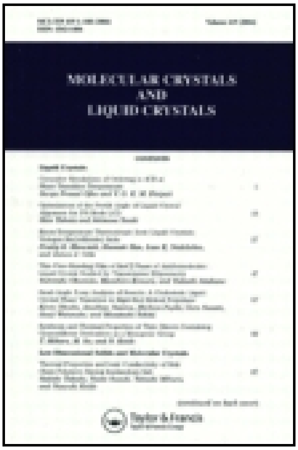

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Electrooptical Devices from Organically Doped Sol-Gel Materials

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Electrooptical Devices from Organically Doped Sol-Gel Materials

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Transparent porous matrices made by the sol-gel method are ideal as hosts for active photoactive or electroactive organic dopants. Sol-gel optics applications are related to an adequate and precise control of the compositional and pore surface variations in the cage of trapped molecules, which is necessary to the preparation of novel optical and electrooptical gel-glasses.

In this paper, gel-glass dispersed liquid crystal (GDLC) with electrooptical properties shall be presented as an application of the sol-gel process for trapping microdroplets of nematogenic organic compounds (i.e., liquid crystals, LCs), GDLC films may be used as electrooptical devices. Upon application of an external electric field, unaltered GDLCs were made to switch from white opaque to colorless transparent states. The different electrooptic features of GDLCs, including GDLC performances for color display applications are reviewed.

Keywords: Gel-Glass Dispersed Liquid Crystals; GDLC; Electrooptic; Sol-Gel

INTRODUCTION

Many papers have recently demonstrated that transparent (SiO_2, Al_2O_3, TiO_2, etc.) matrices made by the sol-gel method are ideal as hosts for photoactive or electroactive organic dopants. The adequate combination of a precise control between the compositional, the pore surface variations in the cage of trapped molecules and the chemical composition of the organic molecules is necessary in the preparation of novel optical or electrooptical gel-glasses[1-3].

In this paper, emphasis is placed on the preparation of organically doped sol-gel materials, describing gel-glass dispersed liquid crystal (GDLC) as electrooptical thin-film devices.

Preparation of GDLCs

For the point of view of electrooptics applications, the sol-gel process[4-7] has been used for trapping microdroplets of nematogenic organic compounds (i.e. liquid crystals, LCs) in a thin-film of a silica-gel based matrix[8,9]. During the first stage of the GDLC preparation, LC compounds are dissolved in the starting mixture (loosing its particular LC properties); further hydrolysis and polycondensation reactions leads to a phase separation that results in the formation of pores which are filled with the organic compound. If adequate processing of the preparation of the microdroplets is achieved, the organic compound recovers its nematic liquid crystal state, its molecules being oriented in microdomains according to the pore inner-surface anchoring (organic group on the walls of the pores, e.g.. $-CH_3$, $-C_2H_3$, $-C_6H_5$, etc.) and orienting properties. Once the phase separation in GDLC formation takes place, the LC microdroplets dispersion (LC concentration used in the starting solution) becomes simply a figure related to the number and density of microdroplets within the silica-gel matrix.

An important factor to avoid textural inhomogeneities in nematic microdomains is the production of a orienting surface, i.e., using $Si-CH_2CH_3$ groups on the pore cage. It may provides a lamellar structure for the LC molecules at the surface, an action that could be called a "molecular hair combing" that is sufficient to obtain molecular orientation and microliquid crystalline phases. In addition, $Si-CH_2CH_3$ groups provides flexibility to the matrix needed for deformations and reorganization of the microdomains at the time that an electric field is applied to the doped thin film. Either single monomers or mixtures of two monomers have been employed to prepare GDLCs with different electrooptical responses[10]. To characterize the orientation and shape of the microdroplets, the samples were switched in a microscope between crossed polarizers. Radial orientation corresponding to a homeotropic surface condition was obtained in all cases, as shown by a characteristic "Maltese cross" pattern in the droplets. Droplets from 0.8 μm to 1.6 μm, which allowed to high contrast GDLC films can be obtained by controlling reaction conditions.

The optical and dynamic performance of GDLC films depend on both, the starting mixture and the film preparation. Changes in the preparation were made according to the characterization of the GDLCs. For example, titanium isopropoxide (TIPO) was added as a dopant for increasing the matrix refractive index and for speeding up the hydrolysis and polymerization reactions, thus reducing the LC droplet size. Additionally, film thickness homogeneity and LC droplet size uniformity are also improved during the sample assembly by controlling the film formation conditions. Following this method, the resulting properties of the LC microdroplets may allow to the use of GDLC films as electrooptical devices (Figure 1).

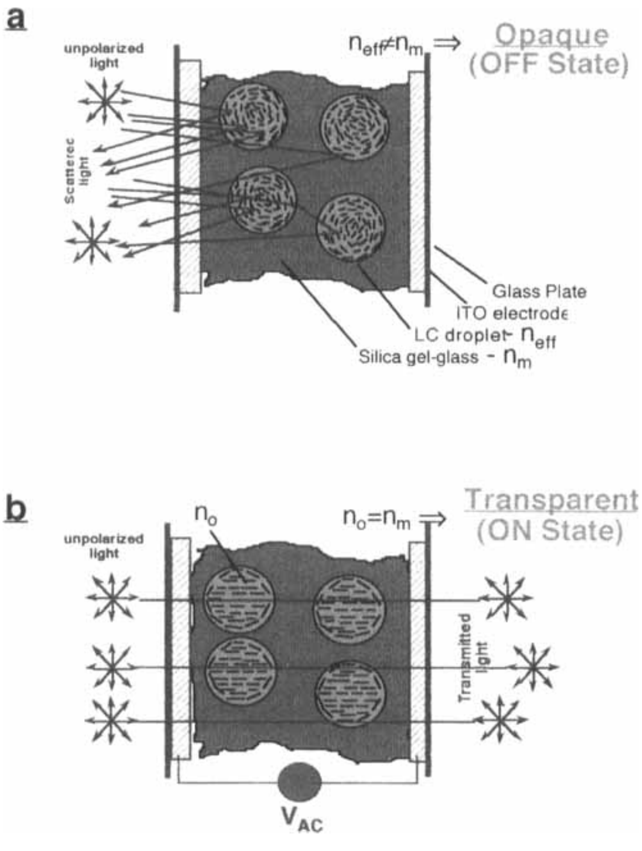

FIGURE 1. Illustration of a switching (opaque/transparent) GDLC. The incoming light is scattered out by the opaque GDLC (a), whereas upon an electric field is applied the optical path for the switched GDLC reach transparent conditions (b).

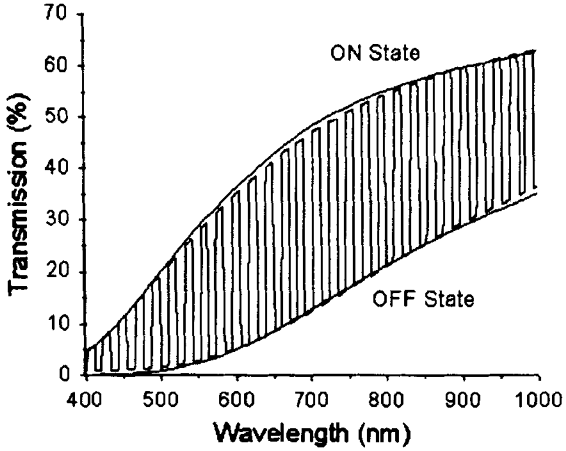

FIGURE 2. Transmission spectra of a 20 μm thick GDLC, showing simultaneous ON and OFF states (switching cycles) with wavelength.

Excellent GDLC dynamic response ($t_{ON(10\text{-}90)}$ is about 1 ms, and $t_{OFF(10\text{-}90)}$ is 0.9-3 ms) have been found under certain conditions of the GDLC preparation[11]. A different electrooptical dynamic response was found when varying the non-reacting organic group of the polymerizing organoacethoxysilane: assuming different anchoring forces in the inner surfaces of the pores, the relaxation time (t_{OFF}) varies with the different substrates.

GDLC Color Projection Displays

Should GDLC materials be used for displays, color need to be incorporated for many applications. Direct-view, backlighted passive displays usually include color filters located between the backlight system and the electrooptic material. In GDLCs, color may be included in the sol-gel matrix or in the liquid crystal itself.

A comparative study of different dyes for GDLC color displays[12] demonstrated that, dyes may be either embedded in the sol-gel matrix or dissolved in the liquid crystal microdroplets. In the first case, the liquid crystal scatters out the backlight when no voltage is applied, whereas a transparent colored pixel is obtained upon switching. In the second case, the dye is oriented by the liquid crystal, its absorption being modified by the liquid crystal reorientation. This affects the display contrast, brightness, and viewing angle.

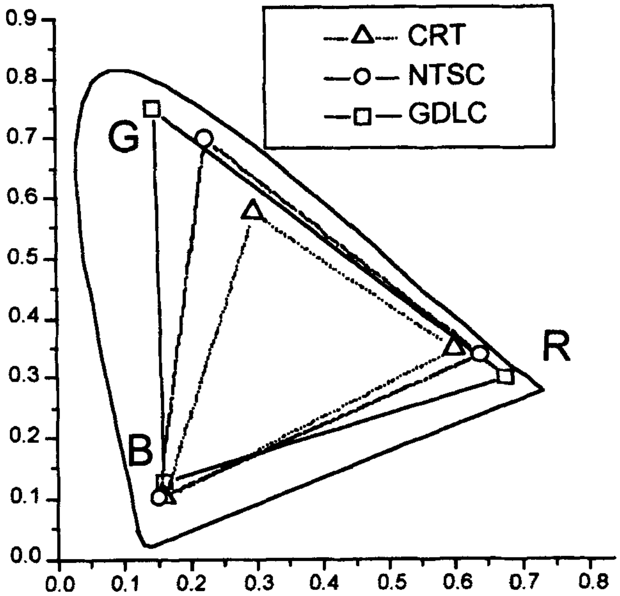

FIGURE 3. CIE 1931 chromaticity diagram of RGB pixels.

A new illumination system for opaque/transparent color emissive displays was recently used[13] by placing fluorescent RGB masks on the back plane. The display is illuminated from the front panel using UV light, and a matrix of fluorescent red, green, and blue dyes is placed in the back panel which excites the chromophors located under switched pixels, whereas unswitched pixels scatter the incoming UV light and the residual fluorescence. This setup may then be used for projection, the display behaving as an emissive display (i.e., like a commercial TV), and takes advantage of the photostability of sol-gel glasses as compared to similar systems. Two distinct sol-gel processes are used for trapping the liquid crystal and for preparing the fluorescent matrix respectively of the GDLC projection display.

The color coordinates and the color triangle achievable with fluorescent dyes is shown in Figure 3, a CIE 1931 chromaticity diagram. CRT and NTSC color triangles are also included for comparison. A number of dyes have been tested for appropriate color coordinates. Fluorescent dyes color coordinates usually lie near the horse-shoe shaped curve corresponding to monochromatic colors, thus giving a fairly large color triangle. The color coordinates obviously depend on the specific dye chosen for each pixel. As shown in the Figure 3, red and green color coordinates are more favorable than blue coordinate.

No serious attempts of display optimization have been included. Indeed, should this system be applied to displays, the blue dye has to be improved, both in color coordinates and in quantum yield. An additional problem derives from the UV excitation chosen for this work, as its peak emission (365 nm) is quite close to blue emission; the absorption band of many blue dyes is located further in the UV. However, this lamp is quite convenient for an eventual commercial system for its price, availability and low biological risks. Besides, the photostability of the LC is lower as the UV wavelength decreases.

The system performance is enhanced by using reflective mode. The incoming UV light is scattered by the (opaque) GDLC, and the residual fluorescence is scattered again by the same GDLC. Should the light wavelength be constant, this arrangement would be equivalent to doubling the GDLC thickness. Taking into account the actual LC microdroplet size (0.6-1 μm), the scattering mechanism is close to Rayleigh scattering for UV-visible light. In this case, UV light scattering is much stronger than visible scattering (Rayleigh scattering is a function of the 4th power of the wavelength). Therefore, the scattering of the system is higher than that of an equivalent reflective system working with visible light at a constant wavelength[14].

Moreover, in order to simplify sample manufacturing, an alternative method of incorporation of colors in GDLCs was used by the preparation of doped gel-glass film containing the dyes, which were coated on the outer side of the GDLC sandwich. This somewhat impairs the transmission and the viewing angle of the fluorescence, for a parallax effect arises. As dyes are trapped into gel, the deposition of the doped gel-glass on the internal surface of the rear glass plate (i.e. between the glass and the GDLC, see Figure 1) should be straightforward. However, the increased sandwich thickness increases the switching voltage.

Conclusions

The number of potential applications of organic doped sol-gel gel-glasses is very large; important possibilities include optics and electrooptics. Development of these applications requires a good understanding of the structure of the doped sol-gel matrices, the properties of the matrices on the molecular level, and the conditions that the oxide network imposes on the optical properties of the dopant. Specific modifications in the sol-gel processing allows the preparation of sol-gel devices for applications, such as emissive/transmissive GDLC color displays, which use the GDLC preparation associated to gel-glasses doped with fluorescent dyes.

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