

The Influence of Crosslinking Agents on the Morphology and Electro-Optical Performances of PDLC Films

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ABSTRACT: The morphology of polymer-dispersed liquid crystal (PDLC) has a major impact on its electro-optic properties. The PDLC was prepared by photochemical polymerization from UV-curable monomers/crosslinking agent/initiator/LC mixture. The influences of crosslinking agents on the PDLC system had been studied. The microstructures of the PDLC were strongly influenced by the insertion of polyethylene glycol (600) diacrylate (PEGDA 600) crosslinker, relatively long and flexible branch, and diethylene glycol diacrylate (DEGDA) cross-

linker along the network bone. The relative weight ratio of crosslinking agents and polymerization temperature had a significant effect on the LC domain size, and which resulted in influencing the electro-optic properties of PDLC. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3434–3440, 2010

Key words: polymer-dispersed liquid crystal; photopolymerization; morphology; electro-optical properties; crosslinking

INTRODUCTION

A liquid crystal (LC) is widely used in electric devices, such as optical display, especially when relatively low power consumption and satisfactory response time are required.^{1–3} Among the electric devices, a polymer-dispersed liquid crystal (PDLC) film has been intensively studied in the past few decades, as it can be switched electrically from a light scattering state to a transparent state. Unlike conventional LC displays, a PDLC film is flexible and easy to prepare, besides being unnecessary for polarizers, alignment layers, and precise control of the spacer between two substrates.^{4–6} Therefore, PDLC film is candidate for several applications such as flexible display devices, optical shutters, and switchable windows.⁷

A PDLC film consists of micron-sized droplets of LC trapped within a polymer matrix.⁸ In an electrical off-condition, a PDLC film is opaque because of

the light scattering caused by the refractive index mismatch between LC droplets and polymer matrix. In an electrical on-condition, a PDLC film becomes transparent because of the long axes of the LC molecules is aligned parallel to the applied electric field and the ordinary refractive index of the LC matches the refractive index of the polymer.^{9–11} It has been found that the electro-optic properties of PDLC films are influenced by the size and morphology of LC domains, the compositions ratios, separation degree, and other parameters.¹²

PDLC can be fabricated using polymerization-induced phase separation (PIPS),¹³ thermally induced phase separation,¹⁴ solvent-induced phase separation,¹⁵ or nematic curvilinear aligned phase.¹⁶ PIPS has been considered to be the most popular way, as the fabrication process is relatively simple, clean, and solvent free. The matrixes in the PIPS can be cured from photo-curable and thermal-curable monomers.⁹ Because of that the cure of the former can be finished in a few minutes at room temperature, whereas that of the latter is usually done for few hours at a higher temperature; the PDLC films of which the matrixes made from photo-curable monomers have being attracted much attention.

In this study, the PDLC film was prepared with PIPS method from monomers/initiator/LC composite. The effects of the relative weight ratio of crosslinking agents and polymerization temperature on the microstructure of the polymer matrix and the electro-optical properties were investigated.

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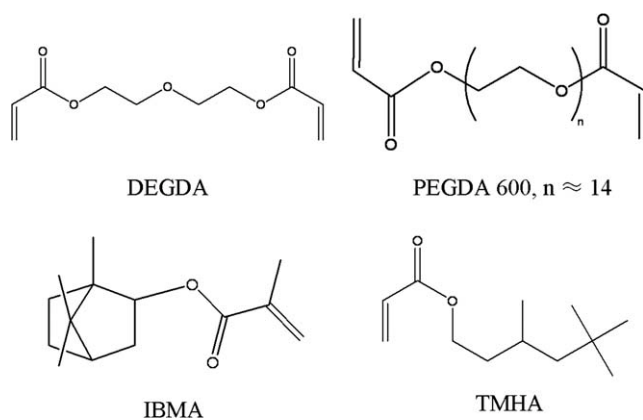


Figure 1 Chemical structures of the photo-polymerizable monomers used.

EXPERIMENTAL

Materials

The nematic LC used in this study was SLC 1717 ($T_{NI} = 365.2\text{K}$, $n_o = 1.519$, $n_e = 1.720$, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. China). Diethylene glycol diacrylate (DEGDA), polyethylene glycol (600) diacrylate (PEGDA 600) (Sartomer, Exton, PA), Isobornyl methacrylate (IBMA), and 3,5,5-trimethylhexyl acrylate (TMHA) (Aldrich, St. Louise, MO) were used as photo-polymerizable monomers, while Irgacure 651 (Ciba Geigy, Jingjiang Hongtai Chem. Co. China) was used as photo-initiator. Figure 1 shows the chemical structures of the photo-polymerizable monomers. All aforementioned materials were used as received without further purification.

Sample preparation

The monomers/initiator/LC mixture was placed between two glass slides coated with a thin transparent layer of conducting indium/tin oxide. The film thickness was controlled by $16 \pm 1\text{-}\mu\text{m}$ -thick polyethyleneterephthalate spacer. The mixture was then exposed to UV irradiation for about 7.0 min at 273.5, 283.0, and 293.0 K from a 35.0 W high pressure Hg lamp, yielding intensities at the cell surface of about 6.0 mW/cm^2 at 365.0 nm. In this study, the ratio between the diacrylate crosslinkers and the comonomers was maintained as the weight ratio of 1/4. The ratio between IBMA/TMHA was fixed. The various weight ratio of DEGDA/PEGDA 600 with the LC contents of 60.0 wt % were studied.

SEM observation

Morphology of the PDLC film was studied by a scanning electron microscopy (SEM) (Leica S440i, Germany). The film was dipped in hexamethylene at room temperature to extract the LC molecules. Then,

the film was sputtered with carbon before viewing under SEM.

Electro-optic measurement

Electro-optic experiments were measured at room temperature by an LCD parameters tester (LCT-5016C, Changchun Liancheng Instrument Co., China). A halogen laser beam at a wavelength of $\lambda = 560\text{ nm}$ orienting the films normal to the incident laser beam. Starting from the electrical off-state, the applied sinusoidal voltage of frequency 100 Hz was increased continuously up to desired maximum value V_{max} . The transmittance of the PDLC films was recorded by a photodiode, and response of the photodiode was monitored by a digital storage oscilloscope. The distance between the sample cell and the detector was $\sim 300\text{ mm}$. The collection angle of the transmitted intensity was about $\pm 2^\circ$ so that principally forward scattering was detected. UV-visible spectra of off-state PDLC films were measured using a UV/visible/NIR spectrophotometer (V-570, Jasco Corp., Tokyo, Japan). The wavelengths of 300.0–800.0 nm were measured and recorded with an incident angle, $\delta = 0^\circ$. The transmittance of air was normalized as 100.0%.

RESULTS AND DISCUSSION

Figures 2–4 show the SEM photos of the morphologies of the PDLC films with different ratios of DEGDA/PEGDA of which the temperatures of UV irradiation were 273.5, 283.0, and 293.0 K, respectively. The LC domain size and morphology of PDLC film are determined while the LC droplet nucleation and the polymer gelation. The LC domain size is influenced by the rate of polymerization, the relative ratios of materials, the types of LC and polymers used, and physical parameters such as viscosity, rate of diffusion, and solubility of LC in the polymer.^{15,17} As shown in Figures 2–4, the LC droplet size is significantly influenced by the crosslinking agents and the curing temperature. Figure 5 shows that the LC domain size decreases with decreasing PEGDA 600 content. For the polymer network, the introduction of PEGDA 600 crosslinker resulted in the insertion of relatively long, flexible branch comprising ~ 14 ethylene oxide repeat units along the network bone. The presence of this long pendant chain led to a systematic increase in LC domain size. On the other hand, the insertion of DEGDA crosslinker, short-branch pendant led to the increase in the crosslinking density, so the LC domain size would decrease. Figure 2 shows that the density of polymer matrix increases with increasing PEGDA 600 content. At 273.5 K, the viscosity of PEGDA 600 is very high, whereas the viscosity of DEGDA is

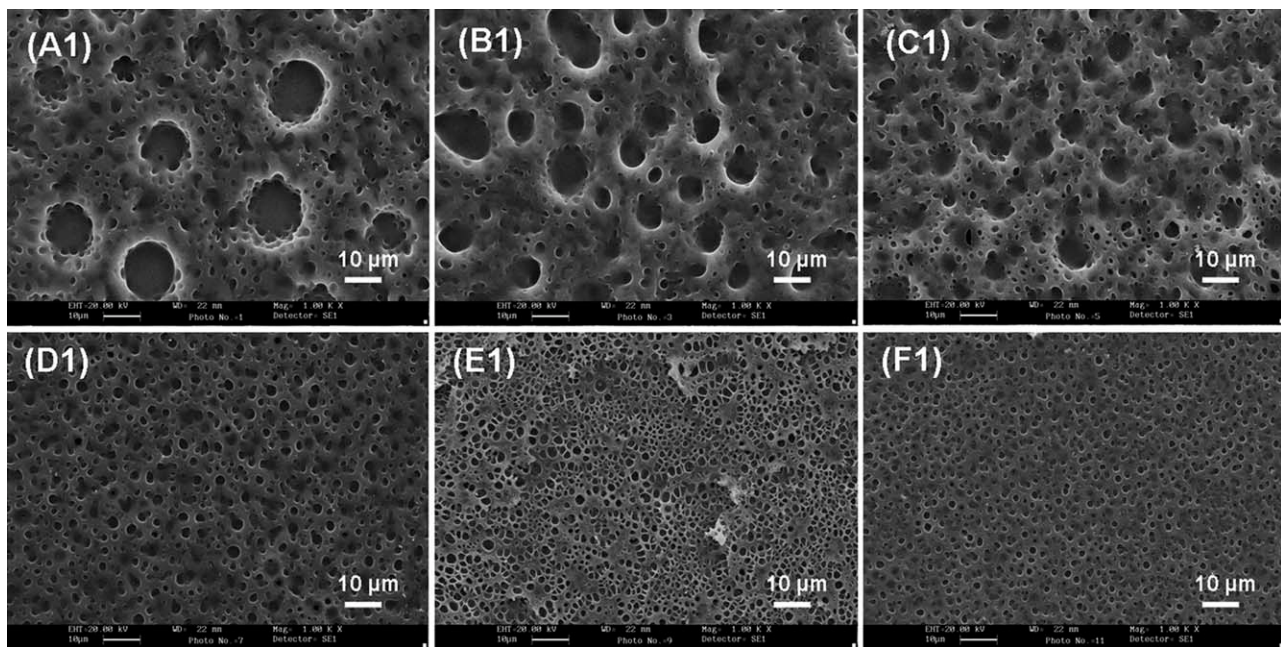


Figure 2 Morphologies of PDLCs for different ratio of DEGDA/PEGDA 600 at UV irradiation temperature of 273.5 K. (A1) 0/5, (B1) 1/4, (C1) 2/3, (D1) 3/2, (E1) 4/1, (F1) 5/0.

very low, so the viscosity of mixed solution increased with increasing PEGDA 600 content, and it led to the increase in the density of polymer matrix. These showed DEGDA and PEGDA 600 crosslinkers had a strong and clear effect on the LC domain size. So, the chain length of crosslinkers and the ratio of PEGDA 600/DEGDA played important roles in the fabrication of the polymer network. Comparing Figures 2–4, it can be found that the

lower the UV irradiation temperature, the bigger the LC droplet size. The polymerization rate $1/\tau$ depends exponentially on temperature

$$\frac{1}{\tau} \propto e^{-E_{\text{act}}/kT}$$

where E_{act} is an activation energy, k is Boltzmann's constant, τ is the cure time constant, and T is the

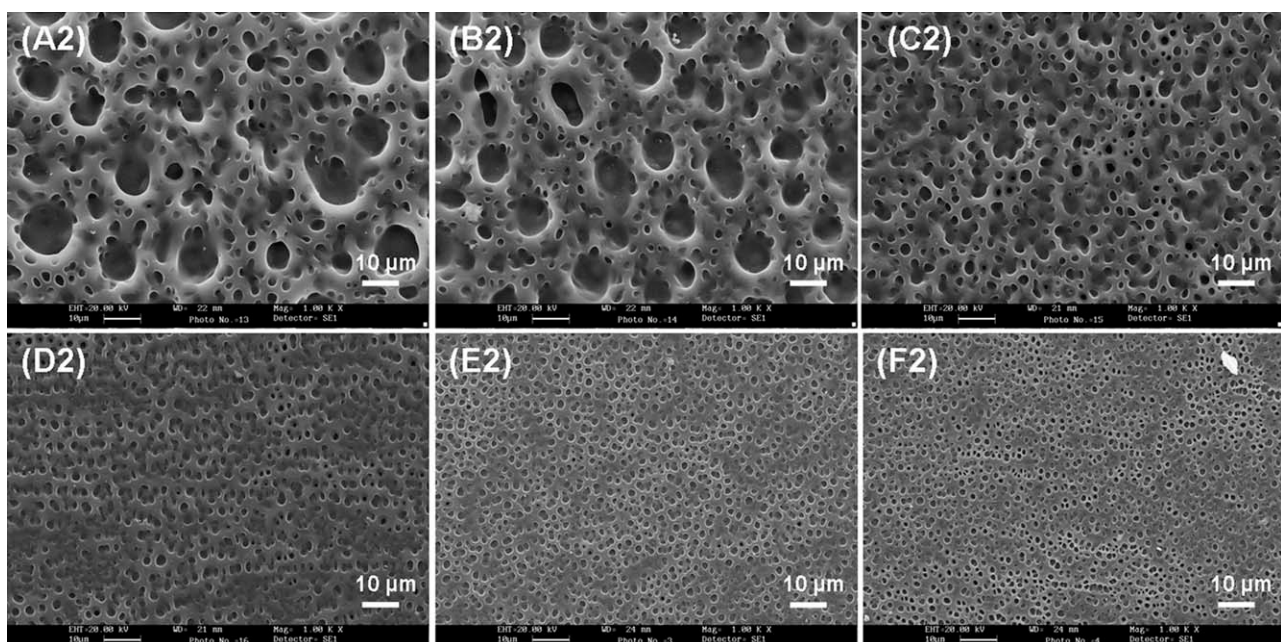


Figure 3 Morphologies of PDLCs for different ratio of DEGDA/PEGDA 600 at UV irradiation temperature of 283.0 K. (A2) 0/5, (B2) 1/4, (C2) 2/3, (D2) 3/2, (E2) 4/1, (F2) 5/0.

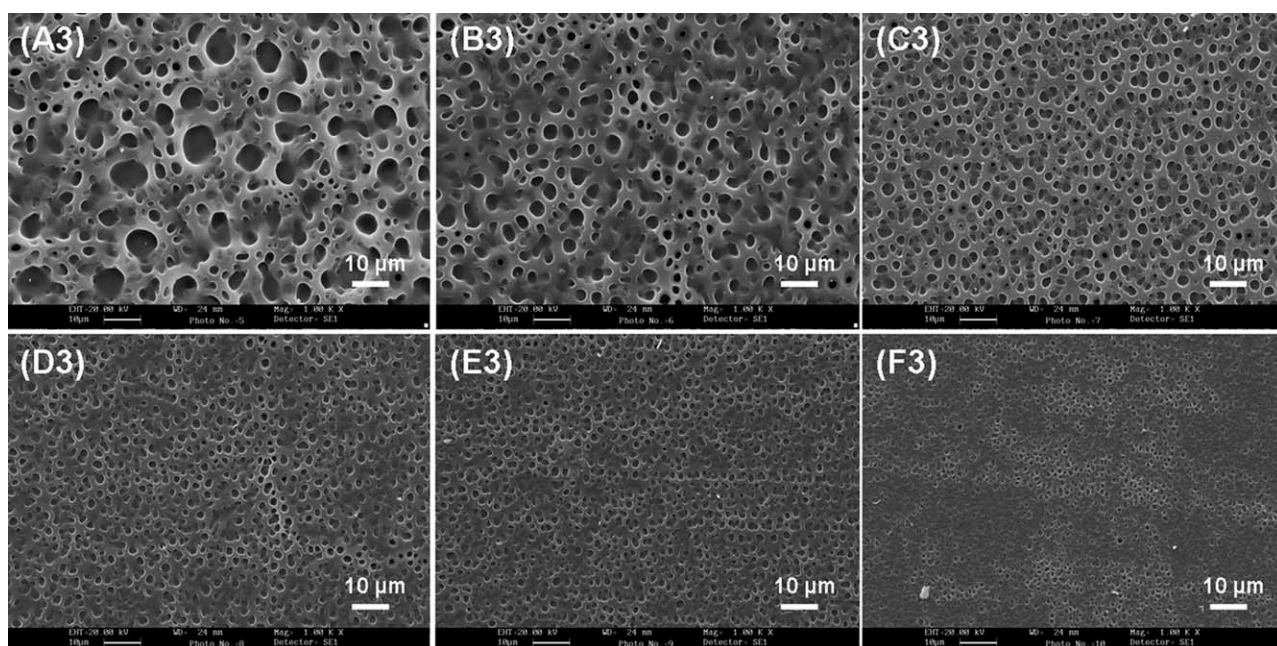


Figure 4 Morphologies of PDLCs for different ratio of DEGDA/PEGDA 600 at UV irradiation temperature of 293.0 K. (A3) 0/5, (B3) 1/4, (C3) 2/3, (D3) 3/2, (E3) 4/1, (F3) 5/0.

absolute temperature, respectively.^{18,19} Along with increasing the temperature during UV irradiation, the polymerization rate of the monomers was increasing. The faster polymerization rate resulted in fabricating smaller LC droplet size. Comparing Figures 2–4, the higher the UV irradiation temperature, the lower the density of polymer matrix. The increase of the curing temperature decreased the viscosity of the mixed solution, and then promoted the diffusion of monomers, so the density of polymer matrix decreased.

Contrast ratio (CR) is an important measure of the electro-optic performance in a PDLC system. CR of PDLC to characterize the different between a transparent and an opaque state is defined as

$$CR = T_{on}/T_{off}$$

where T_{on} and T_{off} are transmittance in the on- and off-state of PDLC films. As shown in Figure 6, along with increasing PEGDA 600 content, the CR decreased, and also the higher the UV irradiation temperature, the smaller the CR. Comparing Figures 2–4 with Figure 7, the morphology of the PDLC has indispensable effect on the electro-optic properties of the PDLC systems. A high value of CR can be obtained when the microstructure of the PDLC film is appropriate.

It is known that the size of the LC droplets plays a fundamental role in determining the electro-optic performance of a PDLC system. The threshold voltage (V_{th}) and the saturation voltage (V_{sat}) are

defined as the electric voltage required for the transmittance to reach 10.0% or 90.0%. V_{th} is inversely proportional to the radius of LC droplets (R) as shown below

$$V_{th} \cong \frac{d}{R} \left[\frac{K(\omega^2 - 1)}{\epsilon_0 \Delta \epsilon} \right]^{1/2}$$

where d , K , ω , and $\Delta \epsilon$ represent film thickness, elastic constant, aspect ratio, and dielectric anisotropy of the LC, respectively.^{3,20–22} Larger LC droplet size

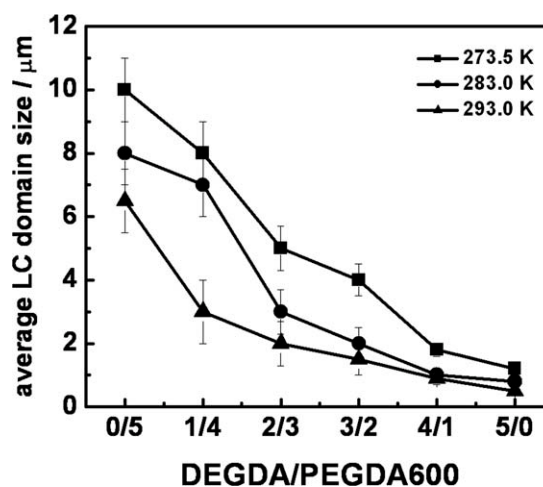


Figure 5 Average LC domain size dependence on different ratio of DEGDA/PEGDA 600 at different UV irradiation temperature.

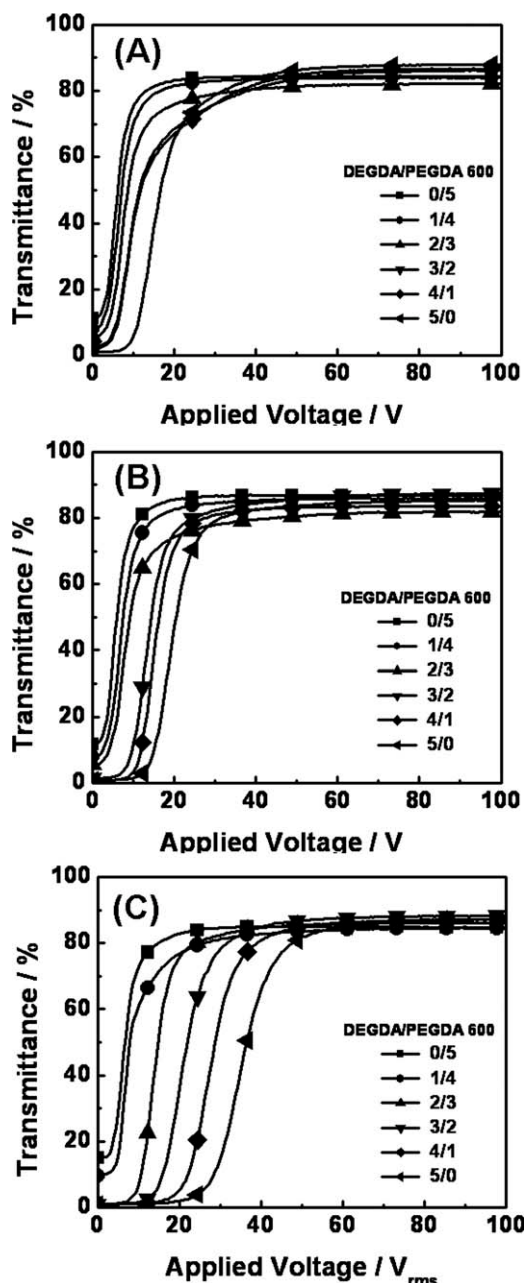


Figure 6 Transmittance dependence on applied voltage for different ratio of DEGDA/PEGDA 600 at different UV irradiation temperature. (A) 273.5 K, (B) 283.0 K, (C) 293.0 K.

leads to lower V_{th} . V_{sat} is affected by the anchoring energy at the polymer-LC interface. In LC cells, there is a relationship between the anchoring strength (A) and V_{sat} as shown below

$$A = \frac{V_{sat} \sqrt{\epsilon_0 \Delta \epsilon K}}{d} \tanh \left[\frac{V_{sat}}{2} \sqrt{\frac{\epsilon_0 \Delta \epsilon}{K}} \right]$$

The stronger the anchoring energy, the higher the electric field strength needs. The anchoring energy is related to the polarity and viscosity of polymer

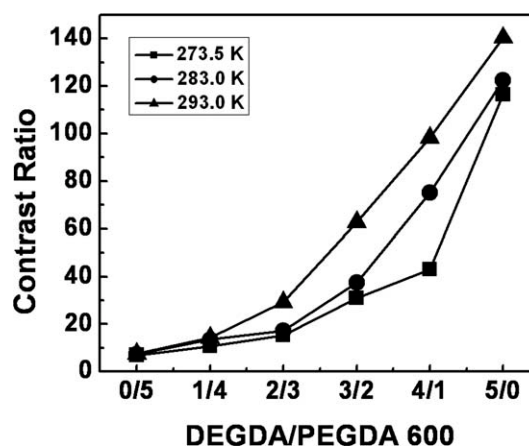


Figure 7 Contrast ratio dependence on different ratio of DEGDA/PEGDA 600 at different UV irradiation temperature.

matrix.²³ As shown in Figures 2, 3, 4, and 8, the V_{th} and V_{sat} generally decreased with increasing the LC domain sizes. V_{sat} increased with the decreased of the LC droplet size, which indicated that the LC domain size has indispensable effect on the anchoring energy. It is shown that the operating voltage of the PDLC film was significantly influenced by the relative ratios of the crosslinking agents and the UV irradiation temperature.

The time it takes to switch to a transparent state (rise time, t_R) or to an opaque state (decay time, t_D) is one of the important factors for evaluating a PDLC performance. These are the times necessary for the LC molecules to align along the electric field or to relax to an arbitrary orientation where the electric field is suppressed. t_R and t_D are defined as the time from 10% to 90% or 90% to 10% of the total

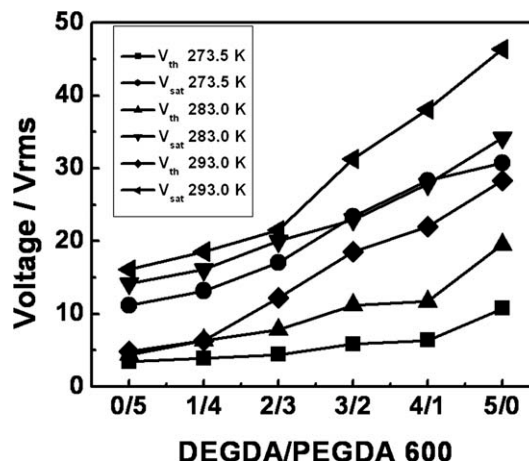


Figure 8 Threshold and saturation voltages, V_{th} and V_{sat} , dependence on different ratio of DEGDA/PEGDA 600 at different UV irradiation temperature.

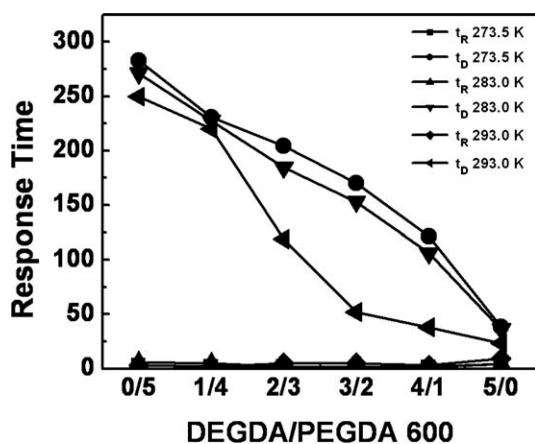


Figure 9 Response times dependence on different ratio of DEGDA/PEGDA 600 at different UV irradiation temperature. The PDLCs were driven by an applied field of 100 V_{rms} .

change between a transparent and an opaque states. t_R and t_D depend on the field strength forcing molecular orientation and the viscoelastic parameters influencing the forces that oppose such orientation.^{13,22} In general, the smaller the LC domain size, the larger the t_R and the smaller the t_D . As shown in Figure 9, along with decreasing the LC domain size, t_R increased and t_D decreased.

As shown in Figures 2, 3, 4, and 10, the transmittance of off-state PDLC films increased with increasing the LC domain size. It was shown that the transmittance of off-state was significantly depending on the morphology of the PDLC film.

CONCLUSIONS

The influences of the relative weight ratio of crosslinking agents and polymerization temperature on the PDLC system have been studied. The microstructures of the PDLC films were strongly influenced by the insertion of PEGDA 600 crosslinker, relatively long and flexible branch, and DEGDA crosslinker, short branch, along the network bone. So, the chain length of crosslinking agents and the relative weight ratio between crosslinking agents had a significant effect on the LC domain size, and which resulted in influencing the electro-optic properties of PDLC films. The UV irradiation temperature had indispensable effect on the viscosity of monomers and polymerization rate, which influenced the morphologies of PDLC films, and then the PDLC performances.

The results presented in this study suggest that it is possible to regulate the LC domain size and optimize the electro-optic properties of PDLC films by

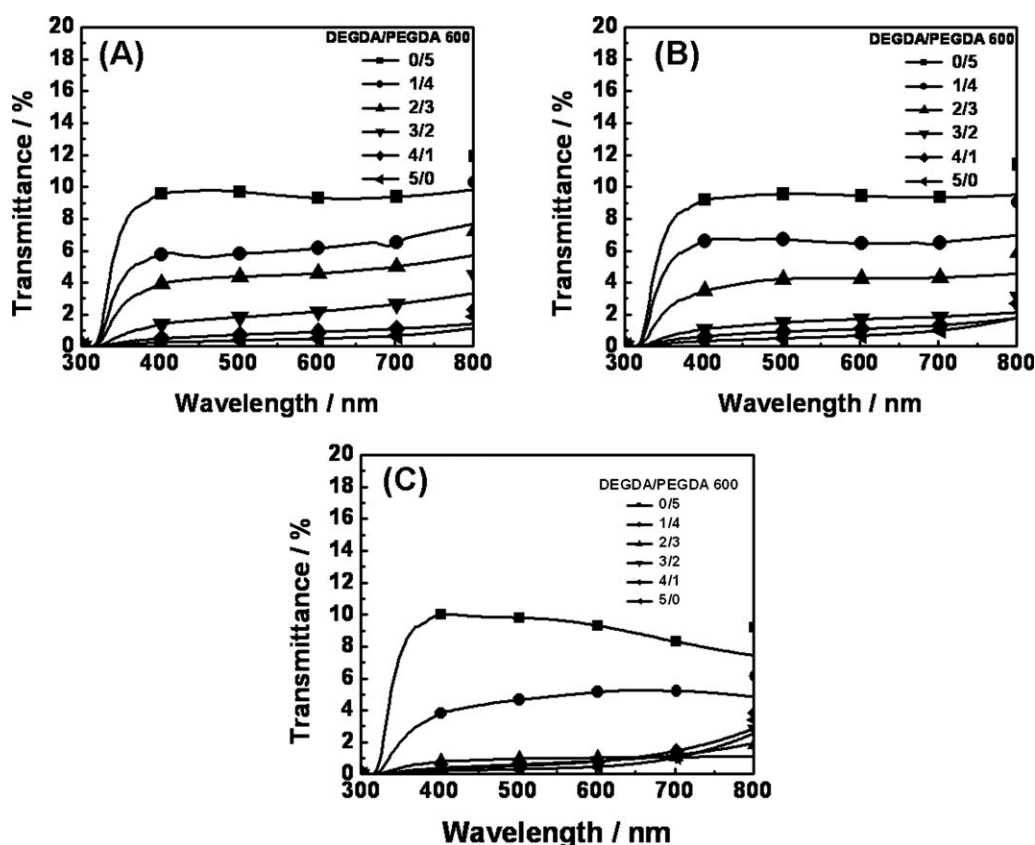


Figure 10 UV-visible spectra of off-state PDLCs dependence on different ratio of DEGDA/PEGDA 600 at different UV irradiation temperature. (A) 273.5 K, (B) 283.0 K, and (C) 293.0 K.

adjusting the chain length and the ratio of crosslinking agents, and the UV irradiation temperature.

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