Electro-optic Response of a Polymer Dispersed Liquid Crystal Film

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Abstract

Polymer dispersed liquid crystal (PDLC) films are potentially useful in electro-optic devices since they can be used for vision products. In this work the PDLC thin films were prepared by a photopolymerization induced phase separation method and electro-optic properties of the films were investigated.

1. Introduction

Polymer dispersed liquid crystal (PDLC) displays are interesting new uses for liquid crystals which could allow liquid crystalline materials to be used in electro-optic applications such as projection displays [1-3]. PDLC displays exhibit several advantages in comparison to conventional displays, one such example being the twisted nematic liquid crystal display [4], where the liquid crystal is sandwiched between two glass plates and placed between two crossed polarizers. In production of the PDLC cells no surface-alignment treatment is required and they can work without polarizers. For that reason, the PDLC devices are currently of high interest [5-7] and they have promising new applications for light control and flexible electro-optic displays.

PDLC films consist of micron sized droplets of liquid crystal dispersed in an optically isotropic polymer matrix, shown schematically in Figure 1. By choosing appropriate combinations of liquid crystal and polymer material, the PDLC film can be electrically switched from a light-scattering or opaque "off state" to a non-scattering or transparent "on state". In the "off state", the PDLC film appears milky white due to the refractive index mismatch encountered by incoming light at the liquid crystal/polymer interface. When an electric field is applied across the film, the liquid crystal molecules within the micro-droplets align with the electric field such that the higher relative permittivity of the

liquid crystal is aligned parallel to the electric field; so the liquid crystal materials which have positive dielectric anisotropy align with their long-molecular axis parallel to the field direction. Thus, in the "on state", if the ordinary refractive index of the liquid crystal within the droplets is sufficiently close to the index of the polymer matrix material, the incoming light is no longer scattered and the PDLC film becomes clear. These films can be used for a wide variety of devices such as switchable windows.
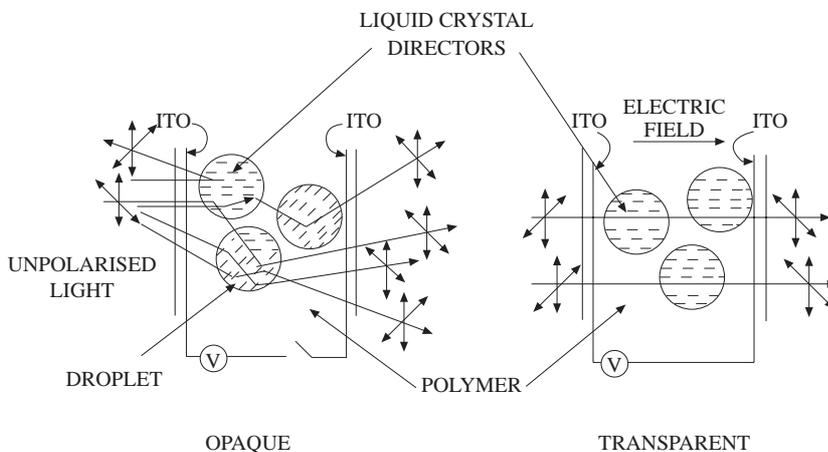

Figure 1. Light transmission characteristics of a PDLC film. Droplets of liquid crystal within a polymer matrix give rise to a strong light scattering; however electrical reorientation of the liquid crystal molecules provides a transparent state

In this paper, the PDLC thin films which have normal mode morphology were fabricated and their electro-optical characteristics were reported. The sample preparation parameters such as liquid crystal concentration and curing time were reported. Polarizing microscopy was also used to study the microstructure of the films and to determine the size of the droplets.

2. Experimental

The PDLC films were manufactured using optical adhesive NOA 65 (Norland) and the liquid crystal E202 (Merck). NOA 65 is an ultraviolet (UV) curable prepolymer that contains no solvent, and due to it being a one part system it is always ready to use without any preparation. The refractive index of NOA 65 is 1.52. The liquid crystal E202 is fast switching mixture and its nematic-isotropic phase transition (clearing point) is 85.9 °C. The material has positive dielectric anisotropy, $\Delta\epsilon = 8.63$ at 20 °C and 1 kHZ. Ordinary and extraordinary refractive indices of E202 are $n_0 = 1.5079$ and $n_e = 1.6764$ (at 20 °C). Thus, it has optical anisotropy, $\Delta n = 0.1685$. The mixture E202 has been developed for wide area applications. This mixture is a capable of giving a nematic phase

of high chemical and photochemical stability in the room temperature. The liquid crystal mixture has white color, and relatively low viscosity ($\eta = 24.7 \ cSt$ at $20\,^\circ$C). It can also be driven at a lower voltage.

The liquid crystal was mixed with NOA 65 in the weight ratio 3:2 and heated to above the isotropic clearing temperature to achieve good mixing. Temperature was controlled by a Linkam microscope hot stage. This mixture was introduced by capillary action into a prepared indium tin oxide (ITO) coated glass cell with an approximate active cell area $1cm^2$ depending on the preparation. Sample thicknesses of 2 and 7 μm were adjusted using glass beads as spacers (E.H.C. Ltd). Two conductive wires were fixed on the ITO layer with a special two-component silver adhesive.

In order to obtain defined active cell area, first the ITO coated glass plates were cut to the optimum size for the experimental set-up. After first cleaning procedure the mask for the electrodes was painted on the ITO coated layer. Therefore a special acid resistant varnish (Lacomit varnish G371) was used. The glass plates were then etched by using HCl and HNO_3 mixture to remove all parts of the ITO layer which were not protected by the varnish. After the etching process, varnish was removed with Lacomit remover. Finally the glass plates were cleaned in several steps within an ultrasonic cleaning bath (Ultrawave Ltd).

The PDLC film was placed on a Peltier hot stage to adjust the curing temperature during the polymerization-induced phase separation (PIPS). The PIPS process is particularly convenient and is a fast method [3] for the production of the PDLC devices. The samples were exposed to UV light by using a 300 W ultra-vitalux Osram halogen lamp. In order to obtain constan UV intensity during the curing process, a filter was placed between UV-lamp and the cell.

Electro-optical properties of the PDLC films were measured using a He-Ne laser ($\lambda = 632.8 \ nm, P = 2 \ mW$) (Polytec Type 710) and a photodiode at room temperature. The experimental arrangement for recording the electro-optic data is shown in Figure 2. The PDLC films were held in a cell holder on an optical bench and measurements were performed in a normal transmission geometry. Laser light was focused on to a silicon photodiode (DET) using a lens (L) after passing a diaphragm (D). A neutral density filter (F) was also used to avoid saturation of the photodiode. In order to investigate switching time characteristics, the electrical signal from a signal generator (SG) whose output was amplified by an amplifier (A) was applied to the PDLC films. The detected signal was observed on a storage oscilloscope (CRT) screen and compared with the original signals applied. Measurements were recorded with a programmable graphic recorder (GR) (Hameg Instruments HM8148-2). Optical transmittance of the films versus wavelength were also measured with a visible spectrometer (Spex Spectrometer 3293).
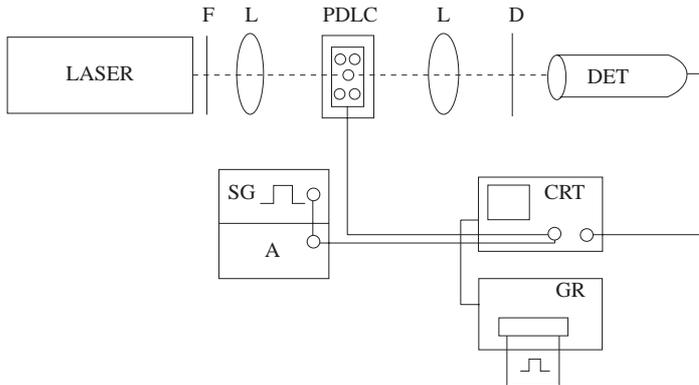
Figure 2. Electro-optic measurement system used during this work

3. Results and Discussion

In order to investigate homogeneity and optical switching behavior of the liquid crystal droplets, the PDLC film was mounted on a polarizing microscope. When electric field applied to the film, switching of the droplets could be easily observed. Macroscopically the films scattered light strongly in the unactivated state, becoming more transparent when electric field applied.

When AC voltages with different frequencies were applied to the cell, switching could be seen by naked eye. It was observed that on removing the electric field liquid crystal relaxed back, so that the orientation direction of the long shaped molecules (viz. director) in each droplet returned their original direction. This effect indicates that director is pinned on to the polymer surface.

A typical PDLC texture, shown in Figure 3, was observed when viewed through crossed polarizers in the transmission microscope (Olympus BH-2). The sample was photographed with the microscope camera assembly. The droplets when viewed under the polarizing microscope were enlarged by a factor of 500. When observed between crossed polarizers, the droplets appeared to be single domains in different sizes. In the texture of Figure 3, average diameter of the microdroplets were about 25 μm. It was found that liquid crystal droplets become uniform if the glass plates were coated with some undercoating film such as polyvinylalcohol before forming the PDLC films. In the experiments it was also observed that the curing intensity and time had a profound effect on the size and shape of the droplets. For our samples curing time war nearly 25 s. Very short curing time resulted in an incomplete polymerization; in comparison, the long time curing resulted in large droplet sizes.

While the most stable structure of the bulk nematic phase is given by a uniform orientation of the director, the confinement of nematic liquid crystals to spherical cavities can lead to a variety of quite complicated director fields. The occurrence of the different

structures depends on the anchoring of the director at the droplet surface, on the size and shape of the droplet and on the elastic properties of the liquid crystal. The droplets are not perfectly spherical and the nematic director is random from droplet to droplet. The orientation of the molecules within the droplets is usually bipolar but other arrangements can also be observed. Some of the droplets shown in Figure 3 are very characteristic for a bipolar configuration. On the other hand, Figure 4 shows only one microdroplet taken under investigation. The picture was assigned to a radial configuration [8].
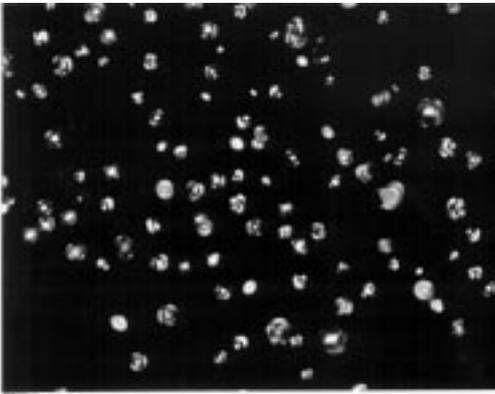

Figure 3. Microscopic view of the UV-cured PDLC sample. E202 liquid crystal droplets in NOA 65 polymer material
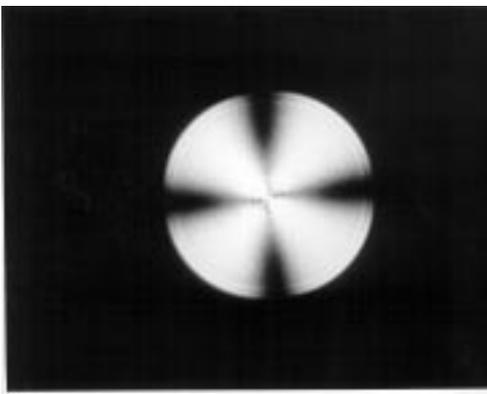
Figure 4. Black and white polarizing microscope photograph of a liquid crystal droplet

When the concentration of the liquid crystal in the film was increased, different types of film morphology were observed. At high concentrations of liquid crystal, polymer networks were obtained. It was seen that light scattering mechanism changed in these films. This is due to the fact that thickness of the polymer matrix between the liquid crystal droplets becomes less than the wavelength of the incident light. The clearest film was the film that contained the lowest concentration of liquid crystal E202.

Threshold voltage was measured by observing microscopically the polarization texture changes of the droplets. At 8 V, droplets started to switch. Transmittance of the film was measured with a visible spectrometer as a function of wavelength. The increase in transmittance with increasing wavelength was observed. The maximum transmitted light was found at 620 nm.
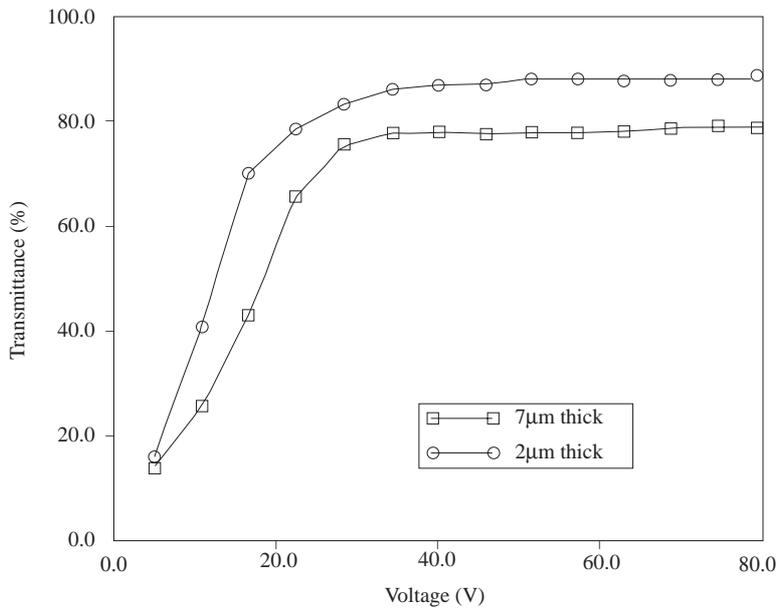
Figure 5. Voltage-transmission curve of a PDLC film made from E202/NOA 65

To determine switching voltage, the light transmittance of the film was measured as a function of applied voltage. Applying a voltage to the PDLC film while monitoring the transmission gives rise to a voltage-transmission curves [9] such as shown in Figure 5. Figure 5 shows voltage-transmission curves for PDLC films with different thicknesses. It can easily be seen that transmittance decreases with increasing cell thickness. Since the transmittance is inverse of the turbidity, a thicker film scatters light more strongly. On the other hand, transmittance increases with increasing applied voltage and reaches 90 per cent in the "on state". The 100 per cent transmittance refers to no cell in the beam, therefore the voltage-transmission curve represents loses caused by cell scattering and reflection from the film substrate. When the voltage is removed the transmittance returns to the initial level. The voltage-dependent optical transmission of the PDLC film was also affected by several parameters, such as droplet shape and size and liquid crystal concentration. The film with high liquid crystal concentration showed more light scattering effect in the "off state" and lower threshold voltage in the "on state". However, when the UV curing time in the preparation of the film process is not controlled, a higher liquid crystal concentration leads to a larger droplet size. The switching voltage is also dependent on some factors, such as resistivity and dielectric properties of the liquid crystal and polymer matrix [10].

The transmittance versus voltage curve in Figure 5 shows no sharp voltage threshold for the onset of transmittance. In the voltage-transmittance measurements, transmit-

tance exhibited a slight hysteresis for increasing the decreasing voltage. This effect might be a consequence of surface morphology of the droplets.

In order to measure the switching time of the PDLC sample, a wave generator giving frequency variable pulse trains of AC square waves up to 100 V was used. In the experiment 100 Hz AC square signals were applied to the cell. Light transmission response was studied on an optical bench equipped with a He-Ne laser and a photodiode to collect the transmitted laser light into a storage oscilloscope. The switching time was measured as the time taken for the light transmission to vary from 10 to 90 per cent. A typical response of the UV-cured PDLC film is shown in Figure 6. The PDLC device showed good electro-optic response at room temperature.
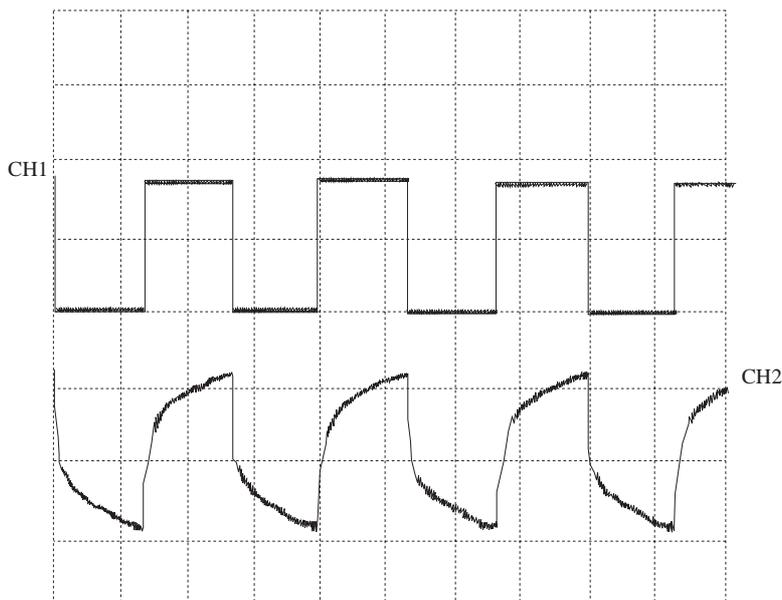

Figure 6. A typical response of a 2 μm-thick PDLC cell. In CH1 (upper trace), the applied voltage scale is 5 V/div. In CH2 (lower trace) the voltage scale is 10 mV/div. The time scale is 10 ms/div. The square wave frequency is 100 Hz

A 2 μm-thick film could be switched by 8 V square signal and showed almost perfect square response when driven at 30 V. Dependence of the switching time on the applied voltage is shown in Figure 7. The switching time decreases when the applied voltage increases. The switching time of a PDLC device is also related to visco-elastic constants of the liquid crystal material and size of the droplets [11].

The differences in the switching behavior of the samples prepared under different

conditions lead to the question of how the droplet shape and size are affected by the curing parameters. Therefore further investigations are under consideration.
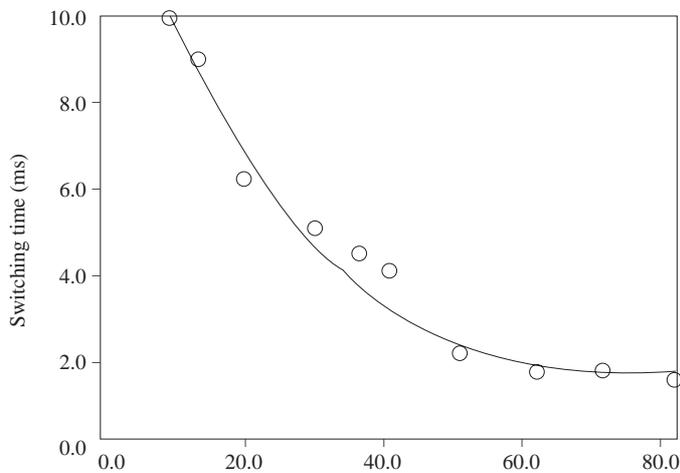

Figure 7. Voltage dependence of the switching time for 2 μm-thick PDLC film

Normal-mode PDLC displays require a nematic liquid crystal with positive dielectric anisotropy. Many of the early publications on the PDLC films using nematic liquid crystals refer to the use of some alkylcyanobiphenyl (for instance, 5-CBP, 7-CBP), or eutectic mixtures of similar compounds such as E7 [12, 13]. The liquid crystal employed in our experiments is a low threshold and fast switching mixture. The mixture E202 has been designed wide area applications. Its clearing temperature point, as indicated before, is very high (85.9 $^\circ C$) and its nematic range extents to below -50 $^\circ$C. In the PDLC applications liquid crystal solubility is an important factor for transmission of the cells. The mixture E202 has good solubility in the prepolymer and is not affected by the curing of epoxy resin. For the PDLC films of wider viewing angle, the liquid crystal materials with a lower birefringence are better. E202 is, therefore, suitable for this aim since it has lower anisotropy. Maximum film clarity occurs when the ordinary refractive index of the liquid crystal equals to the refractive index of the polymer. However, the slight difference between the ordinary refractive index of E202 and refractive index of NOA 65 gives rise to loss of clarity in the on-state of the PDLC film.

To conclude the PDLC films play fundamental role in the electo-optic applications of the liquid crystal materials. These devices have a high potential for flat panel displays without the use of an active matrix substrate.

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