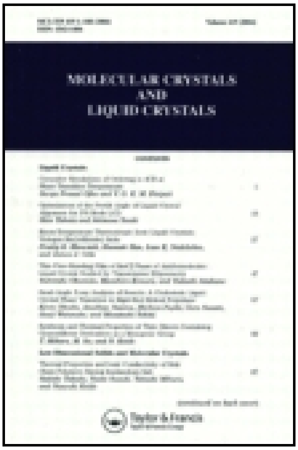

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Electrooptical Characterization of Various PDLC Materials

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Electrooptical Characterization of Various PDLC Materials

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PDLC materials are prepared by various methods: Polymerization Induced Phase Separation (PIPS), Solution Induced Phase Separation (SIPS) and encapsulation. The aim of the present study was to compare and optimize the electrooptical and switching properties of the PDLC samples.

The electrooptical and switching properties of PDLC films show a strong dependence on curing time of the polymer matrix, which my be explained by the effective increase of anchoring strength at the interface of the polymer and liquid crystal, depending on the area fraction of the interface, size and shape of LC droplets, the polymer stiffness and resistivity changing in the course of crosslinking polymerization.

PDLC films prepared from flexible amorphous polyester resin containing dispersed nematic LC have shown the best electrooptical and switching properties in the case of polyester resin crosslinked with diacrylane and nematic LC mixture (W-52) with matched refractive index to polyester matrix ($n_p \approx n_0$, $n_p = 1.505$, $n_0 = 1.509$);

Keywords: Polymer Dispersed Liquid Crystals; electrooptical and switching studies; effect of temperature; LC content; curing time

INTRODUCTION

In the mid 1980 's a novel class of electrooptical materials was introduced [1-3]. They consist of low molecular weight nematic liquid crystalline (LC) microdroplets dispersed in a solid polymer matrix called PDLC (polymer dispersed liquid crystal). PDLC films find several applications as optical switches, large scale flexible displays, variable transmittance windows, membranes, sensors and others [4].

A PDLC device operates by changing and matching the refractive index of LC phase with an optically transparent polymer matrix. In the absence of an electric field PDLC films are opaque. The nematic director is randomly distributed in the droplets which induces a mismatch of LC and polymer refractive indices and light scattering. When an electric field is applied across the film thickness, the directors orient parallel to the field direction ($\Delta\varepsilon_{LC} > 0$). In this state the film becomes transparent due to matching between the ordinary refractive indices of LC and polymer.

PDLC films are prepared by induced phase separation of LC occurring in a homogeneous solution of the two - or three - component system: polymer / liquid crystal in a molten state – the separation follows by cooling (TIPS – thermally induced phase separation); oligomer or prepolymer / liquid crystal – the separation follows by polymerization (PIPS – polymerization induced phase separation); polymer / liquid crystal / common solvent – the separation follows by solvent evaporation (SIPS – solution induced phase separation); polymer / liquid crystal / polymer solvent – LC encapsulation in polymer solution (heterogeneous solution), solidification of matrix follows by evaporation of solvent .

A wide variety of PDLC structures are possible to obtain depending on materials properties (both LC and polymer), LC concentration and method of their preparation. The aim of this study is to compare and optimize the electrooptical and switching properties of various PDLC systems obtained in our laboratory during the last decade[5-9].

EXPERIMENTAL

Initial Materials

Polymers

a) Photopolymerized polyester resin (Polimal 102) crosslinked by styrene (with a cure agent); b) Photopolymerized polyester resin crosslinked by diacrylane (with a cure agent); c) Polycarbonate; d) Polyvinyl alcohol.

Nematic liquid crystals

a) mixtures of isothiocyanates: (W-52) T_{NI}=60°C, $\Delta\varepsilon$=13,0; (M-419) T_{NI}=125°C, $\Delta\varepsilon$=9,8;

b) 6 CB ($T_{NI} = 29°C$), $\Delta\varepsilon = 11.5$,

LC samples were supplied by the Military Technical Academy in Warsaw.

Table I. Sample characterization.

Sample No.	Polymer	LC	LC content c [wt %]	Film thickness d [μm]
1.	Polyester resin crosslinked by styrene[5]	M – 419	10– 30	20
2.	Polyester resin crosslinked by styrene, various curing times[7]	W – 52	10– 40	10 – 75
3.	Polyester resin crosslinked by diacrylane[6]	W – 52	40	20
4.	Polyester resin crosslinked by diacrylane, various curing times[8]	6 CB	20–40	10 – 20
5.	Polycarbonate[9]	W – 52	20-40	30
6.	Polyvinyl alcohol[11]	W – 52	40	30

Sample 1 – the curing time equals to 15 min; sample 3 – the curing time equals to 20 min.

Because of limited size of presented paper more details on the characterization, preparation and operation of the PDLC's can be found elsewhere [5-9].

PDLC preparation

1. PIPS separation: oligoester resins with W-52, M-419, 6 CB.
2. SIPS separation: polycarbonate with W-52. Common solvent – methylchloride.
3. Encapsulation: polyvinyl alcohol water solution with W - 52.

Optical Studies

Thermooptical - Mettler photocell analyzer FP 90 and optical microscope. Electrooptical and switching analyzer consists of He/Ne laser, ac voltage generator (frequency used equals to 2 kHz), digital oscilloscope, photomeasuring cell. Experimental set - up for electrooptical and switching studies of the samples are used without polarizers (He/Ne laser light) except sample No. 5 which was studied using a photocell and white light in an optical microscope with crossed polarizers.

The direction of beam of the incident light was perpendicular to the sample surface using diaphragm with aperture of 0.3 cm^2 for transmitted light. The incident laser light intensity was 2.01 mW (λ = 632.8 nm).

RESULTS AND DISCUSION

1. Morphological structure

Figure 1 shows micrographs of a morphological structure of some PDLC films prepared in different conditions and methods. The samples differ in the morphological structure distribution of the dispersed LC droplets embedded in various polymer matrices.

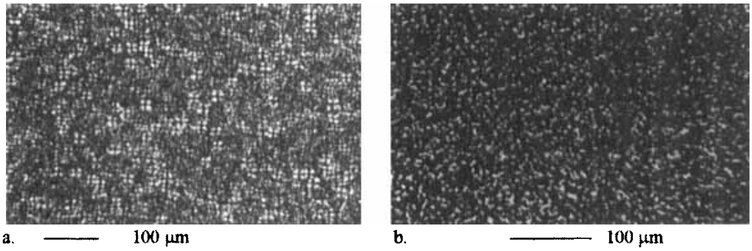

FIGURE 1. Micrographs of PDLC films.
a. sample No. 5 b. sample No. 3

2. Electrooptical properties

The electrooptical properties of PDLC films are controlled by the conditions of both preparation and operation, i.e. by LC content and size of LC droplets, film thickness, temperature and solidification (also by curing) time of a resulting polymer binder. Threshold voltage – minimum voltage required to switch the PDLC is described[10] by Eq. (1) in the case of a more frequent bipolar configuration of LC in the droplets:

$$U_{th} = \frac{d \cdot \left(\frac{\varsigma_P}{\varsigma_{LC}} + 2\right)}{3 \cdot a} \cdot \left[\frac{K \cdot (l^2 - 1)}{\varepsilon_0 \cdot \Delta\varepsilon}\right]^{\frac{1}{2}} \tag{1}$$

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

2.1. Effect of temperature

When temperature increases, a character of the electrooptical curves changes and the threshold voltage decreases (Fig. 2). It is due to a lowering K / $\Delta\varepsilon$ value and anchoring forces on the boundary walls (decreasing stiffness of the polymer matrix). On the other hand, the resistivity of the liquid crystal (liquid) seems to decrease more rapidly with increasing temperature than the resistivity of the crosslinked polymer (solid) so that $\varsigma_P / \varsigma_{LC}$ ratio could have an opposite effect on U_{th} value.

2.2. Effect of thickness

The linear dependence between film thickness and threshold voltage is predicted according to Eq. (1). Figure 3 presents an example of relative transmittance as a function of applied voltage related to various film thickness. U_{th} dependence on film thickness d becomes nonlinear for films thicker than 50 μm due to a more complicated multiple light scattering.

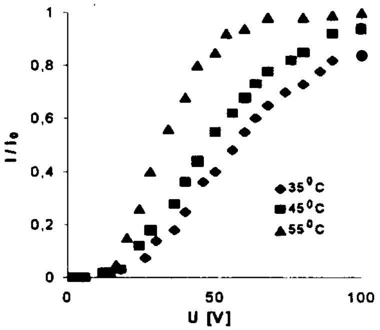

FIGURE 2.
Temperature effect on electrooptical properties; sample No. 3.

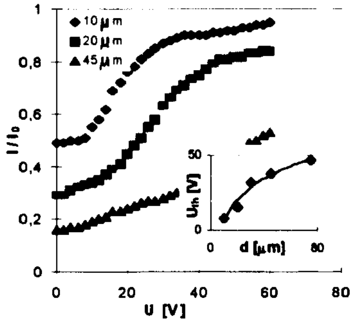

FIGURE 3.
Thickness effect on electrooptical curves; Inset: threshold voltage versus film thickness; sample No. 2.

2.3. Effect of LC content

Figure 4 shows the electrooptical curves of PDLC samples drawn as a function of LC content in the PDLC film. The observed change of electrooptical behavior can reflect a possible difference in the size and concentration of birefrigent LC droplets (here crossed polarizers) with an increasing amount of LC in the initial blends.

Some amount of LC is not separated from the solution (here about 20 % wt.).

2.4. Effect of curing time

Figure 5 presents the electrooptical curves of PDLC samples related to PDLC films prepared at various curing times of the polyester matrix ranging from 40 s to 15 min. The inset shows the increase of the threshold voltage U_{th} with the curing time. It is determined by a cooperation between changing the droplet size (decreasing with curing time) and increasing the resistivity ratio $\varsigma_P / \varsigma_{LC}$. Also a surface anchoring on the interface varying in the course of polymer curing plays an important role in controlling the U_{th} which is neglected in Eq. (1).

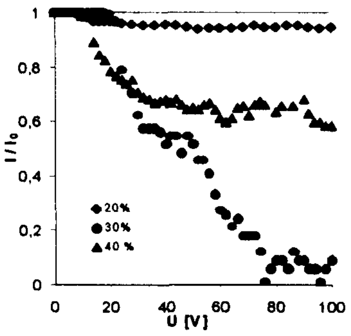

FIGURE 4.
LC concentration effect on electro-optical behavior; sample No. 5.
(crossed polarizers)

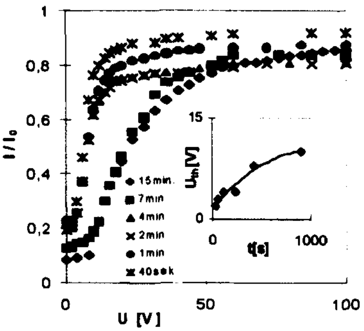

FIGURE 5.
Electrooptical curves related to various curing time; sample No. 4.

3. Switching results

Response times of PDLC film (τ_R – rise time which is usually defined as the time needed to reach 90 % of the on state transmission when an alternative voltage is applied and τ_D – decay time is the time needed in the off state to reach 10 % of the on - state transmission) depend on some LC and polymer parameters according to Eq. (2) drawn in the case of bipolar configuration (the anchoring effect is neglected):

$$\frac{1}{\tau_R} = \frac{9 \cdot \varepsilon_0 \cdot \Delta\varepsilon}{\gamma \cdot (\frac{\varsigma_P}{\varsigma_{LC}} + 2)^2} \cdot E^2 + \frac{1}{\tau_D}$$
$$\tau_D = \frac{\gamma \cdot a^2}{K \cdot (l^2 - 1)} \qquad (2)$$

where:

$\Delta\varepsilon$ - dielectric anisotropy of LC
E - electric field, U/d
d - film thickness
U - voltage applied
γ - viscosity coefficient

ς_P / ς_{LC} – resistivity ratio
K – elastic constant
a – major dimension of LC droplet
l – aspect ratio (major to minor dimension)
τ - decay time

Rise time τ_R is mainly a function of electric field U / d, viscosity γ, resistivities ratio ς_P / ς_{LC} and dielectric anisotropy $\Delta\varepsilon$. Decay time depends on the viscosity to elasticity ratio as well as on the shape and size of droplet. The effects of voltage, temperature and curing time of matrix on τ_R are presented in Figs. 6 through 8.

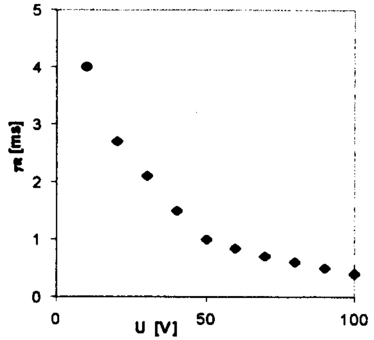

FIGURE 6.
Rise time τ_R versus voltage; sample No. 3.

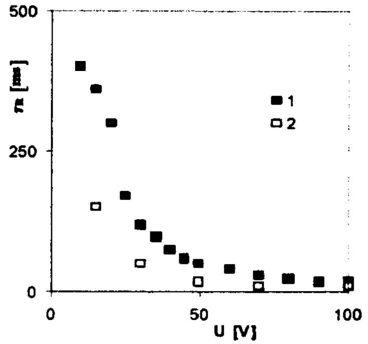

FIGURE 7.
Rise time τ_R versus voltage
1. T= 25°C 2. T= 53°C; sample No. 1.

3.1. Effect of voltage applied

Figure 6 presents the result of the rise time τ_R with increasing voltage obtained for sample No. 3. The dependence $1 / \tau_R$ versus U^2 is in good agreement with Eq. (2) (not presented in this paper).

3.2. The effect of temperature is shown in Fig. 7. The experimental results show that increasing temperature reduces the rise time τ_R probably due to a decrease in viscosity coefficient γ of LC and matrix stiffness.

3.3. The effect of curing time of matrix on τ_R is presented in Fig. 8. It shows a set of curves presenting τ_R obtained for various curing time from 40 s to 15 min. The stiffer matrix the longer τ_R is observed for various voltage applied. From the slope of the reciprocal τ_R drawn versus U^2 the values of the resistivity ratio ς_P / ς_{LC} were calculated [8] and drawn in Fig. 9 versus curing time. The solidification of the matrix is complete after 3 min. and then ς_P / ς_{LC} ratio reaches a constant value.

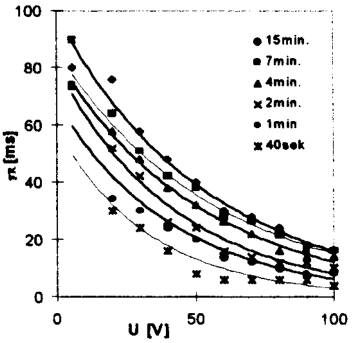

FIGURE 8.
Effect of curing time; rise time versus voltage, sample No. 4.

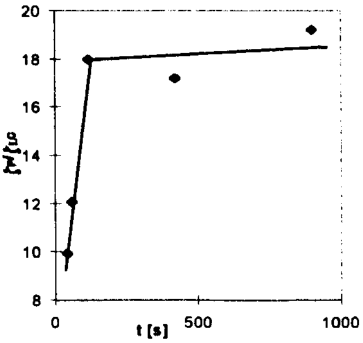

FIGURE 9.
Effect of curing time; resistivity ratio ζ_P/ζ_{LC} versus curing time t; sample No. 4.

4. Attenuation coefficient μ

The attenuation coefficient μ of PDLC film (sample No. 3) was calculated according to the following equation:

$$I = I_0 \cdot e^{-\mu d} \qquad (3)$$

where I, I_0, μ, d are the light intensities (I_0 – incident and I – transmitted light intensities), attenuation coefficient and film thickness respectively.

It was found that μ depends on wavelength λ and voltage applied which is presented in Figs. 10 and 11.

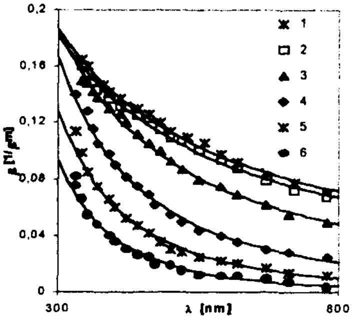

FIGURE 10.
Attenuation coefficient μ versus wave length λ in off state U=0 (curve 1) and on state, U=10, 30, 50, 70 and 100V (curves 2-6); sample No. 3.

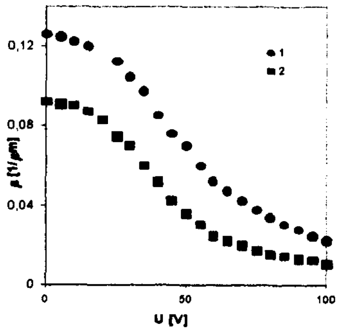

FIGURE 11.
Attenuation coefficient μ versus voltage applied U for λ=454 nm (curve 1) and λ=625 nm (curve 2); sample No. 3.

CONCLUSIONS

1. The electrooptical and switching properties of PDLC films show a specially strong dependence on curing time of the polymer matrix.

2. The results are explained by the effective increase of anchoring strength at the of the polymer and liquid crystal interface depending on the area fraction of the interface, size and shape of LC droplets, the polymer stiffness and resistivity changing in the course of crosslinking polymerization.

3. Morphological structure of PDLC films (also size of LC droplets) can be modified by the concentration of LC the conditions (temperature, curing rate) and methods of PDLC preparation.

4. Electrooptical and switching properties depend also on temperature, LC concentration and voltage applied.

5. PDLC films prepared from flexible amorphous polyester resin containing dispersed nematic LC have shown the best electrooptical and switching properties in the case of a) polyester resin crosslinked with diacrylane and b) LC, W-52 with matched refractive index to polyester matrix, ($n_p \approx n_0$, $n_p = 1.505$, $n_0 = 1.509$).

The best results: $V_{th} = (8 - 12\text{ V})$, $\tau_R = 0.4 - 4$ ms (100 – 20 V), $\tau_D = 70$ ms.

Film transparency is controlled by ac electric field as follows: in opaque state (off) the films attenuate 90 % and in transparent state (on) they transmit 70 - 90 % of the incoming intensity (in the visible range). Contrast ratio $C_r = I_{max} / I_{min} \approx 7\text{-}9$.

Acknowledgments

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References

[1] J.W. Doane, A.N. Vaz, B.G. Wu, S. Žumer, *Applied Physical Letters*, **48,** 269 (1986).
[2] N. A. Vaz, G. W. Smith and G. P. Montgomery, *Molecular Crystals and Liquid Crystals*, **146,** 17 (1987).
[3] P. S. Drzaic, *Applied Physics*, **60,** 2142 (1986).
[4] L. Bouteller and P. Le Barny, *Liquid Crystals*, **21,** 157 (1996).
[5] M. Mucha, *Journal of Applied Polymer Science*, **43,** 175 (1991).
[6] M. Mucha, *Polimery, Tworzywa Wielkoczqsteczkowe*, **37,** 258 (1992) (Polish).
[7] M. Mucha, E. Nastał (Grosicka), *Liquid Crystals*, **23, 5,** 749 (1997).
[8] M. Mucha, E. Nastał (Grosicka), E. Žurańska, *Journal of Applied Polymer Science*, **71,** 455–463 (1999).
[9] E. Nastał -Grosicka and M. Mucha, *SPIE – The International Society for Optical Engineering, "Liquid Crystals: Materials Science and Applications"* (in press).
[10] J.W. Doane, *Liquid Crystals Applications and Uses*, vol. 1, ed. B. Bahadur, Singapore, World Scientific (1990).
[11] E. Grosicka (Nastał), M. Mucha, in preparation.