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High Contrast Reverse Mode PDLC Films: A Morphologic and Electro-Optical Analysis

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Reverse Mode Polymer Dispersed Liquid Crystal films obtained by the photo polymerization of homeotropically aligned Liquid crystal solutions, have been investigated in order to optimise their optical contrast with the aim of their application as windows able to be switched from an high transparent state into a very opaque state by an appropriate electric field. An excellent optical contrast has been obtained by varying the amounts of two different liquid crystal diacrylate monomers in the starting solutions as precursors of the final polymer matrix. Morphology of the film has been investigated to account for the electric threshold field needed to operate the film. A simple model has been proposed to describe the threshold field and the behaviours of the dynamic response times as a function of the polymer composition. A novel type of morphology which opens the field for deeper investigation, has been found, where two different segregations of the liquid crystal into the polymer matrix coexist.

Keywords: electro-optical device; liquid crystal; PDLC reverse mode

INTRODUCTION

Composite systems consisting of polymers and low-molecular-weight liquid crystals have attracted increasing interest over the last years, providing a new field of liquid crystal science and technology. Liquid crystal-polymer composites include standard polymer-dispersed liquid crystals (PDLCs) [1–5] and polymer stabilized liquid crystals (PSLCs) [6]. High concentration of polymer (preferably more than 20 wt%) is used in PDLCs to confine the liquid crystal, while PSLCs are produced

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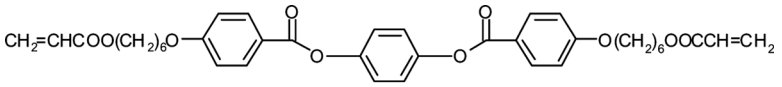
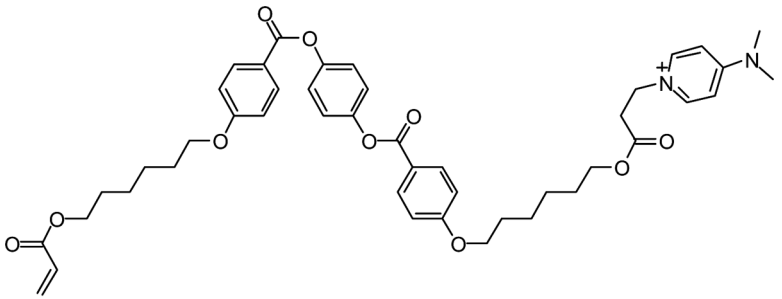
by smaller amounts (usually $< 10\,wt\%$) of polymers. In this work attention has been devoted to a particular type of reverse mode PDLC film developed by the photo-polymerization of mixtures of liquid crystal diacrylate monomers and a low molecular mass liquid crystal having negative dielectric anisotropy [7–9]. The advantage of this type of cell with respect to other reverse mode liquid crystal scattering devices, is linked to the easiness of manufacturing the cell. Up to now a key product used to produce the cell has been the UV curable liquid crystal monomer 1,4-phenylene bis[4-6(acryloyloxy)hexyloxy)-benzoate] (PAHB) [10] (product **I**):



(I)

The nematic temperature range of the product (**I**) is comprised between 116°C and 155°C.

Nevertheless we have recently discovered that synthesis impurities such as 1-[2-[6-(4-[4-[4-(6-Acryloyloxy-hexyloxy)-benzoyloxy]-phenoxycarbonyl]-phenoxy)-hexyloxycarbonyl]-ethyl]-4-dimethylamino-pyridinium (product **II**) [11]:



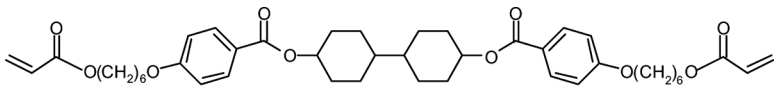
(II)

accompanying compound (**I**), are able to align, in an uniform homeotropic configuration a liquid crystal solution where (**I**) is contained even at relatively low concentration (about 5 wt%). The ZLI 4788-000 Merck nematic mixture is an appropriate complementary partner (a non polymerisable negative dielectric anisotropy liquid crystal) of (**I**), in the starting liquid crystal solution. Indeed, this product is the only available liquid crystal having a quite large negative dielectric anisotropy ($\Delta\varepsilon$ (1 kHz, 20°C) $= -5.7$) and a very wide nematic temperature range (from 30 to 83°C). Reverse mode PDLC electro optical cell were obtained from a nematic solution of (**I**) and/or similar

compounds (including impurities (**II**), or other aligning compounds) in the ZLI 4788-000, inserted between two ITO-coated glass slabs. The cell thickness was regulated by means of appropriate spacers. From our experience a minimum thickness of 25 microns is required in order to get an uniform contrast trough the surface of the cell. The temperature of the cell is kept at around 120°C, in order to ensure a perfect solubility of I into the ZLI. To avoid crystallization of (**I**) it is worth to fill the cell at a temperature where the mixture is into the isotropic phase and then to low the temperature until the nematic phase is reached. At this temperature the liquid crystal film orients with the director axis perpendicular to the cell surface. Afterwards the cell is cured by UV polymerization of I. While PAHB polymerizes building up a continuous polymer fractured lattice across the film, the ZLI liquid crystal remains entrapped in this polymer lattice keeping a homeotropic orientation. The working principle of the cell is based on the fact that an incoming beam of light going trough the equilibrium configuration of the film experiences the n_0 refractive index of the ZLI and the n_0 refractive index of the polymer, which should be the more possible similar. In this conditions the film will appear transparent. If an electric field, able to give a 90° tilt of the ZLI director, is applied to the cell, the light beam will experience, in this case, the extraordinary refractive index n_e of the fluid liquid crystal and the n_0 of the polymer. If a relevant difference between these indices occurs the film is shifted in an opaque state as a result of the strong light scattering introduced by the refractive index mismatching on the incoming light.

A preliminary investigation of the electro-optical and morphology properties of reverse-mode PDLC films obtained by processing a mixture of (**I**) with the ZLI 4788-000 liquid crystal, according to the above outlined procedure has been recently presented [12]. The electro-optical response has been correlated to the changes of the morphology induced by different UV curing powers. In this paper it was demonstrated that only by using high power UV irradiation it is possible to obtain high contrast cell. In this conditions, due the high speed of polymerization of (**I**) a great part of the ZLI remains dissolved in the polymer matrix, thus a better matching of the n_0 indices is obtained in the equilibrium configuration. Nevertheless, in these manufacturing conditions the electric conductivity of the cells may increase almost of an order of magnitude with respect to lower UV power irradiation conditions, due to molecular fragmentation introduced by UV photons. Thus high power UV irradiations must be, in principle, avoided in order to reduce the power consumption in an operational state. A correct strategy to increase the optical contrast of the cell is to optimize

the composition of the casting solutions in order to get an optimal index matching between the n_0 index of the ZLI and that of the polymer matrix (containing variable quantities of ZLI depending on the polymerization conditions) in the final cured film. We have explored the possibility to fulfill this objective by introducing a new synthesized liquid crystal monomer: the bis{4-[6-(acryloxy)hexyloxy]benzoate}-4,4′-bicyclohexyl (**AHBB**) (product **III**):



(**III**)

which, having two cyclohexyl rings in the molecular framework, is expected to have a much lower n_0 refractive index with respect to the monomer (**I).** The chemical synthesis of product (**III)** has been described elsewhere [13].

In this paper, a detailed investigation of the effect produced on the electro-optical performance and morphology of PDLC cells by changing the relative amounts of monomer (**I)** and monomer (**III)** in the starting mixtures is reported.

Scanning electron microscopy (SEM) was used to observe the polymer network in PDLC films. The correlation between film morphology and electro-optic properties was also discussed in the framework of a simple model.

EXPERIMENTAL

The nematic liquid crystal used in this work was ZLI 4788-000, a commercially available nematic liquid crystal having a negative dielectric anisotropy $\Delta\varepsilon = -5.7$, supplied by Merck.

The acrylate monomers PAHB an AHBB were synthesized by the Polymer Synthesis Group of University of Calabria. Monomer mixtures were prepared by mixing the monomers PAHB and AHBB in the weight ratios ranging from 9 to about 0.7 (see Table 1).

The reverse mode device was realized by adding the liquid crystal ZLI 4788-000 and about 2% of photoinitiator, Irgacure 651 to the monomer mixture. Resulting solution was stirred at 120°C. The composition of the reverse-mode PDLC films was 16% of monomer component and 84% of nematic liquid crystal (w/w). The isotropic solution was introduced by capillarity into home-made cells, whose thickness

TABLE 1 AHBB Percentages with Respect the Monomer Composition

Sample	AHBB (wt%)
1	0
2	40
3	50
4	60
5	70
6	90

was set about 25 μm, by means of glass spheres. The cell walls had an indium tin oxide (ITO) conductive substrate, which was 120 nm thick. The samples were cooled until they reached a homeotropically aligned nematic state, and they were cured for 10 minutes at 45°C using an UV lamp at uniform power of about 0.5 mW/cm^2.

The morphological analysis of the reverse-mode films was performed by a Leica Leo 420 scanning microscope (SEM). Polymerized films were cut after immersion in liquid nitrogen, and fixed on microscope stubs. Cross sections of the films were left under vacuum at 10^{-3} Torr for several hours in order to extract the liquid crystal; successively they were gold coated, and finally examined.

The electro-optical properties of the reverse-mode films were measured at room temperature. The experimental set up for the electro-optical measurements is made up of a He-Ne Laser (632.8 nm), as light source, with a power of 2 mW. The light beam goes through the chopper rotating disk, and enter in a diaphragm able to eliminate reflections. Successively, the ray is directed in a beam expander in order to correct the intrinsic laser divergence, obtaining a collimate beam, and goes through a second diaphragm, which reduces the dimension of laser beam incident on the film. Transmitted light is collected by a detector, converted in an electrical signal and sent to a lock-in-amplifier, and controlled by the reference chopper signal.

The output signal is sent to a computer and recorded. The applied voltage is controlled by a Digital Analogical Converter (DAC). The measurements were performed using an alternating signal at 1 kHz.

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. The intensity of the incident light measured with no sample in place was assumed as full-scale intensity.

RESULTS AND DISCUSSION

Figure 1 shows the dependence of transmittance an the electric field of PDLC films containing different amounts of the monomer AHBB. It is possible to observe a considerable increase of the OFF state transmittance (still 92%), due to the addition of the liquid crystal monomer AHBB. Nevertheless, the effect of AHBB monomer on the electro optical performance of the PDLC films is more complex with respect to what expected, as it is shown in Figure 2 where the OFF and ON states (related to an applied field of 6 volts/μm) transmittances as well as the optical contrast (ratio between the ON and OFF states transmissions) are reported. In fact, for AHBB percentages ranging from 40 to 70 the films are not only much more transparent in the OFF state, but also become gradually more transparent in the ON state, with a dramatic decreasing of the optical contrast. The opacity of the film, in the ON state, returns to be sufficiently high when the AHBB percentage reaches the value of 90. An opposite trend shows the threshold field required to reorient the local director of the ZLI liquid crystal with respect to its equilibrium configuration (from the homeotropic alignment to a parallel orientation with respect to the cell surface), see Figure 3. In the same figure the OFF states decay time as a function of AHBB percentage is reported. As the AHBB concentration increases, the threshold E_{th} of the Fréedericksz transition, here defined as the electric field required to reach 90% of the maximum

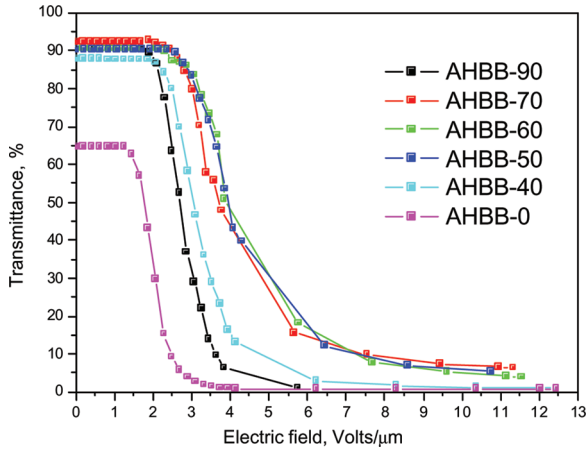


FIGURE 1 Transmittance dependence on the applied electric field of homeotropically aligned PDLCs for different AHBB contents.

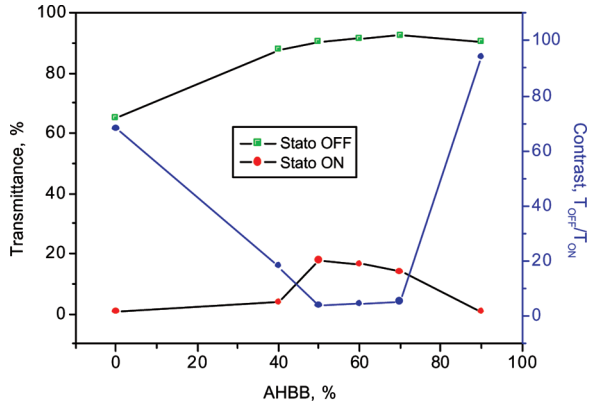


FIGURE 2 OFF and ON state transmittances and contrast ratio as a function of AHBB percentages.

transmittance, increases up to a maximum of about 3.3 volts/μm and than decreases, as shown in Figure 3.

A detailed study of the film morphology of the sample specimens 5 and 6 are shown in Figure 4 for different viewing directions and different magnifications. Top figures a and b, at low magnification, highlight a first interesting feature of the composite film. Both the samples appear to be made by fractured polymeric structures separated by channels. We will call "void channels" these regions which

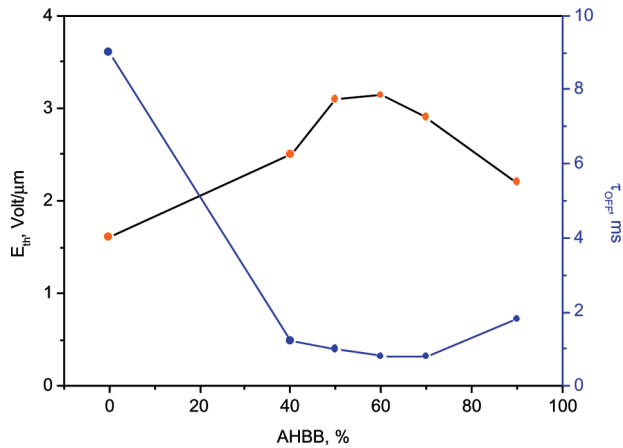


FIGURE 3 Threshold electric field, E_{th}, and decay time, τ_{OFF}, as a function of AHBB percentages. total monomer composition.

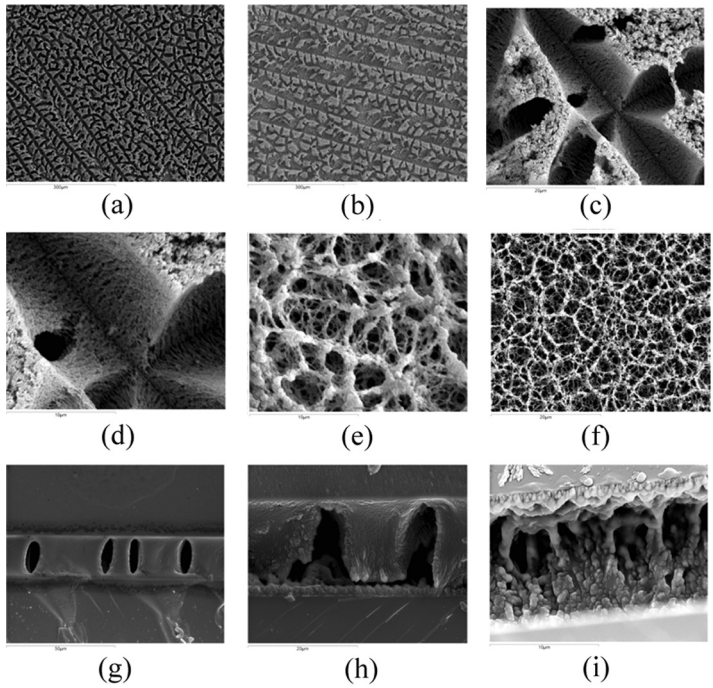


FIGURE 4 SEM images of samples 5 (a, c, e, g) and 6 (b, d, f, h) prepared from solutions containing 70% and 90% respectively of AHBB with respect to the total monomer component; (a, b) film surfaces with bar equal to 300 microns; (c, d) film surfaces with bar equal to 20 and 10 microns; (e, f) film surfaces with bar equal to 10 and 20 microns; (g, h) film cross section with bar equal to 50 and 20 microns; (i) cross section of the film obtained from only the monomer PAHB, the bar is equal 10 micron.

were full of ZLI liquid crystal before the film manipulation for SEM investigation. The shape of polymer dense structures, separated by the void channels, seems to be not periodic going from one dominium to another. This type of morphology never appeared before when a single monomer was inserted in the film formulation, at least for UV power irradiation similar to that used in the present work. Indeed voids have been observed in single monomer film only for irradiation power above 100 mw/cm^2 [14]. So we are leaded to think that the long range spatial heterogeneity of the film is strongly linked to the presence of two different monomers having a different reactivity with respect to the polymerization reaction. The structure of the void channels is better illustrated in Figures 4c and 4d. It is possible to see that the voids have an almost regular elliptic shape. This feature

of the samples appears very interesting for future investigation since work could be done to achieve a regular repetition of the large channels in order to obtain regular birefractive optical devices without recurring to complex laser techniques which hardly can be applied on large surface devices. At the moment this was far beyond the aim of the present work and it is important, for now, only to underline the presence of the channels to explain one of the effects observed in the optical response reported in Figures 1 and 2, i.e., the lost of scattering efficiency of the film in ON state in the range of film composition comprised between 40 and 90 of AHBB. It is evident from Figures 4a and 4b, even if peaces of the polymer dense structures remained glued to the upper glass support (removed for SEM manipulations), that the fraction of volume occupied by the void channels is much greater in sample 5 (70 PAHB wt%) than in sample 6 (90 PAHB wt%). The estimation of void volume fraction in the different sample drives to the conclusion that in sample 2–5 the large channels occupy a fraction of volume of about 50%, while in sample 6 such volume fraction reduces to less than 20%. In sample 1 no voids were observed. A simple explanation is found with respect to the reduced ON state light scattering of samples 2–5: large channels, having an elliptic shape where the minor transversal dimension is around 5 microns, do not efficiently scatter light. This effect becomes dramatic in samples 2–5, but is almost absent in sample 6, where the void volume fraction is reduced. Let us go now to comment the rest of the electro optical features shown by the analyzed samples. Again we got inspiration from the SEM photographs shown in Figure 4. And in particular from Figures 4c–f. From Figures 4c and 4d appear evident that the inner surfaces of voids are make by elongated polymer filaments developing perpendicularly to the film surface, while the central part of the polymer structures, observed by cutting the film with a blade razor in direction parallel to the surface, shows that the polymer network contains smaller voids (black spots in Figures 4e and 4f). These features suggest that a good model to apply to have a quantitative interpretation of the electro optical response (threshold voltage and decay time) can assume that the liquid crystal, remained more finely entrapped into the polymer structure, is dispersed as a multitude of elongated elliptic droplets according to Figure 5, where the nematic director, in the OFF state, is parallel to the major axis. Useful equations to model the threshold voltage and the decay time for elliptic droplets PDLC have been derived time ago in the case of normal mode PDLC films [2,15]. In our model, we consider a single elliptic droplet of dimensions a, the length of the semi-major axis, and b (the length of semi-minor axis) according the experimental observation. Indeed,

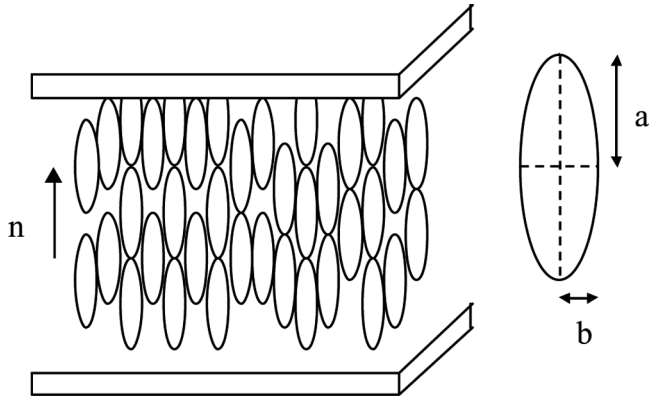


FIGURE 5 Modelization of the liquid crystal distribution into the polymer matrix.

by observing the SEM images of samples at different liquid crystal concentrations result evident that single droplet are separated between each other by the polymer layer. In this case the threshold voltage needed to reorient the nematic director along the semi-minor axis ($\Delta\varepsilon$ is negative in our case), and the time required to turn the director back on the equilibrium configuration, after removing the electric field, are given by the following Eqs. (1) and (2) respectively.

$$E_{th} = F(\rho_p, \rho_{CL}, r_p, r_{CL}) \cdot 1/a \cdot \left(\frac{K \cdot (l^2 - 1)}{\Delta\varepsilon}\right)^{\frac{1}{2}} \tag{1}$$

$$\tau_{OFF} = \frac{\gamma \cdot a^2}{K(l^2 - 1)} \tag{2}$$

The term $1/a \cdot (K \cdot (l^2 - 1)/\Delta\varepsilon)$ in Eq. (1) is the critical field required into the elliptic droplet to balance the torque moment exerted by the elastic force to tilt the nematic director. Here K is the elastic constant, a is the length of the ellipsis major axis and l is the ratio of the nematic ellipsoid: $l = a/b$, where b is the length of the minor axis. The function F represents a scalar factor between the external threshold field and the critical field acting in the droplet. This is due to a pure electric effect and depends on the polymer and liquid crystal resistivity (ρ_p and ρ_{CL}) as well as on the relative thickness r_p and r_{CL} (the ratio between the average thickness of each material with respect to the full film thickness) of the polymer and liquid crystal mixed in the film. In order to have an idea of the order of magnitude of the F function value, we can estimate it on the basis of a simple model, assuming that the

film, from an electric point of view, can be assimilated to a couple of resistors (one for each material mixed in the film). Having defined the meaning of ρ_p, ρ_{CL}, r_p, r_{CL} it is easy to show, on the basis of a simple circuit analysis that:

$$F = \left(\frac{\rho_p}{\rho_{CL}} \cdot r_p + r_{CL}\right) \tag{3}$$

When considering Eq. (2) we need only to remind that γ is the rotational viscosity of the liquid crystal. We can further simplify the above written equations by considering that, in the present case is evident from the SEM analysis of the films $l \gg 1$. Then, in first approximation, Eqs. (1) and (2) can be simplified in the following Eqs. (4) and (5):

$$E_{th} = F \cdot \left(\frac{K}{\Delta\varepsilon}\right)^{\frac{1}{2}} \cdot b^{-1} \tag{4}$$

$$\tau_{OFF} = \frac{\gamma}{K} b^2 \tag{5}$$

According to this simplified model the threshold field and decay time should depend only on the value of the elliptic minor semi axis. In order to check the proposed interpretation of the electro optical properties of the films, we derived the value of b using Eq. (5) and τ_{OFF} values reported in Figure 3 and Table 2, by assuming Merck values of γ and K equal respectively to 225 mP sec and 18.9 N. Having the b values, obtained in such a way we used them to calculate E_{th}, letting F to vary in order to reach the best fitting of the experimental data. The results obtained by this approach are shown in Table 2.

As it is possible to see from the results shown in Table 2 the differences between the calculated and experimental E_{th} values are, on average, of the order of 16% maximum. We consider this result a positive test of the applied model for at least two main reasons. First of all it must be considered that the experimental data are chosen in a very

TABLE 2 Experimental Theoretical Values of E_{th} and τ_{OFF}

Sample	τ_{OFF} (ms)	b	$E_{th\ (exp)}$ (ms)	$E_{th\ (calc)}$ (ms)	$\Delta E_{th(\%)}$
1	9.00	0.90	1.60	1.50	+6.70
2	1.20	0.33	2.50	2.54	−1.60
3	1.00	0.30	3.10	2.67	+16.10
4	0.75	0.26	3.14	2.87	+9.40
5	0.75	0.26	2.90	2.87	+1.00
6	1.7	0.39	2.20	2.34	−5.98

arbitrary way, assuming that the threshold field corresponds to the value of the field required to obtain a reduction of the 10% of the light transmission. As a second point it must be underlined that the model has been chosen on the basis of the morphology characterization of the films containing two different monomeric precursors of the polymer matrix which has been deeply discussed above. Sample 1 is, instead, obtained from a single monomer (PAHB) and the morphology in this case is quite different, as it is shown in Figure 4i. The morphology of sample 1 is more next to that of a PSLC systems, where isolated polymer filaments are able to contain the liquid crystal phase without interrupting the continuity of the phase. Then, for sample 1, here reported only for comparison, a different model should be applied: for example that reported by Kossyrev *et al.* [16]. In the bi-monomer films, part of the liquid crystal transfers into the large channel, and part remains finely dispersed into the polymer matrix cannot be considered as a PSLC. Another important point to underline is the value of the F function which has been used to calculate the threshold field of Table 2. The best fit is actually obtained when F is equal to 1. This value is the limit value of the function when the thickness ratio of the polymer r_p goes to zero, since contemporaneously r_{CL} goes to 1. This means that even the liquid crystal dominion finely dispersed into the polymer can be considered as an elliptic droplet joining the two opposite surface of the film (a = film thickness). This is an advantage for this kind of systems, since the applied field can reach the liquid crystal without any shield due to the polymer matrix. Nevertheless, the operational voltage is quite high, since the minor axis of the liquid crystal aggregate are quite small and the elastic force require a quite high balancing electric field.

CONCLUSIONS

We have shown that very high contrast Reverse Mode PDLC films can be obtained by matching appropriately the refractive indices of the polymer and the liquid crystal. We have also clarified the morphology of the films obtained by polymerizing two liquid crystal monomers in the presence of a non polymerizing liquid crystal. The morphology investigation has been found very useful to suggest the way to rationalize the factor influencing the operational electro optical parameters.

It has been further shown that the morphology is characterized by the presence of two type of liquid crystal segregations: one corresponding to large liquid crystal longitudinal channels and the other one vertical submicron channels, which are responsible of the electro optical contrast of the film. We believe that what reported on this paper opens

a new challenging research argument: how to optimize the size and geometrical features of the large channels. It could be interesting to obtain ordered oriented channels in order to get different optical properties and different modulation possibility for these regions. In order to reach this goal, work must be done to understand what are the physical parameters which control the morphology. Of course it is possible to hypothesize that among these parameters a critical role must be plaid by the polymerization speed of the monomers, the diffusion coefficient of the reactants and the relative concentration of the components. Investigations will follow on this subject in the next future.

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