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Electrically switchable chromogenic materials for external glazing

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ABSTRACT

The development of chromogenic materials is important for their potential applications as electrically adjustable or thermally self-adjusting light and heat filters in the external glazing of buildings. Recently, we have reported our investigations on electrolyte–liquid crystal dispersions, which show independent electro-optical and electrochromic properties characterized by fast bleaching times. Nevertheless, for the external glazing of buildings, it is recommended to have a transparent off state, which turns opaque upon application of the external field. In this paper, we present our efforts to homeotropically align by rough surfaces fluid mixtures of a low molecular mass liquid crystal with a negative dielectric anisotropy, a liquid crystalline monomer, and electrolyte molecules in order to obtain transparent films after a polymerization process. Upon application of an ac electric field, the device becomes opaque and if a dc field is added, the cell changes colour too. We have also investigated the relationship between electro-optical/chromogenic response and physical chemical properties of the components.

1. Introduction

Electrically switchable chromogenic materials (ESCMs) are glazing devices that change either their colour or transmittance upon application of a suitable electric field. The most important types of such devices are electrochromic windows, which change their colour, and dispersed liquid crystal and dispersed particles that allow controlling the scattering of the impinging light. ESCMs can be used as "smart windows" for building and automotive applications in order to control incident daylight and glare [1–3], according to occupant comfort. ESCMs are currently limited to side and rear-view mirrors, sunglasses, sun-roofs and, in general, small area glazing. They are also expected to lower the demand on precious non-renewable fuels for lighting and cooling.

Both inorganic- and organic-based electrochromic windows are the most popular ESCMs as confirmed by large number of scientific publications in recent years [4–8]. The major advantage of electrochromic materials is that the low electric field must be applied only during the switching operations. Organic electrochromics are based on bipyridilium systems, conducting polymers, quinones, phthalocyanines, terephthalates, tetrathiafulvalenes, and cyanobiphenyls, which are molecules able to change their colour in response to oxidation/reduction processes.

The physical principle used in all liquid crystal-based systems is the electrically driven reorientation of liquid crystal directors, which results a change in their transmittance values [9,10]. Among them polymer dispersed liquid crystals (PDCLs) 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, or by liquid crystal that fills the voids and crevices of a polymer network. 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 between the refractive indices of liquid crystal and polymer matrix is fulfilled. Reverse mode operation PDLCs are devices which are transparent in the OFF state and turn opaque in the ON state. They allow overcoming some drawbacks of direct mode PDLCs such as the opaque unpowered state and the large values of haze. Reverse mode shutters have been obtained by using dual frequency addressable liquid crystals [11,12], by polymerizing nematic emulsions [13], and by functionalizing the liquid crystal/polymer matrix interface [14]. Recently, we proposed a reverse mode device obtained by the photopolymerization of mixtures containing a low-molecular-mass liquid crystal with a negative dielectric anisotropy, and a liquid crystalline diacrylate monomer homeotropically aligned by means of rough surfaces [15]. The alignment is achieved through typical grooves present in the substrates, which promote an excellent anchoring and an easy

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axis almost perpendicular to the cell glass plates. Such preferential alignment can be stored if crosslinkage of the polymerizable component is performed.

The use of rough surfaces allows an easier and faster preparation since neither surface treatment of supports nor the use of external aligning fields is required. In addition, no limit is theoretically imposed on the dimensions of devices.

More recently, we have shown that electrolyte/liquid crystal dispersions are able to give both an independent and fast switching from a scattering opaque state to a transmissive transparent state, owing to liquid crystal director reorientation, and a colour change, due to the electrochromic reactions occurring at the electrodes [16]. Both changes are obtained with rather fast switching and relaxation times: few milliseconds and few seconds for the electro-optical and electrochromic responses, respectively. The origin of electrochromism can be attributed to the formation of coloured complexes between phenyl rings and ammonium ions, as reported by Nakamura et al. [17,18]. The bleaching occurs when the dc field is removed and is attributed to the diffusion of halide molecules produced by oxidation at the anode and their reaction with coloured species. In this paper we will show our efforts devoted to the fabrication and characterization of electrically switchable chromogenic cells suitable for external glazing obtained by doping with electrolytes reverse mode operation PDLCs. They are really bifunctional devices characterized by a transparent OFF state, which can become opaque upon application of an ac field and can independently turn coloured, if a dc field is applied. Such "smart windows" could be used both for building and automotive applications allowing a controlled comfort from daylight and glare.

2. Experimental part

The nematic liquid crystal used in this work was the eutectic mixture ZLI 4788-000 (Merck) characterized by a negative dielectric anisotropy ($\Delta\varepsilon = -5.7$). Liquid crystalline monomer, 1,4-bis {4-[6-(acryloyloxy)hexyloxy]benzoyloxy} benzene (Fig. 1), was synthesized in agreement with literature [19]. 1% of ammonium salts, tetrabutylammonium tetrafluoroborate, tetrabutylammonium hexafluorophosphate, tetrabutylammonium perchlorate, octadecyltrimethylammonium bromide, and didodecyldimethylammonium bromide (Aldrich) were dissolved in liquid crystal by stirring at 65 °C. The choice of ammonium salt can produce a change in the intensity and shade of the cell colour [15]. Mixtures were prepared in vials by mixing the appropriate amounts of liquid crystalline monomer, 16 wt%, and ammonium salt-doped ZLI 4788-000, 84 wt%, and subsequently stirring them at 100 °C. Then, a small quantity of mixtures was introduced by capillarity into home-made cells whose thickness was set to 60 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 allows the alignment of liquid crystalline mixtures perpendicular (homeotropic) to glass substrates [15]. After checking 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/cm^2) in order to induce the phase separation between the liquid crystal and the polymer. The electro-optical properties of samples were measured with the optical setup previously reported [20] and the colour changes were monitored as a function of time and applied dc fields with a YASCO V550 UV–Vis spectrometer. The intensity of the incident 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 ($\nu = 1$ kHz, $E_{pp} = 4\,V\,\mu m^{-1}$) and the response of the photodiode using a digital storage oscilloscope.

3. Results and discussion

1,4-bis{4-[6-(acryloyloxy)hexyloxy]benzoyloxy} benzene is known to allow and keep after the polymerization, a good homeotropic alignment of liquid crystal on rough substrates covered by indium tin oxide [15,21,22]. In fact, highly transparent (OFF state transmittance, T, around 80%) and uncoloured PDLC films were obtained after the polymerization-induced phase separation process. If an ac external field is applied ($\nu = 1$ kHz), liquid crystal directors will reorient perpendicularly to the field direction because of its negative dielectric anisotropy, increasing the light scattering and reducing the transmittance values (about 1% for an electric field of 1.8 V μm^{-1}). Fig. 2 reports the typical field-dependent transmittance of a cell and shows that there is no

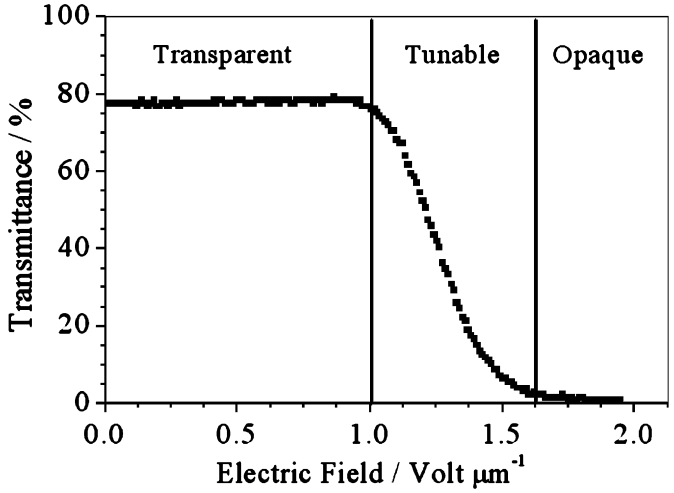

Fig. 2. Typical electric field-dependent transmittance of our ESCM.

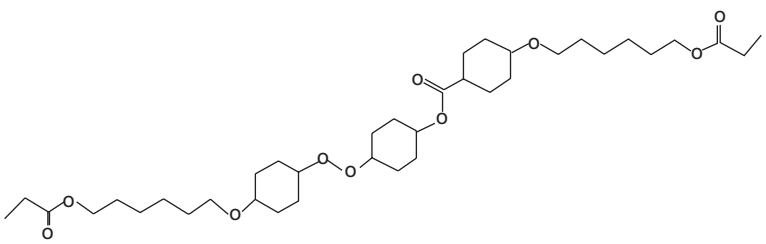

Fig. 1. Molecular structure of used liquid crystalline monomer, 1,4-bis{4-[6-(acryloyloxy)hexyloxy] benzoyloxy} benzene.