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Improvement of the diffraction properties in holographic polymer dispersed liquid crystal bragg gratings[☆]

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Abstract

Holographic polymer dispersed liquid crystal (HPDLC) is a new kind of holographic material. It can be fabricated by the photo-initiated polymerization-induced phase separation. HPDLC Bragg grating is composed of parallel, periodic polymer-rich and liquid crystal-rich lamellae. The diffraction efficiency (DE) can be switched by the application of electric field. HPDLC devices are potentially useful for optical communication, information storage and display. How to increase the diffraction efficiency is the key to application. We investigated the dependence of DE on different monomers, liquid crystal content, exposure intensity and time, and exposure temperature. The best conditions were founded to make the diffraction properties improved. Now the highest DE was 80.2%. The HPDLC grating morphologies were also observed and analyzed by scanning electron microscope (SEM).

Keywords: Holographic polymer dispersed liquid crystal; Diffraction efficiency; Phase separation; Morphology

1. Introduction

Conventional PDLC has been studying since it was first described in 1985 [1,2]. Most attention has centered around switchable windows, whose clarity can be varied from opaque to transparent by applying an electric field. In conventional PDLC systems, phase-separated droplets can be formed through a variety of techniques and the droplet sizes are the order of micrometer (usually 2–5 μm).

Unlike conventional PDLC, since Sutherland et al. [3–5] reported the results of holographic studies in a acrylate photopolymer system containing a nematic liquid crystal in 1993, the holographic PDLC systems attract more attention, which have been investigated recently for numerous applications in optical data storage, diffractive optics and optical communications [6–8]. Here we describe switchable HPDLC volume phase Bragg gratings which are holographically recorded in a simple single-step process. In Fig. 1, we show the

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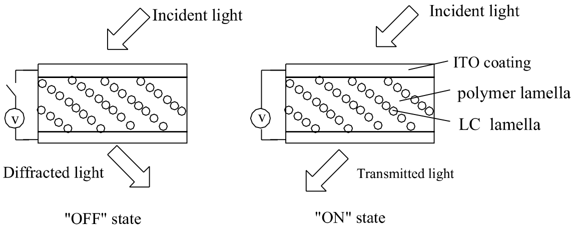

Fig. 1. The operation mechanism of HPDLC transmission Bragg grating.

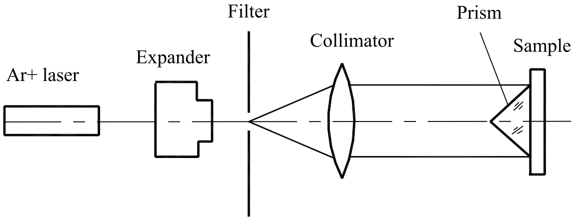

Fig. 2. Holographic recording experimental setup.

operation mechanism in switchable HPDLC volume phase Bragg grating. The prepolymer/LC syrup irradiated by two interfered beams will form a volume transmission Bragg grating with alternation of LC-rich lamella and polymer-rich lamella by photo-initiated polymerization-induced phase separation (PIPS) [2,9]. This periodical arrangement will produce a refractive index modulation. The diffracted light outputs in the first order diffraction direction when inputting an incident light with Bragg angle. When applying an electric field, the LC molecules will again align the direction of the electric field and the index modulation will disappear (suppose $n_p = n_o$). The light transmits in the zero order direction. So the HPDLC Bragg grating is a switchable grating which can be controlled by an electric field.

For the practically switchable volume gratings, DE is a very important parameter. Here, it is defined as the diffracted power in the first order divided by the incident power. Selection of a proper monomer and control of the LC content, exposure intensity and time, and exposure temperature are typically used to control the resulting morphology (domain size, domain shape, volume fraction) which in turn effects DE. In this letter we explored the effects of these factors on DE and found the best experimental conditions. Presently, the highest DE is 80.2%.

2. Experiment

The prepolymer consists of monomer, photoinitiator Rose Bengal (RB), cross-linking monomer *N*-vinylpyrrollidone (NVP), coinitiator *N*-phenylglycine (NPG) and surfactant Octanoic Acid (OA), all from Aldrich. In prepolymer, monomer/NVP/OA/NPG/RB was 62/25/10/2/1 by weight. The LC E63 was obtained from Merck with $n_o = 1.517$, $\Delta n = 0.2272$.

Prepolymer/LC syrup was sandwiched by two ITO glasses and placed behind the base of a right angle prism and then exposed to laser irradiation from 514.5 nm Ar ion Laser, as shown in Fig. 2. After exposure, the samples were further cured for 5 min by mercury lamp.

All samples were 22 μm thick. The theoretical grating spacing was 0.57 μm which could be calculated from the geometry of our recording setup. This grating spacing was in good agreement with the SEM photos. The samples were probed by p-polarized He–Ne laser with the exact Bragg angle and only one diffraction peak was observed. The morphology of the samples was investigated by low-voltage, high resolution SEM from Philips. Samples with the ITO glass eliminated were soaked in the ethanol for more than 12 h in order to remove the LC. After drying, the samples were observed by SEM.

3. Results and discussion

3.1. Selection of the monomer

In our configuration the polymer refractive index n_p is equal to the ordinary refractive index n_o of LC. This can make the grating applied electric field become very transparent. What's more, we should make LC's optical anisotropy Δn as large as possible in order to improve DE. In this case, we selected 5 kinds of acrylate monomers and their refractive indices are, respectively, $1^{\#}$ (Dipentaerythritol penta-/hexa-acrylate) 1.490, $2^{\#}$ (Pentaerythritol

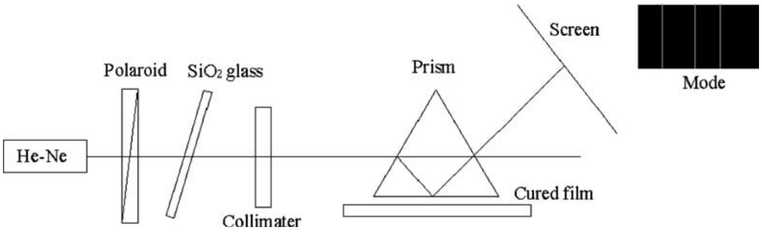

Fig. 3. The measuring setup of the refractive index n_p.

Table 1
DE as a function of different monomer refractive indices

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	40.8%	50.0%	60.0%	11.6%	22.2%

triacrylate) 1.484, $3^{\#}$ (Trimethylolpropane triacrylate) 1.474, $4^{\#}$ (Pentaerythritol tetraacrylate) 1.487 and $5^{\#}$ (Tricpropylene gly(ol)diacrylate) 1.450. Because the prepolymer syrup included some other components (such as photoinitiator, coinitiator, and so on), the refractive index would change from liquid to polymerization. The prepolymer syrup refractive indices were measured by Abbe refractometer. Then the syrup was cured on the SiO_2 substrate and formed a thin film (the refractive index of the film is n_p). The n_p was measured by m-line method and the setup of measurement was shown in Fig. 3. Samples with the prepolymer/LC = 70/30 by weight were made at $I = 10$ mw/cm^2 and $t = 90$ s and the results are shown 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 monomer, on an average increased by 0.03–0.05. In our experiment the n_o of LC is 1.517. Only the $3^{\#}$ monomer was nearest to 1.517 and the experimental result proved that DE was highest with the $3^{\#}$ monomer.

3.2. Effect of the exposure intensity on DE

The exposure intensity decides the rate of polymerization, LC diffusion and cross-linking, which decides the degree of phase separation and morphology of the droplets, and then decides DE. If the intensity is too small, the induced energy will not be enough and will slow the rate of polymerization and then make the growth time of the droplets be longer. Finally, the size of LC droplets will be greater and the scattering will increase and DE will be lower. On the contrary, too great intensity will promote the rate of polymerization. The liquid crystal microdroplets do not have sufficient time to grow and diffuse because of the rapid cross-linking of this photopolymer system, so many droplets were trapped in the polymerized regions. The buried droplets will form a center of scattering and lower DE in the same. So a suitable exposure intensity will be needed to make the rate of polymerization and diffusion approximately equal and then form a clear and smooth grating structure. As reported before [3], the laser intensity was varied between 0.1 and 100 mw/cm^2, with exposure time of typical 30–120 s. In our experiment, we selected different intensities and time in making HPDLC samples and statistically obtained the peak DE in the case $I =$ 10 mw/cm^2 and $t = 120$ s with the $3^{\#}$ monomer and prepolymer/LC = 70/30.

3.3. Effect of LC content on DE

We found that the effect of LC on the DE was dramatic. In the pure polymer gratings, the peak DE was typically $\sim$1%. With different LC contents of 20–40 wt%, DE was very different. Samples with the $3^{\#}$ monomer were made at $I = 10\ \mathrm{mw/cm^2}$ and $t = 120$ s. Fig. 4 showed the effect on DE in different LC contents. The peak DE was obtained with the content of 28 wt%. The morphology of the samples was shown in Fig. 5. From Fig. 5 we can see that if the LC content is too high, the volume fraction of LC lamella throughout the bulk of the film will increase and the size of the droplet will be greater, making the scattering increase and DE lower. However, if the content is too low, the volume fraction of LC will lower and the size of droplet will be smaller. Within the LC-rich lamellae, a great deal of polymer will exist and lower the index modulation and then DE will also decrease. So a suitable content of the LC is needed in order to obtain a good grating structure and high DE.

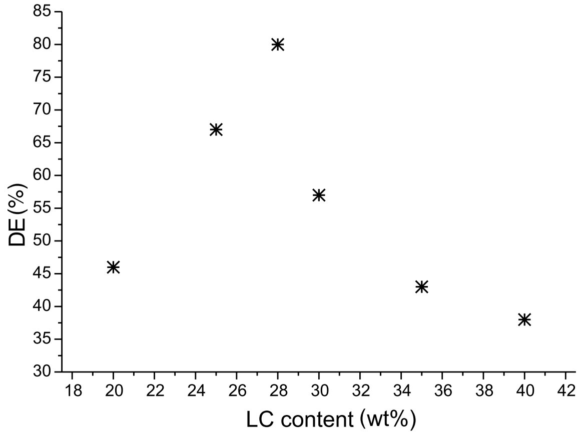

Fig. 4. Effect of the LC content on DE.

3.4. *Effect of the exposure temperature on DE*

For the same prepolymer/LC syrup and the same exposure intensity, different exposure temperatures also effect the DE of the grating, so the effect of the temperature was investigated on the DE. Samples with the $3^{\#}$ monomer and prepolymer/LC = 72/28 were fabricated at $I = 10\ \mathrm{mw/cm^2}$ and $t = 120$ s. The result was shown in Fig. 6 and in the condition of $T = 40$–50 °C, we obtained the

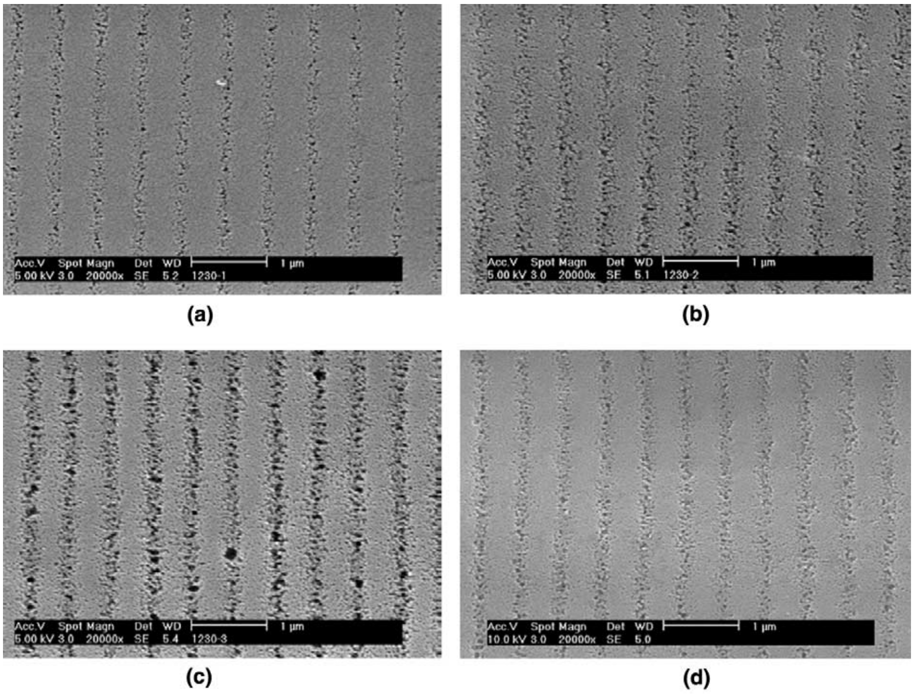

Fig. 5. The same magnification SEM photographs of the surface of HPDLC Bragg grating of different LC contents: (a) 20 wt%, (b) 30 wt%, (c) 40 wt%, and (d) 28 wt%.

best DE. For E63, the clear point is 82 °C. In the low temperature case, thermally induced phase separation (TIPS) may play an important role in the process of polymerization. This is not favorable for HPDLC system in which PIPS should play an absolutely important role. TIPS makes some LC remain in the polymer matrix. In addition, it is possible that LC droplets may contain some of the polymer. For a temperature approximate or above the clear point, we find that the HPDLC system polymerizes so rapidly that the grating structure will not form at all.

3.5. Electric field effects

For switching operation of HPDLC gratings it is of greatest interest to understand the dependence of DE on external electric field. Here, the threshold electric field is defined as DE begins to decrease. The switching electric field is defined as DE reaches a minimum. We applied the field perpendicularly to the sample surfaces. Fig. 7 showed the electric field effects of the HPDLC grating. The sample in Fig. 7 is 22 μm thick and was recorded at 514.5 nm with 10 mw/cm^2 for 120 s and has 28 wt% LC content. The monomer was $3^{\#}$ and exposure temperature was 40–50 °C. The grating was read with p-polarized 632.8 nm light. The threshold electric field was about 2.5 V/μm and the switching electric field was 27 V/μm. When the electric field continued to increase, the DE increased again because the direction of the LC molecule had an angle with the direction of the incident light, which made an index mismatch.

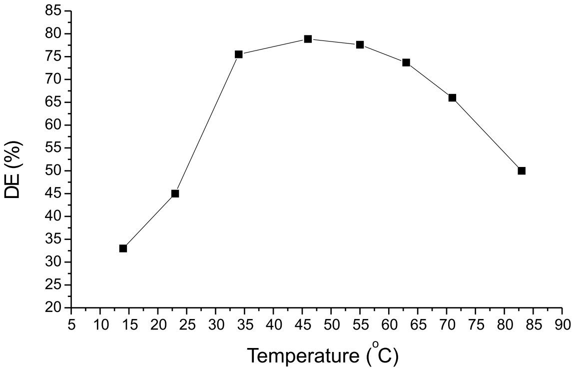

Fig. 6. Effect of the exposure temperature on DE.

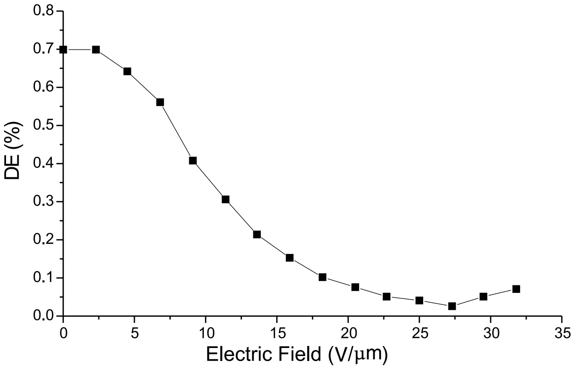

Fig. 7. DE as a function of electric field.

4. Conclusions

The HPDLC is a novel opto-electrical material. The continuing marriage of electronics and optics is a perfect setting for the development and commercialization of new broad application for HPDLC. We have demonstrated that transmission gratings can be recorded in these materials with high diffraction efficiency in films of reasonable optical quality. In this letter, we have explored the effect on DE of primary factors such as the kind of monomers in the recipe, exposure intensity and time, the LC content, and exposure temperature. We obtained peak DE = 80.2% for $\lambda = 632.8$ nm in the conditions $I = 10$ mw/cm^2 and $t = 120$ s, $T = 40$–50 °C, LC content = 28 wt%.

References

[1] J.L. Ferguson, SID Int. Symp. Dig. 16 (1985) 68.
[2] J.W. Doane, N.S. Vas, B.G. Wu, S. Zumer, Appl. Phys. Lett. 48 (1986) 269.
[3] R.L. Sutherland, L.V. Natarajan, V.P. Tondiglia, Chem. Mater. 5 (1993) 1533.
[4] L.V. Natarajan, R.L. Sutherland, T.J. Bunning, V.P. Tondiglia, SPIE 3292 (1998) 44.
[5] V.P. Tondiglia, L.V. Natarajan, R.L. Sutherland, Opt. Lett. 20 (1995) 1325.
[6] L. Domash, G. Crawford, A. Ashmead, R. Smith, M. Popovich, J. Storey, SPIE 4107 (2000) 46.

[7] F. Simoni, G. Cipparrone, A. Mazzulla, P. Pagliusi, Chem. Phys. 245 (1999) 429.

[8] L.H. Domash, Y.M. Chen, B. Gomatam, C. Gozewski, R.L. Sutherland, L.V. Natarajan, V.P. Tondiglia, T.J. Bunning, W.W. Adams, Proc. SPIE 2689 (1996) 188.

[9] C.C. Bowley, G.P. Crawford, Appl. Phys. Lett. 76 (2000) 2235.