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Influence of partial matrix fluorination on morphology and performance of HPDLC transmission gratings

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Abstract

The morphology and the electro-optical performance characteristics were investigated in holographic polymer-dispersed liquid crystal (HPDLC) transmission gratings with partially fluorinated polymer matrices. HPDLC transmission gratings were prepared using standard UV curable monomer mixtures along with mono-functional fluorinated acrylate monomers and a nematic liquid crystal, TL203. Partial fluorination of the host polymer matrices by incorporating hexafluoroisopropyl acrylate (HFIPA) or trifluoroethyl acrylate (TFEA) in the standard formulation has been found to influence the morphological and the electro-optical properties of the resulting HPDLC transmission gratings. Significant decrease in switching voltages and higher relaxation times were observed in fluorinated HPDLCs. Conversely, an addition of methyl acrylate (MA), a non-fluorinated monomer with a similar structure in the standard formulation, resulted in an increase in the switching voltage and produced no significant change in the relaxation time in the HPDLC gratings. Presence of fluorine atoms at the polymer-liquid crystal (LC) interface not only decreased the surface anchoring strength but also influenced the orientation of LC droplet directors. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Holographic polymer-dispersed liquid crystal; Transmission grating; Fluorination

1. Introduction

Polymer dispersed liquid crystals (PDLCs) have been extensively studied for various electro-optical applications [1]. A modification of PDLC is the holographically formed PDLC or HPDLC. HPDLCs are produced using holographic techniques to create a stratified composite of alternating layers of liquid crystal (LC) and polymer [2]. HPDLCs have potential in diverse applications such as reflective flat-panel displays [3–5], switchable lenses [6], optical switches for telecommunication [7,8], reflective strain gauge technology [9], application-specific lenses [10], spatially patterned devices [11], image capture systems [12], remote sensing [13], switchable photonic crystals [14,15] and in many other electro-optical applications.

HPDLC gratings are formed in single step by exposing a homogeneous mixture of photo-reactive monomer and LC with an interference fringe pattern created by a holographic exposure apparatus. In the hologram writing process, the photo-polymerization preferentially initiates at the high intensity regions. The consumption of monomers in those regions gives rise to the diffusion of reactive monomers from the low intensity regions to the high intensity regions, thereby causing a periodic spatial modulation of the polymerization kinetics. As the LC molecules do not participate in polymerization, their chemical potential increases in the high intensity regions. Therefore, the LC molecules diffuse to the low intensity regions in order to equilibrate the chemical potential across the holographic writing area. Consequently, the low intensity regions become enriched with LC molecules. As the polymerization proceeds, the miscibility gap between the LC and its polymer host increases and finally LC molecules phase separate, creating alternating layers of polymer and LC rich lamellas [16]. In general, the LC rich layers consist of randomly oriented sub-micrometer sized LC domains. The grating morphology depends on the functionality of the constituting monomers, the fraction of LC in the pre-polymer syrup, the intensity and duration of irradiation and the curing temperature. Since the morphology is largely

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responsible for the electro-optical performance, control of LC domain size and their distribution is of paramount interest in optimizing the over-all performance of the HPDLC gratings.

Several investigators have explored different types of photo-reactive monomers and nematic LC combinations and studied the holographic writing mechanism and structure property relationships. Recently, Schulte and his co-workers [17] used fluorine substituted acrylate monomers in the conventional formulation with LC E7 to prepare HPDLC gratings with visible radiation. The motivation of using fluorinated monomers for the preparation of HPDLC was driven by the hypothesis that the chemical incompatibility between the hydrocarbon and the fluorinated compounds may enhance the LC phase separation. Moreover, the presence of fluorine atoms at the LC/polymer interface of the HPDLC gratings may lower the LC anchoring strength thus lowering the switching voltage. Schulte and others reported that partial fluorination of the polymer matrix practically resulted in an increase in the switching voltage of the HPDLC cells [17]. The earlier publications by this group on conventional PDLC systems reported enhanced phase separation of LCs, improved optical properties and more distinct morphologies with partial matrix fluorination [18,19].

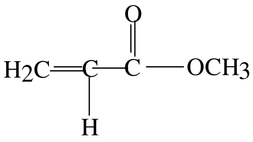
In this contribution, we focus on UV curable systems and fluorinated acrylate monomers for the preparation of HPDLC transmission gratings. It has been observed that holograms with considerable diffraction efficiency ($>50\%$) are generated from the standard visible formulations with average functionality greater than 4.0 [20], whereas, the UV formulations require monomers with average functionalities less than 2 [21]. Such difference in functionality of the constituent monomers in UV and visible radiation curable systems causes holograms with radically different morphological features and electro-optical performance parameters.

This contribution describes the influence of partial fluorination of the polymer matrix on the morphological and electro-optical properties of HPDLC transmission gratings. In this study, the effect of methodically replacing the standard monomer mixtures with hexafluoroisopropyl acrylate (HFIPA) and trifluoroethyl acrylate (TFEA) was examined. HFIPA is considered to have twice as many fluorine atoms as TFEA comonomer. For comparison purposes, a non-fluorinated and structurally similar monomer, methyl acrylate (MA) was used as an additive. The incorporation of MA in the pre-polymer syrup rendered the same change in average functionality as caused by the addition of identical quantity of HFIPA or TFEA. In order to understand the consequence of the matrix fluorination, it is crucial to compare fluorinated and non-fluorinated systems with the same functionality since the average functionality of the pre-polymer formulation tends to strongly influence the performance of the resulting gratings [21]. Instead of adding conventionally used inert LCs (for example, E7), a mixture of fluorinated mesogens, TL203, was selected for this study. The fluorinated LC molecules were expected to further enhance the phase separation from the partially fluorinated polymer matrix and would reduce the switching voltage of the gratings. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to explore the change in grating morphology and surface topology, respectively with the matrix fluorination. Dependence of the electro-optical performance on the level of fluorination was also studied.

2. Experimental

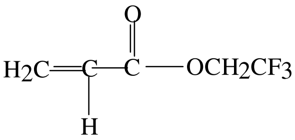
2.1. Materials and sample preparation

The formulations used in this study for the preparation of HPDLC gratings consisted of commercially available constituents. The nematic LC component used here was TL203, a mixture of fluorinated mesogens, procured from EM industries. The physical characteristics of TL203 are the following: $T_{\mathrm{N-I}} = 77\ ^\circ\mathrm{C}$, $\Delta n = 0.2013$, $\varepsilon_{\|} = 15.2$ and $\varepsilon_{\perp} = 4.2$. The control monomer mixture consisted of 80 wt% of 2-ethylhexyl acrylate (EHA), 5 wt% of trimethylolpropane triacrylate (TMPTA); both from Aldrich and 15 wt% of Ebecryl 8301, a hexa-functional aliphatic urethane acrylate oligomer, procured from UCB Radcure [22]. Ebecryl 8301 is a commercially available material, which has been used in many H-PDLC devices to date [9,11,13,15]. Although it would be more appropriate to calculate the average functionality using the mole fraction, we do not have the exact molecular weight of this material. Therefore we simply use weight fraction in this contribution, which has also been used in these materials [13] and other formulations [18]. The monomer mixture has an average functionality of 1.85 as calculated from the mass fraction of each component. Previous experiments with this control monomer mixture together with LC TL203 in 1:1 ratio resulted in HPDLC gratings of high diffraction efficiency and low switching voltages [21]. Our preliminary studies showed that the pre-polymer formulation with same monomer components but with higher average functionality (>2.0) had solubility issues with fluorinated additives and the low functional (≤ 1.4) mixtures gave rise to mechanically weak samples. The control monomer mixture was partially replaced with mono-functional fluorinated monomers: 1,1,1,3,3,3 hexafluoroisopropyl acrylate (HFIPA) and 2,2,2 trifluoroethyl acrylate (TFEA) and with a structurally similar non-fluorinated monomer, methyl acrylate (MA). Fig. 1 shows the chemical structures of the monomer additives. They consist of approximately the same chemical constitutions but differ only in the number of fluorine atoms per monomer unit. The refractive indices of MA, TFEA and HFIPA at 20 °C are 1.402, 1.350 and 1.319, respectively, as reported by the supplier. Mixtures ranging from 5 to 40 wt% of HFIPA, TFEA and MA were each used to incrementally substitute the control monomer mixture in order to generate



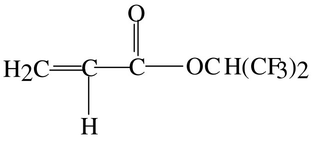
$\mathrm{H_2C{=}C(H){-}C({=}O){-}OCH_3}$

Methyl Acrylate (MA)



$\mathrm{H_2C{=}C(H){-}C({=}O){-}OCH_2CF_3}$

2,2,2 Trifluoroethyl Acrylate (TFEA)



$\mathrm{H_2C{=}C(H){-}C({=}O){-}OCH(CF_3)_2}$

1,1,1,3,3,3 Hexafluoroisopropyl Acrylate (HFIPA)

Fig. 1. Chemical structures of monomers additives.

various experimental formulations as shown in Table 1. The components of the monomer mixtures together with 2 wt% of Darocur 4265 photo-initiator (from Ciba Specialties) were at first mixed homogeneously for 3 min in a glass vial. This isotropic mixture was then thoroughly mixed with 50 wt% of the LC TL203. It has to be noted that the concentration of the monomer additives (fluorinated or non-fluorinated) mentioned in the subsequent text represents their weight percentages loading in monomer mixture, not in the pre-polymer syrup with LCs.

The pre-polymer syrups were prepared under diminished lights absent of UV to eliminate any unwanted photo-polymerization reaction. A few drops of the monomers–LC mixture were placed between indium–tin oxide (ITO) coated glass slides separated by 5 μm glass spacers to control the thickness. The glass slides used here have an anti-reflection coating on the outer surfaces and an index-matching layer over the inner ITO sides. These index matching coatings greatly reduce the internal reflection during the laser exposure that compromises the quality of the holograms.

2.2. Formation of gratings

Holographic transmission gratings were recorded by interfering two beams (Ar$^+$ laser, $\lambda = 351$ nm) of equal intensity with a total power of 100 mW. After accounting for the optical losses, there was a power of approximately 22 mW in each recording beam. Typical recording time was 30 s. For transmission gratings, the holographic fringes are normal to the substrate. After recording, all of the HPDLC cells were post cured for 2 min under a UV lamp to stabilize any unreacted functional groups from further photo-induced reactions.

Table 1
Experimental formulations and average functionalities

Type of monomers	Concentration of additives (wt%)	Average functionality[a]
–	0	1.85
MA	6.6	1.79
MA	11.8	1.75
MA	15.0	1.72
MA	20.2	1.68
MA	25.9	1.63
MA	30.2	1.59
MA	35.1	1.55
MA	40.9	1.50
TFEA	6.5	1.79
TFEA	11.3	1.75
TFEA	16.8	1.71
TFEA	20.3	1.68
TFEA	25.4	1.63
TFEA	30.1	1.59
TFEA	35.2	1.55
TFEA	41.0	1.50
HFIPA	6.6	1.79
HFIPA	10.6	1.76
HFIPA	15.1	1.72
HFIPA	20.3	1.68
HFIPA	25.1	1.64
HFIPA	30.3	1.59
HFIPA	35.3	1.55
HFIPA	40.0	1.50

[a] Calculated from the mass fraction of each component [21].

2.3. Characterization of gratings

Several experimental techniques were used to characterize the HPDLC transmission gratings. Morphologies of the HPDLC samples were examined with scanning electron microscope (SEM) (JEOL 840F). The samples used in the SEM studies were prepared by freezing and fracturing the HPDLC cells using liquid nitrogen, and extracting the LC with reagent-grade methanol. The exposed surface was coated with a very thin layer of Au–Pd to minimize artifacts associated with sample charging. AFM (Nanoscope III, Digital Instrument Inc.) was employed to determine the surface topology of the transmission gratings. The HPDLC cells were disassembled and flushed with methanol several times to remove the LC in preparation for AFM analysis.

Electro-optical performance parameters of the HPDLC gratings were determined by probing the HPDLC cells with a *p*-polarized He–Ne ($\lambda = 632$ nm) laser beam. A gated 1 kHz square wave voltage was applied across the HPDLC cell. The first-order diffracted intensities were monitored as a function of applied voltage. The relaxation times of the HPDLC cells were monitored using an oscilloscope. The relaxation time is defined as the time taken to relax from 90 to 10% of the maximum switching difference under an electric field. To ensure that the electro-optical properties were reasonably stable at the time of testing, all the samples were aged for 5 days prior to any characterization.

The diffraction efficiencies of the HPDLC gratings were

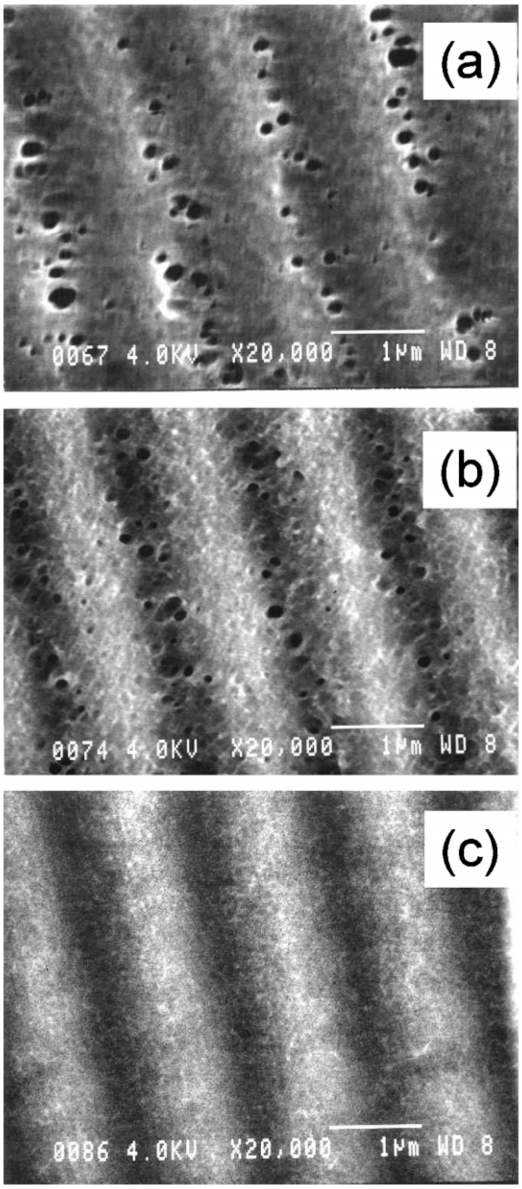


Fig. 2. SEM micrographs of HPDLC transmission gratings prepared by substituting the control monomer mixture with 20 wt% of (a) HFIPA (b) TFEA (c) MA.

measured with a photo-diode. The input beam from a He–Ne laser ($\lambda = 632$ nm) was either p-polarized (in the plane of incidence) or s-polarized (perpendicular to the plane of incidence). The intensity of the diffracted beam was normalized with respect to the sum of the diffracted and directly transmitted beam intensities. The external Bragg angles were adjusted by rotating the samples until the maximum efficiency was observed.

3. Results and discussion

Fig. 2 shows the effect of partial matrix fluorination on the morphology of the HPDLC transmission gratings. Fig. 2(a) and (b) represents the SEM photographs of HPDLC gratings, each prepared by adding 20 wt% of fluorinated monomers HFIPA and TFEA, respectively, to the control monomer mixture. An SEM micrograph of HPDLC grating, prepared with the same amount of non-fluorinated monomer (MA) is shown in Fig. 2(c). The darker regions of the micrographs are representative of the original location of the LC. It has been observed from Fig. 2 that the fluorinated systems display very different morphology in comparison with the non-fluorinated systems with same additive concentration (i.e. with the same average functionality). With the fluorinated monomers the grating microstructures consist of spherical LC domains separated by polymer 'walls' (Fig. 2(a) and (b)) However, with the same amount of non-fluorinated monomer, MA, bi-continuous layers of polymer and LC have been observed without any resolvable features. The LC rich regions with MA are devoid of any specific LC domains (Fig. 2(c)). The average size of LC domains found with HFIPA (Fig. 2(a)) is slightly larger than that found with TFEA (Fig. 2(b)). Fig. 3(a)–(g) shows the gradual change in grating morphology with the incremental addition of HFIPA in the control monomer mixture. The morphology of the HPDLC gratings made from the control formulation (without any fluorinated or non-fluorinated additive) is shown in Fig. 3(a). The LC-rich regions are composed of very small, discrete and nearly spherical domains of size 0.07–0.1 μm. The width of the LC-rich channels are approximately 0.3 μm separated by dense polymer walls with the width of ~1 μm. Up to the addition of 20 wt% of HFIPA (Fig. 3(c)), the grating microstructure does not change considerably except for a slight increase in size and number of LC domains in the LC-rich channels. The concentration and the size of the LC droplets as well as the width of LC-rich channels increase abruptly with 25% HFIPA loading (Fig. 3(d)). With 35 wt% of HFIPA (Fig. 3(f)), the size and shape of the LC domains become very irregular and the holographic planes become highly distorted. The width of the LC channels becomes as large as 0.8–1.0 μm. Beyond 35 wt% of HFIPA loading, no gratings are formed at all. The SEM images of the film with 40 wt% of HFIPA (Fig. 3(g)) resemble 'sponge-like' morphology typical for conventional PDLC film. It is apparent from the SEM micrographs that with the increase in the degrees of fluorine substitution, the size and distribution of the nematic domains, and the LC volume fraction increase in the transmission grating.

It has been seen through SEM that the grating morphology does not change significantly with incorporation of non-fluorinated additive, MA. The LC domains found in the control film (Fig. 3(a)) completely disappeared beyond 20 wt% of MA loading (Fig. 2(c)). This result is in line with our previous observations in which the LC domain size decreases with the increase in the amount of mono-functional acrylates, which eventually caused the average functionality of the system to decrease [21].

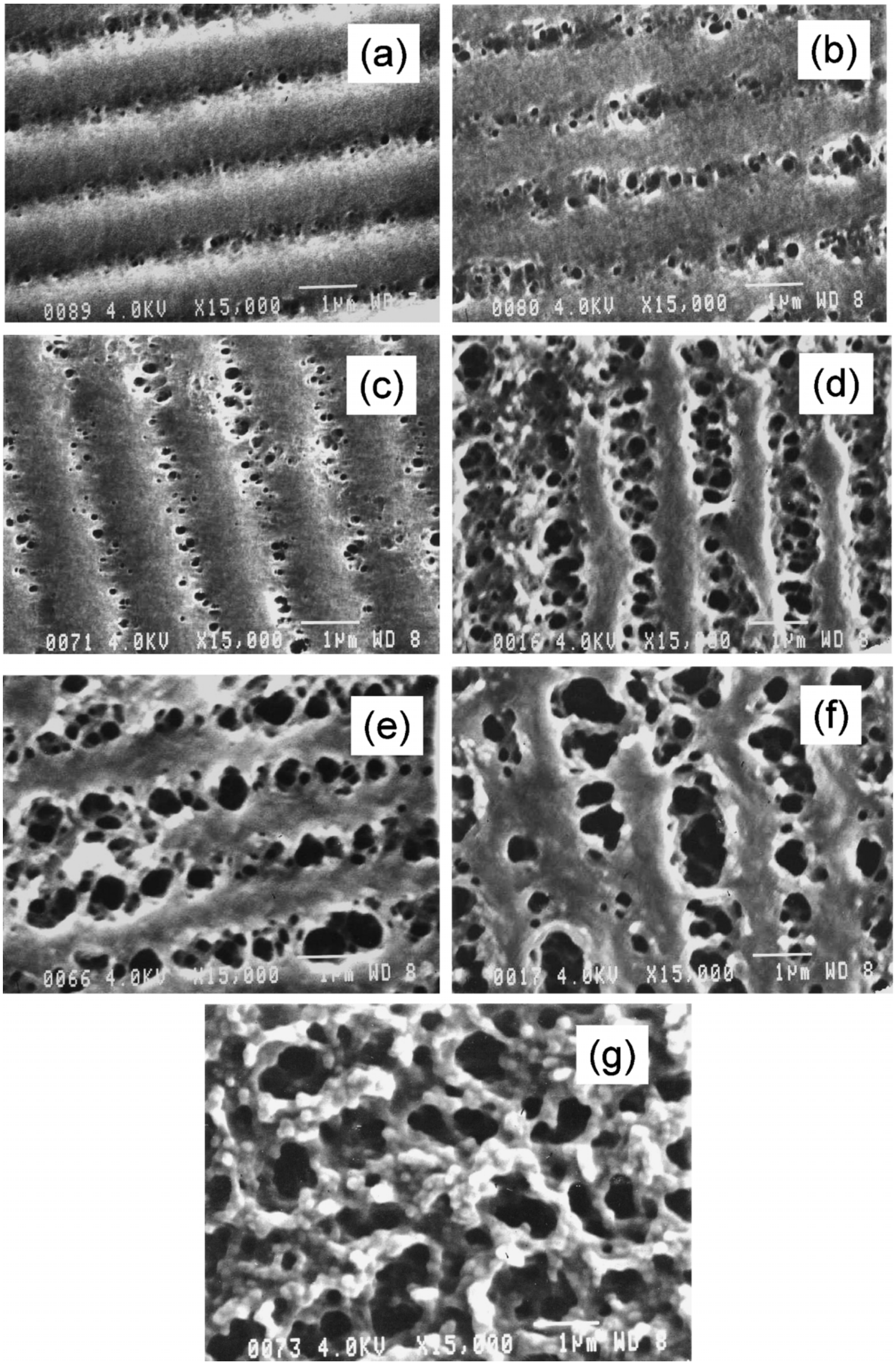


Fig. 3. SEM micrographs of HPDLC transmission gratings prepared (a) from control monomer mixture and substituting it with (b) 10 wt% (c) 20 wt% (d) 25 wt%, (e) 30 wt%, (f) 35 wt% and (g) 40 wt% of HFIPA.

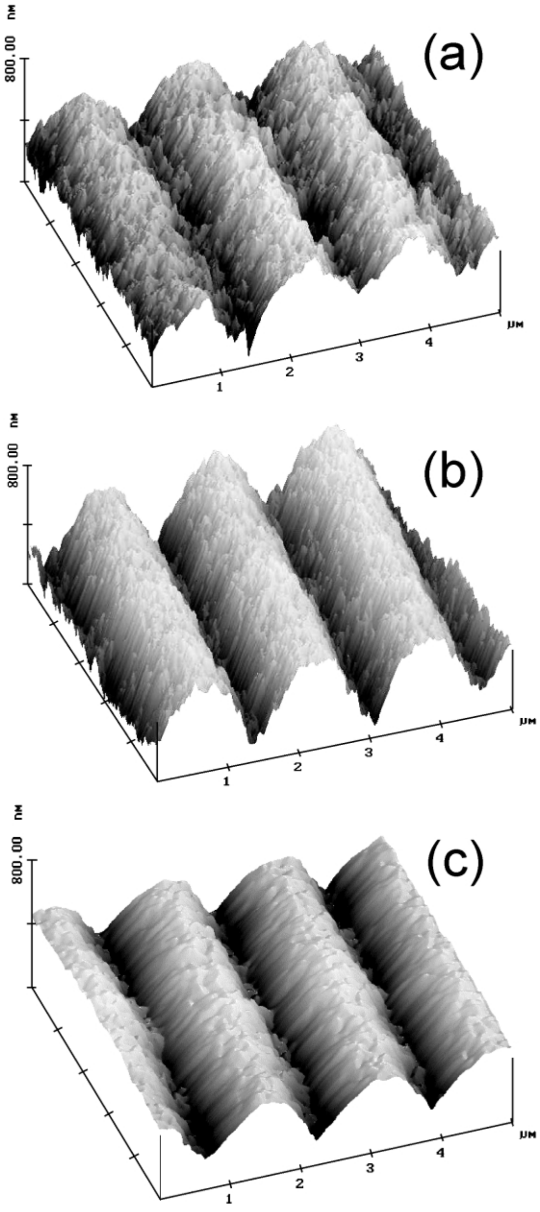


Fig. 4. Atomic force microscope profiles of the HPDLC transmission gratings prepared by substituting the control monomer mixture with 20 wt% (a) HFIPA (b) TFEA and (c) MA.

During the hologram writing process, the average functionality of the monomers dictates the cross-link density, thereby influencing the incipient formation of LC droplets. The higher the average functionality of the system, the higher the cross-link density, and the more LC will be forced out from the polymer matrix ensuing in bigger droplets. However, our present studies show that by adding fluorine containing mono-functional monomers in the pre-polymer formulation, the LC domain size increases significantly in the resulting gratings though their addition causes a decrease in average functionality of the system (Table 1).

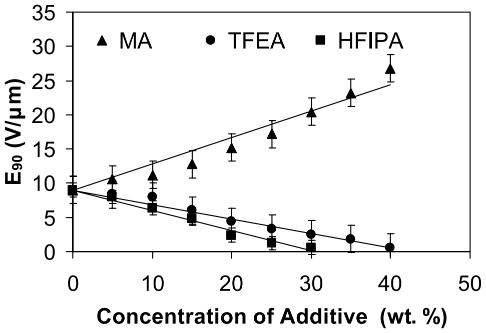


Fig. 5. Influence of additive concentrations on the switching properties of HPDLC transmission gratings.

In order to study the consequences of partial matrix fluorination on the surface topology of the HPDLC gratings, the AFM was performed in the tapping mode. Fig. 4(a)–(c) shows the three-dimensional view of the transmission gratings formed by substituting the control monomer mixtures with 20 wt% of HFIPA, TFEA and MA monomers, respectively. The surfaces of all the gratings show sinusoidal type profiles. The AFM image for the grating made with 20 wt% of HFIPA (Fig. 3(a)) demonstrates a very uneven and heterogeneous texture. The grainy appearance of the surface relief is attributed to the presence of LC domains in the polymer matrix. Conversely with 20 wt% of MA, the grating surface appears to be very smooth (Fig. 3(c)). The grating made with TFEA shows intermediate behavior. An interesting feature observed in AFM is that the depth of the gratings apparently increases with matrix fluorination. The average depth of grating with 20 wt% MA has been found to be 0.25 µm (Fig. 4(c)). With the same amount of TFEA, the grating depth becomes 0.47 µm (Fig. 4(b)). Due to the surface irregularities associated with transmission gratings prepared using HFIPA, it is difficult to measure the depth of the grating grooves accurately. However, from the two dimensional surface profile over a relatively larger area (not shown here), the average depth of the grating made with HFIPA has been found to be around 0.45 µm. The AFM observation of higher depth of grating associated with partial matrix fluorination indicates better phase separation between the LC and the fluorinated polymer host. The enhanced phase separation can be interpreted by considering the reduced solubility of the fluorinated LC in the partially fluorinated polymer matrix.

Fig. 5 shows the effect of the additive concentration on the HPDLC electro-optical performance. The parameter E_{90} is defined here as the electric field required attaining 90% zero field efficiency of the first order diffraction peak. It has been observed that E_{90} steadily decreases with increasing amount of fluorinated monomers. On the contrary, E_{90} increases progressively with the increase in MA loading. The reduction in E_{90} is more pronounced with HFIPA compared to that in TFEA. The control HPDLC grating made without any mono-functional monomer additive possessed E_{90} of 9 V/µm. With the addition of 30 wt% of TFEA and HFIPA, E_{90} values have significantly decreased to 2.5 and 0.6 V/µm, respectively. Interestingly, the addition of the same amount of MA to the formulation leads to an increase in E_{90} to approximately 20 V/μm.

The switching performance of HPDLC gratings, in general, diminishes with the decrease in the size and distribution of LC domains [20]. In the present study, the decrease in E_{90} with the increasing level of fluorination can be attributed to the significant increase in the size and distribution of nematic domains, as well as the increase in the amount of phase separated LC with incorporation of fluorinated additives. It has also been observed through SEM that the size of the LC domains decreases with the addition of non-fluorinated monomer MA, which justifies the increasing of E_{90}.

For the PDLC or HPDLC systems, the anchoring strength between the nematic LC domains and the polymer host plays a very important role to dictate the electro-optical properties. If the anchoring strength between the LC molecules and polymer matrix is weakened, less voltage is required to re-orient the LC molecules with applied field. For the organic surfaces, it has been established that the surface energy decreases with increasing fluorine content in the following order: $CH_2 > CH_3 > CF_2 > CF_3$ (36:30:23:15 dyn/cm, respectively) [23]. Based on this observation, we believe the decrease in surface energy of the polymer matrix with partial fluorination will reduce the anchoring strength of the LCs. From our switching results, it is reasonable to speculate that the substantial decrease in E_{90} with the matrix fluorination may not only be caused by the larger nematic domains from better phase separation but it also could be due to the weakening of the surface anchoring strength with matrix fluorination. We invoked here a very simple calculation to get a rudimentary estimation of how the anchoring strength between the LC molecules and polymer host changes with fluorination. We adopted an expression for anchoring density (W) of the nematic LC on polymer matrix as [24]

$$W = \frac{3\varepsilon_0\varepsilon_P\left[\dfrac{3\varepsilon_P(\varepsilon_\parallel - \varepsilon_\perp)}{(\varepsilon_\parallel + 2\varepsilon_P)(\varepsilon_\perp + 2\varepsilon_P)} + C(f,\lambda)\right]}{8\pi}E_{th}^2 \qquad (1)$$

where $\varepsilon_\parallel, \varepsilon_\perp$ are the dielectric constants parallel and perpendicular to nematic director, ε_P is the dielectric constant of the polymer matrix, ε_0 is the permittivity of vacuum, $C(f,\lambda)$ is a function of the droplet volume fraction f and the micro-geometrical parameter λ. E_{th} represents here the threshold electric field for the Freedericksz transition for the confined LC droplets in PDLC systems and experimentally we take E_{90} as E_{th} for this simple estimation. The droplets are assumed here to be bipolar, mono-dispersed and nearly spherical.

We extended the expression of W to our HPDLC systems and assumed E_{th} to be the switching threshold electric field required for our HPDLC transmission gratings. For simplicity, the $C(f,\lambda)$ term is neglected. We can rewrite Eq. (1) as

$$W = \frac{9\varepsilon_0\varepsilon_P^2(\varepsilon_\parallel - \varepsilon_\perp)}{8\pi(\varepsilon_\parallel + 2\varepsilon_P)(\varepsilon_\perp + 2\varepsilon_P)}E_{th}^2 \qquad (2)$$

Since the volume and the surface area for a nearly spherical nematic droplet with average radius R are approximately $4\pi R^3/3$ and $4\pi R^2$, respectively, the surface anchoring strength between the LC droplet and the polymer matrix, W_s is related to the anchoring density W as

$$W_s = \frac{WR}{3} \qquad (3)$$

Therefore, the anchoring strength is given by

$$W_s = \frac{3\varepsilon_0\varepsilon_P^2(\varepsilon_\parallel - \varepsilon_\perp)}{8\pi(\varepsilon_\parallel + 2\varepsilon_P)(\varepsilon_\perp + 2\varepsilon_P)}E_{th}^2 R \qquad (4)$$

The permittivity of the vacuum ε_0 is 8.85×10^{-12} F/m. It is evident that the incorporation of fluorine in polymer matrix would modify the magnitude of the dielectric constant of the polymer matrix ε_P. However, from Eq. (4) it is apparent that the small variation in ε_P does not affect W_s to a large extent, therefore we assume $\varepsilon_P \approx 3$ through out our calculations of W_s.

Putting all the constants in Eq. (4), we can write

$$W_s = 0.484 \times 10^{-6} E_{th}^2 R \qquad (\mathrm{N/m}) \qquad (5)$$

The average droplet radius R (in μm) is obtained from the SEM micrographs and E_{th} (in V/μm) is obtained from our electro-optical measurements. Fig. 6 shows the change in anchoring strength as a function of concentration of HFIPA in the control monomer mixture. In this simple model, it can be seen that with partial matrix fluorination the anchoring strength decreases.

Relaxation times were measured to assess the effect of matrix fluorination on the response of HPDLC gratings to the applied electric field. There is an increase in relaxation time with the incremental addition of fluorinated monomers TFEA and HFIPA (Fig. 7). The HPDLC gratings prepared from the control monomer mixture (without any monomer additive) shows a relaxation time of 1.6 ms. With 35 wt% of TFEA, the relaxation time has increased to 18 ms. A 35 wt% of HFIPA causes an even stronger effect and the

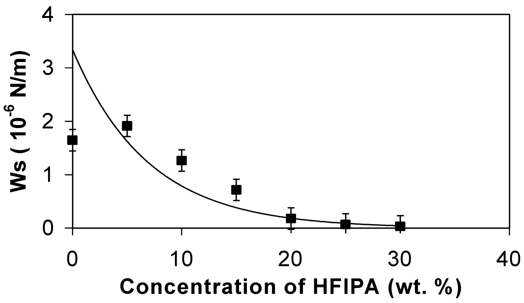


Fig. 6. Plot of anchoring strength as a function of concentration of HFIPA additive. A best fit line has been drawn through the experimental points to show the trend.

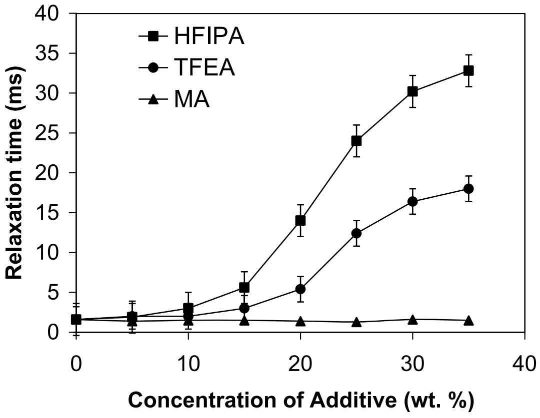


Fig. 7. Influence of additive concentrations on the relaxation times of HPDLC transmission gratings.

relaxation time becomes 33 ms. On the other hand an incorporation of non-fluorinated MA does not cause any substantial change in relaxation time. It is well known that the relaxation time is governed by the surface anchoring energy, elastic free energy, viscosity as well as the size of the LC droplet [1]. In our system, the decrease in surface anchoring strength and the increase in size of the nematic domains with matrix fluorination both accounts for the increase in relaxation time.

Fig. 8(a) and (b) demonstrates the influences of additive concentration on the 1st order diffraction efficiencies of the HPDLC gratings with *p*- and *s*-polarized light, respectively. HPDLC grating prepared from control formulation without any mono-functional additives possess diffraction efficiencies of 58% with *p*-polarized light and only 2% with *s*-polarized light. In general, with fluorinated monomers, irrespective of the polarization of the probe beam, the diffraction efficiency increases initially, reaches its maximum at a particular concentration and decays rapidly with further addition. The optimum concentration required to achieve maximum efficiency depends on the fluorine content of the additive. It is interesting to notice that at the intermediate concentrations, ranging 5–20 wt% for HFIPA and 10–30 wt% for TFEA, the diffraction efficiencies with *p*-polarization decrease, whereas, with *s*-polarization the efficiencies show an increasing trend. The changes in diffraction efficiencies for both *p*- and *s*-polarizations with an addition of 5–20% of HFIPA are shown as an inset of Fig. 8(b). With incremental addition of non-fluorinated monomer MA, the diffraction efficiency with *p*-polarization increases gradually and saturates after 20 wt% and with *s*-polarized beam, the diffraction efficiencies remain almost unchanged upon its addition.

The calculated refractive index of the control monomer mixture was 1.44. All the monomer additives (non-fluorinated or fluorinated) possess refractive indices ranging from 1.40 to 1.32. Therefore, the addition of monomer additives in the control mixture results in an overall decrease in refractive index. Hence the initial increase in diffraction efficiency with the addition of mono-functional additives, shown in Fig. 8, can be attributed to the improved optical index modulation. With a higher loading of fluorinated monomers (e.g. >20 wt% of HFIPA), the nematic domains present in the HPDLC cells become larger and very irregular in shape. The large sized nematic domains account for the high scattering loss, hence, the diffraction efficiency of the grating decreases drastically, irrespective of the polarization of the probe.

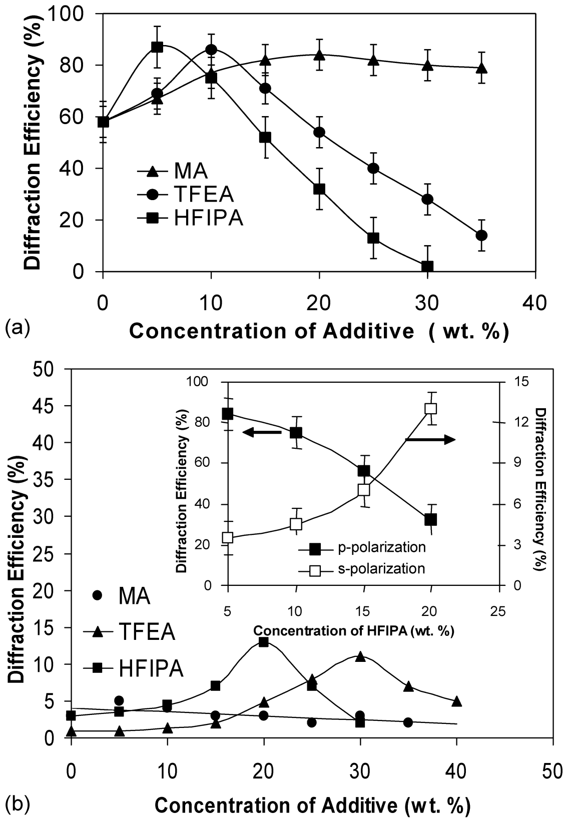


Fig. 8. Influence of additive concentrations on the diffraction efficiencies of the HPDLC transmission gratings measured with (a) *p*-polarized beam, (b) *s*-polarized beam. The inset of (b) shows the change in diffraction efficiencies with addition of HFIPA with both *p*- and *s*-polarizations.

An effort has been taken to explain the polarization dependencies of the diffraction efficiencies of the HPDLC cells in the intermediate level of fluorination by considering the orientation of LC inside the domains. At any instance during the holographic writing process, the concentration of mono-functional monomers (low molecular weight) would be higher in the high intensity regions. On the other hand, the multifunctional monomers with more cross-link sites get attached with growing polymer chains fairly easily and their movements thereby become restricted. The higher functionality monomers thus cannot diffuse readily out of the low intensity regions. As a result, the extent of diffusion towards high intensity regions is much less with higher functionality monomers compared to that of low functionality ones. Since the pre-polymer syrup contains both mono- and multi-functional (hexa- and tri-) monomers, a significant modulation of cross-link density across the grating is created [25].

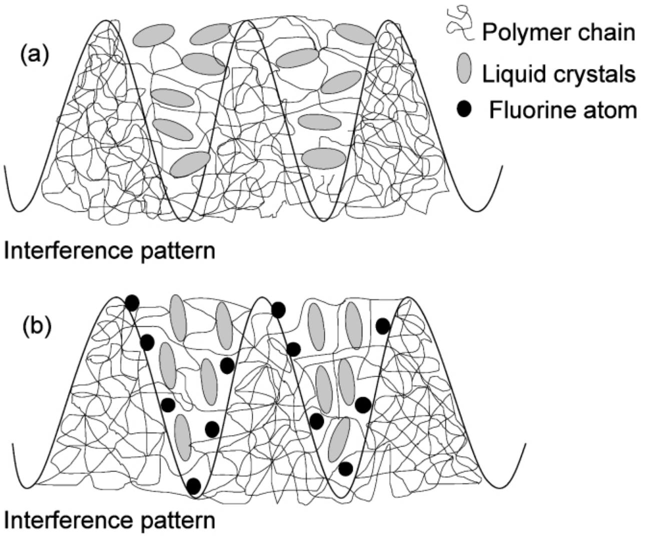


Fig. 9. Schematic representations of HPLDC gratings (a) before and (b) after partial matrix fluorination.

The dark fringes are composed of greater concentration of tri- and hexa-functional acrylates whereas the bright fringes are predominantly composed of mono-functional monomers. Our pre-polymer syrups consist of two mono-functional monomers with different reactivity and rate of diffusion. We have EHA, from the control mixture and one of the mono-functional fluorinated or non-fluorinated monomer additives. Fluorinated monomers, particularly HFIPA containing six fluorine atoms per molecule are expected to have low reactivity in comparison to EHA because of the high electron-withdrawing effect of the fluorine atoms from the adjacent reactive double bonds. In the PDLC systems, it has been reported that the slower reacting monomers preferentially incorporated at the LC–polymer interface [26]. Therefore, we can assume that in our transmission gratings the fluorinated polymer chains will reside near the interface of ‘LC rich’ and ‘polymer rich regions’ with highly electronegative fluorine atoms segregating at the interface in order to circumvent the strong electro-static repulsions present in the bulk. Consequently, the interface will selectively become enriched with fluorine. Our assumption is consistent with the fact that the fluorinated polymer chains preferentially resides at the less-polar interface rather than present in the bulk [27]. The results obtained here from the switching voltage and relaxation time measurements point toward the fact that with partial fluorination of polymer matrix the LC–polymer interface becomes rich with fluorine. It is well known that the chemical nature of the polymer surface influences the LC alignment at the interface [28]. Therefore, it is logical to speculate that the fluorine atoms present at the LC/polymer interface will also manipulate the surface alignment of LCs. The strong *p*-polarization dependence of the diffraction efficiency of the gratings made from the control formulation (without any additives) indicates that the average droplet directors are aligned orthogonal the holographic planes, as shown schematically in Fig. 9(a). In the case of fluorinated HPDLCs, it has been observed that the surface anchoring energy is substantially reduced. Hence, with an increasing level of matrix fluorination the order of LC droplet directions decreases. Under that condition, the *s*-polarized light-waves will interact more effectively with the LCs, resulting to an increase in diffraction efficiency. This interpretation based on the relaxation of the alignment of LC droplet directors supports our experimental observations of the simultaneous decrease and increase in diffraction efficiencies measured with *p*- and *s*-polarized lights, respectively in the intermediate fluorination level.

We investigated the IR spectra under our present experimental condition and found that almost all the double bond are consumed irrespective of presence of fluorinated/non-fluorinated additives. IR spectra of our samples did not show any significant peaks in the regions of $\sim 1640\ \mathrm{cm}^{-1}$ (C=C stretching vibration) and $\sim 970\ \mathrm{cm}^{-1}$ (alkene C–H vibration), indicating completion of polymerization. We believe that the increase in diffraction efficiency shown in Fig. 8 is due to the over-all decrease in refractive index with addition of fluorinated monomers.

4. Conclusions

Partial fluorination of the polymer matrix demonstrated significant effects on the morphology and electro-optical performance of the HPDLC transmission gratings. The morphology of the fluorinated transmission gratings displayed an enhanced phase separation as manifested in a significant increase in nematic domain size and the LC volume fraction. The incorporation of fluorinated monomers in the standard UV HPDLC formulation reduces the switching voltage considerably. The relaxation time also increases with fluorination. These results strongly indicate that significant amount of fluorine atoms resides on the polymer–LC interface. The presence of fluorine atoms at the interface can manipulate the surface anchoring strength and alignment, causing a re-orientation of the original configuration of the LC droplet directors.

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