

Temperature stability of electro-optic properties of polymer dispersed liquid crystal with different crosslinking monomer in PN393 base pre-polymer

Young-Seok No, Jae Hong Kim, Chan-Wook Jeon[†] and Si-Hyun Park*

School of Display and Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Korea

*Department of Photonic Engineering, Chosun University, Gwangju 501-759, Korea

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Abstract—The electro-optic properties of polymer-dispersed liquid crystals (PDLCs) fabricated by photo-induced phase separation have been investigated. A mixture of TL205 (80 wt%) liquid crystal and PN393 (20 wt%) pre-polymer having different crosslinking monomers was used for producing various PDLCs to compare its temperature stability. As a reference, a commercialized PN393 formulation was closely examined to compare the effects of replacing the crosslinker. The liquid crystal domain size varied from 3.5 μm to 10.3 μm depending on the crosslinker used. The larger domain size of PDLCs consisting of vinyl ether shows higher contrast ratio but faster response time and higher turn-on voltage, which is contrary to the prediction. Acrylate-based PDLCs were found to be turned on, although abruptly increasing below 20 °C, and also showed heavy variation of other electro-optic over a wide operation temperature range. By substituting a vinyl-ether for the acrylate crosslinker, the temperature behavior was greatly improved.

Key words: PDLC, Crosslinker, PN393, TMPTA, DEGDVE

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) is a mixed phase of polymer and liquid crystal, which can be switched by applying an external electric field. The interest in the material stems from the possible application to electronic paper or flexible displays, which are believed to be the next generation display formats [1,2]. Since the PDLC exhibits a switchable electro-optic effect based on a change in scattering cross-section, no polarizer is required, making PDLC easy to produce a flexible device. PDLCs can also give high contrast in reflective mode devices based on passive lighting, eliminating the need for integrated backlighting that adds to weight and power consumption. The transmittance of PDLC cells can be controlled by an external electric field, because of the refractive index difference of the liquid crystal domain, which is anisotropic with its orientation direction, and the surrounding polymer network is adjustable. The liquid crystal domains, which are separated from a homogeneous solution of liquid crystals and monomers by photo-induced phase separation method, take a random distribution of their orientation directions, which are determined by averaging the molecular orientation of liquid crystals contained in a domain. With no electric field applied to the cell, the incident light will interact with two optical media and hence be scattered. An electric field that is sufficient to force the liquid crystal molecules align along the field, together with the ordinary refractive index of liquid crystal matched to that of surrounding polymer, leaves only one optical medium and hence most of the incident light will pass through the cell.

The two-phase composite is usually made by the phase separation technique starting from mixing liquid crystals and a pre-polymer, which consists of several monomers including a crosslinking agent. PN393, one of the commercial pre-polymers, was provided

by Merck, specially designed for application to TFT-PDLC devices. This formulation includes polyester acrylate resin of Ebecryl 1810, acrylate monomer of 2-ethylhexyl acrylate (EHA), acrylate monomer of trimethylolpropane triacrylate (TMPTA) as crosslinker, and a mixture of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and 2-hydroxy-2-methylpropiophenone (Darocur4265) as photoinitiator. While the polymerization of acrylate-based formulations is known to be very fast via radical propagation, it can be inhibited by oxygen present either in the surrounding or inside the bulk of pre-polymer [3]. Oxygen inhibition could give the PDLC film critical defects especially for the flexible devices produced by a roll-to-roll process, which is usually done in the air.

In this study, we examined the EO properties of several PDLCs fabricated with different pre-polymer formula by changing crosslinker material in the standard PN393 composition. To verify the effect of crosslinker, other components were the same as that of PN393. Although as little crosslinker as 2%-10% was added, the EO properties of PDLCs were found to exhibit heavy change with material selection.

EXPERIMENTAL

PDLC cells are prepared by sandwiching a mixture of pre-polymer and liquid crystal between two transparent indium tin oxide (ITO) coated glass plates with a 7 mm cell gap thickness. In order to avoid any uncertainty induced from cell gap nonuniformity, commercial liquid crystal test cells (Solomon Goldentek Display Ltd.) without an alignment layer were used for the study. We prepared three sets of mixtures using 80 wt% TL205 (Merck) and 20 wt% PN393 (Merck) with various crosslinking monomers, trimethylolpropane triacrylate (TMPTA, 2 wt%), 1,6-hexanediol di-acrylate (HDDA, 2 wt%), and diethyleneglycol divinyl ether (DEGDVE, 10 wt%). The structures of the crosslinkers are shown in Fig. 1. The mixture was introduced into the cell by capillary action and photo-

[†]To whom correspondence should be addressed.

E-mail: cwjeon@ynu.ac.kr

Table 1. The electro-optic properties of PDLCs with different crosslinker measured at 25 °C

Crosslinker	Cloud point (°C)	Domain size (μm)	T_o (%)	T_{sat} (%)	Contrast ratio	On-time (msec)	Off-time (msec)	V90 (V)
TMPTA	18.3	3.5	22	98	4.5	1.4	84	2.5
HDDA	19.0	3.7	17	99	5.7	2.3	33	3.6
DEGDVE	18.0	10.3	6	96	15.6	1.4	16.8	6.5

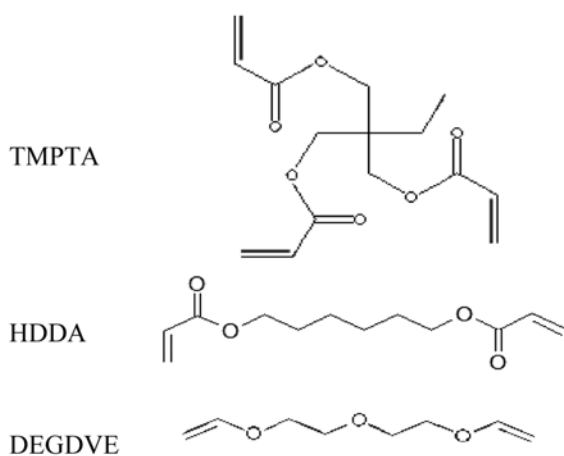
polymerized by illuminating with a UV lamp (365 nm peak wavelength) of 1 mW/cm² intensity for 10 minutes. During the UV curing, the temperature of the sample was fixed at 22 °C by using Linkam PE120 hotstage. The film has a typical PDLC morphology with domain sizes on the order of 3–10 μm diameter.

Electro-optic properties were characterized by using a linearly polarized 632 nm laser (Newport laser diode module, 5 mW) of 0.1 mW output power. By applying a gated 1-kHz sinusoidal voltage to the PDLC, the transmittance variation and the response time (defined as sum of rise and fall time) were measured. Rise and fall times are defined as the time for the transmitted light intensity to go from 10% to 90% (or vice versa) of the maximum transmitted light intensity. The contrast ratio was calculated by dividing the measured on-state transmittance (T_{sat}) by off-state transmittance (T_o). The turn-on voltage of V_{90} , where the transmittance hits 90% of T_{sat} , is taken from the voltage-transmittance curve.

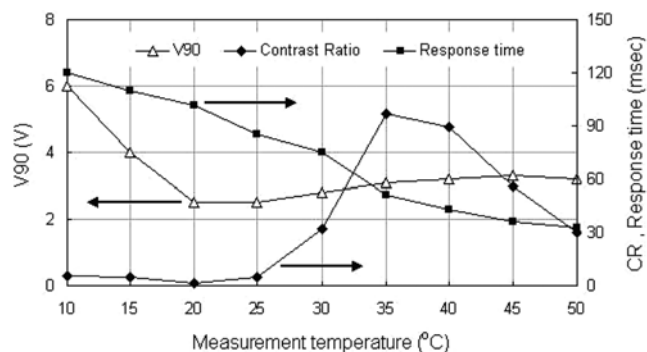
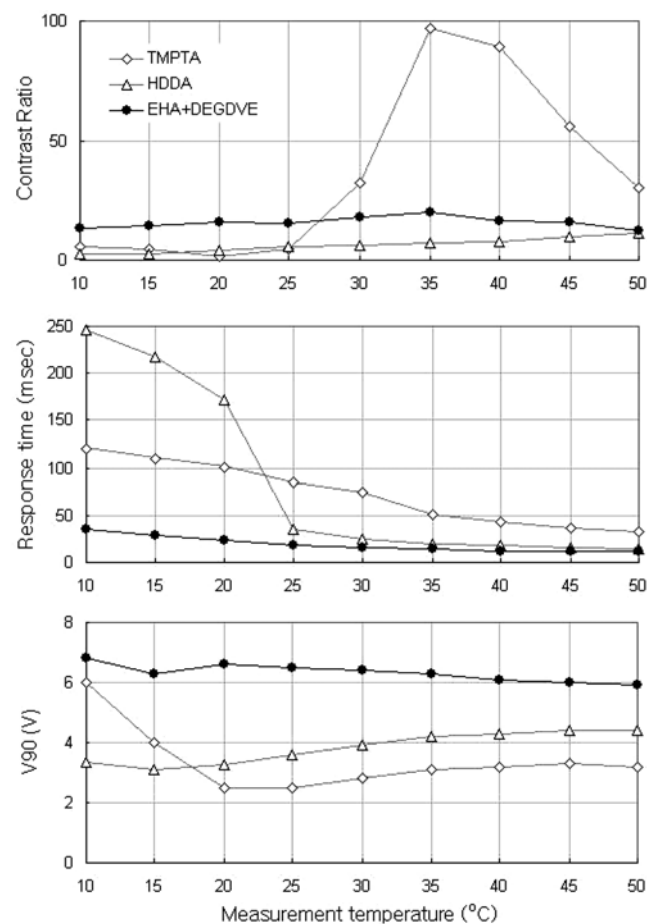
RESULTS AND DISCUSSION

The typical electro-optic (EO) properties of three different PDLC cells are summarized in Table 1. The PN393 with TMPTA is the commercialized pre-polymer, and its turn-on voltage is the lowest among the three; however, a long response time will produce a poor video image for TFT-based display applications. While the response time can be lowered down to 35 msec by replacing TMPTA with HDDA, it is still far longer than 60 Hz frame rate. In terms of the response time, DEGDVE has been found to be the best monomer for PN393 base pre-polymer. Although the turn-on voltage is almost double that of the others, considering the relatively thicker cell gap than the commercial TFT-LCD cell, it's moderately high for display.

The advantage of using DEGDVE comes from the temperature

**Fig. 1. Chemical structure of various crosslinking monomers.**

stability of the PDLCs. Over the temperature range of 10 to 50 °C, TMPTA-PDLC revealed a heavy variation of contrast ratio, response time, and turn-on voltage as shown in Fig. 2. The contrast ratio was

**Fig. 2. Electro-optic characteristics of PDLCs made of standard PN393 formulation.****Fig. 3. Variation of electro-optic properties of PDLCs: (a) contrast ratio, (b) response time, and (c) turn-on voltage.**

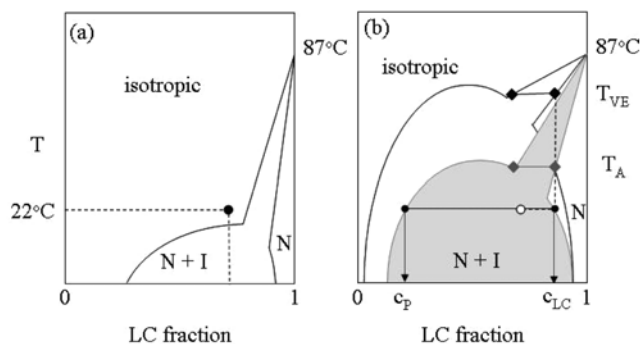


Fig. 4. (a) The pseudobinary phase diagram for the PDLC mixture before the UV irradiation. The black circle indicates the initial composition at the curing temperature. N and N+I denote pure nematic phase and nematic+isotropic binary phase, respectively. (b) The hypothetical phase diagram after finishing the UV curing. The shaded area and open area correspond to the TMPTA-PDLC and DEGDVE-PDLC. T_A and T_{VE} are the starting temperature where the secondary phases emerge, which are symbolized by the gray diamonds (TMPTA) and the black diamonds (DEGDVE).

measured as peaking around 37 °C and the response time decreases with the operating temperature. Although its turn-on voltage is very low and stable at an elevated temperature, the voltage increases abruptly below 20 °C. Moreover, the high turn-on voltage region coincides with the longer response time zone, which possibly results in a sudden stop of the PDLC display operation or failure of gray scale realization. Fig. 3 shows the effect of changing the crosslinker on the display characteristics. HDDA-PDLC performs better than TMPTA-PDLC in terms of temperature stability of turn-on voltage and contrast ratio; however, it reveals an abrupt increase of response time below 25 °C. Compared to these two, DEGDVE-PDLC shows no big change in its EO properties, which means that it can reasonably work well as designed under a wide temperature range.

Amundson et al. reported that the anchoring transition temperature of PDLC containing 2-ethyl hexyl arylate (EHA) as the major component in PN393 base pre-polymer is around 23 °C [3]. Upon cooling the PDLC below this temperature, which is well below the nematic-to-isotropic transition temperature of liquid crystal, the director field can reorient, for example, homogeneous to homeotropic, and the PDLC will lose much of the scattering power and will be turned on at even lower voltage. However, in this study, even the standard PN393-based PDLC behaves in the opposite way to the expectation, which may be attributed to the smaller domain size. The phenomenon was discovered from the PDLC having larger domain size enough to touch down to the two ITO surfaces, while the PDLC in this study has small domain compared to the cell gap.

An alternative way to explain the temperature instability may come from the phase diagram of the composite mixture. Fig. 5(a) shows the pseudobinary phase diagram for the mixture of TL205 and PN393 before the UV curing [4-6]. The mixture of 80% LC at 22 °C, where the UV curing takes place, is in the isotropic phase. The immiscibility gap is extended to the nematic-isotropic transition temperature (T_N) of the TL205 used in this study. After photopolymerization is completed, the immiscibility gap expands due to the lowered solubility of LC in polymer, and the initial composition

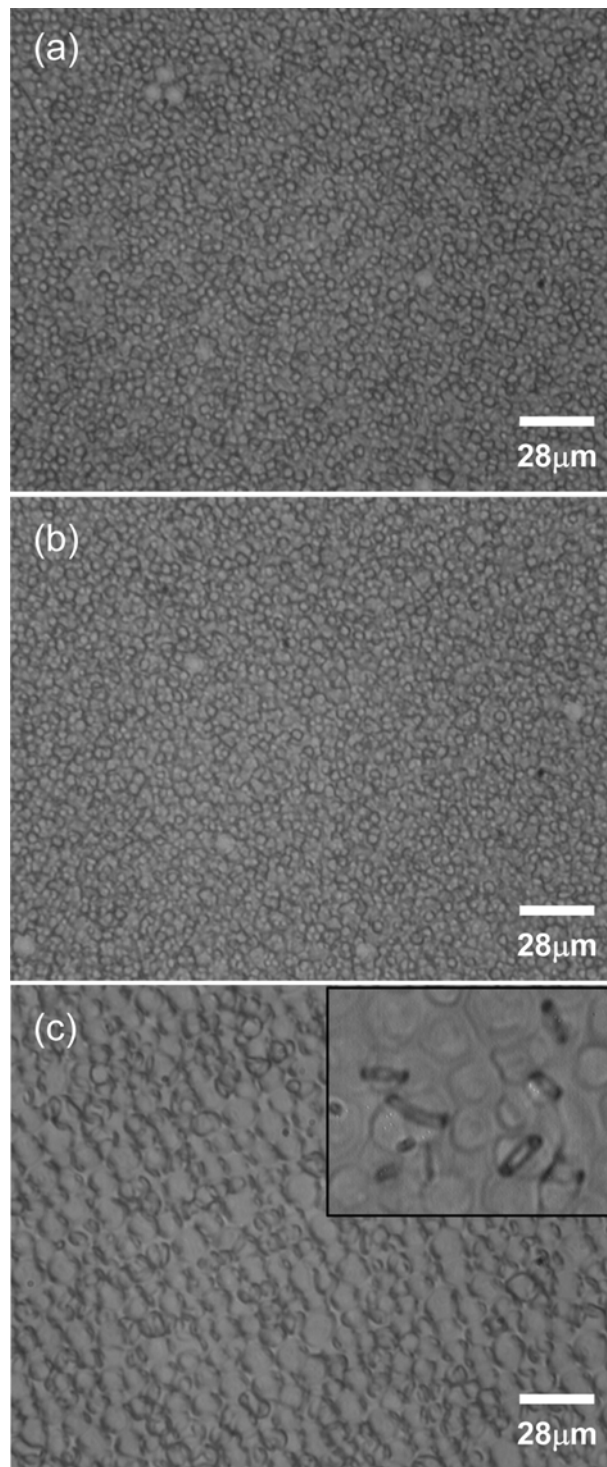


Fig. 5. Optical micrographs of PDLCs having various crosslinking agents of: (a) TMPTA, (b) HDDA, and (c) DEGDVE. The inset in (c) is a twice-enlarged section of the cell biased at 2 Volts.

falls into the binary phase area so that the polymer phase with a composition of c_p and the LC phase of c_{LC} can be separated, as shown in Fig. 5(b) [3]. At an elevated temperature, the c_p phase transforms to a single isotropic phase; however, c_{LC} phase will be separated into newly formed phase above T_A . In this situation, the TMPTA-

PDLC layer consists of three different phases, which are supposed to have totally different anchoring energy from the original phase, so that TMPTA-PDLC may show the extreme variation of EO properties [6].

Considering the temperature stability of DEGDVE-PDLC, it is assumed that the immiscibility gap of DEGDVE-PDLC is much taller than TMPTA-PDLC as depicted in Fig. 5(b). While secondary phase separation can take place, the phase transformation temperature (T_{VE}) would be much higher than T_A so that the PDLC can be stable even at higher temperature and hence its EP properties in turn. The reason why the TMPTA-PDLC has a narrower immiscibility gap is not clear yet. However, we presume that the degree of polymerization would be relatively low in acrylate-PDLC (TMPTA- and HDDA-) due to the oxygen inhibition effect. It is known that the polymerization of vinyl ether-based formulation is not affected by oxygen dissolved in the mixture [7]. Therefore, DEGDVE can lead to higher degree of polymerization so that the immiscibility gap is much wider.

The morphology of DEGDVE-PDLC is somewhat different from acrylate-PDLC. As shown in Fig. 5, the domain size is measured to be more than double by using an optical microscope, which might reduce the contrast ratio. Bosc et al. reported that the most efficient PDLC films must follow the optimization relation, $a(\Delta n)/\lambda = 0.3$, where a is droplet radius, Δn is the liquid crystal anisotropy, λ is wavelength [8]. According to the relation, the domain size of the liquid crystal phase should be less than 2 μm in diameter to get the highest contrast. Otherwise, the lowered scattering power of PDLC will decrease the off-state transmission and the contrast ratio in turn. Fig. 5 shows the effect of crosslinker selection on the variation of domain size. Contrary to the prediction, the contrast ratio of VE-based PDLC cells having the biggest domain among the three was measured to be much higher compared to the other two acrylate-based PDLCs. This might be explained by the shape of polymer construction inside the liquid crystal domain. The domain size value is usually calculated by analyzing the polarized optical micrograph taken at no electric field, where the liquid crystal domains appear as colored area due to the interference and the polymer matrix as dark area. However, even the colored area can contain polymer texture as shown in the inset image in Fig. 5(c). The seams inside the domain are supposed to be of filamentary polymer construction, and the arrangement of liquid crystal molecules deviates from the direction of domain director. For drops much larger than the wavelengths of light, the stronger deviation due to the polymer filaments inside the domains will increase scattering power and hence the contrast ratio [9].

CONCLUSIONS

We compared the electro-optic properties of PDLCs prepared by

using PN393 pre-polymer having different crosslinker monomers. While TMPTA or HDDA containing PDLCs shows considerable variations in contrast ratio, response time and turn-on voltage depending on the operation temperature, DEGDVE-PDLC exhibits stable electro-optic characteristics over a wide temperature range. Enhanced degree of polymerization by replacing TMPTA with DEGDVE may play a major role in stabilizing EO properties. Examination of optical micrographs of DEGDVE-PDLC reveals that polymer filaments are contained inside of the domains so as to exhibit similar contrast ratio as acrylate-PDLC in spite of the much larger domain structure.

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NOMENCLATURE

c_p	: composition of polymer phase
c_{LC}	: composition of liquid crystal phase
T_A	: temperature beginning to show the secondary phase separation in acrylate containing PDLC [$^{\circ}\text{C}$]
T_o	: off-state transmittance [%]
T_{sat}	: on-state transmittance [%]
T_{VE}	: temperature beginning to show the secondary phase separation in vinyl-ether containing PDLC [$^{\circ}\text{C}$]
Δn	: refractive index anisotropy of liquid crystal
λ	: wavelength [nm]

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