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

Monitoring of Photopolymerization Through Dielectric Spectroscopy

D. Schuele [a] , R. Renner [a] & D. Coleman [a]
[a] Department of Physics, Case Western Reserve University, Cleveland, OH, 44124

Version of record first published: 04 Oct 2006

To cite this article: D. Schuele, R. Renner & D. Coleman (1997): Monitoring of Photopolymerization Through Dielectric Spectroscopy, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 343-352

To link to this article: http://dx.doi.org/10.1080/10587259708042013

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 343–352
Reprints available directly from the publisher
Photocopying permitted by license only

MONITORING OF PHOTOPOLYMERIZATION THROUGH DIELECTRIC SPECTROSCOPY

D. SCHUELE, R. RENNER AND D. COLEMAN
Department of Physics, Case Western Reserve University, Cleveland, OH 44124

Abstract

Polymer stabilized liquid crystal cells containing by weight 88.4% E48, 8.4% CB15 and 2.8% DSM monomer with photoinitiator are monitored by dielectric spectroscopy during polymerization by UV radiation. During the polymerization process, the dielectric loss decreases by approximately 50% independent of the UV intensity with only a slight change in capacitance. Optical and dielectric studies of the cured cells indicate that the morphology of the polymer gel is a function of the intensity of the UV radiation.

INTRODUCTION

Research in the flat panel display area has undergone rapid growth along with the commercialization of these devices. A recent advance has been the introduction of a small amount of polymer into the liquid crystal sample in order to stabilize the liquid crystal through the resultant polymer structure.(1-3) An advantage of the polymer stabilized cell is the wide viewing angle as compared to polymer dispersed liquid crystal cells. In the PDLC cell there is diffuse scattering at non normal incidence due to the index of refraction mismatch between the anisotropic liquid crystal and the polymer matrix. Due to the small amount of polymer in the stabilized cell the mismatch is relatively insignificant. This paper reports on a method using dielectric spectroscopy to monitor the state of polymerization during cell production.

EXPERIMENTAL PROCEDURE

The polymer stabilized cholosteric texture (PSCT) samples contained a liquid crystal mixture of nematic E48 (88.4wt%) and chiral CB15 (8.4wt%) with an addition of DSM monomer (2.8wt%) with photoinitiator. The samples were filled by capillary action into etched ITO cells consisting of two parallel plates separated by 6.0 μm Mylar spacers placed outside the active region and held together with Hysol epoxy. The virgin materials were studied in similar cells with a 6.0 μm spacing for DSM and 12μm spacing for E48 and CB15. The UV source of 366mμ wavelength was a UVGL-58 MINERALIGHT lamp. Three levels of intensity were used in the time studies of the PSCT cells - .366, .023 and .0027 mW/cm ^{2} and .050 mW/ cm ^{2} for the DSM sample.

A CGA-83 precision ratio-arm bridge with 17 fixed frequencies in a logarithmic scale over the frequency range 10Hz to 10^5 HZ was used to measure the complex dielectric properties as a function of frequency. The excitation level was kept quite low and varied between 9 and 95 milli volts depending on frequency. An H-P 4284A was used to measure the dielectric response at 500Hz and 15 volts rms excitation during UV radiation and to measure the AC voltage level dependence after polymerization.

Dielectric measurements are usually displayed in terms of the complex dielectric constant which consists of the dielectric constant ε' and the loss factor or imaginary part of the dielectric constant ε''. In this study most of the measurements will be reported in terms of the capacitance and loss in capacitive units. The dielectric constants can be obtained from these measurements by dividing by the empty cell capacitance. The parallel resistance of a cell is calculated from the dielectric loss by calculating the impedance using the loss in capacitive units.

The optical switching measurements used a METROLOGIC laser diode as source and a NEWPORT photodiode as receiver. The amplitude transmission response was measured at 500Hz square wave excitation on the cells and the transient time response had 15 volt square excitation at a number of frequencies.

VIRGIN MATERIALS

E48

The real and imaginary parts of the dielectric constant are shown in Figure 1. E48 acts as a relatively good dielectric material with low loss above 100Hz. The increased loss below 100Hz is probably due to ionic impurities.

CB15

The dielectric constants are shown in Figure 2 and indicate a material which is highly conductive at low frequency, having a resistive impedance which is about a factor of 7 lower than the capacitive reactance at 10Hz. These measurements indicate that this material contains a substantial concentration of ions and probably accounts for the low frequency loss in the polymerized cells. At 100Hz The phase angle is 45 degrees and above 300Hz this material appears as a good dielectric.

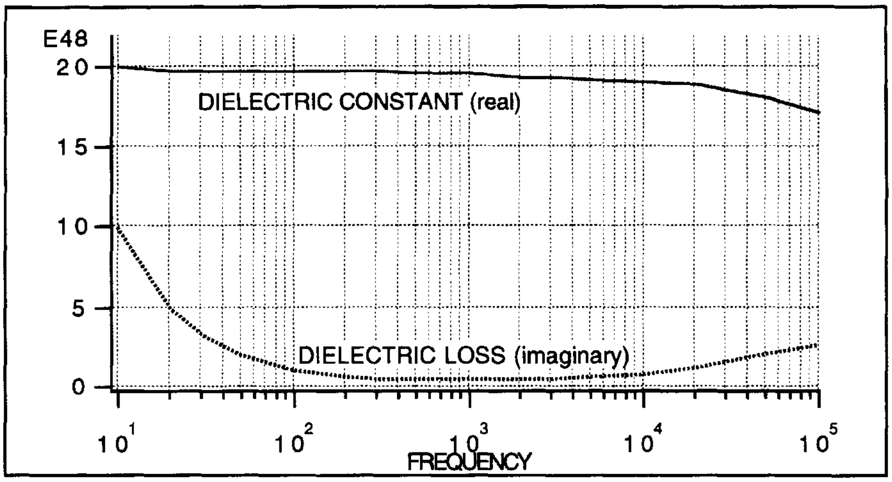

Figure 1. The real and imaginary parts of the dielectric constant of E48 as a function of frequency as measured in a cell with no surface treatment.

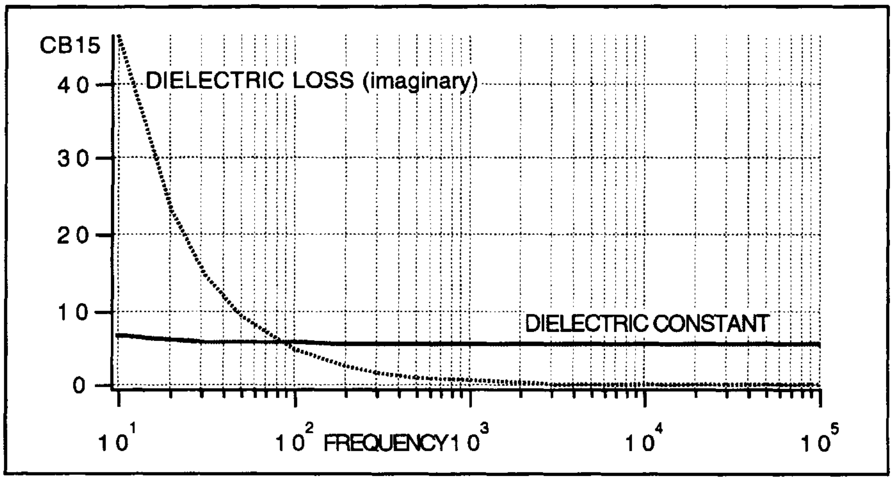

Figure 2. The real and imaginary parts of the dielectric constant of CB15 as a function of frequency as measured in a cell with no surface treatment.

DSM

The DSM monomer containing photoinitiator was developed and supplied by Dr. L. C. Chien of Kent State University. The dielectric spectrum before and after exposure to UV radiation is shown in Figure 3.

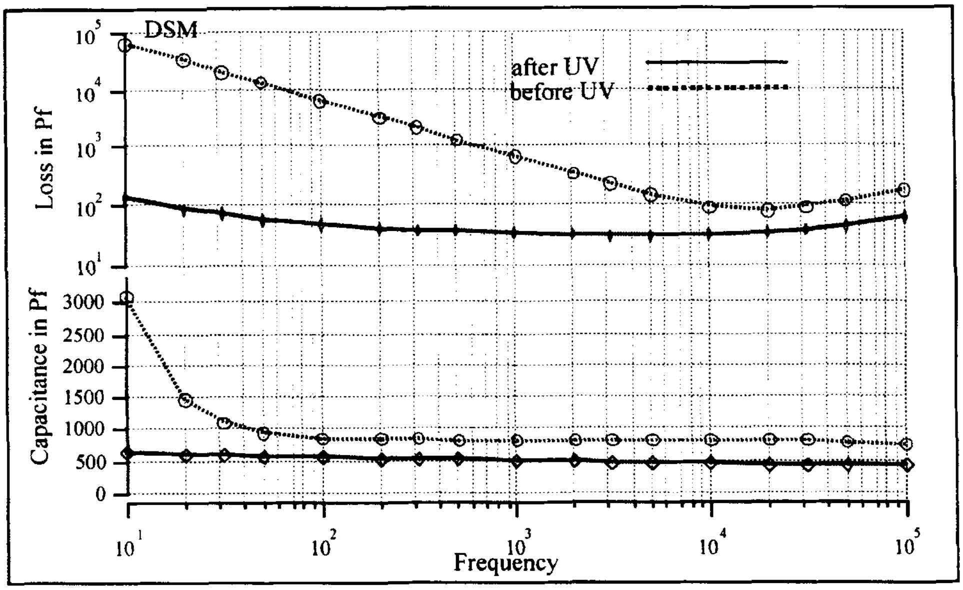

Figure 3. Dielectric spectra of DSM before (dashed line) and after (solid line) UV radiation. Note the log scale on the loss.

Prior to polymerization the monomer is highly conductive as indicated by the linear region in the log-log loss plot and exhibits a substantial Maxwell-Wagner effect at low frequencies. After polymerization the loss is reduced by almost three orders of magnitude at 10Hz. In terms of the resistance of the cell, prior to polymerization it had a resistance of 2.4KΩ and after 120MΩ. The dielectric constant in the frequency region above the Maxwell-Wagner effect is reduced by about 40%. Essentially the conductive components in the monomer are bound up by the polymerization.

The time evolution of the dielectric properties at 500Hz during polymerization with a UV source intensity of .05mW/cm^2 are shown in Figure 4. The radiation experiments were carried out at room temperature and no attempt was made to sink the temperature. The sequence of steps was an initial measurement at low voltage for comparison with the full spectrum followed by an increase in voltage to 15 volts with a short wait prior to radiating the sample. In contrast with the liquid crystals the monomer showed no voltage dependence in the loss or capacitance. the sample shows no change for 60 seconds after exposure and then undergoes a precipitous change in the loss by a factor of 25 over a period of the next 60 seconds. The capacitance shows no change until the point at which the loss begins its dramatic change. In this region the capacitance shows a small increase followed by a decrease with a long exponential tale well beyond the time at which the loss remains constant resulting in a 40% reduction. After polymerization the epoxy has the dielectric characteristics of a relatively low loss dielectric.

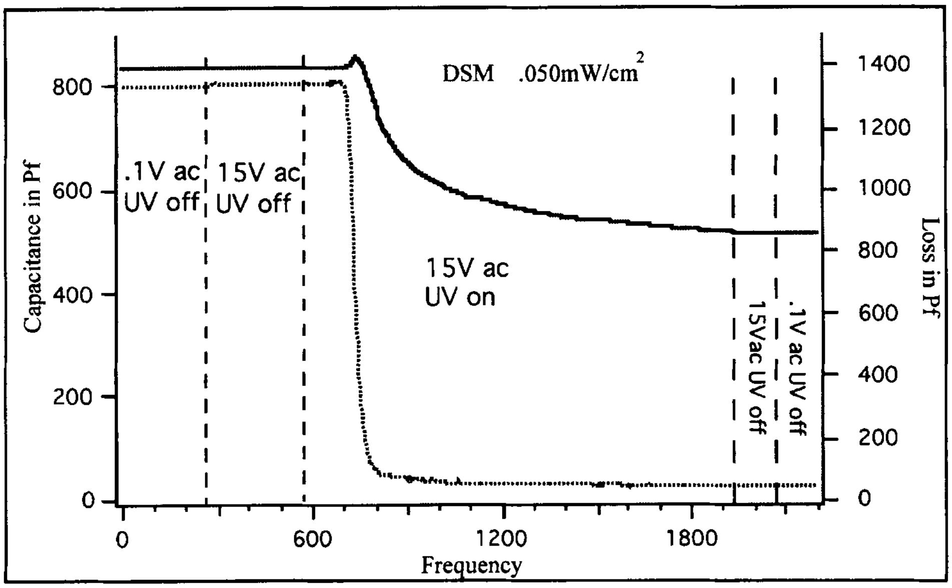

Figure 4. Radiation time study of DSM. The capacitance is the solid curve and the loss is the dashed curve.

Two components, CB15 and DSM, of the virgin materials add significantly to the dielectric loss while E48, the major component of the mixture, does not contribute. After polymerization, the bulk sample of DSM exhibits low loss.

PSCT CELLS

The samples were studied at three different UV intensities which varied by a factor of 100 each with the same time sequence of AC voltage and exposure. The time sequence was essentially the same as that used in the DSM study. Dielectric spectrums were taken before and after polymerization. Complete data will be presented for the sample exposed to the mid range intensity, .023mW/cm^2.

The dielectric spectrum before and after exposure is shown in Figure 5. The sample exhibits a high loss in the low frequency region before polymerization which is reduced by about 40% during polymerization. In terms of the components of the sample this is what one would expect assuming that DSM no longer contributes to the loss after polymerization. All three samples exhibited the same characteristics in the loss, however the capacitance of the high and low intensity irradiated samples had a larger capacitance in the low frequency region after polymerization than before.

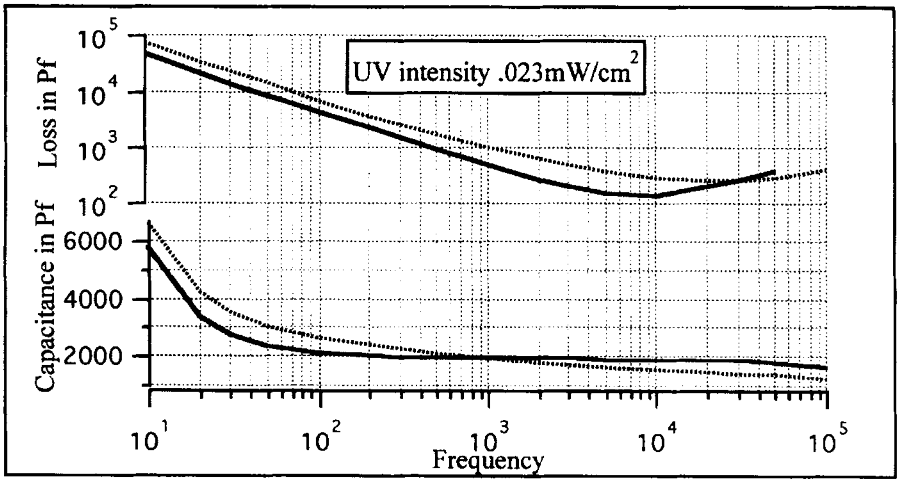

Figure 5. Dielectric spectrum of the PSCT sample irradiated with UV intensity of .023mW/cm^2. The dotted line is before radiation and the solid line is after.

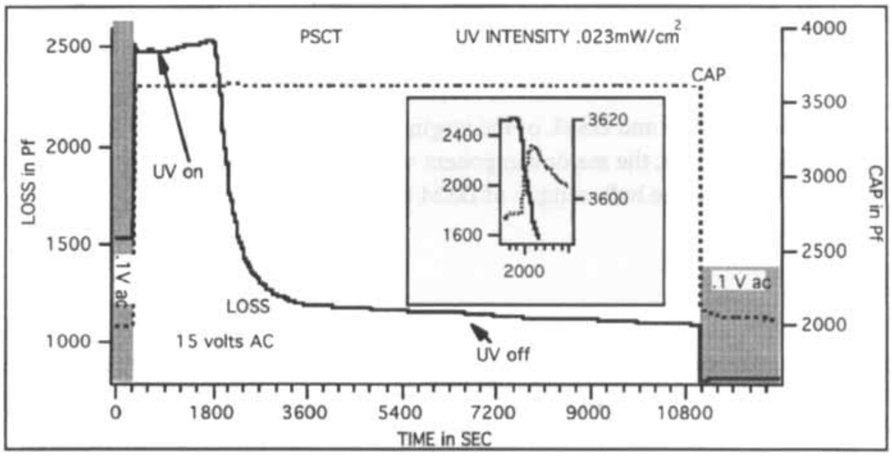

Figure 6. time study of a PSCT sample. The insert is an expansion of the region of the rapid fall off in the loss. The dashed curve is the capacitance and the solid curve is the loss.

The time study is shown in Figure 6. When the AC signal is increased to 15 volts from .1 volts there is a substantial increase in the capacitance which is due to the alignment of the liquid crystal. Along with this increase is an increase in the loss which indicates that the ions have a higher mobility in the environment of an aligned liquid crystal. After application of the UV radiation there is a long time period of approximately 15 minutes when one observes a slight increase in the loss with no change in the capacitance. Over the next 15 minutes the loss undergoes a substantial reduction of about 50% while the capacitance change is less than one percent as expected from the bulk measurement of DSM. After this transition and over the next two hours there is a slight reduction in the loss and no change in the capacitance. Following a removal of the radiation there is a slight change in the loss over the next two hours. Reducing the AC signal back to .1 volts results in a large decrease in the capacitance due to the randomness in the alignment of the liquid crystal with a corresponding decrease in the loss as a result of the decrease in the mobility of the ions.

Figure 7 is a composite of the three samples with normalized capacitance and loss. The normalization of a sample is obtained by dividing the capacitance as a function of time by the value prior to the onset of the loss decrease. The loss is normalized with respect to the maximum value of the loss. Thus the curves are capacitance and loss ratios.

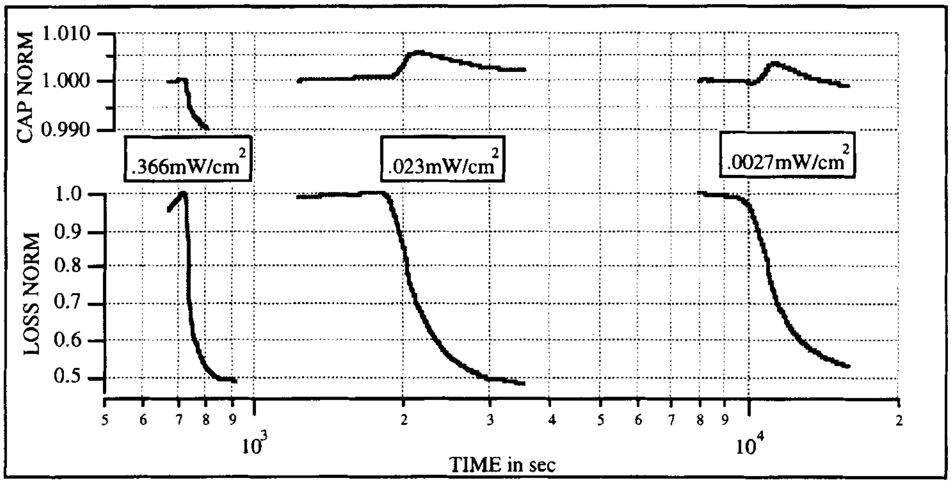

Figure 7. Composite of the normalized loss and normalized capacitance of the three samples. Note the logarithmic time scale.

The general characteristics of the dielectric loss as a function UV intensity follows. The change in loss during the photo-polymerization is approximately 50% independent of the UV intensity. The time to the onset of the large change in the loss is inversely proportional to the intensity and the intensity time product to the midpoint of the loss change is approximately constant. This implies that the incident UV energy per unit area to produce the same change in loss is constant. The time it takes the loss to change from the 90% to 10% point is approximately equal to the time of the onset of the fall off in loss. The initial characteristics of the change prior to the large fall off depends on the incident intensity. For large intensities there is an increase in loss prior to the fall off and as the intensity is reduced this transforms over to a continuous small decrease up to the time of the sharp decrease. This characteristic is probably due to the UV phiotoionization. While the loss exhibits substantial change, the capacitance shows structure but the total change is less than one percent. Clearly the loss serves as an excellent indicator of the processes taking place during photo-polymerization and can serve as a useful monitor.

PSCT CELL RESPONSE

The formulation of the cells places them in the scattering mode with no field applied. On application of a suitable AC field, the cells switch to the transparent or transmitting state. To characterize the cells, measurements were made of the capacitance and optical transmission as a function of applied voltage. The capacitance measurements were made at 500Hz rms signals while the optical measurements were made with square wave excitation at a variety of frequencies. Optical time response was also measured by applying a burst of 15 volt square waves and measuring the rise and fall times of the transmitted light.

The capacitance of the samples as a function of the ac voltage is shown in Figure 8a and the relative optical transmittance as a function of ac voltage at 1000Hz is shown in figure 8b. The relative transmittance is the ratio of the transmitted intensity to the maximum transmitted intensity for each cell. The optical transmission range of the cells is about 10 to 1. The .023mw/cm^2 cell's capacitance has the lowest voltage turn on point in terms of its increase in capacitance and this correlates well with the optical transmission measurements. Also this cell has the steepest increase in optical transmission as a function of the excitation voltage.

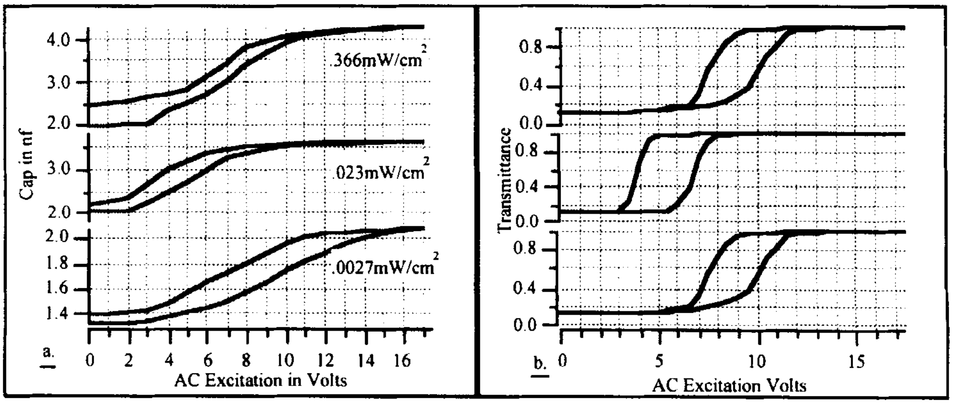

Figure 8. The capacitance as a function of excitation level at 500Hz is shown in a and the relative optical transmission as a function of excitation level at 1000Hz is shown in b. For each cell the lower curve is increasing voltage and the upper curve is the decreasing voltage.

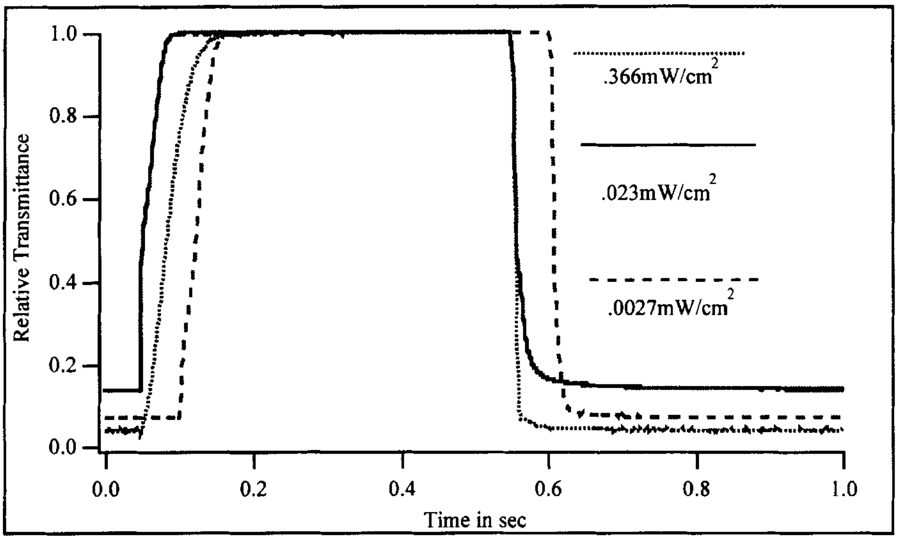

Figure 9.

Figure 9 is a plot of the optical response to a 1000Hz 15 volt square wave burst. The 10% to 90% turn on time varies from 25.7 msec to 52 msec with the .023mW/cm^2 sample having the fastest turn on. The turn off times were independent of sample and were of order 20msec. In terms of the optical quality of a window, the middle exposure sample has the best characteristics which would also be predicted from the voltage capacitance measurements.

From the optical and dielectric measurements it appears that the morphology of the polymer gel depends on the intensity of radiation during polymerization. Optical microscopy data seems to verify this conjecture, however final verification will require electron microscope studies which are underway.

CONCLUSION

The dielectric loss can serve as a monitor of the state of the gel polymerization during photo-polymerization of PSCT cells. This technique may have applications in the commercial manufacture of these devices. studies are underway to use this technique to examine the effect of cell temperature on the polymerization process.

Supported by the National Science Foundation Science and Technology Center
ALCOM DMR89-20147

REFERENCES

1. Liquid Crystals in Complex Geometries , edited by G. Crawford and S. Zumer, (Taylor and Francis, Bristol, PA, 1996).
2. R. A. M. Hikmet, Liquid Crystal, 9, 405 (1991).
3. D. K. Yang, L. C. Chien and J. W. Doane,Applied Physics Letters, 60, 3102-3104 (1992).