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### UV-CURED POLYMER DISPERSED LIQUID CRYSTALS WITH NANOSIZED DROPLETS

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*The spectral selectivity of the light transmitted by Polymer Dispersed Liquid Crystal films with nanosized liquid crystalline droplets is investigated. We focus on the impact of the method of preparation on the optical transmission versus wavelength. Materials elaborated from selected mixtures of resin A\**

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*and the liquid crystal E7 are considered. A UV-vis spectrophotometer is used to evaluate the spectral transmission of light of the fabricated films in the range of wavelengths from 200 to 1100 nm. Spectral responses are examined in terms of the curing conditions of the initial monomer/liquid crystal/photoinitiator mixtures. The concentrations of photoinitiator and liquid crystal were changed in order to find the best conditions to obtain nanosized droplets within the polymer matrix. The salient features of the method of preparation adopted to obtain PDLC films with nanosized droplets and controlled distribution are discussed.*

*Keywords:* light transmission; nanosized liquid crystalline droplets; PDLC; UV-curing

## INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs) are composite materials consisting of liquid crystal droplets distributed randomly in a solid polymer matrix. These materials are the subject of extensive research in the literature because of fundamental interest and applications involving specific optical and electro-optical properties [1–4]. Recently, more emphasis has been put on the case of PDLCs with droplets having sizes in the scale of nanometers. These systems are sought for their potential use in non-linear optical devices being low scattering of visible light [5–7]. If the size of droplets is comparable to the wavelength of light, the scattering is strong and the film is opaque. On the other hand, for initially transparent films and mean droplet sizes much less than the wavelength of incident light, then the films remain transparent even by applying an electric field.

Optical properties of these materials are intimately related to the nature of molecular species in the compounds and the methods of preparation. In the present work, we report first results evaluating some effects of these methods on the properties of PDLCs with nanosized droplets. The criteria for evaluating these effects are based on the variation of transmitted intensity versus wavelength of the incident beam. The considered films are fabricated according to the classical method of Polymerization Induced Phase Separation (PIPS) of a reactive monomer/liquid crystal/photoinitiator blend exposed to UV light. Different types of reactive monomeric species have been investigated but only the results corresponding to a mixture called A\* are presented in this communication.

## EXPERIMENTAL PART

### Materials

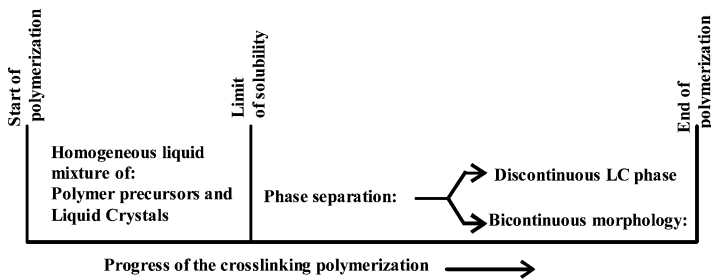
The precursor systems consist of mixtures of commercially available reactive species designated A\*, the liquid crystal mixture E7 (Merck,

Germany), and the photoinitiator Darocur 1173 (Merck, Germany). Several LC compositions are considered besides three different concentrations of the photoinitiator. The results for 0.5 wt.-%, 1.5 wt.-%, and 5 wt.-% Darocur 1173 are presented noting that these concentrations are calculated relative to the amount of A\*.

Recall that the LC E7 is an eutectic mixture of cyanoparaphenylenes exhibiting a single nematic to isotropic transition at 61°C and no other transitions in the entire range of temperature explored in this work. Its glass transition temperature is near -62°C.

## Sample Preparation and Photocuring

The preparation of PDLC films is based upon PIPS mechanism combined with UV curing. A scheme describing the main steps of this procedure is given in Figure 1. First, the LC and the photoinitiator is dissolved in the resin A\* at appropriate quantities, and the resulting blends mechanically stirred for some hours until they become homogeneous. A drop of a mixture is applied on an ITO coated glass plate and sandwiched with a second glass plate prior to radiation exposure. The film thickness was set to 25  $\mu\text{m}$  for all samples considered using calibrated adhesive stripes as spacers. To cure the initial reactive mixtures, two different UV light sources were employed. The first one is a polychromatic source (Minicure Model MC4-300 from Primarc UV technology), delivering a dose of 100  $\text{mJ}/\text{cm}^2$  at 80  $\text{W}/\text{cm}^2$ . A fraction of this energy only is available for photoinitiation in the appropriate wavelength range for the photocuring mechanism. The second source is a fluorescent lamp TL08 (Philips) with a wavelength  $\lambda = 350 \text{ nm}$ , a power output of 1  $\text{mW}/\text{cm}^2$ , and an exposure time of one hour. Due to its weak power output, the latter UV equipment leads to a much slower photopolymerization process. A spectrophotometer of the

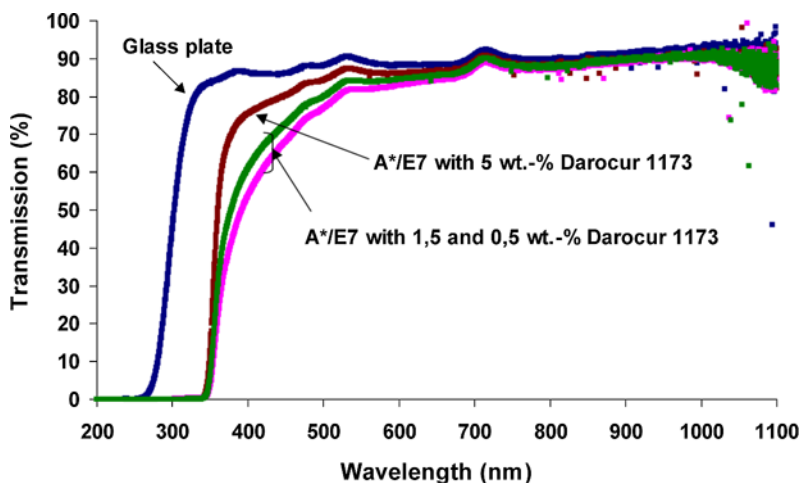


**FIGURE 1** Schematic representation of different steps in the preparation of PDLC films with nanosized droplets by a combination of the PIPS method and UV curing.

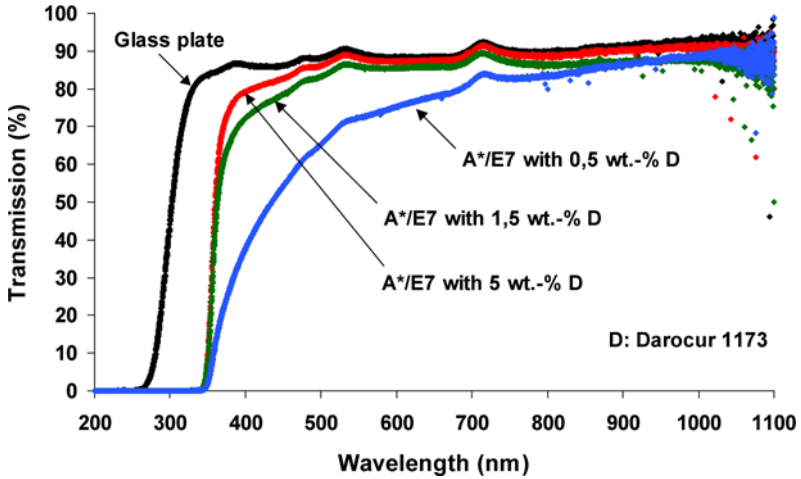
type Varian Cary 50 was used to evaluate the light transmission as a function of the wavelength in the range 200–1100 nm.

## RESULTS AND DISCUSSION

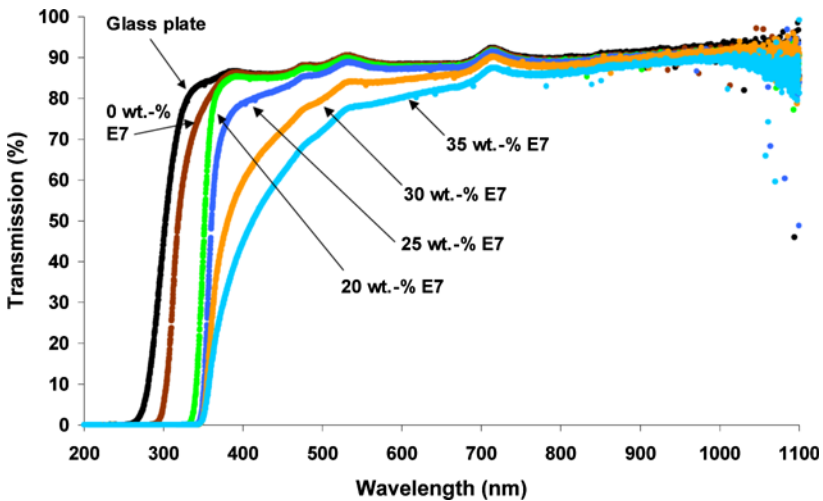
Figure 2 exhibits the light transmission versus wavelength for the 75 wt.-% A\*/25 wt.-% E7 system exposed for one hour to the TL08 UV light. Three different quantities of photoinitiator were employed spanning the concentration range from 0.5 to 5 wt.-%. Only a small variation of the transmission versus wavelength curves was found after curing by changing the amount of photoinitiator from 0.5 wt.-% to 1.5 wt.-%. On the other hand if a concentration of 5 wt.-% Darocur is used in the initial blend, the transmission curve shifts sensitively to higher values. These effects are more pronounced if the Minicure UV source is used instead of the TL08 lamp. Figure 3 shows clearly a strong dependence of the transmission versus wavelength curves on the photoinitiator concentration. The film containing 0.5 wt.-% Darocur 1173 scatters light in the wavelength range of visible light roughly from 400 to 700 nm expressed by relatively low transmission values, whereas the 5 wt.-% Darocur 1173 sample already reaches high transmission values around 400 nm. For a given illumination time, higher photoinitiator concentrations lead to a more crosslinked polymer. As a consequence, droplet sizes will become smaller thus not furthermore



**FIGURE 2** Transmitted light (in %) versus wavelength for the system 75 wt.-% A\*/25 wt.-% E7 exposed to the TL08 UV lamp using three concentrations of photoinitiator. (See COLOR PLATE II)



**FIGURE 3** Transmitted light (in %) versus wavelength for the system 75 wt.-% A\*/25 wt.-% E7 exposed to the Minicure UV source ( $100 \text{ mJ/cm}^2$ ) using three concentrations of photoinitiator. (See COLOR PLATE III)



**FIGURE 4** Transmission versus wavelength for the A\*/E7 system (5 wt.-% Darocur 1173) exposed to the Minicure UV source ( $100 \text{ mJ/cm}^2$ ) using several LC concentrations. (See COLOR PLATE IV)

scattering the visible light. The highest transmission vs wavelength values have been obtained using the Minicure apparatus with a dose of  $100 \text{ mJ/cm}^2$  and 5 wt.-% photoinitiator included in the mixture. In order to modify the density of droplets, the LC concentration dependence has been investigated using the same experimental conditions i.e. 5 wt.-% Darocur and a Minicure dose of  $100 \text{ mJ/cm}^2$ . The results are displayed in Figure 4 where the concentration of LC has been varied from 20 to 35 wt.-%. As expected, the transmission vs wavelength curves tend to lower transmission values if the LC content increases especially in the 350–600 nm range. Plateau values higher than 80% for the transmission are obtained for all LC concentrations investigated considering wavelength ranges higher than 600 nm.

## CONCLUSIONS

This paper reports a selection of results obtained recently on PDLC films with nanosized droplets. The aim of this study was to identify the important parameters that control the size and distribution of droplets within the polymer matrix. The focus here was put on photoinitiator and liquid crystal concentration and the source of radiation curing. The selection criterion was the variation of the intensity of transmitted light versus wavelength. Extension of this work is under progress looking at the variation of morphologies (SEM observations) depending on several parameters: concentration of photoinitiator, LC, UV intensity.

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