Holographic PDLC Containing Fluorine Segments

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Transmission gratings of holographic polymer dispersed liquid crystals (HPDLCs) have been designed and fabricated based on partial fluorination of the polymer matrix using three types of fluorinated monomers carrying different numbers of fluorine atoms and structures, viz. 2-(perfluoroalkyl)ethyl methacrylate (PFEMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), and 2,2,2-trifluoroethyl acrylate (TFEA). Addition of fluorinated monomer gave long saturation time, increased off state diffraction efficiency, small anchoring strength and driving voltage. Anchoring strength and driving voltage of methacrylate monomers (PFEMA and TFEMA) were lower than that of TFEA, implying that the fluorine segments of these monomers are preferentially exposed to the interfaces. HPDLC film having low driving voltage and response time of below 10 ms has been fabricated with 20 wt % PFEMA at 40 wt % LC.

Holographic polymer dispersed liquid crystals (HPDLCs) have a number of potential applications such as displays and optical shutters. In such applications, high diffraction efficiency and low driving voltage are highly desired.[1–3] Diffraction efficiency generally increases when the mismatch of refractive indices between polymer and LC is high,[4] which results from good phase separation of LC from polymer. Upon photopolymerization, the chemical potential of the monomer in bright regions is decreased compared to that in dark regions. Conversely, chemical potential of LC increases in bright regions due to the consumption of monomer. Since the system attempts to equalize the chemical potentials of each component, monomer diffuses into the bright regions and LC toward the dark regions, which are periodically formed.

The incident light is refracted due to the difference in the refractive indices of the polymer and LC. Therefore, a key parameter to control the diffraction is the clean phase separation between polymer and LC regions by decreasing miscibility of the two components.[5–7] However, when the miscibility is too small the prepolymer mixture can phase separate before curing.

Electro-optical properties of HPDLC films are of practical importance.[8,9] Upon applying an electric field, LC molecules near the center quickly orient along the field direction giving a fast optical response. However, LC molecules at the surface layer are rotated slowly giving a long optical response. Upon removal of the electric field, the center of the droplet can quickly relax while the rest moves slowly since the LC molecules are anchored on the resin surface.[3] Therefore, it is important to reduce the anchoring strength of the system to lower the driving voltage and response time of LC.[10] Crawford et al.[11] added fluorinated monomers to a conventional HPDLC formulation and reported significant decrease in switching voltages and higher relaxation times, together with extensive morphology study.

In this experiment, we incorporated various amounts and types of fluorinated monomers carrying different numbers of fluorine atoms and structures, viz. 2-(perfluoroalkyl)ethyl methacrylate (PFEMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), and 2,2,2-trifluoroethyl acrylate into the polymer matrix, and the influences have been studied in terms of the off state diffraction efficiency, morphology, anchoring strength, and electro-optical property of the films. Results were also interpreted in terms of solubility parameter (SP) gap between polymer and LC.

Experimental

Materials and Oligomer Synthesis. Poly(urethane acrylate) (PUA) oligomers were synthesized from poly(propylene glycol) (PPG, $M_n = 300$) and a molar excess of hexamethylene diisocyanate (HDI) to form isocyanate terminated prepolymers, followed by capping with hydroxyethyl methacrylate (HEMA). Detailed synthetic procedures are described in our earlier paper.[12,13]

The composite films were prepared from a homogeneous prepolymer mixture consisting of a PUA oligomer, the nematic LC (E7), and reactive diluents viz., *N*-vinylpyrrolidone (NVP) and dipentaerythritol hexa/pentaacrylate (DPHPA) were used to control the viscosity and functionality of prepolymer respectively. The prepolymer composition was fixed at 4/3/3 (oligomer/DPHPA/NVP) by weight. Three types of fluorinated monomer viz. 2-(perfluoroalkyl)ethyl methacrylate (PFEMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), and 2,2,2-trifluoroethyl acrylate (TFEA), were incorporated for partial fluorination of the host polymer (Figure 1).

E7 ($n_o = 1.5216$, $n_e = 1.7462$, and $T_{NI} = 61\,°C$) was used as LC at two loadings viz. 40 and 45%. Rose Bengal (RB) and *N*-phenylglycine (NPG) were respectively used as photoinitiator and co-initiator for holographic recording with an Ar-ion laser.

Grating Fabrication. Cells were constructed by sandwiching the PUA oligomer, reactive diluents (DPHPA and NVP), fluorinated monomer, and LC mixture between two indium tin-oxide (ITO) coated glass plates with a gap of 10 µm, adjusted by a bead spacer.[14] The interference of the two beams establishes a periodic

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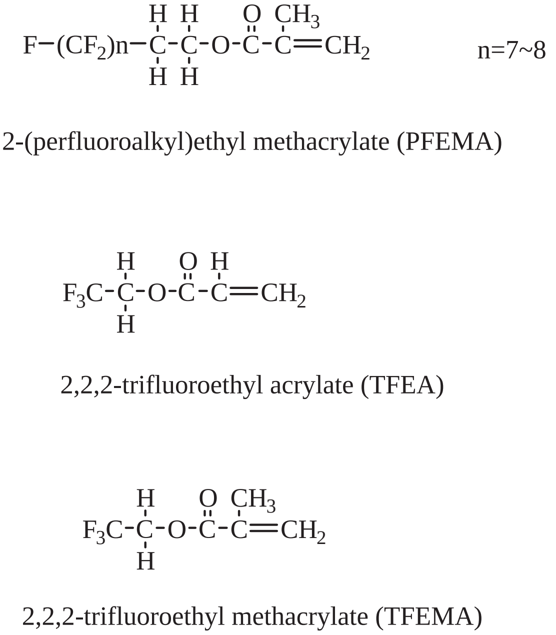


Figure 1. Chemical structures of fluorinated monomers.

pattern according to Bragg's law,[15] which is approximately 514 nm at 100 mW cm^{-2} with exposure times of 3 min. The intersection angle (θ) of the two beams outside the cell was fixed at 30°.

Measurements. Reading was accomplished by using the 514 nm beam from an Ar-ion laser, positioned at the Bragg angle, the same angle as the recording beam. The diffraction beam was detected by a photodiode detector. Diffraction efficiency was determined upon dividing the diffracted beam intensity of the sample cell by the transmitted beam intensity of a blank cell.[16,17] The saturation time of the diffracted beam was monitored by a detector at a probing wavelength of 633 nm from a He-Ne laser.

For electro-optic measurement, an electric field was applied across the film from 0 to 65 V. Response time was monitored with a digital storage oscilloscope (Hitachi VC-6023).

To obtain atomic force microscopy (AFM) images, LC was first extracted in methanol for 24 h before the cells were fractured in liquid nitrogen. The average droplet size can be obtained from the AFM image. For this, AFM images of LC channels were taken. Then, a number of straight lines were drawn on the micrograph and average size of particles lying on the line was calculated. Finally, the average of all the lines was calculated to report the average droplet size of the sample.

Results and Discussion

Miscibility. The miscibility of a polymer and LC can be approximated by the SP gap. The SP is the square root of the cohesive energy density (E_c) which can be calculated by group contribution theory.[18] SP of LC is 20 (J cm^{-3})$^{1/2}$ and that of PUA is 22 on average, whereas those with TFEMA, TFEA, and PFEMA are respectively 16.54, 16.37, and 15.53 (J cm^{-3})$^{1/2}$. So, the SP gap and polymer–LC immiscibility increase along

$$\text{PUA} < \text{TFEMA} < \text{TFEA} < \text{PFEMA}. \tag{1}$$

Saturation Time of Diffraction. The reactive sites are included in HEMA termini of oligomer, reactive diluents and fluorinated monomers. The overall reaction is governed by the slowest reaction step which is the addition reaction of fluorinated monomer onto the propagating oligomer chains. And statistically, the fluorine segments become the chain termini of the polymer. As expected, saturation time increased with fluorinated monomer due to low reactivity (Table 1). Moreover, saturation time increases as the SP gap decreases. By far the slowest saturation (101 s) of TFEMA comes from the combined effects of small miscibility gap and slow reaction due to the steric hindrance of the methyl group on the vinyl group. The fluorinated monomers exert dual effects: they retard reaction and accelerate phase separation.

Table 1. Saturation Time of Diffraction Efficiency Monitored by a He-Ne Probe (Oligomer/DPHPA/NVP = 4/3/3)

Fluorinated monomer		LC content /wt %	Saturation time of diffraction efficiency/s	Run number
Type	Content /wt %			
w/o	—	40	21	1
		45	15	2
PFEMA	20	40	26	3
	20	45	19	4
	40	40	31	5
	40	45	21	6
TFEA	20	40	35	7
TFEMA	20	40	101	8

High LC content generally induces fast saturation (Runs 1–6). LC lowers mixture viscosity and augments mobility of the reactive mixture[19] which leads to fast diffusion, fast polymerization, and fast phase separation. The law of mass action states that rate of reaction increases with reactant concentration. However, our results support that the effect of viscosity is much more pronounced than that of reactant concentration. Thus, saturation time of diffraction efficiency becomes shorter with more LC.

Diffraction Efficiency. Diffraction efficiencies of the HPDLC films prepared with various types and contents of fluorinated monomer are shown in Figure 2. With the addition of fluorinated monomer, diffraction efficiency increases over PUA and reaches a maximum of over 80% with 5 wt % PFEMA and TFEMA, and over 90% with 20 wt % TFEA, indicating that the proper immiscibility introduced by the fluorine segment increases phase separation. However, beyond the maximum concentration, diffraction efficiency decreases below that of PUA. The decrease is due to slow reaction and great droplet coalescence. The earlier maxima obtained with the methacrylate monomers are due to their low reactivity. However, the small SP gap of TFEMA leads to a long saturation time and small droplet size, whereas the large SP gap of PFEMA gives short saturation time allowing droplet coalescence. On the other hand, reactivity of TFEA is much greater than TFEMA due to the absence of the pendant methyl group, which induces optimum monomer concentration much greater than TFEMA.

Anchoring Strength and Electro-Optical Properties. Threshold voltage (E_{th}) and surface anchoring strength (W_s) are related by the following equation.[11,20]

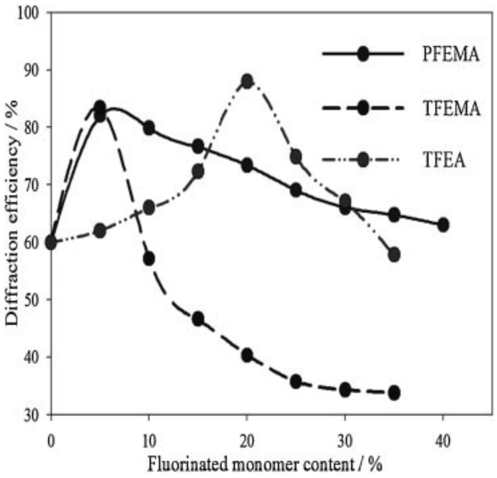


Figure 2. Diffraction efficiency vs. content and type of fluorinated monomer (40 wt % LC).

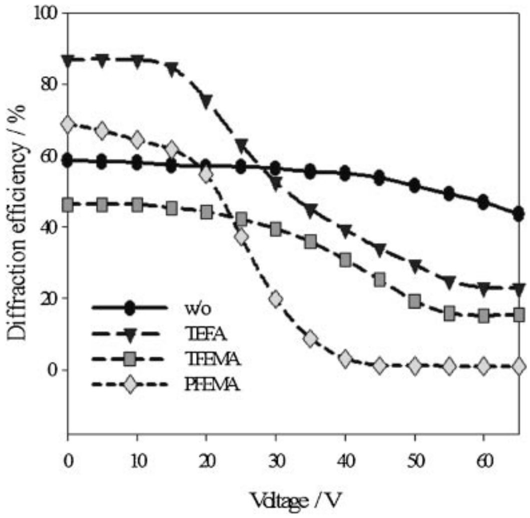


Figure 3. Diffraction efficiency vs. applied voltage according to the type of fluorinated monomer (40 wt % LC, 20 wt % fluorinated monomer).

$$E_{\mathrm{th}}^2 = \frac{8\pi W_{\mathrm{s}}(\varepsilon_\parallel + 2\varepsilon_{\mathrm{P}})(\varepsilon_\perp + 2\varepsilon_{\mathrm{P}})}{3R\varepsilon_{\mathrm{o}}\varepsilon_{\mathrm{P}}^2(\varepsilon_\parallel - \varepsilon_\perp)}, \tag{2}$$

where ε_{o}, ε_{p}, $\varepsilon_\parallel$, $\varepsilon_\perp$, and R are respectively vacuum permittivity, dielectric constant of polymer, the dielectric constants parallel and perpendicular to the nematic director of LC, and average radius of LC. In our experiment, ε_{o}, ε_{p}, $\varepsilon_\parallel$, and $\varepsilon_\perp$ are 8.85×10^{-12}, 3, 19.0, and 5.4. The R and E_{th} are obtained from AFM morphology and Figure 3, respectively.

Table 2. Droplet Size and Anchoring Energy of HPDLC Film Prepared from Various Types of Fluorinated Monomer (20 wt % Fluorinated Monomer, 40 wt % LC)

Prepolymer	Type of fluorinated monomer	Droplet size/nm	Anchoring strength /$\times 10^{-6}$ N m^{-1}
	w/o	215	2.6
Oligomer /DPHPA/NVP	PFEMA	263	0.5
	TFEA	232	1.4
	TFEMA	206	0.9

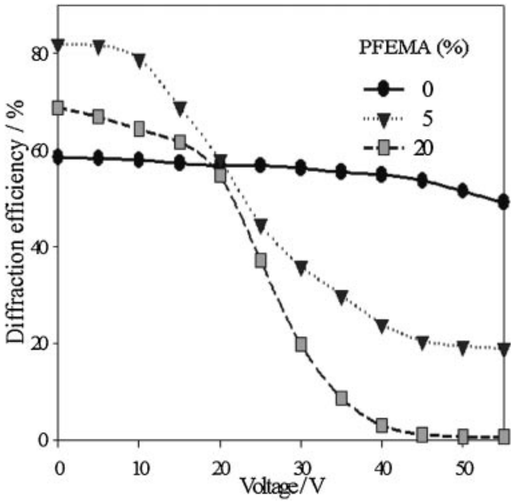


Figure 4. Diffraction efficiency vs. applied voltage according to PFEMA content (40 wt % LC).

Table 2 shows droplet size of LC and anchoring strengths calculated using eq 2 for various types of fluorinated monomer. Droplet size increases according to

$$\text{TFEMA} < \text{PUA} < \text{TFEA} < \text{PFEMA}, \tag{3}$$

the order corresponding to increasing SP gap (immiscibility) except PUA due probably to its greater SP than LC. Apparently, the droplet size is governed by the miscibility as in polymer–polymer blends. However, in HPDLC large droplets are obtained by coalescence, whereas the droplet size is determined by miscibility of the blend components in the polymer blend.

Anchoring strengths (W_{s}) calculated from eq 2 increase along the order of

$$\text{PFEMA} < \text{TFEMA} < \text{TFEA} < \text{PUA}. \tag{4}$$

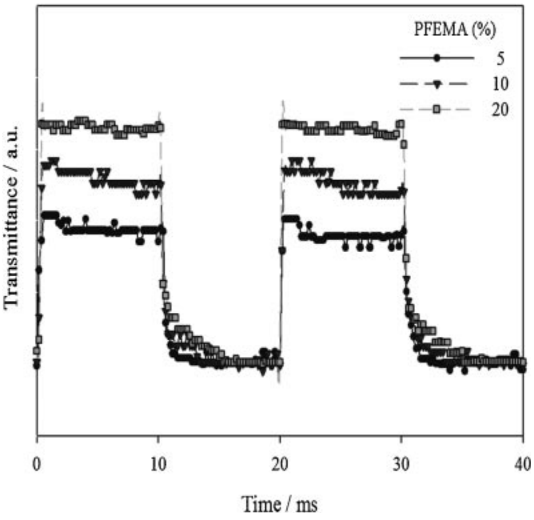
The fluorinated monomers lower anchoring energy since these monomers are added to the oligomers at the last stage of reaction to form the chain termini which are preferentially exposed to the surface by the low free energy of fluorinated monomer. It is noted that methacrylate monomers induce still lower anchoring energy due to their low reactivity. This, together with the largest number of fluorine atoms, PFEMA induces the lowest anchoring strength.

Figure 3 shows the applied voltage dependence of the diffraction efficiency according to the type of fluorinated monomer. When a voltage is applied across the film, diffraction efficiency decreases due to the orientation of LC molecules along the electric field direction.[21–23] Therefore, interface anchoring is a most important fact in driving the HPDLC film. It is seen that the driving voltage of film increases with increasing anchoring strength as above. Generally, driving voltage increases with decreasing droplet size.[24,25] However, driving voltage of TFEMA is lower than that of TFEA despite the small droplet size of TFEMA. As is indicated by eq 2, this is attributed to its lower surface anchoring strength (Table 2).

Effect of fluorinated monomer content on the switching voltages has been studied with PFEMA in Figure 4 where measurements were made at two monomer concentrations. Off state diffraction efficiency showed a maximum at 5% PFEMA (Figure 2) and decreased asymptotically to about 20%, indicating that the orientations of LC molecules were not completed. However, at 20% PFEMA droplets coalesce and the polymer interfaces include more fluorinated segments. This lowers anchoring strength and gives more or less perfect orientation of the LC molecules giving diffraction efficiency close to zero.

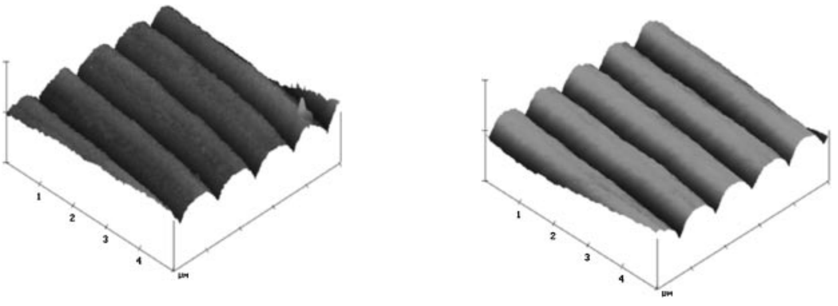
Figure 5 shows rise time (τ_R) and decay time (τ_D) of the HPDLC films. Rise time decreases and decay time increases with applied voltage[26] and the response time ($\tau_R + \tau_D$) is less than 10 ms. Rise time rapidly decreases with increasing PFEMA content due to the decreased anchoring strength. However, decay time gets larger with increasing PFEMA content, implying that distortion energy of LC droplets decreased by low anchoring strength as well as increased droplet size.

Morphology. AFM morphologies of the holograms are shown in Figure 6 where dark channels represent those previously occupied by LC and bright ones by polymer. It is seen that AFM morphologies show the size of LC droplets, Bragg period as well as polymer–LC interfaces. Grating images of PFEMA, TFEA, and PUA are fairly well fabricated. However, gratings TFEMA are a bit distorted and not uniform along the grating direction, which leads to a lower diffraction efficiency compared with others (Figure 2). Also, droplet size of the films increases with the addition of PFEMA (263) and TFEA (232) and decreases with TFEMA (206 nm) as compared with PUA (215 nm). The depth profile of grating from the AFM image also agreed with the droplet size although there is no direct evidence of a relationship between the droplet size and depth.



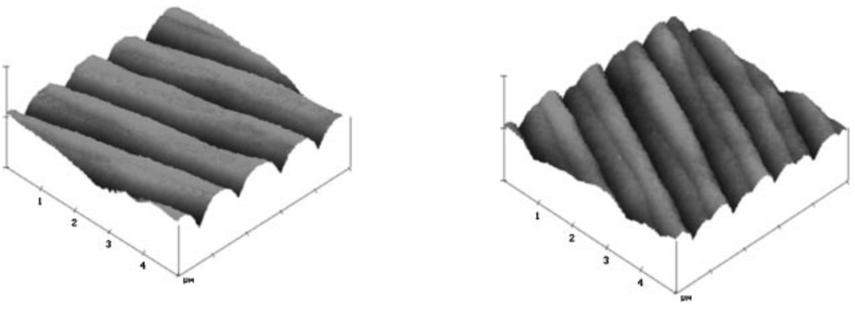
PFEMA (%)	Rise time (µ s)	Decay time (ms)
5	900	2.3
10	700	4.5
20	400	6.8

Figure 5. Response time vs. PFEMA content for the HPDLC films (40 wt % LC, 40 V).



(a) R=215 nm

(b) R=232 nm



(c) R=263 nm

(d) R=206 nm

Figure 6. AFM morphology of HPDLC film w/o fluorinated monomer (PUA) (a), w/ TFEA (b), PFEMA (c), and TFEMA (d) (40 wt % LC, 20 wt % fluorinated monomer, $\theta = 30°$).

Conclusion

HPDLCs have been fabricated by introducing a number of different types and lengths of fluorine segments at the polymer–LC interfaces based on the poor solubility and reactivity of fluorine monomers, and low free energy of chain ends.

The addition of fluorinated monomer to the conventional formulation based on PUA exerted dual effects on the off state diffraction, i.e., delayed saturation due to its low reactivity and increased efficiency by the decreased miscibility of polymer matrix with LC.

With increasing amount of fluorine monomer, the off state diffraction efficiency increased over PUA and showed a maximum due to the decreased miscibility and increased phase separation. However, beyond the maximum concentration, gratings were hardly formed either by slow reaction or extensive droplet coalescence due to the great immiscibility.

Driving voltage decreased with the addition of fluorinated monomer due to decreased anchoring strength. Also, anchoring strength and driving voltage of methacrylate monomers (PFEMA and TFEMA) were lower than that of TFEA, implying that the pendant methyl group decreases monomer reactivity. Statistically, low reactivity monomers are reacted at the last stage of reaction to form chain termini which are exposed to the interfaces and reduce anchoring strength.

HPDLC film having driving voltage of about 4 V μm^{-1} and response time below 10 ms has been fabricated with 20 wt % PFEMA at 40 wt % LC.

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