Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Morphology and electro-optical properties of reverse mode polymer dispersed liquid crystals

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) 'Morphology and electro-optical properties of reverse mode polymer dispersed liquid crystals', Liquid Crystals, 27: 10, 1337 — 1341
To link to this Article: DOI: 10.1080/026782900423395
URL: http://dx.doi.org/10.1080/026782900423395

LIQUID CRYSTALS, 2000, VOL. 27, NO. 10, 1337–1341

Morphology and electro-optical properties of reverse mode polymer dispersed liquid crystals

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

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

(*Received 13 March 2000; accepted 27 April 2000*)

We have investigated the morphology and electro-optical properties of reverse mode polymer dispersed liquid crystals as a function of liquid crystal loading. Reverse mode shutters have been obtained by a polymerization-induced phase separation of mixtures, consisting of a liquid crystalline monomer and a non-reactive nematic liquid crystal, placed between rough conductive surfaces. Such surfaces are able to keep the photopolymerizable mixtures homeotropically aligned without the use of any aligning polymer substrate. OFF state transmittances are always larger than 80% and the switching fields decrease if the non-reactive liquid crystal percentage is increased. Both rise and decay times are always lower than 10 ms. The electro-optical properties have been related to the sample morphology and a simple mode is proposed.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) are composite materials formed by liquid crystal and polymer. They can exhibit either a droplet morphology [1], in which droplets of liquid crystal are embedded in a polymer matrix, or a polymer ball morphology [2], in which the liquid crystal takes up the voids and the crevices of a network structure formed by small polymer balls. PDLCs can be distinguished also for their operation mode. A normal mode operation PDLC is characterized by an opaque OFF state, which can be turned into a transparent ON state by applying a suitable electric field. A reverse mode operation PDLC is transparent in its OFF state and can be turned into an opaque ON state. Great interest has been aroused in reverse mode shutters [3–10] for their use in a wide range of applications that need a transparent state in the absence of any applied voltage. Several procedures have been proposed for the manufacture of reverse mode devices including the modification of the surface energy of PDLC droplets [3], the use of dual-frequency addressable liquid crystals [5, 8], the polymerization of nematic emulsions [9], and the use of mesogenic networks with a larger liquid crystal loading [4, 6, 7]. More recently, we have proposed a reverse mode polymer dispersed liquid crystal shutter made by using the alignment properties of rough surfaces [10]. In fact, mixtures of a low molecular mass liquid crystal and a liquid crystalline monomer can be homeotropically aligned by the 'natural' grooves present on glass substrates covered by conductive indium tin oxide (ITO) films. Such spontaneous alignment avoids orientation control by means of any aligning polymer substrates. The initial homeotropic alignment can be stored by the polymer matrix obtained from the UV irradiation of cells. Such reverse mode PDLCs are characterized by a polymer ball morphology and, as a consequence, by a lower drop in the off-normal transmittance (haze). Our previous investigation [10] was focused on the effects induced in a single mixture by substrates with a different average roughness. In particular, it was found that rougher substrates were able to give devices with high optical contrast, good adhesion, long time stability, reduced haze at large angles, low switching electric fields, and easier preparation.

In this paper we present a detailed investigation of the morphology and electro-optical properties of reverse mode polymer dispersed liquid crystals characterized by a different weight ratio of the two liquid crystalline components in the mixtures, but obtained with the same orientation-controlling ITO substrates. It will be shown that switchable devices with good electro-optical properties can be obtained only for concentrations of the non-reactive liquid crystal larger than 75 wt %. We will find an excellent agreement between the experimental data and the theoretical forecasts.

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

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals

2. Experimental

The nematic liquid crystal used in this work is EN-40 (Lixon) characterized by a negative dielectric anisotropy ($\Delta\varepsilon = -2.7$). The liquid crystalline diacrylate monomer 1,4-phenylene bis[4-(6-acryloyloxyhexyloxy)benzoate], (C6H), was synthesized in the Chemistry Department of the University of Calabria according to the procedure outlined in [11]. Its molecular formula is given in figure 1.

Mixtures were prepared by weighing the appropriate amounts of the components and stirring them at 120°C. About 1.5 wt % of photoinitiator (Irgacure 651, Ciba-Geigy) was added. A small quantity of mixture was introduced by capillarity into home-made cells, whose thickness was about 40 μm. The cell walls had an ITO conductive substrate, which was 120 nm thick (Balzers). These substrates are characterized by an average roughness of ≈2.6 nm as determined by atomic force microscopy (Nanoscope III, Digital Instruments) and are able to induce a good homeotropic alignment of nematic mixtures [10]. Then, such samples, homeotropically aligned in their nematic state, were cured at 80°C using a 10 mW cm^{-2} UV source (HPK 125, Philips) for 15 min. The electro-optical properties of irradiated samples were measured using the optical line reported in previous work [12]. The intensity of incident light measured with no sample in place was taken as the full-scale intensity. The rise and decay times of samples, i.e. the time required to drop to 10% on applying a suitable driving voltage at 1 kHz frequency and to reach 90% of the maximum transmittance after field removal, respectively, were determined. Morphology analysis was performed on cross sections of PDLC films, cut after immersion in liquid nitrogen, left under vacuum for several hours in order to extract the liquid crystal, gold coated, and finally examined by a Leica LEO 420 scanning electron microscope (SEM).

3. Results and discussion

After performing the polymerization of the samples we obtained transparent PDLCs (transmittance ≈82% at zero field). The electro-optical behaviour of such cells was investigated by determining their optical transmittance as a function of applied electric field and their response times. Figure 2 reports the typical optical transmittances of samples with different liquid crystal contents. It is possible to detect an electro-optical response only in samples with a non-reactive liquid crystal loading larger than 60 wt %. A soft response is observed for samples whose liquid crystal content ranges from 60 to 75 wt %. On the contrary, PDLCs with a high contrast and a low switching electric field are obtained for EN-40 percentages larger than 78 wt %.

The electro-optical response of samples of the last kind is reported in figure 3, together with the applied driving electric field. It is possible to observe that the rise time is always less than 2 ms, while the decay time increases with EN-40 percentage (from 3 to 10 ms). Such times are faster than those shown by conventional reverse mode PDLCs (some tens of ms).

In addition, all our samples are characterized by a low decrease in the OFF state transmittance as a function of viewing angle. Figure 4 shows the dependence of transmittance on the tilt angle for different PDLCs in their OFF state [5]. It is evident that the haze is less than in conventional reverse mode shutters.

This electro-optical behaviour can be explained by assuming that the increase in EN-40 content leads to a larger quantity of liquid crystal separated from a polymer ball matrix (obtained from the UV photopolymerization of the diacrylate monomer). In fact, it is known that reverse morphology PDLCs are characterized by a lower haze value as the thin liquid crystal layers which surround the polymer balls do not give rise to a large phase shift of the light [1]. The morphology analysis agrees with these electro-optical previsions. Figure 5 shows SEM photographs of reverse mode PDLCs for different EN loadings.

No phase separation is present in samples with a liquid crystal content lower than 50 wt %. Samples

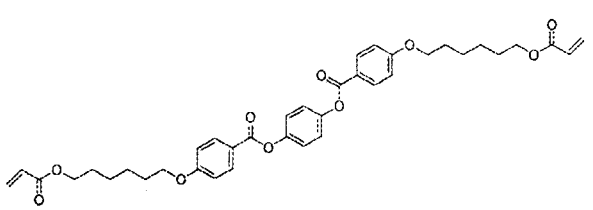

Figure 1. Molecular formula of 1,4-phenylene bis[4-(6-acryloyloxyhexyloxy)benzoate].

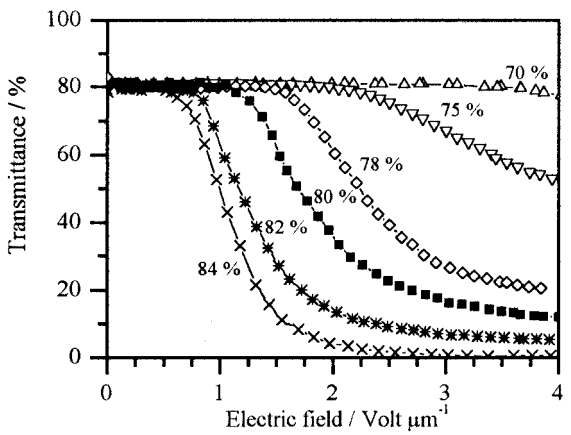

Figure 2. Transmittance dependence on the applied electric field of reverse mode PDLCs aligned by means of rough surfaces for different EN-40 contents.

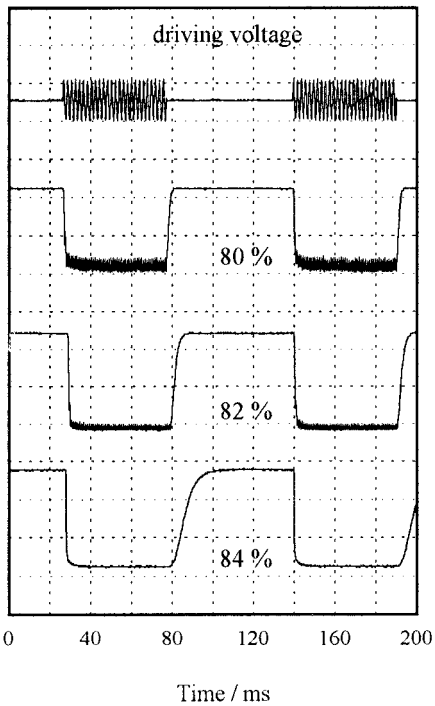

Figure 3. Electro-optical response for reverse mode PDLCs aligned by means of rough surfaces for different EN-40 contents. The driving voltage is a sine wave of 100 V_{rms} at a frequency of 1 kHz.

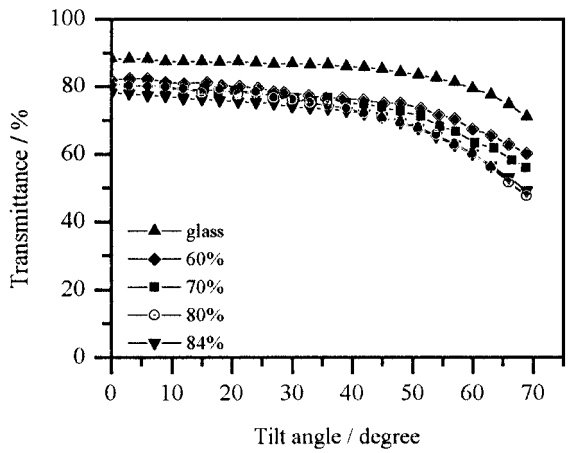

Figure 4. OFF state transmittance dependence on tilt angle for reverse mode PDLCs aligned by means of rough surfaces for different EN-40 contents. The transmittance through a glass substrate is reported for comparison.

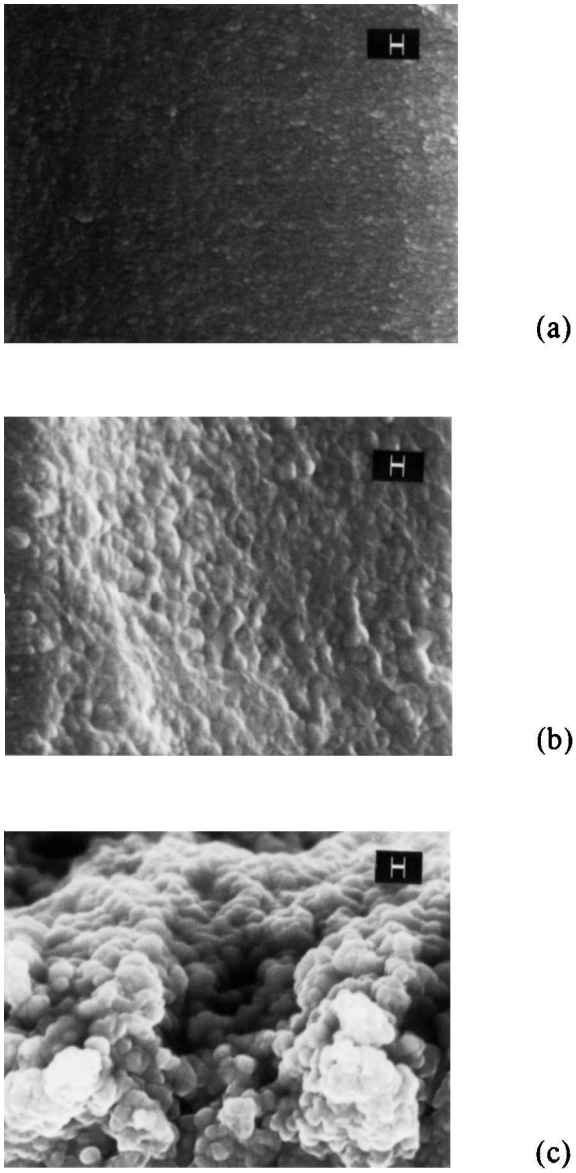

Figure 5. Scanning electron microscopy photographs of reverse mode PDLCs aligned by rough surfaces for different EN-40 contents: (*a*) 60 wt %, (*b*) 70 wt %, (*c*) 80 wt %. The bar is 400 nm.

are characterized by a reverse morphology for EN-40 loadings larger than 50 wt %. Very small polymer balls (average radius $\approx 0.2\,\mu m$) form an irregular network with the liquid crystal filling the voids and crevices. Such a structure does not give rise to a significant loss in the angular transmittance even at large tilt angles. A larger liquid crystal shell around the polymer balls can also account for the increase in decay times with EN-40 percentage. The liquid crystal in thicker shells is less anchored to the polymer ball surfaces and, consequently, a lower electric field is required for PDLC switching. After removal of the electric field, a lower restoring force will act and give rise to a slower realignment of the liquid crystal molecules. A similar behaviour has been previously reported for droplet PDLCs. Their rise and decay times, τ_{rise} and τ_{decay}, calculated by balancing

electric, elastic, and viscous torques, scale as [1]:

$$\tau_{rise} \approx \frac{\gamma}{\varepsilon_0 \Delta\varepsilon(\mathbf{E}_{appl}^2 - \mathbf{E}_{th}^2)} \quad (1)$$

$$\tau_{decay} \approx \frac{2\gamma}{\varepsilon_0 \Delta\varepsilon \mathbf{E}_{th}^2} \quad (2)$$

where $\mathbf{E}_{appl}$ and $\mathbf{E}_{th}$ are the applied and the threshold (i.e. the field required for reorienting a droplet) electric fields, respectively, and γ is a rotational viscosity coefficient. $\mathbf{E}_{th}$ is inversely proportional to droplet radius [13] and consequently larger droplets are characterized by a longer decay time. On the contrary, the rise times are strongly influenced by the applied electric field rather than the threshold electric field and consequently do not show a strong dependence on the radius.

As further confirmation we calculated the light scattered by a model system as a function of the applied electric field. A polymer ball surrounded by a shell of axially aligned liquid crystal [13] with a negative dielectric anisotropy is subjected to an increasing electric field, **E** (figure 6).

The polymer balls are characterized by a radius, r_0, while the shell parts extend between r_0 and $r = r_0/(1-\phi)^{1/3}$, where ϕ is the liquid crystal percentage separated from the polymer matrix. Adapting the model of Li *et al.* [14] for the optical transmittance of droplet PDLCs in a magnetic field, we assumed that the light transmittance T, obeys the following exponential behaviour:

$$T = \exp(-\beta\sigma d) \quad (3)$$

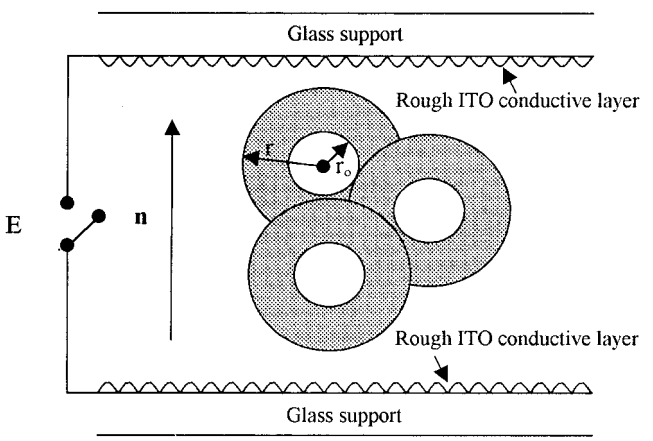

Figure 6. A simple model for a reverse mode PDLC. Each polymer ball of radius r_0 is surrounded by a shell of liquid crystal with negative dielectric anisotropy, whose thickness is $r - r_0$. Liquid crystal directors are assumed to be axially aligned along a direction perpendicular to the glass support. The transparent OFF state can be turned into an opaque OFF state by means of a suitable electric field as the dielectric anisotropy of the liquid crystal is negative.

where β is the polymer ball number density, σ is the scattering cross section, and d is the sample thickness. The scattering cross section can be expressed as a function of a reduced field, h:

$$h = (\mathbf{E}_{th} - \mathbf{E}) r (1 - x_0) \left(\frac{\Delta\varepsilon}{k}\right)^{1/2} \quad (4)$$

where k is the elastic constant of the liquid crystal in the one constant approximation, $x_0 = r_0/r$, and $\Delta\varepsilon$ is the liquid crystal dielectric anisotropy. In the anomalous diffraction approximation [15], which holds in the limit $2\pi r/\lambda \gg 1$ (λ is the wavelength of the impinging light), σ can be written as:

$$\sigma(h, r) = \pi r^2 (1 - x_0^2) \int_0^{\pi/2} \times \left\{ 1 - x_0^2 - \frac{2\sin[v(1-x_0^2)^{1/2}](1-x_0^2)^{1/2}}{v} + 2\frac{1 - \cos[v(1-x_0^2)^{1/2}]}{v^2} \right\} \sin\theta \, d\theta \quad (5)$$

with

$$v(h, r, \theta) = 2kr(1 - x_0^2)\frac{(n_e - n_o)}{n_p} \times \left[1 - \frac{h^2 + \cos 2\theta}{(h^4 + 2h^2 \cos 2\theta + 1)^{1/2}} \right] \quad (6)$$

where v is the phase shift term, n_e and n_o are, respectively, the extraordinary and ordinary refractive indices of the liquid crystal, n_p is the polymer ball refractive index, and θ is the angle between the applied external field and the liquid crystal director. A random final distribution of directors was assumed in the model. It should be noted that equation (5) reduces to the well known scattering cross section of Zumer for a droplet if $x_0 = 0$ [15]. Calculations were carried out using the known refractive index values ($n_e = 1.655$, $n_o = 1.518$, and $n_p = 1.530$) and assuming the liquid crystal solubility in the polymer matrix to be about 50 wt %. Results are shown in figure 7, where a Gaussian distribution of the polymer ball radius, with a mean value of 0.20 μm and a standard deviation of 0.05 μm, was assumed. The size distribution was used, as the fits with a monodisperse polymer ball sample exhibited sharp ON-OFF transitions. The behaviour of the fits is in excellent agreement with experimental results.

4. Conclusions

We have investigated the morphology and electro-optical properties of reverse mode polymer dispersed liquid crystal films aligned by means of rough conductive supports as a function of non-reactive liquid crystal

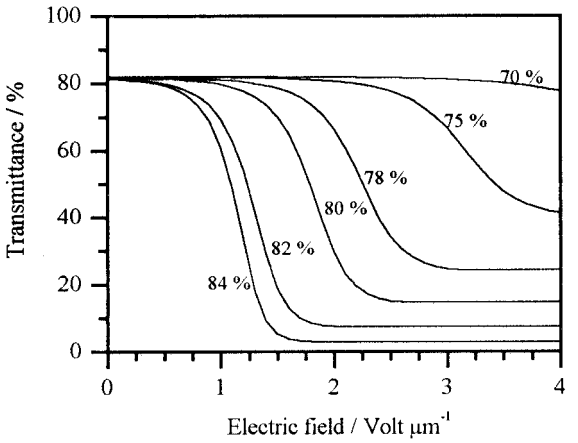

Figure 7. Fits of the electric field-dependent transmittances of reverse mode PDLCs aligned by rough surfaces for different EN-40 contents (cf. figure 2).

content. We found that the phase separation of liquid crystals from a reverse morphology polymer matrix starts at 50 wt % of non-reactive liquid crystal. Low switching fields and fast response times can be obtained for samples with a liquid crystal content ranging from 78 to 84 wt %. In this range the reverse mode optical shutters are also characterized by a high optical contrast, good adhesion both on glass and plastic supports, long term stability, and reduced haze even at large tilt angles. The use of rough surfaces for orientation control in reverse mode polymer dispersed liquid crystal films could make the production of large area displays and shutters easier and faster.

This work was supported by MURST, the Italian Ministry for University Research (project VARILUX, #1262/153).

References

[1] Drzaic, P. S., 1995, *Liquid Crystal Dispersions* (Singapore: World Scientific).
[2] Yamagishi, F. G., Miller, L. J., and van Ast, C. I., 1989, *Proc. SPIE*, **1080,** 24.
[3] Ma, Y. D., Wu, B. G., and Xu, G., 1990, *Proc. SPIE*, **1257,** 46.
[4] Hikmet, R. A. M., 1990, *J. appl. Phys.*, **68,** 1.
[5] Nolan, P., and Coates, D., 1991, *Mol. Cryst. liq. Cryst. Lett.*, **8,** 75.
[6] Hikmet, R. A. M., and Zwerver, B. H., 1992, *Liq. Cryst.*, **12,** 319.
[7] Yang, D. K., Chien, L. C., and Doane, J. W., 1992, *Appl. Phys. Lett.*, **60,** 3102.
[8] Gotoh, T., and Murai, H., 1992, *Appl. Phys. Lett.*, **60,** 392.
[9] Nicoletta, F. P., De Filpo, G., Lanzo, J., and Chidichimo, G., 1999, *Appl. Phys. Lett.*, **74,** 3945.
[10] Macchione, M., Cupelli, D., De Filpo, G., Nicoletta, F. P., and Chidichimo, G., *Liq. Cryst.* (in the press).
[11] Broer, D. J., Boven, J., Mol, G. N., and Challa, G., 1989, *Makromol. Chem.*, **190,** 2255.
[12] Chidichimo, G., Huang, Z., Caruso, C., De Filpo, G., and Nicoletta, F. P., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 379.
[13] Huang, Z., Chidichimo, G., Nicoletta, F. P., De Simone, B. C., and Caruso, C., 1996, *J. appl. Phys.*, **80,** 6155.
[14] Li, Z., Kelly, J. R., Palffy-Muhoray, P., and Rosenblatt, C., 1992, *Appl. Phys. Lett.*, **60,** 3132.
[15] Zumer, S., 1988, *Phys. Rev. A*, **37,** 4006.