Preparations of Polymer Dispersed Liquid Crystals Using the Liquid Crystals with negative dielectric anisotropy

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Abstract

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

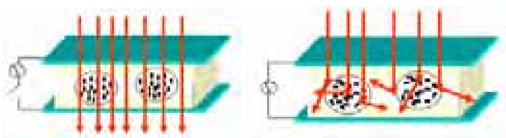
1. Introduction

In recent, a great attention has been paid to the fabrication of display devices using the Polymer Dispersed Liquid Crystals(PDLCs) because of potential applications such as optical shutters, flexible displays and etc. due to their interesting electro-optical properties, and simplicity in process.

PDLCs are the dispersion of liquid crystal micro-droplet into the polymer matrix based on phase separation phenomenon.[1-3] Under an external electric field, PDLC films can be switched between translucent and transparent states according to the mismatch or match between the refractive indices of liquid crystal and polymer matrix. That is, the birefringent liquid crystal droplets form light scattering centers, and their scattering properties can be switched on and off by applying an electric field across the film. The detailed electro-optical properties of PDLC films 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 droplet will experience different constraint under different interface environment(different droplet size and morphology).[6,7] Therefore, it is very important to investigate the effect of interfacial characteristics such as the properties of polymer domain or the size and morphology of LC droplet, for the purpose of preparing the PDLC device with optimal electro-optical characteristics.

On the other hand, the PDLC systems in this work have contained liquid crystals with negative dielectric anisotropy. In PDLCs of negative dielectric LCs, LCs tend to align temselves with the directors perpendicular to field direction. Therefore, under the presence of electric field, the PDLC films will be translucent by scattering the incident light. On the contrary, under the absence of electric field, they will be transparent if alignment layer is used to align LCs vertically. A schematic representation of reverse mode PDLC was presented in Figure 1. Reverse mode PDLC has some advantages over normal mode PDLC in that power consumption could be seriously lessened because incident light is transmitted in the absence of electric field – normally tranparent.

In this work, in order to prepare reverse mode PDLC and investigate the effect of interfacial environment, polymerization rate has been carefully controlled by varying the preparation conditions such as resin composition, film thickness, alignment layer and so on. And also prepolymers with only mono/di-functional groups have been selected to reduce the cross-linking density.



(a) (b)

Figure 1. Schematic representation for reverse mode PDLC; (a) under no electric field, and (b) under electric field.

2. Experimentals

The present PDLC systems were prepared 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 a eutectic mixture of liquid crystals, 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% by weight) with the uncured resin component(60% by weight) until obtaining a complete homogenization of the mixture. In every composition of resins, prepolymer ratios of TPGDA/EHA were the same as 3:1 , while the ratios of prepolymer/HMPPO were varied to 99:1, 80:20, 70:30, 60:40, 50:50, and 40:60, respectively, to control the rate of polymerization. The mixtures were then sandwiched between two transparent conductive glasses spaced at 4.2nm and 10nm, respectively, by appropriate spacers, and cured by UV irradiation of 365nm 1.5mW/cm^2 for 5 min.

Morphology of the films was studied using a scanning electron microscopy (SEM, Jeol JSM820) and polarized microscope. For the measurement of SEM, UV-cured cells were first fractured in liquid nitrogen. Then, LC was extracted in n-hexane for 24h, and cells were cleaned in an ultrasonic cleaner. Samples were sputtered with gold before measurement. Transmitted light intensity without any polarizer was measured with a photodiode after the UV-cured PNLC films sandwiched between two ITO-coated cells were placed normal to the direction of collimated beam of He/Ne laser(λ=632.8nm). The drive signal and the response of the photodiode were monitored with a digital storage oscilloscope(Hitachi VC-6023).

3. Results and Discussion

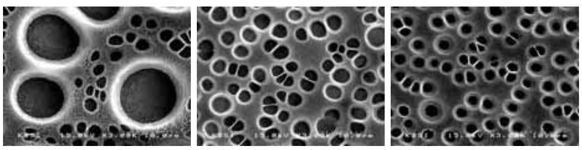
In Table 1, the variations of transmittances upon the amount of HMPPO were listed. It was found that off-state transmittance was increased with the increment of the amount of photo-initiator. As the amount of photo-initiator was increased, the rate of polymerization will be faster and the droplet size smaller, which consequently leads to the increase of off-state transmittance by inducing the more ordered alignment of LCs in perpendicular direction under no electric field. It is also notable that PDLC with 60 % of HMPPO showed contrast ratio, ca. 19:1.

Table 1. Transmittance in off-state and on-state upon the amount of photo initiator(HMPPO)

HMPPO (part %)	Transmittance (%)	
	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

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 trend was in a good agreement with the expectation from above results. The size of droplet also showed smaller and monodisperse distribution with the increment of initiator contents. As the size of droplet became smaller, the 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 increase of the amount of initiator, HMPPO.



(a) (b) (c)

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

This observation are caused by 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.

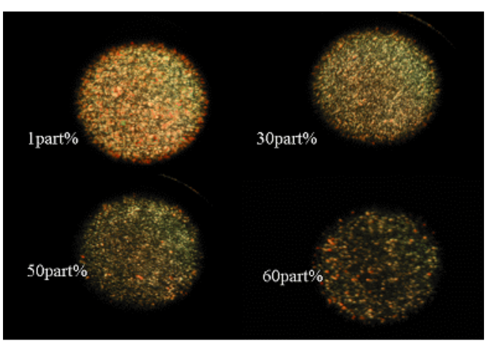
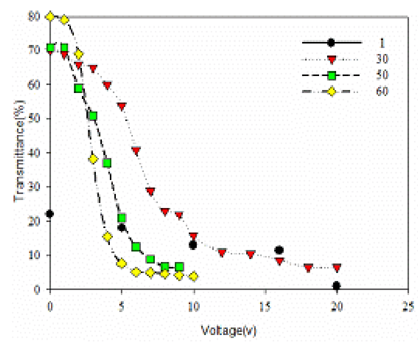


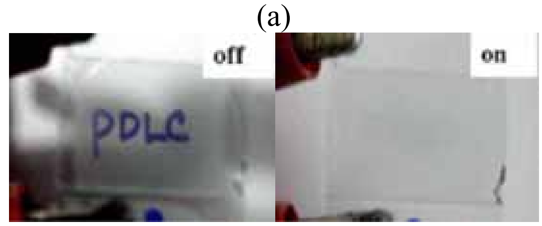
Figure 3. Polarized microscopic images according to the amount of initiators

Figure 4(a) shows transmittance-voltage (V-T) relationships according to the amount of initiator. It was found that the driving voltages were reduced to 10V for above 50% of HMPPO. This can be explained to be due to the reduction of anchoring energy at interface between polymer and LC domain as the degree of polymerization became lower with the increment of the amount of initiator although the size of droplet became smaller.

The photographs of the PDLC cell corresponding to HMPPO 60 part % in electric field-off and on states, respectively, were presented in Figure 4(b). In the absence of electric field, ordinary refractive index(n_o) of LC and that(n_p) of polymer was well matched with each other, which leads to transparent mode. On the contrary, in the presence of electric field, light was scattered because of the mismatch between the refractive indices by the perpendicular alignment of LCs to electric field, which leads to non-transparent state.



(a)



(b)

Figure 4. (a) Transmittance vs applied voltage relationship according to the variation of the contents of initiator, HMPPO, and (b) Photographs of PDLC cell under electric field on and off states, respectively

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

In this work, film thickness and alignment layer has been also varied to investigate their effect on optical properties. The effects were listed in Table 2.

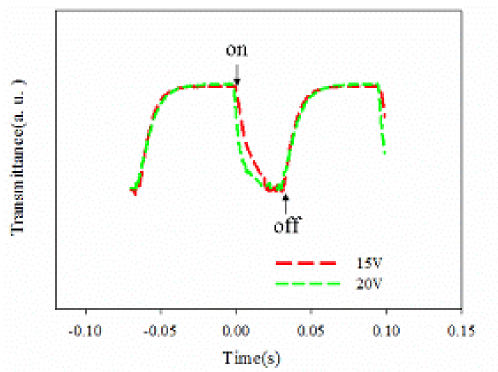


Figure 5 Response time upon the strength of electric field (TPGDA/EHA=3/1, HMPPO 50 part %)

Note how transmittance changes according to presence/absence of alignment layer. Irrespective of film thickness, transmittance in off-state is higher in PDLC with alignment layer, which implies LCs are more well aligned vertically by alignment layer and so the refractive indices of LC and polymer are well matched. On the other hand, transmittance in on-state became higher, as the film thickness decreased, because the effect of alignment layer got more effective in thinner film.

Table 2. The effects of film thickness and alignment layer upon transmittance.

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

3. Conclusion

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. From the morphological examination, it was confirmed that uniform and smaller droplets were stably embedded in each of polymer matrix as the increase of the amount of initiator. A good electro-optical property and driving voltage were obtained by the control of the degree of polymerization in spite of smaller droplet size.

4. Acknowledgements

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5. References

[1] P.S.Drzaic, Liquid crystal dispersions Singapore:World Scientific Publishing, (1995)

[2] J. Ding, Y. Yang, Mol. Cryst. Liq. Cryst., 238, 47, (1994)

[3] P. S. Drzaic, Liq. Cryst., 3, 1543, (1988)

[4] B.K.Kim, Y.H.Cho, J.S.Lee, Polymer, 41,1325 (2000)

[5] R.S.Justice, D.W.Schaefer, R.A.Vaia, D.W.Tomlin, T.J.Bunning, Polymer, 46, 4465 (2005)

[6] G. P. Montgomery, J. L. West, W. Tamura-Lis, J. Appl. Phys. 69, 1605, (1991)

[7] J. B. Whitehead, S. Zumer, J. W. Doane, J. Appl. Phys., 73, 1057, (1993)