
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# The Effect of Partial Fluorination on the Performance of Epoxy Based PDLC Films

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Version of record first published: 04 Oct 2006.

To cite this article: Scott D. Heavin , Bing M. Fung , James J. Sluss Jr. & Theodore E. Batchman (1994): The Effect of Partial Fluorination on the Performance of Epoxy Based PDLC Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 238:1, 83-91

To link to this article: http://dx.doi.org/10.1080/10587259408046917

*Mol. Cryst. Liq. Cryst.*, 1994, Vol. 238, pp. 83–91
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Printed in the United States of America



# The Effect of Partial Fluorination on the Performance of Epoxy Based PDLC Films

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*(Received September 2, 1992; in final form April 8, 1993)*

Changes in the electro-optic performance of polymer dispersed liquid crystal (PDLC) films caused by partial fluorination of the epoxy polymer binder have been investigated. The switching performance of the PDLC films was characterized by threshold voltage, rise time, fall time and contrast ratio. The results indicate that fluorine substitution in the polymer can cause a better phase separation, resulting in significant increases in the contrast ratio as well as large decreases in the fall time.

## INTRODUCTION

PDLC films are a special type of material for electro-optic devices composed of tiny droplets of liquid crystals randomly dispersed in a transparent polymer matrix.[1-6] In the absence of an electric field, the nematic directors in different droplets point in random directions and cause the film to scatter light, giving it an opaque, milky white "off" state appearance. Nematic droplets with a positive dielectric anisotropy would align in an externally applied electric field so that the liquid crystal directors are parallel to the field. In this "on" state configuration, if the isotropic refractive index of the polymer is similar to the ordinary refractive index of the liquid crystal, the film will transmit light.

Several different types of polymers including epoxy resins, poly(methylmethacrylate), polyvinyl alcohol, and various photo curable resins, have been used as the binding matrix of PDLC films.[7-9] The choice of the polymer has a large impact

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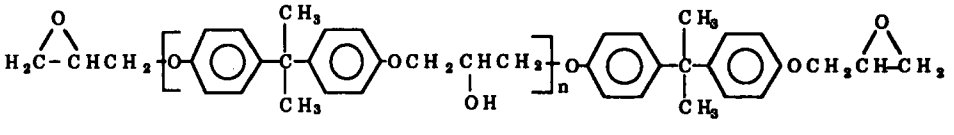
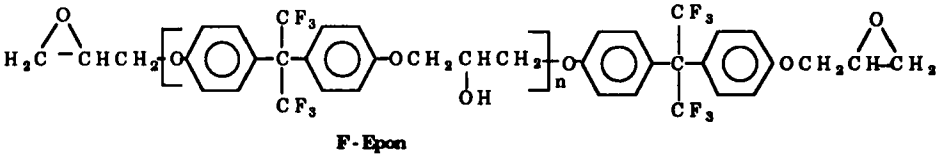
on the optical performance of the PDLC film since this component can account for as much as 50% of the total mass of the film. One polymer which has been used extensively to prepare PDLC films is the epoxy based Epon 828/Capcure 3-800 (Shell Chemical Company, Diamond Shamrock) thermoset. The resin, Epon 828, is the diglycidyl ether of bisphenol A, and the curing agent, Capcure 3-800, is a thiol terminated liquid polymer (Figure 1). These two precursors combine readily with the eutectic liquid crystal mixture E7 (BDH) to form a homogeneous solution. The mixture undergoes nearly complete PIPS (polymerization induced phased separation)[7] within 24 hours at 70°C. PDLC plates prepared with this system are relatively easy to construct and exhibit low threshold voltages. Problems with the system include long response times and inhomogeneous appearance associated with the sample "off" state. The "off" state defects are probably due to areas of inhomogeneous phase separation, resulting in inconsistencies in the light scattering efficiency of the sample. These areas are sometimes observed in electron micrographs of the system as broad bands of the polymer matrix with a much smaller number of liquid crystal droplets than other parts of the film.

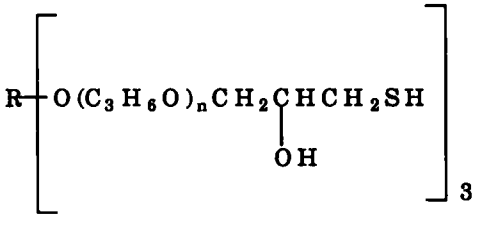
Because fluorination can affect many properties of a polymer, we have investigated the effect of partial fluorination on the electro-optic performance of an epoxy-based PDLC system, and the results are presented here.



Epon



F-Epon



R = Aliphatic Hydrocarbon

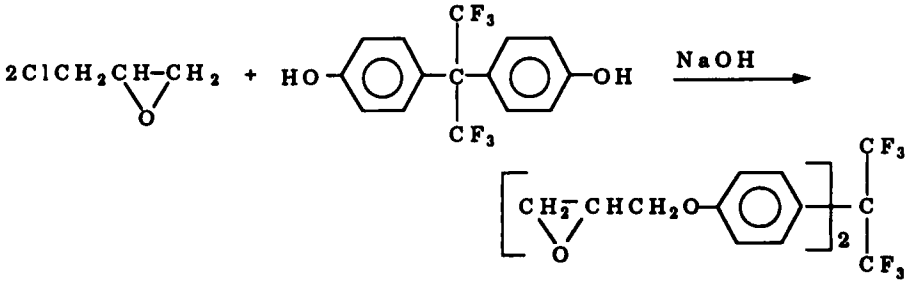
n = 1 - 2

Capcure 3-800

FIGURE 1 Chemical structures of Epon, F-Epon and Capcure 3-800.

## EXPERIMENTAL

To investigate the effects of fluorination on the Epon PDLC system, a partially fluorinated homologue of Epon 828 (Figure 1) was prepared. The synthesis of 2,2-bis-4-(2,3-epoxypropoxyphenyl)hexafluoropropane (F-Epon) follows a general procedure outlined by Sandler and Karo.[10] 2,2-Bis-(4-hydroxyphenol)-hexafluoropropane (hexafluorobisphenol A), obtained from PCR Company (0.030 moles) was combined with epichlorohydrin (0.416 moles) and 1.2 ml of distilled water in a 500 ml 3-neck round bottom flask. The mixture was stirred at room temperature until a homogeneous dark brown solution was obtained. Following the addition of 0.7 g sodium hydroxide, the temperature of the solution was increased to 95–100°C. An additional 0.42 g of NaOH was added in 6 separate increments and the solution was stirred for 30 additional minutes. The excess epichlorohydrin was removed using a water aspirator while the temperature of the solution was maintained at 85°C. The brownish white residue was redissolved in 100 ml benzene and filtered. The remaining solid was washed with an additional 50 ml benzene. The benzene was then removed by rotory-evaporation and the product was vacuum dried overnight. The brown viscous product was purified by passage through a silica gel column using a 1:1 mixture of hexane and ethylacetate as eluent. Retention time in the column was 1.5 hours. 50 ml fractions from the column were monitored by thin layer chromatography under UV light. After removal of the solvent, the product, a tan-brown powder, was washed with 250 ml hexane. Removal of the hexane yielded a cream-white colored powder.




The reaction of epichlorohydrin with bisphenol A would often produce Epon oligomers as shown in Figure 1, with $n = 0–2$. However, we have found that the reaction with hexafluorobisphenol A yields mainly monomers ($n = 0$), as determined from element analysis, which was performed by Midwest Microlab. $C_{21}H_{18}F_6$: Calc. C: 56.24, H: 4.05, F: 25.42. Found C: 56.14, H: 4.00, F: 25.24.

All experimental plates were constructed using polymerization induced phase separation as described by West.[7] The pre-polymer/liquid crystal mixture was composed of a 1:1:1 by weight ratio of E7, Capcure 3-800 and F-Epon/Epon 828. These components were thoroughly mixed and placed between two ITO (indium tin oxide) coated glass electrodes separated by 25 micron microfiber spacers (EM Industries). Each glass cell was then placed under a ca. 155 g steel weight and cured in an oven at 70°C for a period of 24 hours. The experimental setup used to measure the transmittance, response time and threshold voltage has been described previously.[11,12] Nine different mixtures composed of 0% to 60% F-Epon by weight were

prepared and six optically switchable plates were constructed and analyzed for each mixture. The percent F-Epon refers to the F-Epon/Epon-828 resin component only and not to the total four component mixture. Mixtures greater than 60% F-Epon were not prepared due to the low solubility of the F-Epon in the Capcure 3-800.

Scanning electron micrographs were taken with an ETEC Autoscan microscope. Feature analysis was performed on a JEOL JSM 880 microscope utilizing Kevex computer software.



## RESULTS AND DISCUSSION

The performance of PDLC films containing the F-Epon resin can be evaluated by measuring threshold voltage, contrast ratio, rise time and fall time. The threshold voltage is defined as the voltage required to achieve 90% of the maximum transmittance ($T_{max}$) that the plate can reach. The rise time is defined as the time required for the minimum transmittance ($T_{min}$) to increase to a value of $T_r$, where $T_r$ is defined as $T_{min}$ + 90% ($T_{max}$ − $T_{min}$) and the fall time is defined as the time required for the maximum transmittance to decrease to a value of $T_f$, where $T_f$ is defined as $T_{min}$ + 10% ($T_{max}$ − $T_{min}$). To maintain consistency, the voltage used to measure the response time of each sample was set at a value of twice the sample's own threshold voltage. The contrast ratio of each sample is defined as $T_{max}/T_{min}$.

The parameters defined above were averaged for each F-Epon mixture and the results are summarized in Table I. To present the data in graphical form, each parameter is plotted as a function of the percent F-Epon contained in the resin component. Figures 2 and 3 indicate that increasing concentrations of F-Epon results in both a decrease in the minimum transmittance and an increase in the maximum transmittance of the PDLC film. The maximum benefit to the "off" state transmittance appears to have been reached when the percent F-Epon reaches about 10%. An increase in the F-Epon composition beyond 10% seems to have little significant effect on $T_{min}$. In contrast, the benefit to the "on" state transmittance appears to reach a plateau at approximately 40% F-Epon. A decrease in $T_{min}$ accompanied by a simultaneous increase in $T_{max}$ results in a large increase in contrast ratio. Figure 4 indicates that the contrast ratio roughly doubles upon the incorporation of only 10% F-Epon. Partial fluorination of the Epon resin also

TABLE I

| % F-Epon | $T_{min}$ | $T_{max}$ | Threshold Voltage | Rise Time (msec) | Fall Time (msec) | Contrast Ratio |
|---|---|---|---|---|---|---|
| 0 | 0.8 | 67 | 30 | 8 | 180 | 80 |
| 4 | 1.0 | 64 | 31 | 7 | 196 | 66 |
| 7 | 0.6 | 75 | 31 | 17 | 259 | 129 |
| 10 | 0.4 | 75 | 33 | 3 | 126 | 168 |
| 20 | 0.5 | 80 | 33 | 7 | 126 | 170 |
| 30 | 0.5 | 83 | 36 | 7 | 70 | 166 |
| 41 | 0.5 | 87 | 33 | 10 | 91 | 181 |
| 50 | 0.4 | 88 | 38 | 21 | 140 | 220 |
| 59 | 0.4 | 88 | 34 | 15 | 67 | 204 |

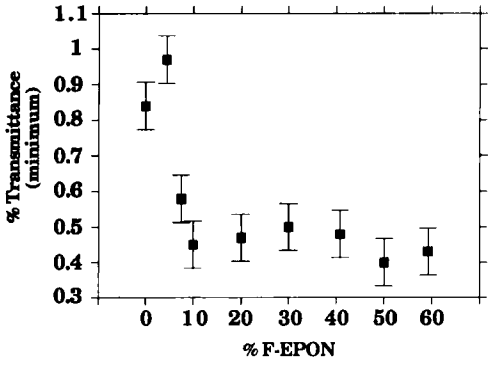



FIGURE 2 Minimum transmittance plotted as a function of %F-Epon contained in the polymer resin.

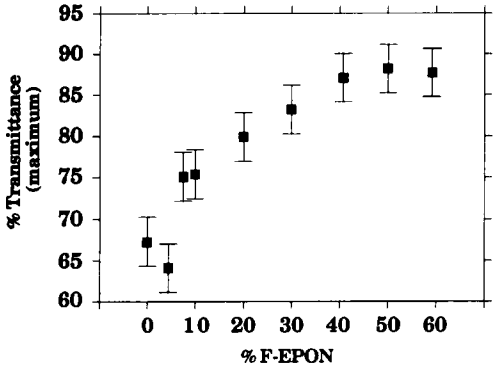



FIGURE 3 Maximum transmittance plotted as a function of %F-Epon contained in the polymer resin.

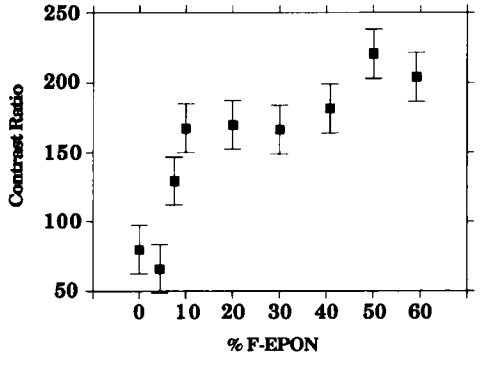



FIGURE 4 Contrast ratio plotted as a function of %F-Epon contained in the polymer resin.

affects the response time and the threshold voltage, but the data are much more scattered. Figures 5 and 6 indicate that the rise time increases and the fall time decreases with increasing percentages of F-Epon. Figure 7 indicates that the threshold voltage increases slightly with increasing percentages of F-Epon.

To study the possible effect of the incorporation of F-Epon on the viewing angle,

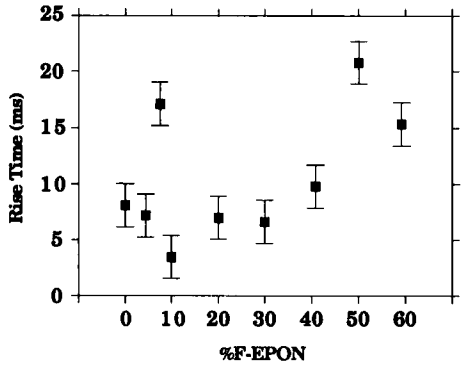



FIGURE 5 Rise time plotted as a function of %F-Epon contained in the polymer resin.

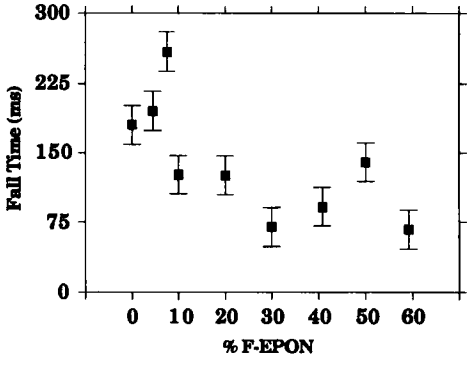



FIGURE 6 Fall time plotted as a function of %F-Epon contained in the polymer resin.

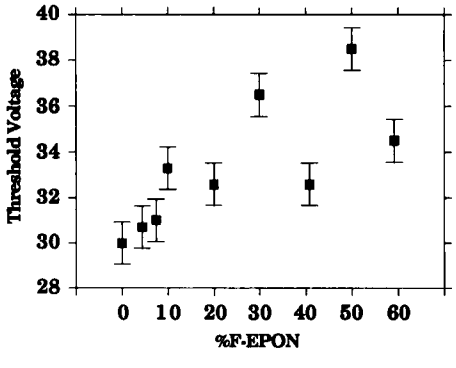



FIGURE 7 Threshold voltage (peak) plotted as a function of %F-Epon contained in the polymer resin.

$T_{max}$ was measured as a function of the angle of incidence formed between the laser beam and the surface of the sample. Data obtained in this manner for two plates containing 0% and 50% F-Epon, respectively, are plotted as contrast ratio versus incident angle in Figure 8. Both sets of data exhibit a sharp decrease in transmittance through the sample when the angle of incidence drops below 45°. In

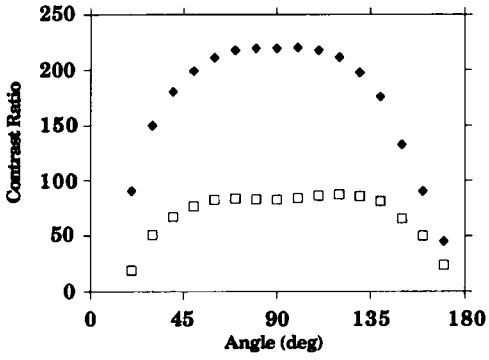



FIGURE 8 Contrast ratio plotted as a function of the angle of incidence made between the laser beam and the sample surface. The data were obtained by dividing the measured $T_{max}$ values of two samples with 0% F-Epon (squares) and 50% F-Epon (diamonds), by the corresponding average $T_{min}$ values listed in Table I.

comparing the two sets of data, the contrast ratio of the 50% F-Epon sample does appear to exhibit a slightly larger angle dependence compared to that of the sample containing no F-Epon. This is due in part to the much larger contrast ratio exhibited by the F-Epon sample between the angles of 45° and 90°.

The results presented here show that the incorporation of small amounts of F-Epon into the polymer binder results in increases in the contrast ratio and threshold voltage. These effects may stem from a decrease in solubility of the liquid crystal in the partially fluorinated polymer as opposed to the unfluorinated polymer, causing more complete phase separation to occur during polymerization. The data for the rise time and fall time are more scattered. In general, there appears to be a small increase in the rise time, and an obvious decrease in the fall time.

To investigate this point, scanning electron microscopy (SEM) was used to examine the difference in phase separation occurring betwen the two PDLC systems. Figures 9A and 9B are SEM pictures of a PDLC sample containing 0% F-Epon and 60% F-Epon, respectively. The density of the liquid crystal droplets associated with the 60% F-Epon sample is clearly much larger than that associated with the 0% F-Epon sample, while the droplet sizes do not appear to be significantly affected. To estimate quantitatively the effect of polymer fluorination on droplet density, feature analysis was performed on the SEM photos of both a 0% and a 60% F-Epon sample. Kevex Feature Analysis is the trade name of a software package associated with the JEOL JSM 880 SEM which enables the computer to distinguish between and count the features in a scanning electron micrograph. The features in the PDLC system are the phase separated liquid crystal droplets. This analysis indicates that there is approximately a 3.7 fold increase in the number of droplets formed in the 60% F-Epon sample compared to the 0% F-Epon sample. This is reflected in a significant decrease in the OFF state transmittance (Figure 2), which is very obvious to the naked eye. The increase in the ON state transmission with the concentration of F-Epon (Figure 3) may be a result of better phase separation, or a change in the refractive index of the polymer upon fluorination, or both. For most PDLC materials, the extraordinary refractive index of the liquid crystal is larger than the refractive index of the polymer binder, which is in turn

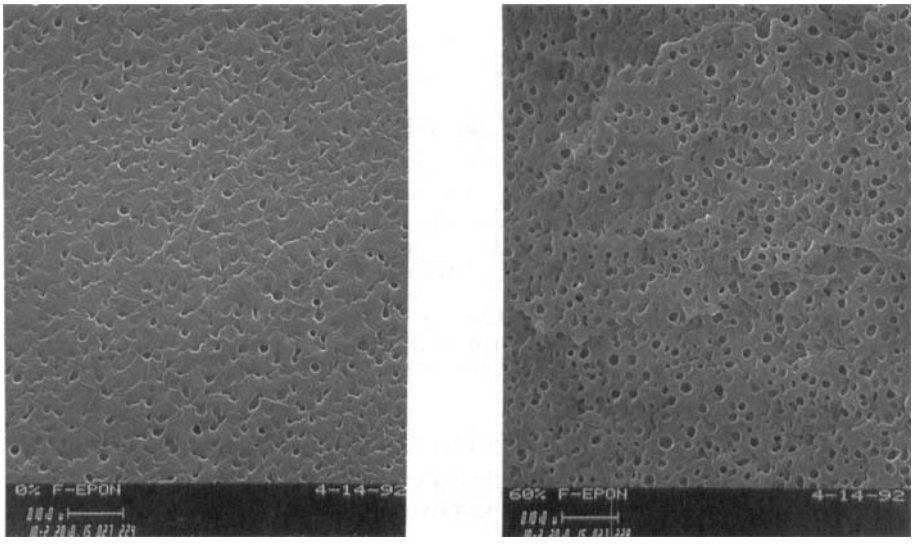



FIGURE 9 Scanning electron micrographs illustrating phase separation in (a) 0% F-Epon sample, (b) 60% F-Epon sample.

larger than the ordinary refractive index of the liquid crystal.[13] Fluorination often results in a decrease in the refractive index of the polymer,[14] making it a better match to the ordinary refractive index of the liquid crystal droplets to increase the ON state transmission.

Because the droplet sizes do not significantly change upon partial fluorination of the polymer, the increase in the threshold voltage and rise time accompanied by the decrease in fall time is likely due to changes in the anchor energy associated with the liquid crystal at the polymer droplet interface. A reduction in the solubility of the liquid crystal in the polymer, as discussed above, may be responsible for an increase in the anchor energy, since the composition of the polymer will certainly affect its interaction with the liquid crystal molecules at the interface. The change in the threshold voltage could also be related to the dielectric properties of the polymer binder[15] upon fluorination.

## CONCLUSIONS

In summary, the incorporation of small amounts of F-Epon into the polymer matrix results in a much better phase separation between the polymer and the liquid crystal. This leads to a significant improvement in the contrast ratio, and a large reduction of the fall time of the PDLC films compared to normal Epon samples. Additionally, phase separation within the F-Epon samples appears to be much more homogeneous, resulting in fewer visual defects in the "off" state appearance of the samples. The increases in the threshold voltage and rise time are disappointing. However,

the increase in the threshold voltage is only about 20% for the incorporation of 60% F-Epon (Figure 7), which is relatively small compared to the gains made in increasing the contrast ratio (Figure 4). The corresponding increase in the rise time is about a factor of two (Figure 5), compared to a reduction in the fall time by about the same factor (Figure 6). Since the fall time is much longer than the rise time, the advantage in reducing the former far outweighs the disadvantage in increasing the latter, and the overall electro-optic performance of the system is improved significantly.

## Acknowledgment

This work was supported by the Oklahoma Center for the Advancement of Science and Technology (OCAST) under grant number AR9-045. The authors thank Bill Chissoe and Greg Strout for providing scanning electron micrographs and for performing the SEM feature analysis.

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