Controlling the anisotropy of holographic polymer-dispersed liquid-crystal gratings

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In this work we investigate the optical properties of electrically switched transmission gratings fabricated holographically using polymer-dispersed liquid-crystal (PDLC) materials. We have found that the PDLC mixture can be used to control the diffractive properties of the liquid-crystal composite gratings. In one limit the gratings are highly isotropic and in the other limit the gratings are highly anisotropic with a large birefringence. The experimental results are compared to theories that include the birefringence of the grating. From theoretical fits to the experimental data, measurements of the liquid-crystal distribution and alignment are obtained.

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Switchable gratings have been under investigation for several applications including time-delay networks [1], optical beam steering, and switching [2,3]. Highly birefringence liquid-crystal composite gratings are attractive because the liquid crystal has a large field-induced birefringence change, which results in large changes in refractive index modulation and, therefore, diffraction efficiency of the composite grating. Switchable gratings have been fabricated holographically using polymer-dispersed liquid crystals (PDLC) [2–8].

In this paper we present the results of an experimental study of the diffractive properties of electrically switched holographic gratings fabricated using polymer-dispersed liquid-crystal mixtures. In a recent series of papers Sutherland and co-workers [5–8] have performed experiments that show that the morphology of a PDLC grating is dependent on the details of the prepolymer syrup. In this study we correlate the changes in the optical properties to the details of the PDLC mixture. In one limit the diffraction from the grating is extremely polarization dependent with high diffraction efficiency for *p*-polarized light and near zero efficiency for *s*-polarized light. In this limit the grating is highly birefringent. In the other limit the diffraction is characteristic of a nonbirefringent grating. By modeling the composite grating we are able to obtain information on the liquid-crystal distribution and alignment.

In a recent paper, Montemezzani and Zgonik [9] present a two-wave coupled wave theory for volume gratings that are fabricated from birefringent materials, which is a modification to the theory of Kogelnik [10] for nonbirefringent gratings. We have previously used the birefringent grating theory to explain the diffraction properties of liquid-crystal composite gratings [11,12]. In this work we have used this theory to model the changes in the optical properties, as the PDLC mixture is changed. For birefringent gratings it is assumed that the relative permittivity tensor of the grating can be written in the form

$$\overleftrightarrow{\varepsilon}(x)=\overleftrightarrow{\varepsilon}_0+\overleftrightarrow{\varepsilon}_1\cos(2\pi x/\Lambda), \tag{1}$$

where $\overleftrightarrow{\varepsilon}_0$ is the average relative permittivity tensor, $\overleftrightarrow{\varepsilon}_1$ is the relative permittivity modulation tensor, and Λ is the grating spacing. The diffraction efficiency of an anisotropic volume grating for light incident at the Bragg angle is given by [9]

$$\eta=\sin^2\frac{\pi d}{\lambda_0\cos\theta}\,\frac{\hat{e}_0\cdot\overleftrightarrow{\varepsilon}_1\cdot\hat{e}_1}{2n_0\cos\delta}, \tag{2}$$

where d is the grating thickness, λ_0 is the free space wavelength, $\hat{e}_0$ and $\hat{e}_1$ are polarization unit vectors for the zeroth and first diffracted orders, n_0 is the average refractive index of the grating, θ is defined as an angle between the grating normal and the energy propagation direction of a diffracted wave, and δ is an angle between the energy propagation direction and the wave vector direction for the diffracted wave. For composite gratings it is important to remember that n_0 depends on θ due to the average birefringence of the grating. In addition, δ is small for the composite gratings considered in this work. From Eq. (2) we see that the predicted diffraction efficiency is highly dependent upon the form of the relative permittivity modulation tensor. For the composite liquid-crystal gratings the form of this tensor is dependent upon factors such as liquid-crystal distribution and the liquid-crystal alignment within the droplets.

In our experimental work we have only studied unslanted gratings and there is no observed coupling between *s*- and *p*-polarized light, which leads us to assume that the average relative permittivity tensor for the composite grating can be written as

$$\overleftrightarrow{\varepsilon}_0=\begin{pmatrix}\varepsilon_{xx}^0 & 0 & 0\\ 0 & \varepsilon_{yy}^0 & 0\\ 0 & 0 & \varepsilon_{zz}^0\end{pmatrix} \tag{3}$$

and the relative permittivity modulation tensor can be written as

$$\overleftrightarrow{\varepsilon}_1=\begin{pmatrix}\varepsilon_{xx}^1 & 0 & 0\\ 0 & \varepsilon_{yy}^1 & 0\\ 0 & 0 & \varepsilon_{zz}^1\end{pmatrix}. \tag{4}$$

In Eqs. (3) and (4) the x direction is parallel to the grating vector and the z direction is parallel to the grating normal.

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The PDLC gratings were fabricated holographically using an argon-ion laser operating at $\lambda = 514.5$ nm. The prepolymer mixture was contained in indium-tin-oxide coated glass cells with a thickness of ~ 11 μm. Volume phase gratings were recorded with a period of 545 nm by exposing the prepolymer mixture to an interference pattern produced by two plane waves derived from the laser. Each of the plane waves subtended an angle of 28° from the recording plane normal; they were incident symmetrically upon opposite sides of the normal. The gratings were typically exposed for a period of 30–60 s. The photocuring of the monomer takes place through free radical polymerization that results in monomers diffusing to the high intensity regions and liquid crystal diffusing to the low intensity regions. The phase separation results in a refractive index modulation, which results in high diffraction efficiency.

The PDLC mixtures that we have used are similar to those of Sutherland *et al.* [13]. The liquid crystal E7 ($n_e = 1.7462$, $n_0 = 1.5216$) and the SR399 monomer are the main elements of the prepolymer syrup. The comonomer 1-vinyl 2-pyrrolidinone is used as a chain extender. The photoinitiator HNU-470 is used to sensitize the solution for the wavelength that we are using for polymerization, and the coinitiator DIDMA from Spectra Group Ltd. aids in dissolving the photoinitiator dye.

The optical properties of the composite gratings depend sensitively on the morphology of the gratings and the alignment of the liquid crystal within the grating. Previous studies have investigated the morphology of PDLC gratings and the effect that changes in the prepolymer syrup have on the resulting morphology [5–8]. These studies have involved the examination of scanning electron micrographs (SEMs) of the gratings. In this work we have characterized the changes in the diffractive properties of the composite. Specifically we have studied the dependence on the comonomer concentration. We have found that at low comonomer concentration the diffractive properties are characteristic of a highly birefringent grating whereas for high comonomer concentration the diffractive properties are characterized by an isotropic grating. We keep other constituents of the mixture constant throughout our investigation.

To obtain information about the components of the permittivity tensors and, therefore, the liquid-crystal alignment for the PDLC mixtures, we measure the diffraction efficiency of the composite grating as a function of angle of incidence for many different wavelengths. The Bragg condition is given by $\sin\theta_B = \lambda_0 / 2 n_0 \Lambda$. From this relation we see that each wavelength will have its own Bragg angle. Thus, by measuring the diffraction efficiency at many different wavelengths we are effectively probing the composite medium at many different Bragg angles, which is a sensitive measure of the relative permittivity modulation tensor and, therefore, the liquid-crystal alignment. For these measurements the liquid-crystal composite grating was sandwiched between two BK7 prisms. The prism coupling was used so the Bragg angle for a wide range of wavelengths could be accessed. The angle within the prism is defined as the angle that the incident beam makes with the grating normal at the prism-sample interface.

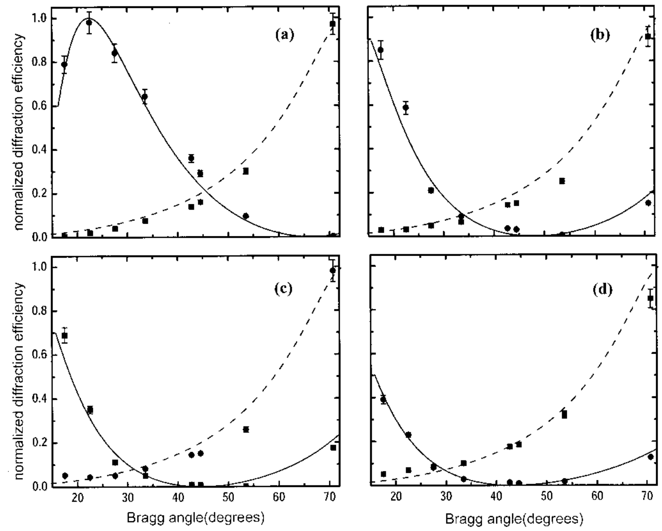

FIG. 1. Normalized diffraction efficiency of PDLC gratings fabricated using E7 liquid crystal and comonomer concentrations of (a) 4%, (b) 8%, (c) 16%, and (d) 24%. The solid circles represent data recorded for the case when no field is applied to the grating and the solid squares represent the case when a switching field of 34 V/μm is applied to the gratings. Theoretical predictions are obtained by modeling the grating as a highly anisotropic composite grating. The solid line represents the theoretical prediction for the case when no field is applied to the sample and the dashed line represents the case when a saturating field is applied to the sample.

The light sources used in this experiment were an argon-ion laser operating at 0.5145 μm, Helium-Neon lasers operating at 0.6328 and 1.125 μm, Nd:YAG (yttrium aluminum garnet) laser operating at 1.06 μm, and semiconductor lasers operating at 0.780, 1.298, and 1.552 μm. Figures 1(a)–1(d) show the experimentally measured values for the normalized diffraction efficiency for *p*-polarized light incident at the Bragg angle for each wavelength for the case no applied field (solid circles) and for the case of a saturating field of 34 V/μm (solid squares). The normalized diffraction efficiency is defined to be equal to the power in the first diffracted order normalized to the total power transmitted through the grating. Figure 1(a) shows the case when the comonomer concentration is equal to 4%. In this limit a striking feature is that, the diffraction efficiency at a Bragg angle of 45° is not equal to zero for either the field off or field on case. For this mixture the diffraction efficiency for *s*-polarized light is near zero for all Bragg angles. These properties are characteristic of highly birefringent gratings. Figure 1(d) shows the case of a grating that is fabricated with a comonomer concentration of 24%. In this case we see that the diffraction efficiency for *p*-polarized light is equal to zero for a Bragg angle of 45° for the case of no applied field. Also for this concentration the diffraction efficiency for *s*-polarized light is increased to 12% that is greater than the diffraction efficiency for *p*-polarized light. These properties are characteristic of an isotropic grating. From these figures we also see that the optical properties for the case of a saturating applied field are characteristic of anisotropic, birefringent gratings for all comonomer concentrations.

By comparing the predictions of the birefringent grating theory [9] to the experimental data we obtain information about the distribution and alignment of the liquid-crystal molecules that are trapped within the droplets. We first make some assumptions about the composite gratings. We assume that the grating is composed of two regions. One region is a solid polymer region that contains no liquid-crystal droplets. This assumption is supported by SEM studies of others [6]. However this region is assumed to contain some liquid crystal that is trapped in the polymer matrix. This trapped liquid crystal is randomly aligned and is not free to rotate with the applied electric field. In conventional PDLC materials ≈20% of the liquid crystal can remain in the polymer matrix and does not phase separate out into the droplets [14]. The index of refraction of the solid polymer region can be written as

$$n_b = n_{P(\mathrm{LC})} = c n_{\mathrm{iso}} + (1-c) n_p , \tag{5}$$

where c is the volume concentration of the liquid crystal, $n_p = 1.49$ for the polymer we have used in this work and $n_{\mathrm{iso}} = 1.597$, which is the three-dimensional average index of refraction of E7 liquid crystal. The other region of the grating is assumed to consist of a polymer matrix containing a volume fraction of liquid-crystal droplets. The refractive index of this region is given by

$$n_a = f n_{\mathrm{LC}} + (1-f) n_{P(\mathrm{LC})} , \tag{6}$$

where f is the filling fraction of the liquid-crystal droplets and $n_{p(\mathrm{LC})}$ is the index of refraction of the polymer matrix.

We obtain values for the two unknowns $n_{P(\mathrm{LC})}$ and f for the various gratings by measuring the diffraction efficiency of the composite gratings at a temperature of 70 °C, which is above the clearing temperature of the E7 liquid crystal. These unknowns characterize the morphology of the grating independent of the alignment of the liquid crystal inside the droplets since at this temperature the liquid crystal contained in the droplets are in the isotropic state with an index of refraction of $n_{\mathrm{iso}} = 1.597$. The average refractive index of the grating can be calculated from the weighted average of the refractive index of the pure polymer ($n_p = 1.49$), and the concentration and index of refraction of the isotropic liquid crystal in the solution. For the gratings studied in this work, the solutions contained 30% E7 liquid crystal. Therefore, the average index of refraction of the gratings for temperatures above the clearing temperature is ≈1.522.

The refractive index modulation of the gratings is obtained by comparing the measured diffraction efficiency to the predictions of coupled-wave theory derived by Kogelnik [10]. This theory can be used since at temperatures above T_c the material is not birefringent. We have characterized gratings for each of the comonomer concentrations. From measurements of the diffraction efficiency we calculate the refractive index modulation of the gratings. Once the average index of refraction and refractive index modulation are found for each of the gratings, the parameters f and c can be calculated using Eqs. (5) and (6),

$$n_0 = \frac{n_a + n_b}{2} \tag{7}$$

and

$$n_1 = \frac{n_a - n_b}{2} . \tag{8}$$

From the fits to the diffraction efficiency at elevated temperatures we calculate $n_p = 1.514 \pm 0.0015$ and $f = 21 \pm 3.6\,\%$. We note that ~20% of the liquid crystal that is added to the original mixture does not phase separate out and, therefore, does not contribute to the diffraction.

The measurements at high temperatures yield information about how much liquid crystal is contained in the droplets of the PDLC. At room temperature the alignment of the liquid crystal is also an unknown that must be taken into account to describe the diffraction. The alignment of the liquid crystal determines the effective refractive indices of the liquid-crystal droplets, which are used in Eq. (6) to calculate the refractive index of the composite region.

From Fig. 1 we note that in the limit of low comonomer concentration for the case when no external field is applied to the grating, the diffraction from the grating is characteristic of a highly birefringent grating. However, in the limit of high comonomer concentration the diffraction properties indicate a nearly isotropic grating. We attribute the change in the anisotropy of the grating to a degradation of the ordering of the liquid crystal as the comonomer concentration is increased. In the limit of low comonomer concentration the diffraction efficiency for p-polarized light at near normal incidence is high that implies the director of the liquid crystal lies predominately parallel to the grating vector. Therefore, the elongated axes of the liquid-crystal droplets are aligned along the grating vector in the x direction. The effective indices of refraction of the droplet depend on a droplet order parameter S_d. We assume that the order parameter of the liquid-crystal droplets varies as the comonomer concentration is changed. The effective refractive indices of the droplets can be written as [15]

$$n_{\mathrm{ed}}(S_d) = \frac{n_e n_o}{\left[n_e^2 + \frac{1}{3}(n_0^2 - n_e^2)(2S_d + 1) \right]^{1/2}} \tag{9}$$

and

$$n_{\mathrm{od}}(S_d) = \frac{2}{\pi} n_o F \left\{ \frac{\pi}{2}, \frac{1}{n_e} \left[\frac{2}{3}(n_e^2 - n_o^2)(1 - S_d) \right]^{1/2} \right\}, \tag{10}$$

where $F(\theta, m)$ is the complete Legendre elliptic integral of the first kind and n_o and n_e are the ordinary and extraordinary refractive indices of the liquid crystal, respectively.

The solid lines shown in Figs. 1(a)–1(d) are fits to the experimental data for the case of no applied electric field. For these fits we use the polymer refractive index and droplet concentration that are obtained from the fits to the diffraction efficiency at high temperature. The droplet order parameter is adjusted to obtain agreement between the experimental data and the theoretical predictions. For an assumed droplet order parameter the effective indices of refraction for the

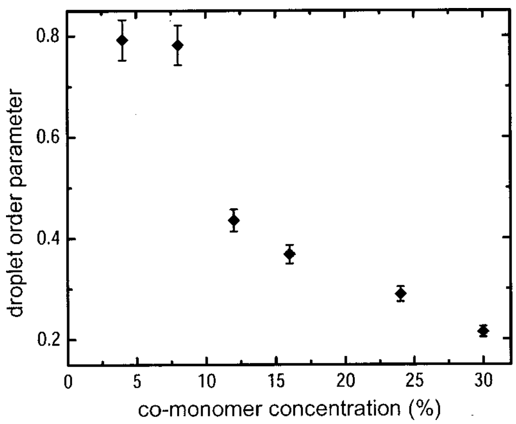

FIG. 2. The change of the droplet order parameter is plotted as a function of comonomer concentration. The droplet order parameter is obtained from the fits of the diffraction efficiency data for each comonomer concentration.

droplets are calculated using Eqs. (9) and (10). These values are then used to calculate the relative permittivities, ε_{ox} and ε_{oz}, and relative permittivity modulation values, ε_{1x} and ε_{1z}, for the composite gratings. Figure 2 shows a graph of the droplet order parameter plotted as a function of the concentration of comonomer concentration that is extracted by fitting the diffraction efficiency data for the case of no applied field. From this figure we see that the droplet order parameter is high for low comonomer concentration, which results in a highly anisotropic grating. As the comonomer concentration is increased the droplet order parameter decreases. At concentrations of ~15% and higher the order parameter is ≈0.3 and the grating properties are not modified significantly by the effects of birefringence. These results agree with the SEM work done by Bunning *et al.* [6] that shows that in the limit of low comonomer concentration, the droplets within the grating are elongated along the grating vector and the droplets become more spherical as the concentration is increased.

The dashed lines on Figs. 1(a)–1(d) represent fits to the experimental data for the case when a saturating electric field is applied to the PDLC grating. To obtain these fits the polymer refractive index and the droplet filling fraction obtained from the high temperature fits are used again. However, for the case with an applied electric field the composite gratings are all highly anisotropic with the director of the liquid crystal oriented parallel to the *z* direction since the liquid crystal trapped inside the droplet aligned parallel to the applied field. Also since the liquid crystal is aligned by the applied field we assume that the droplet order parameter is high and is nearly equal for all cases. The best fits to the experimental data were obtained for a droplet order parameter of $S_d = 0.848$.

In summary we have shown that the diffraction properties depend sensitively on the details of the PDLC prepolymer syrup. We have found that at low comonomer concentration the gratings are highly birefringent and are optimized for steering *p*-polarized light. At high comonomer concentrations we find that the gratings are not highly birefringent and the diffraction properties are characteristic of isotropic gratings. In this limit the refractive index modulations that are obtained are much lower since the liquid crystal trapped in the droplets is randomly aligned. We have also shown that there is a smooth progression from the highly birefringent limit to the highly isotropic limit and this progression can be characterized by a change in the droplet order parameter.

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[1] T. W. Stone, J. C. Kralik, and M. S. Malcuit, Proc. SPIE **3463**, 86 (1998).
[2] R. L. Sutherland, V. P. Tondiglia, L. V. Natarajan, T. J. Bunning, and W. W. Adams, Appl. Phys. Lett. **64**, 1074 (1994).
[3] T. W. Stone, J. C. Kralik, R. C. Veitch, and M. S. Malcuit, Proc. SPIE **4112**, 38 (2000).
[4] R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, and T. J. Bunning, Proc. SPIE **2689**, 158 (1996).
[5] T. J. Bunning, L. V. Natarajan, V. Tondiglia, R. L. Sutherland, D. L. Vezie, and W. W. Adams, Polymer **36**, 2699 (1995).
[6] T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, G. Dougherty, and R. L. Sutherland, J. Polym. Sci., Part B: Polym. Phys. **35**, 2825 (1997).
[7] R. T. Pogue, L. V. Natarajan, V. P. Tondiglia, S. A. Siwecki, R. L. Sutherland, and T. J. Bunning, Proc. SPIE **3475**, 2 (1998).
[8] L. V. Natarajan, S. A. Siwecki, V. P. Tondiglia, R. L. Sutherland, and T. J. Bunning, Polymer **41**, 733 (2000).
[9] G. Montemezzani and M. Zgonik, Phys. Rev. E **55**, 1035 (1997).
[10] H. Kogelnik, Bell Syst. Tech. J. **48**, 2909 (1969).
[11] J. J. Butler and M. S. Malcuit, Opt. Lett. **25**, 420 (2000).
[12] J. J. Butler, M. S. Malcuit, and M. A. Rodriguez, J. Opt. Soc. Am. B **19**, 183 (2002).
[13] R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, and T. J. Bunning, Chem. Mater. **5**, 1533 (1993).
[14] P. S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, Singapore, 1995).
[15] F. Simoni, *Nonlinear Optical Properties of Liquid Crystals* (World Scientific, Teaneck, NJ, 1997).