Electro-optic Properties of Reflective HPDLC with Fluorinated Polymer Matrices

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Abstract

We modified the molecular structure of urethane acrylate oligomer by varying raw materials. Also fluorination of the host polymer matrices has been found to influence the morphological and the electro-optical properties of the resulting HPDLC grating. The incorporation of fluorinated monomers in HPDLC formulation enhance the LC phase separation and improved elctro-optical properties.

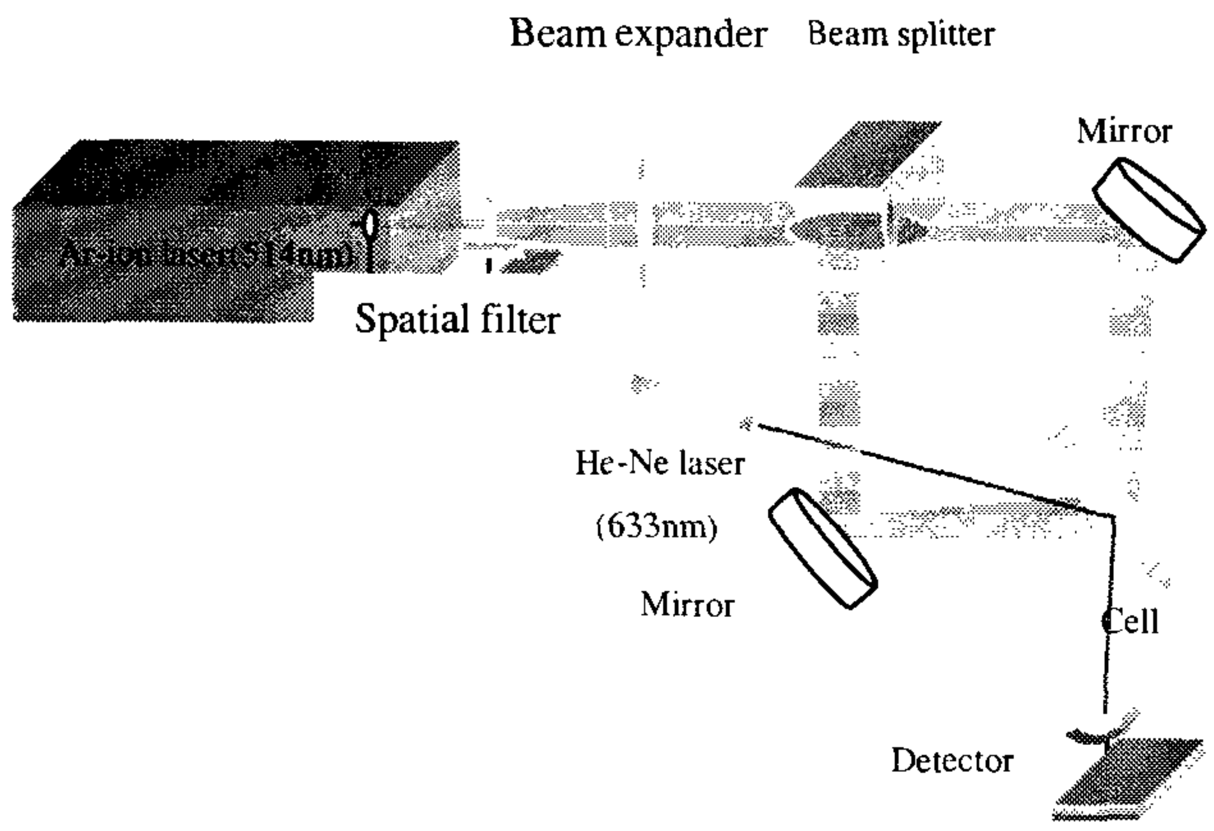
1. Introduction

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 are micrometer films containing liquid crystal and photoreactive prepolymer that are exposed to a coherent interfernce pattern generated by a laser.[3] In this contribution we only consider a two beam exposure, but it has been shown the multidimensional HPDLCs can be created by three of more exposing laser beam.[4] The development of periodic arrays of PDLC droplet embedded in a polymer matrix results in refractive index profile across the film giving rise to diffraction of light. If monomer polymerizes on exposure to spatially modulated light, a concentration gradient of this monomer is produced because more monomers are consumed in the region of higher intensity of the sample. Then counter diffusion of monomer and LC occurs due to the concentration gradient formed by the polymerization. It should be emphasized that there is a distribution of droplet sizes within typical PDLC films which is related to the kinetics of the phase separation process.[5] The liquid crystal rich regions result in randomly oriented submicrometer droplets where the size of droplets depends on a number of factors; most importantly exposure time, laser beam intensity, and the concentration of liquid crystal and polymer. Figure 1 shows the experimental setup we used to fabricate a reflective HPDLC.

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[6] used fluorine substituted acrylate monomers on 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 fluorinated compounds and LC 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.[7,8]

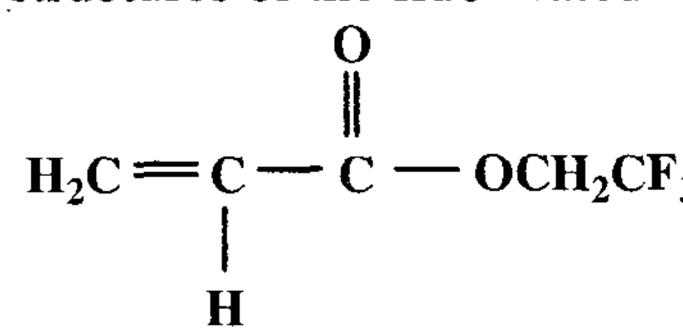
This study reports the effects of fluorinated polymer matrices on the electro-optic properties of reflective HPDLC. 1,1,1,3,3,3 hexafluoroisopropyl acrylate(HFIPA) and 2,2,2 trifluoroethyl acrylae(TFEA) are used as fluorinated monomers. Polymers which are highly or completely fluorinated exhibit properties of stability at very high temperatures, toughness and flexibility at low temperatures, nonadhesiveness, very low friction properties, low dielectric losses, high dielectric strengths.[9] The content of fluorinated monomer has been systematically varied for HPDLC, and electro-optic properties of these HPDLC films have been studied with an emphasis on the role as polymer matrix.



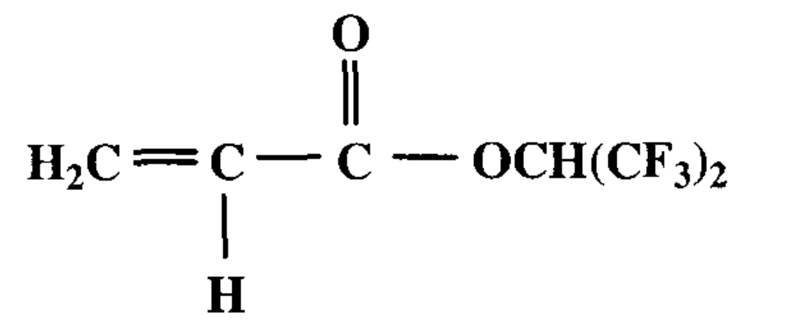
2. Experimental

To form a HPDLC device, a homogeneous mixture of a fast-curing multi-functional monomer, a reactive diluent, a photoinitiator dye, a coinitiator, and a LC is prepared. The photoinitiator requires good absorption at the writing wavelength of the laser and the ability to react with the coinitiator to produce a free radical. So, in our experiments, we used Rose Bengal (RB, TCI) known as an ideal initiator for holographic recording with an Ar-ion laser as it displays a broad absorption spectrum with a peak molar extension coefficient of ~10^4 $M^{-1}cm^{-1}$ at about 490nm.[10] To this, a millimolar amount of N-phenyl glycine (NPG, TCI) as a coinitiator was added.[11] Free-radical addition polymerization of multifunctional monomers leads to the formation of polymers of high molecular weight in a few seconds. Multifunctional PUA monomers are effective in this regard. PUA is a segmented polymer tipped with acrylate functionality. Bifunctional polypropylene glycol(PPG) were reacted with molar excess of hexane diisocyanate(HDI) for over 1h at 80°C to abtain isocyanate(NCO) terminated polyurethane prepolymer. Then the reaction mixture was cooled down to 40°C and hydroxyl ethyl acrylate(HEA) was added to obtain HEA-capped urethane acrylate oligomer. This urethane acrylate oligomers are highly viscous and immiscible with LC. Mono-functional monomer helps to dissolve different compounds in the mixture and form homogeneous syrup. It is also essential to reduce the viscosity of an LC/monomer mixture. NVP has been used as mono-functional monomers.

Also, mono-functional fluorinated monomers (1,1,1,3,3,3 hexafluoroisopropyl acrylate and 2,2,2 trifluoroethyl acrylae) were added to the monomer mixtures ranging from 10 to 30 wt%. Figure 2 show the chemical structures of the fluorinated monomer.



2,2,2 trifluoroethyl acrylae(TFEA)



1,1,1,3,3,3 hexafluoroisopropyl acrylate(HFIPA)

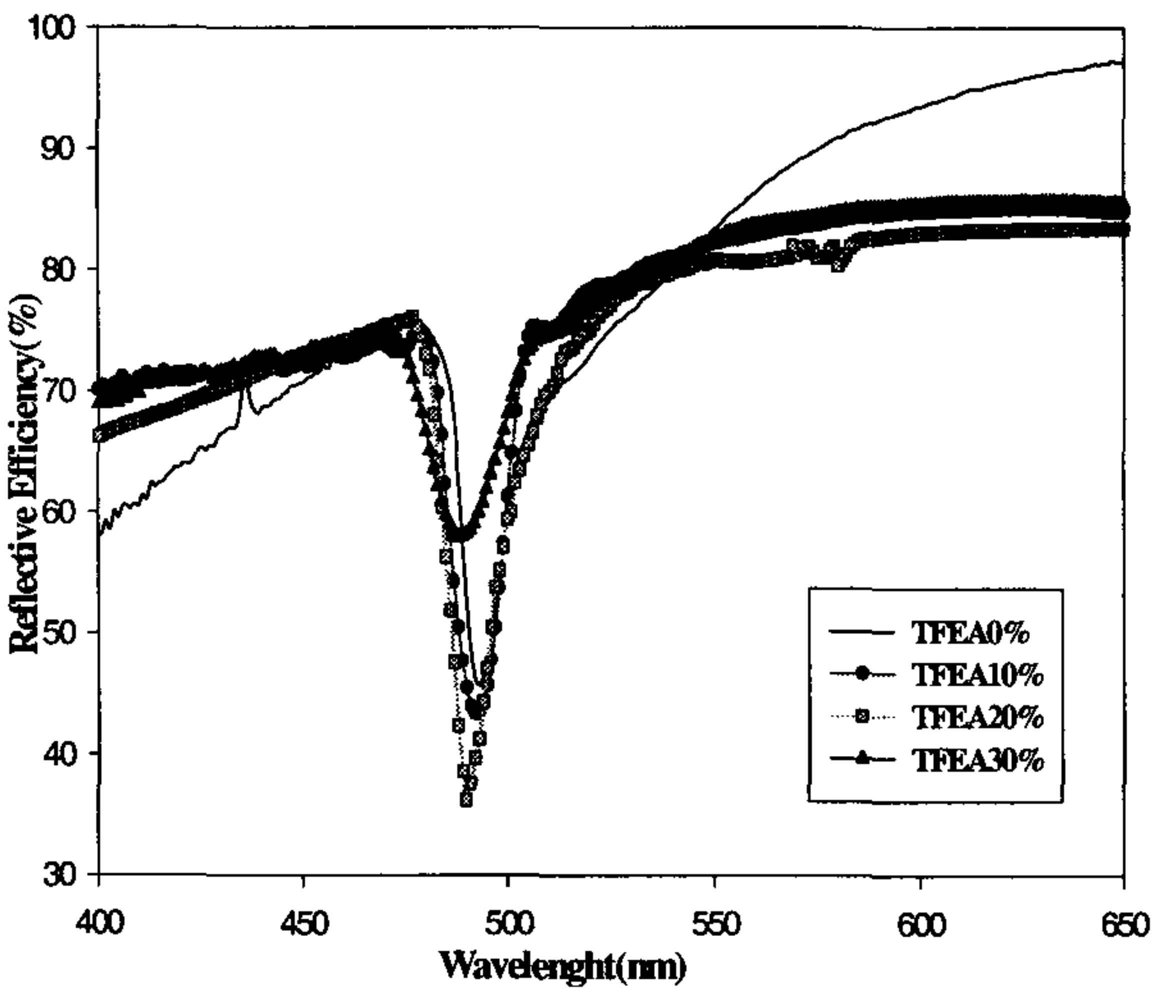
Figure 2. Chemical structures of fluorinated monomer

The choice of the liquid crystal plays a very important role in the electro-optical performance and diffraction efficiency of the HPDLC. We have used E7 (BL001, Merck), an eutectic mixture of four cyanobiphenyl and a cyanoterphenyl mixture with T_{KN} = -10° C, T_{NI} = 50.5° C, $\varepsilon_{\parallel}$ =19.0, and $\varepsilon_{\perp}$=4.2.[12,13]

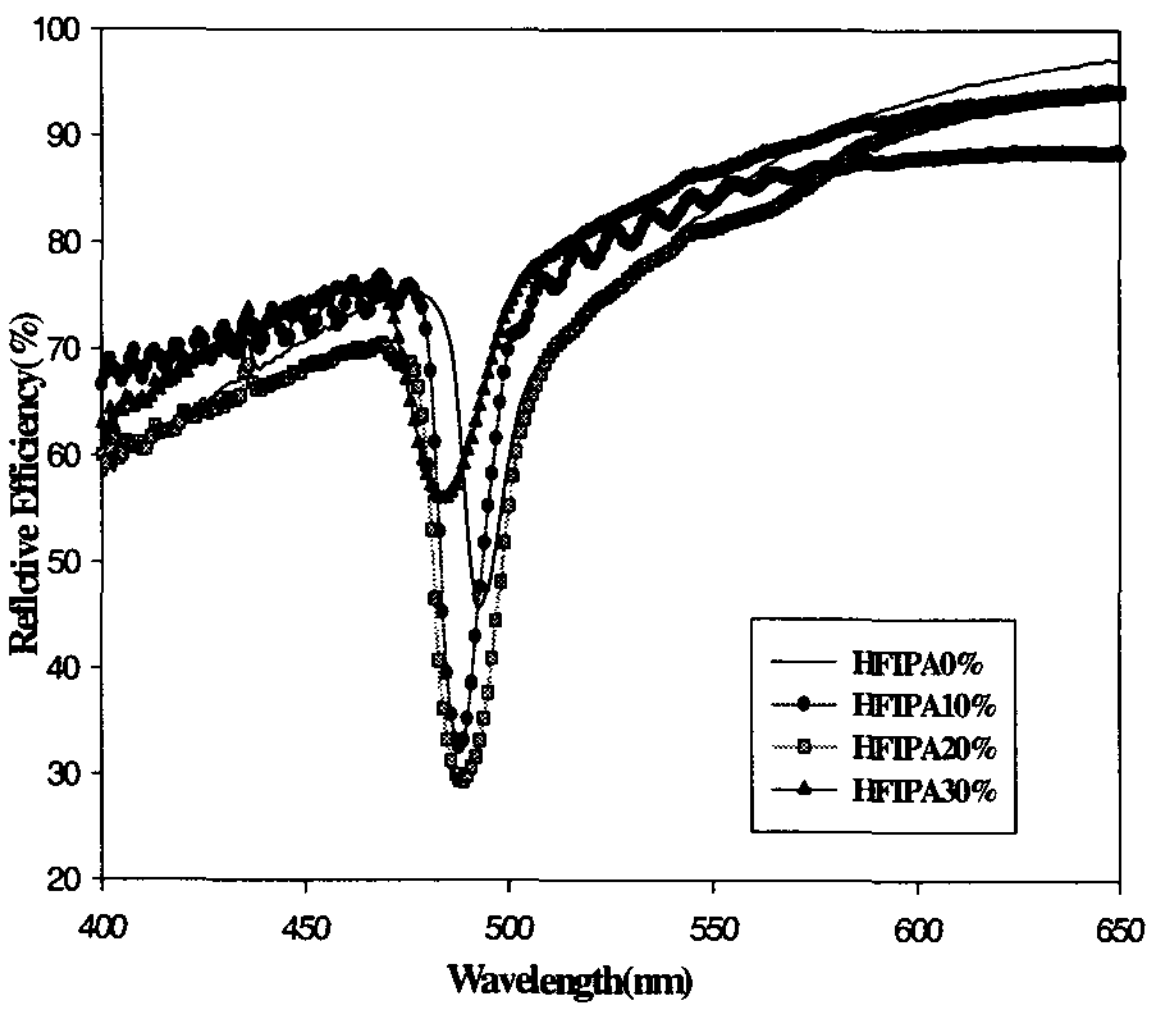
The cell was constructed by sandwitching the prepolymer syrup/LC mixture between the two indium-tin-oxide(ITO) coated glass plates, with a gap of 5μm, adjusted by a bead spacer. The LC content was about 35wt%. The prepolymer mixtures have been irradiated with an Ar-ion laser(514nm), with exposure times of typically 30s~180s. Interference pattern was made according to the Bragg law($\Lambda=\lambda/2\sin\theta$)

3. Results and discussion

In reflective HPDLC, reflection efficiency should depend on LC droplet size and density. Small droplet size and high droplet density generally increase the reflection efficiency. The increased hydrophobicity of polymer matrix with the increase in the degrees of fluorine substitution should give decreased interactions with LC molecules which are highly polar, and consequently large droplet size and small droplet density could be expected. So, the rate and extent of polymer-LC phase separation should be great with increasing chemical immiscibility which would give clean phase separation and reflection.



(a)



(b)

Figure 3. UV-visible spectra of reflective holographic grating at 150mW/cm^2;
(a) according to TFEA contents, and (b) HFIPA contents.

Figure 3 shows the reflection efficiency vs wavelength relationships of the composite films prepared from two different fluorinated monomers (TEHA and HFIPA) of various contents. In both cases, it is seen that the reflection efficiency increases with increasing content of fluorinated monomers up to 20wt%. This is due to the chemical incompatibility between fluorinated compounds and LC. This may enhance the LC phase separation. But beyond 20wt% of fluorinated monomers loading, reflection efficiency deacrease due probably to the coalescence of LC droplets.

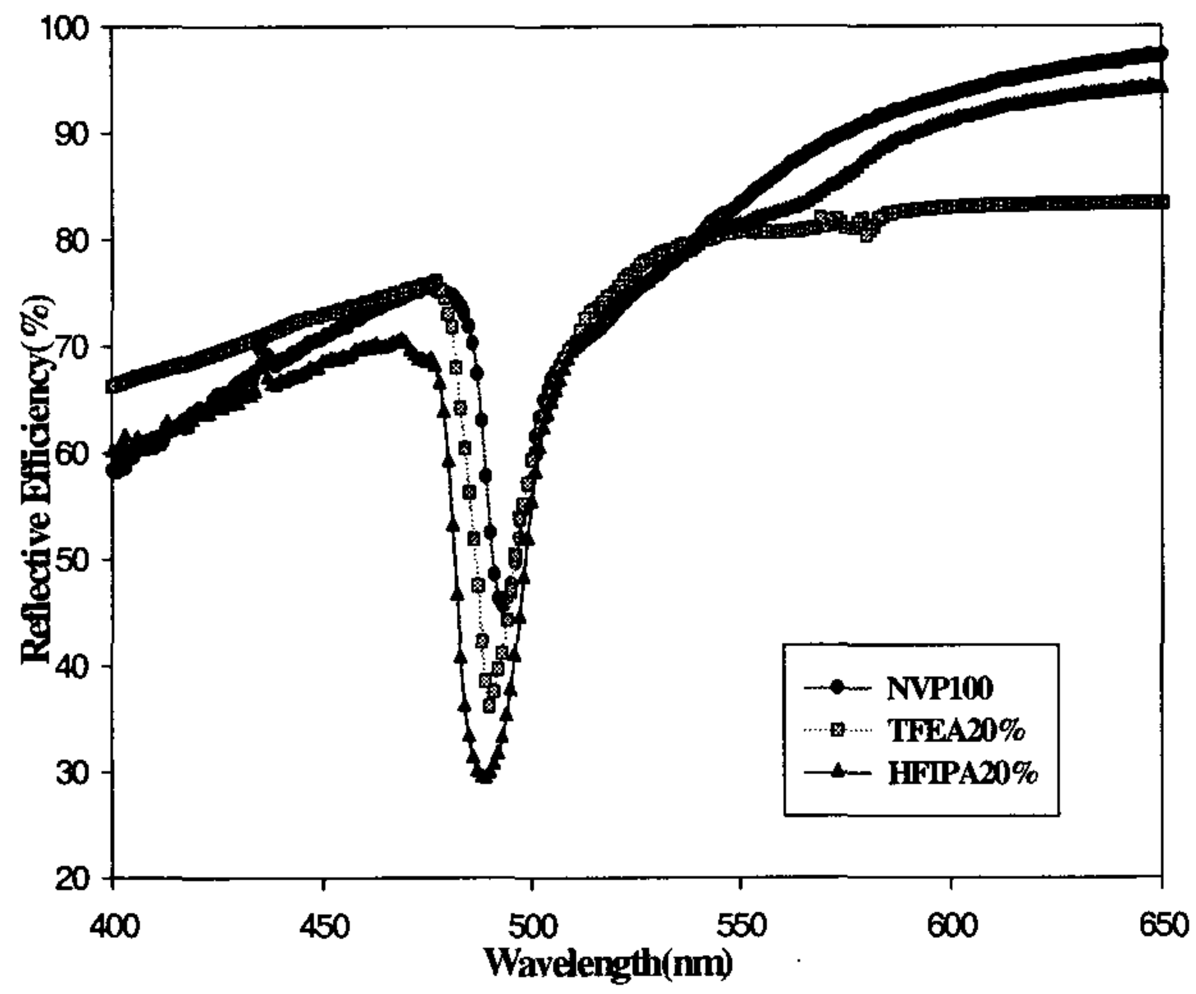


Figure 4. Effect of fluorinated monomer on reflection efficiency of HPDLC films.
(LC35%, 150mW/cm^2)

Figure 4 illustrates the UV-visible spectra of the films to confirm the reflection by holographic gratings prepared from 35wt% LC and PUA prepolymer. It is seen that the peak position and intensity are different depending on the content of fluorinated monomer although they were grated using the same laser of 514nm. It is clearly seen that the reflection efficiency increases with increasing the content of fluorinated monomer. This is due to the increased hydrophobicity of polymer matrix with the increase in the degrees of fluorine substitution and this may enhance the phase separation between polymer and LC. The number of fluorine atoms in HFIPA is considered twice of that in TFEA monomer.

4. Conclusion

Investigation of the effects of varying prepolymer molecular structure has been conducted in holographic PDLC gratings. The increased number of fluorine atoms with the polymer matrice of the HPDLC gratings may enhance the LC phase separation and improved optical properties.

5. Acknowledgements

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6. References

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