Switchable gratings by spatially periodic alignment of liquid crystals via patterned photopolymerization

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Spatially periodic patterning of the anchoring condition of a nematic liquid crystal (NLC) within a polymer matrix via a patterned photopolymerization affords a novel and facile method to prepare electrically switchable diffraction gratings. UV irradiation through a photomask of two comonomers, with opposite tendencies to align the NLC and also with different reactivity ratios, leads to definition of areas with either homeotropic or planar alignment of the NLC. Photopolymerization-induced diffusion of the monomers accounts for the spatial distribution of the concentration of these monomers. The resulting diffraction gratings are switchable under low electric fields and possess structural stability offered by the polymer matrix. © 2006 Optical Society of America

OCIS codes: 160.3710, 230.1950.

Calamitic liquid crystals (LCs) consist of molecules with highly anisotropic structures. Their use in optical or electro-optical devices relies on the alignment of these elongated molecules by external fields and by the influence of surface anchoring forces.[1] Control of surface anchoring is important in the preparation and operation of any LC-based electro-optical devices. In conventional LC displays, mechanical rubbing of polymer layers is the dominant technique by which to achieve uniform, slightly tilted anchoring.[2]

Electrically switchable LC devices with spatially periodic modulation of refractive index have recently attracted attention due to their potential applications in optical communications, displays, holograms, and optical storage.[3,4] Periodic structures can be obtained by either spatially modulating the concentration distribution of LC in a polymer matrix[4,5] or spatially patterning the LC alignment. Examples of the latter include LC diffraction gratings and Fresnel lens arrays, which are fabricated by combining a surface alignment technique[6] with various patterning methods such as microcontact printing, photolithography,[3,7] laser scanning,[8] atomic force microscope patterning,[9] and holographic recording.[10] However, with the exception of the method using photoinduced alignment and holographic recording, these techniques still require multiple processing steps or sophisticated experimental setup.

We report a simple and novel approach to pattern the alignment of LCs in a periodic way, to produce a field-switchable diffraction grating, by photopolymerization of a mixture of a nematic LC and acrylate monomers through a photomask in a single step. We have demonstrated that anchoring of nematic LC in contact with poly(alkyl acrylate) matrices is sensitive to the length and branching of the polymer side chains;[11,12] and to the copolymer composition.[13] The hometropic-to-planar anchoring transition temperature (T_t) of the nematic LC can be tuned at will

across a wide temperature range by changing the composition of the copolymer.[13] By using two comonomers with different reactivity, we have created a periodic variation in the copolymer composition, resulting in a spatially periodic variation of anchoring to produce a diffraction grating. Pretreatment or patterning of the substrate is not necessary, as the alignment is determined by the encapsulating polymer matrix formed *in situ*. Compared with diffraction gratings based on holographic polymer-dispersed liquid crystals, the device that we report here can be readily switched with a much lower field.

The nematic fluid TL205 (EM Industries; refractive index $n_e = 1.744$ and $n_o = 1.527$ at 20°C, $\varepsilon_{\parallel} = 9.1$ and $\varepsilon_{\perp} = 4.1$ at 20°C and 1 kHz; nematic at –20–87°C) was used. The reaction mixtures consist of TL205, monofunctional acrylates (2-ethylhexyl acrylate (2-EHA), *n*-octyl acrylate (C8A)), 1,1,1-trimethylolpropane triacrylate (Scientific Polymer Products) with a fixed weight ratio of 80:18:2, and a photoinitiator (Darocur 1173, Ciba, Inc. 0.5% by weight of the total acrylate monomers). The mole ratio of two monofunctional acrylates (2-EHA and C8A) was varied to study the effect on the anchoring of LCs in the LC–polymer composite films. The triacrylate was added as a cross-linking agent (at 10 wt. % of the total acrylates) to provide rigidity to the film. The monomer mixtures are homogeneous and isotropic at room temperature.[14] The mixtures were placed between glass substrates with a transparent (indium tin oxide) conductive coating, spaced by 15 μm diameter glass microbeads with a narrow diameter distribution (Duke Scientific). Polymerization was induced with UV (360 nm) at low intensity ($\approx$0.5 mW/cm^2) and a photomask consisting of 80 μm spaced parallel fringes placed on top of the glass slide to obtain a closed-cell morphology (typically 30–60 min). The mask was then removed, and the film was fully cured at much higher UV intensity (16 mW/cm^2) at room

temperature for 15 min to enhance the rigidity of the film.

The morphology and the anchoring of TL205 in the final LC–polymer films were observed by polarized optical microscopy (Fig. 1). When the ratio of 2-EHA:C8A in the initial comonomer mixture is in the range from 80:20 to 90:10 (mol/mol), the photocopolymerization leads to alternating stripes consisting of regions in which the LC is aligned perpendicular to the substrate (homeotropic anchoring) and parallel to the substrate (planar anchoring), as shown in Fig. 1(c).

These results can be understood in terms of polymerization rate, monomer diffusion, and the relationship between the anchoring condition and copolymer composition.[13] Irradiation through a mask creates periodic modulation of the UV intensity across the film. The polymerization is first initiated in the exposed regions corresponding to the open fringes of the mask. The consumption of the monomers in these stripes gives rise to diffusion of monomers from the neighboring stripes beneath the blocked fringes. The reactivity ratios of 2-EHA and C8A, calculated for free radical copolymerization,[15] are 0.90 and 0.05, respectively. As a result, the copolymer composition in the stripes below the open fringes is richer in the fast-reacting monomer, 2-EHA, than the global composition of the monomer mixture. Planar anchoring at room temperature is therefore obtained in these regions (Fig. 1). In contrast, the copolymer formed in the stripes below the blocked fringes is richer in C8A, which favors homeotropic anchoring. The LC cells in the stripes with homeotropic anchoring are larger than those in the neighboring stripes. This is because a slower polymerization-induced phase separation occurs beneath the blocked fringes during mask exposure, allowing for coalescence of the LC domains

prior to extensive cross linking of the polymer matrix.[16]

The difference in copolymer composition between the two stripes is limited by the reactivity ratios of the two comonomers, the balance between diffusion and polymerization, and the timing when solidification occurs.[16] If the composition of the starting monomer mixture has less than 80 mol.% 2-EHA, the anchoring transition temperature of the encapsulated LC phase, T_t, is far above room temperature,[13] and the resulting film shows only homeotropic anchoring. Similarly, if the monomer composition is above 90 mol.% 2-EHA, only planar anchoring is obtained.

The differences in LC alignment and polymer concentration between the adjacent stripes generates spatially periodic modulation of refractive index that constitutes a good diffraction grating, as shown in Fig. 1(e). The periodicity of the grating, ρ, was calculated from the Bragg equation for normally incident light, $\rho = m\lambda/\sin(\beta_m)$, where m is the order of diffraction, λ is the wavelength, and β_m is the corresponding diffraction angle. The calculated value of ρ is consistent with that directly measured by optical microscopy and with the photomask spacing. The transmitted and diffracted intensities of a 1 mW He–Ne laser were monitored as a function of the applied voltage (1 kHz square wave AC voltage ramping from 0 to 10 V). The polarization of the incident laser was set parallel to the orientation of the periodic stripes of the film. When a 6 V potential (i.e., an electric field strength, E, of 0.40 V μm^{-1}) is applied, the contrast in the birefringence is lowered [Fig. 1(d)] and the diffracted intensity is greatly diminished [Fig. 1(f)], because most of the LC molecules are aligned parallel to the field direction.

The first-order diffraction efficiency, DE_1, defined as the percentage of the total intensity of the first-order diffraction spots to the intensity of the incident beam, shows a maximum value of 3.4% at approximately 2 V ($E = 0.13$ V μm^{-1}) and a minimum at 6 V [Fig. 2(a)]. DE_1 then increases slightly and reaches an asymptotic value of 0.3% at higher voltages. The weak diffraction at higher voltages arises from a small difference between the refractive index of the polyacrylate matrix (1.46–1.50, Ref. 17) and the ordinary refractive index of TL205.

The modulation of the DE with the applied voltage can be understood on the basis of LC alignment being perpendicular to the substrate due to the applied field. This decreases the overall refractive index variation in the film, thereby reducing scattering loss (i.e., increasing the total diffracted and transmitted intensity). On the other hand, decreasing the refractive index difference between the adjacent stripes also reduces the diffraction effect. Therefore, a maximum is observed for the first- and third-order diffraction intensity due to these two opposing trends, whereas a monotonic increase of the zeroth-order (transmitted) intensity was obtained.

The switching times of the LC diffraction gratings were determined by monitoring the response of the zeroth-order diffraction to an electric field switching between 0 and 0.47 V μm^{-1} with a photodetector con-
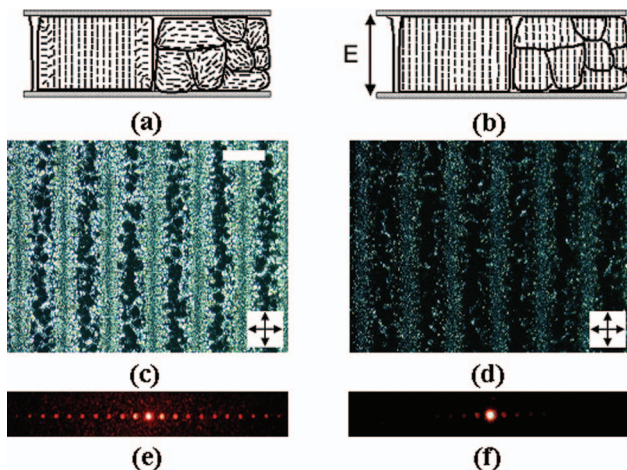

Fig. 1. (a), (b) Schematic of the side view of the LC–polymer film with two alternate stripes of different anchoring and morphology. (c), (d) Light micrographs of the LC–polymer grating film between crossed polarizers. (e), (f) Diffraction patterns of the same film with a normally incident 633 nm He–Ne laser. (a), (c), (e) Electric-field off state; (b), (d), (f) with an electric field **E** of 0.40 V μm^{-1} (square-wave AC) across the thickness. The scale bar in (c) is 80 μm. The sample thickness is 15 μm.
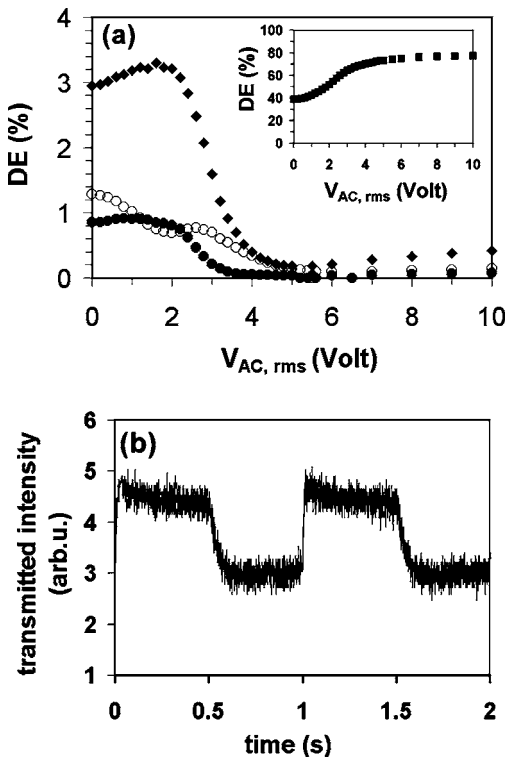
Fig. 2. (a) Plot of the zeroth- (■, the inset), first- (♦), second- (○), and third-order (●) diffraction efficiencies (DEs) as a function of the root mean square values of the applied voltage. (b) Response of the zeroth-order diffraction corresponding to switching between $E = 0$ and 0.47 V μm^{-1}.

nected to a digital oscilloscope. The rise time was defined as the time from turn-on until the signal reaches 90% of the asymptotic value. The fall time was measured from turn-off to the 10% level of asymptotic signal. The measured rise and fall times are 25 and 110 ms, respectively. The longer fall time is typical for a PDLC device because the relaxation of the LC without an electric field is determined only by LC elasticity and surface anchoring at the polymer interface.

In summary, we have demonstrated a facile and operationally simple method to prepare electrically switchable diffraction gratings by periodic spatial alignment of LC based on the polymerization-induced phase separation of a LC and copolymer. The advantages of the procedure reported here include ease of

manufacturing, low switching voltages, the structural stability offered by the polymer matrix, and compatibility with plastic substrates.

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