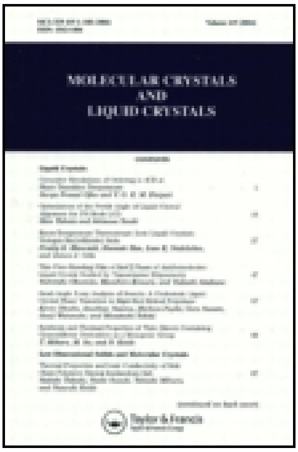

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Effects of Monomer Structure on Morphology and Electro-Optical Properties of Polymer/Liquid Crystal Systems

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Effects of Monomer Structure on Morphology and Electro-Optical Properties of Polymer/Liquid Crystal Systems

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The relationship between chemical structures of monomers, especially their alkyl chain length, with morphology and electro-optical properties of the corresponding polymer/liquid crystal (LC) films were investigated. A dependence of electro-optical properties on the type of monomer used to prepare the films is demonstrated and explained. We report on the memory effect of polymer/LC films, which are prepared using four biocompatible acrylic and methacrylic monomers. These results were correlated with observations of the sample morphologies by polarizing optical microscopy. Samples based on acrylic and methacrylic monomers and 5CB were studied after polymerization, with and without application of an electric field.

Keywords Electro-optical properties; liquid crystals; morphology; optical memory effect; phase separation; polymers

1. Introduction

In recent years a high level of activity has characterized the field of research on polymer dispersed liquid crystals (PDLCs) which are potentially useful for a variety of electro-optical applications including switchable windows, displays and other devices [1–7].

These applications include large-scale flexible displays that do not require polarizers and are simple and cost effective to fabricate. Switchable coatings for windows to be used for controlling daylight or interior lighting, privacy, cosmetics, solar heat gains, security, etc. provide a totally new application of LC materials.

The main electro-optical effect observed in nematic-containing PDLC is called electrically-induced light transmission [5] and consists in a transition from scattering to transparent state or *vice versa* induced by electric field due to a change of intrinsic

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LC molecular arrangement. An applied electric field aligns the nematic droplets to yield a non-scattering or transparent state without polarizers and alignment layers [8,9]. Improved electro-optical properties have been reported for new applications [10,11]. Fan *et al.* [12] reported scattering-free PDLC systems for infrared light modulators. Nicoletta *et al.* [13] investigated the application of polymer/LC materials for electro-chromic devices.

The electro-optical properties of polymer/LC films are determined in large part by the size, shape, and packing of the embedded LC domains. Typically, as the electric field aligns the LC molecules in the segregated domains, the scattering power of the film decreases substantially, bringing the film from a highly scattering state to transparency. Therefore, an understanding of the relationship between processing, morphology, and electro-optical performance is crucial for controlling film properties.

It has been shown that in such systems applied external electric field causes transparent state which under some conditions can be retained after the field is off, which is called memory effect [14–21]. The memory effect is generally interpreted using the fact that the LC molecules do not completely relax back to their initial scattering off-state, if a sufficiently high electrical field has been applied. They remain partially aligned in the direction of the applied field even after it is removed. In this case, it can be assumed that the effective refractive index of this portion of the LC molecules is still close to the refractive index of the polymer matrix.

The memory effect can be utilized for large area outdoor displays with high power consumption, which can be significantly reduced by utilizing the memory effect of polymer/LC films in the field off state. For spherical aerosol particles, it has been found that essential contribution to the memory effect is achieved due to formation of ordered branched network of the aerosol particles in the LC matrix [22].

This work is part of a systematic investigation to understand structure-property relationships of elaborated polymer/LC films, based on selected acrylic or methacrylic monomers and 5CB as model LC. In particular our interest is focused on the dependence of the molecular structure of the monomers (presence of hydroxyl groups, variation of the alkyl chain length,...) on the electro-optical properties of polymer/LC films, which were investigated by measuring transmission-voltage dependencies. These observations were correlated with the sample morphology which was obtained via polarizing optical microscopy (POM).

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), and was obtained from Synthon Chemicals GmbH (Wolfen, Germany). 5CB exhibits a crystalline to nematic transition temperature at $T_{CrN} = 23°C$, and a nematic to isotropic transition temperature

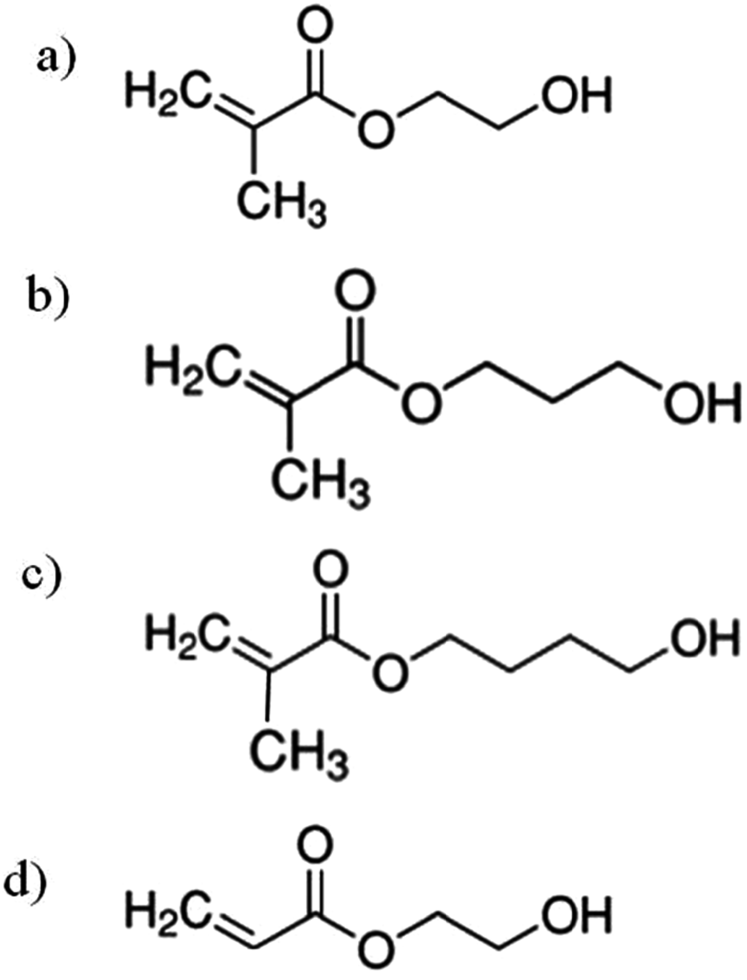


Figure 1. Chemical structures of the hydroxyalkyl acrylate and methacrylate monomers used in the preparation of polymer/liquid crystal systems: (a) 2-hydroxyethyl methacrylate (HEMA), (b) hydroxypropyl methacrylate (HPMA), (c) hydroxybutyl methacrylate (HBMA), and (d) 2-hydroxyethyl acrylate (HEA).

at $T_{NI} = 35.5°C$. The chemical structures of the different monomers are given in Figure 1.

2.2. *Polymer/LC Sample Preparation by PIPS*

Phase separation by polymerization is useful when prepolymer materials are miscible with low molecular weight LC compounds. In polymer/LC systems, the initial mixture consists of LC mixed with a UV curable monomer (usually a photoinitiator is added).

In this work, the PIPS technique was applied to blends where the LC to monomer ratio was taken as 6/4. A small amount of Darocur 1173 (2 wt.% compared to the monomer) was added to the initial blends. The homogeneous mixtures were sandwiched between Indium-Tin-Oxide (ITO) coated glass substrates so that the monomer/LC mixtures 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 $\lambda = 365\,\text{nm}$ and an intensity $I_0 = 1.5\,\text{mW/cm}^2$. 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 irradiations 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. Size 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 $\lambda = 632.8\,\text{nm}$ 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 micro-computer using an interface card (DAS 1602). For electro-optical measurements, an external electric field was applied across the PDLC film. The output of a frequency generator was amplified and used to drive the shutter device. Starting from the electrical off-state, the applied sinusoidal 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 120 s with an additional measuring time of 60 s 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. 6a).

The memory parameter was obtained for various polymer/LC systems, before and after relaxation. This parameter is defined by Eq. (1):

$$M = \frac{T_m - T_0}{T_S - T_0} * 100 \tag{1}$$

where T_0, T_s and T_m are the initial transmittance of the sample, the transmittance of saturation in an electric field and the residual transmittance after removing the field, respectively [23].

2.4. *Polarizing Optical Microscopy*

Characterization of the sample morphologies was performed by observations via a polarizing optical microscope (POM) in the electrical off-state and upon application of an electrical field with varying amplitude. Micrographs were taken using a POM equipment Olympus BX-41, equipped with a Q-Imaging numerical camera (3.3 MB). Several duplicate samples were considered systematically to check reproducibility.

3. Results and Discussion

Figure 2 presents transmittance values of the initial OFF state and ON state of UV irradiated polymer/LC films versus film thickness, obtained from initial mixtures containing hydroxy alkylmethacrylate and hydroxy alkylacrylate as monomers, and 60 wt% 5CB. The results of T_{ON} are presented in a logarithmic scaling. Generally the transmittance in the OFF state was found to be low which indicates phase separation, keeping into mind that the sensibility of human eyes is important in the range of visible wavelength around 550 nm. For thin films the transmittance in the OFF state can reach up to 10%. The polymeric systems studied here show almost no dependence on film thickness in the off state. Interestingly, the system including HBMA reached the highest T_{ON} values compared to the other systems.

Generally transmittance values in the ON state (T_{ON}) were found to be around 90–100%. Only the acrylic HEA system shows a lower level of T_{ON} in comparison with the methacrylic monomers.

The difference between saturation voltage V_{90} and threshold voltage V_{10} (at 9090 and 10% of transmittance, respectively) is shown in Figure 3, as a function of film thickness. These values were taken from the very first application of a voltage ramp (10 V) starting from the initial off-state, since the presence of the memory effect will not allow to compare the electro-optical response of all systems for applications of higher voltages.

It was found that the difference V_{90}-V_{10} is small, the values are situated between 2 and 6 V. Interestingly all systems investigated exhibit approximately the same V_{90}-V_{10} values. Only a small dependence on film thickness can be noticed for HPMA polymer/LC and HBMA polymer/LC systems.

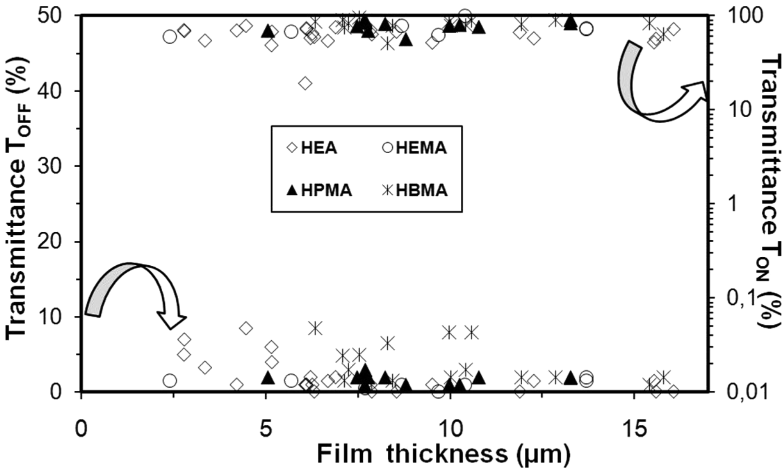


Figure 2. OFF state (T_{OFF}) and ON state (T_{ON}) transmission versus film thickness of cured 5CB/monomer systems. The incident light had a wavelength of $\lambda = 632.8$ nm, and a frequency of $\nu = 145$ Hz.

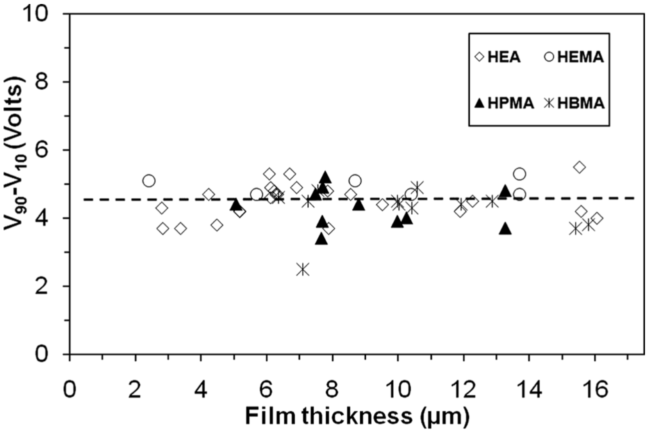


Figure 3. The difference between saturation and threshold voltages V_{90}-V_{10} versus film thickness for the cured systems with 60 wt.% 5CB. The maximum voltage application was fixed at 10 V ($\lambda = 632.8$ nm, $\nu = 145$ Hz).

The most interesting result of this work can be found on Figure 4 showing important transmittance memory effects as a function of applied voltage for cured HEA-, HEMA-, HPMA- and HBMA-LC systems. In these experiments, the voltage maxima of the scan up/down cycles, V_{max}, were chosen in the following consecutive order: 10 V, 20 V, 30 V, 40 V, ... up to 150 V. The values of T_{off} (transmittance memory effect) in Figure 4 were taken 60 s after the end of the application of the different voltage scan up/down cycles (see insert of Fig. 4), in order to elucidate

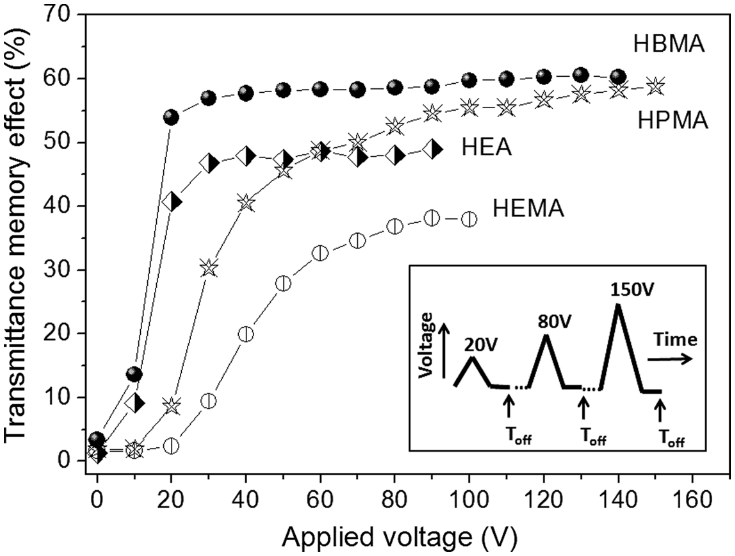


Figure 4. Dependence of the transmission memory effect in the off states (T_{off}) of polymer/liquid crystal systems on the maxima of the applied voltage scan up and down cycles. The continuous lines are guides for the eye. For the sake of comparison, film thicknesses around 6 µm were chosen here.

the relaxation time of LC molecules in the domains. It should be mentioned that Figure 4 shows representative results chosen from at least 8 to 10 samples for each polymer/LC system.

Different observations can be deduced from this figure, concerning the memory threshold voltage, the plateau value, and the general shape of these curves:

3.1. *Memory Threshold Voltage*

With increasing length of the alkyl chain, the threshold voltage becomes smaller and smaller, for example HPMA samples need much lower voltages to reach the plateau values than HEMA samples.

3.2. *Plateau Value*

The value of the transmittance memory effect depends on the structure of the methacrylic monomer. An increase of the alkylic chain length (ethyl-propyl-butyl) leads to a more important memory effect. At a given voltage interval, for instance 40–80 V, the slope of the curves decreases in the following order: HBMA-HPMA-HEMA.

3.3. *General Shape*

Figure 4 shows two different regions. A drastically increase of the transmittance memory effect between 0 to 30 V for all polymer/LC systems. After this first region the polymer prepared by the acrylic monomer shows a plateau while the polymers prepared with methacrylic monomers do not exhibit constant transmittance memory effects. It can be noticed that the plateau values continue to increase with applied voltage and that the uptake of these curves is more important in the case of HEMA, less in the case of HPMA and still lower in the case of HBMA. As an example it was found that the transmittance of 60 wt.% 5CB/40 wt.% HBMA samples reached a horizontal plateau at about 60% in the OFF state and the transmittance values T_{off} of these samples increased from 13% at 10 V to 54% at 20 V before reaching a plateau.

In order to get a deeper insight of the observed optical memory phenomena, sample morphologies were investigated by POM. As an example, Figures 5a–h show micrographs (in the crossed polarizer/analyzer mode) of a film consisting of 60 wt.% 5CB and 40 wt.% HEMA which was prepared between two ITO glasses. Figures 5a and 5h represent micrographs before and after application of an electrical field, respectively. An electrical field was applied in the case of the micrographs shown in Figures 5b–5 g. A sinusoidal voltage of 145 Hz with varying amplitude was applied in the following consecutive order: 5 V (Fig. 5b), 10 V (Fig. 5c), 15 V (Fig. 5d), 20 V (Fig. 5e), 25 V (Fig. 5f), 30 V (Fig. 5g). From these micrographs it is difficult to discern LC domains in the polymer matrix which are probably characterized by the blue areas. Here, we are more interested in macroscopic changes of morphologies rather than in the corresponding microstructure. Indeed, strong variation of overall sample morphology was obtained with increasing applied electrical field up to 30 V. Beyond this value the observed structures were recovered. Interestingly if the voltage was cut down (Fig. 5h) the obtained sample morphology seems to be close to that of Figure 5g but completely different compared to the initial OFF state (Fig. 5a), thus clearly demonstrating the existence of a memory effect.

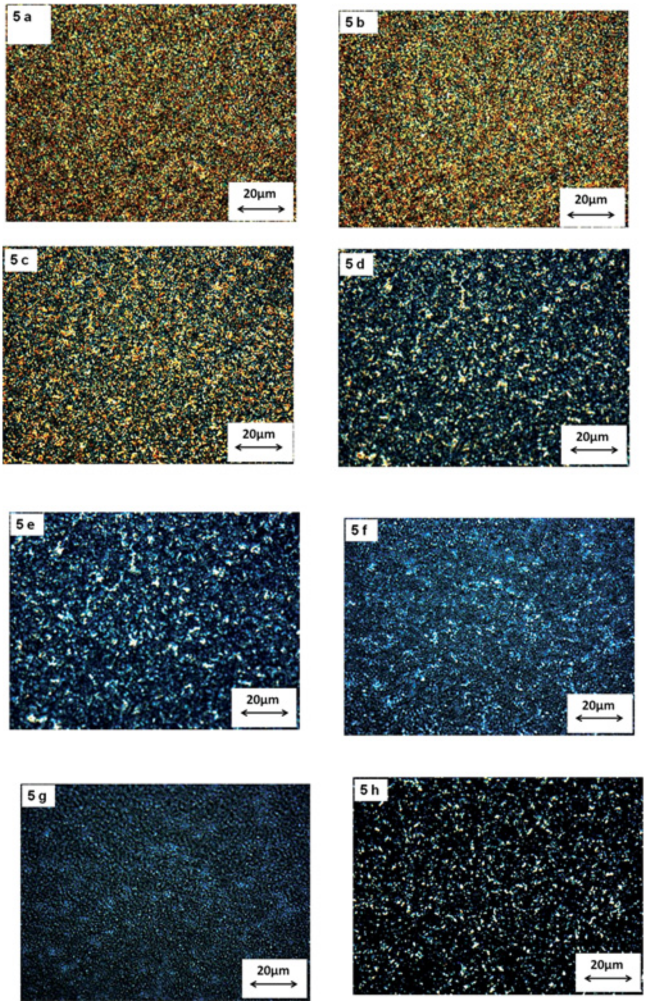
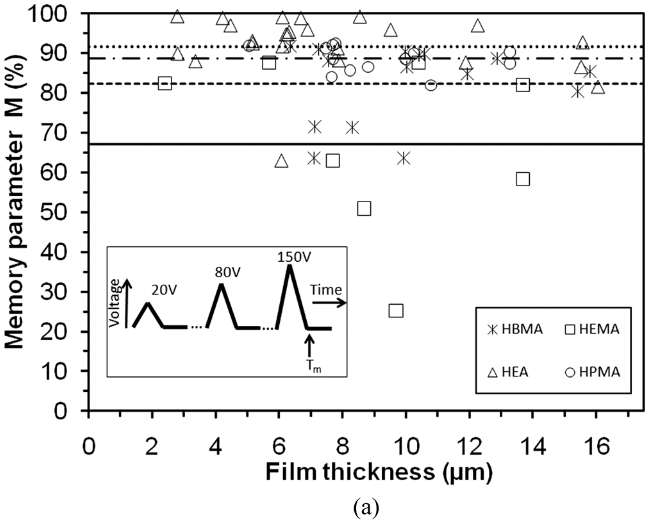
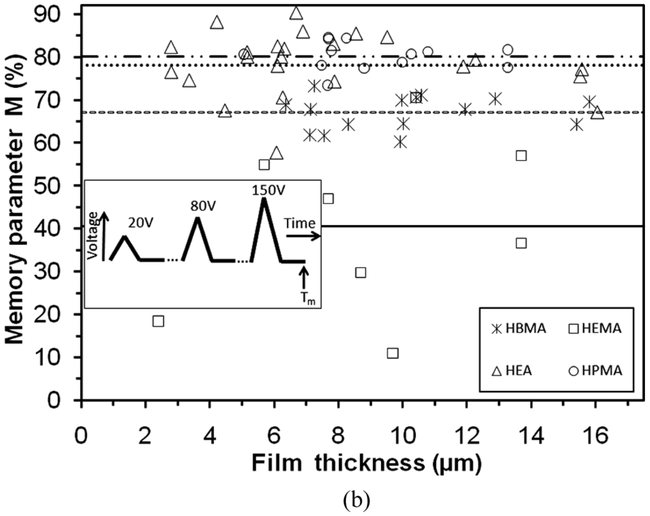


Figure 5. Film morphologies obtained by the POM technique in the transmission mode (crossed polarizer/analyzer) of a polymerized HEMA/5CB (40/60) system: (a) before application of an electrical field, (b) after applying 5 V, (c) after applying 10 V, (d) after applying 15 V, (e) after applying 20 V, (f) after applying 25 V, (g) after applying 30 V, and (h) after returning to 0 V.

Results from all methacrylic and acrylic systems were plotted in Figures 6a and 6b, where the calculated memory parameter M (Eq. 1) is given as a function of film thickness. In Figure 6a the calculation was made by using the transmittance values measured immediately after the end of the voltage cycle with a maxima of 150 V (T_m) as it is shown in the insert of this figure. Relatively high values of the memory parameter were observed in all cases considered here, particularly for the HEA system. Methacrylic polymers also show high memory parameters except HEMA, which present a strong dispersion of the results. Generally, the transparent state is preserved without electrical field over a period of days and sometimes even for a couple of weeks.



(a)



(b)

Figure 6. (a) Memory parameter "M" as function of film thickness taken immediately after scan up and down cycle (see insert). (b) Memory parameter "M" as function of film thickness taken after a relaxation of 60 s, after the voltage scan up and down cycles were finished (see insert). The average values of each system are plotted as lines. Dashed line is for HBMA, straight line stands for HEMA, dotted line represents HEA, dashed dotted line is for HPMA.

Figure 6b represents the memory parameter M of all systems taking into account an additional relaxation time of 60 seconds after the electrical field was cut down (see insert of Fig. 6b). The polymer/LC system with initial composition 60 wt.% 5CB/40 wt.% HEMA show a strong decrease of the M values. For the systems with initial composition 60 wt.% 5CB/40 wt.% HBMA, 60 wt.% 5CB/40 wt.% HPMA, and 60 wt.% 5CB/40 wt.% HEA the decrease of the memory parameter was less important.

4. Conclusions

The electro-optical responses as well as the sample morphologies of UV-cured methacrylate/5CB and acrylate/5CB films were investigated as function of the applied electrical field. A strong optical memory effect was found in all cases considered here, which was preserved for a long period. In particular, the relationship between the memory effect and the chemical structure of the monomers was investigated. The presence of hydroxyl groups seems to be a necessary condition to obtain a memory effect whereas only some dependence of the variation of the alkyl chain length on the preserved transmittance states was found here.

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