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# Relaxation time of polymer ball type PDLC films

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'Polymer ball' polymer dispersed liquid crystal (PDLC) samples were fabricated by the photopolymerization induced phase separation method and their relaxation behaviour was studied. It was found that upon removal of the applied electric field, the transmittance of the 'polymer ball' PDLC sample decays exponentially from  $T_{on}$  to  $T_{memo}$  with a relaxation time constant in the order of msec. It was found that the measured relaxation time constant decreases as the curing time increases and the LC concentration increases.

#### 1. Introduction

In recent years, the liquid crystal display (LCDs) has emerged as the most important commercial product in the flat panel display market. However, the conventional twisted nematic liquid crystal (TNLC) light valve used in these LCDs requires two polarizers. These two polarizers limit the transmittance of the TNLC light valves and at most only half of the incident beam can be utilized. Therefore, the efficiency of TNLC light valves is seriously limited. Recently, much attention has been focused on using composites of liquid crystals and polymers to generate optical displays and light valves [1-4]. These electro-optical materials consist of dispersions of LC droplets in polymer films, and are referred to in the literature by the terms NCAP (nematic curvilinear aligned phase) or PDLC (polymer dispersed liquid crystal). These droplets have a positive dielectric anisotropy and their sizes can be preselected to between  $0.1 \,\mu\text{m}$  and  $10 \,\mu\text{m}$  in radius. A light value is constructed by sandwiching the PDLC material between two transparent conducting electrodes. The principle of operation of the valve is to control the light scattering crosssection of the LC droplets by applying a voltage between the electrodes. In the rest state, the film is opaque because the light is scattered by the randomly oriented LC in the droplets. The application of an electric field across the film causes the LC molecules in each droplet to align in the direction parallel to the field. If the ordinary refractive index of the birefringent nematic LC matches the refractive index of the polymer material, the film will become transparent. Compared with conven-

tional TNLC light valves, PDLC light valves are brighter, switch faster, have an improved viewing angle and are easily manufactured over large areas. Other than the 'droplet' PDLC, a different kind of PDLC with a distinct type of polymer morphology, which is referred to as 'reverse' or 'polymer ball' morphology, has also been reported [5-8]. Instead of forming microdroplets, these PDLC films form narrow and irregular voids and crevices filled with LC. The optical properties of the 'polymer ball' PDLC is also different from those of the conventional 'droplet' PDLC. The 'polymer ball' PDLC has a memory effect in which a transparency is preserved in the memory state for a long period of time after the applied electric field is removed. The transparent memory state can be erased and returned to the original opaque state by heating and cooling the film without applying an electric field. Figure 1 shows a typical voltage-transmission characteristic of a 'polymer ball' PDLC sample. In this figure, the ON state transmittance  $T_{\rm on}$  is 90 per cent while the memory state transmittance  $T_{\rm memo}$  is 70 per cent. After the applied electric field is removed, the film will be switched from the ON state to the memory state and the transmittance of the film will change from  $T_{on}$  to  $T_{memo}$  with a relaxation time constant. Previously, it has been reported that the sample preparation parameters of the 'polymer ball' PDLC films are important and can profoundly affect the optical properties [9, 10]. It was found that a low curing intensity or a short curing time will result in an incomplete polymerization and some monomer will remain within the liquid crystal. In such a case, the optical properties of the PDLC film will degrade. However, the effects of the sample preparation parameters on the relaxation time

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memory state

has not yet been studied. In this work, we will report upon the measurement of the relaxation time constant of the 'polymer ball' PDLC sample and its dependence on the sample preparation parameters.

#### 2. Experimental

The samples used in this study were prepared by the photo-polymerization induced phase separation (PIPS) method. To synthesize the 'polymer ball' PDLC films, we have used the UV curable 2-hydroxyethylmethacrylate (HEMA) as the monomer material, and a mixture of E7 and K15 as the nematic LC material [9]. The photoinitiator used in this study was 2,2-diethoxyacetophenone (DEAP). The mixture of monomer and LC with a few weight percentage of photoinitiator was then cured between two ITO-coated glass substrates. A UV lamp, HPA400/30S produced by Philips with an output wavelength centred at 348 nm, was used for curing, and a UV photodector G3641 was used to monitor the curing intensity. Throughout this study, the mixing ratio between E7 and K15 was fixed at E7:K15=1:1, and the photoinitiator concentration fixed at  $5\cdot36$  per cent. To understand the effects of sample preparation parameters on the relaxation time constant, six samples were prepared as listed in tables 1 and 2. The first set of samples were used to study the effect of LC concentration and the second set of samples were used to study the effect of curing time. The film thickness of these samples was fixed at  $12 \mu m$ .

#### 3. Results and discussion

To measure the relaxation time constant of the sample, an electric field larger than the saturation field was first applied across the sample so as to switch the film to the ON state. When the applied electric field was removed, the relaxation behaviour of the film was monitored by measuring the transmittance change of the sample. If  $\tau$ is the relaxation time constant, then the transmittance as a function of time after the removal of the applied electric field can be expressed as

or

$$\frac{T(t) - T_{\text{memo}}}{T_{\text{on}} - T_{\text{memo}}} = \exp\left(-t/\tau\right).$$

 $T(t) = T_{on} - (T_{on} - T_{memo}) (1 - \exp(-t/\tau))$ 

The measured voltage-transmission properties in the ON state (filled symbols) and in the memory state (filled symbols) for samples listed in table 1 are shown in figures 2(a) and 2(b), respectively. As reported previously [9], sample A with a small amount of liquid crystal has a higher OFF state transmission. On the other hand, although sample C, with a large amount of liquid crystal,

Table 1. 'Polymer ball' PDLC samples prepared with different curing times.

Sample	E7:K15	HEMA: (E7 + K15)	Curing intensity/mW cm <sup>-2</sup>	Curing time/min
A	1:1	7:3	15	30
В	1:1	1:1	15	30
<u>C</u>	1:1	3:7	15	30

Table 2. 'Polymer ball' PDLC samples prepared with different LC concentrations.

Sample	E7:K15	HEMA: (E7 + K15)	Curing intensity/mW cm <sup>-2</sup>	Curing time/min
D	1:1	1:1	3	3
E	1:1	1:1	3	15
F	1:1	1:1	3	30



100

90

80

70

60

50

40

30

20

10

0

Transmission / %

on state



Figure 2. The (a) ON state (filled symbols) and (b) memory state (open symbols) transmission for samples prepared with different monomer/liquid crystal ratios.

has a small OFF state transmission, its threshold and saturation voltages are high. To determine the relaxation time constants of these samples, we first drove the samples into saturation (80 V), and then measured the transparency dynamics upon removal of the electric field. Figure 3 shows the measured  $(T(t) - T_{memo})/(T_{on} - T_{memo})$  as a function of time after the removal of the applied electric field for samples listed in table 1. We can clearly see that the measured transmittance indeed



Figure 3.  $(T(t) - T_{memo})/(T_{on} - T_{memo})$  as a function of time after the removal of the applied electric field for samples listed in table 1.



Figure 4. Measured relaxation time for samples listed in table 1.

decays exponentially from  $T_{on}$  to  $T_{memo}$ . The relaxation time constants of these three samples were determined from the slopes in figure 3 and are plotted as a function of LC concentration in figure 4. It can be seen that the relaxation time constants of these 'polymer ball' PDLC samples are in the order of msec, and that they decrease as the LC concentration increases. The measured voltage-transmission properties in the ON state (filled symbols) and in the memory state (open symbols) for the samples listed in table 2 are shown in figure 5. As reported previously [9], sample D, with a larger curing time, has a larger optical transmission in both the ON and memory state. It also has a lower threshold voltage. Again, we first drove the samples into saturation (80 V), 90

Figure 5. Voltage-transmission property in the ON state (filled symbols) and in the memory state (open symbols) for 'polymer ball' PDLC samples cured with different curing times.

50

Volt/v

60

70 80

and then removed the electric field to study the dynamic behaviours of the samples. Figure 6 shows the measured  $(T(t) - T_{memo})/(T_{on} - T_{memo})$  as a function of time after the removal of the applied electric field for the samples listed in table 2. The relaxation time constants of these three samples were also determined from the slopes in figure 6 and are plotted as a function of curing time in figure 7. It can be seen that the relaxation time constant decreases as the curing time increases. For 'droplet' PDLC samples, it has been previously reported [11,12]



Figure 6.  $(T(t) - T_{memo})/(T_{on} - T_{memo})$  as a function of time after the removal of the applied electric field for samples listed in table 2.



Figure 7. Measured relaxation time for samples listed in table 2.

that the switch-off time  $T_{off}$  is determined by the anchoring force at the LC/polymer interface, and the shape and size of the droplet. A higher anchoring force will force the LC molecules to realign faster and thus a shorter  $T_{off}$ . For 'polymer ball' PDLC samples, the relaxation behaviour should also be influenced by a similar interface anchoring force. In this study, the polymerization process of the sample cured with a short curing time (sample D) is incomplete [9]. Such an incomplete polymerization will result in a weaker anchoring force at the polymer/LC interface and thus a longer relaxation time constant was observed as shown in figure 5.

#### 4. Summary

In summary, 'polymer ball' PDLC samples were fabricated by the PIPS method and their relaxation behaviour studied. It was found that upon removal of the applied electric field, the transmittance of the 'polymer ball' PDLC sample decays exponentially from  $T_{\rm on}$  to  $T_{\rm memo}$  with a relaxation time constant in the order of msec. It was found that the measured relaxation time constant decreases as the curing time increases and the LC concentration increases.

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100

90

80

70

60

50 40

30 20

10

0 L 0

10 20 30 40

Transmission/%

- time: 30min - - time: 30min - - time: 15min - - time: 15min

-d-- time: 3min -d-- time: 3min

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