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## Liquid Crystals

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# The effect of fluorine-substituted acrylate monomers on the electro-optical and morphological properties of polymer dispersed liquid crystals

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The effects of fluorinated acrylate monomers on the electro-optical and morphological properties of polymer dispersed liquid crystal (PDLC) films are reported. The partial fluorination of host polymer matrices resulted in improved optical properties and better defined morphologies. An enhancement in contrast ratio was observed for fluorinated systems containing trifluoroethyl acrylate (TFEA) and hexafluoroisopropyl acrylate (HFIPA). Conversely, the incorporation of methyl acrylate (MA), a chemically similar non-fluorinated acrylate, resulted in no appreciable change in contrast ratio and an increase in relaxation time. Scanning electron microscopy morphological studies were conducted to understand further the influence of fluorinated monomers in PDLC systems.

## 1. Introduction

Polymer dispersed liquid crystals (PDLCs) constitute a distinctive class of composite materials which consist of liquid crystal droplets randomly dispersed in an amorphous polymer matrix [1]. If the droplets are on the order of a micrometer in diameter, spatial refractive index inequalities among liquid crystal ( $n_{LC}$ ) and polymer ( $n_p$ ) phases result in the scattering of normal incident light [2, 3]. In this state, such films have a white, opaque appearance. Conversely, optical transmittance is realized when the ordinary liquid crystal ( $n_o$ ) and polymer matrix refractive indices are equal and the liquid crystal directors are aligned parallel to the direction of an applied electrical field.

Several phase separation techniques may be used to obtain PDLCs. Irrespective of the methodology, each generally commences with an isotropic solution of liquid crystal and matrix-forming component. Solvent induced phase separation (SIPS) involves the evolution of constituent phases with the loss of a solvent. Initially, a thermoplastic polymer and liquid crystal are dissolved in a common solvent. Evaporation of the solvent causes the system to cross the miscibility gap, resulting in liquid

crystal droplets randomly dispersed in a polymer binder. Droplet shape and density depend on the rate of solvent loss and physical properties of the components [4]. Thermally induced phase separation (TIPS) produces phase separated LC domains by cooling an initially isotropic solution of thermoplastic and liquid crystal below an upper critical solution temperature. As the system cools, it passes through the miscibility gap and liquid crystal droplets form. Polymerization induced phase separation (PIPS) was first reported in 1986 by Doane *et al.* [5] where the chemical potential of the solution changes after polymerization has been initiated. Subsequently, liquid crystal solubility in the growing polymer chains decreases [6, 7]. The solution passes through the miscibility gap and phase separation occurs by either spinodal decomposition or nucleation and growth [7, 8]. Droplet growth continues until the matrix solidifies, thus securing the morphology [9].

An intriguing application of PDLCs is in holographic volume gratings (HPDLCs). These devices may be used in reflective displays, switchable notch filters for computing and diffractive filters. HPDLCs are composed of parallel, periodic liquid crystal and polymer-rich planes [10, 11]. In this manner, the refractive index is modulated throughout the volume of the material. In the off-state, a phase grating is produced by an index modulation

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between the LC and polymer-rich planes. The application of a sufficiently strong electric field causes LC directors to orient parallel to the field for positive dielectric liquid crystals, reducing the index modulation. In this state, the film appears transparent to normal incident light if  $n_p \approx n_o$ .

Two types of planar HPDLC gratings exist: transmission and reflection geometries. For reflective geometries, HPDLCs interact with light according to the Bragg condition, ( $\lambda = 2nA$ ), where  $\lambda$  is the wavelength of incident light,  $n$  is the average refractive index and  $A$  is the grating period. Thus, for reflected light of  $\lambda = 500$  nm with  $n = 1.52$ , the Bragg period must be approximately 165 nm. This grating spacing comprises both polymer-rich and LC-rich regions where the LC domains are typically half the size of the grating spacing. These very small domains possess high surface-to-volume ratios and result in inherently high device driving voltages [12], making significant issues of power consumption and heat dissipation.

One possible means of lowering the switching voltage is to reduce the surface anchoring energy of the LC molecules at the droplet interface. Several research groups have explored the use of fluorinated materials as a means of improving the electro-optical performance of PDLC devices. Heavin *et al.* observed improvements in phase separation, contrast ratio and response time with partial matrix fluorination using the liquid crystal mixture E7. E7 is a eutectic mixture of cyanobiphenyl (CB) moieties consisting of 5CB (51 wt %), 7CB (25 wt %), 8OCB (16 wt %) and 5-cyanotriphenyl (8 wt %) [13, 14]. Yamada *et al.* reported a reduced operating voltage with the addition of a fluorinated acrylate monomer to a photo-initiated PIPS system containing fluorinated liquid crystals [15]. Finally, Coates *et al.* noted improved contrast ratio and reduced driving voltage when novel fluorinated liquid crystal mixtures were used in conjunction with PN393 [16].

The objective of this investigation was to explore the effect of partial matrix fluorination on the electro-optical and morphological properties of floodlit PDLCs. The motivation is driven by the hypothesis that fluorinated monomers may lower LC anchoring strength, thus lowering device driving voltage, and may also enhance phase separation due to chemical incompatibility. Both of these possible effects would be beneficial in optimizing the electro-optical behaviour of HPDLCs. Since the anisotropic polymerization and subsequent phase separation associated with HPDLCs is extremely complex, experiments described in this work focused first on floodlit films (PDLCs). The validity of the above hypothesis was examined by determining the effect of systematically replacing the multifunctional acrylate matrix monomers typically used with hexafluoroisopropyl acrylate and

trifluoroethyl acrylate. Polymerization conditions remained the same. In all cases, a non-fluorinated, chemically similar acrylate additive, methyl acrylate (MA), was used as a control. Optical and electro-optical comparisons were used to assess the influence of fluorine on the refractive index matching. High resolution morphological studies were used to investigate subtle changes in the sub-micron microstructure.

## 2. Experimental

### 2.1. Materials

PDLC prepolymer formulations consisted of a homogeneous mixture of several vinyl-terminated monomers, photoinitiator, co-initiator and liquid crystals. Preliminary experiments in this investigation with halogenated liquid crystals resulted in low contrast ratios and high driving voltages. For this reason, investigations using E7 were pursued. The standard recipe for PDLC films consisted of 50 wt % inert liquid crystal E7 (EM Industries) and 50 wt % prepolymer solution. The latter consisted of 0.25 wt % photoinitiator rose bengal from Spectra Group, 2.0 wt % co-initiator *N*-phenylglycine (NPG), 0–20 wt % 1,1,1,3,3,3-hexafluoroisopropyl acrylate (HFIPA), 2,2,2-trifluoroethyl acrylate (TFEA) or methyl acrylate (MA), 16 wt % *N*-vinyl-2-pyrrolidinone (NVP), and the balance, a multifunctional acrylate monomer mixture consisting of 87 wt % dipentaerythritol penta-acrylate (DPHPA) and 13 wt % pentaerythritol tetra-acrylate, both from Sartomer. The chemical structures of the vinyl-functional components are shown in figure 1. The average functionality ( $f$ ) of this mixture was determined as 4.73 by

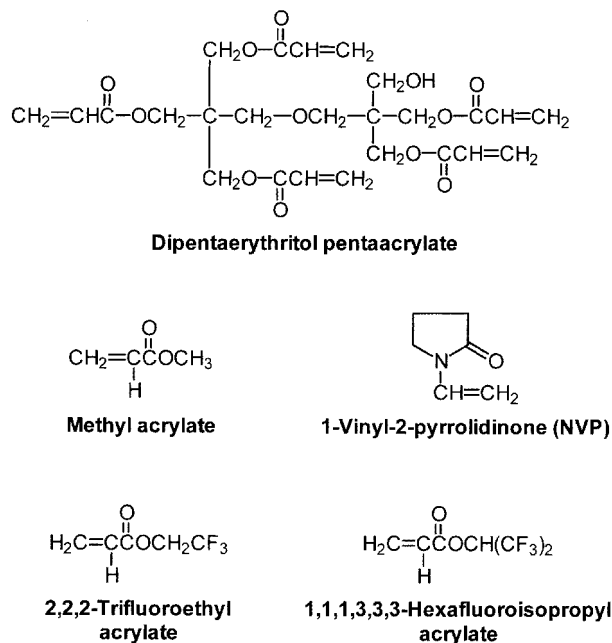


Figure 1. Chemical structures of the vinyl-functional matrix materials.

high performance liquid chromatography (HPLC) and liquid chromatography–mass spectrometry (LC-MS). NVP, MA, HFIPA, TFEA and NPG were purchased from Aldrich. All materials were used as received without further purification. Standard formulation specimens were prepared in the absence of monomeric acrylate additives. A shaker mill was employed to ensure that components were thoroughly mixed and homogeneous. Syrups were then centrifuged for 1 min to remove undissolved gases.

## 2.2. Sample preparation

PDLC cell preparations were carried out under strict darkroom conditions. ITO-coated glass slides were thoroughly cleaned with methanol. Glass spacer rods, utilized to achieve uniform film thickness, were deposited about the perimeter of an ITO-coated slide using a mixture of 15  $\mu\text{m}$  glass rods and dichloromethane (DCM). After evaporation of the DCM, approximately 25  $\mu\text{l}$  of prepolymer syrup was placed in the centre of the substrate. A top slide was carefully placed over the first and the excess prepolymer forced out through the sides. The assembled unit was placed in a custom-made aluminum holder that applied constant pressure to the perimeter of the cell during exposure.

All PDLC films considered in this study were of the floodlit variety. Specimens were illuminated for 8 min at a constant distance from a 20 W unfiltered incandescent halogen white light source such that the incident energy was 315  $\text{mW cm}^{-2}$ . A randomly polarized HeNe laser beam ( $\lambda = 632 \text{ nm}$ ), offset 25° from the sample normal, passed through the cell for real-time transmittance monitoring during writing and for 2 min thereafter. Since the wavelength of the probing beam was well beyond the peak absorption wavelength of the photoinitiating dye, it had no appreciable contribution to the polymerization reaction. Samples were then removed from the holder and post cured for 5 min at a distance of 6 in from an unfiltered, 50 W incandescent flood lamp.

## 2.3. Characterization

The PDLC films were characterized by determining the threshold voltage, response time, contrast ratio and morphological properties. A series of time-dependent electro-optical tests proved that substantial changes in properties occurred up to 24 h after writing. These changes were thought to be due, in part, to continued liquid crystal domain growth, polymerization and phase separation. To ensure that electro-optical properties were reasonably stable at the time of testing, all samples were aged 10 days prior to characterization.

A *p*-polarized HeNe laser beam was used to probe the films during electro-optical characterization. Fast photodiodes were utilized to monitor the intensity of the

probing beam. Calibration was accomplished by placing a clean ITO slide in the path of the beam to determine the maximum transmittance value or calibration constant. Normalization of the experimental data was accomplished by dividing the experimental values by this value.

Electro-optical performance was determined by assessing the threshold voltage, contrast ratio and response time. All tests utilized a 1 kHz a.c. square wave across the thickness of the film. The threshold voltage,  $V_{90}$ , is the voltage required for a device to achieve 90% of its maximum transmittance ( $T_{\text{max}}$ ). Film response times of experimental interest typically include rise and fall times. The rise time ( $\tau_{\text{on}}$ ) is defined as the time necessary for the minimum transmittance ( $T_{\text{min}}$ ) to reach a value of  $T_{\text{min}} + 0.9(T_{\text{max}} - T_{\text{min}})$ . The PDLC devices of the nature described in this communication typically display rise times < 55  $\mu\text{s}$ . This is very near the capability limit of the characterization equipment employed. For this reason and the fact that charge-carrying contaminants can result in anomalous rise-time behaviour, characterization efforts focused on the relaxation time. The relaxation time ( $\tau_{\text{off}}$ ) is defined as the time necessary for a device at  $T_{\text{max}}$  to return to a value of  $T_{\text{min}} + 0.1(T_{\text{max}} - T_{\text{min}})$ . These determinations were made by driving devices at their measured threshold voltages.

The contrast ratio is a dimensionless parameter used to assess the on- and off-state optical performance of PDLC films and is defined as ( $T_{\text{max}}/T_{\text{min}}$ ). Since these values are dependent on the optical performance in both the on- and off-states, each condition must be examined individually to provide insight into factors that affect film properties. The contrast ratio, *CR*, serves as a means of making a general evaluation of optical performance.

Low voltage, high resolution scanning electron microscopy (SEM) was employed for morphology studies using a Hitachi S-900 scanning electron microscope with a 1 keV accelerating voltage. Films were prepared for SEM analysis by first peeling them from the glass substrate with a razor blade. The liquid crystal was then extracted over a 12 h period by immersing the free films in methyl alcohol. Dried films were mounted on metallic sample trays with silver paint, followed by fracturing in liquid nitrogen to yield an interface that was representative of the bulk morphology. A 2–5 nm thick coating of tungsten was deposited using a dual ion beam sputter coating apparatus to minimize artifacts associated with sample charging.

## 3. Results and discussion

Floodlit PDLC electro-optical parameters were taken as the average value of three specimens and plotted as a function of additive alkene mol %. These data are given in the table for all formulation series. Standard PDLC

Table. PDLC film optical performance parameters as a function of additive mol %.

Additive	Concentration /mol %	Minimum transmittance ( $T_{\min}$ )/%	Maximum transmittance ( $T_{\max}$ )/%	Contrast ratio	Threshold voltage ( $V_{90}$ )/V $\mu\text{m}^{-1}$	Fall time / $\mu\text{s}$	Average functionality ( $f$ )	Matrix refractive index ( $n_p$ )
N/A	N/A	12	88	7.6	10.8	156	4.1	1.539
MA	1.4	12	89	7.3	10.9	158	4.0	1.535
MA	6.7	15	90	6.3	10.9	159	3.9	1.524
MA	13.2	16	92	5.8	10.4	177	3.6	1.512
MA	25.5	25	93	3.9	7.2	212	3.2	1.494
TFEA	0.8	12	90	7.7	9.9	158	4.1	1.536
TFEA	3.9	9	90	10.3	10.2	154	3.9	1.526
TFEA	7.8	7	92	13.6	11.0	149	3.8	1.515
TFEA	16.1	2	95	39.5	9.6	158	3.5	1.495
HFIPA	0.5	10	88	8.8	11.0	150	4.1	1.537
HFIPA	2.7	10	89	8.8	11.6	136	4.0	1.528
HFIPA	5.6	10	94	10.0	11.2	144	3.9	1.518
HFIPA	11.7	4	93	21.3	10.8	149	3.6	1.500

films possessed an average contrast ratio of 7.6; a general increase was observed with incremental addition of fluorinated monomers, as indicated in figure 2. TFEA- and HFIPA-containing films demonstrated contrast ratio improvements up to 5.2 and 2.8 fold, respectively. This is a significant finding since devices for display application require high contrast ratios. Conversely, the addition of methyl acrylate resulted in diminished values with respect to the standard formulation. Since the contrast ratio is dependent on  $T_{\min}$  and  $T_{\max}$  ( $CR = T_{\max}/T_{\min}$ ), the on- and off-state transmittance of each series was examined to explain the origin of the observed differences.

Standard formulation PDLC films possessed an average on-state transmittance of 88%. A common increase in  $T_{\max}$  with additive concentration was observed for all three monomers as indicated in figure 3. The phenomenon of increasing transmittance with the addition of a low refractive index additive is indicative of improved index

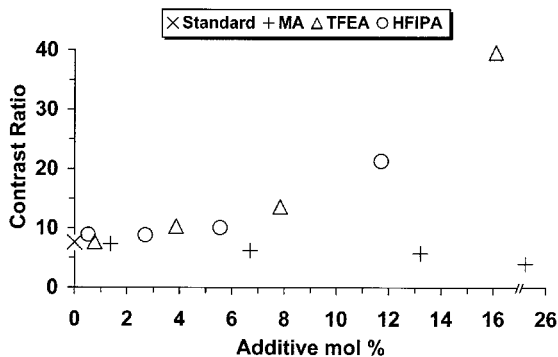


Figure 2. Contrast ratio versus additive mol % for PDLC films.

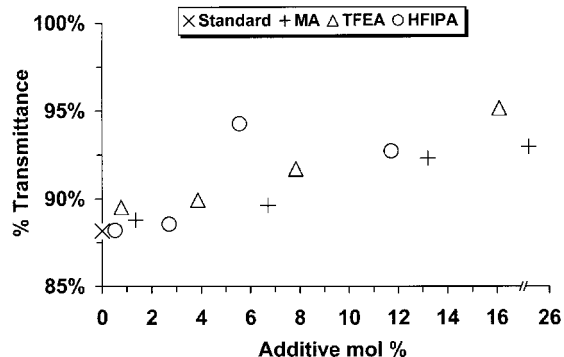


Figure 3. On-state transmittance versus additive mol % for PDLC films.

matching as described in a later portion of this report. An interesting point in figure 3 is a transmittance maximum which occurs around 6 mol % HFIPA. Typically, a transmittance maximum occurs when  $n_o$  and  $n_p$  are closely matched. One plausible explanation for this peak is that the low refractive index monomer serves better to match the LC and matrix indices at low concentrations ( $\approx 6$  mol %). For significantly higher additive concentrations,  $n_p$  and  $n_o$  begin to deviate from one another and the transmittance once again decreases. Therefore, figure 3 suggests that HFIPA has a more pronounced effect on refractive index matching than TFEA or MA. This was later shown to be due to a higher degree of fluorine substitution and therefore increased incompatibility with the LC phase. To investigate further differences between the fluorinated monomers and the MA control, the off-state transmittance of all films was also examined.

The average off-state transmittance of each series was examined to understand the CR trends. The average off-state transmittance decreased with the degree of matrix fluorination as shown in figure 4. As mentioned in §1, off-state scattering is optimized when the difference between  $n_{LC}$  (the average refractive index of the LC domains) and  $n_p$  (the refractive index of the polymer matrix) is maximized. Thus, an increase in contrast ratio with matrix fluorination is due to the simultaneous increase in maximum transmittance and decrease in minimum transmittance. Interestingly, MA-containing films revealed increasing transmittance with additive concentration. Therefore, negligible changes in contrast ratio for MA formulations are due to the simultaneous increases of both the maximum and minimum transmittance. Since the refractive index of MA is lower than that of the DPHPA matrix precursor, and therefore should result in a larger difference between  $n_{LC}$  and  $n_p$ , the increase in off-state transmittance suggests that MA must have a higher solubility in the LC phase than the fluorinated monomers. This possibility is explored below.

Since on- and off-state transmittances are dependent on the refractive indices of the LC domains and polymer matrix, the theoretical polymer matrix refractive index was examined as a function of additive mol %. The theoretical refractive index was calculated based on component molar concentration. These calculations assume that 25% of the liquid crystal remains dissolved in the matrix and a refractive index increase of 0.02 occurs with polymerization. The average refractive index of E7 ( $n_{LC} = 1.596$ ) was calculated using equation (1):

$$n_{LC}^{av} = (2n_o + n_e)/3. \quad (1)$$

The values of  $n_o$  (LC ordinary refractive index) and  $n_e$  (LC extraordinary refractive index) were taken as 1.521

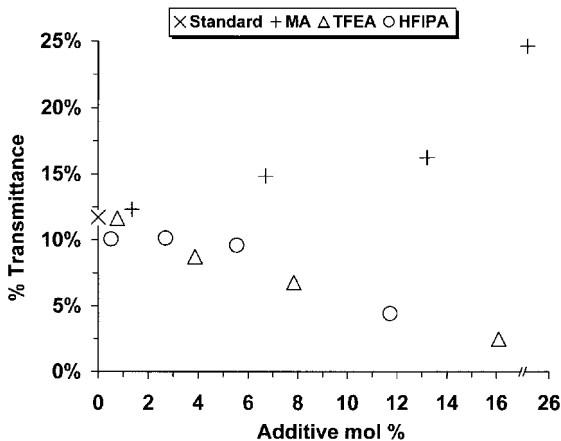


Figure 4. Off-state transmittance versus additive mol % for PDLC films.

and 1.746, respectively, as indicated by the manufacturer. The refractive indices of MA, TFEA and HFIPA were taken as 1.402, 1.35 and 1.319, respectively.

The theoretical matrix refractive index decreases with increasing additive concentration as shown in figure 5. The dashed line at  $n_p = 1.521$  corresponds to  $n_o$  for E7. Thus, as monofunctional components are incrementally added to the PDLC formulation, the effective polymer matrix refractive index should decrease and at some concentration,  $n_p \approx n_o$ . At this point, the indices are matched, resulting in an on-state transmittance maximum. For higher additive concentrations,  $n_p$  and  $n_o$  diverge and on-state properties diminish.

Comparison of figures 3 and 5 shows that the on-state transmittance corresponds reasonably well with the predicted matrix refractive index for HFIPA. Specifically, figure 5 predicts that at a concentration of nearly 6 mol % HFIPA, the matrix refractive index will approximately equal that of the ordinary liquid crystal. Figure 3 shows, in fact, that a transmittance maximum occurs approximately at this concentration. However, the correlation is not as strong for TFEA and MA films. This suggests that  $n_o$  must be slightly lower than the value of pure E7 due to the dissolution of additives. The plausible explanation for this is that these monomers have a high solubility in the LC phase, thus lowering  $n_o$ . As described in §1, a transmittance maximum is reached when  $n_o \approx n_p$ . This is because a monomer with refractive index  $n_m$  such that  $n_m < n_o < n_e$ , will effectively decrease  $n_e$  and  $n_o$  when dissolved in the LC phase [17]. As a result, a transmittance maximum occurs for TFEA and MA at concentrations which are higher than those predicted in figure 5. This would also require that less additive is being incorporated into the matrix. Therefore, the actual matrix index would actually be slightly higher than predicted. Thus, comparison of figures 3 and 5 support the argument that the more extensive the degree of additive fluorination, the lower the solubility in the LC

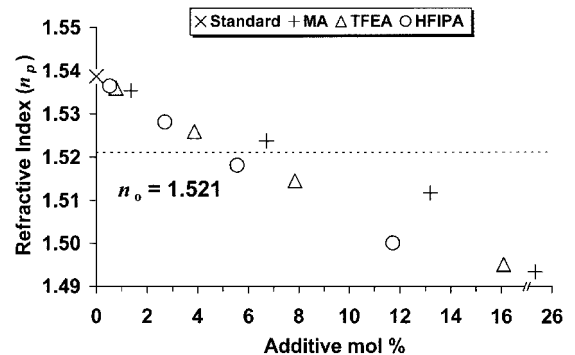


Figure 5. Theoretical polymer matrix refractive index versus additive mol % for PDLC films.

phase. In order to verify this, trends in the off-state transmittance were also compared with the polymer matrix refractive index model.

PDLC off-state transmittance is minimized when the absolute difference between  $n_p$  and  $n_{LC}$  is at a maximum. As anticipated, the off-state transmittance decreases with matrix fluorination as shown in figure 4. Surprisingly, little difference is demonstrated in the trend among the fluorinated monomers. This is a strong indication that  $n_p$  and  $n_o$  must differ substantially, due in part to a high degree of monomer incorporation into the matrix. However, MA-containing films display increasing off-state transmittance with additive concentration. This supports the argument that the polymer matrix refractive index is lowered by fluorinated additives. This suggests that  $n_{LC}$  is actually less than 1.596 as calculated for pure E7, an observation consistent with the hypothesis that a sufficient quantity of MA remains dissolved in the LC phase such that  $T_{min}$ ,  $T_{max}$  and subsequently, contrast ratio, are affected.

Since the addition of fluorine was observed to have a significant effect on  $T_{min}$  and  $T_{max}$ , the threshold voltage of all films was determined to investigate possible changes in driving voltage with matrix fluorination. Standard formulation PDLC films possess an average threshold voltage of  $10.8 \text{ V } \mu\text{m}^{-1}$ . The high values are mainly the result of the very small domains as will be shown later through SEM studies. Partial matrix fluorination with TFEA or HFIPA has no appreciable effect on the driving voltage as shown in figure 6. Similarly, equivalent additions of MA result in no significant changes in driving voltage. This indicates that if partial fluorination is affecting surface anchoring, then changes in either morphology or matrix conductivity are counteracting the effect. Often, relaxation time measurements serve as good qualitative indications of changes in surface anchoring.

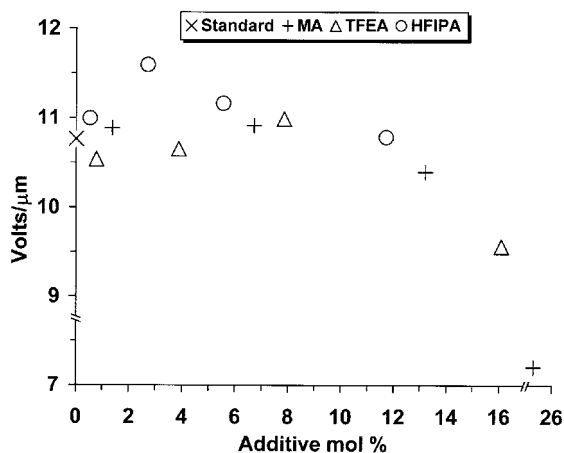


Figure 6. Threshold voltage ( $V_{90}$ ) versus additive mol% for PDLC films.

Relaxation times were determined to assess the effect of fluorinated additives on film response. Standard formulation films possessed an average relaxation time of  $156 \mu\text{s}$ . A faster relaxation time was observed with HFIPA addition as indicated in figure 7, suggestive of increased anchoring strength, with the shortest relaxation time of  $136 \mu\text{s}$  measured for an approximately 3 mol% addition. This is interesting since the associated SEM photomicrographs demonstrate no apparent changes in morphology. This observation is at odds with the premise of this investigation, suggesting that partial fluorination may actually increase surface anchoring strength. The addition of TFEA to the standard formulation elicited no significant change in the relaxation time. This is further evidence that partial matrix fluorination does not reduce LC anchoring strength. However, MA-containing formulations displayed an increase in relaxation time ( $177 \mu\text{s}$  for an additive concentration of 13 mol%). This is believed to be due to MA dissolved in the LC phase [16] as described above.

The off-state response time,  $\tau_{off}$ , is governed by a balance between the surface anchoring energy, elastic free energy and viscous torque of the liquid crystal [18]. Additives may serve to plasticize the matrix, thereby decreasing the anchoring potential, resulting in an increase in relaxation time. As mentioned above, monomers or oligomers dissolved in the LC domains can serve to change the viscosity, resulting in an increase in relaxation time. The increase in fall time with incremental MA addition further supports the supposition of LC phase contamination [19].

SEM was employed to study the effect of fluorinated additives on floodlit PDLC film morphology. Polymeric aggregates on the order of several hundred nanometers in diameter are observed in standard films as shown in figures 8(a) and 8(c). Also apparent is a highly interconnected, yet porous, polymeric phase (light regions) surrounded by relatively small LC domains (dark regions).

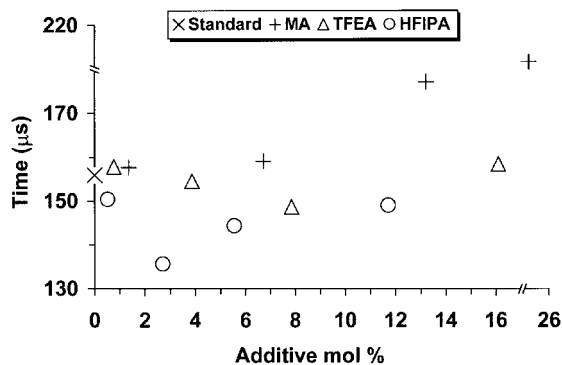


Figure 7. Relaxation time versus additive mol% for PDLC films.

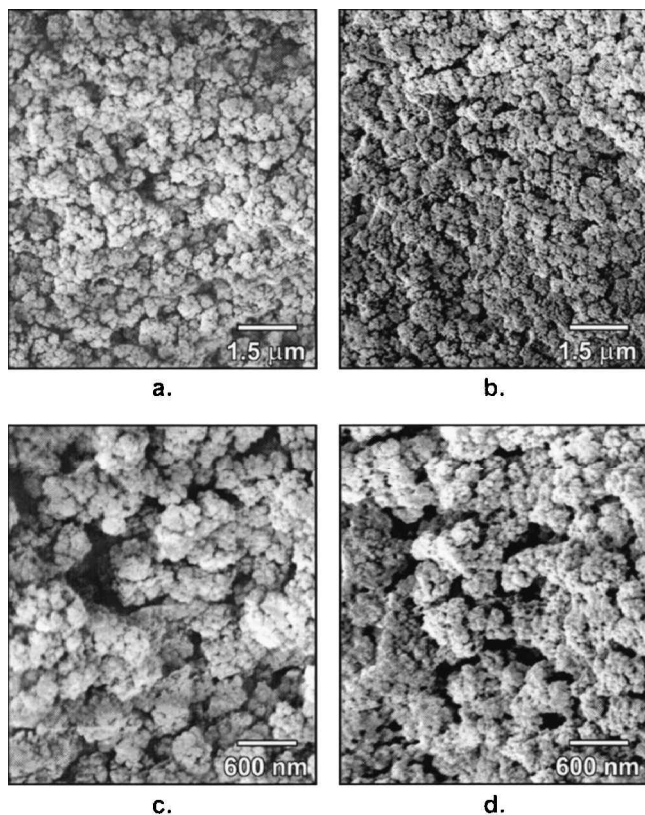


Figure 8. SEM photomicrographs for a standard formulation (a and c) and 13 mol % MA PDLC films (b and d).

Overall, a low LC volume fraction is seen and the polymer matrix is a porous, continuous phase. Since these features do not relate closely with respect to the wavelength of the probing HeNe laser beam, standard films have relatively weaker scattering properties with respect to fluorinated films (as evidenced by contrast ratio values in figure 2). In addition, the small LC droplets contribute to high driving voltage and fast response times as described above [20].

Gradual changes in morphology were commonly observed with increasing monomer concentration. These typically included an increase in LC volume fraction and improved polymer aggregate definition. The addition of MA resulted in increased polymer bead porosity and a slight increase in LC volume fraction as depicted in figures 8(b) and 8(d). It is noted, however, that an increase in LC volume fraction and polymer aggregate size was not accompanied by improvement in off-state scattering properties. This is further support that the scattering efficiency of the system is being affected by changes in  $n_{LC}$  [21, 22].

The addition of TFEA to the standard PDLC formulation resulted in improved aggregate definition, figures 9(b) and 9(d), and increased LC volume fraction. In these systems, polymer aggregates are larger in size and

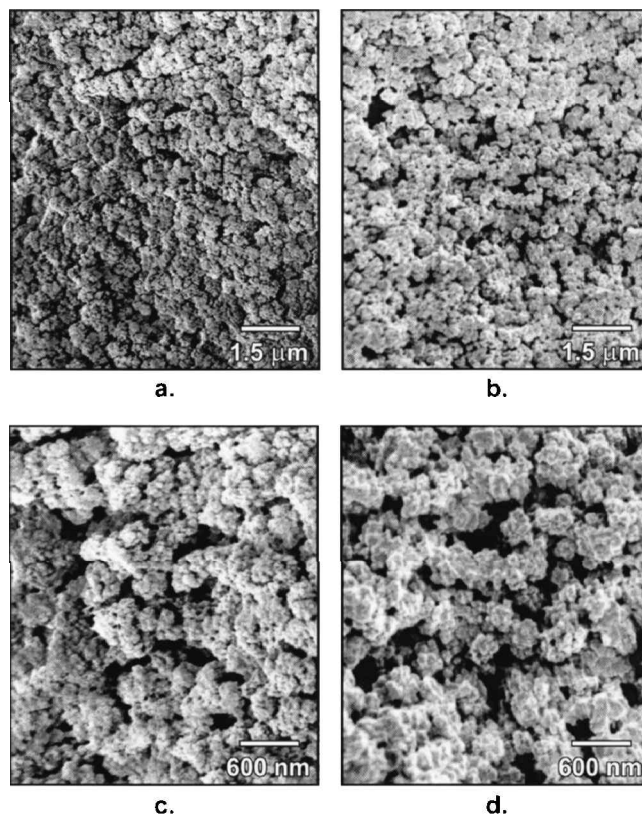


Figure 9. SEM photomicrographs of PDLC films containing 13 mol % MA (a and c) and 16 mol % TFEA (b and d).

appear to be more dense than MA films of comparable additive concentration. Similarly, the addition of HFIPA resulted in enhanced phase separation as indicated by an increase in LC volume fraction, figures 10(b) and 10(d). Polymeric domains measuring around 600 nm in diameter are very dense compared with analogous MA- and TFEA-containing films.

Two major types of floodlit morphologies are often observed in PDLCs. When the LC concentration is relatively low (< 35%) and high molecular weight polymer is not achieved until late in the polymerization process, the so-called 'Swiss cheese' morphology often results. This type of morphology is typified by discrete LC droplets randomly dispersed throughout the polymer matrix. Conversely, if the LC concentration is high and/or high molecular weight polymer is achieved in the early stages of polymerization, a 'polymer bead' morphology often dominates [22, 23]. In these systems, polymeric bead-like structures become dispersed throughout a semicontinuous LC phase. This is often the case with free-radical addition polymerizations that feature highly functional monomers such as tetra- or penta-acrylates. The combination of both high functionality and LC loading causes the formation of nano- or micro-gel polymeric domains which are soluble in the prepolymer solution



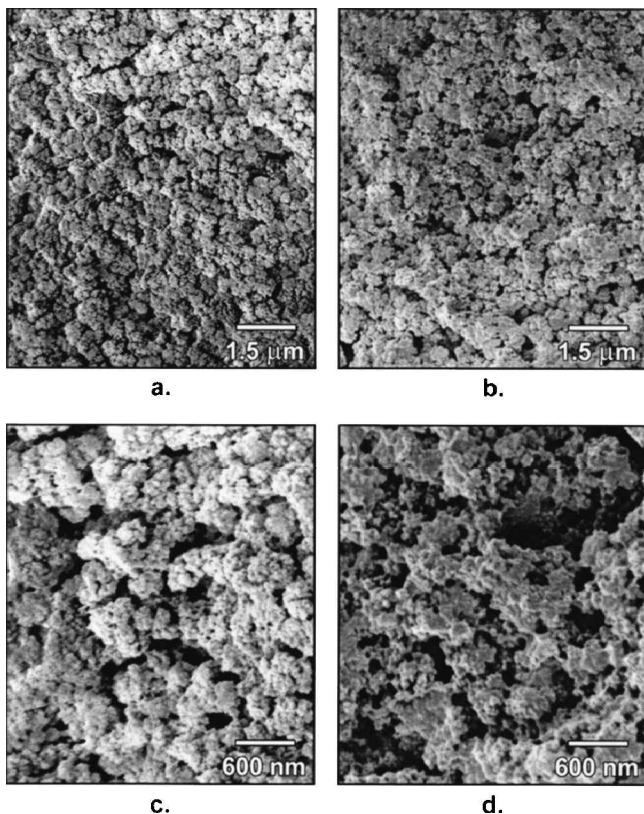


Figure 10. SEM photomicrographs of PDLC films containing 13 mol% MA (a and c) and 11.7 mol% HFIPA (b and d).

only at very low conversions [24]. The miscibility gap is quickly breached and nano-scale polymeric domains densify and grow amidst oligomers and prepolymer components [25]. Finally, aggregates combine leading to macroscopic gelation, typically at low vinyl conversions (< 10%).

The fluorinated systems studied here display an increase in LC volume fraction in comparison with non-fluorinated systems of comparable additive concentration. This is believed to be due to decreased compatibility of the fluorinated polymer with the prepolymer solution. As a result, aggregates become tightly grouped and expel the prepolymer during densification, resulting in low porosity polymer networks. To insure that differences were not due merely to changes in average system functionality ( $f$ ), this value was computed for each additive series as shown in the table. There is close agreement in average  $f$  between series of comparable additive concentrations. For instance, the average functionality of 13.2 mol% MA and 11.7 mol% HFIPA films are identical ( $f = 3.6$ ), yet the morphologies of these films, as shown by SEM studies, are notably different. This further supports the belief that differences are, in fact, due to partial matrix fluorination. Presently, real-time

scattering studies are being conducted to determine the effect of partial matrix fluorination on scattering properties. The findings from these studies will be reported later.

Morphology studies showed that matrix fluorination promotes enhanced phase separation. It was therefore of interest to determine whether fluorinated and non-fluorinated films with similar morphological characteristics had comparable electro-optical properties. To explore this possibility, 25.5 mol% MA was incorporated into the prepolymer syrup to achieve a morphology similar to that of 16 mol% TFEA films. The morphology of these non-fluorinated films are depicted in figures 11(a) and 11(c). These films possessed very low contrast ratios (< 6), consistent with the previous MA films. As described earlier, the explanation for the poor optical properties lies in fundamental differences in  $n_{LC}$  due to a high solubility of MA in E7. As a result, a slight decrease in threshold voltage was observed for an average value of 7.2 V  $\mu\text{m}$ , as well as a relatively long relaxation time of 212  $\mu\text{s}$ .

#### 4. Conclusions

Fluorine-substituted monofunctional acrylate monomers have been demonstrated to have significant effects

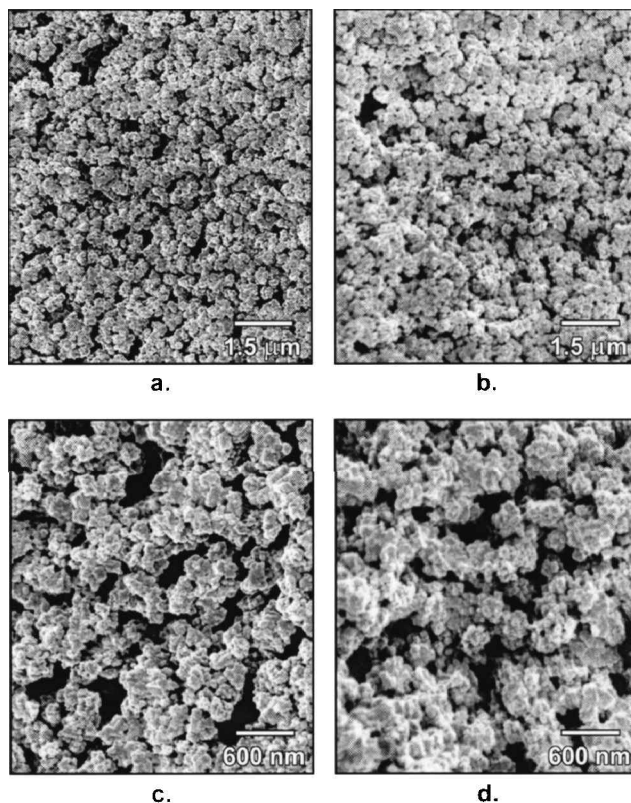


Figure 11. SEM photomicrographs of PDLC films containing 25.5 mol% MA (a and c) and 16 mol% TFEA (b and d).

on the electro-optical and morphological properties of floodlit PDLC films. The inclusion of fluorinated monomers in the standard formulation resulted in improved refractive index matching between the liquid crystal and host polymer matrix. Furthermore, the LC volume fraction increased with the degree of monomer fluorine substitution as evidenced by SEM analysis. Specifically, HFIPA films resulted in a higher LC volume fraction than TFEA films. As a result, the contrast ratio improved due to a simultaneous increase and decrease in  $T_{\max}$  and  $T_{\min}$ , respectively. The larger LC domains and polymer aggregates of fluorinated films resulted in improved optical properties with respect to the standard formulation. Conversely, formulations containing MA resulted in relatively poor electro-optical properties due to a high additive solubility in the liquid crystalline phase. Despite improved optical properties with partial matrix fluorination, there was no indication that partial matrix fluorination serves to decrease surface anchoring energy. Presently, holography experiments are being conducted using the same monomers; the results will be compared with those presented in this report at a later date. In addition, differential photo calorimetry and real-time light scattering experiments are presently being considered for an investigation of the kinetics and morphological development of fluorinated films.

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