Memory effects of polymerized 2-hydroxyethylmethacrylate/4-cyano-4’-pentyldibiphenyl mixtures

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Abstract

Polymer dispersed liquid crystal (PDLC) films are heterogeneous composite materials consisting of micron-sized droplets of liquid crystal dispersed in a continuous polymer matrix. They are formed by a phase separation process of the LC component from the polymer. PDLC films can be switched from a light scattering off-state to a transparent on-state, when a sufficiently high electrical field is applied. Polymerization Induced Phase Separation (PIPS) using UV-light is one of the most common methods to prepare PDLC films and the polymerization is induced by decomposition of the photoinitiator in a mixture of LC with functional monomers.

Polymer/liquid crystal (PDLC) films were prepared by a PIPS process of a mixture composed of the nematic LC material 4-cyano-4’-pentyldibiphenyl (5CB), 2-hydroxyethylmethacrylate (HEMA) as monomer, and a photoinitiator (Darocur 1173). Ultra-violet (UV) radiation was employed to initiate the PIPS process. The electro-optical behaviour of the films obtained was investigated as function of applied voltage and frequency. Strong memory effects have been observed in the case of samples prepared from 60 weight.-% 5CB and 40 weight.-% HEMA.

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1. INTRODUCTION

Liquid crystals (LCs) have anisotropic dielectric properties which can allow an applied electric field to cause an orientational change in the molecules of the LC phase and thus an orientational change in the refractive index indicatrix (matrix of indices) which causes incident light to see a different refractive index. Polymer as an important component of polymer dispersed liquid crystal (PDLC) materials has a great influence on electro-optical properties. The confinement of electro-optical materials in polymeric matrices has raised special interest due to their...
technological applications. It is part of systematic studies undertaken in our laboratory to explore the physical properties of composite materials made of polymers and low molecular weight LCs [1,2]. In the absence of an electric field (OFF state), PDLC films appear opaque due to the mismatch of refractive indices of the polymer matrix and the LC. When an electric field is applied, the PDLC films turn into a transparent state (ON state). The electro-optical characteristics of a PDLC film depend on a variety of material and fabrication parameters such as choice of polymer, choice of LC, solubility of LC in polymer, shape and density of the LC droplets, temperature etc. During the preparation process, randomly orientated LC droplets will be separated from the polymer by either polymerization induced phase separation (PIPS), thermal induced phase separation (TIPS), or solvent induced phase separation (SIPS). However, it is well-known that the most convenient method used for the preparation of PDLC films is the polymerization induced phase separation (PIPS) of mixtures composed of reactive polymer precursor and LC.

Only a limited number of reports are known combining synthetic polymeric hydrogels with opto-electronic materials [3-8]. The manifest interest in hydrogels derives from their characteristics, particularly biocompatibility and non-toxicity [9,10]. Hydrogels based on Poly (2-hydroxyethylmethacrylate) (PHEMA) have been effective in ophthalmology field, due to their mechanical stability, high refractive index at room temperature (n=1.512), and oxygen permeability.

In our research, the electro-optical properties of elaborated polymer/LC films based on HEMA and 5CB have been experimentally investigated, and their transmission-voltage dependence has been studied in detail.

2. EXPERIMENTAL PART

2.1 Materials

The monofunctional monomer 2-hydroxyethylmethacrylate (HEMA) was purchased from Sigma-Aldrich and used without further purification. To initiate the reaction of free radical photopolymerization, 2-hydroxy-2-methyl-1-phenyl-propanone-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).

![Chemical structures of the components of the initial mixtures prior to UV radiation exposure: a) the monomer 2-hydroxyethyl methacrylate, b) the photoinitiator Darocur 1173, and c) the LC 5CB.](image-url)
5CB exhibits a crystalline to nematic transition temperature at $T_{\text{CrN}}=23^\circ\text{C}$, and a nematic to isotropic transition temperature at $T_{\text{NI}}=35.5^\circ\text{C}$. The chemical structures of the different components are given in Figure 1.

### 2.2 PDLC film preparation

Polymer/LC samples were prepared using the PIPS technique, starting from blends where the LC to monomer ratio was taken as 60 weight-% (wt.-%)/40wt.-%. A small amount of Darocur 1173 (2 wt.-% compared to HEMA) 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 samples were exposed to UV radiation, using Philips TL08 UV lamps with a $\lambda=365\text{nm}$ and an intensity $I_0=1.5\text{mW/cm}^2$. The exposure time was fixed at 10min and the sample thickness was 10.4μm.

### 2.3 Electro-optical measurements

Electro-optical experiments were performed at room temperature by measuring the transmission of an unpolarized HeNe laser light at a wavelength of $\lambda=632.8\text{nm}$ orienting the films normal to the incident laser beam. The distance between the sample cell and the detector (silicon photodiode) was approximately 30cm. The collection angle of the transmitted intensity was about $\pm 2^\circ$. The uncorrected intensity of transmitted light was recorded on a micro-computer using an interface card (DAS 1600-2).

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 145Hz was increased continuously up to a desired maximum value $V_{\text{max}}$. 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 behaviour of the transmittance in the off-state. The maxima of the voltage of the scan up/down cycles, $V_{\text{max}}$, were chosen in the following consecutive order: 10V, 20V, 30V, 40V.

### 3. RESULTS AND DISCUSSION

Kinetic swelling experiments from polymerized pure HEMA (PHEMA), conducted in the LC solvent 5CB as function of temperature, revealed only a weak effect of swelling and deswelling in the whole range of temperature explored, from 0°C to 100°C. Since PHEMA samples were prepared in the absence of any crosslinking agent, the obtained polymer was only loosely crosslinked, probably due to the presence of small amount of difunctional impurities. These results are in strong contrast with earlier investigations of the swelling behaviour of chemically crosslinked polybutylacrylate networks in LC solvents, where a strong increase of swelling was found around the nematic-isotropic transition temperature $T_{\text{NI}}$ [11]. From these findings it can be assumed that the PHEMA/5CB interactions were rather strong. Following these lines, it would be interesting to investigate in-situ polymerized HEMA/5CB systems since LC will be forced to phase separate to a great extent from the formed PHEMA. Indeed, rather strong light scattering polymer/LC samples were obtained after UV-exposure of HEMA/5CB mixtures and the electro-optical response of these heterogeneous films was investigated as a function of applied electrical field.
In our electro-optical experiments, the maxima of the voltage of the scan up/down cycles, $V_{\text{max}}$, were chosen in the following consecutive order: 10V, 20V, 30V, 40V. until a plateau value of the transmittance was obtained. Figure 2 shows the evolution of the transmittance as a function of voltage at a low (20V) and a high value of $V_{\text{max}}$ (160V) for polymerized 60wt.-% 5CB/40wt.-% HEMA films. Starting from the electrically off state, samples became more transparent by increasing the applied voltage. At $V_{\text{max}}$=20V, transmittance evolves from 0% to 35%. If the voltage will be subsequently removed, transmittance in the electrical off-states will be identical to the initial $T_{\text{off}}$ values. By successive increase of the electrical field, it was found that the transmittance of the samples reached a horizontal plateau at about 80% in the on-state by applying voltages above 40V. When the voltage was removed, the transmittance did not return back to the initial level, but remained at a level of about $T_{\text{off}}$=68%, as shown in Figure 2 for $V_{\text{max}}$=160V. This transparent state is preserved over a period of days.

Figure 3 shows the evolution of the transmittance as a function of time measured immediately after scan up and down voltage cycles with maxima of 20V and 160V for polymerized 60wt.-% 5CB/40wt.-% HEMA films. It can be clearly seen that the transmittance decreases from an initial value of 68% to 55% at t=60s for $V_{\text{max}}$=160V, whereas a constant value of transmittance was observed in the case of $V_{\text{max}}$=20V.
Fig. 3: Transmittance as a function of time after removal of the applied electrical field for a UV-irradiated 60wt.-%/40wt.-% 5CB/HEMA film. The transmission values at 0s correspond to the values at the electrical off-state after the end of the voltage scan up/down cycle on Figure 2, as expected.

Fig. 4: Memory effect: Dependence of the transmission values in the off states ($T_{\text{off}}$) on the maxima of the applied voltage scan up and down cycles for a UV-irradiated 60wt.-% 5CB/40wt.-% HEMA film. The continuous lines are guides for the eye.
In relation with Figure 3, Figure 4 illustrates the variation of the transmittance in the off state (T_{off}) as function of the voltage maxima applied (V_{max}). The values of T_{off} in Figure 4 were taken at the beginning of the application of the different voltage scan up/down cycles as shown in the scheme on the figure. This figure shows two different regions. Below a voltage maximum value of approximately 30V, the same transmittance values before and after applying the electrical field were obtained, for a given film, and these data were identical compared with the initial T_{off} values. Above V_{max} = 30V, the film exhibits continuously increasing T_{off} values in the field off state by further increasing the maxima of the voltage cycles applied. The transmission values T_{off} of the samples increased from 2% at 30V to 52% at 160V, and a plateau was obtained. This behavior is known as memory effect and has been investigated by some authors [3-8]. 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 polymer/LC film prepared from initial mixture 60wt.-% 5CB/40wt.-% HEMA conserves, therefore, its transparent state to some extent. Memory states of these films are maintained for more than several days at room temperature.

Strong interactions between PHEMA and LC molecules might be the reason for the observed memory effect. Furthermore, it cannot be excluded that these UV-cured systems do not reach a chemically stable state under the given radiation conditions.

4. CONCLUSION

Polymer-dispersed liquid crystal (PDLC) films were prepared by UV-light-induced polymerization of photopolymerizable HEMA and nematic LC 5CB.

The electro-optical properties of these films were investigated as function of the applied electrical field. The transmission versus voltage curves show considerable differences between different voltage cycle applications for samples prepared from 60wt.-% 5CB/40wt.-% HEMA. In particular, a strong memory effect was observed for V_{max} values above 30V, so that the electrically actived films preserve their transparent state to some extent.

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