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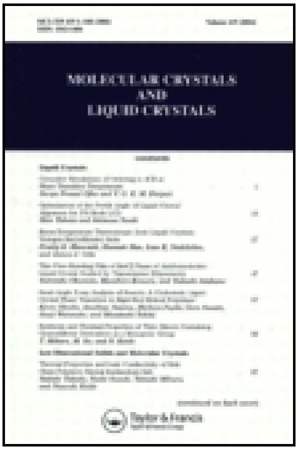

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Investigation of Polymer Dispersed Liquid Crystal films exhibiting nanosized liquid crystalline domains

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INVESTIGATION OF POLYMER DISPERSED LIQUID CRYSTAL FILMS EXHIBITING NANOSIZED LIQUID CRYSTALLINE DOMAINS

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Elaboration of Polymer Dispersed Liquid Crystals (PDLCs) was implemented via radiation curing of a selected mixture of thiolene and the liquid crystal (E7). It is made according to the process of Polymerisation Induced Phase Separation (PIPS) under the conditions where the size of the liquid crystal domains was in the nano-meter scale. Typically, the Scanning Electron Microscopy gives a distribution of nearly spherical droplets of mean diameter in the range of 90 nm. The spectral reflectivity of a Fabry Perot cell of the nanosized materials was obtained by UV-vis spectroscopy in the range of wavelengths roughly between 200 and 1000 nm. The electro-optical response of this cell was investigated in terms of the variation of the reflectivity as a function of the applied electrical field and the change of the mean refractive index was deduced from these measurements.

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Keywords: electro-optical response; nano-sized droplets; polymer dispersed liquid crystals; spectral reflectivity

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1. INTRODUCTION

This paper reports results of the morphology and the electro-optical response of Polymer Dispersed Liquid Crystals (in short PDLCs) exhibiting nano-sized droplets. These systems consist of droplets filled with a low molecular weight liquid crystal (LC) that are randomly distributed throughout a solid polymer matrix [1–4]. The particular interest on PDLCs with nano-sized droplets originates mainly from their applications in non-linear optical devices and telecommunication systems due to variations of the mean refractive index upon application of an electrical field [5–9]. Droplets of size comparable to the wavelength of incident light generate a strong scattering while those of mean diameter much smaller than the wavelength lead to a weak scattering with and without an external electric field.

In this work, we report results establishing correlation between the method and conditions of preparation of these compounds and their morphology and electro-optical properties. PDLC films exhibiting nanosized LC domains were prepared by radiation curing of a selected reactive monomer/LC/photoinitiator mixture under Ultraviolet (UV) light exposure. The reflectivity of a Fabry Perot cell which include the nanocomposite material was measured as a function of the wavelength of the incident light, with and without the applied field. Curves representing the variation of the mean refractive index with the applied field are deduced.

2. EXPERIMENTAL SECTION

2.1. Materials

The polymer precursor was a mixture of commercially available thiolene compounds designated A*. The eutectic LC mixture E7 was obtained from Merck Eurolab (Darmstadt, Germany) including three cyanobiphenyls and a cyanoterphenyl. E7 exhibits a nematic – isotropic transition temperature at 61°C and a glass transition temperature at -62°C. Recall that E7 presents a high birefringence $\Delta n_{\mathrm{LC}} = n_{\mathrm{e}} - n_{\mathrm{o}} = 0.22$ at a wavelength $\lambda = 632\,\mathrm{nm}$ and room temperature, where n_{e} and n_{o} are the extraordinary and the ordinary refractive indices, respectively. The photoinitiator Darocur 1173 was purchased from Merck Eurolab (Darmstadt, Germany), and added to the initial mixture with a quantity of 5 weight -% (wt-%) with respect to A*.

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2.2. Sample Preparation

Preparation of the PDLC films was made according to the Polymerisation Induced Phase Separation mechanism (PIPS) under radiation curing by UV light. 65 wt.-% of the resin A*, 35wt.-% of the LC E7, and the photoinitiator were mixed together and mechanically stirred for several hours until the blend became homogeneous. A small quantity of this mixture was introduced by capillarity into commercially available standard sample cells from EHC (Tokyo, Japan). The sample thickness was 15 µm and the cells were coated with Indium – Tin – Oxide (ITO) so that an electrical field could be applied.

The samples were exposed during 2 s to a polychromatic source of UV radiation (Minicure MC4-300 from Primarc UV technology). A dose of 200 mJ/cm^2 was applied and the polymerization processes were conducted at room temperature.

2.3. Techniques

2.3.1. SEM Analysis

Samples for Scanning Electron Microscope (SEM) studies were prepared by sandwiching a drop of the initial mixture between two glass plates prior to radiation exposure. Thickness of the films was set to 25 µm by applying calibrated adhesive stripes. After UV exposure was finished, the sample cell was cutted in two pieces allowing to reveal the sample morphology. These pieces were immersed in ethanol in order to dissolve the LC. The sample preparation technique as described above lead to the appearance of empty cavities that were once filled with LC. The PDLC samples were coated by a thin gold/palladium layer and characterized by means of a standard scanning electron microscope. The magnification used in our experiments was about 20000x using an acceleration voltage of 20 kV. The obtained images have been analyzed and the results of the granometrical analysis were collected as histograms.

2.3.2. Reflectivity Measurements

A spectrophotometer Varian Cary 50 was used to evaluate the reflectivity of a Fabry-Perot cell as a function of the wavelength in the range 200 – 1100 nm. The measurements were made in the off-state (no electric field) and under application of an electrical field. Starting from the electrical off-state, the applied sinusoidal voltage with frequency 145 Hz was increased in steps of 25 volts until a further increase of voltage did not vary the reflectivity values. After the first scan up cycle, the voltage was decreased in the same way before another scan up cycle was performed.

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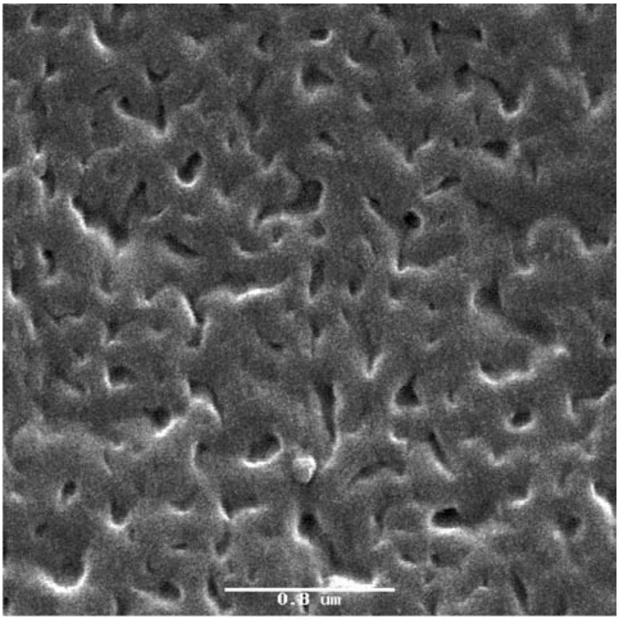
The variation of the mean refractive index Δn was obtained by measuring the spectral shift of the oscillations in a Fabry-Perot cell.

3. RESULTS AND DISCUSSION

Figure 1a gives a typical example of the observed sample morphologies. It shows an SEM micrograph of the thiolene/E7 system (65wt% thiolene/ 35wt% E7) cured with the Minicure UV source in the presence of the photoinitiator Darocur 1173. The obtained results were analyzed by a granulometric method allowing for example to quantify droplet sizes. Figure 1b shows the dependence of the number of droplets as a function of the average diameter of the droplets, where the values were extracted from the micrograph of Figure 1a. The histogram in Figure 1b exhibits a nearly symetrical distribution of the droplet sizes with a maximum at 90 nm. Only few droplets were larger than 200 nm which means that practically all LC domains are in the nanosize range thus generally suitable for



(a)

FIGURE 1 a) SEM micrograph of the thiolene system (65wt%)/E7(35wt%)/ Darocur1173 cured with the Minicure UV-unit. b) Histogram showing the size distribution of the droplets. The data were extracted from a).

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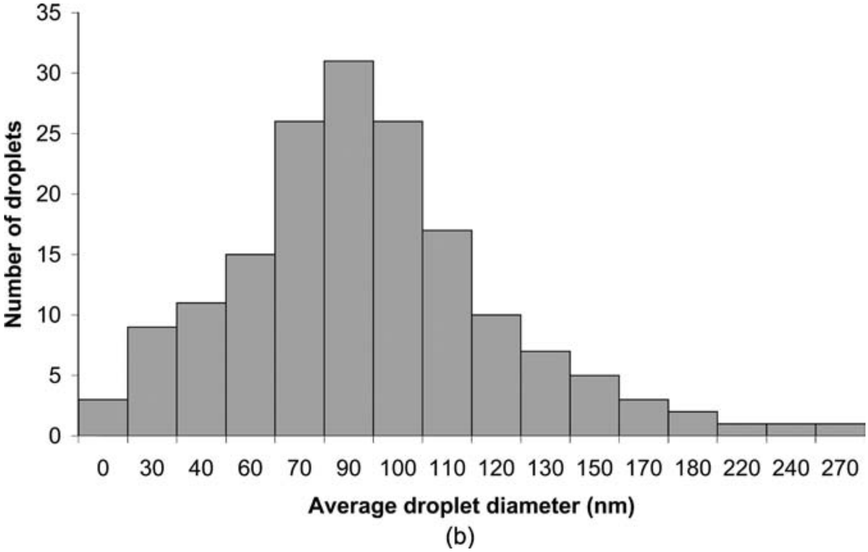

FIGURE 1 Continued.

telecommunication applications. Details of the morphology and mean size of droplets depend on the composition of the sample and its conditions of preparation.

In order to investigate if the obtained samples fulfill the criteria for the desired application that means showing a variation of the mean refractive index upon application of an electrical field without changing the transmission values, samples for optical and electro-optical studies were prepared using standard Fabry-Perot cells. The same experimental conditions as described before were applied to obtain cured samples. Figure 2 shows a representative example of the reflectivity of a Fabry-Perot cell in terms of the wavelength in the off-state and when applying an alternating signal with voltage 350 V and frequency 145 Hz. The response curve is quite sensitive to the amplitude of voltage. It shows oscillations that are shifted when applying an electric field. This shift is used to determine the variation of the mean refractive index Δn. Indeed, the distance between consecutive maxima of the oscillating signal is directly related to Δn as indicated on this figure. A value of $\Delta n = 0{,}022$ was deduced from the experimental curves presented in Figure 2.

The variation of Δn with the applied voltage is exhibited in Figure 3. Each value displayed in this figure was obtained from reflectivity vs wavelength curves at the choosen value of the applied voltage compared to the corresponding curve without application of an electrical field. For example,

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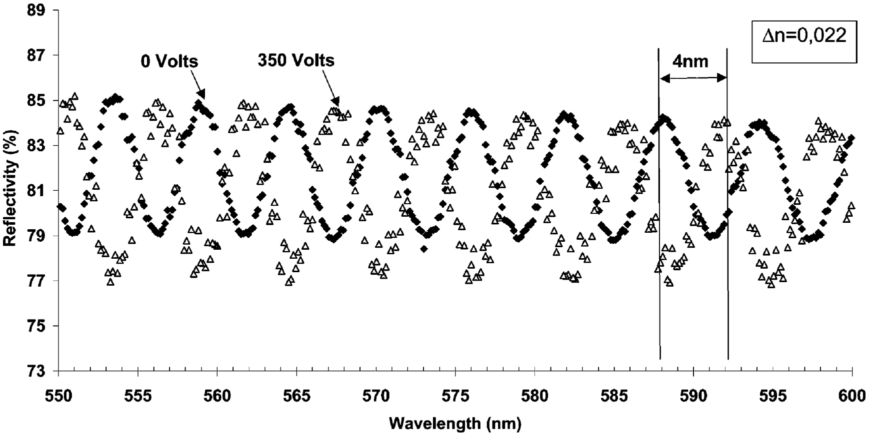

FIGURE 2 Reflectivity of the thiolene/LC system (thiolene (65wt%)/ E7(35wt%)/ Darocur1173 in the off-state and when applying an alternating voltage of amplitude 350 V and frequency 145 Hz.

the result deduced from Figure 2 represents the data couple (x/y) (Voltage = 350 V/Δn = 0,022) in Figure 3.

The bottom curve in Figure 3 corresponds to the first voltage scan applied to the film. Above approximately 250 V the wavelength shift

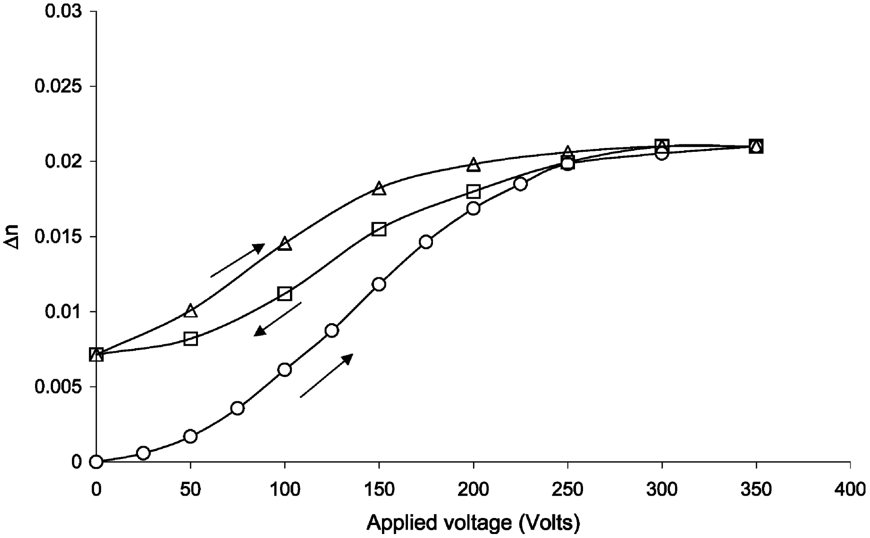

FIGURE 3 Δn versus applied voltage for the thiolene/LC system (thiolene (65wt%)/E7(35wt%)/Darocur1173). The applied signal has a frequency of 145 Hz.

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remains constant and thus Δn exhibits a plateau value. Interestingly the first scan of the voltage is quite different from the subsequent ones. First, Δn increases from zero steadily towards a plateau value as mentioned before. A finite value of Δn was obtained in the descending ramp after reaching zero voltage. Subsequent scans yield a different curve that remains unchanged upon repeating voltage scans up and down. This behavior can be explained by a combination of phenomena reminiscent of hysteresis and memory effects familiar in common PDLC systems [1,4]. The hysteresis comes from the fact that Δn is higher in the direction of increasing voltages compared to the ramp down.

Note that the same plateau value for voltages higher than 250 V was obtained for all scans. Regarding these results together with the high value of Δn compared to other systems under investigation, these findings confirm that the cured thiolene/E7 sample represents a good candidate for telecom applications.

4. CONCLUSIONS

This paper reports results concerning morphology and electro-optical response of PDLC films with nano-sized droplets. The precursor system is made of a selected thiol-ene/E7 mixture polymerized with UV light in the presence of Darocur 1173 as photoinitiator. The morphology obtained by SEM shows a rather uniform distribution of nano-sized droplets throughout the polymer matrix. This was confirmed by looking at the SEM pictures and by analyzing the results using the histogram method. The curves representing the mean refractive index against the applied voltage (i.e., Δn versus voltage curves) exhibit a hysteresis behavior with a strong memory effect.

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