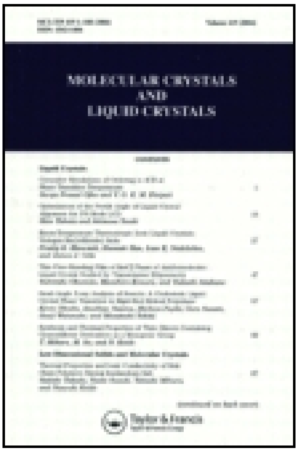

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Electro-Optical Memory Effects of Polymerized Methacrylate/Liquid Crystal Systems

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Electro-Optical Memory Effects of Polymerized Methacrylate/Liquid Crystal Systems

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The effect of the chemical structure of the initial species on the electro-optical properties of polymer/liquid crystal (LC) films was investigated. The latter were prepared by polymerizing/crosslinking reactions of low molecular weight LC/monomer blends involving irradiation processes. Several selected methacrylates as monomers and a pure nematic LC (4-cyano-4'-pentylbiphenyl = "5CB") were mixed together where the LC to monomer ratio was taken as 7:3 and 6:4.

The electro-optical properties of the obtained phase separated polymer/LC blends were measured as function of the choice of the monomer, sample composition and applied sinusoïdal voltage of the electrical field. The transmission versus voltage curves show a strong optical memory effect for some polymer/LC systems involving especially hydroxyl and methylacrylate groups. A particular attention was paid to correlate the obtained results with sample composition and chemical nature of the monomer.

Keywords Contrast ratio; electro-optical properties; morphology; optical memory effect; polymer/liquid crystal films

1. Introduction

Polymer Dispersed Liquid Crystal (PDLC) materials are still promising materials for the preparation of electro-optical devices such as displays and electrically controllable light shutters [1–4]. The list of polymer/LC combinations reported in literature and patents is very long. It is well established by prior works [5–7], as well as by our recent publications [8–11], that electro-optical properties of polymer/LC composites depend both on LC and polymer phases. They can be influenced dramatically by size, shape and distribution of the LC domains, which are controlled by several factors, e.g., concentration of the curing material, viscosity of the polymer, the make-up of the starting solution, as well as the anchoring characteristics of the LC at the polymer surface, determining thus the suitability for application of the polymer/LC system. In addition, the structural aspects of the polymer

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film morphology, the polymer–LC compatibility, and the phase separation processes are very important parameters.

Commonly used polymer/LC composite preparation methods are (1) polymerization-induced phase separation (PIPS), (2) thermally induced phase separation (TIPS), and (3) solvent-induced phase separation (SIPS). The PIPS method is often used to prepare polymer/LC composite films since it generally forms LC domains with reproducible size distribution and density, if the starting mixture of monomer and LC is optically homogeneous. In particular, UV light-induced polymerization is presently the most common technique to induce PIPS.

In our previous reports [8–11], an effort was made to correlate the chemical structure of acrylic monomers used in the fabrication of polymer/LC films, with the electro-optical properties of these devices. Especially in [11] it was shown that the presence of hydroxyl groups seems to be a necessary condition to obtain an optical memory effect whereas only a small dependence of the variation of the alkyl chain length on the preserved transmittance states was found.

In this paper, experimental results will be presented dealing with electro-optical and morphological properties of polymer/LC samples prepared in our laboratories, consisting of nematic LC domains in acrylate or methacrylate resin binder [12,13]. The sample morphology of the elaborated polymer/LC films will be analyzed by scanning electron microscopy (SEM). In particular, the contrast ratio will be taken into account as an important parameter to measure the performance of the electro-optical devices. This parameter, which will be considered for various polymer/LC systems, can be defined by writing:

$$\mathrm{CR} = \mathrm{T_S}/\mathrm{T_0} \qquad (1)$$

where $\mathrm{T_S}$ represents the maximum transmission obtained, and $\mathrm{T_0}$ is the initial off-state transmittance in the field off state.

2. Experimental Part

2.1 Materials

All monofunctional acrylic and methacrylic monomers (2-hydroxyethyl acrylate “HEA”, 2-hydroxyethyl methacrylate “HEMA”, hydroxypropyl methacrylate “HPMA” and hydroxybutyl methacrylate “HBMA”) were purchased from Sigma-Aldrich and used without further purification. To initiate the reaction of free radical photopolymerization, 2-hydroxy-2-methyl-1-phenyl-propane-1 (commercial designation Darocur 1173, from Ciba-Geigy) was employed. The nematic LC used in this work was 4-cyano-4’-pentylbiphenyl (5CB), which was obtained from Synthon Chemicals GmbH (Wolfen, Germany). 5CB exhibits a crystalline to nematic transition temperature at $T_{\mathrm{CrN}} = 23^{\circ}\mathrm{C}$, and a nematic to isotropic transition temperature at $T_{\mathrm{NI}} = 35.5^{\circ}\mathrm{C}$. The chemical structures of the different monomers are given in Fig. 1.

2.2 Polymer/LC Sample Preparation by PIPS

The well-known technique of phase separation induced by polymerization reactions is particularly useful when prepolymer materials are miscible with low molecular weight LC compounds. In photopolymerized polymer/LC systems, the initial mixture consists generally of a LC mixed with a UV curable monomer together with a suitable photoinitiator.

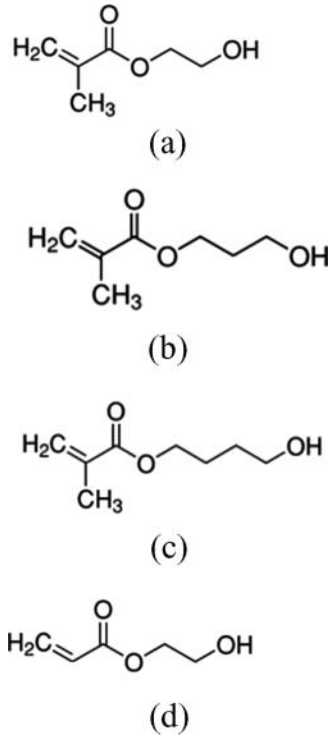


Figure 1. Chemical structures of the hydroxyalkyl acrylate and methacrylate monomers used in the preparation of polymer/LC systems: (a) 2-hydroxyethyl methacrylate (HEMA), (b) 2-hydroxypropyl methacrylate (HPMA), (c) 2-hydroxybutyl methacrylate (HBMA), and (d) 2-hydroxyethyl acrylate (HEA).

In this work, the PIPS technique was applied to blends where the LC to monomer ratio was taken as 7/3 and 6/4. A small amount of Darocur 1173 as photoinitiator (2 wt.% compared to the monomer) was added to the initial blends. The homogeneous initial mixtures were sandwiched between Indium-Tin-Oxide (ITO) coated glass substrates so that the monomer/LC blends were in contact with both transparent conducting ITO layers.

The UV exposure was performed in the absence of an applied field, using Philips TL08 UV lamps characterized by $\lambda = 365$ nm and an intensity of $I_0 = 1.5$ mW/cm^2. The obtained sample thicknesses were found between 2 and 18 μm. The film thickness was measured by a micrometer calliper (Mitutoyo; uncertainty: $+/-1$ μm).

The UV irradiation processes provoke the formation of polymers, at the same time as the phase separation occurs. The solubility of the LC decreases in the growing polymer until the LC phase separates, forming generally LC domains inside the polymer matrix. The size of these domains is controlled by the rate of polymerization, the relative concentration of materials, the type of LC and monomer used, and by such physical parameters as viscosity, rate of diffusion, and solubility of the LC in the polymer.

2.3 Electro-Optical Measurements and Memory Effect

Electro-optical experiments were performed at room temperature by measuring the transmission of an unpolarized He-Ne laser light at $\lambda = 632.8$ nm orienting the films normal to the incident laser beam. A silicon photodiode used as a detector was set at the location of diffraction maxima to measure intensity, and the distance between the sample cell and the detector was approximately 30 cm. The collection angle of the transmitted intensity was about ±2°. The uncorrected intensity of transmitted light was recorded on a microcomputer using an interface card (DAS 1600–2). For electro-optical measurements, an external electric field was applied across the polymer/LC composite film. The output of a frequency generator was amplified and used to drive the shutter device. Starting from the electrical off-state, the applied sinusoïdal voltage of frequency 145 Hz was increased continuously up to a desired maximum value V_{max}. It was subsequently decreased in the same way. The whole scan up and down ramp took 120s with an additional measuring time of 60s allowing to follow the relaxation behavior of the transmittance in the off state. The maxima of the voltage of the scan up/down cycles, V_{max}, were chosen in the following consecutive order: 10 V, 20 V, 30 V, 40 V... ... .150 V (see scheme included in Fig. 3).

2.4 Scanning Electron Microscopy

Samples for scanning electron microscope (SEM) studies were elaborated in the same way as described above for electro-optical measurements. The films prepared for SEM analysis exhibited thicknesses around 25 μm. After irradiation exposure was finished, the sample cells were opened and immersed in isopropanol as organic solvent in order to extract the LC. The samples were then coated by a thin platinum layer and characterized by a SEM (Hitachi S-4700 field emission gun). This sample preparation technique leads to the appearance of dark holes that were once filled with LC. The magnification used in our experiments was about 2000x, using an acceleration voltage of 5 kV.

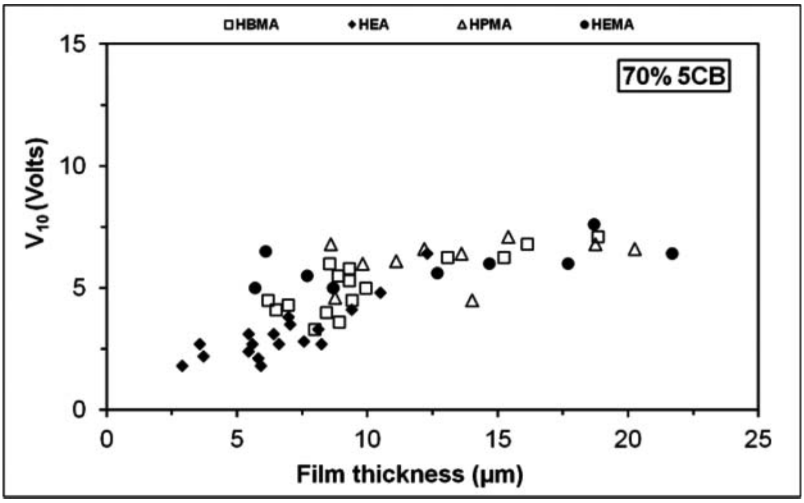
3. Results and Discussion

3.1 Electro-Optical Investigation

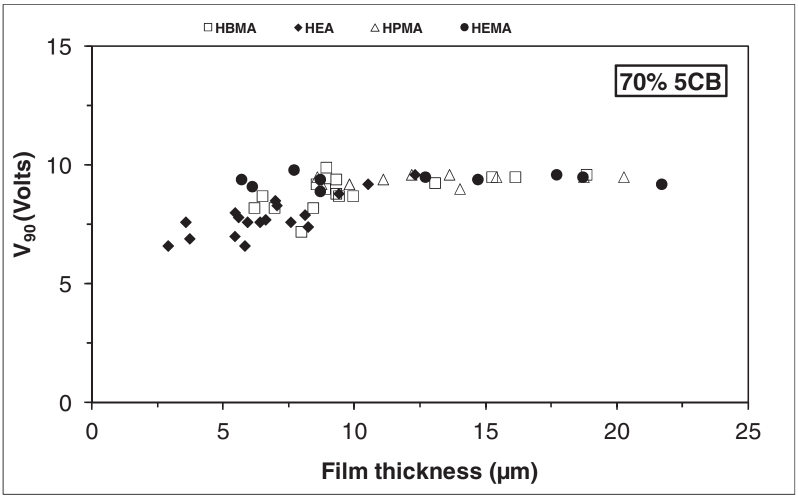
Figures 2 (a) and (b) present experimentally determined values of the threshold voltage (V_{10}) and the saturation voltage (V_{90}) at 10% and 90% of the film transmittance, respectively, of UV-irradiated polymer/LC films, as function of film thickness. These data were obtained from initial mixtures containing 30 wt.% hydroxy alkylmethacrylates and hydroxy alkylacrylates as monomers, and 70 wt.% of 5CB. The threshold voltages were found to be low indicating that the analyzed films need only a small voltage to switch from an opaque scattering OFF-state to a transparent ON-state. V_{10} and V_{90} values were taken from the very first application of an electrical field (10V), starting from the initial OFF-state, since the presence of the memory effect will not allow to compare the electro-optical response of all analyzed polymer/LC systems for higher voltage applications. V_{10} and V_{90} were found to be relatively close together which could be very important for potential applications such as electro-optical display devices.

Generally, values for V_{10} were found to be around 2–6 Volts, and V_{90} values were situated around 10 Volts. For both V_{10} and V_{90}, the obtained results obviously do not exhibit a dependence on film thickness beyond a thickness of 12 μm.

Only the acrylic HEA monomer shows lower levels of V_{10} and V_{90} in comparison with the methacrylic monomers. The latter present roughly the same threshold and saturation voltages, indicating the existence of a certain relationship on the presence/absence of methacrylic groups.



(a)



(b)

Figure 2. (a) Threshold voltage (V_{10}) and (b) saturation voltage (V_{90}) versus film thickness of UV-exposed polymer/LC films for an initial composition of 70 wt.% 5CB and 30 wt.% acrylate monomers.

Transmittance values of initial and final T_{OFF} states were presented in Fig. 3 as a function of film thickness for samples containing 70 wt.% 5CB. It was found that the initial transmittance values T_{OFF} were rather low; the values were situated between 0 and 10%. Interestingly all systems investigated exhibit approximately the same initial transmittance (T_{OFF}) values. Figure 3 shows also transmittance values in the final off-state, displayed using the same scales, which were measured after the end of the complete voltage application cycle with a maximum of 150 V as shown in the insert of Fig. 3. The systems including

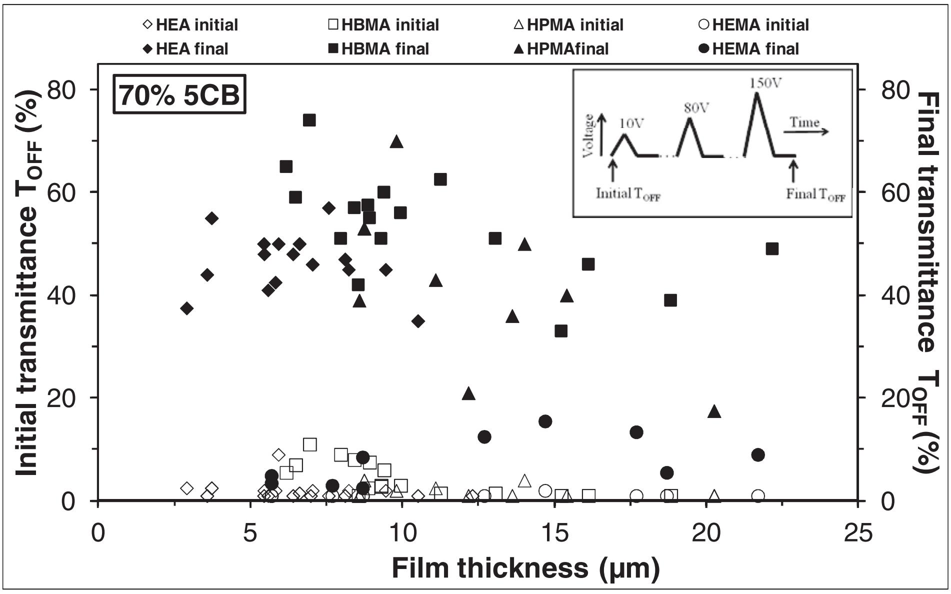


Figure 3. Initial and final transmittances of polymer/LC systems with 70 wt.% of 5CB, as function of the film thickness. The insert shows the voltage application as a function of time.

HPMA and HBMA reached the highest final T_{OFF} values (70%), compared to the other systems.

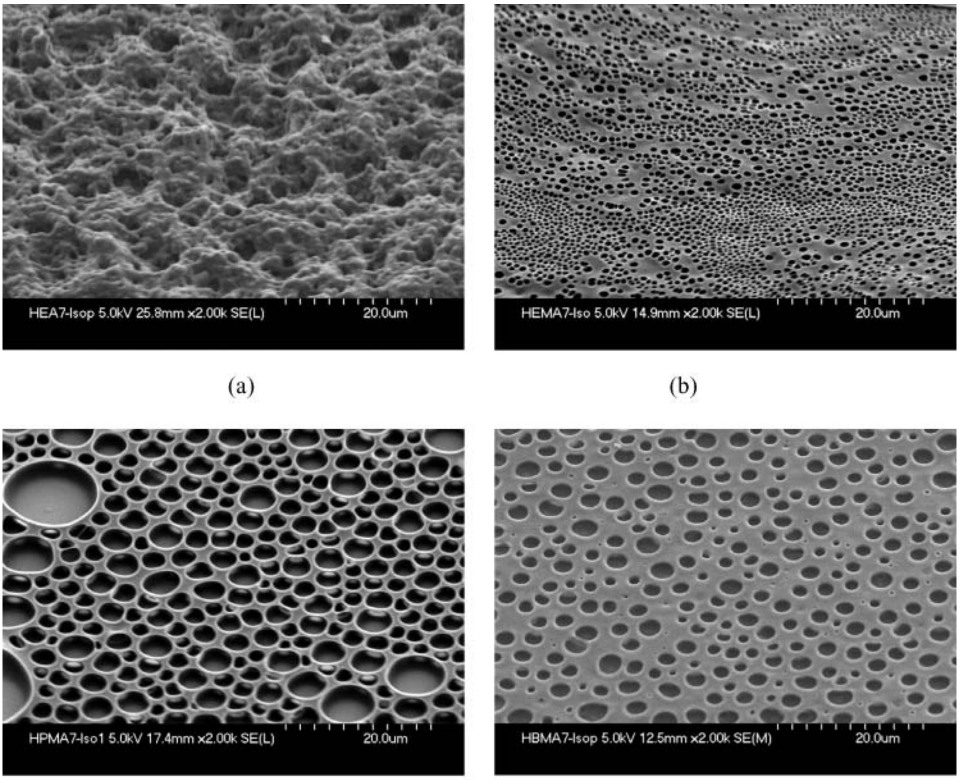
Generally it was found that switching from an opaque to a transparent state occurred during a relatively small voltage range i.e. threshold and saturation voltages were close together. An increase of the film thickness results in a decrease of the transmission values in the OFF- and ON-states. Furthermore, thicker films require higher voltage for their electro-optical activation but the general shape of the transmittance versus voltage curves remains the same independent of the sample thickness.

3.2 Morphology of Polymer/LC Composite Materials

The morphologies of the elaborated polymer/LC samples were investigated by Scanning Electron Microscopy (SEM). Representative examples of the obtained structures are shown in Fig. 4. Using an acceleration voltage of 5keV, the analysis was performed both on the sample surface and on the cross section.

These investigations were carried out on polymer/LC samples which were prepared under the same conditions as those used for the electro-optical experiments. The dark domains shown in Fig. 4 correspond to the empty cavities after removal of the LC and the brighter surroundings represent the polymer matrix. The LC domains seem not to be interconnected and regular shapes of nearly spherical domains were observed especially for methacrylic polymers. Moreover, it can be assumed that these LC domains are uniformly dispersed within the polymer matrix and do not exhibit a preferential orientation of their major axis length.

Photographs corresponding to the morphologies of the methacrylic polymers show similar results; i.e. a rather homogeneous dispersion of nearly spherical domains exhibiting sizes between 0.1 μm and 12 μm. Such types of morphologies have already been observed



(a) (b)

(c) (d)

Figure 4. Microphotographs obtained from SEM observations of UV-treated polymer/LC samples containing 70 wt.% 5CB and 30 wt.% acrylate monomers: (a) HEA, (b) HEMA, (c) HPMA, and (d) HBMA.

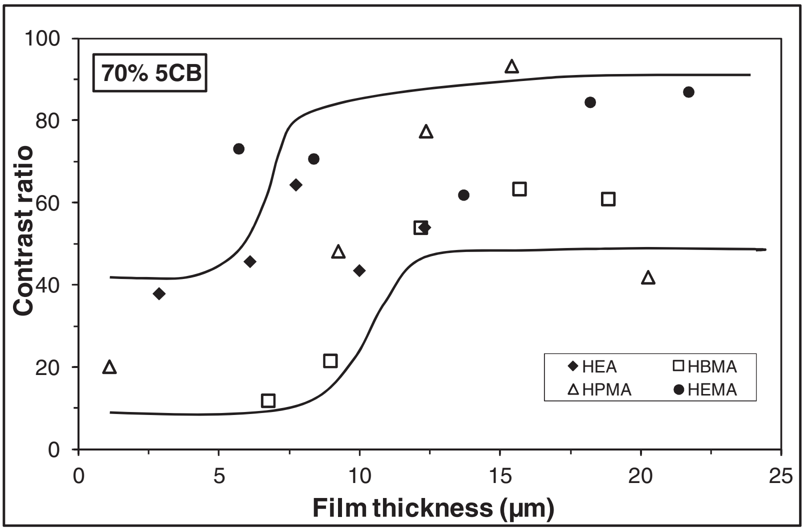
in the case of binary systems composed of a linear polymer and a low molecular weight LC [8,14].

Figure 4a, corresponding to the HEA based system, shows a completely different morphology than Figs 4b-d, exhibiting a relief-like structure with undefined domain shapes with a certain dispersion of domain sizes. SEM observations made on UV-cured difunctional acrylate systems revealed similar results due to the presence of a strong chemically cured polymer network. It can be noticed that the domain sizes are rather small in the case of the HEMA film (Fig. 4b), and become large in the case of HPMA (Fig. 4c) and HBMA (Fig. 4d).

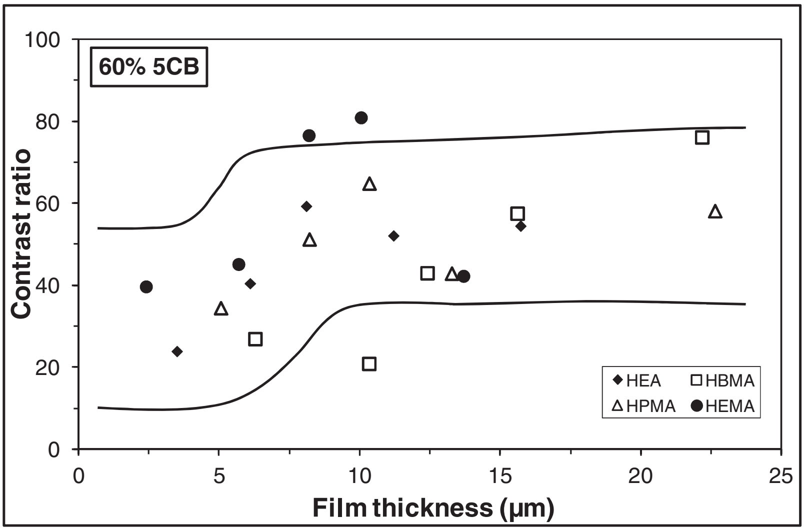
3.3 Contrast Ratio

The contrast ratio (T_S/T_0) was measured to investigate the effect of the monomer structure on the electro-optical properties. Figure 5 (a and b) shows the dependence of this parameter on the film thickness of polymer/LC systems with 60 wt.% and 70 wt.% of 5CB, respectively.

The four polymer/LC systems show low contrast values (between 25 and 40) for thicknesses ranging from 2 to 6 μm, and beyond this latter value one notices an increase of the value of the contrast ratio that can reach up to 95% in some cases.



(a)



(b)

Figure 5. Contrast ratios as function of film thickness for polymer/LC systems with a) 70 wt.% of 5CB and b) 60 wt.% of 5CB. In each case, the continuous lines represent a zone including the majority of the results.

Figure 5 (a) illustrates the contrast ratio as a function of thickness for polymer/LC films with 60 wt.% 5CB. The values of all systems are similar, they are situated in the range from 25 to 75%, except some results of the HEMA system which come out of the zone between the two lines, that has been drawn as an indication for the eyes.

In the case of samples including 70 wt.% 5CB (Fig. 5b), the contrast ratios were somewhat higher than those obtained with 60 wt.% 5CB. The polymer/LC system based on HBMA shows the lowest values of the contrast ratio, and even for high thicknesses, the corresponding value does not exceed 61%. The acrylic monomer HEA exhibits also rather low values, between 37 and 65%, while the two methacrylic monomers HEMA and HPMA show the highest contrast ratios.

The phase separation processes and the obtained morphologies vary by changing the LC content in the initial mixture, which leads to changes of the density and size of segregated domains. As a result, quantities such as the transmittance in the OFF- and initial ON state also vary and can produce the changes observed for the contrast ratios, comparing the results from samples with 60 wt.% and 70 wt.% 5CB.

4. Conclusions

In this study efforts were made to correlate the chemical structure of some selected monomers, used in the fabrication of polymer/LC composites, with the electro-optical and morphological properties of the corresponding films. The study shows that the absence of the methacryl group (HEA) strongly influences the morphology of the films: both size and shape of the segregated domains were different compared to the methacrylic systems. The systems which presented the additional methyl group in their acrylic group showed all the same morphology with approximately similar sizes of the domains, especially composites made of HEMA and HPMA.

The contrast ratio of polymer/LC composites in the case of 70 wt.% of LC is higher than that with only 60 wt.% of LC. The values of the contrast ratio present only a little dependence on the structure of the monomer used in the fabrication of the polymer/LC systems. A slight dependence on the alkyl chain length and the thickness of the films was noticed as well.

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