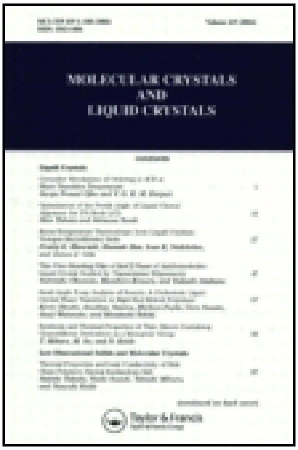

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New PDLC-Films Doped by Black Dye

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Dichroic-dye doped PDLC films were obtained by polymerization-induced phase separation method with two types of dichroic dyes, including a black mixture. The electro-optic characteristics of these films were investigated for different concentrations of liquid crystal in polymer matrix. A strong memory effect was found in such systems, depending on LC concentration and on the type of dichroic dye.

Keywords: PDLC; dichroic dye; EO-characteristics; memory effect

INTRODUCTION

Droplets of nematic liquid crystals (NLC) in a polymer matrix attracted the attention as new class of materials suitable for light valves and displays [1-4]. These devices consist of micron-sized droplets distributed inside a transparent polymer film which typically possesses a highly scattering off- state. It can be switched from opaque to clear transparent state upon application of a voltage to the electrodes. After removal of the applied voltage, the film returns to its original opaque state. Usually, these devices do not exhibit any significant hysteresis.

There are known three methods of such films preparation: the first consists of filling the polymer micropores with a liquid crystal (LC) [5], the second involves the formation of PDLC films from an aqueous emulsion [1], whereas the third way to prepare these films is the polymerization-induced phase separation (PIPS), which occurs when a homogeneous mixture of monomers/oligomers and liquid crystals is polymerized [3,4]. Despite the differences in preparation, the physical properties of the devices formed by these three methods are the same.

PDLC films with dichroic dye (DD) dissolved in the liquid crystal (dichroic-dye-based PDLC) possess a controllable absorbance as well as controllable scattering. This combination can be used to produce high contrast displays [6].

The aim of our work was to obtain and to investigate various PDLC films doped by individual DD or black mixture of DD and to study the influence of dichroic dyes at different LC concentration on electro-optic (EO) characteristics of PDLC films as well.

EXPERIMENTAL

In our work we used phased-separation method for preparing the dichroic-dye-based PDLC films. These films include LC material doped by DD dispersed in the polymer matrix. The solution of LC doped by DD in monomer-oligomer mixture had been polymerized by UV light.

As NLC material we used ZhKM-1289 (commercial production of NIOPIK). As dichroic-dye-guest in LC material we used KD-184 and black mixture BDD-24p (both are commercial production of NIOPIK as well). Monomer-oligomer mixture consisted of monomethylether-methylacrylate and aromatic/aliphatic epoxyacrylates which were specially synthesized. The composition of this mixture was varied in order to match its refractive index n_p to ordinary refractive index n_o of ZhKM-1289.

2.5% wt. of the KD-184 or BDD-24p were preliminary solved in ZhKM-1289 by heating up the mixtures to clearing point. Then these compositions were added to monomer-oligomer mixture. It was prepared three types of films with concentration of LC material with DD guest in prepolymer mixture as 30%, 50% and 70%. The solution was placed in the cell, which consisted of two glass plates with a thin electrically conductive coating of indium-tin-oxide (ITO). The gap between the cell glass plates was 20 μm.

The cell was placed under UV-light source (2 x 1000 W) with the most intensity on 365nm and irradiated (7 mW/sm^2).

Electro-optical properties were measured using a He-Ne laser (632.8nm, 1mW) and silicon photodiode. The laser beam was transmitted through the PDLC sample. The beam was directed with normal incidence with respect to the sample. The PDLC sample was driven by a sinusoidal voltage. For all measurements reported below the driving frequency was 1 kHz. The intensity of the light transmitted through the sample was recorded as a function of the applied voltage on a XY-recorder. For all measurements, a neutral filter was placed between the laser and the sample to ensure a linear output of the photo-cell with the light intensity over the range used. The beam intensity measured without sample corresponds to 100% transmittance.

RESULTS AND DISCUSSION

In our experiments we have used three concentrations of LC doped by dichroic dye (30%, 50%, 70%).

The results of the experiments are demonstrated on Figures 1-3. The figures show the transmittance intensity of PDLC films vs applied voltage for each concentration.

The curves relating to PDLC without DD are denoted by letter "a", PDLC with KD-184 by letter "b" and with BDD-24p by letter "c". The curves "1" - represent the data obtained with the first increasing of the voltage. The curves "2" show the data corresponding to decreasing of the voltage. The curves "3" demonstrate the results of the second increasing of the voltage.

The curves 2 and 3 do not change with further decreasing and increasing of the voltage. From Figure 1 it can be seen that PDLC films with 30 % of LC have following features:

1) The initial off-state is not very opaque;
2) After the first applying and subsequent removing of the voltage, the PDLC film doesn't return to its initial off-state, but keeps a memory state which is rather transparent between the initial off-state and the on- state;

3) A small hysteresis for the second and further switches of PDLC films is observed;

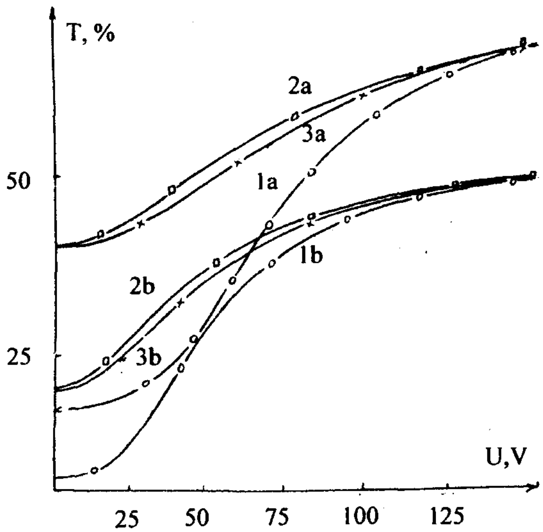

Figure 1. Transmittance vs. voltage for PDLC films with 30 % of LC. a and b denote PDLC films without-DD and with BDD-24p respectively. 1, 2, 3 denote the 1st-increasing, the 1st-decreasing and the 2nd-increasing of the voltage, respectively.

4) Incorporating of dichroic dye leads to the expected enhance of the contrast for the first application of the voltage and for the further ones as well.

Figure 2 shows the results for PDLC with 50% of LC. It is evident, that for 50% PDLC films the electro-optical characteristics differ from the ones with 30% of LC in PDLC films. The features of 50% PDLC films are the followings:

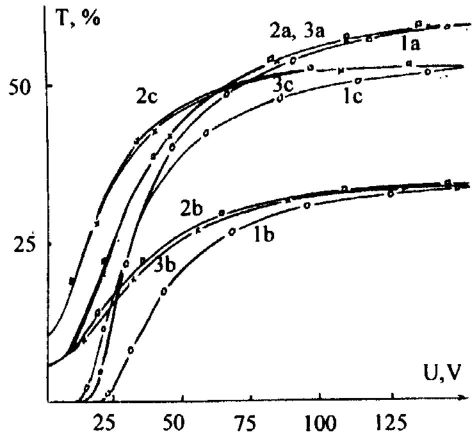

Figure 2. Transmittance vs. voltage for PDLC films with 50 % of LC. a, b, c denote PDLC films without-DD, with BDD-24p and with KD-184 respectively. 1, 2, 3 denote the 1st-increasing, the 1st-decreasing and the 2nd-increasing of the voltage, respectively.

1. The initial off-state of PDLC without DD is very opaque. The transmittance intensity is only 0.03%. of the one measured without PDLC sample;
2. The initial off-state of dye-doped PDLC has the same opaque level as for PDLC without DD;

3. The transmittance of the memorized state for dye-doped PDLC is lower than for non-doped one and both values are lower than for PDLC with 30% of LC;
4. Incorporating of dichroic dye leads to small, but unexpected diminishing of the contrast for the first application of the voltage and for the further ones as well.

In the figure 3 the data are shown for PDLC films with 70% of LC, and one can see that:

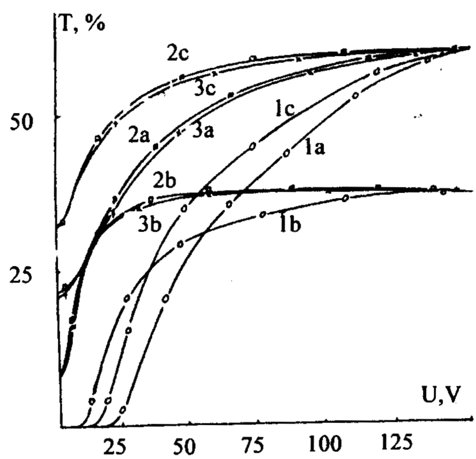

Figure 3. Transmittance vs. voltage for PDLC films with 70 % of LC. The meaning of the letters is the same as in Figure 2.

1. The PDLC sample without DD has the initial off-state with very low transmittance (about 0.02%). The transmittance does not achieve the saturation in on-state even at 150V. In the memory state the

transmittance is higher than the transmittance for PDLC with 50% of LC, but lower than for PDLC containing 30% of LC;

2. The PDLC sample doped by dichroic black mixture BDD-24p has the initial off-state more transmitting (about 0,4%) than PDLC without DD. Its memory state has rather high transmittance (30%). After the first application of the voltage its transmittance curve has no hysteresis and reaches the saturation at sufficiently low voltage (25V);
3. The PDLC sample doped by individual dichroic dye KD-184 has the same initial off-state as PDLC without DD. It has memory state with very high transmittance (45%). Its transmittance curve exhibits a small hysteresis.

It should be noticed that memory effect in PDLC films have been observed by several authors [7,8]. When PDLC films are prepared by polymerization-induced phase separation (PIPS) method they have so called "polymer ball" morphology. This morphology is characterized by continuous spreading of LC with polymer micro-spheres connected by a small quantity of polymer binders. This structure has irregular cavities. The wall forces in these cavities strongly differ at various point, and the LC can accommodate these forces in different ways through a complicate distortion. The applying of an electric field leads to an alignment of LC molecules. After the field is removed, the LC orientation doesn't return to the initial state, but remains in another stable alignment. This alignment always is more transmitting than the original one. This stable state has local energy minimum which is higher than the energy of the initial off-state, but is separated from the latter by an energy barrier. After heating up to the clearing point and subsequent cooling back to the room temperature the PDLC films always return to the initial highly opaque state.

Our results demonstrate that the memory state transmittance strongly depends on the LC concentration. For 30% of LC the transmittance of the memory state is high, but the transmittance of the initial off-state is also not so low. The increasing of the LC concentration from 30% to 50% leads to the decreasing of the memory state transmittance. Nevertheless, the further increasing of the LC concentration to 70% leads to the increasing of the memory state transmittance.

The influence of dichroic dye on PDLC film EO-characteristics is not so obvious. The doping of PDLC by DD leads not only to the contrast enhance due to anisotropic absorbance, but also changes the contrast as a result of the DD influence on PDLC features (size of scattering centers, anchoring energy, degree of prepolymer double-bond conversion and so on). In order to find out the actual mechanism of DD influence on PDLC film EO-characteristics further investigation should be done.

CONCLUSION

In this work it have been shown that EO-characteristics of PDLC films obtained by PIPS method strongly depend on the concentration of LC in the polymer matrix.

The influence of dichroic dye included in PDLC film on EO-characteristics has a complicated aspect and leads to a modification of PDLC physical parameters.

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References

[1] J.L. Fergason, *SID Int. Symp. Dig. Tech. Pap.*, **16**, 68, (1985).
[2] P.S. Drzaic *J. Appl. Phys.*, **60**, 2142 (1986).
[3] J.W. Doane, N.A. Vaz, B.G. Wu, and S. Zumer, *Appl. Phys. Lett.*, **48**, 269 (1986).
[4] N.A. Vaz, G.W. Smith, and G.P. Montgomery, *Mol. Cryst. Liq. Cryst.*, **146**, 1 (1987).
[5] H.G. Craighead, J. Cheng, and S. Hackwood, *Appl. Phys. Lett.*, **40**,22 (1982).
[6] P.S. Drzaic, R. Wiley, and J. McCoy, *Proc. SPIE*, **1080**, 41 (1989).
[7] F.G. Yamagushi, L.J. Miller, and C.I. van Ast, *Proc. SPIE*, **1080**, 24 (1989).
[8] R. Yamaguchi and S. Sato, *Jpn. J. Appl. Phys.*, **30**, L616 (1991).