different lengths of the alkyl group were synthesized. The suffix number indicates the number of the alkyl carbon units for each azobenzene derivative. We also synthesized AzoA and AzoB azobenzene derivatives containing chiral (–)-amyl and (–)-bornyl groups, respectively. The synthetic process is shown in Scheme 1. The azobenzene derivatives were used as photochromic dopants to produce optical image storage films. The UV absorption around 370 nm is a $\pi-\pi^*$ transition band and around 450 nm is an $n-\pi^*$ transition band of azocompounds. Scheme 1 shows the synthesis process of the azoderivatives of AzoA and AzoB. Molecular structures of difunctional monomers and azocompounds used in this investigation are shown in Scheme 2.

Ethylene glycol dimethacrylate (EGDMA) was purchased from Acros (Geel, Belgium) and used without

further purification; 4,4'-bis[6-(acryloyloxy)hexyloxy]biphenyl (BAHB) was synthesized according to the method reported.^{24,25} The difunctional monomers were used as precursor materials to form the polymer matrices; 2,2'-azobisisobutyronitrile (Showa, Tokyo, Japan) was used as a photoinitiator. E7, a eutectic mixture of several low molecular weight liquid crystals, was purchased from Merck (Darmstadt, Germany) and used as a host liquid crystal without further purification. The liquid crystal reveals a nematic phase between -20 and 61°C .

4-hydroxy-4'-ethoxycarbonyl azobenzol (1)

Ethyl 4-aminobenzoate (10 g, 60.0 mmol) was dissolved in 1M aqueous HCl (100 mL) and kept in the ice bath at 0°C . NaNO_2 (4.2 g, 60.8 mmol), dissolved in water (30 mL), was added dropwise to the solution and stirred for 30 min. Sodium hydroxide (7.2 g, 0.18 mol) and phenol (5.8 g, 61.7 mmol) were dissolved in water (80 mL) and then stirred for 30 min at 0°C . The former solution was added dropwise to the later solution; the temperature was kept at 0°C and stirred for 1 h. The resulting mixture was pored into water and the solution was neutralized with 5% aqueous HCl. The precipitated crude product was filtered and recrystallized twice from ethanol. Yield: 11.8 g (72%).

IR (KBr): 3419 cm^{-1} (—OH). $^1\text{H-NMR}$ (CDCl_3 , = ppm): 1.38 (s, 3H, — $\text{C}-\text{CH}_3$), 4.35 (s, 2H, — OCH_2 —), 7.01–8.18 (m, 8H, aromatic).

Ethyl 4-(4-hexyloxyphenylazo)benzoate (2)

Compound 1 (8.1 g, 30 mmol) was dissolved in DMF (70 mL). Potassium hydroxide (2.52 g, 45 mmol), dissolved in DMF (50 mL), was added dropwise to the solution. Potassium iodide (0.83 g, 5 mmol) and 1-bromohexane (4.95 g, 30 mmol), dissolved in DMF (20 mL), was then added. The solution was heated to 80°C and kept at that temperature for 24 h with stirring. The

TABLE I
Phase-transition Temperatures of Azobenzene Derivatives

Sample	Heating cycle		Cooling cycle	
	$T_{\text{C-N}}$ ($^\circ\text{C}$)	$T_{\text{N-I}}$ ($^\circ\text{C}$)	$T_{\text{C-N}}$ ($^\circ\text{C}$)	$T_{\text{N-I}}$ ($^\circ\text{C}$)
AzoC3	— ^a	— ^a	93.5	99.3
AzoC4	104.2	109	75.8	106
AzoC5	104.2	109.2	81.3	106.1
AzoC6	94.5	101.4	74.2	98.8
	$T_{\text{C-I}}$ ($^\circ\text{C}$)	$T_{\text{C-I}}$ ($^\circ\text{C}$)	$[\alpha]_D^b$	
AzoA	85.8	72.3	$[\alpha]_D = +6.8$	
AzoB	120	90.6	$[\alpha]_D = -53.2$	

^a Nematic phase cannot be found.

^b Specific optical rotation of azobenzene derivatives.

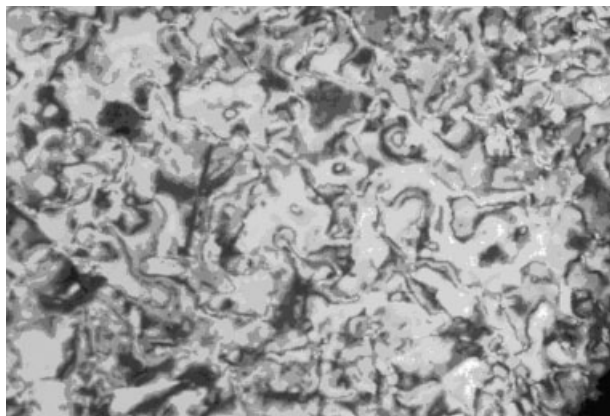


Figure 1 Optical texture observed for AzoC5 at 90°C between crossed polarizers in the polarizing microscope.

resulting mixture was poured into water and extracted twice with CHCl_3 . After evaporation, the crude product was recrystallized twice from ethanol. Yield: 8.1 g (77%).

IR (KBr): 3405 cm^{-1} ($-\text{OH}$), 2975 cm^{-1} ($-\text{CH}_2$), 1688 cm^{-1} ($-\text{C}=\text{O}$). $^1\text{H-NMR}$ (acetone- d_6 , $\delta = \text{ppm}$): 1.36–1.40 (m, 3H, $-\text{CH}_3$), 4.35–4.40 (q, 2H, $\text{O}-\text{CH}_2-$), 7.01–7.05 (d, 2H, aromatic), 7.88–7.94 (d, 4H, aromatic), 8.16–8.18 (d, 2H, aromatic).

4-(4-hexyloxyphenylazo)benzoic acid (3)

Compound 2 (9.0 g, 25.4 mmol) was dissolved in ethanol (50 mL). Potassium hydroxide (10 g, 178.5 mmol), dissolved in ethanol, was then added and the mixture was heated at reflux for 6 h. The suspension was poured into ethanol containing 10% water, and the solution was neutralized with HCl diluted with ethanol containing 10% water. The solution was extracted twice with CHCl_3 , washed with water, dried over magnesium sulfate, and evaporated. Yield: 6.9 g (83%).

IR (KBr): 2948, 2861 cm^{-1} ($-\text{CH}_2$), 1692 cm^{-1} ($-\text{C}=\text{O}$). $^1\text{H-NMR}$ (acetone- d_6 , $\delta = \text{ppm}$): 0.85–1.77 (m, 11H, $-\text{C}_5\text{H}_{11}$), 4.06–4.09 (t, 2H, $\text{O}-\text{CH}_2-$), 7.12–7.14 (d, 2H, aromatic), 7.87–7.92 (m, 4H, aromatic), 8.09–8.11 (d, 2H, aromatic).

Amyl 4-(4-hexyloxyphenylazo)benzoate (AzoA)

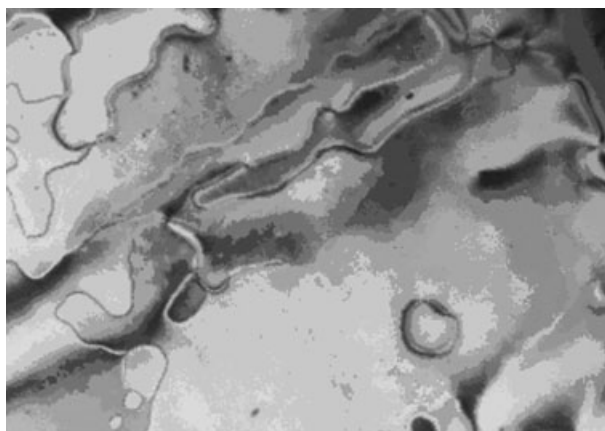
Compound 3 (3.26 g, 10 mmol) and amyl alcohol (0.9 g, 10.2 mmol) were dissolved in CH_2Cl_2 (30 mL) at room temperature; N,N' -dicyclohexylcarbodiimide (DCC) (3.09 g, 18.9 mmol) and 4-dimethylaminopyridine (DMAP) (0.1 g, 0.82 mmol) were then added to the solution. The mixture was stirred for 7 h at 30°C. The resulting mixture was then washed with water, dried over magnesium sulfate, and evaporated. The crude product was purified by column chromatogra-

phy (Merck-2000 silica gel, $\text{MeOH}/\text{CHCl}_3 = 1/20$). Yield: 2.1 g (51%).

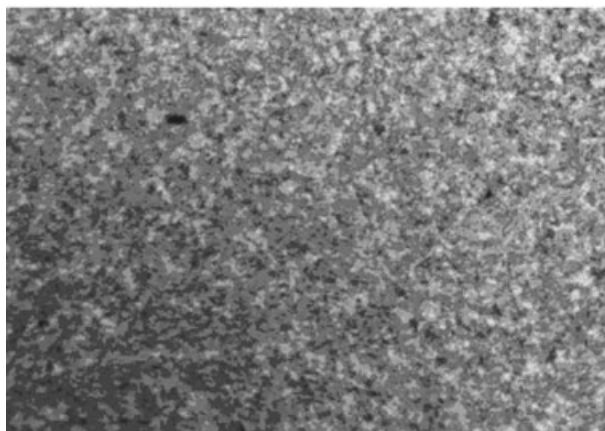
IR (KBr): 2948, 2869 cm^{-1} ($-\text{CH}_2$), 1710 cm^{-1} ($-\text{C}=\text{O}$). $^1\text{H-NMR}$ (acetone- d_6 , $\delta = \text{ppm}$): 0.90–2.09 (m, 20H, $-\text{C}_5\text{H}_{11}$, $-\text{C}_4\text{H}_9$), 4.06–4.09 (m, 4H, $\text{O}-\text{CH}_2-$), 6.99–7.03 (d, 2H, aromatic), 7.89–7.99 (m, 4H, aromatic), 8.16–8.18 (d, 2H, aromatic).

Borneol 4-(4-hexyloxyphenylazo)benzoate (AzoB)

Compound 3 (3.26 g, 10 mmol) and borneol (1.7 g, 10.3 mmol) were dissolved in CH_2Cl_2 (30 mL) at room temperature; DCC (3.09 g, 18.9 mmol) and DMAP (0.1 g, 0.82 mmol) were then added to the solution. The mixture was stirred for 7 h at 30°C. The resulting mixture was then washed with water, dried over MgSO_4 , and evaporated. The crude product was purified by column chromatography (Merck-2000 silica gel, $\text{MeOH}/\text{CHCl}_3 = 1/20$). Yield: 1.58 g (33%).



(a)



(b)

Figure 2 Optical textures observed for the mixture of AzoC6 and E7 at 90°C between crossed polarizers in the polarizing microscope (a) before and (b) after UV irradiation.

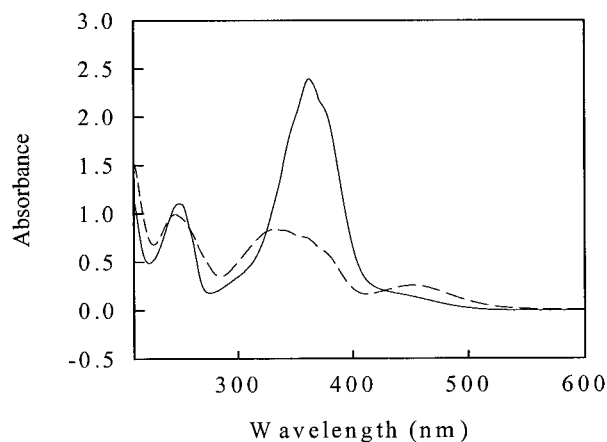


Figure 3 UV spectra of AzoC5 (a) before (solid line) and (b) after (dotted line) UV irradiation.

IR (KBr): 2954, 2861 cm^{-1} (—CH), 1702 cm^{-1} (—C=O). $^1\text{H-NMR}$ (acetone- d_6): δ = 0.90–2.50 (m, 27H, — C_5H_{11} , — C_9H_{16}), 4.04–4.07 (t, 4H, —O— CH_2 —), 5.12–5.16 (m, 1H, —O—CH—), 7.00–7.03 (d, 2H, aromatic), 7.90–8.19 (m, 6H, aromatic).

Preparation and measurements

The PDLC films were prepared from the mixture of difunctional monomers/azobenzene derivatives/E7/AIBN in various weight percent ratios as those described in the Results and Discussion section. Liquid crystal in composite films is around 80 wt %. The mixture was ultrasonic-treated to form a homogeneous solution and then injected into a glass cell separated by a 15- μm spacer. The samples were thermal-cured in an oven. After completing the polymerization, PDLC composite films could be fabricated.

The optical switching behaviors of the PDLC films were investigated using the equipment shown in Scheme 3. A high-pressure mercury lamp (100 W) with a filter was used as a pumping light source to allow the samples to be irradiated with 366-nm light, which could isomerize the *trans*–*cis* structures of the azobenzene derivatives. The optical change of the samples induced by photoirradiation was followed by detecting the intensity of the probe light transmitted through the samples with the photodiode. The intensity of the probe light in the absence of the samples is defined as 100% light transmittance. The optical texture of the composite films was observed under crossed nicols with a polarizing microscope. The morphological observation of the solid polymer in the composite films was performed with a scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The thermal properties of the azobenzene derivatives are listed in Table I. The azoderivatives of AzoC3,

AzoC4, AzoC5, and AzoC6 synthesized in this investigation all have a nematic liquid crystal phase under the observation of a polarized optical microscope (POM). The phase transition temperatures were estimated using a DSC analyzer. As can be seen in Figure 1, AzoC5 shows the marbled texture of the nematic phase at 90°C during the cooling cycle. AzoA and AzoB, with a chiral tail, do not have a liquid crystalline phase. In general, the existence of a high steric hindered structure in molecules may disturb the orientation of liquid crystal molecules. The optical rotation of chiral azobenzene derivatives was estimated using a JASCO DIP-360 automatic digital polarimeter with readings to $\pm 0.001^\circ$.

PDLC composite films were fabricated by thermal polymerization. Figure 2 shows the texture change of the composite films [Fig. 2(b)] under a POM from a mixture of liquid crystals and AzoC6 [Fig. 2(a)]. Phase separation of the polymer matrix may generate a net-like structure and limit the orientation of liquid crystal molecules, leading to a change of their texture. As can be seen in Figure 2(b), polymeric film still reveals an anisotropic optical texture. The bright pattern means that the composite film is an anisotropic membrane even though the liquid crystal was separated as domains in the polymer matrix.

The photoresponsive behavior of AzoC5 was investigated using a UV spectrophotometer. Figure 3 shows the UV spectra of AzoC5 before and after UV ($\lambda = 365$ nm) irradiation for 2 min. After UV irradiation, as shown in Figure 3, AzoC5 may isomerize from a *trans* to a *cis* structure, leading to a decrease in its peak around 370 nm. All azobenzene derivatives synthesized in this investigation showed a similar UV absorption spectrum. The bulky and the branched tails in AzoA and AzoB seemed to not affect the *cis*–*trans* isomerization. Photoisomerization can also be seen in these azobenzene derivatives. Absorption at the visible wavelength region of the azobenzene derivatives, as can be seen in Figure 3, reveal a colored appearance.

To investigate the optical switching behavior of the PDLC composite films, the mixture of difunctional

TABLE II
Compositions of Sample Composite Films

Sample	BAHB (wt %)	EGDMA (wt %)	Azo (wt %)	E7 (wt %)
Sample 1		14	AzoC6 3	83
Sample 2		14	AzoC6 6	80
Sample 3		14	AzoC6 9	77
Sample 4		14	AzoC6 12	74
Sample 5	14		AzoC6 6	80
Sample 6		14	AzoC6 6	80
Sample 7		14	AzoC5 6	80
Sample 8		14	AzoC4 6	80
Sample 9		14	AzoC3 6	80
Sample 10		14	AzoA 6	80
Sample 11		14	AzoB 6	80

TABLE III
Clearing Temperature of Composite Films Before and After UV Irradiation

Sample	Monomer	Azo	T_c^a (°C)		t_{on} (s) ^d
			Before ^b	After ^c	
Sample 5	BAHB	AzoC6	62	54	82.4
Sample 6	EGDMA	AzoC6	61.5	52.2	138.5
Sample 7	EGDMA	AzoC5	61.3	54.8	75.8
Sample 8	EGDMA	AzoC4	61.7	53.1	115.5
Sample 9	EGDMA	AzoC3	60.5	52.6	99.4
Sample 10	EGDMA	AzoA	58.5	53	83.2
Sample 11	EGDMA	AzoB	59	56.5	82.3

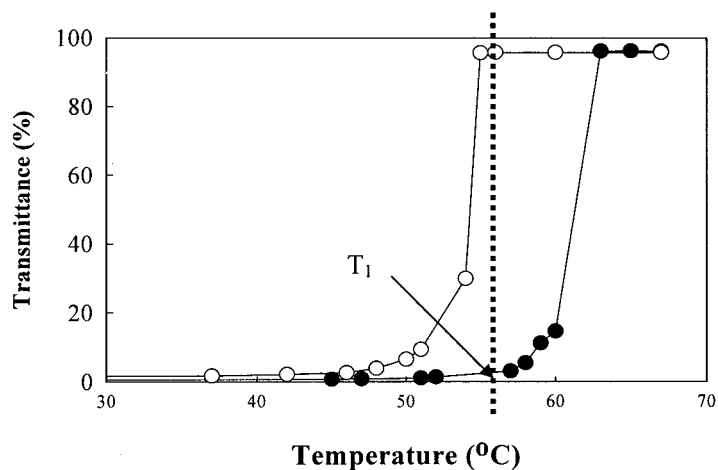
^a Clearing point.

^b Before UV irradiation.

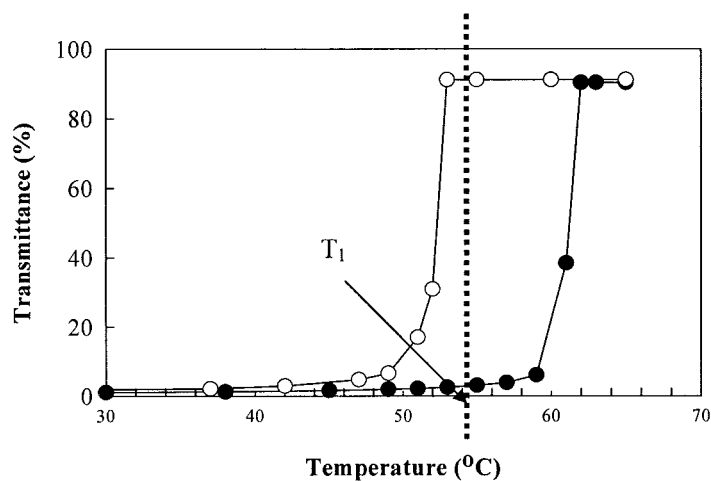
^c After UV irradiation.

^d Response time required from opaque to saturated clear while irradiated with UV.

monomers, azobenzene derivatives, E7 liquid crystal, and the initiator AIBN was mixed and then polymerized in glass cells. The compositions of the composite samples are summarized in Table II. To evaluate the optimal weight ratio of azobenzene derivatives in composite films, the first four samples were mixed with various Azo/E7 ratios. Due to the solubility of azobenzene derivatives in liquid crystals, 6 wt% of azobenzene derivatives were chosen as the optimal composition to investigate the optical behavior of the composite films. As shown in Table III, after UV ($\lambda = 365$ nm) irradiation, the clearing point (T_c) of the composite films decreased. The dependence of the transmittance of the composite films on temperatures before and after UV irradiation is shown in Figure 4. The decrease of the clearing temperature (T_c) can also be seen in the figure. The results suggest that UV irradiation may cause the azobenzene derivatives to



(a)



(b)

Figure 4 Thermal stability of composite films (○) before and (●) after UV irradiation for (a) sample 5 and (b) sample 6.

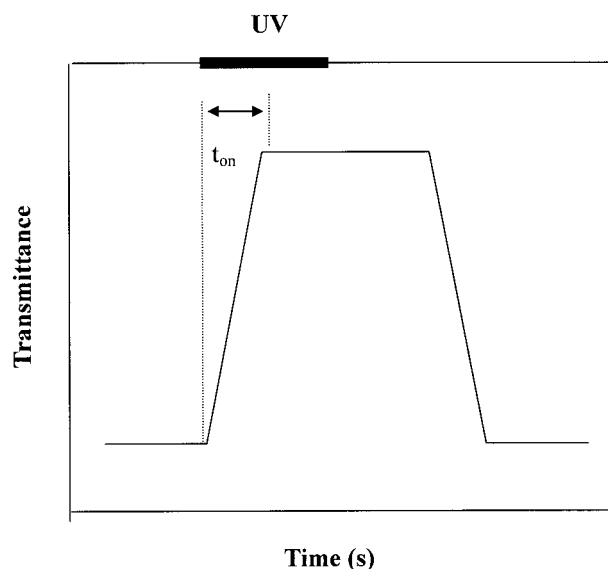


Figure 5 Response time for composite films estimated at T_1 during UV irradiation.

undergo isomerization from *trans* to *cis* and lead to a disturbance in the liquid crystal molecules.

The response time (t_{on}) means the time required for the composite film to go from opaque to saturated transparent during UV irradiation at 365 nm. The response times in Table III were estimated at the central temperature (T_1), as indicated in Figure 4. The time required (t_{on}), as shown in Figure 5, was estimated as the response time. The response time for every sample is shown in Table III. The existence of the *cis*-form azobenzene derivatives due to UV irradiation may disturb the order of the liquid crystal molecules, leading to the change of the film transparency.

Composite films were prepared by heating the sample mixtures at 90°C for various times. Figure 6 shows

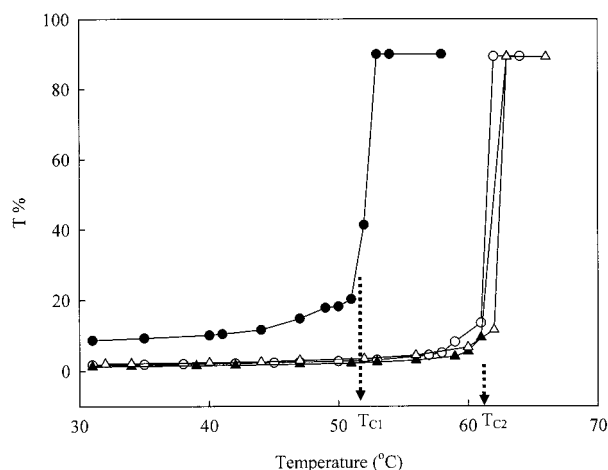
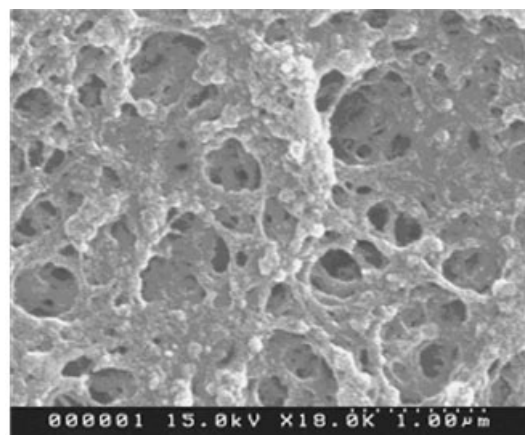
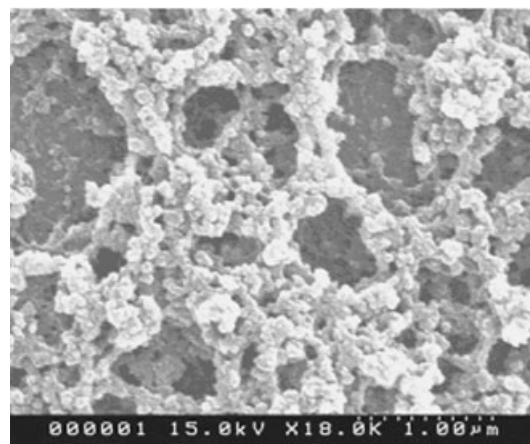


Figure 6 Effects of curing time on the thermal stability of composite films.



(a)



(b)

Figure 7 Morphological network structure of the composite films from (a) sample 5 and (b) sample 6.

the effects of the curing time on the thermal stability of the composite films. The clearing points (T_c) of the composite films were found to increase with increase in the thermal polymerization. During polymerization, anisotropic domains of the composite were more finely subdivided with increases in the polymerization time, resulting in an increase of T_c of the composites. T_c ultimately reaching some constant values and the initial homogeneous state, was transformed into a PDLC in a homogeneous state, in which the composite films consisted of crosslinked polymer-rich isotropic matrices and LC-rich anisotropic domains. As can be seen in Figure 6, the composite films were considered as the fully cured films because T_c no longer changed even though the unreacted monomer might remain in the LC domains. We believe that the increase of T_c (from T_{c1} to T_{c2}) is due to phase separation of the LC domains from the polymer matrices since the LC domains contain much fewer unreacted monomers as the polymerization proceeds.

To investigate the morphological structure of the composite films prepared at various conditions in the

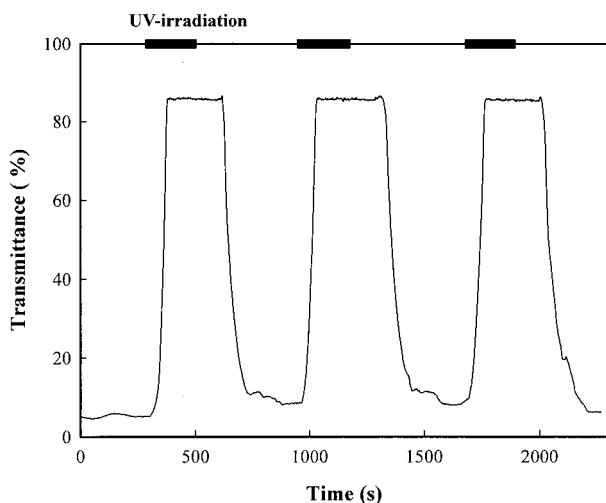


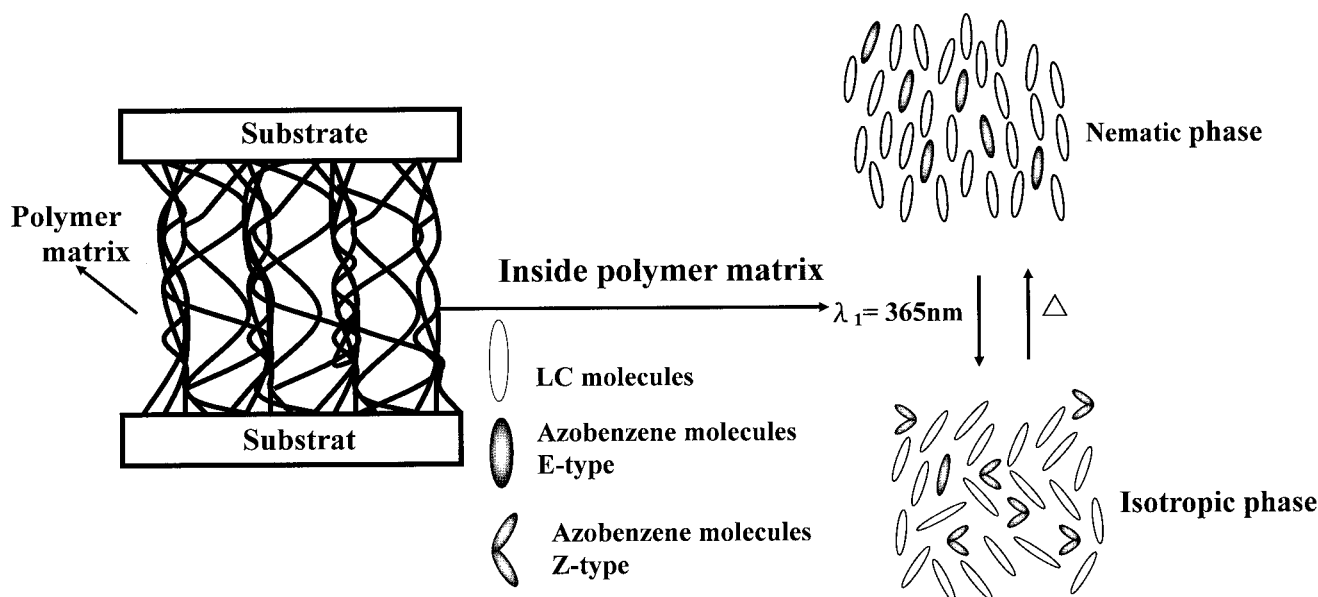
Figure 8 Reversible and repeatable change in transmittance between the light-scattering state and the transparent state of sample 7 composite film by periodic UV irradiation at 57°C.

fully cured state, electron microscopy was used. Figure 7 shows the structure of the resultant polymers in the composite films of samples 5 and 6 with BAHB and EGDMA as the difunctional monomers, respectively. The bare polymers showed network structures interconnected three-dimensionally, which contained continuous LC channels in their pores. It was found that an increase in the concentration of LC gave larger LC channels in the less aggregated solid network. The rate of polymerization seems to be a very important factor for the optical properties of the resultant composite films and is, in fact, affected by the curing temperature and the rate of initiation of the radical

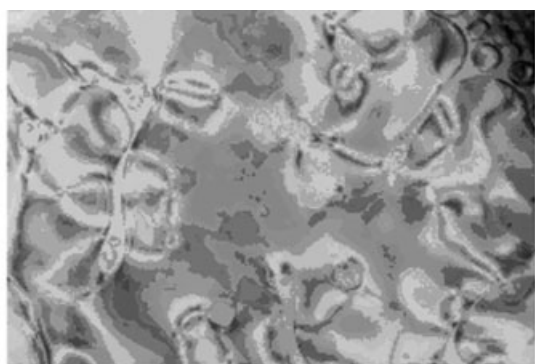
polymerization. As shown in Figure 7, polymer matrices from samples 5 and 6 with different pore sizes and appearance were obtained.

The optical behavior of the composite films on photoirradiation was investigated through a change in the transmittance of the probe light triggered by UV (365 nm) irradiation. Figure 8 shows the result of the change in transmittance as a function of time. Before UV irradiation, the transmittance was not detected because the probe light was strongly scattered by the composite film. However, photoirradiation brought about an increase in the transmittance until a saturated value was obtained. In the saturated state, the composite film showed a clear transparent state. When UV irradiation ceased, the transparent film reverted thermally to the initial opaque light-scattering state. The response between these two different optical states was reversible and repeatable by periodic UV irradiation as shown in Figure 8.

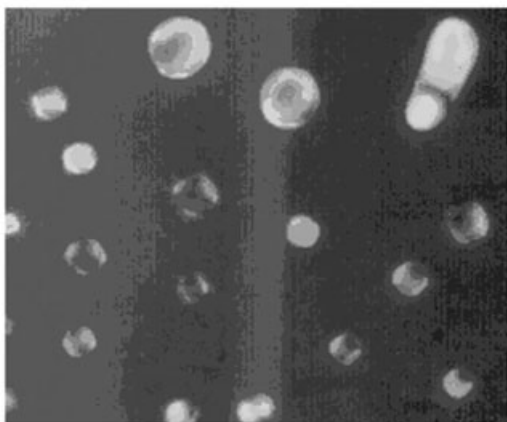
The reversible change is attributed to the phase transition between the liquid crystal and the disordered isotropic phase which is induced by the reversible change in the molecular shape of the guest azobenzene derivatives. Scheme 4 shows a possible mechanism for the optical response of the composite films. The mixture of liquid crystals and azobenzene derivatives are dispersed in the crosslinked polymer matrices. In general, the anisotropic liquid crystal phase is an ordered assembly of rod-shaped molecular units, having anisotropic optical properties. Therefore, *trans*-azobenzene derivatives are favorable for the stabilization of the liquid crystal phase of their rodlike shape. The composite film exhibits a light-scattering state due to the presence of the anisotropic domains with a



Scheme 4



(a)



(b)



(c)

Figure 9 Optical textures observed for E7/Azo-C6 mixture (a) before UV irradiation, (b) after 90 s, and (c) 150 s UV irradiation at 55°C between two crossed polarizers in the polarizing microscope.

nonuniform distribution of the liquid crystal directors. On the other hand, the *cis*-azobenzene derivatives produced by UV irradiation causes destabilization of the liquid crystal phase, resulting in the N-I (nematic-to-isotropic) phase transition. The increase in transmittance on UV irradiation is due to the N-I phase transition induced by the forming of *cis*-azobenzene derivatives. The recovery of the light-scattering state is caused by the thermal *cis*-*trans* back isomerization of the azobenzene derivatives.

The dependence of the optical behavior of the composite films on UV irradiation was investigated using a polarizing microscope. Figure 9 shows a change in the optical texture of nematic E-7 with Azo-C6 at 55°C when it was irradiated at 365 nm for various time periods. A nematic texture of the liquid crystal was observed before UV irradiation [Fig. 9(a)]. The bright texture of anisotropic domains disappeared gradually with increase in the UV irradiation time [Fig. 9(b)], and, finally, the liquid crystal domains changed completely to the isotropic phase [Fig. 9(c)]. Figure 10 shows the result of image recording of the sample 7 composite film after UV irradiation at 25°C for 50 s. A mask with letters "NCKU" was used. As can be seen in Figure 3, absorption at the visible wavelength changed while the composite film was irradiated with UV light. At room temperature, interactions between the liquid crystal molecules are strong. UV irradiation may cause the *cis*-*trans* isomerization of azobenzene derivatives but the mechanical power from the isomerization does not appear strong enough to disturb the orientation of liquid crystal molecules. Hence, a color change can only be seen as shown in Figure 10.

CONCLUSIONS

A series of azobenzene derivatives of AzoC3, Az0C4, AzoC5, and AzoC6 were synthesized. PDLC composite films with various azobenzene derivatives were fabricated by heat curing. The rate of polymerization was found to be a very important factor for the optical properties of the resultant composite films and is, in fact, affected by the curing temperature and the rate of initiation of radical polymerization. A reversible and repeat-

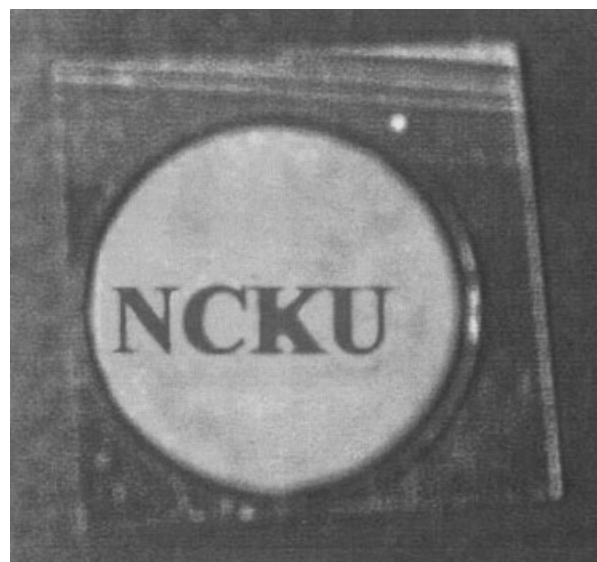


Figure 10 Image recording of the sample 7 composite film with a mask bearing the letters "NCKU."

able change in transmittance between the light-scattering state and the transparent state of the composite film was obtained by periodic UV irradiation. Image recording of a composite film with a mask bearing the letters "NCKU" was achieved by UV irradiation.

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