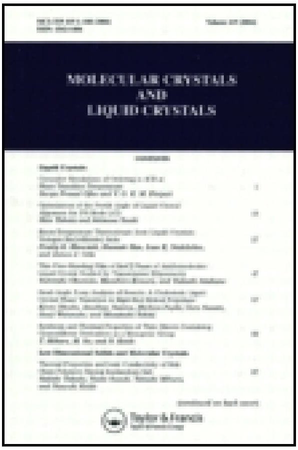

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OFF State Alignment In PDLCs by Polymerization of Monomer Additives

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OFF State Alignment In PDLCs by Polymerization of Monomer Additives

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We have investigated the electro-optical properties of polymer dispersed liquid crystal films obtained by a two step phase separation process. Strong OFF state alignments of the liquid crystal were obtained by the application of an electric field during the photo-polymerization step. This memory effect is not present when the monomer molecules show a low solubility in liquid crystal droplets. The influence of monomer concentration on the OFF state alignment of the liquid crystal has been also discussed.

Keywords: PDLC; Liquid crystals; Composite materials

PACS number: 78.20.Jq; 64.70.-p; 61.30.-v

I. INTRODUCTION

Polymer dispersed liquid crystal (PDLC) films are of particular interest for their applications in electro-optics.[1–3] They are formed by micron-sized liquid crystal droplets dispersed in a polymer matrix. It has been observed that aligned nematic droplets can be obtained if PDLC films are phase separated in the presence of an external force field. The application of either a magnetic or electric field during the phase separation process[3–4] determines an increase of the zero field transmittance. Such an increase is due to the alignment of the liquid crystal molecules induced by the droplets′ walls. The scanning electron microscope (SEM) analysis confirmed that the alignment of the liquid crystal molecules cannot be attributed to a shape deformation of the droplets.

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Recently, Crawford et al.[5] have investigated with optical polarizing microscopy the order of a polymer network and the effect of the application of electric fields during the cure process. Their main result was that the crosslinked polymer network assumes the orientational order imposed by the aligned liquid crystal molecules in the droplets.

Kawatsuki and Ono[6] have shown that the formation of a thin polymerized layer, at the interface between the liquid crystal droplet and the polymer matrix, modify the boundary interactions with a consequent change in the switching fields and response time values.

More recently, it has been observed[7] that the presence of small percentages of monomer additives in polymethylmethacrylate (PMMA) based PDLCs results in a reduction of their switching fields and rise times. The increase of decay times suggests that the monomer contamination of both polymer matrix and liquid crystal in droplets can determine a reduction of PMMA-liquid crystal boundary interactions.

The purpose of the present work is to investigate the effects produced on PDLCs by the polymerization of monomer additives after the thermally induced phase separation of the liquid crystal from the PMMA matrix. Hereafter, these films will be referred to as two step PDLCs.[6] A further aim is to study how the monomer concentration and the application of external fields, during the UV polymerization step, could affect the electro-optical behavior of PDLC films. As shown in our results, strong OFF state alignments of liquid crystal can be obtained when an electric field is applied during the photo-polymerization process. Such memory effect is dependent on the monomer concentration.

II. EXPERIMENTAL PART

Polymethylmethacrylate (Aldrich) and TN10427 (Rolic) nematic liquid crystal were used in the weight ratio 40:60 to prepare control PDLC films by thermally induced phase separation (TIPS). NOA65 (Norland), tripropyleneglycol diacrylate, and tri-methylolpropane triacrylate (both from Aldrich) were used as monomer substituents of PMMA (0 – 15 wt. %). All such monomers are soluble both in liquid crystal and PMMA. Mixtures were fabricated from dichloromethane solutions of PMMA, monomer, and liquid crystal at fixed liquid crystal concentration (60 wt. %). About 1 wt. % of UV initiator (Irgacure 651, Ciba-Geigy) was added in order to perform the second step polymerization. A small quantity of mixtures was introduced in home made cells whose thickness was about 15 μm.

It is known that TIPS films are characterized by a smaller droplet size if they are prepared with rapid cooling rates. Therefore, as a first step of the phase separation process, samples were slowly cooled at a controlled rate in order to achieve droplets of liquid crystal, monomer, and UV initiator with an average diameter of about 1 μm. In fact, the best electro-optical performance of a PDLC is obtained around such droplet size.[1] The electro-optical properties of such one step PDLCs were measured with the optical line described in a previous work.[8] The intensity of incident light measured through pure PMMA cells was assumed as a full scale intensity.

Then samples were UV irradiated with an 80 W high-pressure mercury lamp (10 mW/cm^2 for about 1 hour). Some cells were kept in the ON state by applying a suitable DC electric field during the UV polymerization. Alternatively, some photo-polymerizations were performed in a 7 Tesla magnetic field whose direction was perpendicular to cell substrates. The electro-optical characterization of these two step PDLCs was achieved through the same area previously marked on the one step PDLCs. Then, samples were cut after immersion in liquid nitrogen and vacuum desiccated. Morphology analysis was performed on gold-coated sections with a Leica LEO420 scanning electron microscope.

III. RESULTS AND DISCUSSION

The optical contrast of a PDLC is defined as the ratio between the light transmitted in the ON state and the light transmitted in the OFF state. The PDLC films produced in this work from mixtures of PMMA, monomer, and liquid crystal by a single TIPS process show large contrast ratios, being their OFF state transmittances around 1% and their ON state values about 90%. As reported in figure 1, all samples are characterized by lower switching fields and steeper OFF-ON transitions than control PDLCs. These properties are dependent on the monomer concentration as they are enhanced when the monomer percentage increases. Such behavior was attributed[8] both to the plasticizer effect of monomer on PMMA polymer matrix (which allows the formation of slightly larger droplets) and to the monomer contamination of liquid crystal (which results in lower anchoring energies at polymer-liquid crystal walls).

Typical electro-optical properties of two step PDLCs are reported in figure 2. It can be observed that it is now present:

1. a further reduction in the switching voltages;
2. a slower OFF-ON transition;
3. a lowering of the ON state transmittances to about 80%.

Figures 3a-b show the electro-optical transmittances for two step PDLCs (based on NOA65 and tri-methylolpropane triacrylate) UV polymerized with an electric field on. Each figure reports also the electro-optical response of a control PDLC.

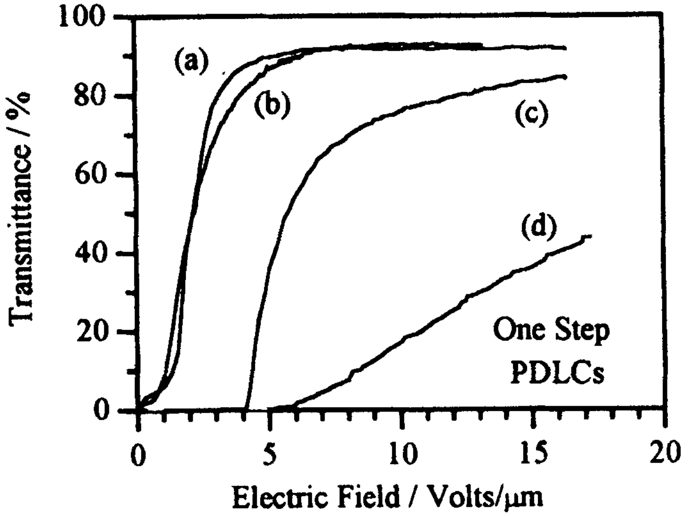

FIGURE 1 Electric field dependent transmittances through PMMA/monomer/TN10427 one step films for a 10 wt. % substitution of PMMA: (a) NOA65; (b) tri-methylolpropane triacrylate; (c) tripropyleneglycol diacrylate. The electro-optical behavior of a control PDLC is also reported (curve d)

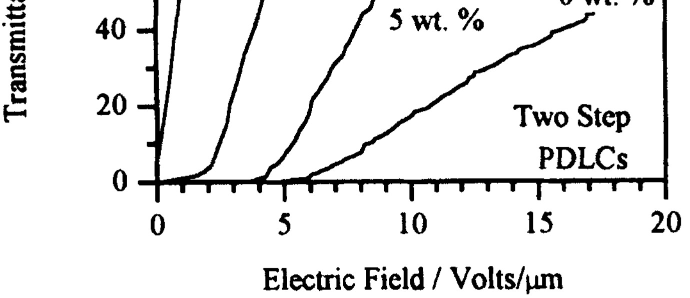

FIGURE 2 Electric field dependent transmittances through PMMA/tri-propyleneglycol diacrylate/TN10427 two step films for different monomer substitutions of PMMA. The electro-optical behavior of a control PDLC is also reported

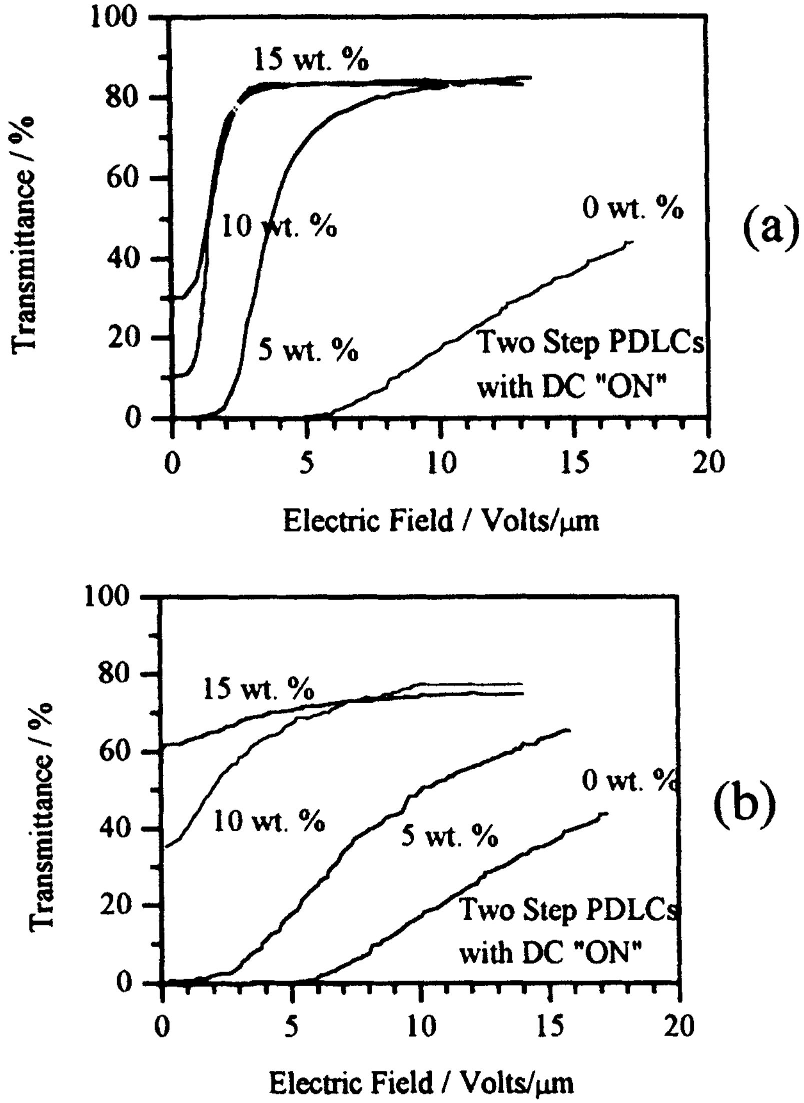

FIGURE 3 Electric field dependent transmittances through PMMA/monomer/TN10427 two step films for different monomer substitutions of PMMA. (a) NOA65; (b) tri-methylolpropane triacrylate. The UV polymerization was performed with samples turned into the ON state by a suitable DC electric field. The electro-optical behavior of a control PDLC is reported in each figure

A large OFF state alignment is present in samples prepared with more than 5 wt. % of triacrylate (T_{OFF}≅35% for 10 wt. % of monomer, and T_{OFF}≅60% for 15 wt. % of monomer). Lower OFF state values are found for samples with NOA65 (T_{OFF}≅10% for 10 wt. % of monomer, and T_{OFF}≅25% for 15 wt. % of monomer). Samples with diacrylate are not characterized by significant electro-optical changes with respect to those reported in Fig. 2 (T_{OFF} less than 5% for 15 wt. % of monomer, data not shown).

When the UV polymerization was performed in the magnetic field, we observed again a reduction in the switching voltages and a slower OFF-ON transition but no evidence of memory effects. We can suppose that the available magnetic field was not able to induce any kind of alignment.

The experimental results are easily explained by assuming the formation in PDLC droplets after the second phase separation of a thin photo-cured polymer layer[6] which:

1. changes the viscosity of the mixture in droplets, which are now purged from monomer molecules;
2. increases the elastic interactions between the PMMA matrix and liquid crystal;
3. causes an optical inhomogeneity[9] of droplets;
4. and is able to keep aligned the liquid crystal molecules.

The presence of a thin polymer layer in two step PDLCs was confirmed by SEM analysis of liquid crystal cavities. Figure 4.a shows a typical photograph of one step sample cavity which results unambiguously spherical and flat. On the contrary, two step PDLCs exhibit corrugated surfaces at the polymer matrix-liquid crystal boundaries (figure 4.b). In fact, it is possible to observe a thin layer of small polymer balls (diameter≅100 nm) coming from the UV polymerization of monomer molecules trapped in the liquid crystal droplets during the first phase separation process. Such layer, grown in the presence of an external field, is the only one responsible of the observed large memory state as there is no evidence of any polymer network inside droplets. In our opinion the alignment of the mesogenic molecules, due to the external field, determines the alignment of the fluid monomer molecules which are trapped within droplets. The UV polymerization turns such a fluid aligned monomer material into a thin polymer layer at the droplet interface which preserves memory of the previous alignment.[10] The imprinted polymer surface keeps the liquid crystal molecules aligned via an interfacial coupling. The strength of surface alignment is related to the polymer thickness and, consequently, to the quantity of monomer molecules which remain dispersed in the liquid crystal droplets after the first phase separation process. It is experimentally evident that samples, characterized by a better solubility of monomer molecules in the liquid crystal and a higher degree of crosslinkage, can develop a thicker shell and a larger memory. As a consequence the order parameter of mesogenic molecules along the field direction can be increased by adding larger amounts of monomer in the mixtures, which lead to a thicker aligned surface bearing a larger imprint.

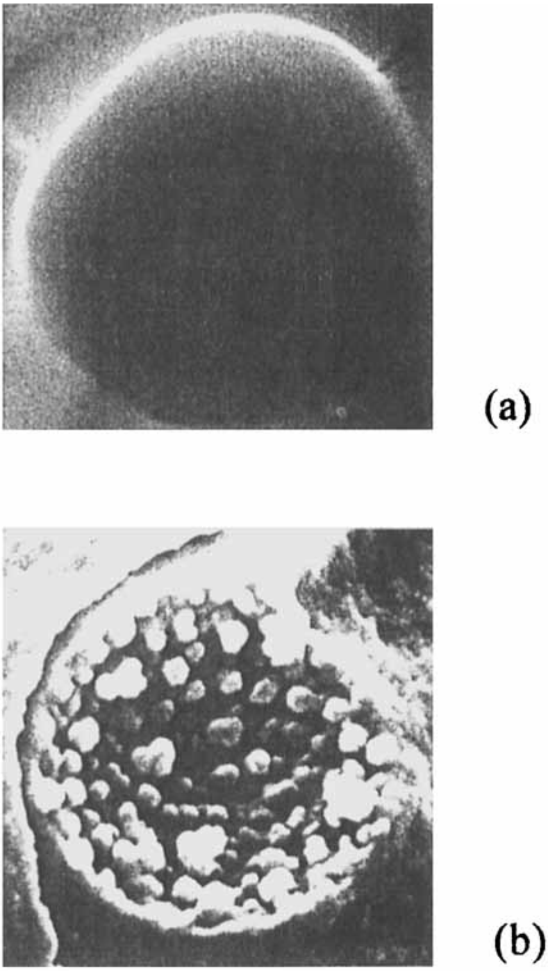

FIGURE 4 SEM photographs of PDLC films: (a) one step PDLC, and (b) two step PDLC. Samples wt. % composition: PMMA: TN10427: tri-methylolpropane triacrylate = 25 : 60 : 15. Droplets diameter $\cong$1 μm. It is possible to observe the presence of a thin layer of small polymer (diameter $\cong$0.1 μm) balls in the two step sample, due to the polymerization of monomer molecules trapped in liquid crystal droplets after the first step phase separation process. The scan area is 1.1 × 1.1 μm^2

IV. CONCLUSIONS

We have observed that the electro-optical properties of two step PDLCs can be affected by the application of an electric field during the UV cure process. The alignment of nematic molecules persists even after the field removal and can be attributed to the formation of an aligned polymer layer at the matrix-liquid crystal boundaries. Therefore, the two step phase separation process can be assumed as a useful tool to modify the properties of conventional PDLCs by an adequate imprinting of the droplet walls.

Acknowledgements

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