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Flow-induced grating from cholesteric mixtures

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In this work we present a new technique for obtaining large diffraction gratings (some cm) by means of a simple filling of cells having a planar treatment of their inner surfaces. A homogeneous mixture, composed of a cholesteric liquid crystal and a nematic liquid crystal monomer, was used. During the filling process, the flow induces a phase separation between the cholesteric liquid crystal and the liquid crystal monomer and, at the same time, the latter is oriented planar to the surfaces of the cell. Phase separation produces alternate arrays constituted by the cholesteric liquid crystal and the nematic liquid crystal monomer. Successive UV polymerization of these films yields a permanent grating. We have investigated the transmitted and first order diffracted beam efficiency for films obtained at different temperatures. The morphology of the films was studied by using an optical microscope equipped with crossed polarizers and by electron microscopy in order to control the shape of the arrays and the alignment of the oriented polymer.

1. Introduction

In the last few years, many scientific groups have developed different techniques to enable spatial light modulation for optical switches and optical data storage. A large number of materials is used for the fabrication of gratings, of which the most widespread are those based on liquid crystals [1–4], photo-chromic materials [5] and micro-fluidic devices [6].

The techniques used to induce a periodic distribution of refractive indices in the films are, essentially, photolithography [7–9], UV polymerization [10–13], UV light combined with a photo-mask [14] and polymerization by laser interference [15]. Moreover, it is well known that mechanically rubbed polyimide on the inner surfaces of a glass cell induces a planar orientation on the liquid crystal molecules [16]. Another technique employed for inducing a high degree of planar alignment on liquid crystal molecules is simply by flow [17].

In this paper we describe the formation of a flow-induced grating from a mixture consisting of a cholesteric liquid crystal and a nematic liquid crystal monomer. In our system we combine the orientational effect of mechanically rubbed polyimide on the inner surfaces of the cell with the molecular alignment induced by flow during the filling of the cell with the liquid crystal mixture.

A cholesteric liquid crystal mixture held between two parallel glass surfaces treated in order to induce planar alignment usually exhibits 'Cano wedges' [18] when observed by optical microscope. These structures are due to different orientations of the cholesteric directors along one direction. This leads to a succession of domains separated by the same discontinuities. When this situation is perturbed by adding liquid crystal monomer, the latter migrates towards the borderlines of such domains. The shape of the latter is usually random, but becomes elongated as a consequence of filling by flow. If the length covered by the flow is sufficient, the cell will show arrays consisting of alternate regions of cholesteric liquid crystal and liquid crystal monomer; the shape of these regions is then like stripes, as schematically shown in figure 1. The cells obtained in such a way were irradiated by UV light in order to induce the polymerization of

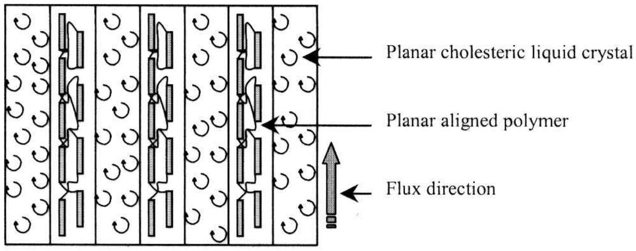

Figure 1. Schematic representation of the grating obtained from the phase separation occurring between the cholesteric liquid crystal and the liquid crystal monomer after the filling process of the cell and subsequent polymerization of the monomer.

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the liquid crystal monomer. The morphology of the resulting films was observed by optical microscopy with crossed polarizers and by scanning electron microscopy (SEM). The electro-optical properties of the device were also investigated in order to measure the dependence of the first order diffracted beam efficiency on filling temperatures.

2. Experimental

The cholesteric liquid crystal mixture was prepared by adding 75 wt % of E49 (a nematic liquid crystal mixture supplied by Merck Ltd UK) to 25 wt % of CB15, (*S*)-(+)-4′-(2-methylbutyl)-4-biphenylcarbonitrile from Aldrich; in this way we obtained a cholesteric liquid crystal with a pitch in the visible region (520 nm). The final mixture was composed of 88 wt % of the cholesteric liquid crystal mixture, 10 wt % of a nematic liquid crystal diacrylate monomer (1,4-phenylene bis-[4-(6-acryloyloxyhexyloxy)benzoate] (C6H) supplied by Hikmet and co-workers [19–21]) and 2 wt % of the UV initiator Irgacure 651 from Ciba Specialty Chemicals. This mixture was heated at 70°C, the transition temperature from cholesteric to isotropic phase, for 2 min and stirred to make it homogeneous. Cells, by Linkam (thickness 5 μm), with planar alignment treatment and having the rubbing direction of the top and bottom substrates mutually parallel, were filled by capillarity with the cholesteric mixture, at different temperatures and rates (20°C–24 μm s^{-1}, 25°C–38 μm s^{-1}, 30°C–49 μm s^{-1}, 35°C–62 μm s^{-1} and 40°C–73 μm s^{-1}). This was done using a hot stage and a temperature control unit by Linkam (PR 600). Polymerization of the liquid crystal in the cells occurred on UV exposure at room temperature for 15 min, using a mercury lamp HPK 125 from Philips. The diffraction patterns, parallel to the rubbing direction, were studied using a He-Ne (632.8 nm) laser beam and the diffracted light of zeroth and first order was measured by means of a photodiode.

The grating was electrically switched by applying an appropriate driving voltage at 1 kHz. The liquid crystal monomer alignment, after polymerization, was observed by optical microscopy with crossed polarizers (Laborlux 12 Pol by Leitz). Film morphology was investigated by means of SEM (LEO 420). A cross-section of the film for SEM observation was obtained after immersion of the cell in liquid nitrogen and washing out the cholesteric liquid crystal with methanol. Such a section was placed under vacuum (10^{-3} Torr) for 12 h in order to eliminate residual methanol and thereafter it was coated with a thin gold film (some hundred Å).

3. Results and discussion

The addition of a small amount (about 10 wt %) of nematic liquid crystal monomer to a cholesteric phase does not disturb the system and the typical 'Cano wedge' texture is preserved. The combined action of the flow during the filling process of the cell together with the aligned polyimide on the inner surface of the cell causes a strong deformation of the 'Cano wedge' structure with formation of alternating regions constituted by nematic liquid crystal monomer.

If during the filling process, the advancing front of the liquid crystal monomer is hindered by a spacer used to fabricate the cell, it becomes divided into two new fronts which can advance in separate ways or recombine to re-establish the original front. This situation is shown in figure 2.

When the filling process is over, we obtain a pattern comprising alternate arrays with two different refractive indices, one related to the cholesteric liquid crystal and the other related to the liquid crystal monomer. The periodicity of the alternating regions is due to the fact that all the cholesteric liquid crystal microdomains present in the 'Cano wedge' structure are constituted by the same amount of substance.

The added liquid crystal monomer in order not to perturb such a situation, migrates towards the microdomain interfaces. Therefore the flow, together with the orientational action of polyimide, does not simply determine a phase separation (which already exists in the mixture immediately after it is stirred at 70°C and cooled to the filling temperatures), but actually causes microdomain deformation into alternate regions of cholesteric liquid crystal and liquid crystal monomer. The periodicity of the stripes (about 5 μm) is, therefore, determined by the amount of material present in the microdomains.

In order to obtain a stable and durable grating, the stripes of fluid liquid crystal monomer were solidified by UV light polymerization of the film. The final structure obtained at the end of these processes, shows regions of

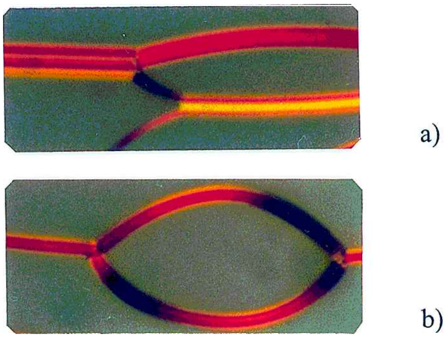

Figure 2. Optical microscopy photographs of the advancing front of the liquid crystal monomer hindered by the presence of a spacer: (*a*) it is divided into two new fronts which can advance in a separate way; (*b*) it may recombine, reestablishing the original front. The magnification is 400 ×.

fluid cholesteric liquid crystal alternating with solid planar oriented polymer. The orientation of the polymer region was verified by optical microscopy with crossed polarizers. The application of an appropriate voltage (40 V at 1 kHz) to the cell gives orientation of the cholesteric liquid crystal molecules parallel to the external electric field and a consequent mismatch between the refractive index of the cholesteric phase and that of the polymer. This situation is shown in figure 3 which depicts two contiguous areas of the same sample in which on the right side there is no electric field, because the ITO surface was removed, and the direction of rubbing with respect to one of the crossed polarizers is 45°. Figure 3 shows that the electric field does not perturb the polymer stripes which remain parallel, aligned to the cell surfaces.

In order to verify the existence of alternate stripes of polymer and fluid cholesteric liquid crystal, we have also examined the cross-section of the film by means of SEM. In figure 4 is shown an SEM image of a cross section of the grating sample filled at 20°C; it is possible to note the presence of alternate empty channels previously occupied by the cholesteric liquid crystal. This photograph does not reflect the volume of the liquid crystal (88 wt %) present in the homogeneous mixture before polymerization, because the polymer matrix is saturated by the liquid crystal, and in fact the matrix has a porous structure.

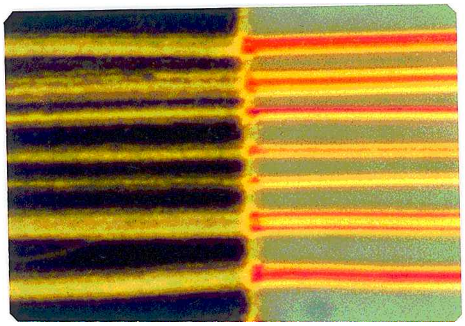

Figure 3. Optical photomicrograph of the grating; on the left side there is an applied external electric field, and on the right side there is no electric field owing to removal of the ITO. The dark areas on the left are attributed to the cholesteric liquid crystal orientation; moreover it is observed that the polymer does not respond to the electric field. The magnification is 400 ×.

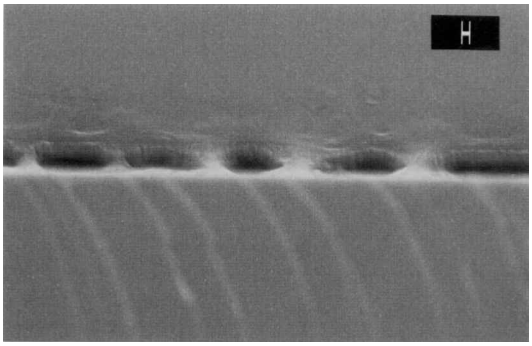

Figure 4. SEM photograph of a cross-section of the polymerized grating. The holes (channels) are due to the cholesteric liquid crystal removed in processing the SEM sample. The bar is equal to 1 μm.

Electro-optical properties of the grating were also investigated, and figure 5 shows the zeroth and first order diffraction efficiency versus external electric field strength. The high degree of diffraction efficiency must be attributed to the mismatch in the refractive indices between the cholesteric liquid crystal phase and the polymer.

The diffraction efficiency η of the grating depends on several parameters, such as the refractive index difference (Δn), the absorption coefficient modulation (Δk), the wavelength of the incident light (λ) and the thickness of the sample (d), as shown in equation (1) [22].

$$\eta = \left(\frac{\pi \Delta n d}{\lambda}\right)^2 + \left(\frac{\Delta k d}{4}\right)^2. \tag{1}$$

According to equation (1), the application of the external electric field changes the liquid crystal orientation, consequently it reduces the value of Δn and the first order diffraction efficiency decreases and that of the zeroth order increases. Figure 5 also shows that the diffraction efficiency is about 35%; this is a good value, even if it seems small when compared with that of gratings obtained using holographic techniques (about 70%) [11, 12]. As equation (1) shows, the efficiency depends only on Δn, remembering that the other parameters are strictly a function of the cell; in order to obtain different Δn values for the same mixture (cholesteric liquid crystal/ liquid crystal monomer), we changed the degree of

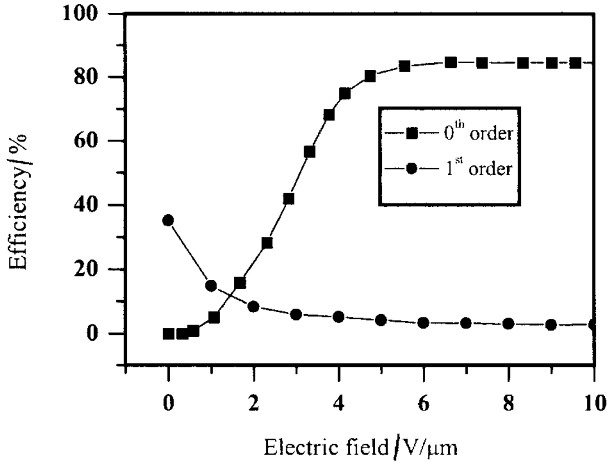

Figure 5. The zeroth and first order diffraction efficiency versus applied electric field strength; the efficiency was normalized with respect to the air.

solubility of the monomer in the liquid crystal phase by varying the temperatures of filling. In fact, an increment in temperature gives a greater solubility of the monomer in the cholesteric phase and at 40°C there is complete miscibility. At temperatures above 40°C, the grating does not form, but there is a mutual dispersion of the liquid crystal monomer and the cholesteric liquid crystal. For a sample filled at this temperature, when the liquid crystal monomer in the cholesteric phase is polymerized, the polymer network hinders the reorientation of the cholesteric liquid crystal in response to an external electric field because, in our opinion, the network inserts itself into the helical structure blocking the system. In this way there is no longer any variation of the efficiency as a consequence of the application of the electric field because Δn is constant. This situation is shown in figure 6 where the first order transmission dependence on the electric field is reported for samples filled with the same liquid crystal mixture at different temperatures.

As may be noted, the maximum variation in efficiency (from 35% to 2.5%), for different values of the electric field, is shown by the sample filled at 20°C, for which there is a very low miscibility between the cholesteric phase and liquid crystal monomer. An increment in filling temperature of the cell gives a lower variation in efficiency until at 40°C, the efficiency of the sample remains constant at a value of about 35% for all values of the electric field.

4. Conclusions

We have demonstrated for the first time that the combination of flow with a planar alignment induced by rubbed polyimide is able to create a grating from a cholesteric liquid crystal mixture. The technique used for the fabrication of our grating is very simple in comparison with other techniques, and allows us to obtain a large surface of grating, some cm, with diffraction efficiency values comparable to any similar devices.

Subsequent polymerization by UV light of the grating obtained by means of the simple cell filling process, is able to make the grating very stable and durable. Moreover, temperature control during the filling process of the cell with the cholesteric liquid crystal mixture, makes it possible to obtain gratings characterized by having different responses of the first order diffracted laser beam transmission through application of an external electric field. The degree of alignment of the polymer and the morphology of the grating have been investigated by optical microscopy and SEM, respectively, and the results discussed. Finally, we have obtained a good diffraction grating that is very simple to fabricate; further investigations are in progress in order to improve the grating efficiency and to have better control of the grating periodicity.

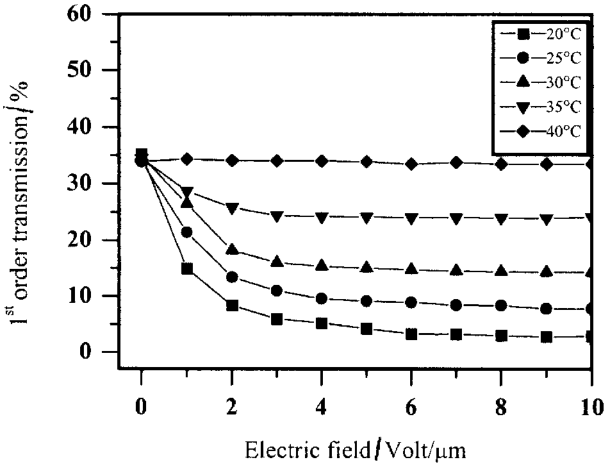

Figure 6. The first order diffraction efficiency of gratings obtained at different filling temperatures versus external electric field strength. The efficiency was normalized with respect to the air.

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