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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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Marialuigia Macchione^a; Daniela Cupelli^a; Giovanni De Filpo^a; Fiore P. Nicoletta^a; Giuseppe Chidichimo^a

^a Dipartimento di Chimica, Universita degli Studi della Calabria, 87036 Rende (CS), Italy,

Online publication date: 06 August 2010

To cite this Article Macchione, Marialuigia , Cupelli, Daniela , De Filpo, Giovanni , Nicoletta, Fiore P. and Chidichimo, Giuseppe(2000) 'Rough surfaces for orientation control in reverse mode polymer dispersed liquid crystal films', *Liquid Crystals*, 27: 7, 917 – 920

To link to this Article: DOI: 10.1080/02678290050043860

URL: <http://dx.doi.org/10.1080/02678290050043860>

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Rough surfaces for orientation control in reverse mode polymer dispersed liquid crystal films

MARIALUIGIA MACCHIONE, DANIELA CUPELLI,
 GIOVANNI DE FILPO, FIORE P. NICOLETTA
 and GIUSEPPE CHIDICHIMO*

Departmento di Chimica, Università degli Studi della Calabria,
 87036 Rende (CS), Italy

(Received 14 October 1999; accepted 14 February 2000)

Reverse mode operation shutters have been achieved with polymer dispersed liquid crystals by means of polymerization-induced phase separation of nematic mixtures consisting of a low molecular mass liquid crystal and a liquid crystalline monomer. Fluid mixtures were homeotropically aligned by rough surfaces and transparent films were obtained after polymerization. Transmittance in the OFF state can be larger than 80% and decreases to less than 1% when an electric field of about $2 \text{ V } \mu\text{m}^{-1}$ at 1 kHz is applied (ON state). Both rise and decay times can be lower than 10 ms and the drop in the OFF state normal transmittance is drastically reduced with respect to conventional polymer dispersed liquid crystals since samples exhibit a reverse morphology. The role played by surface roughness is also discussed.

1. Introduction

The production of large area displays and variable transmission devices has achieved great interest among electro-optical applications. Liquid crystals are not suitable materials for this sort of application because of their fluid nature, the need for surface treatments, and the use of polarizing layers which greatly reduce the light transmittance. Accordingly, in the last fifteen years considerable efforts have been made to obtain composite materials with the optical properties of liquid crystals and the mechanical properties of solids.

Polymer dispersed liquid crystals (PDLCs) are composite materials formed by liquid crystal and polymer in order to combine the above mentioned requirements [1, 2]. PDLCs can exhibit either a droplet morphology [3], in which the liquid crystal is separated as distinct droplets within the polymer matrix, or the opposite morphology [4] in which the liquid crystal exists in the voids of a network structure formed by small polymer balls. Both PDLC types are generally characterized by an opaque OFF state, which can be turned into a transparent ON state by application of a suitable voltage (normal mode operation PDLC). A reverse mode PDLC on the other hand is one which exhibits a transparent OFF state and an opaque ON state. Reverse mode devices can be obtained by the modification of the surface energy of the liquid crystal/polymer interface [5], by the use of a dual-frequency liquid crystal [6, 7],

by the polymerization of nematic emulsions [8], and by the formation of mesogenic network composites [9–14]. The reverse mode devices developed according to the above methods may show one or more disadvantages such as low optical contrast, bad adhesion to supports, high driving electric field, chemical instability and long decay time.

Polymer networks are characterized by only a few percent of highly crosslinked polymer, for which the orientation and structure are stable over long periods of time and practically unaffected by the presence of external fields or changes in temperature. Hikmet has investigated the properties of mesogenic network composites obtained using low molar mass mesogens and liquid crystalline diacrylates. The anisotropic gels were obtained by photopolymerizing the liquid crystalline mixtures containing the liquid crystalline diacrylates, either in a planar uniaxially oriented state (normal mode device) [9] or in a homeotropically oriented state (reverse mode device) [11]. The orientation control in both devices was achieved by using transparent electrodes with rubbed polymer substrates. The shutters described by Hikmet could be characterized by a high contrast ratio, low switching voltages, and short decay times depending on the UV intensity and polymer concentration.

In this paper we propose a reverse mode device obtained by the photopolymerization of mixtures of a low molecular mass liquid crystal with a negative dielectric anisotropy and a liquid crystalline diacrylate

* Author for correspondence; e-mail: defilpo@unical.it

monomer. Nematic mixtures were homeotropically aligned by means of surface interactions with rough conductive supports before the polymerization took place. The alignment was preserved even after the crosslinking of the liquid crystalline monomer and gave reverse mode operation films with a high optical contrast, good adhesion on supports, fast response times, and long stability. The orientation control, and consequently the electro-optical performance, depended on the roughness of the supports used.

2. Experimental

The liquid crystalline diacrylate monomer used in this work was 1,4-phenylene bis[4-(6-acryloyloxyhexyloxy)-benzoate] (C6H) as used by Hikmet and co-workers [9–11]. It was synthesized according to the procedure outlined in [5]. Samples were prepared in home-made cells (thickness $\approx 15 \mu\text{m}$) by mixing the appropriate amounts of C6H and EN-40 (a commercially available liquid crystal with negative dielectric anisotropy, Lixon) in vials, and subsequently stirring them at 100°C . In this paper we limit our investigation to samples with 84 wt % of EN-40. The effect due to different liquid crystal loadings on the morphology and electro-optical properties of PDLCs will be published elsewhere [16]. About 1.5 wt % of photoinitiator (Irgacure 651, Ciba-Geigy) was added. The cell substrates had different indium tin oxide (ITO) conductive layer thicknesses (0, 20, 45, and 120 nm, Balzers). The average roughness of the surfaces was determined by atomic force microscopy (Nanoscope III, Digital Instruments) in the contact mode at constant vertical force. UV irradiation was from a mercury lamp (Philips, model HPK 125) for 15 min.

The electro-optical characterization of PDLCs was performed by using the optical line reported in previous work [17]. The light intensity, transmitted without any sample, was assumed to be full-scale intensity. The normal haze of the PDLC films was measured with a Macam LSO-4514 haze-meter. The haze was calculated by measuring the transmitted light scattered more than 2.5° from the direction of incidence with respect to the total transmitted light (ASTM D 1003). The rise and decay times of samples, i.e. the time required to drop 10% and reach 90% of the maximum transmittance after field removal, were determined by applying a suitable driving voltage of 1 kHz. Morphology analysis was performed on cross sections of PDLC films using a Leica LEO 420 scanning electron microscope (SEM).

3. Results and discussion

The table reports the average roughness of the cell substrates used to prepare PDLC films.

It can be seen that the larger the ITO layer thickness, the higher is the roughness, due, in our opinion, to the

Table. Average roughness of the substrates investigated as determined by software treatment of atomic force microscopy images.

Sample	ITO thickness/nm	Average roughness/nm
a	120	2.6
b	45	2.0
c	20	1.9
d	0	0.5

coating technique. Once the cells were filled by capillarity, we observed that rougher surfaces were able homeotropically to align the nematic mixtures (nematic phase ranges from 67 to 88°C). Such orientation control, due to the interactions between the rough surfaces and the first layers of nematic material, was maintained even during and after the UV polymerization of the contents of the cells, carried out at 81°C .

Figure 1 shows the typical optical transmittance of PDLC samples as a function of the applied electric field.

After having performed the polymerization, transparent PDLCs were obtained at room temperature with a transmittance at zero field which decreases if cells with lower ITO layer thickness are used. In particular, sample 'a' (ITO layer thickness ≈ 120 nm) show 82% transmittance in the OFF state. When a 1 kHz signal is applied, the transmittance of all samples (except sample 'd', which had no conductive substrate) decreases to less than 1% for a driving electric field of about $2 \text{ V } \mu\text{m}^{-1}$, due to the 90° rotation of the liquid crystal molecules.

The OFF state optical transmittance decreases as a function of the viewing angle (figure 2).

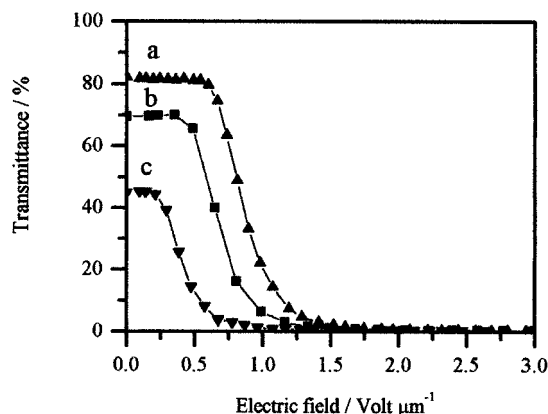


Figure 1. Transmittance dependence on applied electric field at 1 kHz for 84 wt % EN-40 films aligned by substrates with different ITO layer thickness 'a' 120 nm, 'b' 45 nm, 'c' 20 nm.

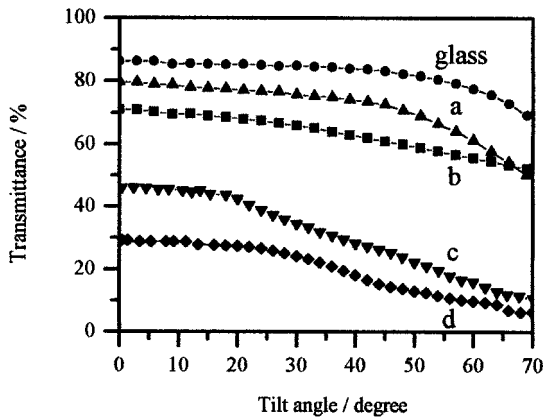


Figure 2. Transmittance dependence on cell tilt angle for 84 wt % EN-40 films aligned by substrates with different ITO layer thickness: 'a' 120 nm, 'b' 45 nm, 'c' 20 nm, 'd' 0 nm. The transmittance through a glass substrate is reported for comparison (curve labelled glass).

Such a decrease is gentler than in conventional reverse mode PDLCs and is about 15% at 60°. The angular dependence for transmittance through a glass substrate is reported for comparison (curve labelled glass).

The electro-optical response of the PDLCs was determined by measuring the rise and decay times. There is no large difference among rise times (less than 1 ms) as shown in figure 3.

In contrast, the decay time, i.e. the time required for the liquid crystal molecules to lose the planar alignment, strongly depends on the liquid crystal alignment, ranging from about 5 ms (sample 'a') to 15 ms (sample 'c'). These response times are slightly faster than those for conventional reverse mode PDLCs (several tens of ms).

The normal haze of PDLCs decreases with the thickness of the ITO coating layer ($\approx 18\%$ for sample 'c' and $\approx 5\%$ for sample 'a'). The very low values of haze can be explained by the reverse morphology of our PDLC films. In fact, it is known that almost haze-free PDLCs can be obtained either in samples characterized by very thin polymer walls or in films where the polymer balls form an irregular network [3] with the liquid crystal filling the voids and crevices of the network.

The presence of a reverse morphology structure in our samples was confirmed by SEM analysis. Figure 4 shows a typical scanning electron microscope photograph.

The matrix consists of small polymer balls (average diameter $\approx 0.3 \mu\text{m}$) merging in a network structure within which the liquid crystal becomes dispersed. Consequently, the liquid crystal does not give rise to a sufficient phase shift of light to cause a significant loss of transmittance even at large tilt angles.

The reverse mode electro-optical cells proposed in this paper show high optical contrasts (larger than 80 for sample 'a'), good adhesion on glass supports (as the

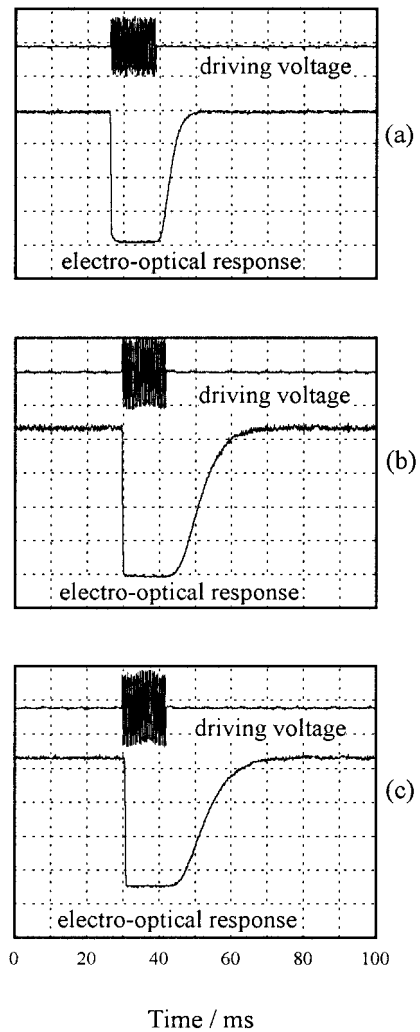


Figure 3. Electro-optical response for 84 wt % EN-40 films aligned by substrates with different ITO layer thickness (a) 120 nm, (b) 45 nm, (c) 20 nm. The driving voltage was a sine wave of $100 \text{ V}_{\text{rms}}$ at a frequency of 1 kHz. The apparent deviation from sinusoidal behaviour is an oscilloscope artefact.

monomer concentration is 16 wt %), long term stability (no evidence of electro-optical change was observed after six months from the time of sample preparation), and reduced haze (less than 5% for sample 'a'). Most importantly, no particular treatment of supports is required.

The main idea for producing our reverse mode shutters consists in using glass substrates with an adequate ITO layer thickness. Due to the coating techniques, the average roughness of the surfaces increases with ITO layer thickness. If the average roughness of the transparent electrodes approximates to that of the molecular length (20–30 Å), the glass substrates are able to control the orientation of nematic mixtures, inducing a good homeotropic alignment. It should be noted that the

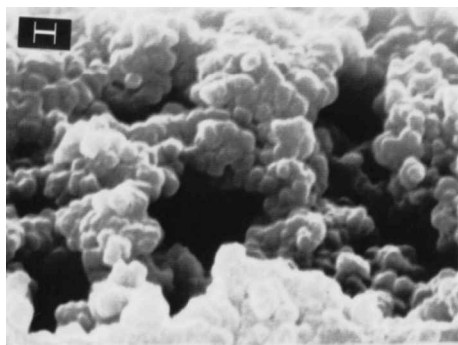


Figure 4. Scanning electron microscope photograph of an 84 wt % EN-40 sample aligned by a 120 nm ITO substrate. The film clearly exhibits a reverse morphology, i.e. the matrix consists of small polymer balls merging in a network structure. The bar is equal to 0.4 μm .

substrates of such electrodes are not treated with polymer [18], and the alignment of the nematic mixtures is not induced by the application of external fields [19], giving consequently an easier procedure for sample preparation. Subsequently, samples are exposed to UV radiation to achieve the phase separation of the liquid crystal from a reverse morphology polymer matrix. The initial homeotropic anchoring for the liquid crystalline mixture (promoted by the grooves present on the ITO coated surfaces) is transferred as an orientational order to the polymer network and stored by the photopolymerization [20]. The separated liquid crystal is now kept homeotropically oriented at the polymer ball surfaces by means of molecular interactions. The final transparent OFF state depends on the initial homeotropic alignment, which is a function of the average roughness of the supports used. Due to the negative dielectric anisotropy, the application of an electric field causes the 90° rotation of the liquid crystal molecules with consequent achievement of an opaque ON state as the extraordinary refractive index of the liquid crystal is mismatched with that of the polymer. The decay times increase when the ITO layer thickness of the supports decreases because, in our opinion, a lower restoring force acts on the liquid crystal molecules in such samples. The lower switching field shown by samples with a lower roughness (figure 1) strengthens this hypothesis. A large haze does not affect such reverse mode shutters as they are characterized by the polymer ball morphology [3].

The use of rough surfaces in the manufacture of reverse mode PDLCS by the procedure outlined offers several advantages with respect to conventional reverse mode devices. In fact, they are characterized by easier and faster preparation (since neither surface treatments of supports [9–11] nor the use of external fields [7, 8] are required), a low switching electric field (~ 2 rather

than $4\text{--}5 \text{ V } \mu\text{m}^{-1}$), high contrast (larger than 20), fast response times (a few ms rather than tens of ms), strong adhesion to supports, and no chemical or physical instability of the samples studied [5].

4. Conclusions

In this work, we have successfully demonstrated that rough surfaces can be used to control the orientation of polymer dispersed liquid crystals. In particular, we obtained reverse mode operation shutters with high performance. It has been shown that larger OFF state transmittances can be achieved by means of rougher surfaces which are able to maintain a better homeotropic alignment of the liquid crystalline material after the polymerization-induced phase separation process. Such films can be turned into an opaque ON state by applying a suitable electric field.

MURST, the Italian Ministry for Universities, is acknowledged for financial support (project 'VARILUX' # 1262/153).

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