

Self-adjusting smart windows based on polymer-dispersed liquid crystals

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ARTICLE INFO

Article history:

Received 9 June 2009

Accepted 3 August 2009

Available online 29 August 2009

Keywords:

Smart windows

Liquid crystals

PDLC

ABSTRACT

The control of sunlight can be achieved either by electrochromic or polymer-dispersed liquid crystal (PDLC) smart windows. We have recently shown that it is possible to homeotropically align fluid mixtures of low molecular mass liquid crystal with a negative dielectric anisotropy, and a liquid crystalline monomer, in order to obtain electrically switchable chromogenic devices. They are new materials useful for external glazing. In fact, they are not affected by the classical drawbacks of PDLCs. In this paper we present a new self-switchable glazing technology based on the light-controlled transmittance in a PDLC device. The self-adjusting chromogenic material, which we obtain, is able to self-increase its scattering as a function of the impinging light intensity. The relationship between the electro-optical response and the physical-chemical properties of the components has been also investigated.

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1. Introduction

Smart windows are used in building and automotive applications in order to control the incident daylight and glare [1–3], according to occupant comfort. The control of sunlight can be achieved by electrically switchable chromogenic materials, which are glazing devices able to electrically change either their colour or transmittance. They are, respectively, based on electrochromic systems, which change their colour as a consequence of REDOX reactions, and liquid crystal systems that allow controlling their transmittance by the electrical-driven director reorientation.

Electrochromic windows are the most popular electrically switchable chromogenic materials [4,5] as they present the advantage that the electric field must be applied only during the switching operations. On the contrary, the physical principle used in nematic liquid crystal-based systems is the electrically-driven reorientation of the liquid crystal director, which results in a change of their transmittance [6]. Recently, Gardiner et al. [7] have presented an interesting device based on an alternative electro-optical effect, which they observed in the smectic A phase. Upon application of a low-frequency voltage, the motion of ionic additives generates highly scattering focal conic textures in the device, becoming opaque. Then, the application of a larger frequency voltage turns the device in the clear state.

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Among liquid crystal-based systems polymer-dispersed liquid crystals (PDLCs) deserve particular mention. They are composite materials, which show both the advantages of a solid polymer and a fluid liquid crystal. In fact, they are formed by either micron-sized liquid crystal droplets embedded in a polymer matrix (“Swiss cheese” morphology), or by liquid crystal that fills the voids and crevices of a polymer network (“polymer ball” morphology), which give them a solid-like nature [8]. In the OFF state PDLCs appear translucent white due to the light scattering. Upon application of a suitable electric field, the molecular reorientation will change the refractive index of liquid crystal domains and the device will appear transparent in the ON state if the optical matching condition is fulfilled. The reorientation electric fields are dependent on several parameters including droplet size and shape, size distribution, anchoring effects at polymer boundary, liquid crystal dielectric and conductive anisotropy, polymer molecular weight and chemical nature. We have recently investigated that the electrical conductivity in polymer-dispersed liquid crystals strongly affect the electro-optical response of PDLCs and can be finely adjusted by adding small amounts of conductive molecules in the polymer matrix [9]. In this way the electric field across the nematic liquid crystal droplets can be increased with a consequent large reduction in the reorientation fields and relaxation times.

For safety reasons, reverse mode operation PDLCs, which are devices transparent in their OFF state and opaque in their ON state, are preferred in building and automotive applications. They allow overcoming some drawbacks of direct mode PDLCs such as opaque unpowered state and large values of haze. Reverse mode

shutters have been obtained by using dual-frequency addressable liquid crystals [10,11], by polymerizing nematic emulsions [12], by functionalizing the liquid crystal/polymer matrix interface [13], and by means of rough surfaces [14]. In this last case, the alignment is achieved through typical grooves present in the substrates, which promote an excellent alignment and an easy axis almost perpendicular to the cell glass plates. Such preferential alignment can be stored if cross-linkage of the polymerizable component is performed. More recently, we have shown that it is possible to combine the electro-optical properties of liquid crystal and the electrochromic properties of electrolyte–liquid crystal mixtures in order to gain the control of incident daylight and glare in building and automotive applications [15].

In this paper we will show our efforts devoted to the fabrication and characterization of self-adjusting electrically switchable chromogenic cells suitable for external glazing. The device was obtained by doping a reverse mode operation PDLC with photoconductive molecules. The optical control of the light-scattering properties of polymer-dispersed liquid crystals can be achieved by fine tuning of the cell electrical properties under light irradiation. In the dark, an electric field, lower than the threshold one, is applied across the film, which, consequently, appears opaque. After irradiation with a light beam, the increased cell electric conductivity enhances the effective field acting on the liquid crystal droplets, making the film transparent. The device can be switched off by turning off either the light source or the electric field. The effects of light intensity and photoconductor amounts on the film performance are also discussed.

2. Experimental part

Mixtures were prepared in vials by mixing the appropriate amounts of liquid crystalline monomer (1,4-bis[4-[6-(acryloyloxy)hexyloxy]benzoyloxy] benzene, 16 wt% and synthesized in agreement with Ref. [16]), and the eutectic nematic mixture ZLI 4788–000 ($\Delta\epsilon = -5.7$, 84 wt%, $\sigma_{\text{avg}} = 2.35 \times 10^{-8} \Omega^{-1} \text{m}^{-1}$), doped with different percentages (up to 10 wt%) of a dispersion of zinc phthalocyanine in ionic liquid (ZP/IL) in the weight ratio 0.5:100 (1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, Merck). Such composition was chosen after a set of trials involving other lipophilic ionic liquids, photoconductive and photochromic molecules, and different concentrations. After stirring at 100 °C, mixtures were introduced by capillarity into homemade cells whose thickness was set to be 30 μm by glass spheres. Glass substrates had a 120 nm indium tin oxide conductive layer (Balzers) with an average roughness of 2.6 nm, which are known [14] to align liquid crystalline mixtures perpendicularly (homeotropically) to them. After having checked the homeotropic alignment of mixtures by polarizing optical microscope, cells were exposed at a controlled temperature (80 °C) to UV light for 15 min (average power 10 mW/cm²) in order to induce the phase separation between liquid crystal and polymer. As the polymerization processes are rather sensitive to thermal fluctuations only samples, which kept a good homeotropic alignment after polymerization process, were considered for the subsequent electro-optical characterization. Obviously, an improvement in the final degree of alignment can be gained by covering glass substrates with alignment promoters as polyimide layers. The electro-optical properties of samples were measured with the optical setup previously reported [17] equipped with a white light source (Linus 1000, Laserpoint, maximum power output 10 mW/cm²) for the measurements under irradiation. Briefly, a He–Ne laser light beam passed through a chopper and a beam expander. The beam diameter was set to be 0.8 mm by a variable iris before impinging on the sample. Then, light coming out from the sample was

collected by a high-speed detector with an acceptance angle equal to 2.5°. The sample was mounted on a computer-controlled rotatable stage to vary the incident angle. The intensity of the incident laser light measured through an empty cell was assumed to be full-scale intensity. The ON and OFF response times, τ_{ON} and τ_{OFF} , defined, respectively, as the time required to drop to 10% of the maximum transmittance and to reach 90% of the optical response after the external field is removed, were determined by monitoring the drive signal ($\nu = 1 \text{ kHz}$, $E_{\text{pp}} = 3 \text{ V } \mu\text{m}^{-1}$) and the response of the photodiode using a digital storage oscilloscope. Conductivity measurements were carried at 1 kHz, which is the typical drive frequency of PDLCs, with a LCR meter (Hewlett Packard 4284A).

3. Results and discussion

Highly transparent (OFF state transmittance, T_{OFF} , larger than 70%) PDLC films were obtained after the polymerization-induced phase separation process at all doping percentages (Fig. 1), i.e. the large additive percentages have no particular effect both on the OFF and ON state transmittance values.

Scanning electron microscopy confirmed the presence of a polymer ball morphology in all our samples: small polymer balls (average radius about 100 nm) merging in a network structure, whose voids and crevices are filled by liquid crystal (Fig. 2). Such a structure allows a large viewing angle as the thin liquid crystal layers around the polymer droplets do not give rise to a sufficient phase shift of the light, as confirmed by the measurements of transmittance as a function of the cell tilt angle in Fig. 3 [18].

If an external field is applied to cells in dark conditions, the liquid crystal director will reorient perpendicularly to the field direction because of the negative dielectric anisotropy, increasing the light scattering and reducing the transmittance values to about 1% for an electric field value inversely dependent on the doping weight percentage. In fact, Fig. 1 shows the typical field-dependent transmittances, which are left shifted as the weight percentage of zinc phthalocyanine/ionic liquid mixture is increased. The electro-optical left shift is easily explained by an increase of cell conductivity as a function of the weight percentage of ZP/IL mixture, which results in a decrease of the reorientation fields, required to make the device opaque [19].

For the sake of completeness, we remind that liquid crystals are anisotropic materials but, being PDLCs rather complex heterogeneous systems and since a complete description of their electrical properties is not known, we have considered PDLCs just as isotropic media (to a first approximation [8]). The measurements of the average conductivities performed on liquid crystal-saturated polymer matrix (liquid crystal 75 wt% and monomer 25 wt%, which is the weight ratio for the onset of an electro-optical response [18]), and liquid crystal with different weight

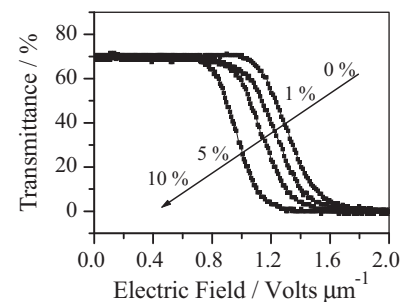


Fig. 1. Transmittance dependence on the applied electric field for increasing percentages of ZP/IL mixture in dark conditions.

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