

Effect of surfactant on the electro-optical properties of holographic polymer dispersed liquid crystal Bragg gratings

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Abstract

The effect of surfactants on the electro-optical properties of holographic polymer dispersed liquid crystal (HPDLC) Bragg gratings was studied in detail. The experimental results showed that surfactants could effectively reduce the driving voltage. The morphologies of HPDLC Bragg grating surface were also investigated by scanning electron microscope (SEM). The threshold electric field was reduced from 13 V/μm to about 2.3 V/μm and the switching electric field was 27.3 V/μm. The rising time and the falling time were 60 μs and 80 μs, respectively.

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1. Introduction

As a new kind of photoelectronic materials, holographic polymer dispersed liquid crystal (HPDLC) attracted more and more attention since Sutherland et al. reported it in the 1990s [1–3]. HPDLC has many advantages such as high diffraction efficiency, fast response and easy fabrication. HPDLC devices are potentially useful in optical communications, flat panel displays, information storage and integrated optics [4–6]. HPDLC gratings are formed by polymerization induced anisotropic phase separation of liquid crystals from a polymer matrix created through free-radical photopolymerization [7]. Bowley et al. even developed a phenomenological diffusion model to reveal a stratified compositional modulation in HPDLC systems enabling optimization of these materials for device applications [8].

However, comparing to the conventional PDLC [9], the driving voltage of HPDLC is significantly higher. Generally, the driving voltage of HPDLC is two orders of magnitude higher than that of PDLC. This disadvantage greatly hinders the applications of HPDLC. How to reduce the driving voltage is one of the keys to application. De Sarkar et al. reported that the driving voltage can be significantly decreased using the partially fluorinated monomers [10]. However, this led to longer relaxation time. In this paper, we shall report a detailed study to lower the driving voltage of HPDLC without deteriorating the response by adding a small portion of various surfactants to the prepolymer.

2. Experimental

The prepolymer consists of monomer, cross-linking monomer, *N*-vinylpyrrolidone (NVP), photoinitiator, Rose Bengal (RB), and coinitiator, *N*-phenylglycine

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(NPG), all from Aldrich. In prepolymer, the ratio of monomer/NVP/NPG/RB was 62/25/2/1 by weight. Three different kinds of surfactants, octanoic acid, #1, S-271 POE sorbitan monooleate, #2, and Tergital Min-Foam 1X, #3 were used for comparison. The liquid crystals used were E7 and BL038 from Merck. Their ordinary refraction index and birefringence were $n_o = 1.521$, $\Delta n = 0.225$ respectively for E7, and $n_o = 1.527$, $\Delta n = 0.272$ respectively for BL038.

The prepolymer and LC were mixed with a 70:30 weight ratio. After mixing, the prepolymer/LC syrup was sandwiched by two ITO glasses with a cell thickness of 18 μm . The laser used to fabricate the volume grating was a 514.5 nm Ar ion laser. The output laser beam was expanded and collimated to achieve a uniform and large area exposure on the LC cell. The holographic interference stripe patterns were obtained by placing the LC cell behind the base of a right angle prism. The intensity of the laser beam irradiated on the LC cell was 10 mW/cm^2 and the exposure time was 120 s. The temperature of the sample was kept at 40–50 $^\circ\text{C}$ during exposure. After exposure, the samples were further cured for 15 min by mercury lamp.

The samples were probed by polarized He–Ne laser with the exact Bragg angle. In our experiment, there was only one diffraction peak that could be observed. For scanning electron microscope (SEM) analysis, samples with one-side ITO glass removed were soaked in the ethanol for more than 12 h in order to remove the LC. After drying, the morphologies of the samples were investigated by a low-voltage, high resolution scanning electron microscope from Philips.

3. Results and discussion

3.1. Selection of the monomer and the LC

In our configuration, the polymer refractive index, n_p , is chosen to be as close as possible to the ordinary refractive index, n_o , of LC. This helps to reduce the diffraction loss in the transparent state. Moreover, the birefringence of LC, Δn , is chosen to be as large as possible in order to improve the diffraction efficiency. In our experiment, five kinds of acrylate monomers were selected and their refractive indices are 1.490 for dipentaerythritol penta-/hexaacrylate (No. 1), 1.484 for pentaerythritol triacrylate (No. 2), 1.474 for trimethylolpropane triacrylate (No. 3), 1.487 for pentaerythritol tetraacrylate (No. 4) and 1.450 for tricpropylene gly(ol)diacrylate (No. 5), respectively. Because the prepolymer syrup includes other chemicals such as photo-initiator, coinitiator, etc., moreover, the refractive index changes during polymerization, in general, the refractive index will be different from the above values for the mixture after polymerization.

Table 1

The refractive index and corresponding diffraction efficiency (DE) for various monomer used

	No.				
	1	2	3	4	5
Monomer	1.490	1.484	1.474	1.487	1.450
Prepolymer syrup	1.501	1.496	1.489	1.498	1.471
Cured film	1.529	1.528	1.522	1.530	1.502
DE for E7	41.2%	56.4%	65.0%	41.6%	32.2%
DE for BL038	61.8%	68.4%	40.2%	51.6%	34.2%

The prepolymer syrup refractive indices were measured by Abbe refractometer. Then the syrup was cured on a SiO_2 substrate to form a polymer thin film, the refractive index, n_p , of which was measured by m-line method [11]. The results are tabulated in Table 1. From the table, we can see that the refractive index n_p of the cured film was larger than that of the corresponding monomer, with an increment of 0.03–0.05 on the average. In our experiment, the n_o of LC E7 is 1.521. The No. 3 monomer was the nearest to 1.521 and the experimental results proved that diffraction efficiency was the highest with the No. 3 monomer. Similarly, for BL038, the n_o is 1.527. Only the No. 2 monomer was the nearest to 1.528 and the experimental result proved that diffraction efficiency was the highest with the No. 2 monomer. According to our selection principle, the No. 3 and No. 2 monomers match with E7 and BL038 liquid crystals respectively.

It is worth to mention that because different kind of monomer has different functionality, the mixture of different monomers with different functionality can improve the morphology and performance of HPDLC gratings. De Sarkar et al. reported that significant performance improvement could be obtained for prepolymers prepared with UV curable monomer mixtures with average functionality ranging from 1.3 to 3.5 [12].

3.2. Effect of the surfactant

For HPDLC gratings, the LC droplets are small and the anchoring energy is high, which results in a high driving voltage. According to Mormile et al., the threshold voltage of PDLC can be written as [13],

$$V_{\text{th}} \approx \frac{d}{r} \left[\frac{K(\ell^2 - 1)}{\varepsilon_0 \Delta \varepsilon} \right]^{\frac{1}{2}} \quad (1)$$

where d is the HPDLC film thickness, r is the droplet radius, K is the effective elastic constant, ε_0 is the vacuum dielectric constant, $\Delta \varepsilon$ is the LC dielectric anisotropy, $\ell = a/b$ is the droplet aspect ratio, with a and b the length of the major and minor axis of the ellipsoid-shaped droplet, respectively.

The LC droplets of conventional PDLC are about 1–5 μm in size. However, the size of HPDLC droplets

is about 0.01–0.1 μm . The size effect on the threshold voltage can be understood by the following comparisons. Using our experimental parameters, the cell thickness, d , is 20 μm , the elastic constant, K , is 1.71×10^{-11} N, the dielectric anisotropy, $\Delta\epsilon$ is 6.49, and assuming an aspect ratio of 1.1, for LC droplets with $r = 2 \mu\text{m}$ and 0.02 μm , the corresponding threshold voltage V_{th} calculated is 2.5 V and 250 V respectively. It can be seen that with the reduction in dimension, the threshold voltage increases linearly. In general, the threshold voltage of nano-PDLC produced by holography is about one or two orders higher than that of normal PDLC.

For practical application of HPDLC, it is desired to reduce the driving voltage. Colegrove et al. reported that by adding a high dielectric anisotropy material ($\Delta\epsilon = 65$), the threshold voltage of HPDLC can be reduced significantly [14]. In addition, adding a small portion of surfactant to the prepolymer/LC syrup also helps to reduce the threshold voltage [15–17]. When phase separation occurs in the homogenous mixture, the surfactant will form an intermediate layer between the polymer and the LC. The anchoring energy at the interface of the LC and the surfactant becomes weaker than that at the interface of the LC and polymer without surfactant. This decrease in anchoring strength may effectively lower the driving voltage.

Fig. 1 shows the diffraction efficiency as a function of driving electric field for three different surfactants. The HPDLC without surfactant is also shown for comparison. The diffraction efficiency is defined by the percentage of the diffracted light intensity over the incoming light intensity. For all samples in Fig. 1, the contents of the surfactants were 8 wt%. It can be seen from Fig. 1 that, the surfactant is effective in reducing the driving voltage. The conductivity of samples with surfactants #1 and #3 was so high that the voltage could not be increased further before they were completely switched. Sample #2 can both keep the high diffraction efficiency and reduce the driving voltage effectively. Comparing these four curves in Fig. 1, surfactant #2 is the best. It reduces the threshold voltage from 13 $\text{V}/\mu\text{m}$ to about 2.5 $\text{V}/\mu\text{m}$. Comparing Fig. 1(a) and (b), we can see that the samples made of BL038 LC have a higher switching voltage than those made of E7 LC. This was because BL038 has a larger viscosity coefficient than E7; the flow viscosity of BL038 and E7 is 72 mm^2/s and 39 mm^2/s at 20 $^\circ\text{C}$, respectively. Thus, the selection of LC should be considered from its physical properties, especially viscosity.

Fig. 2 shows the diffraction efficiency as a function of the surfactant content for samples containing #2 surfactant. With the increase of the content, the diffraction efficiency reduces. Generally, when the surfactant content was less than 8 wt%, the HPDLC Bragg gratings could still keep higher diffraction efficiency.

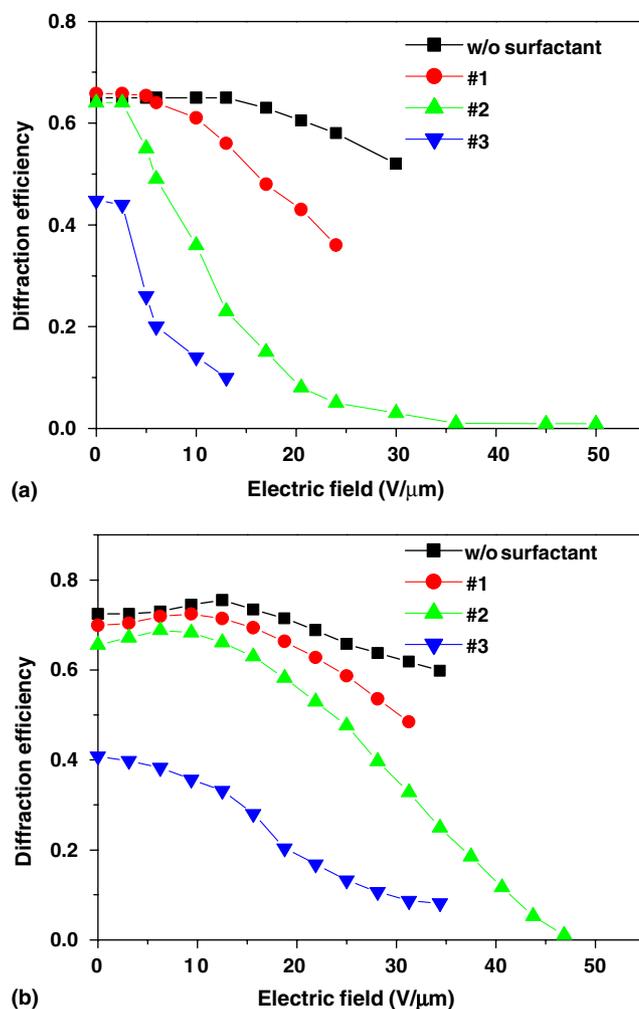


Fig. 1. Diffraction efficiency versus the electric field curves for Bragg gratings made of E7 (a) and BL038 (b) liquid crystals with three different kinds of surfactants. The diffraction efficiency without surfactant is also shown for comparison. The monomers used are No. 3 and No. 2 (Table 1) for E7 and BL038 respectively.

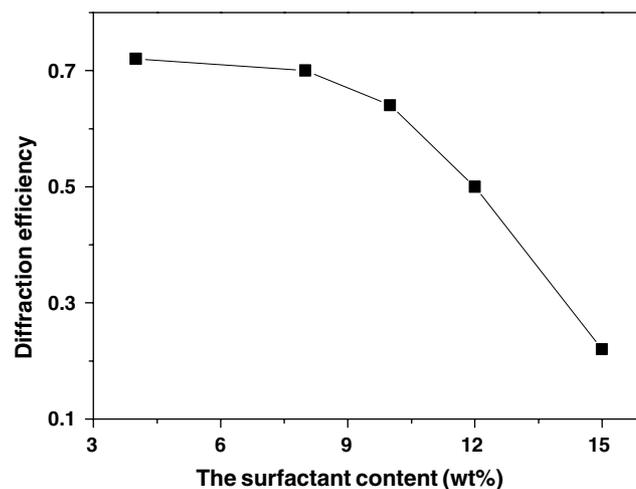


Fig. 2. Diffraction efficiency as a function of the surfactant content for surfactant #2. The monomer and liquid crystal used are No. 3 (Table 1) and E7 respectively.

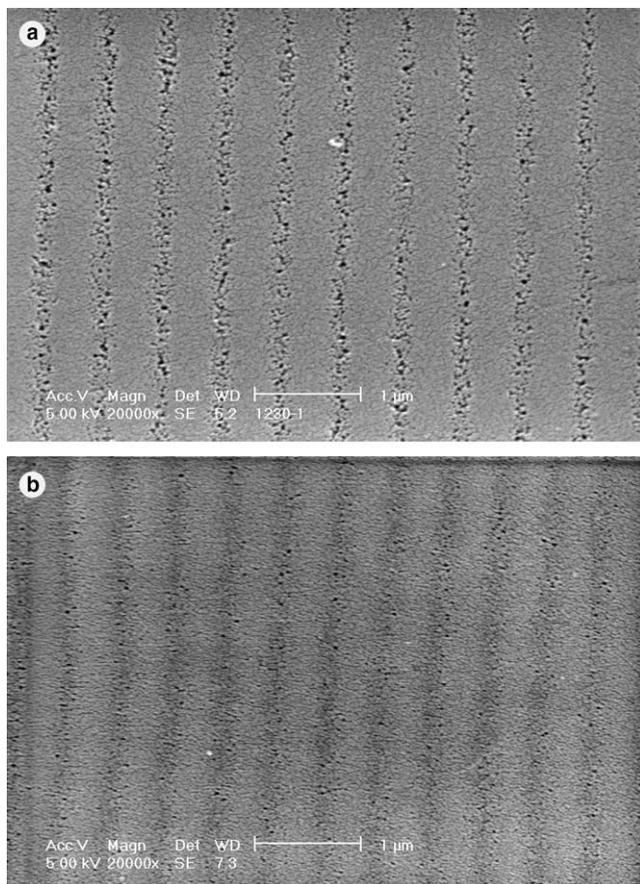


Fig. 3. SEM images of the HPDLC Bragg gratings consisting 8 wt% (a) and 15 wt% (b) of surfactant #2. The monomer and liquid crystal used are No. 3 (Table 1) and E7 respectively.

Fig. 3(a) and (b) show the SEM morphologies of the HPDLC gratings, which contain 8 wt% and 15 wt% of surfactant respectively. From Fig. 3, it can be seen that the surfactant affects the grating significantly. With more surfactant, the polymer regions contain more LC droplets. Thus the surfactant affects the LC movement during polymerization. Fig. 3(a) has a clearer grating structure than Fig. 3(b), which indicates that the grating in Fig. 3(a) has better diffraction properties. In our experiment, when the surfactant content was around 8 wt%, the HPDLC Bragg gratings could both keep high diffraction efficiency and have excellent electro-optical properties.

3.3. The responses to driving voltage

The advantage of HPDLC Bragg gratings is that its diffraction can be switched by an electric field. Fig. 4 showed the diffraction efficiency versus external electric field. In our experiment, the threshold electric field obtained was $2.3 \text{ V}/\mu\text{m}$ and the switching electric field was $27.3 \text{ V}/\mu\text{m}$. When the electric field continued to increase, the diffraction efficiency increased again because

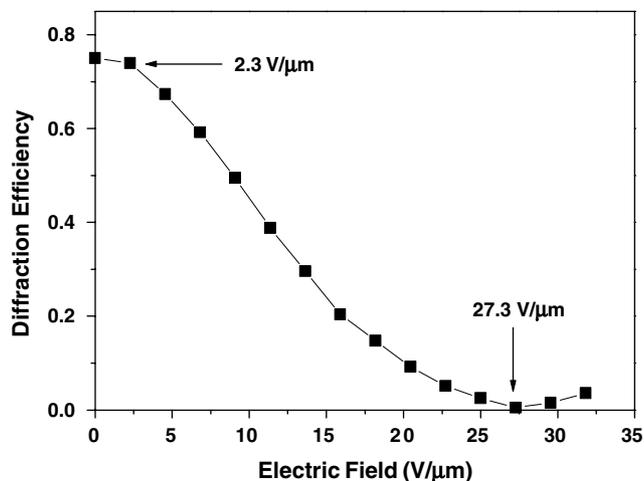


Fig. 4. Diffraction efficiency as a function of the electric field for the grating consisting 8 wt% of surfactant #2. The monomer and liquid crystal used are No. 3 (Table 1) and E7 respectively. The threshold field and switching field are indicated.

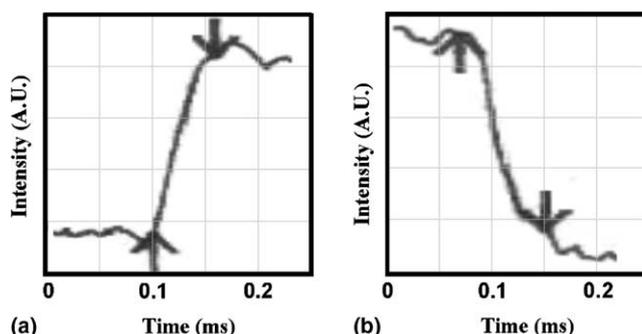


Fig. 5. The rising (a) and falling (b) edges of the diffraction beam intensity responding to a square driving voltage. The arrows are used to indicate 10% and 90% transmittance.

the electric field and the incident light are not parallel, which leads to an index mismatch.

The response time was also measured directly by an oscilloscope. Fig. 5(a) and (b) show the rising edge and falling edge of the detected signal respectively. The rising time (10% to 90% intensity change) and the falling time (90% to 10% intensity change), are $60 \mu\text{s}$ and $80 \mu\text{s}$, respectively. This switching speed is faster than that of the conventional PDLC because of the small droplets in HPDLC.

4. Conclusion

We investigated the effect of surfactant on the electro-optical properties of HPDLC in detail. The experimental results showed that adding a small portion of surfactant to the prepolymer is an effective method to reduce the driving voltage of HPDLC. The threshold electric field

was reduced from 13 V/ μm to 2.3 V/ μm and the switching electric field was 27.3 V/ μm . The rising time and the falling time were 60 μs and 80 μs , respectively.

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