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UV tuning of the electro-optical and morphology properties in polymer-dispersed liquid crystals

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Polymer-dispersed liquid crystal (PDLC) films operating in reverse mode are transparent electro-optical devices, which can be turned into an opaque state by application of a suitable electric field. The effect was investigated of different UV powers, used during the polymerization process, on the electro-optical and morphology properties of PDLCs, working in reverse mode operation. Films were obtained by UV polymerization of mixtures of a low molecular weight nematic liquid crystal and a photopolymerizable liquid crystal monomer, homeotropically aligned by rough conductive surfaces. The electro-optical and morphology properties of samples were related to the polymerization conditions. Samples polymerized by lower UV powers exhibited "polymer ball" morphology and an electro-optical response due to the liquid crystal director reorientation, whereas samples obtained at higher UV powers showed a "Swiss cheese" morphology and an electro-optical response due to dynamic scattering. In addition, we observed by conductivity and IR measurements that UV exposure induces a degradation of the nematic liquid crystal.

1. Introduction

In the development of electro-optical applications, the production of large-area displays has attracted considerable interest. Liquid crystals are unsuitable materials for this sort of application because of their fluid nature, the need of surface treatments and the use of polarizing layers, which largely reduce the light transmittance. In contrast, polymer-dispersed liquid crystals (PDLCs) are devices that are able to combine the optical properties of liquid crystals with the mechanical performance of solids [1, 2]. They can exhibit either a droplet morphology ("Swiss cheese") [3], in which the liquid crystal is separated as distinct droplets within the polymer matrix, or a reverse morphology ("polymer balls") [4], in which the liquid crystal fills the voids in a polymer ball network. Both PDLC types are generally characterized by an opaque OFF state, which can be turned to a transparent ON state by application of a suitable electric field (normal mode operation PDLC). A reverse-mode PDLC exhibits a transparent OFF state and an opaque ON state. Reverse-mode devices have been 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], by the formation of mesogenic network composites [9–14] and by the use of rough conductive substrates [15–17]. Following this last method, reverse-mode PDLCs have been prepared by photopolymerizing the liquid crystalline mixtures, containing a liquid crystal diacrylate monomer and a liquid crystal with negative dielectric anisotropy, homeotropically aligned by "natural" roughness of the conductive substrates used.

The use of rough substrates has allowed some drawbacks to be overcome that were present in previous methods, e.g. low optical contrasts, bad adhesion to supports, high driving electric fields, chemical instabilities, long decay times.

In this paper we report a preliminary investigation of the electro-optical and morphology properties of reverse-mode PDLC films obtained using rough substrates and cured with different UV light powers. The different electro-optical responses have been correlated to the changes in the morphology induced by the different UV powers and to a chemical decomposition of the liquid crystal, as confirmed by infrared and conductivity measurements.

2. Experimental

The liquid crystal monomer used in this study was 1,4-phenylenebis[4-(6-acryloyloxyhexyloxy)benzoate] (C6H),

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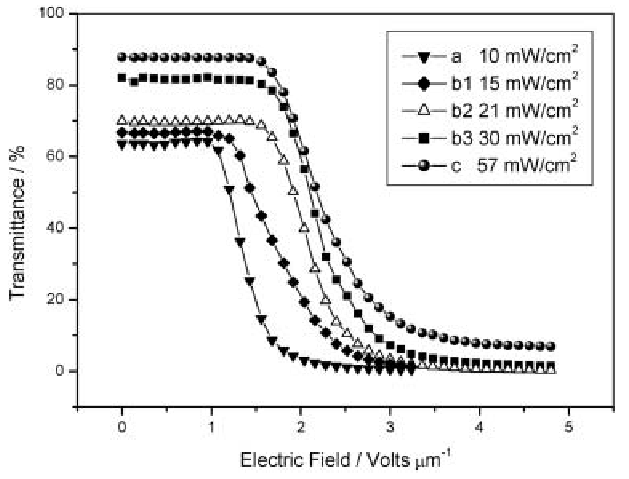

Figure 1. Electro-optical response of reverse-mode PDLC films cured with different UV powers.

synthesized according to the procedure outlined by Broer *et al.* [18]. The low molecular weight liquid crystal used was ZLI 4788-000, a commercially available nematic liquid crystal with a negative dielectric anisotropy, $\Delta\varepsilon = -5.7$, supplied by Merck. Mixtures were prepared by weighing, mixing and stirring the appropriate amounts of the components at 120°C. The composition of the reverse-mode PDLC films was 16% monomer and 84% nematic liquid crystal (w/w). About 2 wt% of photoinitiator (Irgacure 651, Ciba-Geigy) was added, in order to obtain the monomer matrix polymerization. A small quantity of mixture was introduced by capillarity into home-made cells of thickness about 25 μm. The cell walls had an indium–tin oxide (ITO) conductive substrate, which was 120 nm thick (Balzer). These substrates are able to induce a homeotropic alignment in the mixture. The samples, homeotropically aligned in their nematic state, were cured at 60°C using a UV lamp (Lot Oriel) at different powers (1–60 mW cm^{-2}).

IR spectra were recorded by a FT-IR BIO-RAD FTS 6000 spectrometer using a small quantity of liquid crystal between two KBr sheets. Conductivity measurements were performed with a LCR meter HP 4284A using a home-made cell filled with the liquid crystal. The morphology analysis was performed by a Leica Leo 420 scanning electron microscope (SEM). Cross-sections of films were cut after immersion in liquid nitrogen, left under vacuum for several hours in order to extract the liquid crystal, gold coated and finally examined. The electro-optical properties of the reverse-mode films were, instead, measured at room temperature using the experimental setup described elsewhere [19]. The intensity of the incident light measured with no sample in place was assumed as full-scale intensity.

3. Results and discussion

The electro-optical behaviour of reverse-mode cells cured with different UV powers (1–60 mW cm^{-2}, average supplied energy 2200 J cm^{-2}) was investigated by measuring their optical transmittance as a function of the applied electric field. Figure 1 shows some electric field-dependent transmittances for selected powers (10, 15, 21, 30 and 57 mW cm^{-2}). Whatever UV power we used, we obtained transparent samples, with a transmittance at zero field that shows a continuous decreasing behaviour for lower powers (see table 1). A possible explanation for such behaviour can be found in a different liquid crystal trapping in the polymer matrix due to the different curing conditions, which can change the value of the refractive index of the polymer matrix. In fact, it is expected that a fast polymerization process will induce a larger shrinking of the matrix and the trapping of a small amount of liquid crystal, with a consequent better matching between the refractive indices of liquid crystal and polymer matrix. When a 1 kHz electric field is applied, the transmittance of the samples decreases to values less than 5%.

SEM analysis performed on cross-sections shows that the different irradiation powers are able to influence the morphology, as evidenced in figure 2 where some typical pictures are presented. Sample **a**, obtained with a low irradiating power (10 mW cm^{-2}), is characterized by a reverse morphology, i.e. by an irregular network within which the liquid crystal is dispersed. More dense matrices are obtained with increasing UV powers (samples **b2** and **c**). Sample **c**, irradiated at 57 mW cm^{-2}, shows a droplet morphology characterized by large diameters (about the cell thickness).

If one applies an ac electric field to sample **a**, characterized by a reverse morphology, the optical transmittance decreases due to the 90° turning of the liquid

Table 1. Some electro-optical properties of reverse-mode PDLC films cured with different UV powers.

Sample	Power/mW cm^{-2}	Morphology	T_{OFF}/%	T_{ON}/%	E_{SW}/V μm^{-1}	τ_{ON}/ms	τ_{OFF}/ms
a	10	Reverse	65	<1	1.1	2	2
b1	15	Intermediate	66	<1	1.2	2	3
b2	21	Intermediate	70	<1	1.6	2	4
b3	30	Intermediate	82	$\cong 3$	1.6	2	4
c	57	Droplet	87	$\cong 5$	1.6	2	6

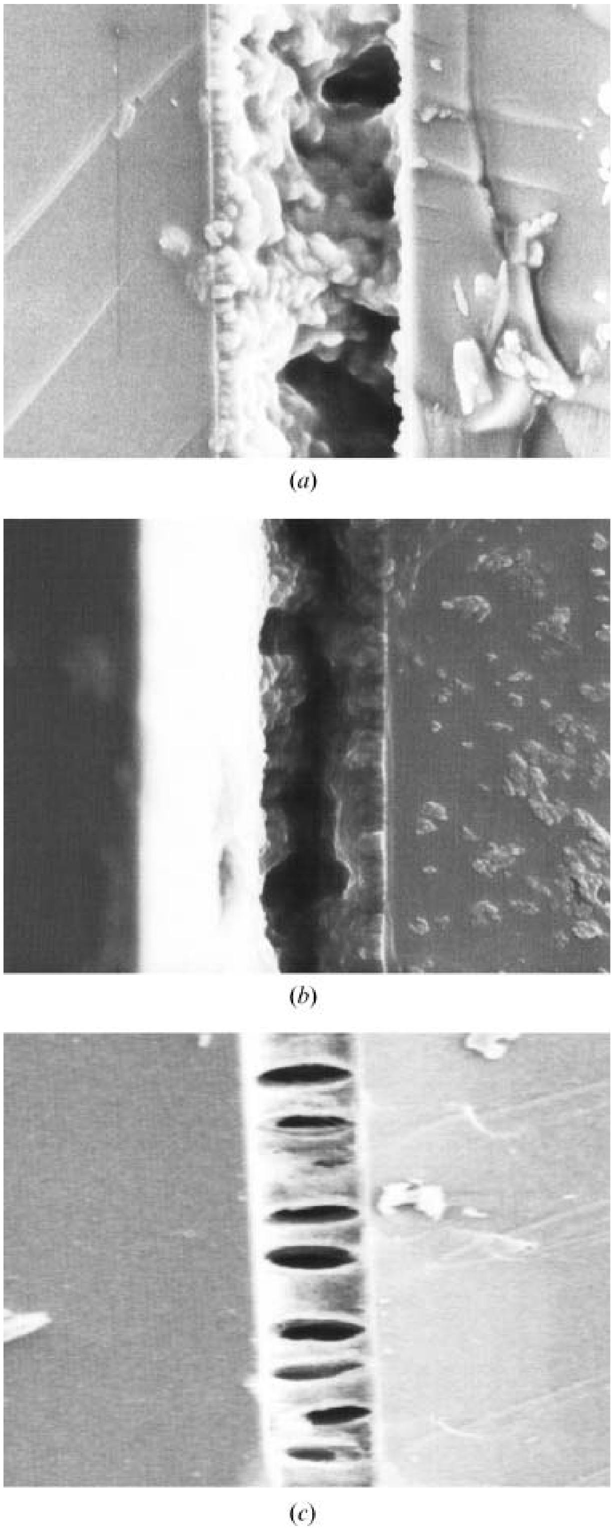

Figure 2. SEM pictures of reverse-mode PDLC films irradiated at different UV power: (a) $10\,\mathrm{mW\,cm^{-2}}$ for 220 s; (b) $21\,\mathrm{mW\,cm^{-2}}$ for 105 s; (c) $57\,\mathrm{mW\,cm^{-2}}$ for 40 s. The average supplied energy was $2200\,\mathrm{J\,cm^{-2}}$.

crystal directors. In contrast, observation of sample **c** in the optical microscope revealed that the application of the electric field induced dynamic scattering that disturbs the liquid crystal director reorientation and increases the switching electric fields (see table 1). By varying the power of the UV irradiation, it is possible to obtain intermediate morphologies, such as that shown by sample **b2**, which was cured at $21\,\mathrm{mW\,cm^{-2}}$. It is characterized by a transparent OFF state higher than that shown by sample **a** and a dynamic scattering lower than that shown by sample **c**. Sample morphology changes in a continuous manner from the pure reverse morphology shown by sample **a** to the pure droplets exhibited by sample **c** when irradiation power varies from 10 to $57\,\mathrm{mW\,cm^{-2}}$.

The rise and decay times of different samples do not show any significant difference: all rise times are about 2 ms, whereas the decay time, i.e. the time necessary for the homeotropic realignment of the liquid crystal directors, ranges from 2 ms (in sample **a**) to 6 ms (in sample **c**, see table 1).

In order to investigate the appearance of dynamic scattering in samples irradiated with powers larger than $10\,\mathrm{mW\,cm^{-2}}$, we performed IR and conductivity measurements as a function of UV irradiation time.

Figures 3 a shows the IR spectra of the nematic liquid crystal, before and after 1 h of UV exposition at $10\,\mathrm{mW\,cm^{-2}}$. It is possible to detect the decrease of the CN signal (figure 3 b) due to bond breaking in the liquid crystal molecules.

Figure 4 shows the changes in resistance, $\Delta R = R(\mathrm{t}_0) - R(\mathrm{t})$, as a function of time for different UV powers. It is evident that there is a decrease in the resistance values as a function of time, which can be attributed to liquid crystal degradation. The higher the UV power, the faster the degradation. The increase of ionic impurities determines the occurrence of dynamic scattering at low electric field and, probably, a change in the optical properties of liquid crystal. As a consequence, by controlling the irradiation power it is possible to tune continuously the morphology, the ionic impurity content and the kind of liquid crystal reorientation in PDLC films. Depending on the device applications, it should be possible to choose either low irradiation powers, which will give less transparent films but characterized by lower switching fields, or high irradiation powers, with cells characterized by higher transmittances and reorientation electric fields.

Conclusions

In this paper we have demonstrated that it is possible, by varying the polymerization conditions, to obtain films with different electro-optical and morphology properties. In particular, samples obtained with low powers show a

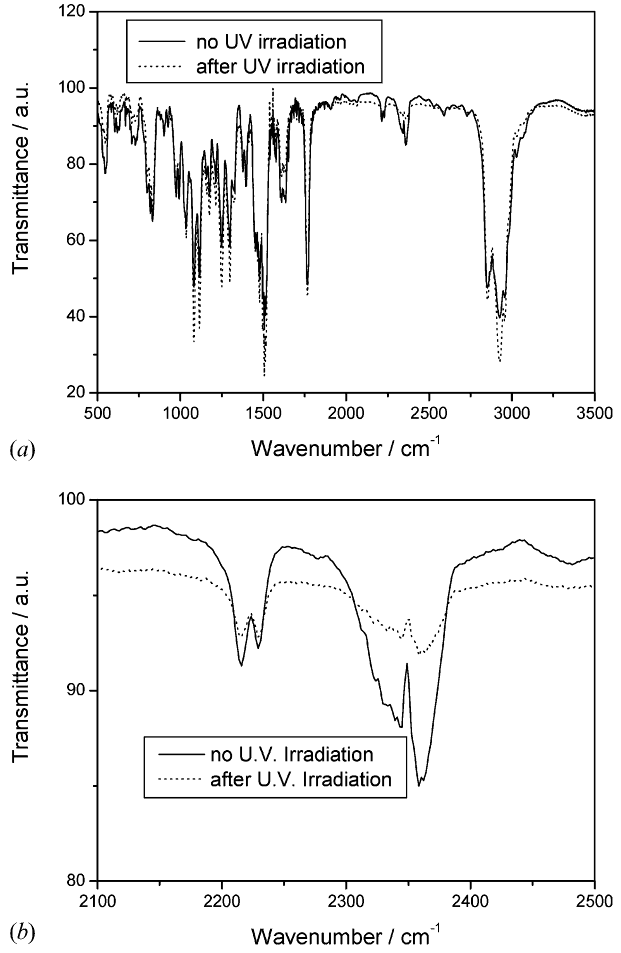

Figure 3. (a) IR spectra of nematic liquid crystal ZLI 4788-000 with no UV irradiation (full line) and after 1 h of UV exposure at 10 mW cm^{-2} (dotted line); (b) enlargement of the region where the CN signal appears (2358 cm^{-1}).

reverse morphology and an electro-optical response due to the liquid crystal director reorientation, whereas at higher powers samples exhibit droplet morphology and dynamic scattering. Intermediate properties are present in samples cured with intermediate UV powers (between 10 and 57 mW cm^{-2}). As a consequence, the electro-optical response of PDLCs can finely optimized by controlling the UV powers used during the polymerization process. Work is in progress to better define the border lines among droplet, reverse and mixed morphologies.

Acknowledgments

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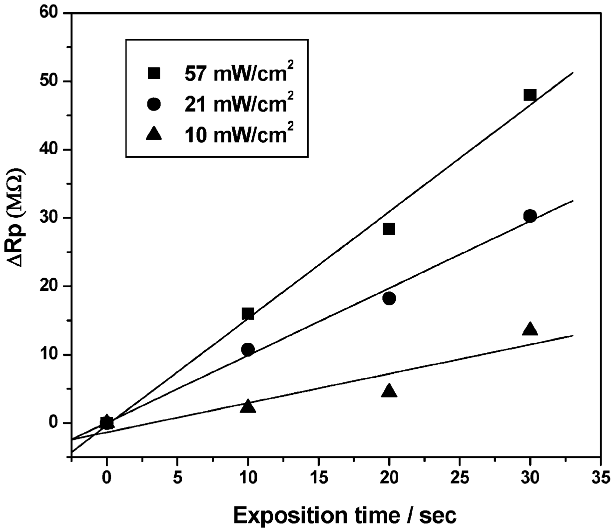

Figure 4. Changes in the resistance of liquid crystal ZLI 4788-000 as a function of exposure time at different UV powers.

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