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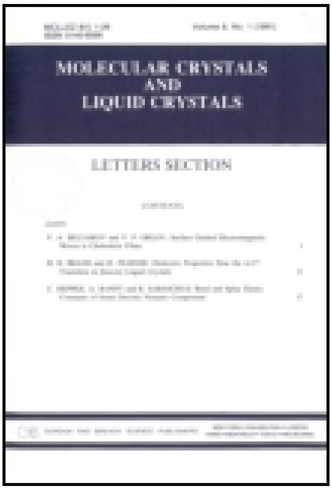

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Effect of Urethane Acrylate Oligomer and UV Curing Temperature on Electro-Optical Property of Polymer-Dispersed Liquid Crystal

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Polymer-dispersed liquid crystal (PDLC) films were prepared by photopolymerization after substituting the reactive diluent monomer 2-ethylhexyl acrylate with an aliphatic urethane acrylate (UA) oligomer in a conventional pre-polymer (PN393). The effects of UA concentration and UV curing temperature on the PDLC films' physical properties were examined. The average LC droplet size decreased with increasing UA concentration. The driving voltage decreased by 30% and the response time increased by 26%. The PDLC films with 30 wt% of UA showed the lowest driving voltage and the highest contrast ratio when the LC pre-polymer mixture was UV-cured slightly above the nematic-isotropic coexistence temperature.

Keywords Polymer-dispersed liquid crystal (PDLC); pre-polymer; urethane acrylate; photopolymerization; electro-optical property; UV curing temperature

1. Introduction

A polymer-dispersed liquid crystal (PDLC) film is a composite material which consists of micron-sized liquid crystal droplets dispersed in a polymer matrix. A PDLC film is used for an electro-optic device since it can switch from an opaque state to a transparent state upon applying an external electric field [1]. Compared to other display devices, its fabrication process is rather simple since its basic operation does not require polarizer or alignment layers. Furthermore, it can also be fabricated on flexible substrates and requires a low driving power. Owing to these advantages, PDLC films have been actively studied for various applications such as projection displays, high contrast reflective displays, smart optical shutters, and privacy windows [2, 3].

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At voltage-off state, a PDLC film is milky white in color since the incident light is diffused because of the refractive index mismatch between the polymer matrix and the randomly oriented liquid crystal (LC) droplets. When voltage is applied between two transparent electrodes, the directors of the LC droplets start to align along the electric field direction. Then, the film becomes transparent since the ordinary refractive index of the LC droplets along the direction of the light propagation is matched with the refractive index of the polymer matrix [2, 3]. If the voltage is turned off, the PDLC film becomes opaque again since the director of each LC droplet returns to a random orientation owing to elastic and viscous forces at the LC-polymer interface. For a practical application of a PDLC film, fabrication optimization for low operation voltage (<10 V), low hysteresis (<0.1 V), high birefringence, and temperature and chemical stability is required [4].

PDLC films are fabricated by phase separation from a homogeneous mixture of liquid crystals and pre-polymers. A pre-polymer normally consists of a certain type of UV curable reactive diluent, cross-linker, and photoinitiators. For example, Merck PN393, a popular PDLC pre-polymer, is a mixture of acrylate monomers. The reactive diluent in a pre-polymer reduces the viscosity and builds up the molecular weight of the polymer by chain reaction for a mono-acrylate or cross-linking for a multifunctional acrylate. The phase separation methods include thermal process [5], photopolymerization [1], or solvent evaporation [6]. The most widely used method is photopolymerization since this phase separation process is simpler and faster than other techniques. During UV curing, the LC phase separates from the growing polymer chain to create LC-rich droplets within the polymer matrix.

The electro-optical and morphological properties of a PDLC film strongly depend on both the physical properties of each component and the detailed fabrication process. The electro-optical properties of PN393-based PDLC films have been reported previously by several groups [7, 8, 9]. However, the experimental data in these studies show wide dispersion in driving voltage, response time, and contrast ratio. This is considered to be mainly due to the temperature sensitivity of the reactive diluent monomer 2-ethylhexyl acrylate (EHA), which is contained in PN393 [10, 11]. In order to improve the stability of PDLC films, a new pre-polymer formulation was prepared by substituting EHA in PN393 with different concentrations (1–30 wt%) of UV curable urethane acrylate (UA) oligomer. The morphology of these PDLC films along with the electro-optical properties and the temperature effect on the UV polymerization process were studied. The PDLC film properties were significantly improved by addition of the UA oligomer and the proper control of the UV curing temperature. The improvements are mainly attributed to the change in the PDLC film morphology and the anchoring properties of the LC-polymer interface.

2. Experiment

In this work, the PDLC film was fabricated by polymerization-induced phase separation (PIPS) method. The liquid crystal was an eutectic mixture of cyanobiphenyl liquid crystal (Merck E7, $n_o = 1.521$, $n_e = 1.746$, $T_{NI} = 61°C$). The pre-polymer was Merck PN393 (2-ethylhexyl acrylate monomer and trimethylolpropane triacrylate cross-linker), which is composed of 2-ethylhexyl acrylate (EHA, 87 wt%, reactive diluent), CYTEC Ebercryl 810 (10 wt%), trimethylolpropane triacrylate (TMPTA, 2 wt%, cross-linker), diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide, and 2-hydroxy-2-methylpropiophenone (Darocur 4265, 1 wt%, photoinitiator) [11]. The reference sample formulation was a mixture of liquid crystal Merck E7 (80 wt%) and pre-polymer PN393 (20 wt%). Pre-polymers of the control samples were prepared by substituting EHA in the PN393 with a commercially available aliphatic urethane acrylate (Photomer6010^{TM}, Cognis) by 1, 5, 10, and 30 wt% respectively. Therefore, the ratio of the liquid crystal (E7) and the pre-polymer in the control samples was also fixed at 80 wt%:20 wt%. The UA additive has a low glass transition temperature (-7°C) and is resistive to scratch and abrasion.

The isotropic LC-polymer mixture was injected into a glass cell (18 mm × 15 mm) coated with rubbing-treated ITO electrodes. The cell was filled by a capillary force. The cell gap between the electrodes was 7 μm. The phase separation of E7 and the pre-polymer was induced by 365-nm UV irradiation (3.6 mW/cm^2, 180 s) at room temperature (23°C) or fixed temperatures using a temperature controller. The LC droplet morphology of the mixture before UV polymerization was examined at different temperatures with a polarized optical microscope, and the surface morphology of the UV-cured PDLC film was characterized by conventional optical microscopy after removing E7 using a solvent. The light transmission as a function of applied voltage, V-T curve, was measured using a He-Ne laser (633 nm) and a photodiode detector while applying ac voltage (1 kHz) between the electrodes. The electro-optical parameters such as contrast ratio and threshold voltage were extracted from the V-T curve. The rise and decay time was obtained from the photodetector signal recorded by a digital oscilloscope.

3. Results and Discussion

The morphology of PDLC films with different UA concentrations are shown in Fig. 1. The LC droplets of polyhedral form are dispersed in the polymer fiber network, and the droplets are separated by polymer walls with a few hundred nanometers in thickness. The average size of the droplets was about 3.0 μm for the reference sample. The droplet size decreased upon adding the UA oligomers. The average diameters were about 2.9 μm for the 1 wt% sample and decreased to 2.3 μm for the 10 wt% sample. However, for the 30 wt% sample, the droplet size increased to 4.0 μm. The droplet size is known to depend on various factors such as the rate of polymerization, the type and relative concentration of LC and pre-polymer, and the physical properties such as viscosity, diffusion rate, and solubility of LC in the pre-polymer [8, 9, 12]. Since the UA oligomer had a much larger molecular mass ($M_w \approx 7000$) compared to the original monomer (EHA, $M_w \approx 180$), it is likely that the chain length increased and solubility decreased. Recently, it was reported that an increase in the mobility of LC molecules and a promotion of LC domain nucleation during UV polymerization due to increased monomer physical length caused an increase in LC droplet size [13]. However, the observation of decreased droplet sizes in this investigation may originate from the high density of cross-linkers or the enhanced reactivity of the UA substitute. Another possible factor influencing the PDLC film morphology is the anchoring of LC droplets to the cell surface. It is known that the droplet size becomes smaller and more uniform for a rubbed cell with high enough anchoring energy [14]. The increased droplet size for the sample with 30 wt% of UA can be explained by the coalescence of LC droplets during UV polymerization from the reduced anchoring energy of LC droplets to the cell surface by the high concentration of UA oligomers.

The optical transmittance as a function of applied voltage for different PDLC formulations is shown in Fig. 2. The addition of UA oligomer significantly improved the contrast ratio by decreasing the initial transmittance (T_0) and increasing the saturation transmittance (T_{sat}). The UA in the pre-polymer formulation increased the surface area of the LC-polymer interfaces by reducing the droplet sizes. The refractivity mismatch between LC droplets and polymer matrix caused light scattering, and the enhanced light scattering at the LC-polymer interface caused a decrease of the initial off-state transmittance. On the other hand, the increase in T_{sat} can be understood in terms of better matching of the refractive

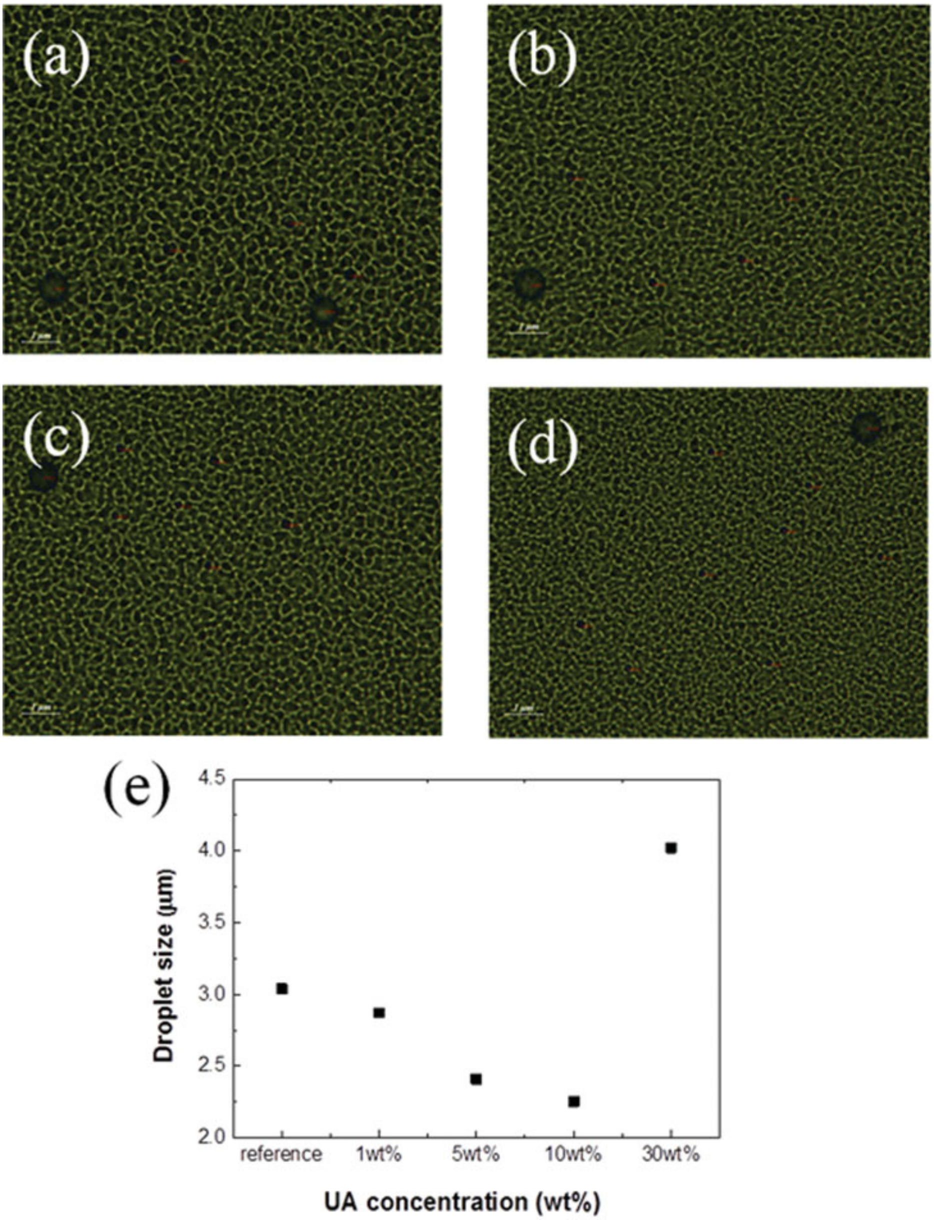

Figure 1. Morphology of the polymer network for (a) the reference sample and the control samples with (b) 1 wt%, (c) 5 wt%, and (d) 10 wt% of UA oligomer in the pre-polymer. (e) Average LC droplet size vs. UA concentration.

index of UV cured polymer matrix with increased UA concentration to the ordinary refractive index of the LC droplets. The PDLC structure with high droplet density and thin polymer walls as shown in Fig. 1 is also known to effectively suppress the light scattering at the saturation state [15]. The change from low transmittance to high transmittance with applied voltage in the control samples showed a sharper transition compared to the

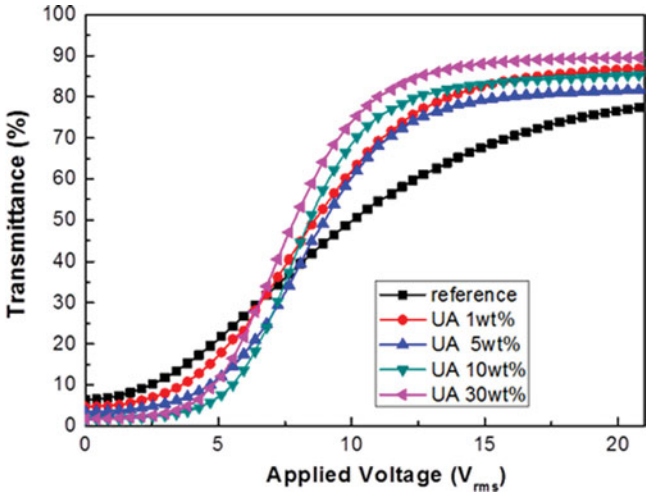

Figure 2. Optical transmittance as a function of applied voltage for PDLC cells with different concentrations of the UA oligomer.

reference sample. Therefore, in addition to a decrease in droplet sizes, the addition of UA oligomer played a role in creating a more uniform distribution of droplet sizes.

Figure 3(a) shows the optical transmittance and contrast ratio (CR) extracted from Fig. 2. In particular, the CR improved because of the increased opaqueness caused by the addition of the UA oligomer. The initial transmittance of the PDLC cells dropped from 6.4% to 1.6% with increased UA concentration up to 10 wt%, resulting in an improvement of the contrast ratio by 420%. Figure 3(b) shows the operation voltages of the PDLC cells with different concentrations of UA oligomer. The driving voltage V_{90} decreased by 30% while the threshold voltage V_{10} increased slightly. The electro-optical property of a PDLC cell is known to be closely related to the film morphology. The threshold voltage tends to decrease with large droplet size as the electrical dipole moment increases with volume. When the anchoring of LC at the interfaces is strong, the driving voltage can be expressed as

$$V_{dr} = \frac{1}{c}\frac{d}{R}(L^2 - 1)^{1/2}\left(\frac{4\pi K}{\varepsilon_0 \Delta\varepsilon}\right)^{1/2} \tag{1}$$

where c is a constant associated with the conductivity of the LC and polymer matrix, d is the film thickness, R is the characteristic radius of LC droplets, L is the ratio between semimajor and semiminor radii of LC droplets, K is the elastic constant, and $\Delta\varepsilon$ is the dielectric anisotropy of an LC droplet [16]. If all other variables are constant, the driving voltage is inversely proportional to the droplet size. Qualitatively, the effect of the droplet microstructure can be understood as the decreased anchoring effect due to the reduced surface to volume ratio in large droplets. However, Fig. 3(b) shows the increase of driving voltage with decreasing droplet size in high concentration of UA oligomer. This result implies that the droplet morphology is not the only factor which influenced the driving voltage in this work since the physical properties of the LC-polymer interface can also be affected by pre-polymer formulation. The UA oligomer may have reduced the elastic force acting on the droplets by decreasing the anchoring energy to the PDLC cell surface causing the observed reduction in the driving voltage.

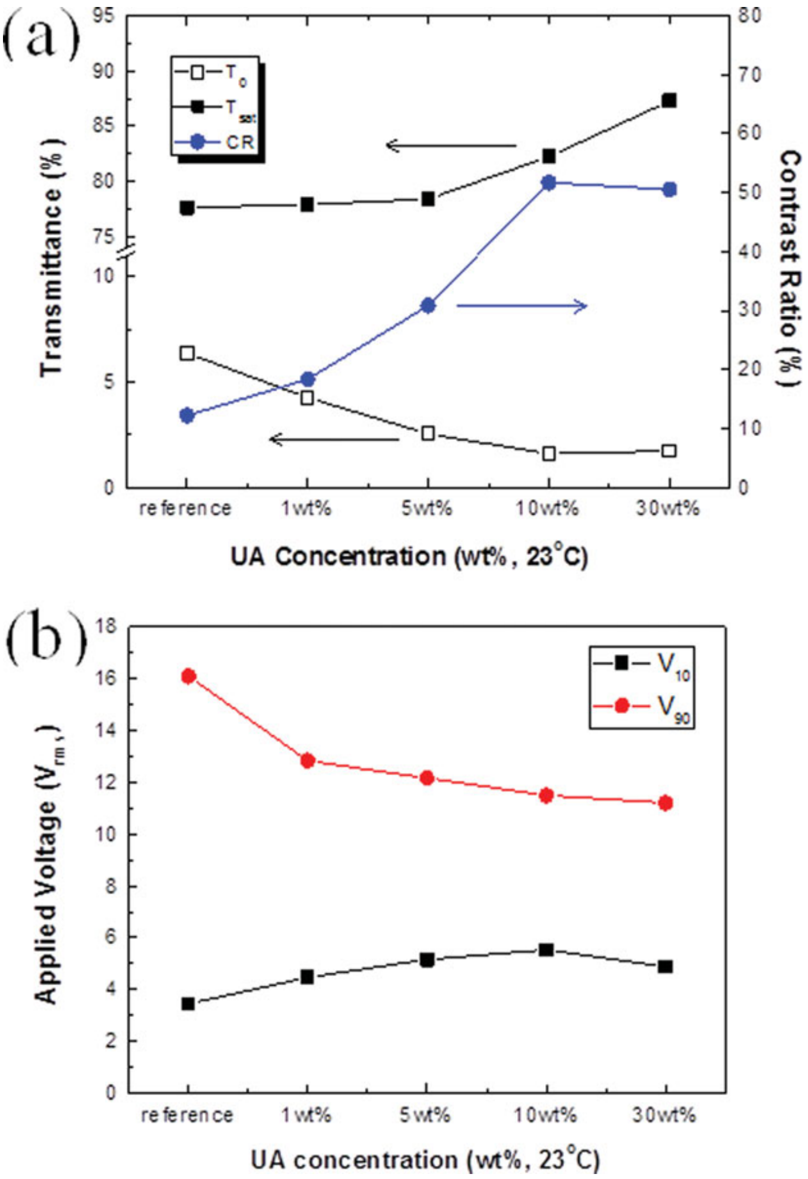

Figure 3. (a) T_0, T_{sat}, and CR of the PDLC cells with different UA concentrations. (b) Operation voltage V_{10} and V_{90} for PDLC cells with different UA concentrations.

Figure 4 shows the temporal response of the PDLC cell with applied voltage. The rise and decay time is defined as the required time between 10 and 90% of transmittance corresponding to the nominally instant changes of applied voltage. The response time is the sum of rise and decay time. The rise time did not depend much on the UA concentration while the decay time showed a strong dependence on the UA concentration. The decay time increased monotonously with UA concentration. The maximum decay time is 110 ms at 30 wt% of UA resulting in a 26% increase in the response time. In general, the response time is mainly determined by the decay time since it is usually an order larger than the rise time.

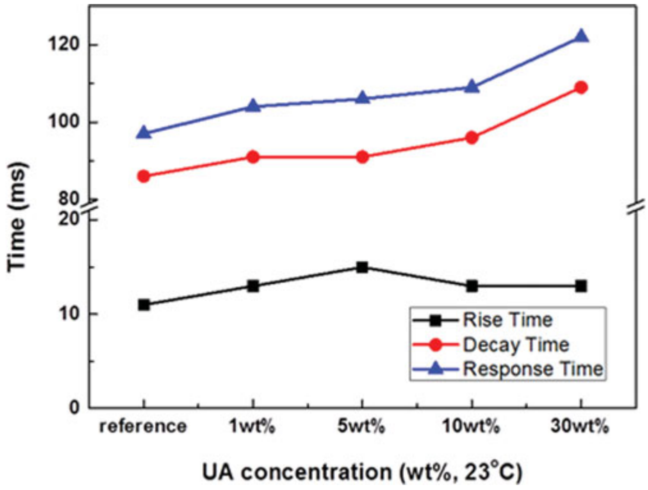

Figure 4. Response time of PDLC cells with different UA concentrations.

The decay time originates from the relaxation against viscous dissipation. Theoretically it can be expressed as

$$t_D = \frac{\eta R^2}{K\left(L^2 - 1\right)} \tag{2}$$

where η is the rotational viscosity of the LC [16]. The expression indicates that response time is proportional to the droplet size if other factors are fixed. However, Fig. 4 shows that response time increased for the smaller LC droplets corresponding to higher concentrations of UA. This departure from theory may be also due to the reduction of anchoring energy at the LC-polymer interface upon adding the UA oligomer. Other factors such as the viscosity within a droplet caused by the polymer dissolved in LC also affect the increase of the response time.

Next the relations between the PDLC film performance and the UV curing temperature were investigated. Figure 5(a) shows the critical temperature of the phase transition of LC droplets from nematic to isotropic state observed by a polarized optical microscope. Compared to the critical temperature of the reference sample ($T_c = 12°\mathrm{C}$), T_c did not change significantly as the UA concentration increased up to 10 wt%. However, for 30 wt%, T_c significantly increased to 22°C. Figure 5(b) shows the dependence of the electro-optical response on the UV curing temperature for the PDLC films with 30 wt% of UA oligomer. The mixture of LC and pre-polymer were photopolymerized at temperatures of 18, 23, 40, and 50°C. The graph shows that the off-state transmittance (T_0) and the CR strongly depend on the UV-curing temperature. T_0 for the samples cured at 40 and 50°C was about 20 and 70%, respectively, while the sample cured at 23°C was very opaque. The performance of the PDLC films were best when cured just above the nematic-isotropic coexistence temperature (22°C) and degraded as the curing temperature increased.

This observation can be explained by the dependence of the LC solubility and the rate of polymerization on the UV curing temperature [12]. In general, during a UV polymerization process, polymer diffuses out of a LC droplet while the LC molecules nucleate to form

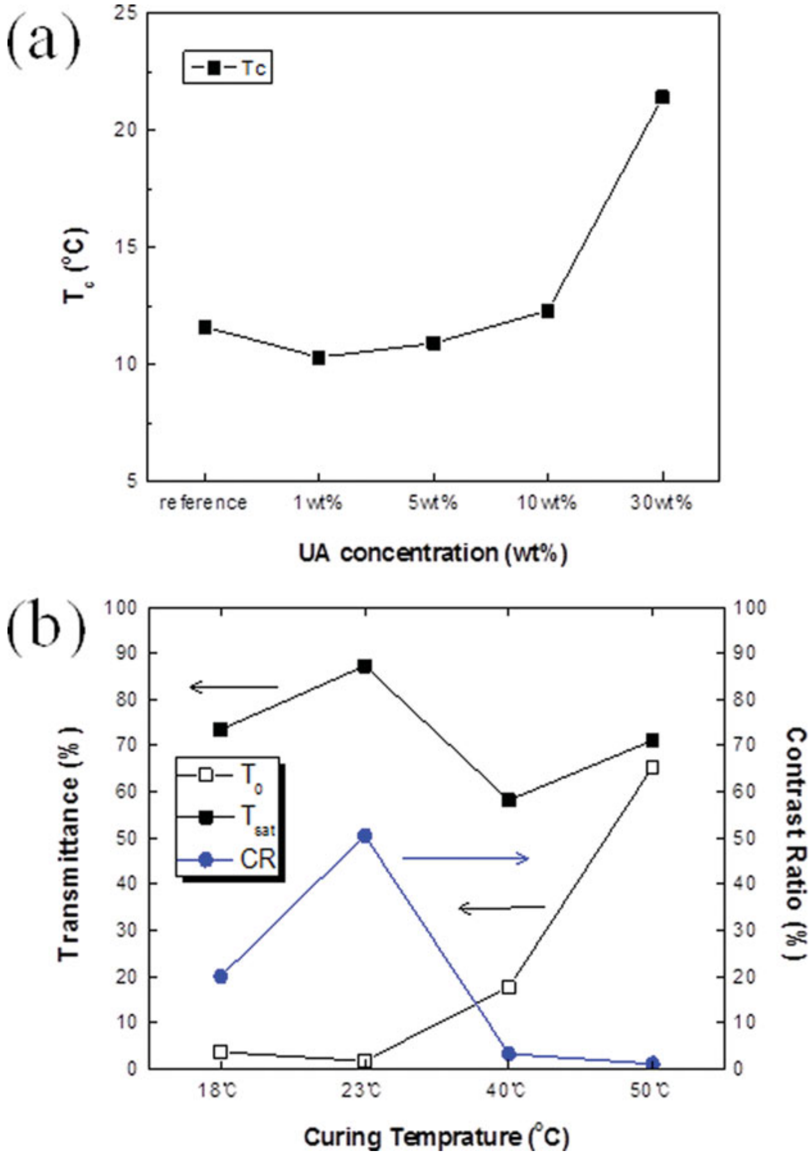

Figure 5. (a) Critical temperature for the nematic-isotropic phase transition of the LC-polymer mixtures with different UA concentrations. (b) Dependence of T_0, T_{sat}, and CR on the UV curing temperature of the PDLC cell with 30 wt% of UA.

droplets. Therefore, if the curing temperature of a certain mixture of LC-polymer is far away from the nematic-isotropic coexistence temperature, the polymerization proceeds and completes before the nucleation of a large LC droplet occurs. Consequently, large droplets are difficult to form and small droplets, in the submicron size range, are created. However, when the droplet size becomes too small compared to the wavelength of the light, the light scattering efficiency is known to become poor [15, 17]. Other research suggests the scattering efficiency begins to drop when

$$kR\Delta n \approx 2 \tag{3}$$

where k is the wave number, R is the average droplet radius, and Δn is the birefringence [15]. In this study, the optimal size for the maximum scattering efficiency occurred when the droplet size was about 1.8–2.7 μm. This data also explains why high transmittance and low CR for the PDLC cured at high temperatures were observed. In contrast, if the UV curing is taken near the coexistence temperature, the droplet formation and coalescence occurs at the early stage of polymerization. Therefore, the degree of cross-linking and the amount of LC in the droplets can be maximized and provides a clear phase separation and better droplet morphology. Consequently the proper size and dispersion of LC droplets formed by the UV curing process at the optimal temperature cause efficient light scattering. This result demonstrates the importance of curing temperature for the control of PDLC film morphology and the electro-optical performance.

4. Conclusion

In conclusion, simple approaches to improve the electro-optical properties of PDLC films were found. Substituting the monomer EHA with a large molecular weight UA oligomer in PN393 to create a new LC-pre-polymer formulation resulted in an increase in the contrast ratio and reduction in the driving voltage. Furthermore, the PDLC film showed the best electro-optical performance when cured at slightly above the nematic-isotropic phase transition temperature. The results showed that the addition of the UA oligomer and the control of UV curing temperature can significantly improve the performance of PDLC films. Experimentation and theory suggest the enhanced behavior resulted from a change in the morphology of PDLC films and the physical properties of LC-polymer interface upon adding UA oligomer. The results also demonstrate that the optimization of the PDLC formulation and the phase separation process are very important for the performance of PDLC display devices.

Acknowledgments

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