Journal of Structural Chemistry, Vol. 34, No. 6, 1993

"GUEST–HOST" EFFECT IN POLYMER-DISPERSED NEMATIC LIQUID CRYSTALS

G. M. Zharkova, S. A. Streltsov, and V. M. Khachaturyan

UDC 621.3.085.3:532.783

In this paper we report on a new optoelectronic material representing a polymer-dispersed liquid crystal (PDLC) film. This material exhibits optical response to the applied electrical field and is useful for displays and light gates. The effect of azo and anthraquinone dyes on the optical density of PDLC films has been studied. The proportion of the dye dissolved in an LC cell and the molar absorption coefficients were determined, and the influence of the dyes on the scattering efficiency of PDLC films was calculated.

INTRODUCTION

At present great attention is paid to a new optoelectronic material – polymer-dispersed liquid crystals (PDLC). These are self-organized assemblies representing small polymeric cells that contain definitely oriented liquid crystals capable of changing their optical properties in the applied electrical field. Such PDLC films are of interest for the design of various optoelectronic devices. They have some distinct advantages over conventional optoelectronic LC materials: unlimited size, any cell seal form, no polarizers, and small turn-on and turn-off times [1, 2].

To expand the contrast range and obtain colored images, various dichroic dyes are incorporated into PDLC cells [3, 4]. In this case, we observe the so-called "guest–host" effect. The essence of this effect is as follows. When a threshold electric field is applied to a PDLC cell, the LC ("host") molecules together with the dichroic dye ("guest") molecules are re-oriented in such a way that the LC director is oriented parallel to the field if the LC dielectric anisotropy is positive. The optical density will decrease or increase depending on the direction of the long-wave absorption oscillator of the dichroic dye. The efficiency criterion of dichroic dyes may be the dichroic ratio or the order parameter of the dye. The higher (with positive dichroism) or lower (with negative dichroism) the ratio, the higher the image contrast in the optoelectronic device [5].

Also, addition of a dye produces a considerable effect on light scattering by the PDLC film [6-8]. Even if the dye has a low order parameter (~0.2) and its dichroic ratio is small (~1.7), its effect is still higher than for the dyes with a high dichroic ratio (~7) in conventional LC materials. This is explained by a more intense dye absorption due to the longer effective path of light passing through the PDLC film, which is reflected many times from cell boundaries. In the case of poorly ordered dyes, it is not important where the dye is dissolved: in a polymer or LC cell. For a dichroic dye, the contrast will be higher if the LC cell contains more dye. Thus, the "guest–host" effect in PDLC films is more intricate and is determined by the chemical properties of the components: LC, polymer, and dye, as well as by the structure of the PDLC film and its morphology since, in the final analysis, the latter determines the path length of the light passing through the film.

This paper is devoted to investigating this effect in PDLC films containing nematic LC, polyvinyl acetate, and some dyes.

Institute of Theoretical and Applied Mechanics, Siberian Branch, Russian Academy of Sciences. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 34, No. 6, pp. 114-117, November-December, 1993. Original article submitted December 10, 1992.

 0022-4766/93/3406-0930 $12.50

MATERIALS AND EXPERIMENTAL PROCEDURE

As PDLC films we used a material obtained by phase separation of LC and polymer by evaporating the solvent. Polyvinyl acetate and 4-pentyl-4′-cyanobiphenyl (5CB) with $\Delta\varepsilon > 0$ were dissolved in an appropriate solvent and applied to a flat surface by casting. After the solvent had been evaporated, a film formed, which was placed between two glass supports with transparent electrodes. As dyes we used azo and anthraquinone dyes, which have positive dichroism. Their long rod-like molecules, consisting of aromatic rings with polar terminal groups (Fig. 1), provide a large dipole moment along the long molecular axis. In these properties the dye molecules are similar to LC molecules with $\Delta\varepsilon > 0$. The wavelengths corresponding to the maximal absorption of these dyes range from 430 to 620 nm. Due to this, almost the whole color spectrum may be used in optoelectronic devices. Using the dyes with many benzene rings, one can obtain dichroic dyes with high order parameters and a sufficient solubility in LC. However, it should be borne in mind that the solubility of a dye in LC decreases with increase in the number of benzene rings in the molecule.

In the process of LC encapsulation in a polymer matrix, the dye added to the solution partly dissolves in the LC cell and partly remains in the polymer matrix. Let us denote the dissolved portion of the dye by X. Then the optical density of the sample in the external field may be written as follows [9]:

$$D_{\text{on}} = \varepsilon_{\perp} Xcd + \varepsilon_i (1 - X)cd, \tag{1}$$

$$\varepsilon_i = (2\varepsilon_{\perp} + \varepsilon_{\parallel})/3. \tag{2}$$

Here $\varepsilon_{\perp,\,\parallel}$ are the molar absorption coefficients measured perpendicularly or parallel to the LC director, $\text{cm}^3/(\text{mole}\cdot\text{cm})$; c is the dye concentration, mole/cm^3; and d is thickness of the PDLC film, cm. The $\varepsilon_{\perp,\,\parallel}$ coefficients are determined from the known dependence of optical density of the LC–dye system on the layer thickness, the dye concentration, and the molar absorption coefficients [10]:

$$D_{\parallel} = \varepsilon_{\parallel} cd, \tag{3}$$

$$D_{\perp} = \varepsilon_{\perp} cd, \tag{4}$$

where $D_{\parallel,\perp}$ are optical densities of the film measured perpendicularly or parallel to the LC director.

In the absence of the electric field,

$$D_{\text{off}} = \varepsilon_{\parallel} Xcd\alpha + \varepsilon_i (1 - X)cd\alpha, \tag{5}$$

where α is the scattering efficiency of the film.

In (1) and (5), the first term specifies the contribution of the LC cell and the second one of the polymer matrix to optical density.

We make appropriate transformations to get

$$D_{\text{off}}/D_{\text{on}} = \alpha/((1 - X) + 3X/(2 + R)), \tag{6}$$

$$R = \varepsilon_{\parallel}/\varepsilon_{\perp} \text{ is the dichroic ratio.} \tag{7}$$

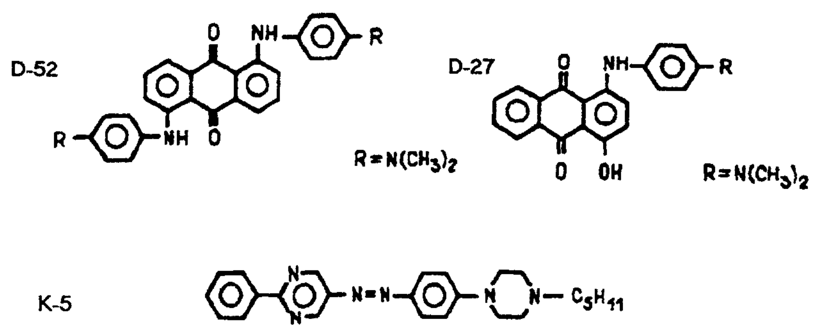

Fig. 1. Molecular structures of the dyes used.

TABLE 1. Characteristics of PDLC Films Containing Different Dyes

Dye	λ_{max}, nm	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	ε_i	R	D_{off}	D_{on}	X	α
		$cm^3/(mole \cdot cm)$							
K-5	460	2.12	0.83	1.69	2.55	0.237	0.085	0.3	2.61
D-27	594	1.47	0.59	0.89	2.49	0.44	0.35	0.16	1.19
D-52	526	0.965	0.52	0.67	1.86	0.37	0.21	0.25	1.65

Thus, to determine the scattering efficiency of the film, it is necessary to find the fraction of the dye dissolved in the LC cell and the molar absorption coefficients.

The molar absorption coefficients were determined using the 5CB solution of dyes. In the absence of the external electric field, the light transmission by a cell with a homogeneous (planar) orientation will depend on $D_{\parallel}$, or on $D_{\perp}$ when the field is applied. The optical densities were measured on an SF-18 spectrophotometer. The electric field was applied in the form of a rectangular bipolar pulse with a frequency of 400 Hz. The dye concentration was 1% LC weight. The homogeneous orientation was achieved by polishing the glass.

After measuring $D_{\parallel}$ (in the off-state) and $D_{\perp}$ (in the on-state) of the LC + dye system, we determine $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, R, and the order parameter $S = (R - 1)/(R + 2)$. Having measured D_{on} and D_{off} of the PDLC film, we calculate X and α.

RESULTS OF EXPERIMENTS AND DISCUSSION

Table 1 gives characteristics of PDLC films containing different dyes. All the dyes studied were mainly dissolved in a polymer matrix. The K-5 dye has a higher order parameter, better solubility in LC, and, as a consequence, the scattering efficiency of the K-5 system is greater. Despite the lower characteristics of the other two dyes, they also markedly increase the contrast. The samples containing these dyes intensively absorb light in the initial state because of the increased path length of the light scattered on cell boundaries. It is seen that the behavior of the three dyes in PDLC films can vary widely. Evidently, the introduction of a dye into a PDLC film affects its optoelectronic characteristics in a more complex way. Due to the presence of a dye, orientation of LC molecules on the cell boundaries can drastically change. Moreover, the presence of a dye must change the size and density of cells in the PDLC film. Therefore these results should be regarded as tentative and only highlighting an increased absorption of the PDLC film due to the increased light path length. It is necessary to examine more closely the interactions of dyes in PDLC films and their "guest–host" effects.

We are grateful to Professor E. P. Fokin and to Doctor M. A. Mikhaleva for providing us with the dye samples and for discussion of the results.

REFERENCES

1. J. W. Doane, A. Golemme, J. L. West, et al., *Mol. Crystal. Liq. Crystal.*, **165**, 511-532 (1988).
2. G. P. Montgomery and N. A. Vaz, *Appl. Optics*, **26**, No. 4, p. 738 (1987).
3. G. H. Heilmeier and L. A. Zanoni, *Appl. Phys. Lett.*, **13**, No. 3 (1968).
4. L. M. Blinov, in: *Electro- and Magnetooptics of Liquid Crystals* [in Russian], Nauka, Moscow (1978).
5. V. V. Titov and A. V. Ivashchenko, *Zh. Vses. Khim. O-va D. I. Mendeleeva*, No. 2, 56-57 (1983).
6. J. L. West, Tamura-Lis, and R. Ondris, *Proc. SPIE*, **1080**, 48 (1989).
7. P. S. Drzaic, R. C. Wiley, and J. McCoy, ibid., **1080**, 41-47 (1989).
8. J. L. West, R. Ondris, and M. Erdmann, *Liquid Crystal Displays*, J. W. Doane and Z. Vaniv (eds.), *Proc. SPIE*, **1257** (1990).

9. J. L. West, R. Ondris, and M. Erdmann, *SPIE Conference*, Santa Clara, CA (1990).
10. I. Ya. Bershtein and Yu. L. Kaminskii, *Spectrophotometric Analysis in Organic Chemistry* [in Russian], Khimiya, Leningrad (1986).

Translated by L. Smolina