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Complex study of reorientational dynamics of the liquid crystal in PDLC films

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Morphological, electro-optical and switching properties of polyester resin/nematic liquid crystal composite films have been studied for varying composition (10–40 wt % of LC), temperature (20–50°C), film thickness (10–75 µm) and UV curing time of the matrix (0.25–12 min). The PDLC films were formed by LC separation in a UV polymerization process of the thin layer of oligoester resin (liquid crystal mixture) between ITO coated glass plates. The electro-optical and response behaviour based on the electric field controlled light scattering of the composite films was observed. The results were interpreted in terms of effective anchoring strength at the interface of the polymer and liquid crystal depending either on the area fraction of the interface in the composite film (dependent on the size and shape of the liquid crystal droplets) or the stiffness and resistivity of the polyester resin changing in the course of the crosslinking polymerization.

1. Introduction

In recent years a high level of activity has characterized the field of research on polymer dispersed liquid crystals (PDLCs) which are potentially useful for a variety of electro-optical applications including switchable windows, displays and other devices [1–13]. These materials consist of micrometre sized nematic droplets dispersed in a polymer matrix and their optical response is based on the electrically controlled light scattering properties of the droplets. An applied electric field aligns the nematic droplets to yield a non-scattering or transparent state. Surface interactions at the droplet wall and a non-ideal spherical droplet shape return the droplets to the original orientation in the absence of the field to yield a scattering or opaque state. A competition between the applied field, and the elastic and viscous torques of the liquid crystal governs the response times and switching voltages of such light shutters. 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 refractive indices of the components. It is reported that the electro-optical properties of PDLC displays depend on LC concentration, film thickness, size and shape of LC droplets, anchoring energy on the boundary surface, and physical properties of both components, e.g. elasticity and viscosity parameters, and dielectric anisotropy of the liquid crystal, and the resistivities and refractive index ratios of the liquid crystal and polymer.

Here we report experimental studies on the electro-optical and switching behaviour of PDLC light shutters controlled by the conditions of their preparation, particularly the effects of the liquid crystal content, film thickness, curing time of the polymer binder and temperature.

2. Experimental

2.1. Sample preparation

The PDLC displays under study consist of a nematic liquid crystal (mixture of isothiocyanates W-52, prepared in the Institute of Chemistry of the Military University of Technology in Warsaw, Poland) randomly dispersed as droplets in polyester resin films. Thin films were prepared by fast mixing of appropriate amounts of the liquid crystal (10–40 wt %) with the polymer precursor (an unsaturated oligoester resin containing styrene and a UV curing agent which is a Polish product obtained from the chemical company, Organika in Nowa Sarzyna) and UV irradiation of the blend between ITO coated glass plates (previously coated by a very thin layer of pure oligoester resin to avoid LC escape) using a spacer to control the thickness of 10–75 µm. Refractive indices of the LC and polymer binder were well matched [6, 7].

2.2. Methods

The morphology of the composite films was studied using a MULTI-SCAN analysis system consisting of a polarizing microscope, video camera and computer. Thermo-optical, electro-optical and switching studies

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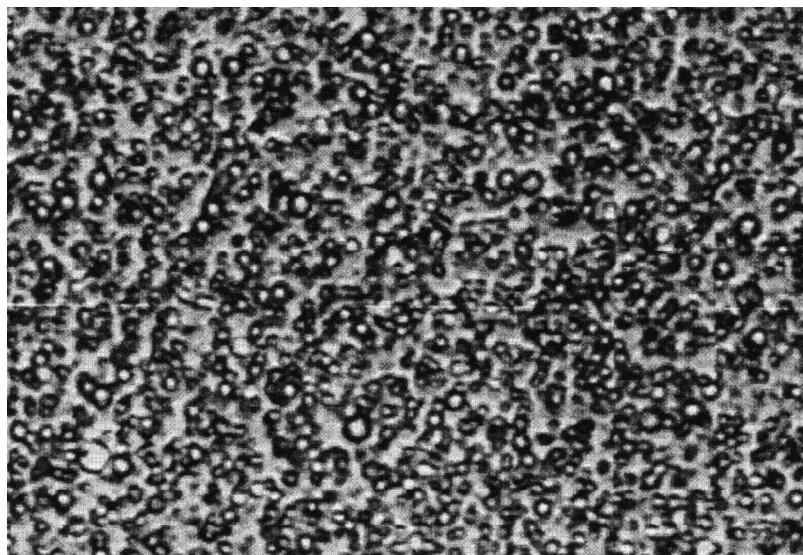
were made using a special device consisting of a He/Ne laser, Mettler heating stage, photodiode, generator, digital oscilloscope and computer. The He/Ne laser beam (wavelength 632.8 nm) was directed normal to the film surface and the transmitted light intensity, without any polarizer, was measured with a photodiode (with changing temperature or driving voltage or time). The output from a function generator (frequency 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).

3. Results and discussion

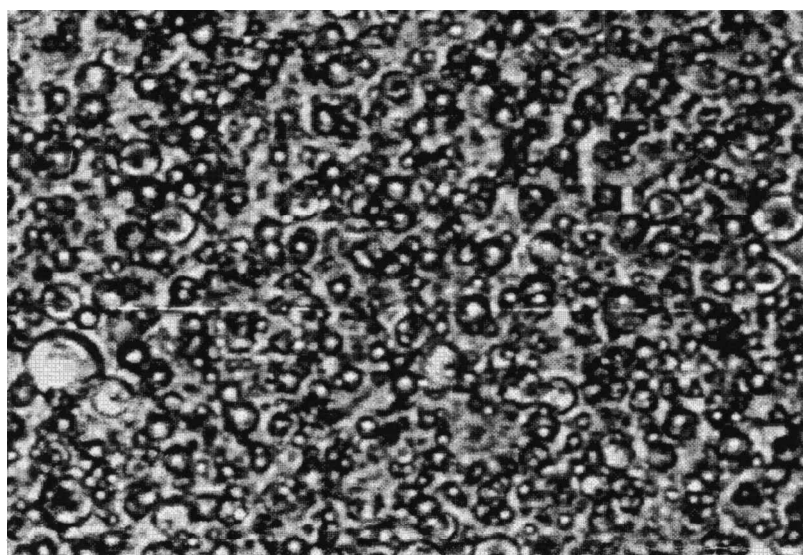
3.1. Morphology and thermo-optical analysis

Figures 1 and 2 show selected micrographs of two composite PDLC films containing different weight fractions of LC, 10 and 30 wt %, respectively, obtained using the same conditions of UV polymerization (curing time



0.1 mm

Figure 1. Micrograph of PDLC film, $c=10$ wt % LC, $d=20$ μm , $t_c=10$ min.



0.1 mm

Figure 2. Micrograph of PDLC film, $c=30$ wt % LC, $d=20$ μm , $t_c=10$ min.

$t_c=10$ min, temperature $T=30^\circ\text{C}$). The size of the LC domains is smaller and more uniform for 10 wt % (figure 1). At higher concentration, a possible coalescence of LC droplets leads to their larger size. A significant difference in size is found with varying curing time t_c of the polymer matrix (LC content remaining the same). The shorter the t_c the larger is the size of the LC droplets due to possible LC coalescence in the still soft matrix.

Figures 3 and 4 present thermo-optical curves in the range of the isotropization temperature T_i of the liquid crystal drawn as a function of LC concentration (figure 3) and film thickness (figure 4). Curing time was 10 min. The observed value of T_i looks independent of film thickness and LC concentration due to the high purity of the LC in the droplets. In figure 4 the log plot of the relative transmittance versus film thickness is drawn. From the slope of the straight line, a turbidity constant was found, $\tau=3.8 \times 10^{-8}$ 1/m according to the following equation:

$$I/I_0 = \exp(-\tau d) \quad (1)$$

where I/I_0 is the relative transmittance and d and τ represent thickness and turbidity constant respectively.

Figure 5 presents thermo-optical curves in the region

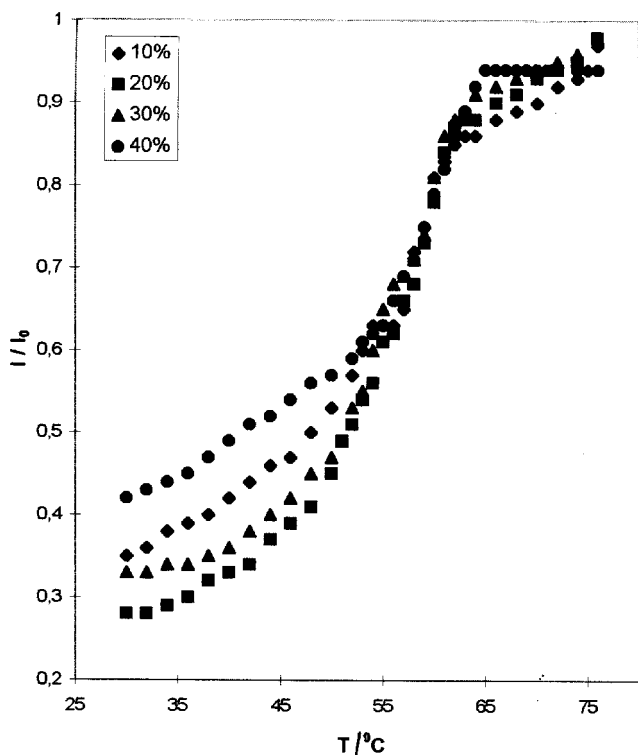


Figure 3. Thermo-optical curves related to various LC contents of 10–40 wt %, $d=20 \mu\text{m}$; curing conditions, $t_c=10$ min at room temperature.

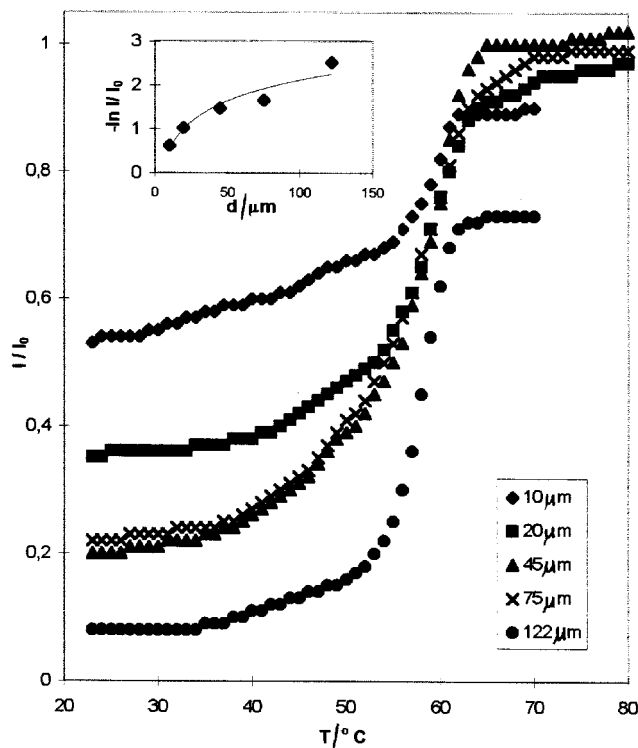


Figure 4. Thermo-optical curves related to various film thicknesses d ; $c=40$ wt % LC; curing conditions, $t_c=10$ min at room temperature. Inset: \ln of relative transmittance versus film thickness.

of LC isotropization related to various curing times. The longer the curing, the higher the T_i observed due to improving purity of the LC in the domains in the course of the polymerization process of the polyester matrix. $T_i=62^\circ\text{C}$ was determined for the pure LC.

3.2. Electro-optical analysis

For the bipolar orientation occurring in most cases and shown in the previous paper [7], the threshold voltage U_{th} (minimum voltage required to switch the liquid crystal) of PDLC films is given by equation (2).

$$U_{th} = dl3a(\zeta_P/\zeta_{LC} + 2)[K(l^2 - 1)/\epsilon_0 \Delta\epsilon]^{1/2} \quad (2)$$

where d , a , ζ , K , l and $\Delta\epsilon$ represent film thickness, major dimension, resistivity, elastic constant, aspect ratio (major to minor dimension) and dielectric anisotropy of the LC, respectively. The nematic director orientation within the LC droplets is determined by competition between elastic and electric forces and surface interaction.

3.2.1. Effect of LC content

Figure 6 shows the transmittance at 20 kHz as a function of the amount of LC in the PDLC film. The

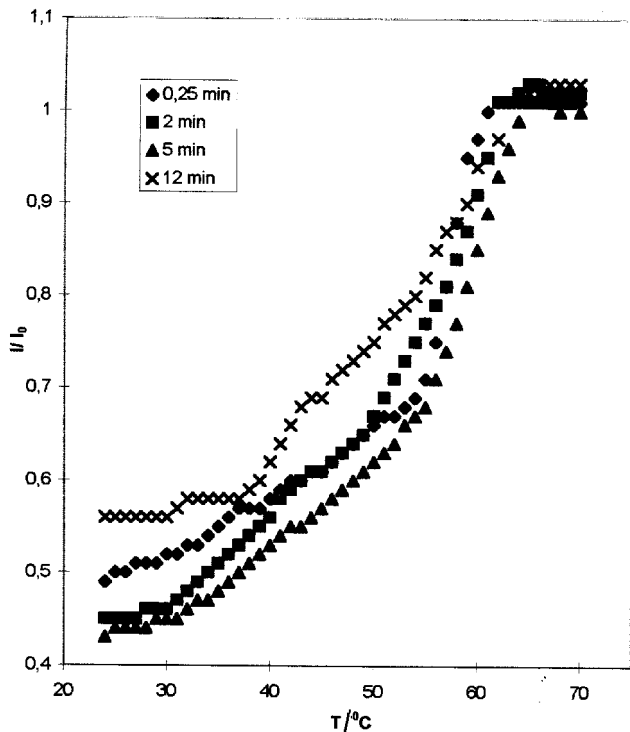


Figure 5. Thermo-optical curves related to various curing times.

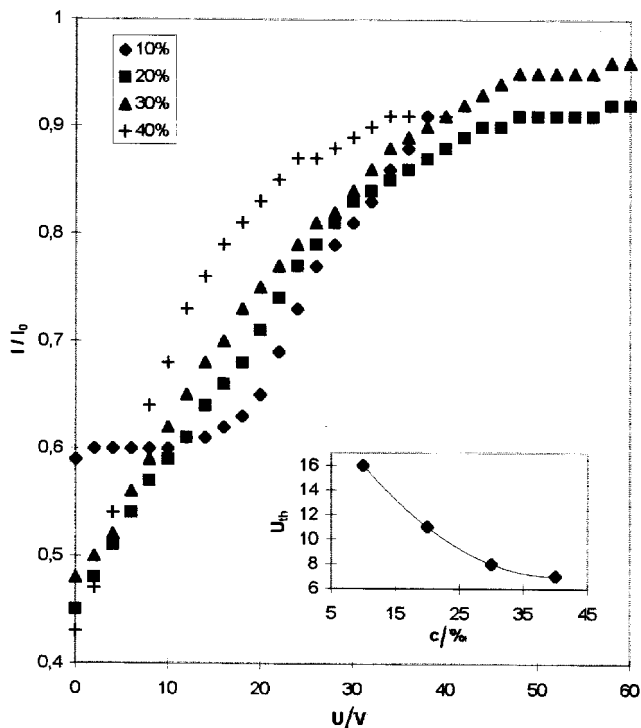


Figure 6. LC concentration effect on electro-optical curves. Inset: threshold voltage versus LC content; $d=20\ \mu\text{m}$, room temperature, $\tau_c=10\ \text{min}$.

inset presents the threshold voltage U_{th} versus LC content.

Equation (2) states the U_{th} depends inversely on the size of a droplet if other parameters have similar values ($d=\text{const}$, $\zeta_p/\zeta_{LC}=\text{constant}$ —dependent on the curing time of matrix, K and $\Delta\varepsilon=\text{constant}$). The increasing U_{th} with decreasing LC content reflects the change of LC size (figures 1 and 2).

3.2.2. Thickness effect

Figure 7 shows the transmittance as a function of applied voltage related to various thicknesses of the films. The inset illustrates U_{th} dependence on film thickness d , which becomes non-linear for films thicker than $40\ \mu\text{m}$ due to more complicated multiple light scattering (also a higher error in the measured transmittance).

3.2.3. Temperature effect

Figure 8 shows electro-optical curves related to the various temperatures under study, if LC content, time of curing and film thickness are kept constant. When the temperature is increased, the threshold voltage decreases as normally reported [6, 8]; the decrease is due to a lower $K/\Delta\varepsilon$ value and anchoring forces. On the other hand, the resistivity of the liquid crystal decreases more rapidly than the resistivity of the polymer so that

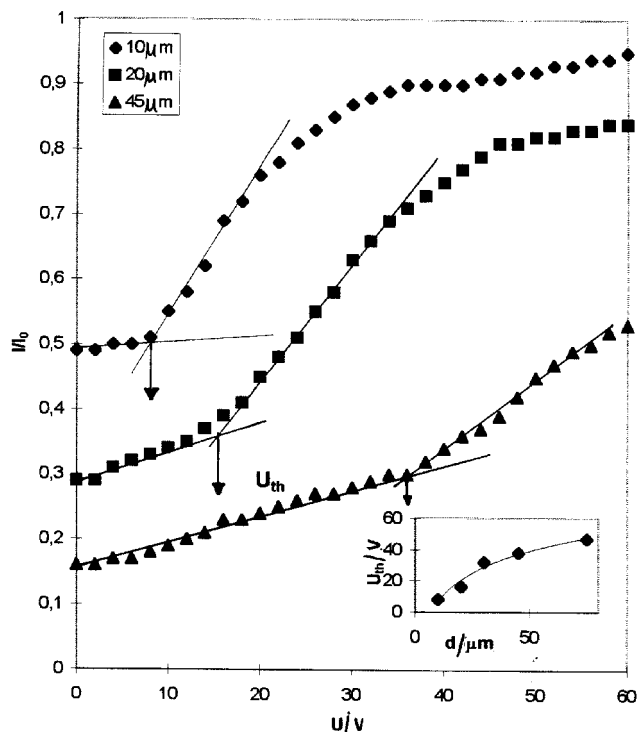


Figure 7. Thickness effect on electro-optical curves. Inset: threshold voltage versus film thickness, $c=40\ \text{wt}\ \%\ \text{LC}$, $\tau_c=10\ \text{min}$.

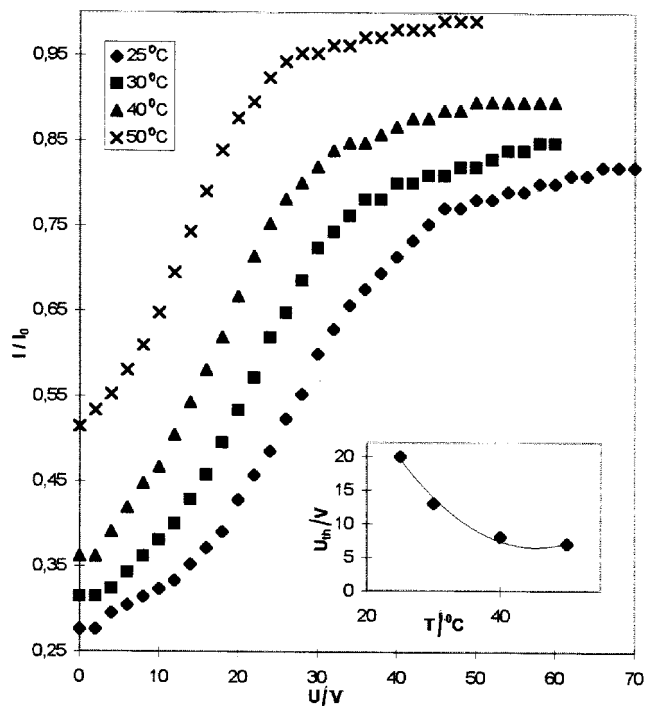


Figure 8. Temperature effect on electro-optical curves. Inset: threshold voltage versus temperature; $d=20\ \mu\text{m}$, $c=40\ \text{wt}\%$ LC, $t_c=10\ \text{min}$.

ζ_P/ζ_{LC} increases. These factors could explain the U_{th} temperature dependence in our case.

Figure 9 presents electro-optical hysteresis curves measured while increasing or decreasing the voltage. As other properties, the hysteresis depends on the measuring conditions, in this case on the temperature. The hysteresis depends also on the natures of the polymer and liquid crystal, and perhaps also on the preparation of the composite. It has been suggested [14] that hysteresis is due to a thin layer of liquid crystal interfacing with the polymer which is not oriented by the field in the same manner as the bulk LC in the droplets. Both curves are obtained at two temperatures below and above the glass transition temperature T_g of the polymer matrix ($T_g \approx 30^\circ\text{C}$) and below and close to the isotropization temperature of the liquid crystal ($T_i=62^\circ\text{C}$). Finally, the existence of the so-called 'memory effect' also shows the importance of anchoring of the liquid crystal.

3.2.4. Effect of curing

According to equation (2), the threshold voltage could be a linear function of the resistivity ratio ζ_P/ζ_{LC} . A linear dependence between U_{th} and resistivity of the crosslinked epoxy-based PDLCs has been observed [15], but the effect of changing the crosslinking density on the chemical nature of the polymer and, thus, on

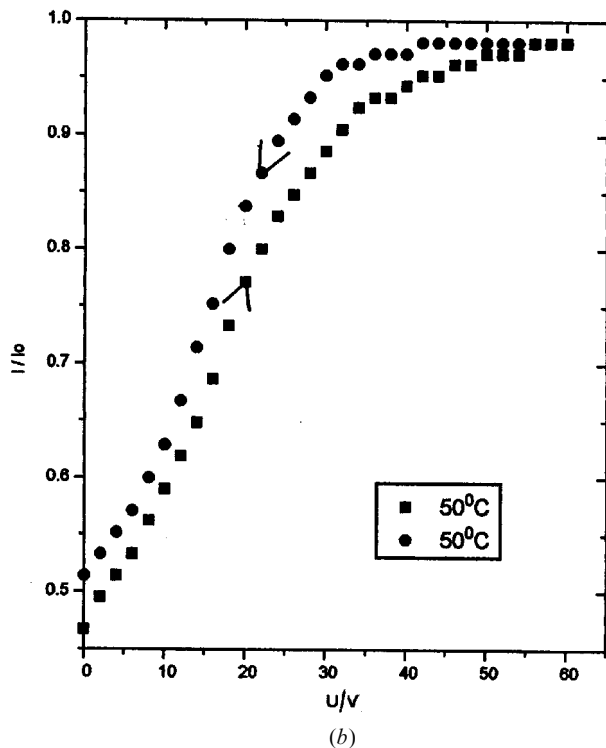
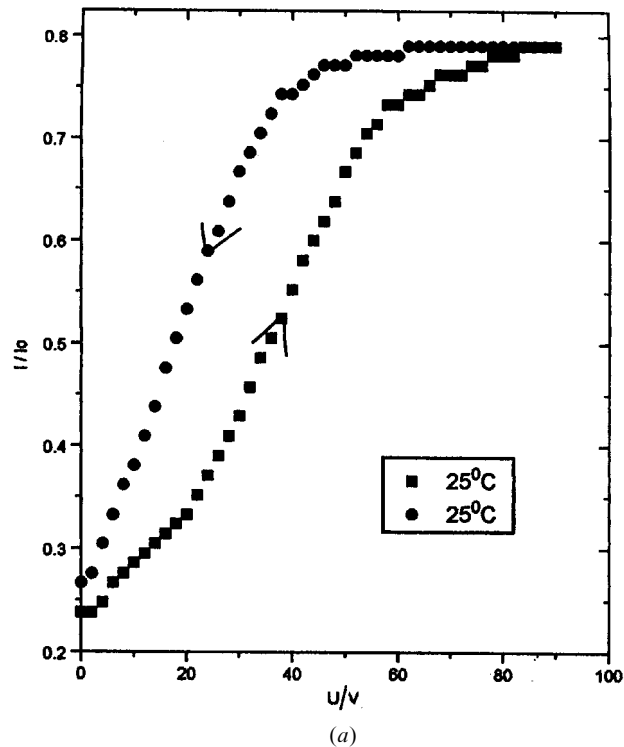


Figure 9. Hysteresis curves: (a) at 25°C , (b) at 50°C ; heating and cooling rate $2^\circ\ \text{min}^{-1}$, $d=20\ \mu\text{m}$, $c=30\ \text{wt}\%$ LC.

the anchoring energy was neglected. Some authors [9, 13] have modified the chemical composition of the polymer and derived conclusions about anchoring. The results indicate that surface anchoring is a dominant factor in controlling U_{th} of the composite film.

Modification of the chemical and physical nature of the polymer binder by increasing its molecular weight and crosslinking density during the UV curing process of the LC-oligoester composites has been studied here. Figure 10 presents electro-optical curves related to PDLC films obtained using various curing times ranging from 0.25 to 12 min. The inset shows the dependence of electro-optical slope on curing time. The threshold voltage shows a small increase, but the slope evidently changes, reflecting the effect of the complex parameter on the electro-optical properties of the PDLC films, and also, indirectly, the importance of anchoring. No visible change in droplet size for the longer times of irradiation is observed. The sample cured for 0.5 min consists of larger droplets due to a coalescence process in the incompletely solidified polymer.

3.3. Switching analysis (rise and decay time)

Rise time (τ_R) is defined as the time needed for the composite to reach 90% of the on-state transmission when an alternating voltage is applied. Similarly, decay

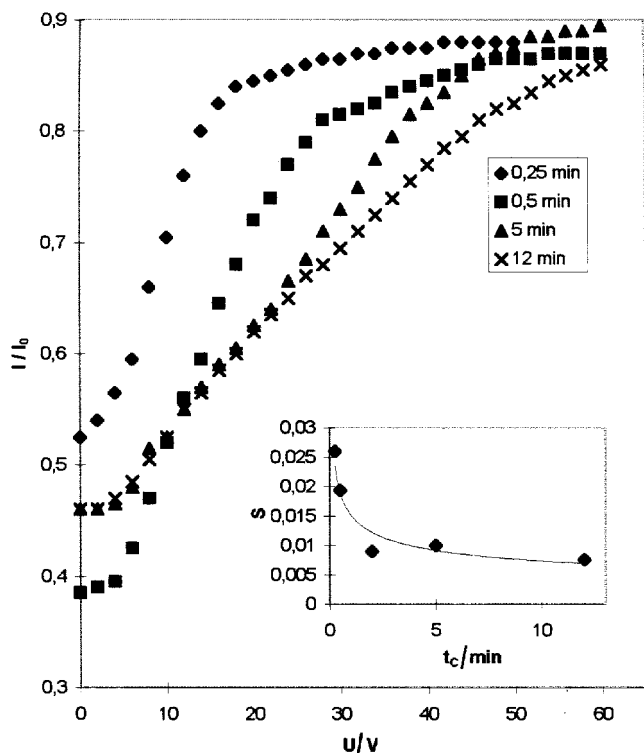


Figure 10. Cure time effect on electro-optical curves; $d=20 \mu\text{m}$, $c=40 \text{ wt } \% \text{ LC}$. Inset: slope of curves versus curing time.

time (τ_D) is the time needed for a composite in the off-state to reach the transmission when the voltage is set to zero. To a first approximation, decay time does not depend on measuring voltage, but rise time is inversely proportional to U^2 . In the case of elongated droplets of bipolar configuration and if liquid crystal anchoring is neglected, it is possible to obtain the equations for response times [14]:

$$1/\tau_R = 9\varepsilon_0 \Delta\varepsilon / \nu (\zeta_P / \zeta_{LC} + 2)^2 (U/d)^2 + 1/\tau_D \quad (3)$$

$$\tau_D = \nu a^2 / K(l^2 - 1) \quad (4)$$

where ν is the rotational viscosity of the liquid crystal. Rise time is mainly a function of electric field U/d , viscosity, resistivities and dielectric anisotropy. Decay time depends on the viscosity and elasticity of the liquid crystal, as well as on the shape and size of the droplet. A set of response curves is presented in figures 11 and 12 in relation to various voltages applied. Curing time, t_c , was constant.

3.3.1. Effect of LC content

Figure 13 shows the voltage dependence of the rise time related to various LC contents in the PDLC films. With increasing LC content, a trend to increasing droplet diameter is observed (figures 1 and 2). Increasing droplet size reduces the magnitude of the surface anchoring effects compared with the bulk effect in LC reorientation,

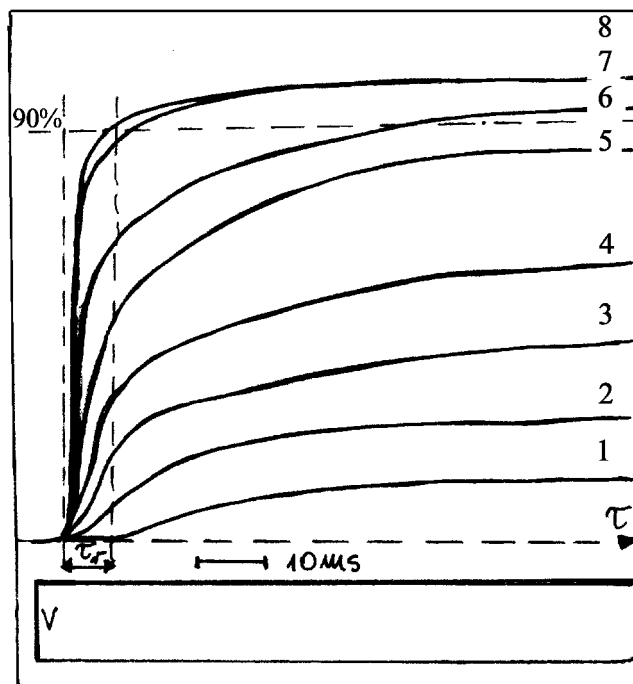


Figure 11. Set of response curves related to various voltages applied; $d=20 \mu\text{m}$, $c=40 \text{ wt } \% \text{ LC}$, $t_c=5 \text{ min}$. Driving voltage $U=10\text{--}100 \text{ V}$ (curves 1–8).

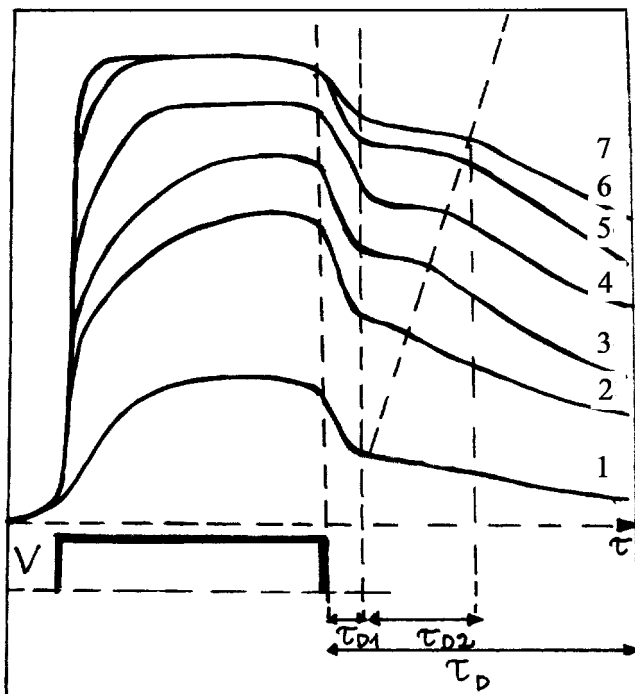


Figure 12. Set of relaxation curves related to various voltages applied; $d=20\ \mu\text{m}$, $c=40\ \text{wt}\%$ LC, $t_c=5\ \text{min}$. Driving voltage $U=10\text{--}100\ \text{V}$ (curves 1–7). Three values of relaxation times are derived (see text).

so that rise time should be expected to decrease. This trend is not clearly seen in the experimental data presented in figure 13. Perhaps other parameters, e.g. droplet shape and various stiffnesses of the matrix lead to the observed behaviour.

3.3.2. Thickness effect

Figure 14 presents the response times as a function of voltage applied for two PDLC films of thicknesses 10 and 20 μm having similar droplet sizes and the same LC contents. That the τ_R value is lower by more than a half for the sample that is thinner by a factor of two can be explained by the higher electric field applied and the possibility of droplet deformation, especially in the case when the droplet size is compared with the film thickness.

Reciprocal τ_R versus U^2 is plotted in figure 15. The lower τ_D is found for the thinner sample, perhaps due to possible droplet deformation and higher aspect ratio l [equation (4)].

3.3.3. Temperature effect

Figures 16 and 17 show the temperature effect presented on the rise time and reciprocal rise time curves. The experimental results show that increasing temperature reduces rise time [8], probably due to a decrease in liquid crystal viscosity ν . The slope in figure 14

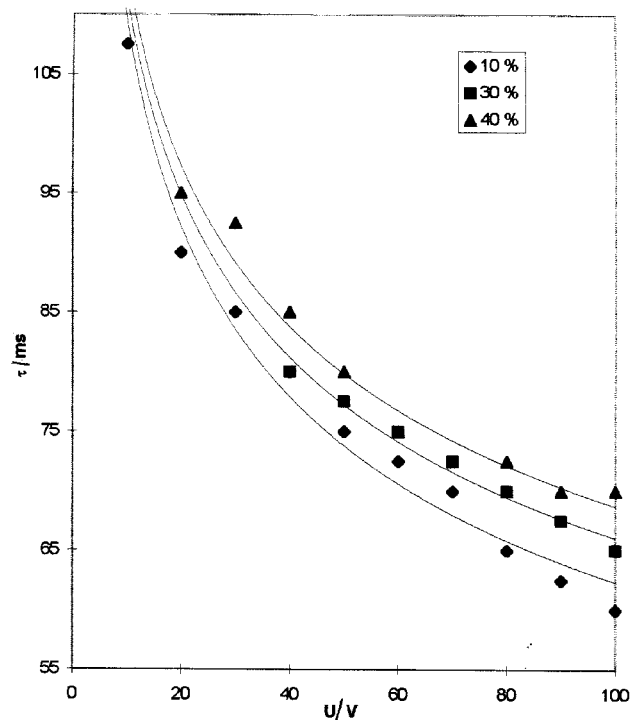


Figure 13. Voltage dependence of rise time related to various LC contents; $d=20\ \mu\text{m}$, $T=20^\circ\text{C}$, $t_c=10\ \text{min}$.

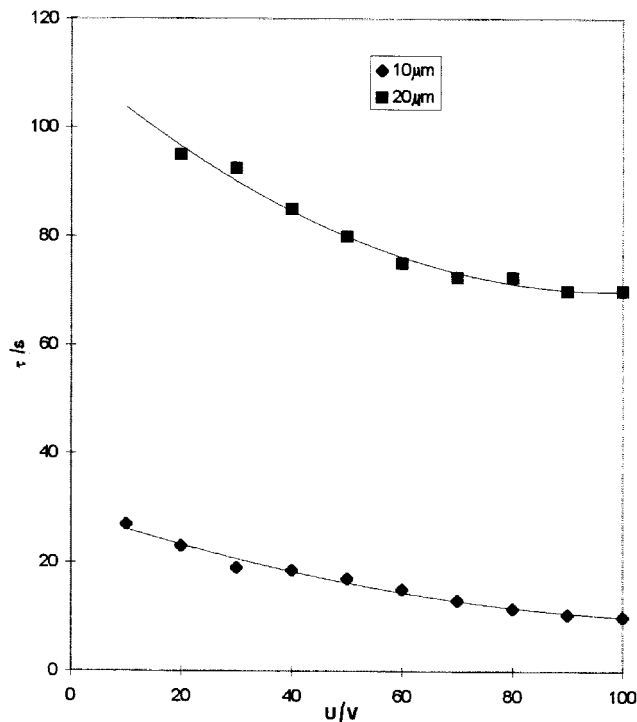


Figure 14. Voltage dependence of rise time related to various thicknesses of PDLC film; $c=40\ \text{wt}\%$ LC, $T=20^\circ\text{C}$, $t_c=10\ \text{min}$.

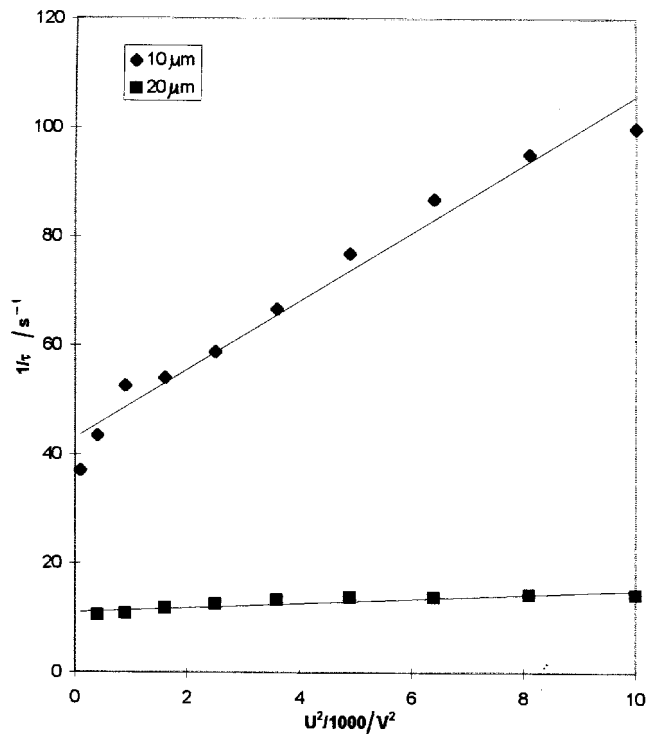


Figure 15. Reciprocal rise time versus square of voltage (samples as in Figure 14).

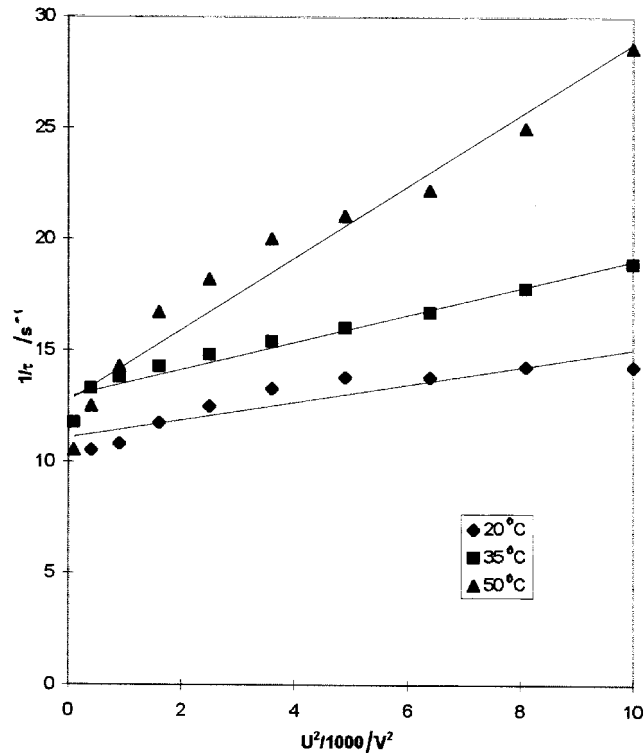


Figure 17. Reciprocal rise time versus square of voltage (samples as in Figure 16).

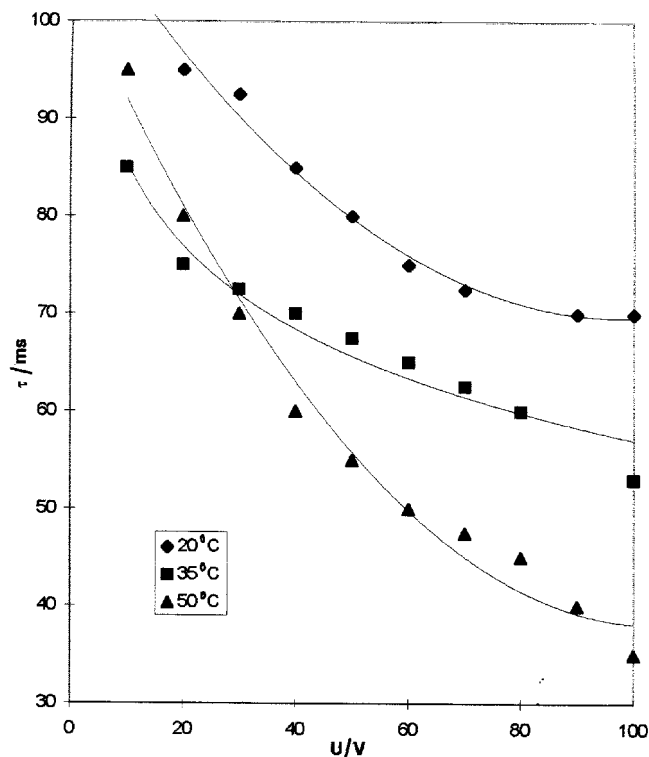


Figure 16. Voltage dependence of rise time related to various temperatures; $c=40$ wt% LC, $d=20$ μm , $t_c=10$ min.

[equation (4)] is inversely proportional to v , if d , $\Delta\varepsilon$ and $\zeta_p/\zeta_{LC} \approx \text{constant}$. Decay time seems to be temperature independent, and the decrease in viscosity may be cancelled by the decrease in elastic constant and anchoring forces.

3.3.4. Effect of curing

A set of response time curves drawn for constant applied voltage and related to various curing times is shown in figure 18. Figures 19 and 20 show the voltage dependent rise times and reciprocal rise times, respectively. Two regions of the rise time are clearly seen here. The first region is for lower applied voltage and the second for higher applied voltage, dependent on curing time of the polymer binders. This may be due to varying resistivities of the polymer matrix ζ_p and anchoring forces on the boundary. In the case of the samples cured for 5 and 12 min, a rise time as long as 40–50 ms is observed up to an applied voltage of 60 V. Above 60 V, the rise time continuously decreases with increasing voltage up to 100 V, where it becomes lower than 20 ms in the case of all samples under study. A slope S of the curves in figure 20 (presented in the inset) reflected the falling ζ_p and increasing anchoring forces, and this decreases rapidly with increasing curing time. A UV curing time of 5 min is long enough for complete

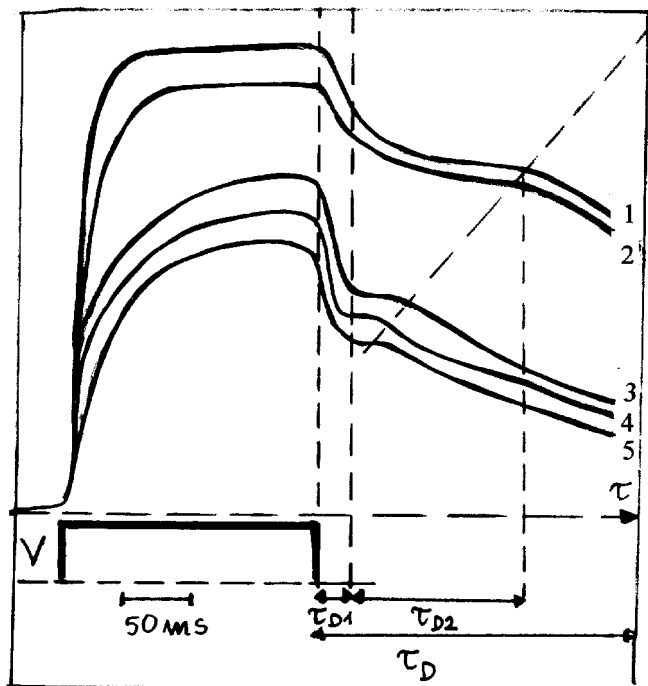


Figure 18. Set of response curves for constant voltage ($U = 40$ V) applied, related to various curing times of the PDLC films (0.25–12 min); curves 1–5, $c = 40$ wt %. Three values of relaxation time are derived (see text).

solidification by crosslinking polymerization of the polyester resin. Three regions in the decay response curves are clearly observed. The first region associated with a very fast time $\tau_{D1} = 20$ ms is independent of applied voltage (figure 12) and curing time (figure 18) which is in agreement with equation (5) and the behaviour of the pure nematic liquid crystal. We suggest that it is due to a possible rapid change of orientation of the nematic director inside the droplets far away from the boundary surface with the polymer binder. The second region (figure 21) for the decay time τ_{D2} is dependent on voltage and curing time which changes from 20 to 120 ms. The third region is for a long relaxation time τ_{D3} leading to initial nematic director orientation in the droplet. Both τ_{D2} and τ_{D3} are dependent on the thin layer of liquid crystal at the interface which is reoriented by the electric field in different ways from the liquid crystal inside the droplets. The whole decay time τ_D plotted as a function of voltage in the on-state shows an increasing trend (Figure 22).

4. Conclusions

Relations between LC content, temperature, film thickness and UV irradiation time, and the electro-optical and switching properties in a UV curable PDLC

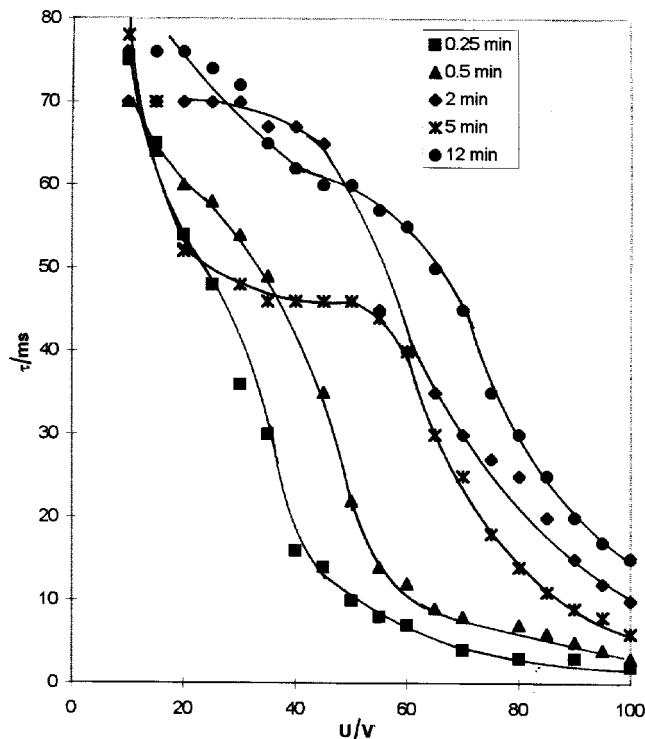


Figure 19. Voltage dependence of rise time related to various curing times $t_c = 0.25$ –12 min, $c = 40$ wt % LC, $T = 20^\circ\text{C}$.

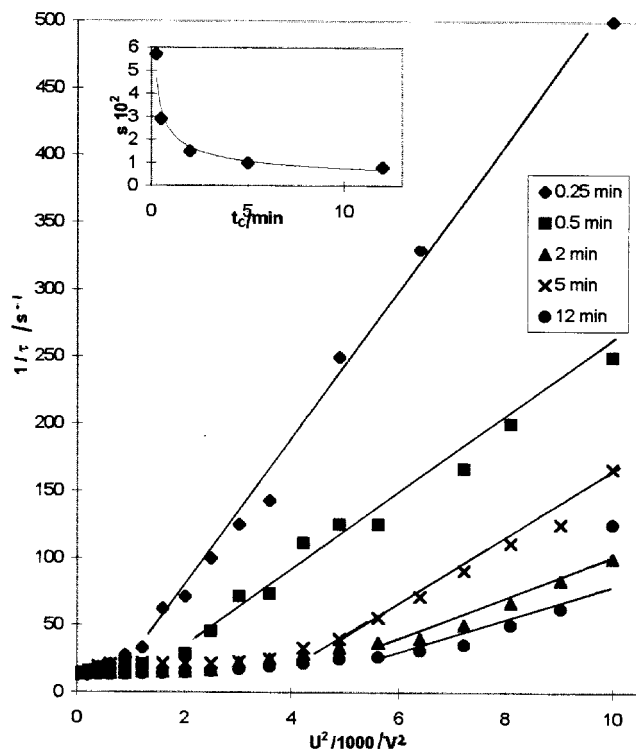
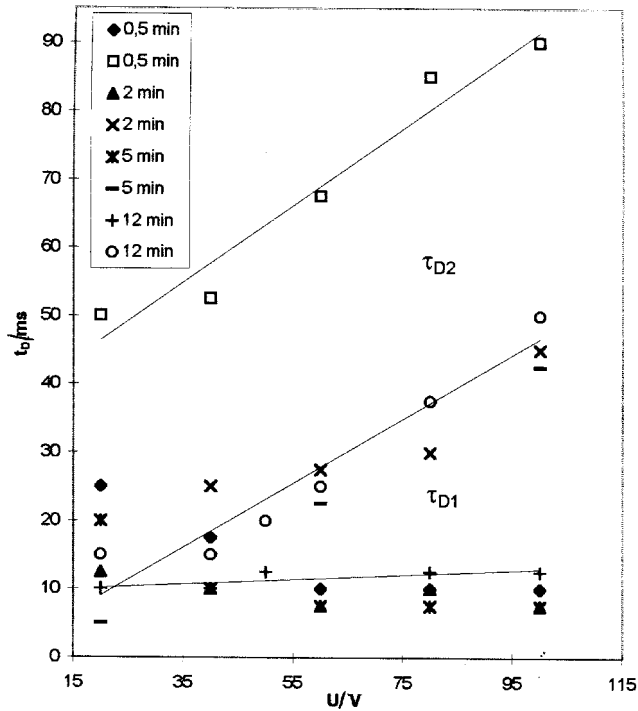


Figure 20. Reciprocal rise time versus square voltage (samples as in figure 19). Inset: slope S (taken in the region of the straight lines) versus curing time t_c .

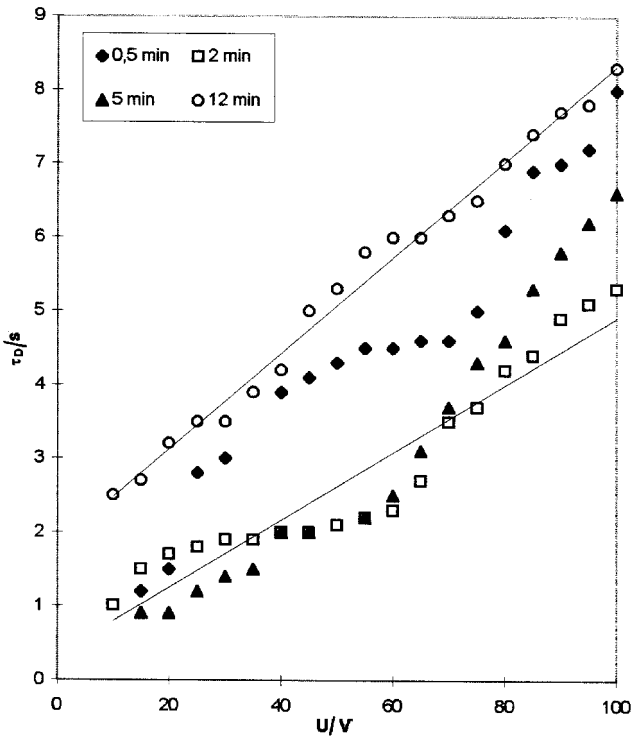
Figure 21. τ_{D1} and τ_{D2} versus voltage.

film have been studied. It was found that the threshold voltage and response time depend mainly on the curing time of the matrix. These electro-optical results could be explained by the effective anchoring strength at the interface of the polymer and liquid crystal depending either on the area fraction of the interface in the composite film (size and shape of LC droplets) or the stiffness of the polymer matrix changing in the course of the crosslinking polymerization.

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Figure 22. Long relaxation time τ_D versus voltage applied.