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Polymer Dispersed Liquid Crystal (PDLC) films, of which the liquid crystal has negative dielectric anisotropy, were prepared from the phase separation between liquid crystal (MJ001317) and the various compositions of resins by common polymerization induced phase separation method. In this work, the effects of resin compositions have been systematically investigated. It was found that the morphology and size of droplets related to electro-optic properties mainly depend on the rate of polymerization and cross-linking density for each resin composition. A reverse mode PDLC films developed from a new formulation containing TPGDA/EHA/HMPPO showed the good off-state transmittance, contrast ratio (19:1), and relatively low driving voltage (10 V).

Keywords: electro-optic property; polymer dispersed liquid crystal (PDLC); polymerization induced phase separation

INTRODUCTION

In recent, a great attention has been paid to the fabrication of devices using Polymer Dispersed Liquid Crystals (PDLCs) because of its

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potential applications, which including smart windows, mobile devices and flexible displays.

PDLCs are the state of things that the micro-droplets of liquid crystal are dispersed into the polymer matrix [1–3]. The transparency of PDLCs can be altered by an external electric fields, which can control the extent of the mismatch of refractive indices between the liquid crystal and polymer matrix. That is, the birefringent liquid crystal droplets form light scattering centers, and their scattering properties caused by the mismatch of refractive indices can be switched on and off by applying an electric fields across the film. The detailed electro-optical properties of PDLC films mainly depend on the chemical nature of the polymer and LC, and preparation conditions, which result in different interface environment between LC and polymer [4,5]. LCs inside the droplets will experience different constraint under different interface environment (different droplet size and morphology) [6,7]. For preparing, therefore, the PDLC devices with optimal electro-optical characteristics, it is very important to investigate the effect of interfacial characteristics such as the properties of polymer domains or the size and morphology of LC droplets.

On the other hand, since LCs in the PDLC systems containing liquid crystals with negative dielectric anisotropy tend to align themselves in direction perpendicular to electric fields, the PDLC films under the presence of electric fields will be translucent by scattering the incident light. On the contrary, they will be transparent under the absence of electric fields because LCs are vertically aligned by alignment layer. A schematic illustration of reverse mode PDLCs was presented in Figure 1. Since reverse mode PDLCs show normally transparent, they have some advantages over normal mode PDLCs in viewpoint of power consumption.

In this work, polymerization rate has been carefully controlled by varying the conditions such as resin compositions, film thickness, and alignment layer to investigate the effect of interfacial environment in preparing with reverse mode PDLCs. Prepolymers with only mono/di-functional groups also have been selected to reduce the cross-linking density.

EXPERIMENTAL

The present PDLC systems were fabricated by the polymerization-induced phase separation process. The tripropylen glycol diacrylate (TPGDA) and 2-ethylhexyl acrylate (EHA) were used as prepolymers, and 2-hydroxy-2-methyl-1-phenyl propane-1-one (HMPPO) as photo initiator. The LC component was an eutectic mixture of liquid crystals,

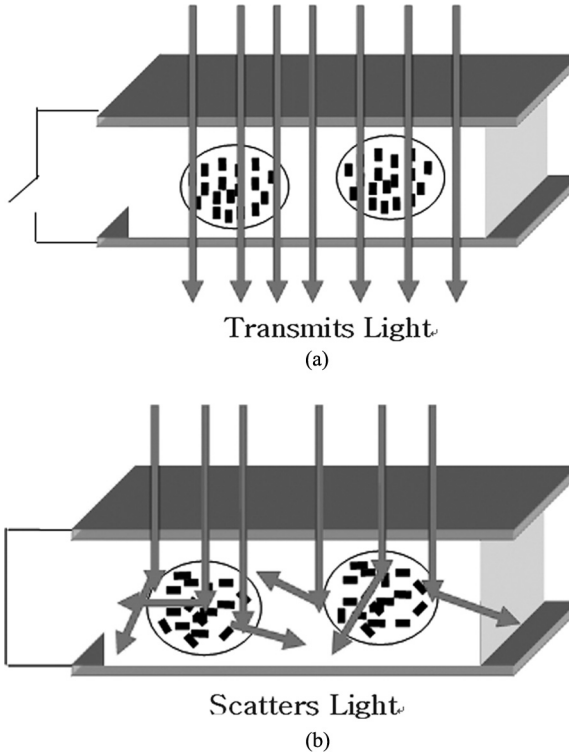


FIGURE 1 Schematic representation for reverse mode PDLCs (a) under no electric fields, and (b) under electric fields.

commercially available as MJ001317 (Merck), which has negative dielectric anisotropy ($n_o = 1.49$, $n_e = 1.6442$ $\Delta\varepsilon = -3.9$).

The PDLCs were prepared by mixing the LC component (40 wt%) with the uncured resin component (60 wt%) homogeneously. Prepolymer ratio of TPGDA/EHA was fixed with 3:1 by weight in all the PDLC formulations. The ratios of prepolymer/photo initiator (HMPPO) to control the rate of polymerization were varied to 99:1, 80:20, 70:30, 60:40, 50:50, and 40:60 by weight, respectively. The mixtures were then sandwiched between two transparent conductive glasses spaced by spacers with the size of 4.2 μm and 10 μm, respectively, and cured by UV irradiation of 365 nm 1.5 mW/cm^2 for 5 min.

Morphologies of the films were studied using a scanning electron microscopy (SEM, Jeol JSM820) and polarized microscope. For the investigations of SEM, UV-cured cells were fractured after quenching by liquid nitrogen. Then, LC was extracted in n-hexane for 24 h, and

the cells were cleaned in an ultrasonic cleaner. Before investigated, the surfaces of samples were treated in a gold sputtering chamber. The intensity of transmitted light was measured with a photodiode after placing PDLC cells normal to the direction of collimated beam of He/Ne laser ($\lambda = 632.8$ nm). The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope (Hitachi VC-6023).

RESULTS AND DISCUSSION

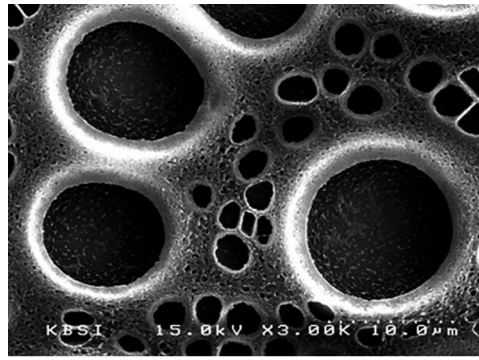
In Table 1, the variations of transmittances upon the amount of photo initiator (HMPPO) were listed. It was found that off-state transmittance was increased with the amount of photo-initiator. The rate of polymerization is getting faster and the droplet size smaller by the increasing amount of photo-initiator, which consequently leads to the increase of off-state transmittance by inducing the more ordered alignment of LCs in perpendicular direction. It is also notable that PDLCs with 60 wt% of HMPPO has shown a contrast ratio, ca. 19:1 calculated from the comparison of off/on-state transmittances in Table 1.

Figure 2 shows the SEM photographs of LC micro-droplets after the LC extraction. It was obviously confirmed that, the more the amount of initiator was, the smaller the size of droplet. The distributions of droplet size in PDLCs prepared from 30 wt%, 40 wt%, and 50 wt% HMPPO, were $2 \sim 9\,\mu$m, $2 \sim 3\,\mu$m, and $1 \sim 2\,\mu$m, respectively. The distribution of droplet size was also narrowed with the increment of initiator contents. The trend was in a good agreement with the expectation from above results. As the size of droplet became smaller, the

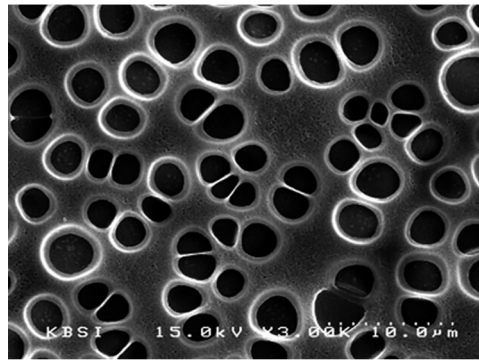
TABLE 1 Transmittance in Off-State and On-State upon the Amount of Photo Initiator (HMPPO)[a]

	Transmittance (%)	
HMPPO (wt%)	Off state	On state
1	22	9.7
20	24	7.8
30	70	6.6
40	70	6.4
50	71	6.6
60	80	4.2

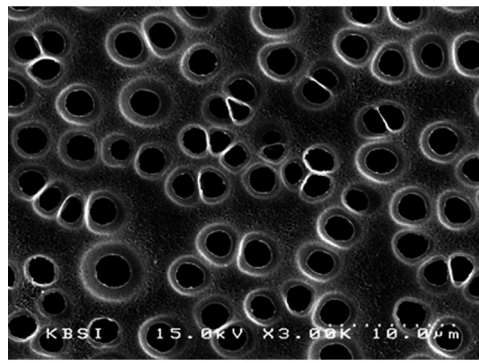
[a]cell gap : 10 μm.



(a)



(b)



(c)

FIGURE 2 Scanning electron microscopic images for (a) 30 wt%, (b) 40 wt%, and (c) 50 wt% of HMPPO, respectively.

number of scattering centers would be increased, which could be expected to be the reason of high contrast ratio.

The optical characteristics of the droplet domains were also observed in Figure 3 by polarized microscope. It was shown that the intensity of reflected light was prominently reduced with the increasing amount of initiator, HMPPO. This observation could be induced from the more ordered vertical arrangement of LCs due to the smaller and uniform size of droplets, for which would make the interaction between alignment layer and LCs more effective. This result is well consistent with previous results, which could be caused by the reduction of anchoring energy at interface between polymer and LC domain as the degree of polymerization was getting lower by the increasing amount of initiator although the size of droplet became smaller.

Figure 4(a) shows the transmittance and applied voltage relationship according to the contents of initiator (HMPPO) in the cell gap of 10μm. According as HMPPO contents increased, LC domain size and the degree of polymerization decreased and anchoring energy was reduced. Therefore, drive voltage showed less than 10 v in contents more than HMPPO 50wt%. The photographs of the PDLC cell corresponding to HMPPO 60 wt% in electric field-off and on states, respectively, were presented in Figure 4(b). In the absence of electric fields, ordinary refractive index of LC (n_o) and polymer (n_p) was well matched with each other, which leads to transparent mode. On the contrary, in the presence of electric fields, light was scattered because

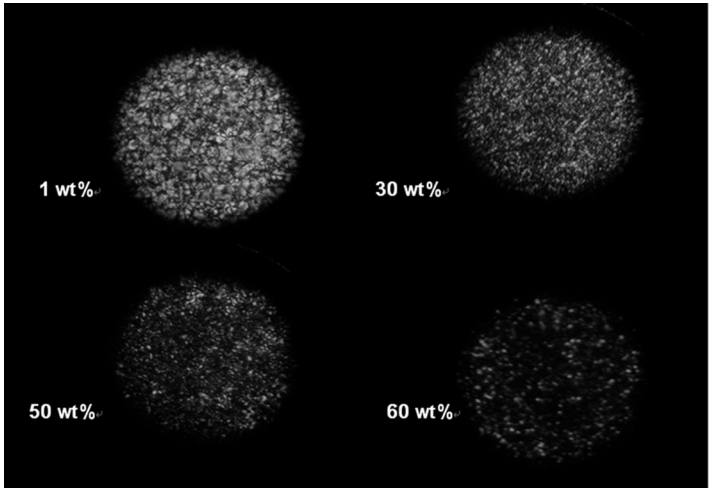


FIGURE 3 Polarized microscopic images according to the amount of initiators.

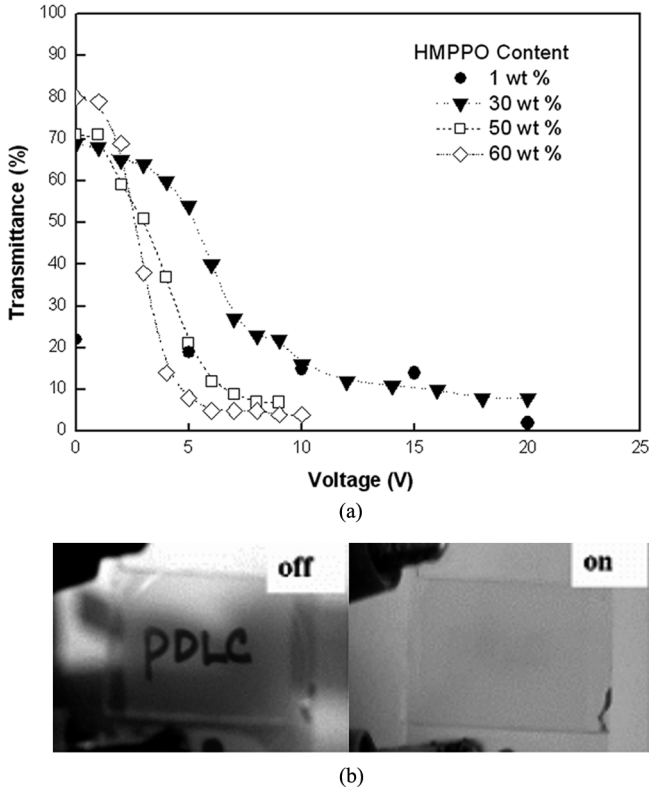


FIGURE 4 (a) Transmittance vs applied voltage relationship according to the contents of initiator (HMPPO) in cell gap of 10 μm, and (b) Photographs of PDLC cell under electric field-on and off states, respectively.

of the mismatch between the refractive indices by the perpendicular alignment of LCs to electric fields, which leads to non-transparent state.

In general, rising time (τ_R) in normal mode PDLCs is proportional to the strength of electric fields, but decay time (τ_D) is inversely proportional to that, because LCs in the droplet, which shows bipolar configuration, experience the change of not only direction but also bipolar axis. In reverse mode, however, τ_D remains unchanged despite of increment of electric fields since LCs can be realigned easily by the interaction with alignment layer, while τ_R still shows the same trends as normal mode PDLCs. As seen in Figure 5, which shows the relationships of response time vs. transmittance, our PDLCs was found to show the response time of 25 ms in 10 μm cell gap.

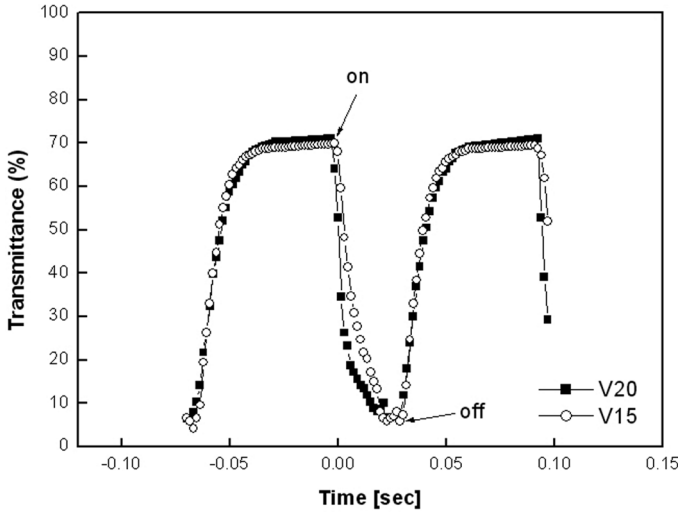


FIGURE 5 Response time upon the strength of electric fields (TPGDA/EHA = 3/1, HMPPO 50 wt%, cell gap : 10 μm).

In this work, film thickness and alignment layer also have been varied to investigate their effectiveness on optical properties. The results were listed in Table 2. Note that how the transmittance changes by alignment layer. Irrespective of film thickness, the transmittance in off-state was higher in the PDLC cells with alignment layer, which implies LCs are vertically aligned by alignment layer and so the refractive indices between LC and polymer are well matched. On the other hand, the transmittance in on-state was decreased with the film thickness because the scattering centers, LC droplets, reduced in thinner film.

TABLE 2 The Effects of Film Thickness and Alignment Layer upon Transmittance[a]

	Transmittance (%)			
	w/alignment layer		w/o alignment layer	
Cell gap (μm)	Off	On	Off	On
4.2	90	21	86	42
10	80	4.2	57	25

[a]HMPPO 50 wt%.

CONCLUSIONS

The reverse mode PDLCs were successfully prepared from newly developed formulations. The size and morphology of micro-droplets were controlled by varying the composition of resin. Uniform and smaller droplets were stably embedded in each of polymer matrix as the increasing amount of initiator. A good electro-optical property (CR. 19: 1) and a low driving voltage (10 V at 10 μm thickness) were obtained by the control of polymerization rate in spite of smaller droplet sizes.

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