Effect of Curing Progress on the Electrooptical and Switching Properties of PDLC System

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Received 9 March 1998; accepted 12 June 1998

ABSTRACT: Experimental studies on the morphology and thermal and electrooptical behavior of PDLC films consisting droplets of nematic LC (6CB) up to a 40% weight fraction in a polyester resin matrix crosslinked by diacrylane are presented. The PDLC samples were prepared by LC separation from a solution in a UV-polymerizing oligoester resin between TIO-coated glass plates. The electrooptical and switching results depending on the UV curing time of the polyester matrix are shown. The curing process of the polymer binder leading to phase separation of the LC causes increasing polymer stiffness affected by the boundary condition on the LC droplets. The reorientational dynamics of LC in PDLC, which reflects the character of switching curves for varying voltage and with progressing curing (varying from 40 s to 15 min), is discussed on the basis of the kinetic analysis of light scattering by the system. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 455–463, 1999

Key words: liquid crystals; polymer-dispersed liquid crystals; polyester resin curing; electrooptical effects

INTRODUCTION

Recently, tremendous activity¹⁻¹⁵ has characterized the field of research on polymer-dispersed liquid crystals (PDLCs) which are potentially useful for a variety of electrooptical applications including light shutters and switchable windows, displays, and other devices. These materials consist of micrometer-size nematic droplets dispersed in a polymer matrix and their optical response is based on the electrically controlled light-scattering properties of the droplets.

The light-scattering state is dependent on optical heterogeneities in the composite film such as a spatial distortion of the nematic director and mismatching in the refractive indices of the components. It was mentioned before⁷⁻¹⁰ that the electrooptical properties of PDLC displays depended on the LC concentration, film thickness, size and shape of the LC droplets, anchoring energy on the boundary surface, and physical properties of both components such as the elasticity, viscosity, and dielectric anisotropy of the LC and the resistivities and refractive index ratio of the LC and the polymer.

Here, we present experimental studies on the morphology, thermal, and electrooptical behavior of PDLC films consisting of nematic LC (6 CB) in the polyester resin matrix. Their properties were controlled by the conditions of preparation, LC content c, film thickness d, temperature, and curing time of the polymer binder. The PDLC samples were prepared by LC separation from a solution of a UV-polymerizing oligoester resin between TIO-coated glass plates. The figures show examples of the electrooptical and switching re-

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Contract grant sponsor: Scientific Research Committee (KBN), Poland; contract grant number: 3 T09B 045 09. Journal of Applied Polymer Science, Vol. 71, 455-463 (1999)

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sults obtained for the 6CB LC in a polyester resin matrix crosslinked by diacrylane depending on the UV-curing time of the matrix.

It was found that the electrooptical and switching properties of PDLC light shutters are controlled by conditions of their preparation. Particularly, the curing process of the polymer binder leading to phase separation of LC causes increasing polymer stiffness affected by boundary conditions. The reorientational dynamics in PDLC, which reflects the character of the switching curves for varying voltage and with progressing curing, is discussed on the basis of a kinetic analysis of light scattering by the system.

EXPERIMENTAL

Sample Preparation

The PDLC displays under study consist of nematic liquid crystal of known characteristics of 6 CB, prepared in a WAT randomly dispersed as droplets in polyester resin films. Thin films were prepared in the following way: First, mechanical mixing of the appropriate amount of the liquid crystals (20-40%) by weight) with the polymer precursor (containing an unsaturated oligoester resin, diacrylane, and UV-curing agent) leads to a homogeneous solution of both components. Then, the mixture was transformed between ITO-coated glass plates (previously coated with a very thin layer of pure oligoester resin to avoid LC escape) using a film spacer to control the thickness of $10-20 \mu m$. Refractive indices of the LC and polymer binder are well matched. UV irradiation in time varying from 40 s to 15 min was applied for curing of the polymer binder and phase separation. Complete phase separation of LC occurs during 40 s of UV radiation (see Fig. 1).

Methods

The morphology of the composite films was studied using a multiscan analysis system consisting of a polarizing microscope, video camera, and computer. Thermooptical analysis was done using a Mettler thermooptical cell. Electrooptical and switching studies were carried out using a special device consisting of a He/Ne laser, Mettler heating stage, photodiode, generator, and oscilloscope. The He/Ne laser beam (wavelength of 632.8 nm) was passed normal to the film surface and the transmitted light intensity without any polarizer



Figure 1 Relative intensity of light transmission versus curing time. Complete phase separation of LC occurs during 40 s of UV radiation.

was measured with a photodiode. The output from a function generator (frequency used: 20 kHz) was used to drive the cell. The drive signal and the response of the photodiode were monitored on a digital storage oscilloscope (Tektronix TDS 310).

RESULTS AND DISCUSSION

Morphological Structure

Figure 2 shows the chosen micrographs of two composite PDLC films containing a weight fraction of UV polymerization versus curing time (2 min, 10 min, temperature 250°C, $d = 10 \ \mu$ m). The size of the LC domains is smaller and more uniform when the curing time t_C of the polymer matrix is longer. The shorter the t_C , the larger the size of the LC droplets, due to possible coalescence in the yet soft matrix.

Thermooptical Analysis

Figure 3 presents thermooptical curves in the range of the isotropization temperature T_i of the LC drawn for 100% LC and 30 and 40% LC in the PDLC. The sample curing time was 15 min, and film thickness, 10 μ m. The observed value of T_i in PDLC decreases only by 2–3°C in comparison to pure LC, presenting a good purity of the LC in the



Figure 2 Micrographs of PDLC films (with 6CB). Thickness $d = 10 \ \mu$ m, curing time $t = 20 \ min$: (a) c = 30%; (b) c = 40%.

droplets. Some small depression of the T_i value in the progress of curing of the matrix is observed.

Electrooptical and Switching Studies

For reorientation by an electric field, it is convenient to discuss film dynamics in terms of electric, elastic, and viscous torques. The elastic-restoring torque per unit volume Γ_d depends on the variation in the elastic free-energy density of the droplet F_k with some orientational parameter λ for the droplet under strong anchoring conditions:

$$\Gamma_{d} = \frac{dF_{k}}{d\lambda}$$

$$F_{k} = \frac{1}{2}\frac{K}{R}$$
(1)

with K the elastic constant and R the droplet radius. The viscous torque can be represented by

$$\Gamma_{\nu} = \gamma \, \frac{d\lambda}{dt} \tag{2}$$

with $(d\lambda)/(dt)$ the rate of reorientation and γ a rotational viscosity coefficient.

The electric torque per unit volume Γ_e depends on the electric-field free-energy density F_e :

$$\Gamma_{e} = \frac{dF_{e}}{d\lambda} = \frac{1}{2} \varepsilon_{0} \Delta \varepsilon \ E^{2} \sin(2\lambda)$$
$$F_{e\text{max}} = -\frac{1}{2} \varepsilon_{0} \Delta \varepsilon \ E^{2}$$
(3)

Surface anchoring parameters are not included in the prediction. It holds for the system where the anchoring is constant and strong. Rise and decay times are determined by balancing all the torques $\Gamma_d + \Gamma_e + \Gamma_v = 0.$

Frequency of Driving Voltage Effect

Figure 4 presents the relative transmitted light intensity versus the frequency of the driving voltage applied to the PDLC system for various values of the driving voltage: 20–50 V. The equilibrium orientation of the LC director for the chosen driving voltage is reached for frequencies higher than 0.5 kHz. For lower frequencies, the electrooptical effect becomes weak because of a pos-



Figure 3 Thermooptical curves in isotropization region of pure 6 CB and in PDLC in heating (h) and cooling (c) regimes.



90 80 • 15min 7min. 70 ▲ 4min. × 2min. 60 • 1min x 40sek 50 $\tau_{\rm R}$ [ms] 40 30 20 10 0 20 40 60 0 80 100 U [V]

Figure 4 Relative intensity of light transmission for various driving voltages (20-50 V) versus voltage frequency.

sible influence of ionic conductivity. For further investigations, f = 2 kHz was applied.

Cure Effect

Figure 5 presents the static electrooptical curves (relative transmittance versus driving voltage) related to PDLC films prepared at various curing



Figure 5 Electrooptical curves of PDLC for various curing times. Inset: Threshold voltage versus curing time.

Figure 6 Rise time versus voltage for various curing times.

times of the polyester matrix ranging from 40 s to 15 min. The inset shows the threshold voltage $U_{\rm th}$ versus the curing time. Increase of $U_{\rm th}$ with the curing time is observed. A minimum voltage required to switch the LC in PDLC films, known as the threshold voltage $U_{\rm th}$ in the case of bipolar configuration, is described by eq. (4):

$$U_{\rm th} = \frac{d\left(\frac{\zeta_{\rm P}}{\zeta_{\rm LC}} + 2\right)}{3a} \left[\frac{K(l^2 - 1)}{\varepsilon_0 \Delta \varepsilon}\right]^{1/2} \tag{4}$$

where d, a, ζ , K, l, and $\Delta \varepsilon$ represent the film thickness, major dimension, resistivity, elastic constant, aspect ratio (major to minor dimension), and dielectric anisotropy of the LC, respectively.

The observed increase of $U_{\rm th}$ with the curing time of the matrix up to a constant value equal to about 10 V is determined by a cooperation between changing the droplet size (observed decreasing *a*) and increasing the resistivity ratio $(\zeta_{\rm P}/\zeta_{\rm LC})$, which reach constant values after some time of curing. However, the effect of surface anchoring on the interface of the LC droplet and polymer matrix varying in the progress of curing the polyester resin can be a dominant factor in controlling the $U_{\rm th}$ of the composite film which is neglected in eq. (4).

Figure 6 shows a set of curves presenting a rise time τ_R dependence on the driving voltage obtained for various curing times of the matrix. In



Figure 7 Reciprocal rise time $1/\tau_R$ versus square voltage $U^2/1000$ for various curing times t.

the case of some elongated droplets of bipolar configuration (when surface anchoring is neglected), the following equation for reciprocal rise time $1/\tau_R$ can be generated:

$$\frac{1}{\tau_R} = \frac{9\varepsilon_0 \Delta \varepsilon}{\gamma \left(\frac{\zeta_P}{\gamma_{\rm LC}} + 2\right)^2} E^2 + \frac{1}{\tau_D}$$
$$\tau_D = \frac{\gamma a^2}{K(l^2 - 1)} \tag{5}$$

where γ is the rotational viscosity. Other symbols are the same as in eq. (4).

The reciprocal rise time (data from Fig. 7) is drawn versus the square driving voltage U^2 in Figure 7. From the slope data of Figure 8 [applying eq. (5)], the values of the resistivity ratio $\zeta_{\rm P}/\zeta_{\rm LC}$ were calculated (data for 6 CB: $\Delta\varepsilon = 11.5$, $\gamma = 4 \times 10^{-2}$ [kg m⁻¹ s⁻¹], $\varepsilon_0 = 8.85 \times 10^{-12}$ [*F*/*m*], $d = 10 \ \mu$ m) and are presented in Figure 8 versus the curing time of the polyester matrix. Increasing resistivity of the polymer $\zeta_{\rm P}$ ($\zeta_{\rm LC}$ remains constant) and surface anchoring on the boundary wall of the droplets have dominant effects on the electrooptical and switching behavior of PDLC films.

INTERPRETATION OF THE SWITCHING RESULTS OF PDLC SYSTEM BY LIGHT-SCATTERING KINETICS

PDLC materials scatter light. For technological and scientific reasons, the light-scattering properties of these films is a topic of great interest. Electrical control of this light scattering is the basis of many devices built with these materials. The light-scattering properties of a PDLC film will depend on many aspects of the film construction. Droplet size, shape and density, and the nematic and polymer refractive indices and wavelength are important parameters in determining the light-scattering properties of a PDLC film. However, the nematic configuration within the droplet dominates the light-scattering properties of a film and allows the film to switch from a strongly scattering to a highly transparent one with an applied field. Several theories on light scattering for PDLC materials have been developed. The anomalous diffraction (AD) approximation assumes that the scattering objects are much larger than is the incident wavelength λ :

$$\frac{2\,\pi R}{\lambda} \gg 1$$

where R is the droplet radius.

There are two contributions to the scattered field: The first contribution is equivalent to light scattered by the scattering particle. The second contribution arises from light undergoing a phase shift Δ which depends on the size and orientation of the nematic droplet:

$$\Delta = \frac{4\pi}{\lambda} \left(\frac{n_{\rm eff}}{n_p} - 1 \right) \tag{6}$$



Figure 8 Resistivity ratio ζ_P/ζ_{LC} versus curing time.



Figure 9 Kinetic curves of reorientational process in PDLC for various voltages applied; curing times $\tau = 12$ min.

For small phase-shift terms, the scattering cross section is equal:

$$\sigma = \left[\frac{R[n_{\text{eff}}(\Theta) - n_p]}{\lambda}\right]^2 \tag{7}$$

In films, at the fields, the clarity of the film depends on the difference in the refractive index $n_{\rm eff}$ (effective refractive index of the droplet) and n_p (the refractive index of the matrix). The value of $n_{\rm eff}$ will depend on the angle of incident light. $n_{\rm eff}$ expressed in terms of the incident angle θ and n_0 and n_e is

$$n_{\rm eff} = \frac{n_0}{\sqrt{1 - \left(\frac{\sin\Theta}{n_P}\right)^2 \cdot \left[1 - \left(\frac{n_0}{n_e}\right)^2\right]}} \tag{8}$$

where n_0 and n_e are, respectively, the ordinary and extraordinary refractive indexes of the LC and n_P is the refractive index of the polymer.

The extraordinary refractive index n_e is associated with the long axis of the molecule, while the direction is perpendicular to the director field. At high fields, light at normal incidence ($\theta = 0$) will be parallel to the nematic director and $n_{\rm eff}$ for the droplet is equal to n_0 .

Experimental switching curves of dynamic LC reorientation obtained for (i) various driving voltages of 20–90 V for a constant curing time of the matrix $t_C = 20 \text{ min } (c = 30\%)$ and (ii) various



Figure 10 Kinetic curves of reorientational process in PDLC for various curing times; U = 50 V.

curing times of the matrix $t_C = 1-15 \text{ min} (c = 40\%)$, with driving voltage of 20 and 50 V, are presented in Figures 9–11. The sample thickness was the same and equal 10 μ m. The effect of the voltage applied and the curing time of the matrix is clearly seen. The transformation of the transmission curve data to the double log scale leads to a linear dependence (Figs. 12–14) according to the equation

$$\lg \left[-\ln \left(\frac{I_{\max} - I}{I_{\max}} \right) \right] = n \, \lg t + \lg k \tag{9}$$



Figure 11 Kinetic curves of reorientational process in PDLC for various curing times; U = 20 V.



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Figure 12 Double lg curves drawn from the kinetic curve data. Inset: lg k (rate constant) versus voltage applied; n = 2.1.

which leads to the following kinetics equation:

$$\frac{I}{I_{\max}} = 1 - e^{-kt^n} \tag{10}$$

where I_{max} is the maximum equilibrium orientation (constant value of transmitted light inten-



Figure 13 Double lg curves drawn from the kinetic curve data. Inset: lg k (rate constant) versus curing time; 4.7 < n < 2.7, U = 50 V.



Figure 14 Double lg curves drawn from the kinetic curve data. Inset: lg k (rate constant) versus curing time; n = 2.2, U = 20 V.

sity) for time equal the rise time τ_R ; k, the rate constant; and n, the slope parameter. The insets present the lg k plots drawn versus the driving voltage (Fig. 12) and curing time (Figs. 13 and 14).

According to Lambert–Beer law, the intensity of light transmitted through the sample thickness d depends on the material turbidity τ if d = cons.:

$$\frac{I}{I_{\max}} = e^{-\tau d} \tag{11}$$

if $I_{\text{max}} \approx I_R$, where I_R is the reference light intensity.

At constant droplet concentration and the absence of multiple scattering (thin sample), turbidity τ will be proportional to the scattering cross section σ :

$$\tau = Nd$$

$$\tau = C_1 \Delta n^2(\Theta)$$

where

$$C_{1} = \frac{NR^{2}}{\lambda^{2}}$$
$$\Delta n(\Theta) = [n_{\text{eff}}(\Theta) - n_{p}]$$

where Θ is the incident angle, and *N*, the number density of scattering objects. Thus,

$$\frac{I}{I_{\max}} = e^{-C_1 d\Delta n^2(\bar{\Theta})}.$$
 (12)

Taking (10) equal to (12),

$$1 - e^{-kt^n} = e^{-C_1 \Delta n^2(\bar{\Theta})d},$$

and for the first approximation,

$$kt^n = 1 - C_1 d\Delta n^2(\bar{\Theta}_0).$$

The change of birefringence with time of reorientation is equal,

$$\Delta n(\bar{\Theta}) = \sqrt{\frac{1 - kt^n}{C_1 d}}$$
(13)

if t = 0:

$$\Delta n(\Theta) = \Delta n(\Theta_0)$$
$$C_1 d\Delta n^2(\bar{\Theta}_0) = 1$$

The initial birefringence

$$\Delta n(\bar{\Theta}_0) = \sqrt{\frac{1}{C_1 d}} \tag{14}$$

for $t = \tau_R \Delta n \rightarrow 0$; thus,

$$k\tau_R^n = 1 \longrightarrow k = \frac{1}{\tau_R^n}$$

$$\lg k = -n \lg \tau_R \tag{15}$$

Figure 15(a,b) reflects the $\lg k = f(\lg \tau_R)$ plots drawn for various voltages applied and curing times of the matrix.

Light scattering as a function of the effective droplet orientations and the sample order parameters is much more complicated than presented here and can be calculated using the anomalous diffraction approximation. Field dependence of the sample order parameter can be presented as a function of the e-reduced electric-field parameter



Figure 15 Lg k versus $\lg \tau_R$ drawn for (a) various voltages applied at curing time t = 20 min and (b) various curing times at U = 20 V and U = 50 V.

$$\begin{split} S_s &= \frac{1}{4} + \frac{33(e^2+1)}{16e^2} \\ &+ \frac{3(e^2+1)(e^2-1)}{32e^3} \ln \frac{e+1}{e-1} \quad (16) \end{split}$$

which depends on both the strength of the applied field and elastic forces responsible for the existing droplet orientation, while the equilibrium orientation depends on the droplet-shape anisotropy. As an external field is applied, the sample order parameter increases as the droplet directors lie in the same direction.

The time dependence of the order parameter S(t) was obtained (16) in the complicated form as follows:

$$S(t) = -\frac{1}{2} + \frac{3}{8\pi} \frac{(1 - wtg\alpha)^2}{(1 + w^2)(1 + tg^2\alpha)} d\Omega \qquad (17)$$

where

$$w = tg(\Theta - \alpha) = tg(\Theta_0 - \alpha)e^{-\sin 2\gamma/\sin 2\alpha t/\tau} \quad (18)$$

and the equation of motion was derived as

$$\dot{\Theta} = \frac{1}{2\tau} \frac{\sin 2\gamma}{\sin 2\alpha} \sin 2(\Theta - \alpha)$$
(19)

where τ is the time characteristic for the droplet, θ is as before, γ is the angle between the applied field and the symmetry axis of the cavity, and α = $f(\gamma, e)$.

CONCLUSIONS

- 1. The electrooptical and switching properties of PDLC films show a strong dependence on the curing time of the polymer matrix.
- 2. The results are explained by the effective increase of anchoring strength at the interface of the polymer and LC depending on the area fraction of the interface, size and shape of LC droplets, and the stiffness and resistivity of polymer changing in the course of crosslinking polymerization. An increase of the glass transition of the polyester resin leads to a change in the droplet surface structure, which, in turn, leads to a change in the surface anchoring energy.
- 3. The kinetic interpretation of the resulting

switching curves was applied to the description of the dynamics of the field-induced reorientational process in the PDLC samples. It allows for a comparison of various switching results in terms of the kinetic rate constant dependent on the voltage applied and the curing time of the polymer matrix.

The authors gratefully thank the Scientific Research Committee (KBN) of Poland for support (Grant No. 3 T09B 045 09).

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