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## Liquid Crystals

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# Photochromic reverse mode polymer dispersed liquid crystals

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Control of light intensity and colour are two of the major features required in the realization of smart windows. We designed a bi-functional polymer dispersed liquid crystal (PDLC) film in order to satisfy such requirements, i.e. it is able both to modulate the optical transmission, if an external electric field is applied, and to change colour if exposed to sunlight. A monomer/liquid crystal mixture was doped with a small amount of photochromic material and homeotropically aligned by means of rough surfaces. A transparent and pale pink coloured film was achieved after photopolymerization. Such a film changes colour upon exposure for some seconds to sunlight or ultraviolet radiation in a persistent but reversible manner. In addition, the film appears transparent without the application of an electric field (OFF state) and becomes opaque on application of a driving voltage of about 75 V (ON state), and thus the film operates in reverse mode with respect to conventional PDLCs.

## 1. Introduction

Photochromic molecules change their chromatic properties upon exposure to both natural and artificial ultraviolet (UV) light [1–4]. The ultraviolet radiation changes the molecular conformation of dye molecules causing a shift of the light absorption peak which causes the colour variation. If the UV source is removed the dyes return to the original state, which may be colourless if no absorption falls in the visible region of the spectrum. A control of light transmittance can be also achieved by both direct and reverse mode PDLCs [5–8]. The operation principle is based on the modulation of light scattering properties of liquid crystal domains dispersed in a polymer matrix by means of a suitable electric field. Direct mode devices show an opaque OFF state and a transparent ON state. By contrast, the application of an electric field to reverse mode PDLCs drives the transition from a transparent OFF state to an opaque ON state. Reverse mode PDLCs are preferable in many applications in which a transparent OFF state is required. Reverse mode devices may be obtained by the modification of the surface energy of the liquid crystal/polymer interface [9], by the use of a dual-frequency liquid crystal [10, 11], by the polymerization of a nematic emulsion [12], and by the formation of mesogenic network composites [13–17]. In this work, we present the results of an investigation devoted to the realization

of smart windows, i.e. devices that are able to regulate the radiation flux in accordance with comfort requirements.

The electro-optical properties of a reverse mode PDLC and the chromogenic properties of photochromic molecules belonging to naphthopyran and oxazine classes [18], are used to control the transmittance and colour of incident light. It is well known that *spiro*-oxazines are promising photochromic compounds with good photo-fatigue resistance [19]. Because the *spiro*-carbon of a *spiro*-oxazine molecule has potential as a chiral centre, they may also be utilized as chiro-optical molecular switches [20].

Their colourless form contains the *spiro*-carbon atom which is  $sp^3$  hybridized and separates the molecules into two halves. In such a geometry (closed form) the molecules absorb in the UV region of the light spectrum, and are colourless (figure 1 state I). The groups,  $R_i$ , may be selected as described elsewhere [21]. The photochromism appears upon exposure to ultraviolet radiation, which causes the rupture of the carbon–oxygen single bond of the oxazine ring (figure 1 state II). As a consequence, the molecular conformation changes into a planar configuration (open form) and the molecular absorption falls in the visible part of the light spectrum. If the UV radiation is removed the carbon–oxygen bond reforms and the molecules relax to the colourless closed form within a few seconds. This process is thermally and photochemically reversible and allows the use of such compounds in many film coloration and bleaching cycles.

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In fact, in the reverse mode PDLC obtained by our method the liquid crystal exists in the voids of a network structure formed by small polymer balls, i.e. the LC is not separated as distinct droplets within the polymer matrix as in conventional direct mode PDLCs; the presence of the LC, mutually and homogeneously dispersed in the film, allows the photochromic molecules dissolved in it to open easily on exposure to UV. By contrast, the photochromic molecules entrapped in the solid phase of the polymeric matrix, are unable to convert from the closed-ring form to the open form.

This conversion produces a change in the visible absorption spectrum of the molecules with an accompanying colour change of the film from pale pink to blue, as shown in figure 3. The spectrum obtained is of the dye contained in the electro-optical film, and not of the dye alone, and represents the real colours observed for our film. In fact, the spectrum of the dye dissolved in a solvent strongly depends on the type of solvent used. We recorded the absorption spectrum of the film under four different experimental conditions, in order to verify whether there exists a dependence of the chromatic properties of the UV irradiated and unirradiated film on the optical transmission.

Figure 4 shows the absorption spectrum of the opaque film, i.e. in the OFF state (0 V applied), both in the clear and in dark conditions; similarly, the absorption spectrum of the transparent film, i.e. in the ON state (75 Volt applied) is also shown. The film is able to modulate, at the same time and independently, both the optical transmission and the colour. In fact, in the clear condition and with no applied external voltage ( $V=0$ ), the film presents an absorbance of 1, and is transparent to light. When the film is UV-irradiated (dark condition), but not subject to an electric field, the absorption spectrum changes, showing an increase of

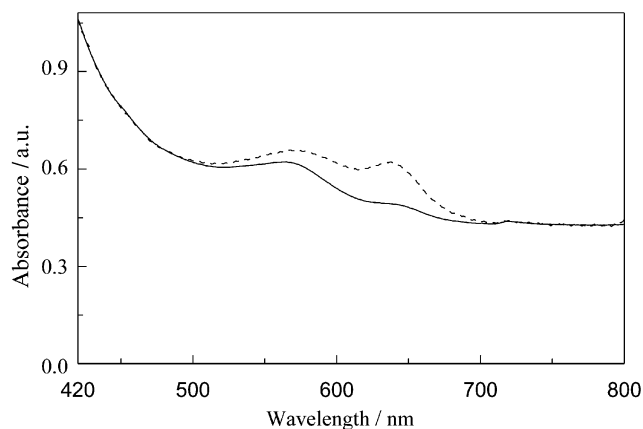


Figure 3. Bi-functional film visible absorption spectra in clear (—) and dark condition (---), corresponding to states I and II of the dye, respectively.

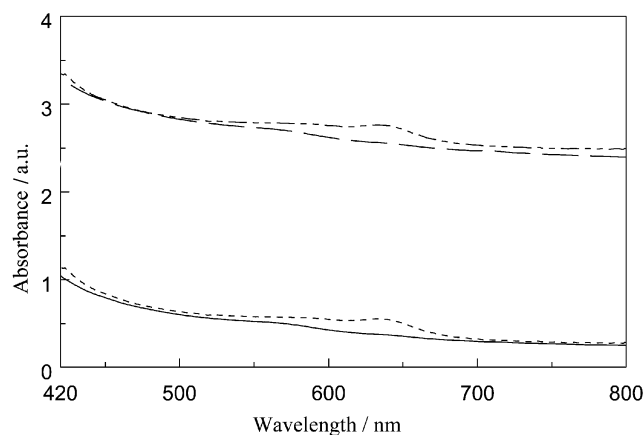


Figure 4. Visible absorption spectra of a reverse mode PDLC containing photochromic dye for two different driving electric fields and under clear and dark condition. — 0 V, UV OFF; --- 0 V, UV ON; - - - 75 V, UV OFF; - · - · 75 V, UV ON.

the absorbance at 640 nm. This provides evidence that the film has turned from pale pink to blue. At the same time, when an external a.c. voltage of 75 V is applied to the photochromic PDLC in clear condition, the absorbance increases to 3.4; this is due to the reorientation of the liquid crystal molecules parallel to the glass surfaces.

In such a condition, the LC refractive index does not match that of the polymeric matrix, and the pale pink film will be opaque. If the film is UV-irradiated, the peak at 640 nm is again evident in the absorption spectrum, and the appearance of the film will be opaque and blue. Figure 5 shows the optical transmission of the film as a function of the applied electric field. The PDLC shows a transmission of 75% with respect to air in the OFF state; when a driving voltage is slowly applied to the film, the transparency of the film

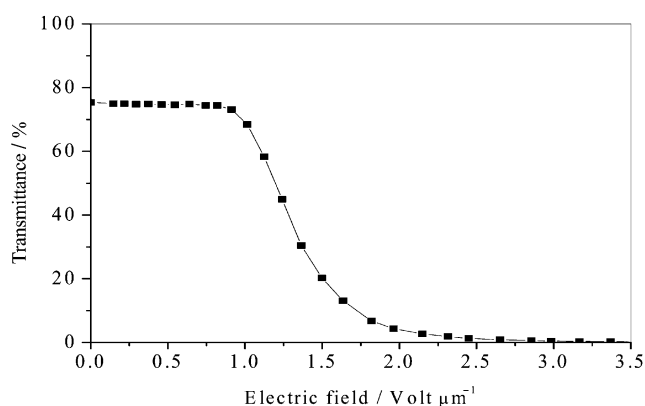


Figure 5. Transmittance dependence on applied electric field at 1 kHz of a reverse mode PDLC film containing photochromic dye.

decreases until the PDLC turns opaque with an a.c. voltage of 75 V. In order to verify whether the isomerization of the dye affects the order parameter of the liquid crystal, we compared the optical transmission, in the OFF and ON states and in clear and dark conditions, of two films with the same thickness (one of these containing the dye).

We observed no difference in transmission, implying that the dye isomerization does not affect the alignment of the liquid crystal dispersed in the polymer matrix. Moreover, we verified that the chromatic properties of the film do not change with the repeated application of the electric field, and at the same time the electrical characteristics of the PDLC also remain unchanged after the repeated exposure of the film to UV radiation.

#### 4. Conclusions

In conclusion, we have investigated the electro-optical properties of reverse mode polymer dispersed liquid crystal shutters aligned by means of rough conductive supports and doped with photochromic molecules. We have shown that it is possible to obtain a bifunctional film able to (i) modulate the light intensity, by means of the reorientation of the liquid crystal molecules resulting from the application of an external electric field, and (ii) achieve chromatic variation by UV irradiation. The use of different photochromic dyes in appropriate ratios would allow the formation of additional colours. The coloured state is achieved in a few seconds on exposure to sunlight or UV, while the bleaching of the dye to its closed form requires several minutes. A detailed kinetic and thermodynamic investigation of the activation and bleaching processes is in progress.

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