

Notes

Effect of Applied Voltage on the Fluorescence Behavior of E7/NOA-65 PDLC Films

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Introduction

In general, a polymer dispersed liquid crystal (PDLC) film is a heterogeneous thin composite film that micrometer sized nematic liquid crystal (LC) droplets are uniformly dispersed in an optically transparent polymer matrix. It is very useful for light control, LC display panels, and other electro-optical applications.^{1,2} The LC droplets in a PDLC film normally have bipolar director configuration.³ In the absence or presence of an external electric field, the LC molecular droplets are randomly distributed (off-state) or aligned along with the field (on-state) in the matrix polymer of a PDLC film. It has been extensively studied that the electro-optical properties of PDLC films depend not only on the analytical factors like applied voltage and frequency, but also on the material factors like LC and matrix polymer types, preparation method, LC concentration, droplet shape and size, film thickness, etc.⁴⁻⁷ However, only a few papers on the fluorescence studies of PDLC films have been reported.^{8,9}

The aims of the present study are primarily to investigate the effect of applied electric field intensity and time on the steady-state fluorescence behavior and also to better understand the LC reorientation occurring in PDLC films with cyanobiphenyl-based E7 and thiol-ene-based NOA-65.

Experimental

A thermotropic nematic liquid crystal (E7, Merck Inc.) used in the present work is a eutectic mixture composed of four different types of liquid crystals, 4-cyano-4'-pentylbiphenyl (5CB: 47 mol%), 4-cyano-4'-heptylbiphenyl (7CB: 25 mol%), 4-cyano-4'-octyloxybiphenyl (8OCB: 18 mol%), and 4-cyano-4'-pentyterphenyl (5CT: 10 mol%). The average molecular weight of E7 was 346.05 g/mol, based on the mole percent of each LC component. A thiol-ene-based photocurable polymer, Norland Optical Adhesive 65 (NOA-65: Norland Products Co.) was used as a matrix component.

The PDLC films used in this work were prepared by a photoinitiated-polymerization induced phase separation (PIPS) method using an E7 and a NOA-65 infiltrated between two indium tin oxide (ITO) glass plates (10×10 mm in size). The mixing ratio of E7 to NOA-65 was 60:40 by weight %. The ITO glass plates bonded together with a sealing material were uniformly apart by 20 μm sized glass bead spacers mixed with the E7/NOA-65 mixture. To prepare the PDLC films, the E7/NOA-65 mixtures were cured for 3 min in an UV chamber equipped with a Hg-UV lamp. The UV light intensity used was 40 W/m².

Each PDLC film was placed on the quartz plate in a dark chamber for fluorescence measurement with fiber-optic light guide equipment. A variety of sinusoidally modulated voltages at 1 kHz were applied using a voltage function generator (HP Model 33120A) and an amplifier. The fluorescence emission spectra were obtained by excitation at 348 nm. An optical cut-off filter of 340 nm was used to minimize the stray light occurring during fluorescence measurement. Two different types of voltages were applied, respectively. One was the cumulatively applied voltage. Here, the voltage applied to the PDLC film was increased stepwise by 2 volts from 0 to 24 volts. The other type was the abruptly applied voltage. Here, in the absence of electric field the given voltages were instantaneously applied to the PDLC film.

The steady-state fluorescence behavior of PDLC films with varying the applied voltages were measured at ambient temperature in air using an Aminco-Bowman Series 2 luminescence spectrometer (Spectronic Ins.) equipped with a 150 W ozone-free xenon lamp. The illumination angle between the fiber-optic light guide and the PDLC film surface in a dark chamber was 90°. The detector angle was also 90°. The distance between the light guide and the film surface was 10 cm. The detector angle was also 10 cm. The slit width of excitation and emission monochromators was 16 nm throughout the measurement.

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Results and Discussion

Figure 1 displays the change of the fluorescence emission intensity as a function of wavelength observed for E7/NOA-65 PDLC films cured by UV irradiation for 3 min in the absence of electric field (0 volt) and also in the presence of various applied voltages (2 to 24 volts). The structureless fluorescence bands with the maximum peak at 388 nm were

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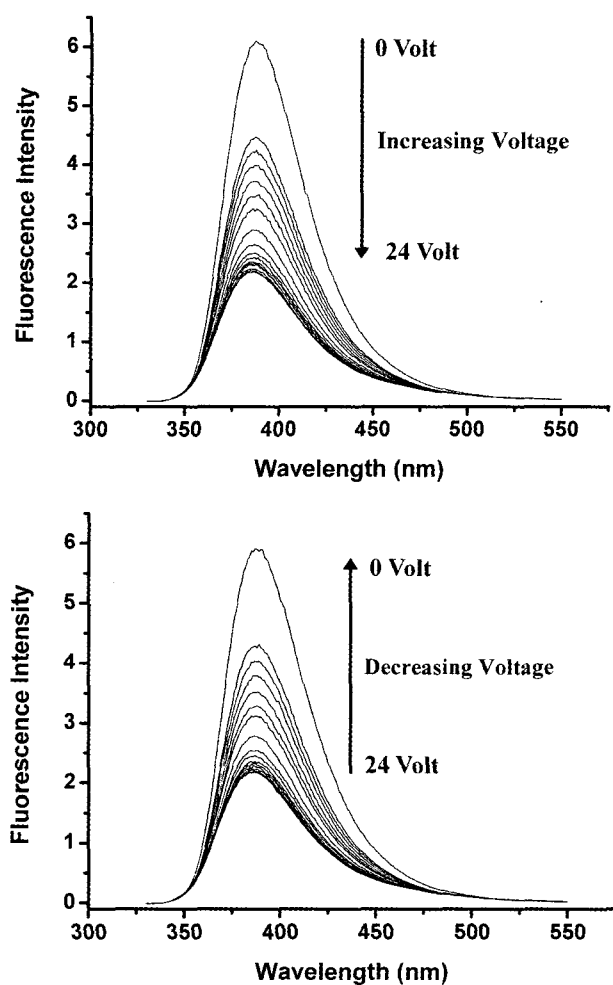


Figure 1. The variation of the steady-state fluorescence spectra observed with increasing (top) and decreasing (bottom) applied voltages for E7/NOA-65 PDLC films.

due mostly to the liquid crystal E7 in the PDLC film, as found in the previous report.¹⁰ The fluorescence intensity observed from the NOA-65 was very weak (close to 0) to be negligible in comparison with that from the E7. As shown in the top of Figure 1, the fluorescence intensity with a maximum peak at 388 nm was obviously decreased with increasing the cumulatively applied voltage, due to the reorientation of the liquid crystal molecules in relation to the polarization of the incident light. Especially, the intensity was greatly decreased with an initial introduction of the electric field and then it was gradually decreased with increasing the voltage. At the later stage of the voltage applied, the intensity was slowly decreased with a smaller extent.

On the other hand, the fluorescence intensity was increased with decreasing the voltage applied, as seen in the bottom of Figure 2. The fluorescence intensity recovered in the absence of applied voltage is ultimately almost same as that obtained from the result in the top of Figure 1. The

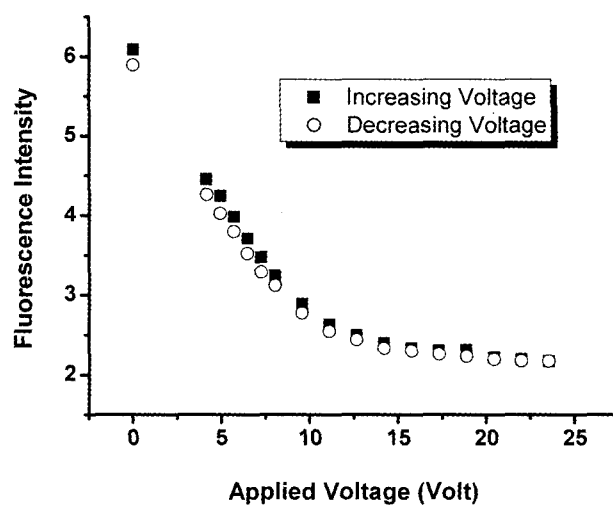


Figure 2. Plots of the fluorescence intensity measured for E7/NOA-65 PDLC films as a function of applied voltage.

result indicates that the orientation and association of E7 molecules dispersed in the NOA-65 matrix of the PDLC film importantly contribute to its electric field-induced reorientation and electro-photophysical response.

Interestingly, the result demonstrates that the fluorescence intensity of the PDLC film was ultimately recovered to its initial state by removing the applied electric field, indicating a photophysical hysteresis phenomenon. Such behavior is directly related with the reorientation behavior of LC molecules dispersed in the PDLC. In the absence of electric field, the E7 LC droplets are randomly distributed in the NOA-65 matrix so that the PDLC film becomes optically opaque. In this case the PDLC film fluoresces with the maximum intensity. This is because individual E7 molecules emit independently without association with other E7 molecules in proximity. On the other hand, the E7 molecules are aligned along with the applied electric field so that the PDLC film becomes optically transparent. In this case, the PDLC film fluoresces with the reduced intensity due to the increased reorientation of E7 molecules with increasing the electric field.

Figure 2 depicts the variation of the fluorescence intensity both with increasing and decreasing the applied voltage. The fluorescence intensity was changed with the almost same tendency against the increasing and decreasing applied voltages. This indicates that the photophysical hysteresis was found with the spectral intensity. Such behavior was found from analysis for the variation of the spectral area as well.

Figure 3 demonstrates that the fluorescence intensity also strongly depends on the voltage abruptly applied to the PDLC film as well as the cumulatively applied voltage above-mentioned. The variation of the fluorescence intensity at 388 nm was monitored with increasing the voltage as a function of data acquisition time. It was clearly found that

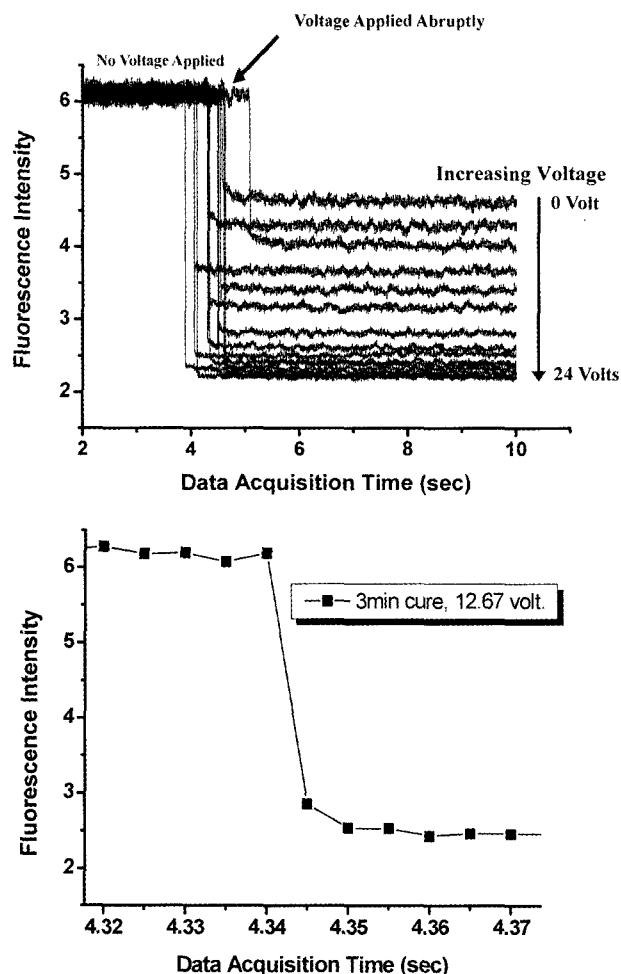


Figure 3. The variation of the fluorescence intensity measured for E7/NOA-65 PDLC films as a function of data acquisition time using a time scan method. The data acquisition time interval was 5 ms.

the fluorescence intensity was not changed in the absence of applied electric field but it was instantaneously dropped down by the voltage applied abruptly after a short period of 4-5 s, depending on the imparted electric field intensity. The fluorescence intensity was gradually decreased with increasing the abruptly applied voltage until the saturation voltage was reached. Near the saturation voltage, the fluorescence intensity was not changed significantly. The result obtained from the time scan in the top of Figure 3 was consistent with that from the emission scan in the top of Figure 1.

A closer inspection of the fluorescence time scan at the instant of voltage application may assist to find out the response time, based on the variation of the fluorescence emission spectrum resulted from the LC molecular reorientation change. The result is shown in the bottom of Figure 3. The photophysical response time was found to be about 0.005 s when 12.7 volts were abruptly applied to the PDLC

film. This means that the rise time, which is defined as the time required for reaching 90% of the on-state transmission from the off-state, was about 0.005 s. This turns out that the E7/NOA-65 PDLC film cured for 3 min may be on-state by 90% within 0.005 s upon application of 12.7 volts. It is noted that the photophysical response time is sensitive to the conformational and microenvironmental changes significantly depending on the local mobility of E7 molecules dispersed in the NOA-65 matrix and the applied voltage as well.

The result demonstrates that the photophysical response occurring in the PDLC film was transient and it was successfully monitored in the present study. Since fluorescence is very sensitive to conformational transition and reorientation of LC molecules occurring for a very short period of time.

Figure 4 shows the variation of the differential fluorescence intensity obtained from the emission scan for the E7/NOA-65 PDLC film as a function of applied voltage. Here, the differential fluorescence intensity is the fluorescence intensity at 0 volt subtracted by that at each applied voltage. It is likely that here the fluorescence behavior shows a S-shaped curve, as similarly found from the typical electro-optical behavior of PDLC in other reports.⁴⁻⁶

The most important impact of the present work is that the fluorescence behavior of E7/NOA-65 PDLC films significantly contributes to evaluating the threshold voltage and the driving voltage, which are key factors for determining the on-off state and the performance of the film. The asymptotic value of the differential fluorescence intensity indicates the maximum of on-state transmission, which is related with

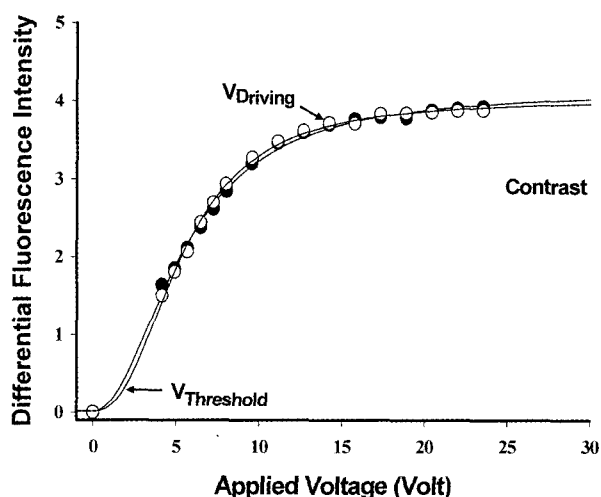


Figure 4. Comparison of the differential fluorescence intensity obtained from the subtraction of the intensity at the given applied voltage from that at zero voltage between two PDLC films scanned by emission (open circles: cumulatively increasing voltages) and time (closed circles: abruptly increasing voltages) methods, respectively.

the contrast. The applied voltage at 10% of the maximum value was determined to be the threshold voltage (V_{10}) and that at 90% was the driving voltage (V_{90}). The slope between the V_{10} and V_{90} values indicates the driving efficiency at a given applied voltage. That is, the stiffer the slope, the lower the driving voltage from the off-state to the on-state. As a result, for the E7/NOA-65 PDLC film in the present work, the V_{10} was 1.9 volts and the V_{90} was 13.8 volts in the case of cumulatively applied voltage (emission scan), whereas the V_{10} was 2.1 volts and the V_{90} was 12.5 volts in the case of abruptly applied voltage (time scan). The result suggests that the cumulatively applied voltage more or less contributes to lowering the threshold voltage, whereas the abruptly applied voltage contributes to lowering the driving voltage.

The result of Figure 4 indicates that the LC molecules in the E7/NOA-65 PDLC film are somewhat easily aligned with the field at a slightly lower initial voltage in the cumulatively applied electric field. On the other hand, the LC molecules need a lower driving voltage to be aligned along the field in the case of abruptly applied electric field. Therefore it may be noted that an abruptly given high voltage is more effective to drive the molecular alignments.

Conclusions

The present result indicates that the steady-state fluorescence behavior of E7/NOA-65 polymer disperse liquid crystal films prepared by a photoinitiated-polymerization

induced phase separation method plays a significant role in understanding electro-photophysical response and hysteresis on varying applied electric fields. The fluorescence technique is sensitive to molecular alignment of LC molecules in the polymer matrix and it also provides useful quantitative information on the rise time, the threshold voltage and the driving voltage of a PDLC system.

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References

- (1) R. A. M. Hikmet, *J. Appl. Phys.*, **68**, 1 (1990).
- (2) D. J. Broer and I. Heynderickx, *Macromolecules*, **23**, 2474 (1990).
- (3) R. Ondris-Crawford, E. P. Boyko, B. G. Wagner, J. H. Erdmann, S. Zumer, and J. W. Doane, *J. Appl. Phys.*, **69**, 6380 (1991).
- (4) L. Bouteiller and P. Le Barny, *Liq. Cryst.*, **21**, 157 (1996).
- (5) C. Grand, M. F. Achard, and F. Hardouin, *Liq. Cryst.*, **22**, 287 (1997).
- (6) U. Maschke, X. Coqueret, and M. Benmouna, *Macromol. Rapid Commun.*, **23**, 159 (2002).
- (7) M. Mucha, *J. Appl. Polym. Sci.*, **43**, 175 (1991).
- (8) S. Kato, B. Lee, and C. Pac, *Liq. Cryst.*, **22**, 595 (1997).
- (9) D. A. Higgins, X. Liao, J. E. Hall, and E. Mei, *J. Phys. Chem. B*, **105**, 5874 (2001).
- (10) G. Yang and D. Cho, *J. Lumin.*, in press.