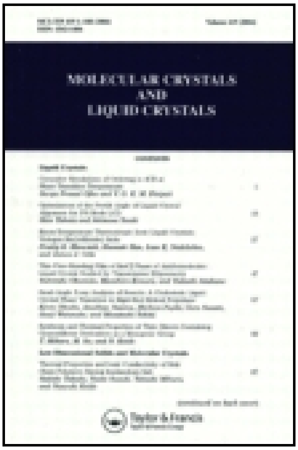

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Improvement of Electro-Optic Properties in PDLC Device by Using New Cross-Linker for the Control of the Contrast Ratio, Response Time and Driving Voltage

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We developed new cross-liker for the PDLC application that includes the bisphenol A and tris(hydroxyphenyl)ethane moieties in the structure with bis- or tris-acrylate at the end of molecules to induce photo-polymerization. Although the cross-linker was added as small as 2% $\sim$ 10% (more ratio) to compare with monomer, the electro-optic properties of PDLCs were found to exhibit significant change with material selection. We found that the more cross-linker added, the droplet size of LC became small which affected the properties of PDLC devices such as response time and driving voltage, directly. We found that tri-functionalized cross-linker synthesized from tris(hydroxyphenyl)ethane moiety could enhance the electro-optic property in PDLC. Also, in the PDLCs containing smaller size of liquid crystal droplets, although the response time and driving voltage were increased, the contrast ratio was enhanced, significantly.

Keywords: cross-linker; electro-optical property; photo-polymerization; polymer dispersed liquid crystal

INTRODUCTION

Polymer dispersed liquid crystal (PDLC) films are of current interest with respect to their potentials for applications such as optical switches, display, and variable transmittance windows due to their unique electro-optical performance [1–5]. Since the PDLC exhibit 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. It can

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Address correspondence to Jae Hong Kim, School of Display and Chemical Engineering, Yeungnam University, 214-1, Dae-dong, Gyeongsan-si, Gyeongsangbuk-do 712-749, Korea. E-mail: jaehkim@yun.ac.kr also give high contrast ratio in reflective mode devices based on passive lighting, eliminating the need for integrated backlighting which can reduce the weight and power consumption in devices.

PDLC films were prepared by the phase separation with dispersed (droplets, swiss cheese) or interconnected (polymer ball) liquid crystal phase in polymer matrixes. If the droplets are on the order of a micrometer in diameter, spatial refractive index inequalities among liquid crystal and polymer phases results in the scattering of normal incident light [6–7]. When the electric field applied in the film, LC molecules are aligned in the polymer matrixes that could make transparent state. Thus, the devices could operate with control for the light scattering property of liquid crystal (LC) domains by dispersed LC phase to match (on-state, transparent) or mismatch (off-state, opaque) with that of an optically transparent polymer matrix, respectively. In its normal state, LC droplets can scatter light strongly that bring about opaque apparently which can be converted to transparent in the electric field with the reorientation of LC molecules at the on-state. It is obvious that the shape, size, chemical interaction and dimensional uniformly of liquid crystal droplets could affect strongly the performance of PDLC devices involving on-off switching time, driving voltage, contrast ratio in on-off state, directly [8–10].

On the other hand, there are several methods manufacturing PDLC cell; Thermally Induced Phase Separation (TIPS); Polymerization Induced Phase Separation of the reactive matrix (PIPS); Solvent-Induced Phase Separation (SIPS); and Encapsulation. The most convenient method to prepare PDLC devices is the photo-polymerization of the mixture of photo-initiation system with reactive monomer, cross-linker and LC molecules by the exposure with the UV-light [11–15].

In this paper, we have developed new cross-liker that includes the bisphenol A and tris(hydroxyphenyl)ethane moieties in the structure with bis- or tris-acrylate at the end of molecules. Although the cross-linker is added as small as $2 \sim 10\%$, the electro-optic properties of PDLCs were found to exhibit heavy change with material selection. We found that the more cross-linker added, the droplet size of LC became small which affected the properties of PDLC devices such as response time and driving voltage, directly.

EXPERIMENTAL

Materials and Equipments

Instruments

Proton NMR was recorded with JEOL 300 NMR spectrometer. Deuterated chloroform ($CDCl_3$) was used as a solvent for recording the spectra. UV-Vis absorption spectroscopic study was performed on a Hewlett Packard 8453 spectrophotometer (PDA type, $\lambda = 190$–1100 nm).

Materials

Triethylamine (TEA), acryloyl chloride, bisphenol A, tris(hydroxyphenyl)ethane were purchased from Aldrich chemical Co. and used without purification. All solvents used in this study were freshly dried by distillation method.

Synthetic Procedure for the Cross-Linkers

Tris-(Hydroxyphenyl)Ethan–Triacrylate (THPETA)

Tris(hydroxyphenyl)-ethane (0.02 mol) was dissolved in presence of triethylamine (0.048 mol) with the dried THF (60 ml). After 10 min stirring under argon atmosphere, acryloyl chloride (4.32 g, 0.048 mol) was added dropwise over 10 min, respectively. The mixture was allowed to stir for 2 h at 25°C. After completion of the reaction, the mixture was filtered and the filtrate was concentrated. It was dissolved in chloroform (100 ml). The solution was washed twice with water (100 ml) and the organic layer was dried over Na_2SO_4. The resulting crude product was purified by silicagel column chromatography (methylene chloride/hexane, 1:1) to yield white crystalline solid. Yield:67%; ^1H NMR (300 MHz, $CDCl_3$):d 2.15 (s, 3H), 5.99 (d, $J = 5.1$ Hz, 3H), 6.30 (dd, $J_1 = 5.1$ Hz, $J_2 = 8.7$ Hz, 3H), 6.57 (d, $J = 8.7$ Hz, 3H), 7.02 (d, $J = 8.2$ Hz, 6H), 7.10 (d, $J = 8.2$ Hz, 6H).

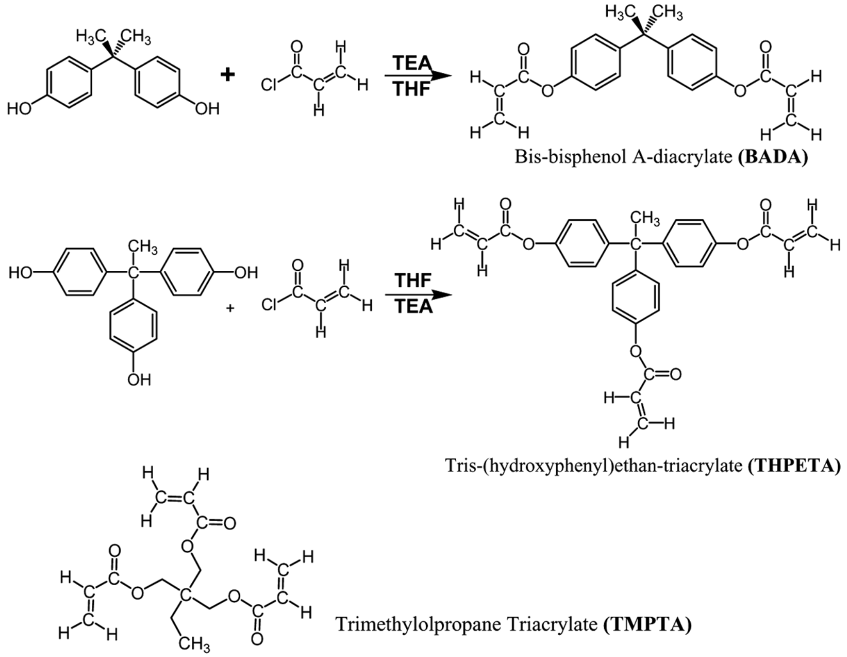
Bisphenol A Diacrylate (BADA)

The same procedure was employed to prepare BADA, instead of tris(hydroxyphenyl)-ethane in THPETA, we used bisphenol A for the synthesis of BADA to yield white solid. Yield:80%; m.p. 88°C; ^1H NMR (300 MHz, $CDCl_3$):d 1.69 (s, 6H), 6.00 (d, $J = 10.2$ Hz, 2H), 6.32 (dd, $J_1 = 10.2$ Hz, $J_2 = 17.4$ Hz, 2H), 6.60 (d, $J = 17.1$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 4H), 7.26 (d, $J = 8.4$ Hz, 4H). FT-IR:1734 cm^{-1} (–COO– stretching), 1605 cm^{-1} (–C=C– in acrylate). Anal.:$C_{21}H_{20}O_4$ (336.38) Calcd.:C 74.98, H 5.99; Found:C 73.90, H 5.32.

Preparation and Characterization of PDLC Devices

PDLC cell is prepared by sandwiching a mixture of pre-polymer and liquid crystal between two transparent indium tin oxide (ITO) coated glass plates with a 7 μm cell gap thickness. In order to avoid any uncertainty induced from cell gap nonuniformity, the 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%) of liquid crystals composed of 80:20 (wt%) mixture with TL205 (Merck) and PN393 (Merck), and 20% of monomer, crosslinker and initiator mixtures with three different mole ratio (monomer:crosslinker; 50:1, 70:1, 100:1), respectively. The content of initiator was fixed with 100:1 (more ratio with mixture of monomer and crosslinker:initiator). The structures of the crosslinkers used in this experiment are shown in Scheme 1. The mixture was introduced into the cell by the capillary action and photo-polymerized by illuminating with a UV lamp (365 nm peak wavelength) of 1 mW/cm^2 intensity for 10 min. During the UV curing, the temperature of the sample was fixed at 22°C using Linkam PE120 hot-stage. The film has a typical PDLC morphology with domain sizes on the order of 3–10 m diameter.

Electro-optic properties were characterized 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,



SCHEME 1 The synthetic procedures for cross-linkers (BADA, THPETA) and the chemical structure of a conventional cross-linker (TMPTA).

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% (vice versa) of the maximum transmitted light intensity. The contrast ratio was calculated by dividing the measured on-state transmittance (Tsat) by off-state transmittance (To).

RESULTS AND DISCUSSION

Synthesis for the Cross-Linker

Bis- or tris-acrylates were synthesized with known method for the application of PDLC as a cross-linker from bisphenol A and tris-(hydroxyphenyl)ethane as shown in Scheme 1.

Acrylate unit can be polymerized easily with the photo-irradiation in the presence of proper sensitizer, 2,4,6-trimethylbenzoyl diphenylphosphine oxide (50 wt%) and 2-hydroxy-2-methyl-1-phenylpropan-1-one (50 wt%) mixture as a initiation system which could induce the phase separation with LC molecules from the mixture. We added aromatic rings in the cross-linker that can act as a rigid-bridge to compare with that of conventional aliphatic cross-linker in the resultant polymer after the photo-polymerization in the cell.

Electro-Optical Properties of the PDLC

We prepared the PDLC devices with the photo-polymerization method in the mixture of photo-initiation system and LC molecules by the exposure with the UV-light. First of all, the incident UV light is absorbed by the photo-initiating system to produce active radical species. Then, monomers and cross-linker start to be polymerized with the radical that induces phase separation with LC molecules. Finally, termination reactions occur either by recombination of the radical species or chain transfer processes in which LC molecules could be separated and build their own domains. Thus, the dimensions and size of LC droplets in PDLC can be affected not only by the manufacturing conditions such as temperatures, light exposure process, but also by the nature and composition of LC molecules, reactive monomer, photo-initiation materials, and cross-linker that could decide the electro-optic properties of PDLC film, crucially.

The content of cross-linker we added was changed to 1–2% (mole ratio) compared with monomer as shown in Table 1. Interestingly, we found that the droplet size of LC was changed with the content

TABLE 1 Electro-Optical Properties of the PDLC Devices

Material	Ratio[a]	T_{init} (%)[b]	T_{sat} (%)[c]	V90 (V)[d]	Times (ms)[e]	D_s (μm)[f]	CR[g]
BADA	50:1	25.7	95.5	4.1	205	1.9	2.8
	70:1	13.0	92.9	3.5	204	2.0	2.3
	100:1	36.7	91.8	3.2	182	2.7	1.7
THPETA	50:1	11.3	95.4	5.1	612	1.6	8.4
	70:1	16.5	96.5	4.3	322	1.9	5.8
	100:1	18.3	95.6	3.8	171	2.0	5.2
TMPTA	70:1	52.0	94.0	3.2	204	2.5	1.8

[a] Mole ratio (monomer:cross-linker).
[b] Initial transmittance values.
[c] Saturated transmittance values.
[d] Applied voltage for 90% transmittance of cells (cell gap:7 μm).
[e] Response time of PDLC cell.
[f] Average diameter of LC droplet.
[g] Contrast ratio, $CR = T_{sat}/T_{init}$.

of cross-linker significantly, as shown in Fig. 1. The more cross-linker added, the average diameter of liquid crystal droplets became small.

It is generally known that the electro-optical performances of the PDLC devices are affected by the size of the LC droplets, morphological shape of the domains, the chemical properties of the LC, composition ratio, and intermolecular interaction between components.

D. Bose *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. According to the

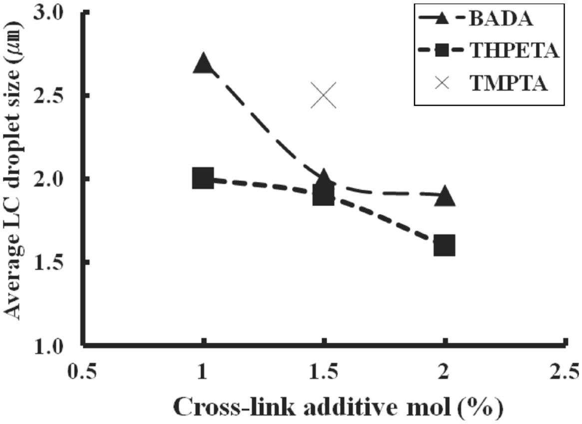


FIGURE 1 The droplet size of LC with the content of the cross-linkers.

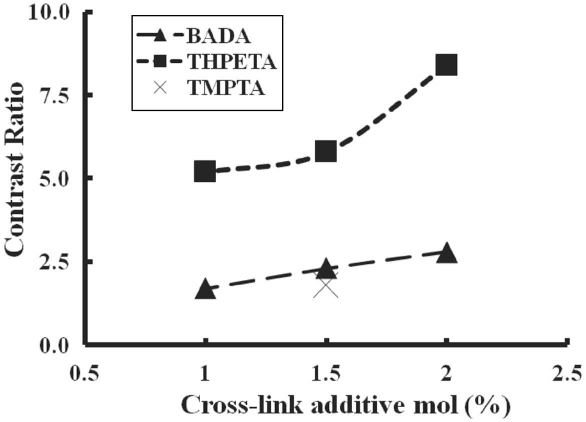
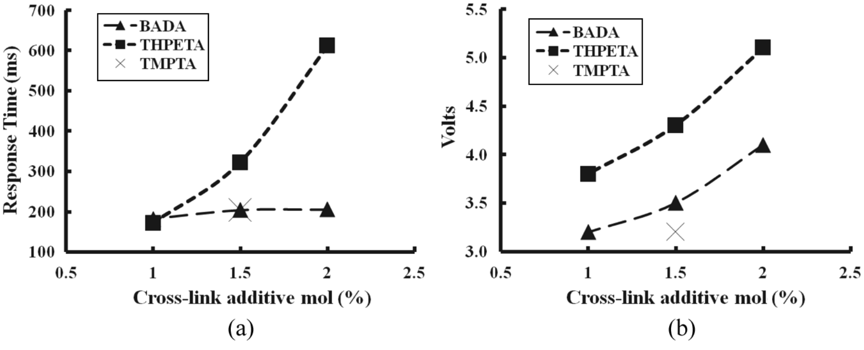


FIGURE 2 The dependence of the contrast ratio with the cross-linker structures and concentrations.

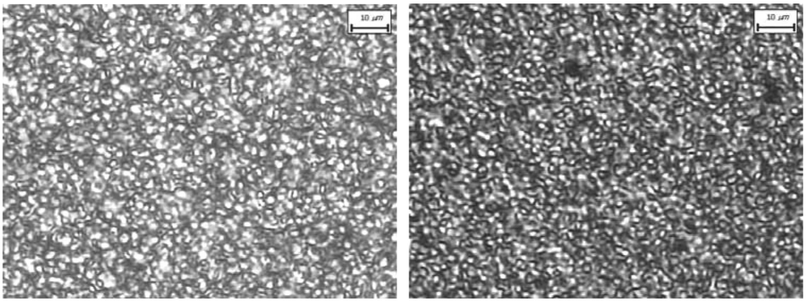
relation, the domain size of liquid crystal phase should be less than 2 μm in diameter to get a highest contrast. Otherwise, the lowered scattering power of PDLC will decrease the off-state transmission and the contrast ratio in turn. Figure 2 shows the dependence of the contrast ratio with the cross-linker structures and concentrations. We could find that tri-functionalized cross-linker enhanced the contrast ratio in PDLC in the concentration of 1:50 (monomer:cross-linker, more ratio).

Figure 3 shows the change of the response time and driving voltage of the cell with the change of cross-linker concentration respectively. It is known that the driving voltage is reverse-proportional relation



(a) (b)

FIGURE 3 The change of the response time (a) and driving voltage (b) of the cell with the change of cross-linker concentration.



(a) (b)

FIGURE 4 (a) Microscopic images of PDLC films made from [BADA]: and (b) [THPETA].

with liquid crystal droplet size in the device. In our measurement results, the driving voltage was decreased with the increase of the droplet size which could be controlled with the content of the cross-linker.

Microscopic images of PDLC films composed of different cross-linker showed in Fig. 4. The device from tris-functionalized cross-linker showed highest contrast ratio to compare with that of bis-acrylate or conventional one.

CONCLUSION

We have developed new cross-liker including bisphenol A and tris-(hydroxypheny)ethane in the structure with bis- or tris-acrylate at the end of molecules, respectively. Although the cross-linker is added as small as $2 \sim 10\%$ (mole ratio) to monomer content, the electro-optic properties of PDLCs were found to exhibit significant changes even with a small change of material composition. We found that the more cross-linker added, the droplet size of LC became small which affected the properties of PDLC devices such as the contrast ratio, response time and driving voltage, directly. In PDLCs composed of the small liquid crystal droplets, the contrast ratio increased significantly. Furthermore, it was obvious that tri-functionalized cross-linker could enhance the electro-optic property in PDLC to compare with that of bis-acrylate cross-linker.

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