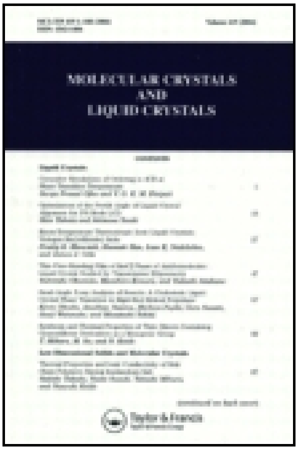

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Alignment of Liquid Crystals Infiltrated into Porous Thin Films with Tailored Nanostructures Grown by Glancing Angle Deposition

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Traditional liquid crystal alignment techniques influence mesogen alignment at the substrate alone, and rely on interactions between molecules to extend that alignment throughout a device's thickness. An alternative approach is the use of a nanostructured host that provides a large surface contact area with a guest liquid crystalline material and can extend for micrometres beyond the substrate. This permits a greater degree of control over the mesogens and allows alignment control throughout the thickness of the nanostructured host. We present the realization and experimental results using hosts fabricated through a specialized thin film process known as glancing angle deposition.

Keywords: alignment; dichroic; nanostructures; porous; switching

INTRODUCTION

It is well known that the ability to control the alignment of liquid crystals (LCs) is fundamental to attaining control over the optical

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and other properties in these unique materials [1]. One class of methods used is surface treatment of the substrates (*e.g.*, surfactants or rubbed polyimide layers [2]). However, these methods work directly only at the surface of the LC film and otherwise rely entirely on the co-operative effects and resulting elastic properties of the LC to influence the molecular alignment within the bulk of the film. Confined geometry systems offer an alternative approach where the high surface contact area between the LC guest and the host material (compared to the volume of LC) permits a much more direct influence on LC structure.

A specialized thin film fabrication technique known as glancing angle deposition [3–5] (GLAD) affords the ability to produce porous, nanostructured, columnar thin films with a high degree of control over porosity and columnar morphology. GLAD-grown thin films have been used in various applications including optical filters and sensors. The structure of a GLAD film host is suited for infiltration by various guest materials including isotropic fluids, polymers, and liquid crystals, as documented in the literature. Previous work has demonstrated that nematic LCs embedded in chiral structured GLAD films caused reduced scattering and enhanced circular birefringence [6, 7]. Most importantly, since the film spans the entire thickness of the cell, one can engineer the structure of the film backbone and hence control the alignment imparted to the LCs, a greater level of control than alignment by substrate surface treatments alone. The present investigation aims to further explore the interaction between GLAD thin films and LCs infiltrated into their pores. Here, we study the optical properties of basic GLAD structural archetypes and their interaction with nematic liquid crystals. In this work, GLAD films of various geometries including biaxial slanted posts, uniaxial vertical posts, and fin-like structures were optically characterized by variable angle spectroscopic ellipsometry (VASE – model V-VASE from J. A. Woollam Co, Inc.). The optical properties were measured for the films as-deposited and again after filling with various nematic LC mixtures with and without the addition of varying concentrations of a dichroic dye [8–10]. The dichroic dye molecules align with the nematic director and, through anisotropic absorption, provide additional insight into how the GLAD film columns influence the LC alignment. Results from measurements on GLAD films of slanted or vertical post morphologies indicate that the LC molecules align with the nematic director parallel to the posts. Application of an electric field across the cell causes the LCs to re-align parallel to the field, enabling the design of devices based on switching of the linear/circular birefringence and/or dichroism.

EXPERIMENTAL

Film Fabrication

Fabrication of the nanostructured hosts was accomplished using SiO_2 and the GLAD process, shown schematically in Figure 1. GLAD uses physical vapour deposition onto an unheated, obliquely held substrate with an angle of flux incidence, $\alpha > 65^{\circ}$, to form a highly porous film. At the onset of film growth, evaporated material nucleates onto the substrate, forming islands of material on the substrate. Because of the low temperature of the substrate, surface and bulk diffusion effects are minimized, and adatom shadowing is the dominant film growth mechanism. Therefore, as new material arrives at the substrate, the nucleated islands shadow the regions behind them, creating regions on the substrate where film growth can not take place. As additional material is deposited, this results in the formation

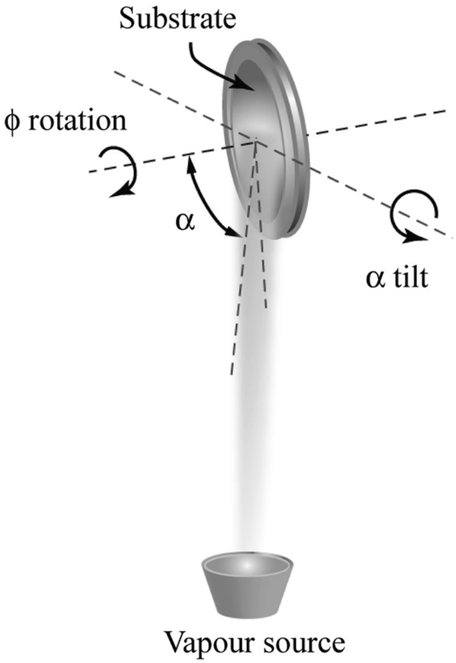
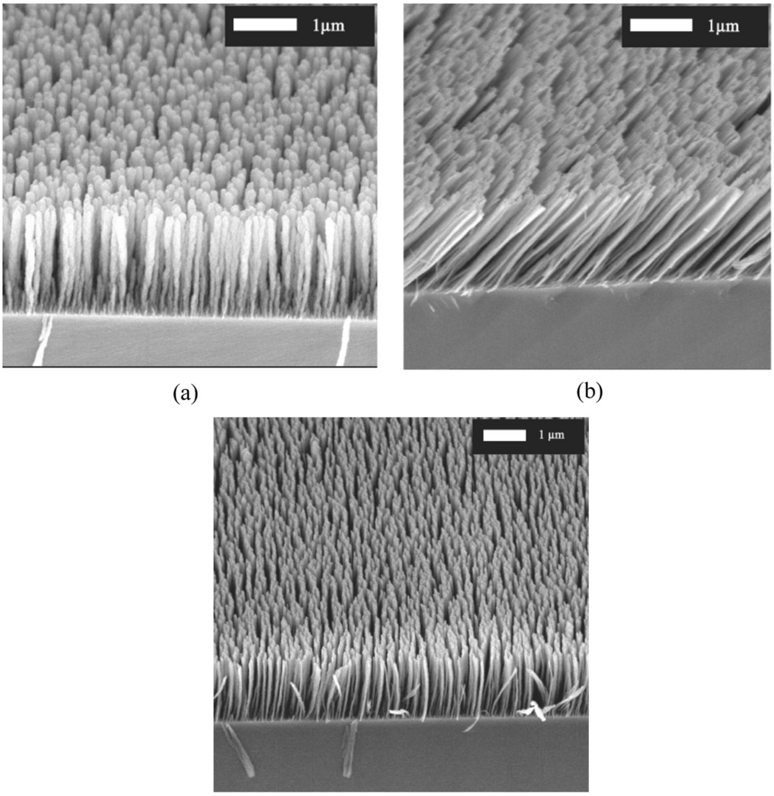


FIGURE 1 Glancing angle deposition. Deposition at large α onto unheated substrates promotes growth based on adatom shadowing, leading to the fabrication of columnar films. In situ variation of α and ϕ allows for the creation of advanced film morphologies.

of columnar structures, oriented toward the vapour source. Larger values of α enable the creation of increasingly porous films. By using simultaneous substrate rotation (ϕ), a wide variety of film structures can be created. The structures investigated in this study include uniaxial vertical posts, biaxial slanted posts and biaxial vertical fin-like structures, deposited at flux angles of $\alpha = 85^\circ$ and $\alpha = 65^\circ$ to examine the effects of film density on optical properties and alignment effects. Examples of these films are shown in Figure 2. More advanced structures, including helices, polygonal spirals and films with variable density are easily fabricated using GLAD.



(a) (b)

(c)

FIGURE 2 Basic film morphologies achievable using GLAD ($\alpha = 85^\circ$). a) Vertical posts – Constant ϕ rotation during deposition ($\sim$1–5 rpm). b) Slanted posts – no ϕ rotation during deposition. c) Fin-like structure – formed by periodic 180° rotations in ϕ during deposition.

LC Infiltration

LCs were incorporated into the voids of the GLAD films using spin coating. The positive $\Delta\varepsilon$ nematic LC E7 ($n_e = 1.75$, $n_o = 1.53$, $T_c = 60.5^\circ C$) was spun onto 1.5 μm thick porous film samples. A major difficulty encountered while filling nanostructured films with LCs is to ensure that a sample has been completely filled with liquid crystal, with no layer of excess LC molecules above the surface of the film, nor an unfilled region below the surface of the film. To achieve this, a simple visual test was employed. An overfilled cell appears quite smooth and glasslike, while the surface of an underfilled sample appears rough. By controlling the viscosity of the LC by diluting it in solvent and varying the spin speed, one can visually determine the crossover point between an overfilled and underfilled cell. For a 50% solution (by volume) of E7 and propylene glycol methyl ether acetate (PGMEA), the required spin speeds for 1.5 μm films fabricated at $\alpha = 85^\circ$ and $\alpha = 65^\circ$ were found to be 2500 rpm and 5000 rpm, respectively. More accurate results for determining the degree of cell filling using interference effects as well as polymerizable LCs are the subject of current experiments.

For certain samples, the dichroic dye molecule shown in Figure 3 was mixed with pure E7. Typical concentrations were 2–3% by weight. The dye molecules align with the LC mesogens and preferentially absorb light polarized along its long axis (positive dichroism). This allows for simple identification of the alignment direction in GLAD films through simple polarized transmission measurements.

Finally, cell structures were fabricated by first depositing GLAD films onto indium tin oxide (ITO) coated substrates that were subsequently glued together using UV cure epoxy. A small fill port was left unsealed, and a drop of the E7 LC/dye mixture was placed at this opening. The mixture was found to quickly fill the cell through capillary action. Using such a structure, the switching behaviour in a filled GLAD film could be investigated. Unfortunately, this approach suffers from the drawback of having a cell thickness that is difficult to determine, as well as the potential for a layer of LCs with an unclear

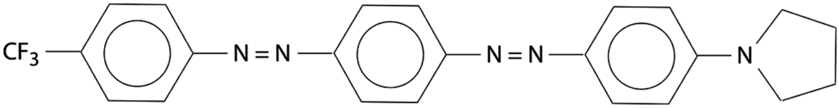


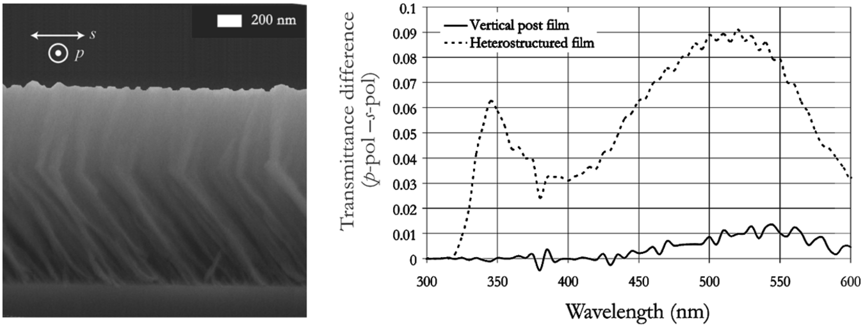
FIGURE 3 Dichroic molecule. The molecule has an absorbance between 400 and 600 nm. The absorbance is strongest parallel to the long axis of the molecule, which is collinear with the long axis of the E7 mesogens.

alignment throughout the center of the cell. Resolution of these issues is the focus of current cell structure redesigns.

RESULTS

Bulk Effect or Surface Effect?

An important question is whether it is the entire host structure that is affecting the alignment of liquid crystals or just the uppermost layer. To determine this, the slanted post/vertical post heterostructure shown in Figure 4a was fabricated and infiltrated with the LC/di-dichroic dye mixture. The difference in transmittance of normally incident light polarized along the *s* and *p* directions through the film was compared to that through a dye-filled vertical post cell, whose morphology is similar to the top layer of the heterostructured film. The results are shown in Figure 4b. Notice that there is almost no distinction between the transmittance of the two polarizations in the circularly symmetric vertical post film. The slight difference that is observed between the two polarizations is due to a slight bias in the tilt of the vertical posts that is a result of the fact that this particular sample was mounted to the side of the ϕ axis. Since the circular symmetry of the topmost vertical post layer does not create any selective transmission of the two orthogonal polarizations, the clear dichroism in the heterostructured film indicates that the lower slanted post structure must be influencing the LC alignment. It is therefore concluded that the effect of the nanostructured film on LC alignment is due to the



(a) (b)

FIGURE 4 a) A slanted post/vertical post heterostructure, formed by combining the morphologies shown in Figures 2a and 2b. b) Transmittance difference between *p* and *s* polarized light ($T_p - T_s$) indicating the effect of the lower, slanted post layer in the heterostructured film.

film structure as a whole, and that we can use such heterostructured films to modify LC alignment throughout a sample's thickness.

Enhanced Birefringence and Reduced Scattering

Certain GLAD films exhibit strong in-plane birefringence. For instance, normally incident light polarized along the long axis of the blades in a fin-like film experiences a higher index of refraction than in the perpendicular direction. A vertical post film, meanwhile, shows no such in-plane birefringence. This "form birefringence" can clearly be seen from the top-down views of the respective structures in Figure 5. However, the porous nature of GLAD films makes them susceptible to a high degree of Rayleigh scattering, and the useful birefringence properties are obscured. This can be alleviated by depositing at lower α, but the lower porosity makes it more difficult to incorporate fluid into the voids. We have used spectroscopic ellipsometry and polar decomposition to examine how infiltration of LCs into porous films enhances the in-plane birefringence, and reduces scattering losses. We can also infer some information over LC alignment from these results. In polar decomposition, we treat the film sample as a combination of a polarizer and a retarding element. By measuring the elements of the 4×4 Mueller matrix [11] of the sample using spectroscopic ellipsometry, and equating them to those of a general cascaded polarizer/retarder combination, we can extract the

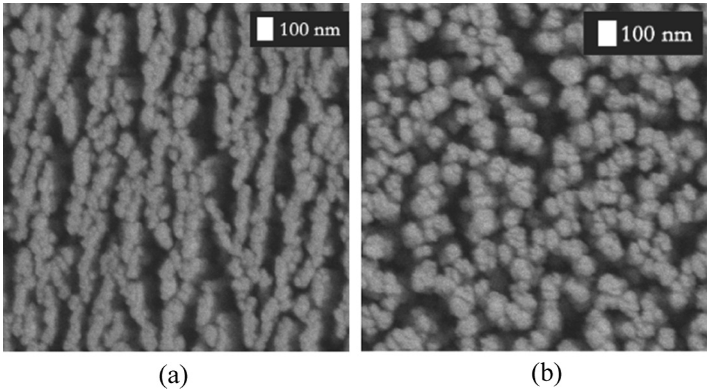


FIGURE 5 Top-down SEMs of GLAD films. a) Fin-like structure. A higher index of refraction is observed for light polarized along the fin blades, as opposed to light polarized normal to them. b) Normally incident light of all polarizations experiences the same refractive index, due to the circularly symmetric cross-section of the structures.

TABLE 1 Birefringence of Various GLAD Film Structures Before and After Infiltration with E7

Film type	α	Δn (no LCs)	Δn (w. LCs)	Alignment
Slanted post	85°	0.012	0.074	Along posts
Fin-like	85°	0.028	0.03	Unclear
Fin-like	68°	0.025	0.068	Along grooves
Vertical post	85°	0.0005	0.0004	Along posts
Vertical post	68°	0.0002	0.034	Along posts (possible pretilt)

Note: Δn is given for $\lambda = 600\,\text{nm}$. Also shown are proposed alignment orientations for the films, as inferred from the results.

retardation of the sample. Knowing the film thickness, we can then extract the sample's birefringence. Results from this procedure for a variety of GLAD films are given in Table 1. The results indicate that the infiltration of LCs into non-circularly symmetric films tends to significantly increase the birefringence of the films, though the overall birefringence still remains less than that of bulk E7 LC. Figure 6 shows the change in transmission through a slanted post film held at 45° between crossed polarizers before and after E7 infiltration, illustrating the combined effects of both the increased in-plane birefringence and the reduced optical scattering to be discussed below. Increased in-plane birefringence is not the case, however, for the circularly symmetric vertical post films. In these films, the addition

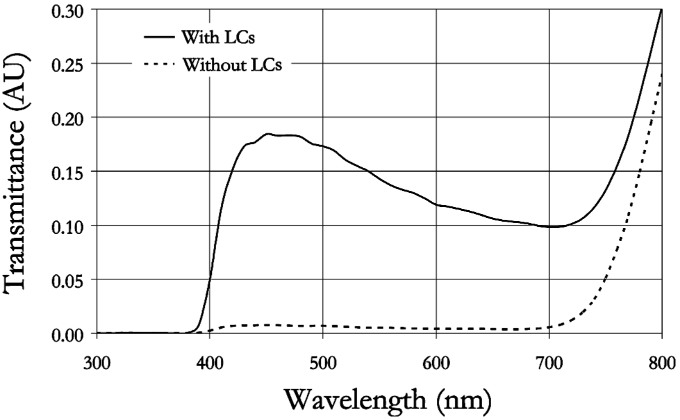


FIGURE 6 Change in transmittance through a slanted post film ($\alpha = 85°$) held at 45° between crossed polarizers. Addition of LCs increases the retardation and reduces optical scattering, both of which lead to an increased transmission of light through crossed polarizers.

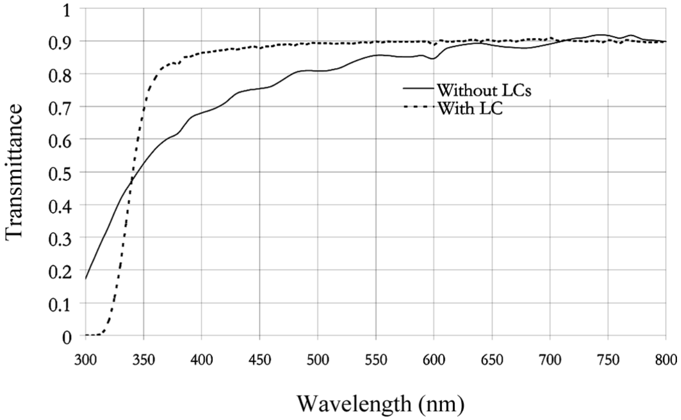


FIGURE 7 Transmittance through a vertical post film ($\alpha = 85°$) before and after LC infiltration. Notice the strong reduction in scattering, particularly at low wavelengths, and the uniform transmittance of the sample after E7 was introduced.

of E7 hardly changed the in-plane birefringence of the films. These results suggest that the long axis of the E7 molecules are aligning with the long axes of the GLAD columns, reinforcing the inherent birefringence of the films. This is not as clear in the 85° fin-like film. In this case, the LCs do not appear to have a favored alignment direction, as the birefringence is hardly altered after LC infiltration. To obtain more concrete evidence with regard to LC alignment, optical measurements at non-normal incidence are required, and are the subject of ongoing investigation. However, it is clear that the addition of LCs to a GLAD film serves as a tool that can be used to enhance the films' birefringence. Further research into different film materials, different LCs and the use of chemical functionalization of the nanostructured columns will permit sophisticated control over the optical properties of GLAD films.

The addition of LCs to GLAD films also reduces the scattering of light traveling through the film. As a result, the sample appears less cloudy, and more light is transmitted through it. The reduction in scattering occurs since the LC mesogens are more closely index matched to the film material (SiO_2, with $n \sim 1.5$), than the void regions that normally make up the film pores. Since scattering is one of the primary reasons that high α films are troublesome for optical applications, the use of LCs to reduce this scattering might enable the use of such films, for instance, where stress concerns in a device design require a porous film. Alternatively, if one can switch between a scattering state and a non-scattering state by applying an external field, one could fabricate a dynamic scattering display. As an example of the advantage of using LCs in a GLAD film to reduce scattering, consider Figure 7, which depicts the transmittance through an $\alpha = 85^\circ$ vertical post film before and after LC infiltration. Notice that the transmission through the filled cell is higher throughout the visible spectrum, with only a 5% variation in transmittance above 450 nm. This is in contrast to the unfilled cell which scatters light strongly at low wavelengths, leading to a greater than 20% variation in transmittance across the visible range. Clearly, the presence of LCs serves to reduce scattering in highly porous GLAD films, and helps to promote a more uniform response across the visible spectrum.

Switching Behaviour

The switching properties of LCs in a GLAD film were examined by using the cell structure described earlier. A 60 V_{rms}, 1 kHz voltage can be applied across the terminals, which aligns the long axis of the E7 molecules with the field lines. The dichroic mixture can be used to easily probe this rearrangement of the LCs, since it is known that the dye molecules orient parallel to the LC mesogens. It is observed that for circularly symmetric structures (*e.g.* vertical posts), no noticeable change in dichroism occurs under an applied field [12], while for an asymmetric structure (*e.g.* slanted posts), a significant change in dichroism occurs. This latter result is shown in Figure 8, which

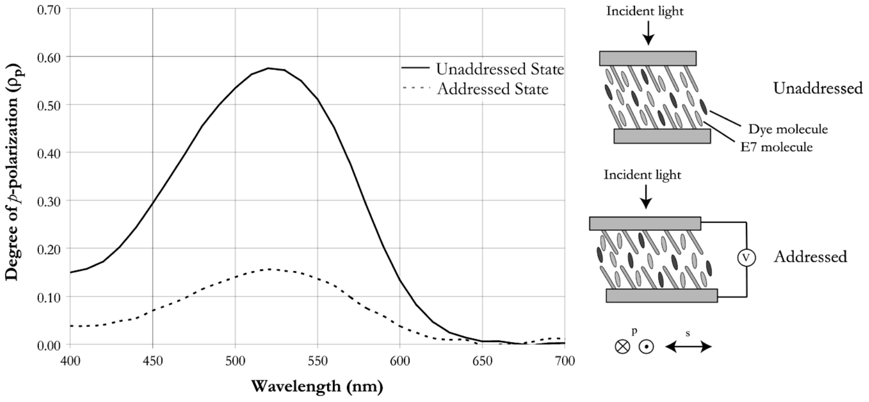


FIGURE 8 Degree of p-polarization for light transmitted through a slanted post cell in the addressed and unaddressed states. Notice the strong reduction in the degree of polarization under an applied field.

illustrates the degree of p-polarized light, ρ_p, given by equation (1). ρ_p varies from 0 when the amount of transmitted s- and p-polarized light is equal, to 1, when the transmitted light is fully p-polarized. The results clearly show that in the unaddressed state, the transmitted light is strongly p-polarized, owing to the dichroism of the film. In the addressed state, the polarization of transmitted light is more evenly spread between the s and p directions, illustrating the ability of the device to act as a polarization switch.

$$\rho_p = \frac{T_p - T_s}{T_p + T_s} \tag{1}$$

The need for a moderately large field (~6V/μm) and the significant dichroism that still remains in the addressed state are concerns that still need to be examined. It is hypothesized that both effects are due to LC molecules that are strongly anchored to the GLAD columns, and are not affected by the electric field. Future experiments with weakly anchoring LCs aim to investigate this possibility. The results presented here confirm that LCs can still be switched in a GLAD film, allowing access to one of the most important features of liquid crystalline materials.

CONCLUSIONS

GLAD films offer a new way of aligning LCs that extends beyond traditional surface treatment methods. Using a mixture of E7 LC with a dichroic dye, it has been shown that a liquid crystal mixture will infiltrate the pores of a GLAD film, and will align with the film structure in a predictable and repeatable manner. The effect of the film structure on LC alignment takes place throughout the thickness of the film, which enables one to modify the alignment of LCs far from the substrate. Future experiments will investigate the behaviour of more advanced GLAD film heterostructures, in hopes of combining the optical properties of different types of LC films in the same cell. At the same time, the addition of LCs to GLAD films has been shown to be a useful and versatile tool for enhancing the optical properties of GLAD films. The research presented here clearly shows that the addition of LCs to a GLAD film can be used to tune the in-plane birefringence of inherently birefringent films, such as slanted post and fin-like films. As expected, no birefringence change was observed in vertical post films, which have circularly symmetric cross-sections. However, presuming that LCs align parallel to the columns of the film, one expects a significant modification to the birefringence encountered by light traveling parallel to the substrate. This could have significant implications for future integrated optics applications of GLAD films. The second major benefit of LC infiltration is a reduction of scattering, due to better index matching between the LC mesogens and the film material. This leads to a more uniform spectral response of the film, and eliminates one of the primary problems encountered in optical applications of highly porous films. Finally, the switching of LCs in a GLAD film under the influence of an applied electric field was examined. Preliminary results have shown that switching remains possible in a GLAD film, and that the addition of a dichroic dye to the LC mixture enables the creation of a polarization switch. Several aspects of such a device still need to be addressed, predominantly the effect of mesogen anchoring to GLAD columns. These early results have shown great promise, and have opened up a potentially rich avenue of research. Future experiments will examine the alignment and optical properties of LCs in more sophisticated GLAD film structures, in an effort to create unique LC alignment patterns with the goal of finding new optical effects and realizing devices based on those effects.

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