

Pixel-isolation liquid crystals formed by polarization-selective UV-curing of a prepolymer containing cinnamate oligomer

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Abstract: A pixel isolated liquid crystal display was fabricated by polarization-selective anisotropic photoreaction of a prepolymer containing a cinnamate oligomer. The cinnamate oligomer was mainly distributed on the surface region of a UV-cured polymer wall. Anisotropic photo-dimerization of cinnamate moiety was achieved by polarized UV exposure. It was found that the polymer walls containing cinnamate dimers formed by polarized UV exposure showed ordered orientation of LC molecules at the boundary of the polymer walls resulting in electro-optic performance improvement.

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1. Introduction

Due to their important features such as light weight, thin packing, bending capability, and portability, flexible displays are gaining much attention in areas of future application, such as portable mobile displays, wearable computers, and smart cards. In particular, flexible displays

based on liquid crystals (LC) have been extensively studied and widely used because of their low-power consumption and potential to produce high-quality images [1,2]. For flexible LC displays, mechanical stability and uniform cell gap between two plastic substrates are critical factors for retaining long-term LC alignment against external perturbations such as pressure, bending distortion, and mechanical shock. In order to solve these problems, several types of polymer walls or networks have been investigated for use as possible support structures. These structures were fabricated using a phase separation method from a LC and polymer mixture by applying a patterned UV exposure [3–6].

The pixel-isolated LC (PILC) mode is one of the leading fabrication methods for flexible LC displays. In this structure, LC molecules are isolated in pixels surrounded by inter-pixel vertical polymer walls. This mode shows not only good mechanical stability but also nearly the same optical behavior as that of the normal LC mode. However, the molecular orientation of the LC molecules at the boundary of the polymer walls is disturbed by the interaction between the LC molecules and the polymer walls [7,8]. In the dark state, this disturbed orientation of LC molecules induces light leakage at the boundary of the polymers wall and the contrast ratio of LC is decreased by the light leakage, which is an important issue for display quality.

In this letter, we propose a polarization-selective anisotropic photoreaction based UV-curable prepolymer system for a pixel isolation wall to improve the light leakage problem at the boundary of the polymer walls. The cinnamate oligomer, which shows the anisotropic photodimerization reaction of cinnamate moiety by polarized UV exposure, was synthesized and applied as an additive to prepare an acrylate prepolymer system that can improve contrast ratio. The distribution of the cinnamate oligomer after UV-curing was confirmed by measuring the water contact angle. The orientation of the LC molecules by polarization-selective distribution of cinnamate dimers in the UV-cured prepolymer was also observed. The prepolymer containing the cinnamate oligomer was used to prepare the PILC and the behavior of LC molecules at the boundary of the polymer walls was investigated.

2. Experiments

2.1. Synthesis and characterization of cinnamate oligomers

Polyethylene glycol (PEG) with cinnamate moiety on both terminals, which was used as the cinnamate oligomer was synthesized using PEG of molecular weight 600 (Aldrich Co.) and cinnamoyl chloride (Aldrich Co.). The synthesized cinnamate oligomer was named poly(ethylene glycol)-dicinnamate (PEG-diCi) (Fig. 1). The photoreactivity of the synthesized PEG-diCi was investigated by measuring the UV-vis spectra with UV exposure from a 4W filtered lamp with a wavelength of 365 nm (Vilber Lourmat, France). PEG-diCi was dissolved in cyclohexanone to prepare a 1 wt% solution. The solution was spread onto the quartz plate (20 mm x 20 mm) and dried for 10 min at room temperature. UV-vis spectra of coated PEG-diCi with the different UV exposure times were collected using a UV-vis spectrometer (Optizen 2120UV plus, Mecasys).

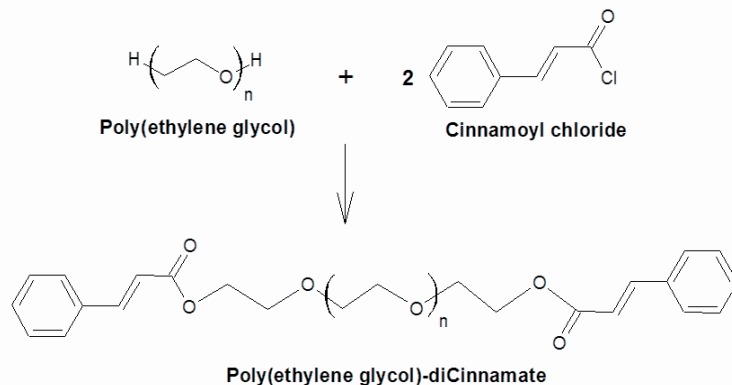


Fig. 1. Synthetic scheme and molecular structure of PEG-diCi

2.2. Preparation of prepolymers

For the preparation of the prepolymer for PILC, bi-component prepolymer was prepared by blending the PEG-diCi and the ethyl hexyl acrylate (EHA, Aldrich Co.) based acrylate prepolymer. EHA, well known as a component of a prepolymer for polymer dispersed liquid crystals (PDLC), was selected for the monomer due to its good phase separation property with LC. The acrylate prepolymer was prepared by mixing 90 wt% EHA, a 9 wt% crosslinker (polyethyleneglycol diacrylate, PEGDA, Aldrich Co.), and a 1 wt% photoinitiator (Darocur4265, Aldrich Co.). Hydrophilicity of the cured bi-component prepolymer was measured by the sessile drop technique using a contact angle analyzer (Phoenix 300 Plus, SEO Co.).

2.3. LC alignment on bi-component prepolymers

The behavior of the LC molecules on the bi-component prepolymer was confirmed by investigating polarized optical microscope images of the LC cell. The bi-component prepolymer was spin coated onto the ITO glass substrate and polarized UV used for irradiation to induce the anisotropic photoreaction of the cinnamate moiety. LC cells were made by assembling a pair of glass substrates coated with bi-component prepolymer; the cell gap between the two ITO glasses was maintained at 5 μm by using polystyrene spacers. Nematic LC (E7, Merck Co.) was injected into the cell by capillary motion at 65°C, upon which the liquid crystals changed to the isotropic phase. This procedure was followed by cooling down of the cell to room temperature.

2.4. PILC device fabrication

To fabricate LC cells with polymer walls, we prepared a mixture of LC and the bi-component prepolymer with a weight ratio of 50:50. The LC cells were prepared by using indium-tin-oxide (ITO) coated glass substrates. A polyimide solution was spin coated on the ITO glass and rubbed. The cell gap between the two ITO glasses was maintained at 5 μm by using polystyrene spacers. The mixture of the LC and the prepolymer was injected into the empty cell by the capillary effect at 100 °C, above the clearing temperature. In order to cure the prepolymer, UV light at 10 mW/cm^2 was irradiated through a photomask while maintaining the sample temperature at 100 °C. The photomask had a pattern of 300 \times 300 μm^2 dark squares with 30 μm spacing. In order to induce the anisotropic photoreaction of the cinnamate moiety, a UV linear polarizer (20LP-UV, Newport) was used for UV exposure.

3. Results and discussion

In order to endow the prepolymer with polarization-selective characteristics, the cinnamate moiety, well known for its anisotropic photo-dimerization reaction by polarized UV, was

attached to the flexible PEG backbone. In order to confirm the photoreactivity of the cinnamate moiety of PEG-diCi, the UV absorption spectrum of PEG-diCi as a function of UV exposure time was investigated (Fig. 2). UV light of wavelength 365 nm was used to irradiate the coated PEG-diCi film. From the UV absorption spectra, maximum peak intensity was observed at 280 nm, which is the characteristic peak of the cinnamate moiety; the peak diminished as the UV exposure dose increased. The decrease of the peak originated from the photo-dimerization reaction of the attached cinnamate moiety of PEG-diCi. From the UV absorption spectrum, it was found that the photo-dimerization reaction of the cinnamate moiety of PEG-diCi successfully occurred due to the UV exposure.

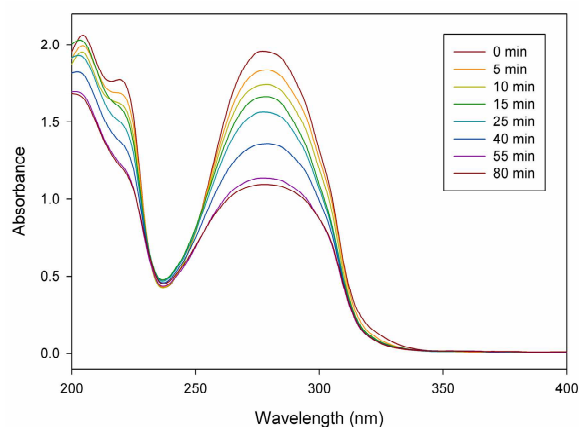


Fig. 2. UV absorption spectrum of PEG-diCi as a function of UV exposure time.

The surface properties of the UV-cured bi-component prepolymer are closely related with the behavior of the LC molecules near the polymer walls. In our work, the surface energy of the polymer surface was investigated by measuring the water contact angle. We measured the water contact angle on the prepolymer film with various amounts of PEG-diCi irradiated by polarized UV (Fig. 3).

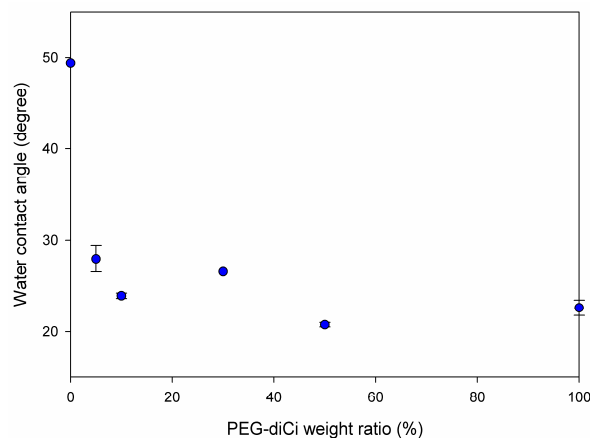


Fig. 3. Water contact angle of bi-component prepolymer films exposed by polarized UV (4 J/cm^2) as a function of PEG-diCi weight ratio.

Due to the hydrophobic alkyl chain of EHA, the water contact angle of the polymer film without PEG-diCi was about 50° . However, the water contact angle of the polymer film containing PEG-diCi dropped below 30° , which illustrates the change in the surface character from hydrophobic to hydrophilic. This change is attributed to the hydrophilicity of the

incorporated PEG-diCi. In spite of the small amount of PEG-diCi (10 wt%), water contact angle on the polymer film showed an abrupt decrease; a further increase of the amount of PEG-diCi showed little effect on the change of water contact angle. From these results, it was determined that the PEG-diCi was well located in the surface region of the polymer film regardless of the amount of PEG-diCi. Consequently, the surface property of the bi-component prepolymer film could be said to be mainly dominated by the cinnamate dimers even if only a small amount of PEG-diCi was used.

The surface-oriented distribution of the PEG-diCi of the bi-component prepolymer film might be closely related with the behavior of the LC molecules at the surface of the bi-component polymer wall. In order to predict the role of the PEG-diCi component on the orientation of LC molecules near the polymer walls, the LC alignment properties of the bi-component prepolymer film were investigated. Figure 4 shows the polarized microscope images of LC cells prepared by using bi-component polymer film irradiated by polarized UV. Polymer film containing no PEG-diCi showed no orientation of LC molecules, while the polymer film containing PEG-diCi showed good orientation of LC molecules. In spite of the small amount of PEG-diCi, PEG-diCi of 10 and 30 wt% showed favorable LC orientation; this is due to the cinnamate dimers distributed on the surface of the polymer film. The cinnamate moiety exposed to polarized UV forms anisotropically distributed cinnamate dimers and LC molecules are aligned by the anisotropic interaction with the cinnamate dimers [9].

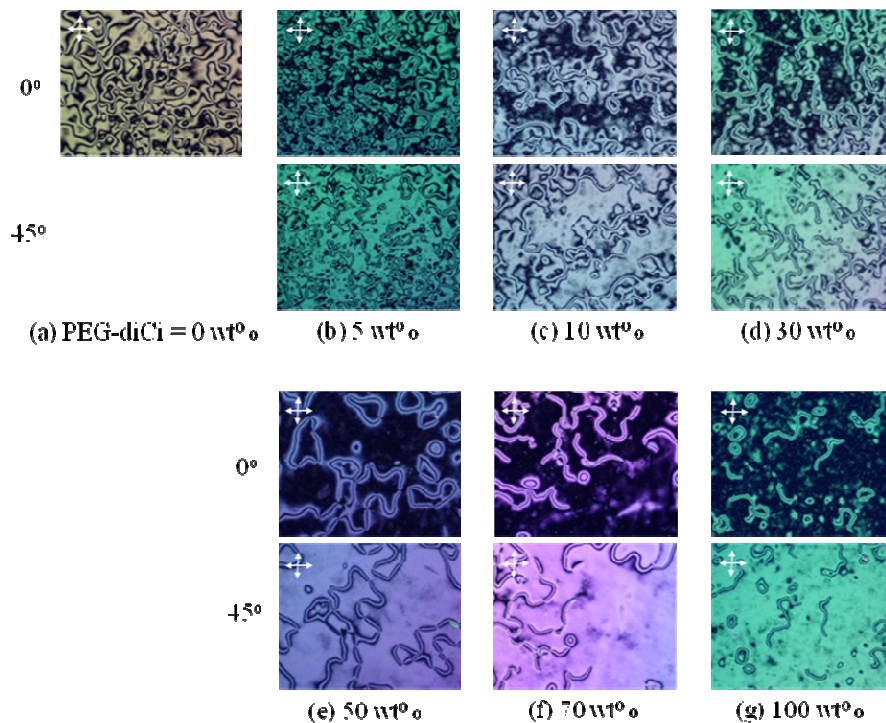


Fig. 4. Polarized optical microscope images of LC cell prepared by using bi-component prepolymer film exposed by polarized UV ($4\text{J}/\text{cm}^2$) as a function of PEG-diCi weight ratio: (a) 0 wt%, (b) 5 wt%, (c) 10 wt%, (d) 30 wt%, (e) 50 wt%, (f) 70 wt%, (g) 100 wt%.

In order to compare the orientation of LC molecules more precisely, the azimuthal anchoring energy was measured, calculated by measuring the width of the Neel Wall [10] of the LC cells prepared by using polarized UV irradiated bi-component polymer film. Figure 5 shows the azimuthal anchoring energy of the polarized UV irradiated prepolymer films containing different amounts of PEG-diCi. In the case of prepolymer containing PEG-diCi, the azimuthal anchoring energy was the same order of magnitude irrespective of the amount of PEG-diCi,

which was in accordance with the surface coverage of the cinnamate dimers. However, polymer film without PEG-diCi showed an abrupt decrease of the azimuthal anchoring energy despite the polarized UV exposure. The cinnamate dimers located in the surface region of the UV-cured bi-component prepolymer film had a dominant effect on the orientation of LC molecules on the polymer film.

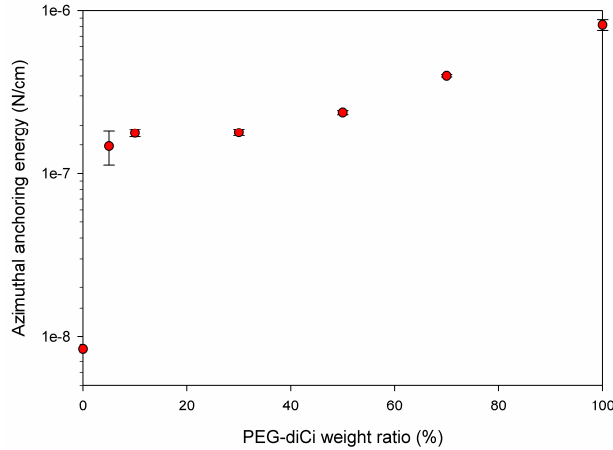


Fig. 5. Azimuthal anchoring energy of LC cell prepared by using bi-component prepolymer film exposed by polarized UV (4 J/cm^2) as a function of PEG-diCi weight ratio.

The state of LC molecules near the polymer walls was investigated by preparing a PILC using a prepolymer containing PEG-diCi. In order to confirm the effect of the anisotropic photoreaction of the cinnamate moiety on the orientation of LC molecules at the boundary of the polymer walls, a linear UV-polarizer was used selectively for the formation of polymer walls. Figure 6 shows the polarized optical microscope images of the PILC structure prepared using a bi-component prepolymer containing PEG-diCi.

All of the samples showed typical pixel isolated polymer walls regardless of UV exposure time or polarization. In the case of unpolarized UV exposure, light leakage at the boundary of the polymer walls was observed in the dark state (45° rotated to the axis of the cross-polarizers of the microscope), which was caused by the disordered orientation of LC molecules at the boundary of the polymer walls [8]. However, unlike the case of unpolarized UV exposure, the polymer walls formed by polarized UV exposure showed little light leakage at their boundary. The polarization direction of the UV exposure was adjusted to the direction parallel to the rubbing direction of the polyimide alignment layer. Because of the polarized UV exposure, the cinnamate moiety distributed near the surface of the polymer wall experienced anisotropic photo-dimerization and the cinnamate dimers had anisotropic orientation as expected from the measurement of the water contact angle and azimuthal anchoring energy. The cinnamate dimers oriented at the boundary of the polymer walls interacted with LC molecules and the LC molecules were aligned parallel to the rubbing direction. Due to the orientation of the LC molecules, light leakage at the boundary of the polymer walls was considerably improved. A small amount of PEG-diCi was sufficient to improve the level of light leakage. This might be attributable to the surface-oriented anisotropic distribution of PEG-diCi in the bi-component prepolymer. From this result, it was determined that the anisotropic photoreaction of a photo-dimerizable prepolymer is a very effective way to improve the interface between LC molecules and the polymer walls of PILC.

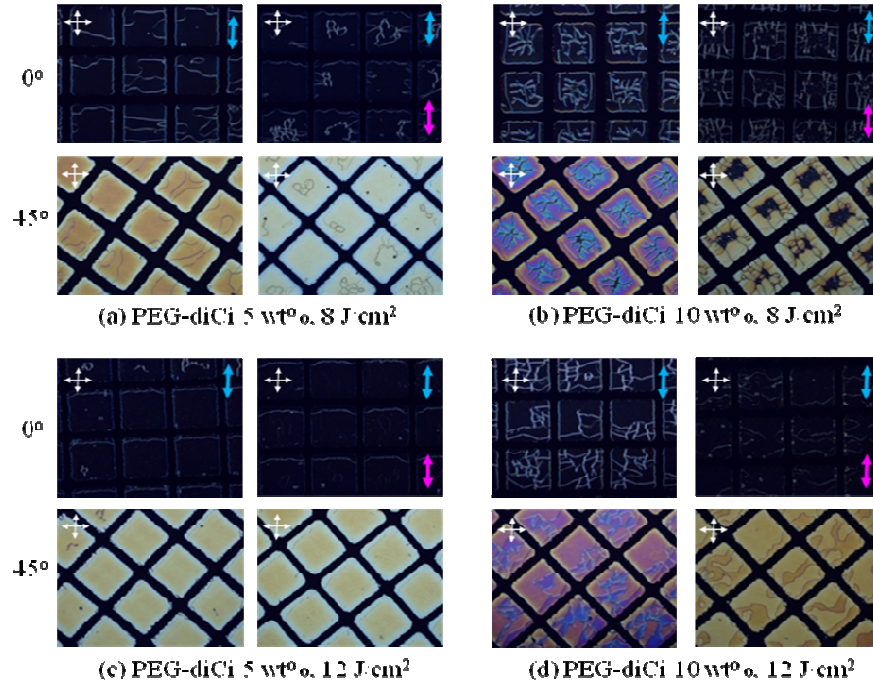


Fig. 6. Polarized optical microscope images of PILC using bi-component prepolymers: (a) PEG-diCi 5 wt%, 8 J/cm², (b) PEG-diCi 10 wt%, 8 J/cm², (c) PEG-diCi 5 wt%, 12 J/cm², (d) PEG-diCi 10 wt%, 12 J/cm². The blue arrow represent rubbing direction and the red arrow represents the polarization direction of UV exposure.

The improvement of the interface between LC and polymer walls is closely related with the display quality of PILC. In order to investigate the effect of the polymer wall interface on the electro-optical performance, V-T curves for PILC devices prepared by using 5 wt% PEG-diCi bi-component prepolymer were measured (Fig. 7). The V-T curve for a normal LC cell without polymer walls was also measured for comparison. All of the LC devices showed almost the same behavior except for the threshold voltage. The PILC device prepared by unpolarized UV exposure showed higher threshold voltage compared with that of the normal LC cell without polymer walls. This means that the movement of LC molecules due to external electric field is considerably disturbed by the interface of the polymer walls. However, PILC devices prepared by polarized UV exposure showed a similar threshold voltage to that of the normal LC cell without polymer walls. The ordered LC molecules near the polymer walls formed by polarized UV might be advantageous for the movement of LC molecules and the threshold voltage did not increase despite the polymer walls.

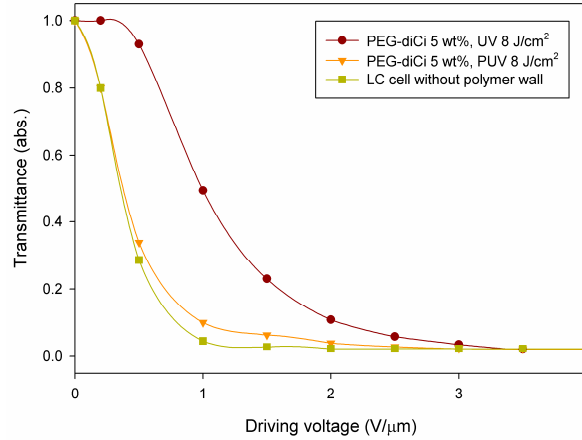


Fig. 7. V-T curves of PILC devices prepared by using 5 wt% PEG-diCi bi-component prepolymers with unpolarized UV (●), with polarized UV (▼) and normal LC cell without polymer walls (■).

In order to confirm the effect of PEG-diCi on electro-optical performance, the contrast ratio and driving voltage of PILC were investigated (Fig. 8). Due to the decreased light leakage at the boundary of the polymer walls, the contrast ratio of the PILC prepared by polarized UV exposure was higher than that of the PILC prepared by unpolarized UV exposure. The prepolymer containing 5 wt% PEG-diCi showed a higher contrast ratio compared with that containing 10 wt% PEG-diCi. This is related to the degree of phase separation between LC and prepolymer. Due to the hydrophilicity of PEG-diCi, PEG-diCi is more compatible with LC molecules and could reduce the degree of phase separation between the LC and the prepolymer [11]. With an increasing amount of PEG-diCi, it is difficult to achieve complete phase separation and electro-optical performance would be deteriorated by the prepolymer residue remaining in the LC phase. Therefore, the 5 wt% PEG-diCi is suitable for improving light leakage without deterioration of electro-optical performance. The driving voltage of PILC was also decreased by using polarized UV exposure and this was related to the improved orientation of LC molecules at the boundary of the polymer walls. In the case of PDLC, the ordering of LC molecules at the boundary of the LC droplet is closely related to the switching characteristics of the LC phase [12]. Due to the presence of ordered LC molecules at the boundary of the polymer walls, LC molecules might be easily switched by an external electric field, decreasing the driving voltage.

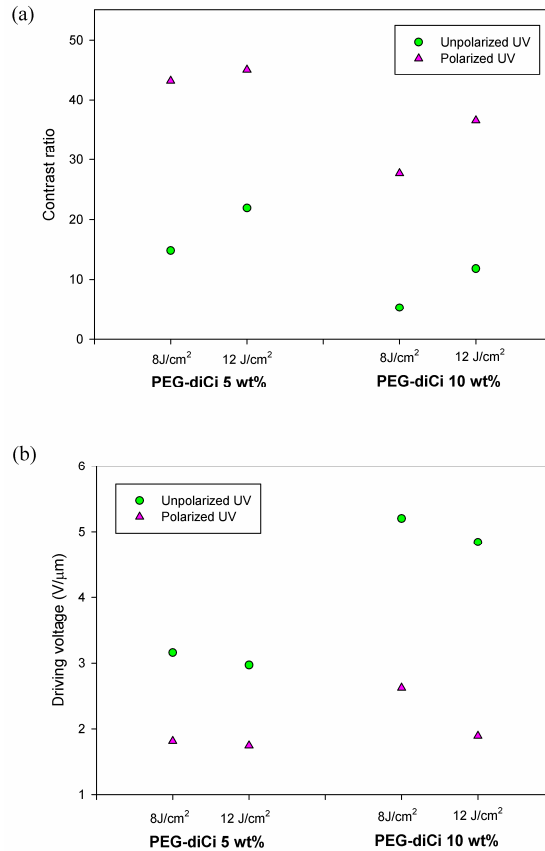


Fig. 8. Electro-optical performances of PILC prepared by using EHA/PEG-diCi prepolymers irradiated by polarized or unpolarized UV: (a) contrast ratio of PILC with driving voltage 2.5V/μm, (b) driving voltage for obtaining contrast ratio 30.

4. Conclusions

In summary, we have proposed a polarization-selective anisotropic photoreaction-based polymer wall formation to improve the electro-optical performance of PILC. A synthesized cinnamate oligomer was used as an additive for the acrylate prepolymer system and the surface-oriented anisotropic distribution of the cinnamate oligomers was demonstrated. Anisotropic photo-dimerization of the cinnamate moiety was achieved by polarized UV exposure; the orientation of LC molecules at the boundary of the polymer walls was controlled. It is expected that polymer wall formation by anisotropic photoreaction can be applied to various types of LC/polymer composite systems to enhance electro-optical performance.

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