

Electro-optic Properties of CO₂ Fixed-Polymer/Nematic LC Composite Films

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ABSTRACT: Bis(cyclic carbonate) was obtained from the epoxide and CO₂ reaction with a quaternary ammonium halide salt catalyst. Cyclic carbonate derivatives were then reacted with amine to obtain quantitatively poly(hydroxy)urethanes that were reacted with isophorone diisocyanate (IPDI) and end capped with acrylate to form prepolymers. These prepolymers were mixed with reactive diluents and nematic LCs, and subjected to UV cure to form polymer/LC composite films in a transparent cell. Three types of diglycidyl ether [poly(propyleneglycol), cyclohexane, bisphenol A], three types of end-capping acrylates [2-hydroxyethyl acrylate (HEA), 2-hydroxypropyl acrylate (HPA), and 2-hydroxyethyl methacrylate (HEMA)], three types of multifunctional diluents [tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), dipentaerythritol hydroxy penta/hexa acrylate (DPHPA)], and three types of photoinitiators (Irgacure-651, Irgacure-184, Darocure-1173) were incorporated to control the morphology, and hence, the electro-optic properties of the polymer/nematic LC composite films. Poly(propylene glycol) diglycidyl ether segment of polyurethane acrylate (PUA) showed lower viscosity and gave larger domain size resulting in lower threshold (V_{10}) and driving (V_{90}) voltages, together with larger nematic–isotropic transition temperature depression. HEA end-capped PUA gave larger polymer–LC phase separation and smaller V_{10} as well as V_{90} . TPGDA-based PUA showed the lowest V_{10} and V_{90} and the shortest response time. Among the three types of photoinitiators used Irgacure-651 showed the larger LC domain, and smaller V_{10} and V_{90} . © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2744–2753, 2001

Key words: PNLC; PUA; CO₂-fixed polymer; threshold and driving voltage; nematic–isotropic transition temperature

INTRODUCTION

Polymer/liquid crystal (LC) composite films have potential for a variety of electrooptic applications ranging from switchable windows to information displays.^{1–4} In one form, they consist of LC droplets dispersed in polymer matrix known as PDLC

(polymer dispersed liquid crystal).^{2–4} In the other form the LC becomes the continuous phase and three-dimensional polymer networks are dispersed in liquid crystals to form PNLC (polymer network liquid crystal).^{5,6} Practically, PDLC saves expensive liquid crystals, whereas PNLC reduces driving voltage and response time. These polymer/LC composite films are self-supporting and need no rubbing process, and this makes the film suitable for the fabrication of large area displays. In addition, polarizer is not used, giving a much brighter film.

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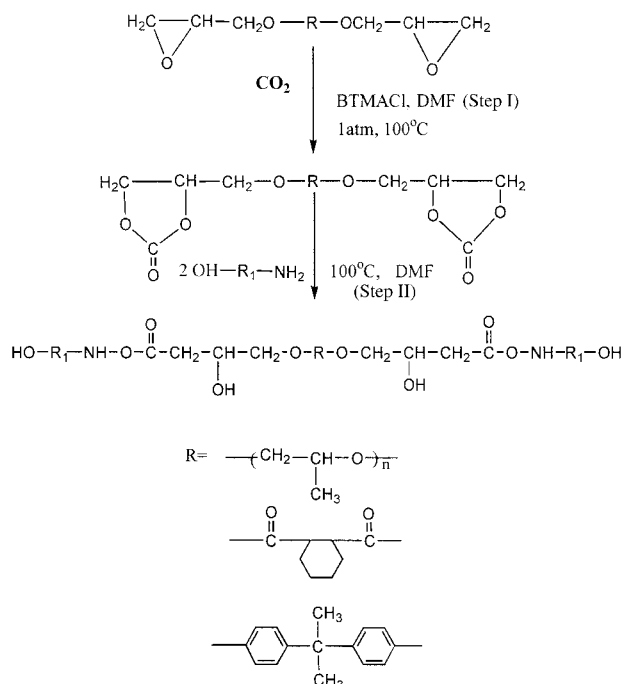


Figure 1 The synthetic process of poly(hydroxy)urethane.

Recently, effective reactions to fix CO₂ have received much attention due to their usefulness in resolving serious environmental and resource problems. Consequently, synthesis of polymeric material, using CO₂-fixed intermediates, has become an emerging area of research. Thus, we consider the use of CO₂-fixed materials as polymer matrices of polymer/liquid crystal composite films for optical displays. Reppel and Rokichi^{7,8} reported that highly selective and reactive cyclic carbonates are prepared from the reactions between epoxide and CO₂. For this report, three types of bifunctional epoxides were reacted with CO₂ to obtain bis(cyclic carbonate), which subsequently were used to obtain poly(hydroxy)urethane. Poly(hydroxy)urethanes were then end capped with acrylates and subjected to UV curing in the presence of reactive diluents and LC.⁹ Types of end-capping acrylate, diluent, and photoinitiator, in addition to the type of epoxides, are variables used to control the morphology, and hence, the electrooptic properties of composite films.

EXPERIMENTAL

Oligomer Syntheses

Syntheses of bis(Cyclic carbonate) (Fig. 1, Step I)

Bis(cyclic carbonate) derivatives have been synthesized from diglycidyl ether derivatives includ-

ing bisphenol A-diglycidyl ether, diglycidyl 1,2-cyclohexanedicarboxylate, and poly(propylene glycol)diglycidyl ether. Diglycidyl ether derivative and dimethyl formamide(solvent) were charged to a flask, equipped with a condenser, gas inlet, and thermometer, and homogenized. Then 5 mol % of benzyltrimethylammonium chloride (BTMAC1) (a phase transition catalyst with relatively high activity) was added with vigorous agitation, together with a continuous supply of CO₂ gas. Reactions proceeded at 100°C for 30 min.

Acetone was added to the reaction products to precipitate the insoluble catalyst, followed by precipitation of the products in H₂O. The crude bis(cyclic carbonate) derivatives synthesized were recrystallized in toluene and dried at 60°C *in vacuo*.

Syntheses of Polyurethane Acrylate

One mol of bis(cyclic carbonate) derivative was reacted with 2 mol of 6-amino-1-hexanol at 100°C for 48 h to obtain poly(hydroxy)urethane (Fig. 1, Step II), which was subsequently reacted with molar excess of isophorone diisocyanate (IPDI) for 3 h at 80°C to obtain isocyanate terminated prepolymers. The reaction mixtures were then cooled to 45°C before end-capping acrylate was added and reacted for 3 h at 60°C with agitation to obtain urethane acrylate oligomers.^{10–12} End-capping acrylate included 2-hydroxyethyl acrylate (HEA), 2-hydroxypropyl acrylate (HPA), and 2-hydroxyethyl methacrylate (HEMA).

The oligomers are highly viscous and immiscible with LC, which necessitate the use of reactive diluents.^{13,14} The reactive diluents used in these experiments were *N*-vinylpyrrolidone (NVP), tripropylene glycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), and dipentaerythritol hydroxy penta/hexa acrylate (DPHPA), and composition of oligomer/monofunctional diluent/multifunctional diluents was 4/3/3 by weight (Table I). A mixture of nematic liquid crystals (Ro521 : La-Rochue, $n_o = 1.499$, $n_e = 1.633$, $T_{NI} = 95^\circ\text{C}$, and $\Delta\epsilon = +6.82$) was employed to prepare the composite films.

Cell Preparations

LCs were then added to the mixture of polyurethane acrylate and diluents at a fixed composition of prepolymer/LC = 3/7 by weight, together with a photoinitiator. Three types of photoinitiators viz.

Table I Formulations to Prepare Polyurethane Acrylate Prepolymer

Run	Polyurethane Acrylate Oligomer							Photoinitiator
	Poly(hydroxy)urethane				End-Capping Acrylate	Monofunctional Diluent	Multifunctional Diluent	
	Bis(cyclic Carbonate)		Amine	Diisocyanate				
	Diglycidyl Ether	CO ₂						
A ₁	PPG-type	CO ₂	6-amino-1-hexanol	IPDI	HEA	NVP	TPGDA	Irgacure-651
A ₂	cyclohexane-type							
A ₃	bisphenolA-type							
B ₁	cyclohexane-type	CO ₂	6-amino-1-hexanol	IPDI	HEA	NVP	TPGDA	Irgacure-651
B ₂					HPA			
B ₃					HEMA			
C ₁	cyclohexane-type	CO ₂	6-amino-1-hexanol	IPDI	HEA	NVP	TPGDA	Irgacure-651
C ₂							TMPTA	
C ₃							DHPHA	
D ₁	cyclohexane-type	CO ₂	6-amino-1-hexanol	IPDI	HEA	NVP	TPGDA	Irgacure-651
D ₂								Irgacure-184
D ₃								Darocure-1173

Oligomer : monofunctional diluent : multifunctional diluent = 4 : 3 : 3.

benzildimethyl ketal (Irgacure 651), 1-hydroxy cyclohexyl phenyl ketone (Irgacure 184), and 2,2-dimethoxy-2-hydroxy acetophenone (Darocure 1174) have been used.¹⁵ The reaction mixtures were mechanically mixed thoroughly before they were filled into the ITO-coated cell by capillary action. Cell thickness was adjusted to 20 μm using glass bead spacers. The mixtures were then cured using a UV lamp (100 mW/cm², 365 nm) for 3 min.

Contact Angles

Contact angles of the films with LC drop were measured using a contact angle meter (ATAGO contact angle meter) at room temperature.

Morphology and Thermal Property

Morphology of the films was studied using a scanning electron microscopy (SEM, JEOL JSM820). UV-cured cells were first fractured in liquid nitrogen, followed by extraction of LC in methanol for 24 h, and were cleaned in an ultrasonic cleaner. Samples were sputtered with gold before viewing under SEM. Thermal property of the films was determined using a DSC (Du Pont 1090) at a heating rate of 10°C/min.

Electrooptic Measurements^{16,17}

The UV-cured PNLC films sandwiched between two ITO-coated cells were placed normal to the

direction of collimated beam of He/Ne laser (wavelength of 632.8 nm). When the effects of temperature were measured, the cells were placed in a heating stage. Transmitted light intensity without any polarizer was measured with a photodiode. The output from a function generator was amplified and used to drive the shutter. The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope (Hitachi VC-6023). The distance between the cell and photodiode was about 300 mm. The lined up facilities, controlled by a laboratory computer, were turned up for about 1 h before the data were taken.

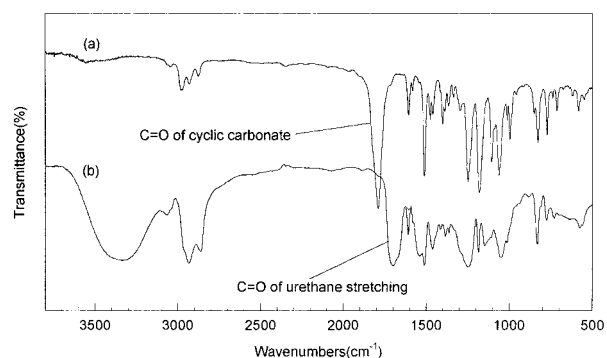


Figure 2 FTIR spectra of cyclic carbonate from bisphenol A-diglycidyl ether with CO₂ (a) and poly(hydroxy)urethane (b).

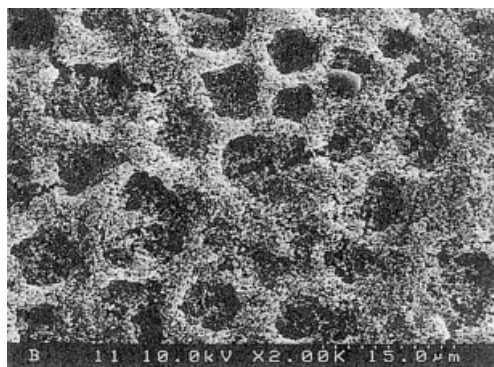
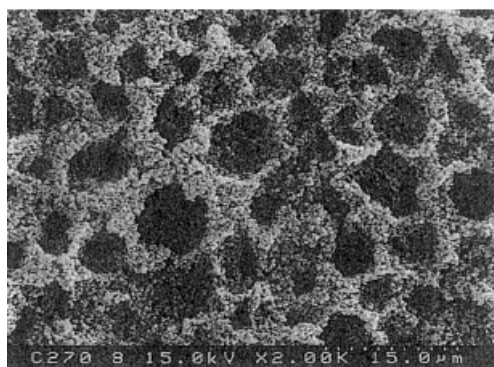
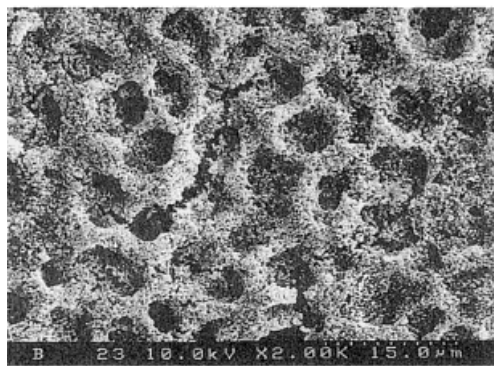
A₁A₂A₃

Figure 3 SEM morphologies of polymer/LC composite films with different types of diglycidyl ether (Series A).

RESULTS AND DISCUSSION

Effect of Diglycidyl Ether Structure

The formation of bis(cyclic carbonate) was confirmed by FTIR measurement [Fig. 2(a)], i.e., a strong absorption peak at about 1800 cm⁻¹ corresponding to the C=O stretch bond indicates that

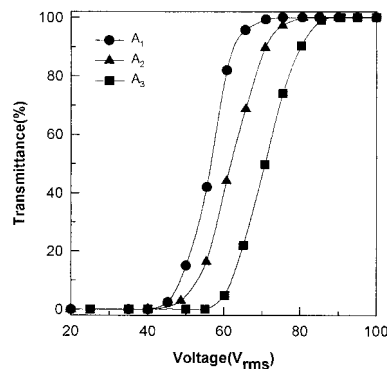
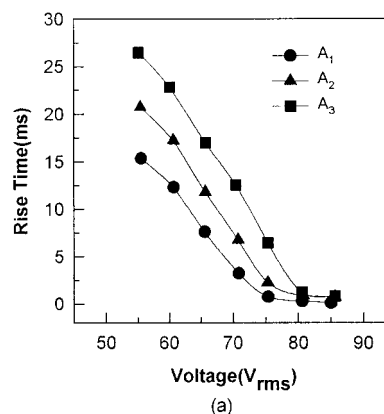
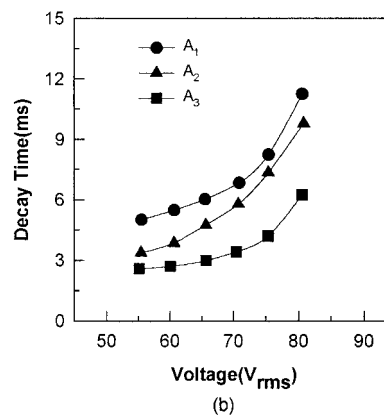


Figure 4 Transmittance vs. applied voltage of polymer/LC films with different types of diglycidyl ether (Series A).

these compounds were obtained from the reactions between epoxide and CO₂. Formation of poly(hydroxy)urethane from cyclic carbonate of bisphenol A–diglycidyl ether and 6-amino-1-hexanol was also confirmed from FTIR measure-



(a)



(b)

Figure 5 Rise time (a) and decay time (b) vs. applied voltage of polymer/LC composite films with different types of diglycidyl ether (Series A).

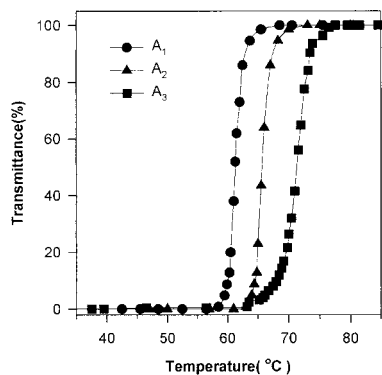


Figure 6 Off-state transmittance vs. temperature during heating of polymer/LC composite with different types of diglycidyl ether (Series A).

ment [Fig. 2(b)]. The C=O absorption peak (1700 cm^{-1}) of cyclic carbonate disappeared, and new peaks at about 1800 and 1540 cm^{-1} , each corresponding to C=O and NH of urethane groups appeared.

Contact angles of LC droplets with PUA films of different types of diglycidyl ether were measured to look at the interactions between them: it was 24° for A_1 (aliphatic), 21° for A_2 (cyclohexane), and 17° for A_3 (aromatic), indicating that the aromatic type gives the greatest interactions with the LC, which mainly are composed of aromatic compounds.

Figure 3 shows the SEM morphology of these films. The domain size decreases in the order of $A_1 > A_2 > A_3$, which is the same order as with the contact angle. It seems that A_3 , having the greatest interaction with LC, gives rise to the smallest domains due to the difficult droplet co-

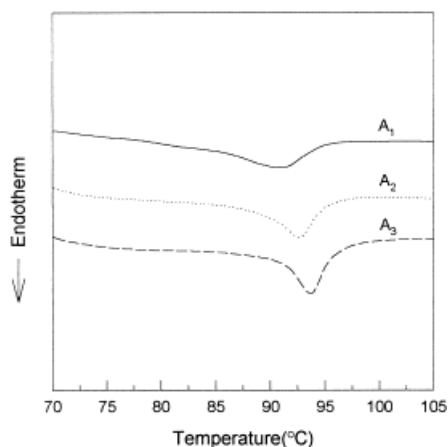
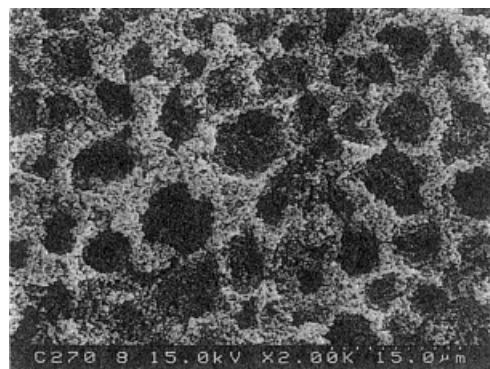
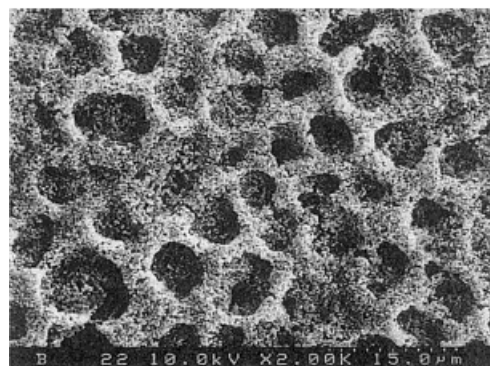


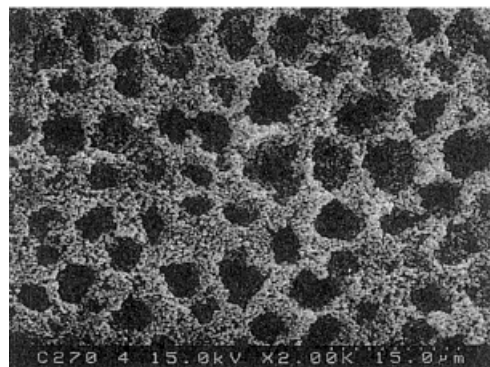
Figure 7 DSC thermograms of polymer/LC composite films with different types of diglycidyl ether (Series A).



B_1



B_2



B_3

Figure 8 SEM morphologies of polymer/LC composite films with different types of end-capping acrylate (Series B).

alescence in the highly viscous A_3 matrix, in addition to the great miscibility between the matrix and LC.

Figure 4 shows the transmittance–voltage (V-T) relationships of these films. Threshold (V_{10}) and operation (V_{90}) voltages of these film increase in the order of $A_1 < A_2 < A_3$, an order of decreasing domain size implying that the elec-

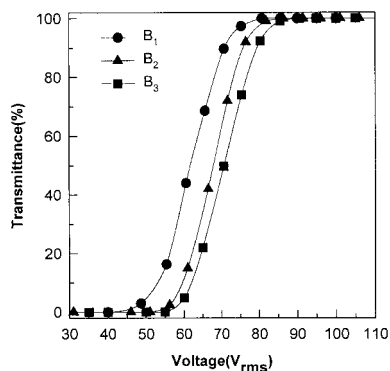


Figure 9 Transmittance vs. applied voltage of polymer/LC composite films with different types of end-capping acrylate (Series B).

trooptic performance of the films is largely governed by the domain size which, on the other hand, can be controlled by the diglycidyl ether segment of the PU. The variation of V_{10} and V_{90} , for aromatic, cycloaliphatic, and aliphatic types of diglycidyl ether, is a direct response to the domain size.

Figure 5 shows the rise time (τ_R) and decay time (τ_D) of these films as a function of applied voltage. Rise time decreases asymptotically with applied voltage due to the rapid alignment of

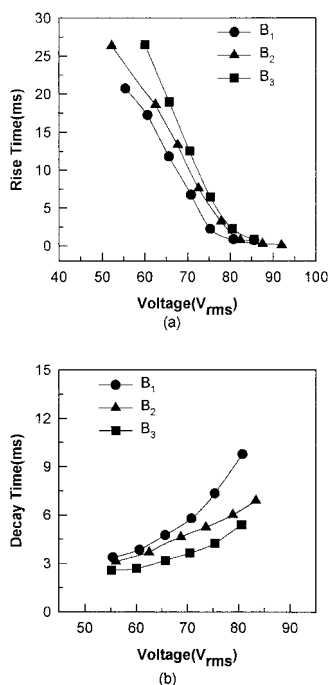
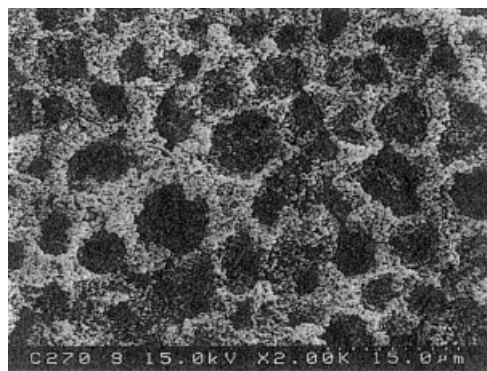
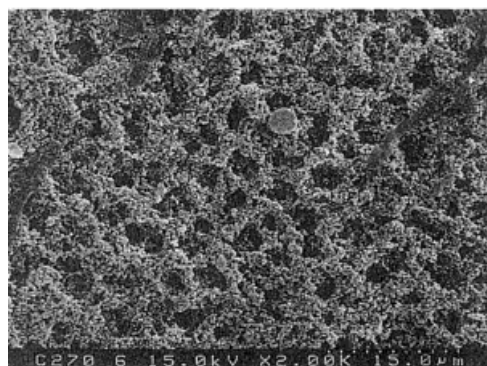


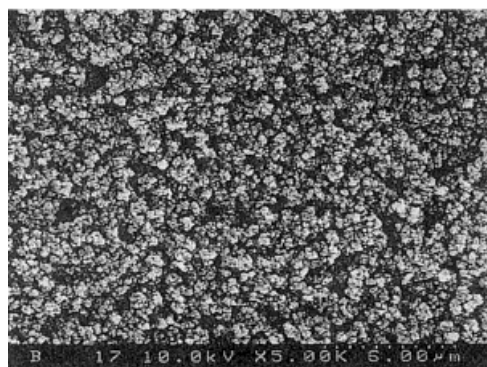
Figure 10 Rise time (a) and decay time (b) vs. applied voltage of polymer/LC composite films with different types of end-capping acrylate (Series B).



C₁



C₂



C₃

Figure 11 SEM morphologies of polymer/LC composite films with different functionality of multifunctional diluent (Series C).

nematic directors along the field direction. Regarding the effect of diglycidyl ether, A₁ gives the quickest response to the electric field due mainly to the morphological effect of this film. In general, smaller domains give larger τ_R , because they have to overcome more surface anchoring energy. Regarding the effect of diglycidyl ether on decay time, A₃ gives the quickest, and A₁ gives the

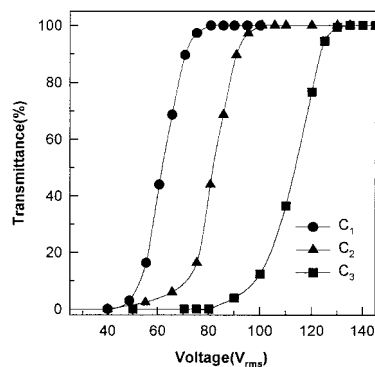


Figure 12 Transmittance vs. applied voltage of polymer/LC composite films with different functionality of multifunctional diluent (Series C).

slowest decay times, in accordance with their domain size. Generally, smaller domain gives smaller τ_D due to the higher elastic energy of the deformed state.

Figure 6 shows the off-state transmittance as a function of temperature during heating. The off-state transmittance shows an abrupt increase in transmittance from opaque to transparent state at a certain temperature. The transition is caused by several factors such as the decrease of birefringence, decrease of refractive index mismatch, and

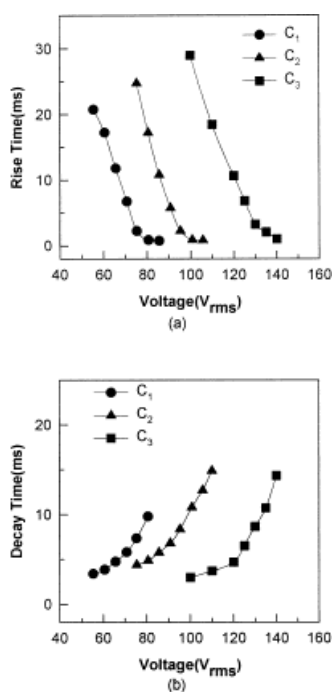


Figure 13 Rise time (a) and decay time (b) vs. applied voltage of polymer/LC composite films with different functionality of multifunctional diluent (Series C).

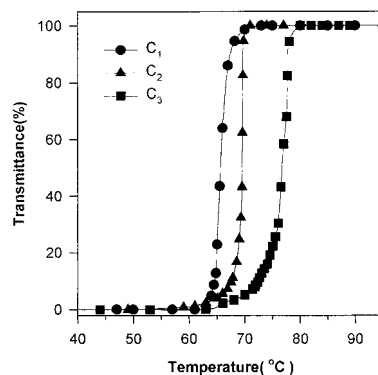


Figure 14 Off-state transmittance vs. temperature during heating of polymer/LC composite films with different functionality of multifunctional diluent (Series C).

increase of mutual solubility. The transition temperature is closely related to the T_{NI} , which may be either depressed, due to the impurity effect of polymer compounds, or raised due to the preferential dissolution of light component of the LC mixture into polymer.^{9,18} The T_{NI} of LC (95°C) decreased in the films, and the order of decrease became larger along A_3 , A_2 , and A_1 . Apparently, flexible polymers with lower interactions with LC showed the greatest drop in T_{NI} . It seems that the lower T_g of aliphatic diglycidyl ether-based polymer is the main reason for the greatest decrease in T_{NI} . The anchoring energy of LC on the polymer wall becomes small with increasing temperature. Hence, polymer of a lower T_g should induce an isotropic state at lower temperature. In general, the transmittance–temperature curve moves towards higher temperature with the increase in T_g . Figure 7 shows the DSC thermogram of the films. The depression of T_{NI} is basi-

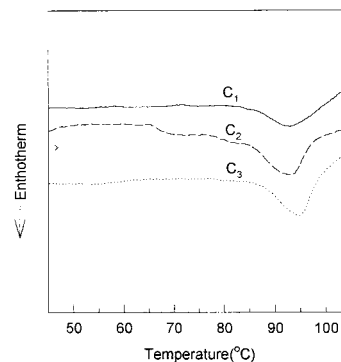


Figure 15 DSC thermograms of the PNLc films with different functionality of multifunctional diluent (Series C).

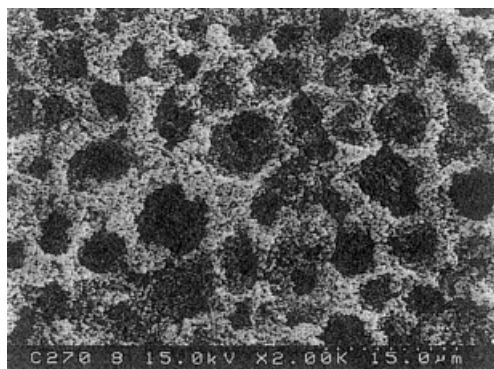
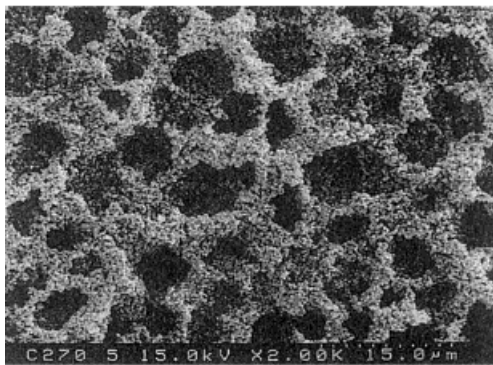
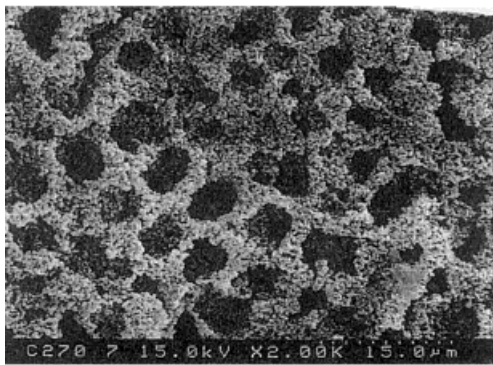
D₁D₂D₃

Figure 16 SEM morphologies of polymer/LC composite films with Series D.

cally in agreement with the above off-state transmittance measurement (Fig. 6).

Effect of End-Capping Acrylate Structure

The structure of end-capped acrylates was varied in series B. The effect was first studied with contact angle measurements. It was 21° for B_1 (HEA), 19° for B_2 (HPA), and 17° for B_3 (HEMA),

implying that polymer–LC interactions are in the increasing order of $B_1 < B_2 < B_3$.

Figure 8 shows the SEM micrographs of the films prepared with different types of end-capping acrylates. HEA end-capped PUA film (B_1) gave the largest LC domain, and the HEMA end-capped one (B_3) gave the smallest domain. This is mainly due to the difference in polymer–LC interactions in accordance with the variation of contact angle.

Figure 9 shows the transmittance vs. applied voltage relationships of these films. It is seen that V_{10} , as well as V_{90} , decreases with the increase in LC domain size in the order of $B_3 < B_2 < B_1$, i.e., B_1 gives the lowest threshold and driving voltages.

Figures 10 shows τ_R and τ_D of these films. τ_R Monotonically decreases with voltage, whereas τ_D increases with voltage. It is seen that the structure of end-capped acrylate exerts a significant effect on τ_R and τ_D . It seems that the response times are very much governed by the domain size, and by polymer–LC interactions to some extent.

Effect of Reactive Diluent Functionality

In series C, the crosslinking density of the polymer matrix was varied by changing the functionality of multifunctional diluent while the type of monofunctional diluent was fixed as NVP. Reactive diluents are typically mono and multifunctional acrylates, and are added for two reasons, i.e., to reduce the viscosity of prepolymer and to build up molecular weight of the polymer by chain extension (monoacrylate) and/or crosslinking

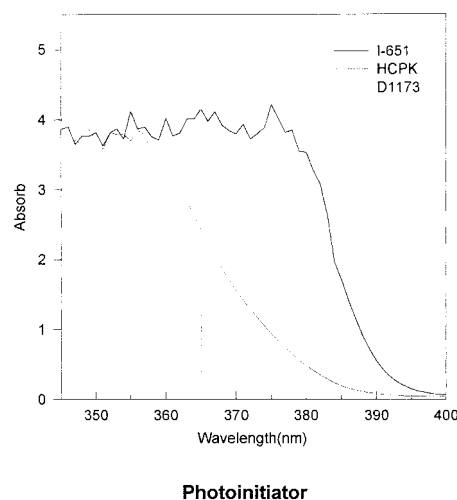


Figure 17 UV absorbances of films with Series D.

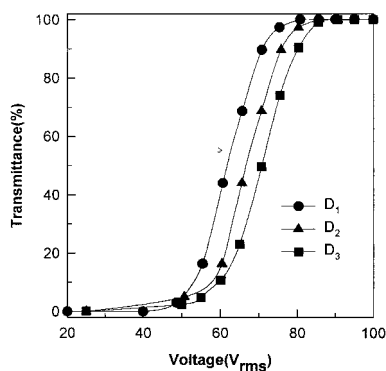


Figure 18 Transmittance vs. applied voltage of polymer/LC composite films with different types of photoinitiators (Series D).

(multifunctional acrylates). The extent of crosslinking, viz. the extent of cure, depends on the average functionality of the reactive diluents. Tripropylene glycol diacrylate (TPGDA, functionality $f = 2$, C_1), trimethylolpropane triacrylate (TMPTA $f = 3$, C_2), and dipentaerythritol hydroxy penta/hexa acrylate (DPHPA $f = 5/6$, C_3) have been incorporated in this series.

Figure 11 shows the SEM micrographs of the films, showing that LC domain decreases in size with increasing average functionality of the diluents. This is because the crosslinking density of the prepolymer domain increases with increasing f .

Figure 12 shows the V-T relationships of these films. As expected, the curves move toward higher V_{10} and V_{90} with the increase in f , due mainly to the decreased LC domain size ($C_1 > C_2 > C_3$). τ_R increases and τ_D decreases with increasing f (Fig. 13). The relatively long τ_D of C_1 is due to the relatively low crosslinking density, providing less interfaces and fewer interactions with LC. Off-state transmittance variation with temperature (Fig. 14) and DSC thermograms (Fig. 15) also show that T_{NI} of LC slightly decreases with increasing f in the film. This implies that the solubility of polymer species in LC is decreased with an increase in crosslinking density.

Effect of Photoinitiator Structure

Among the effects of photocuring conditions, the effect of the photoinitiator has been examined in series D. Figure 16 shows that the LC domain size with Darocure 1174 (D_3) is smaller compared with Irgacure 651 (D_1) and Irgacure 184 (D_2). This is simply because Irgacures have stronger

absorptions at 365 nm (radiation source) wavelength (Fig. 17) for a complete cure. Electro-optic performance of this series follows the morphology effect; i.e., Irgacure 651 gives the lowest V_{10} , V_{90} (Fig. 18), and τ_R , and highest τ_D (Fig. 19).

CONCLUSIONS

Electro-optic properties of CO_2 -fixed polymer/nematic LC have been studied as responses of chemical composition, end-capping acrylate, crosslinking density of the polymer matrix, and photoinitiator structure. Among the three types of diglycidyl ether incorporated, bisphenol A type gave the smallest domain size and greatest threshold and driving voltage due to the greatest interactions with LC molecules, evidenced by the contact angle measurements.

The type of end-capping acrylate also exerted a significant effect on interaction with LC. HEMA, containing two pendant groups compared with one for HEA and HPA, showed better interactions with LC, leading to smaller domain and contact angle, and larger V_{10} and V_{90} .

High functionality diluents gave small domain size and large V_{10} and V_{90} , due to the difficulty in

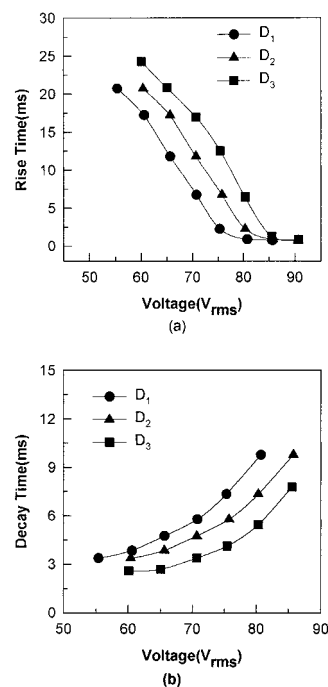


Figure 19 Rise time (a) and decay time (b) of polymer/LC composite films with different types of photoinitiators (Series D).

droplet coalescence in the highly crosslinked polymer matrix. Photoinitiator, with high absorption at the radiation source wavelength, gave a more complete cure of the matrix, leading to smaller domain size and high V_{10} and V_{90} .

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