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Morphological and Electro-Optical Properties of Polymer Dispersed Liquid Crystals Cured by High Intensity Laser Radiation

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We have studied the morphology and the electrooptical properties of Polymer Dispersed Liquid Crystals prepared by the Polymer Induced Phase Separation technique under high-intensity UV laser curing. Photoinduced thermal convective motions have been observed in the directly illuminated area, which originates unusual morphological patterns consisting of *ordered* and/or *disordered* structures, depending on the curing intensity. We show that transition between ordered (columnar) and disordered (turbulent) motion is possible by increasing the laser beam intensity and the flow patterns associated to both these regimes can be frozen in by the photo-polymerization process. We show also that localized high-intensity curing generates a gradient of the droplet-size distribution outside the directly irradiated area essentially due to the non-uniform spatial-distribution of scattered intensity. This complex morphology reflects into a peculiar electrooptical behavior that could find potential application in new optical devices.

Keywords: PDLC; morphology; electrooptical properties; UV laser curing

INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs) are composite materials consisting of droplets of low molecular weight liquid crystals dispersed in a polymeric matrix. In recent years a great deal of interest has been addressed to the morphological and electro-optical properties of these materials because of the great potentialities in many technological fields [1][2].

Polymer Induced Phase Separation (PIPS) activated by incoherent UV radiation is one of the most commonly used techniques to prepare PDLCs samples which exhibit good mechanical and electrooptical properties. During such process the separation of the liquid crystal (LC) droplets is induced by photo-polymerization and cross-linking of a polymer precursor that is mixed with the LC. Whereas the morphological and physical properties of these samples have been widely investigated in the past, the effects of a coherent UV curing source on the morphology and electrooptical behavior of PDLCs is a subject of investigation still widely unexplored. In this paper we report the morphological and electrooptical properties of PDLCs cured by high intensity coherent laser radiation. We show that whereas low-intensity laser radiation originates the usual droplet morphology, high-intensity curing gives rise to completely new morphologies which exhibit peculiar electrooptical properties.

EXPERIMENTAL

The PDLC samples were prepared using two conductive glasses (3 cm x 1.5 cm) filled by capillarity with a mixture (50% in weight) of the nematic liquid crystal E7 (Merck) and the NOA-65 UV (Norland) photo-curable commercial optical adhesive. The cell thickness was 23 μm. Samples were fixed in the vertical position and were irradiated with a Ar^+ ion laser beam (λ = 333.6-363.8 nm) impinging perpendicularly on the glass plates. Temperature was set at 30°C (±0.1 °C), the exposure time was varied between 8 and 30 seconds and light power varied in the range 6 mW - 400 mW. The diameter of the laser beam on the sample was 1.5 mm. The photopolymerization process starts from the center of the spot and propagates in the plane parallel to the glass substrates with a velocity vector-field characterized by circular symmetry. The morphology of the samples was studied by Scanning Electron Microscopy (SEM). The LC ordering within the polymeric matrix was

investigated by optical microscopy and X-ray diffraction as reported in ref.[3]. The electrooptical properties and the spatial velocity of polymerization were measured using the experimental setup reported in ref.[4]. The intensity profiles of the transmitted beam was detected by a CCD camera and analyzed by means of the IMAGE Pro-plus software.

RESULTS AND DISCUSSION

The experimental results revealed an extremely interesting and unexpected morphology in the volume of the sample directly illuminated by the beam, which involves the formation of peculiar *disordered* or *ordered* structural patterns, depending on the curing light intensity. In fact, in this volume the typical droplet-morphology of PDLCs could not be observed because of the convective motions induced by the strong thermal gradient present in the illuminated region. In our samples two different principal morphological patterns were observed.

When low laser intensity is used, the viscosity of the starting monomer+LC isotropic mixture is high, the fluid velocity is relatively low and the resulting thermo-convective motion is *columnar*[5]. Raising the laser intensity reduces the viscosity of the mixture and consequently increases the fluid velocity.

When the intensity becomes greater than ≈ 5 W/cm^2 the drastic reduction of the viscosity leads to a fluid velocity above the threshold for the onset of *turbulent* motion. The thermo-convective motions are slowed down and finally quenched by the polymerization of the matrix and the consequent structural patterns remain frozen in stable configurations.

These latter consist of well-ordered polymeric *channel* structures, in the case of columnar motion (fig. 1A), and of a typical *disordered* pattern, in the case of turbulent motion (fig. 1B).

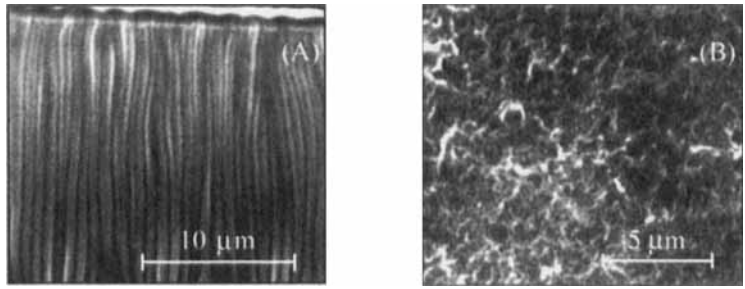

FIGURE 1 SEM micrographs (cross sections) showing the different PDLC morphologies observed in the illuminated regions: (A) ordered *columnar* channel structure and (B) *turbulent* pattern.

In both cases, the irradiated region results transparent to the visible light: in the latter case this occurs because of the formation of submicro-sized LC domains that do not scatter the visible light, in the former case, the reason of the transparency lies in the alignment of the LC molecules along a preferential direction, as will be discussed in the following. Further, the experimental results indicate that with intermediate curing intensities the two morphological patterns were observed simultaneously (fig. 2).

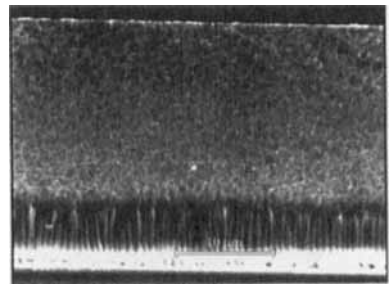

FIGURE 2 SEM micrograph (cross sections) showing at the same time both PDLC morphologies. The curing intensity was 11 W/cm^2

Concerning the morphological properties outside the directly irradiated volume, a gradient of the droplet-size distribution was observed in this region [4] due to the non-uniform spatial-distribution of scattered intensity and of the thermal gradients around the irradiated area (fig. 3).

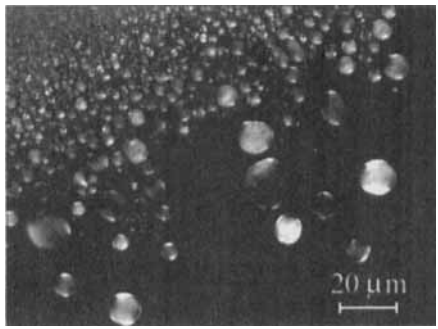

FIGURE 3 Optical micrograph showing the typical PDLC morphology outside the laser-spot area. The dimension of the liquid crystal droplets increases on moving away from this area.

The regular increase of the average droplet's radius that is observed on moving away from the laser-spot is related to the curing technique. In fact, the photopolymerization process outside the irradiated volume of the sample is activated by the light scattered from the high-power direct beam. The intensity of the scattered UV light reduces with the distance from the illuminated region and consequently the average droplet size increases. The spatial extent of this droplet-size gradient was found to be strongly affected by the spatial velocity of polymerization which in turn depends on the intensity of the curing laser beam. This dependence has been investigated in detail by means of a properly designed experiment reported elsewhere [4]. Figure 4 reports the spatial velocity of polymerization, v, against the curing power, measured at two points located at different distances, namely 2 mm and 4.5 mm, from the center of the Ar^+ spot. The lowering of v with increasing the distance d from the spot is due to the reduction of the laser light intensity whereas the increase of v with the laser power is related to the higher polymerisation rate.

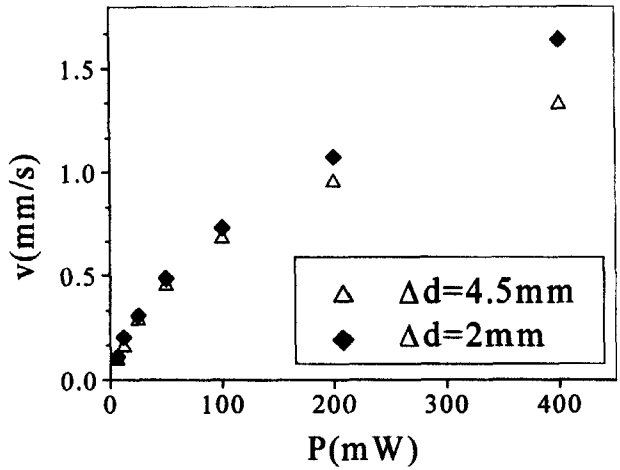

FIGURE 4 Spatial polymerization velocity as a function of the curing power: the symbols (♦) and (△) refer to the He-Ne spots located at Δd=2 mm and Δd=4.5 mm, respectively, from the center of the Ar^+ spot.

The peculiar morphology observed in these samples reflects into unique properties. In the irradiated area, the most relevant consequence of regular motion driven by convective heat transfer process is the formation of a highly-ordered columnar polymeric structure along which the LC molecules are forced to orient. This leads to a macroscopic orientation of the LC director, without application of mechanical or electric/magnetic external fields. The alignment of the LC director inside the polymeric channels has been revealed by conoscopic analysis and X-ray diffraction measurements [3]. The electrooptical properties of these samples can be conveniently discussed with reference to figure 5, where the two-dimensional (2D) light intensity distribution of the transmitted He-Ne probe laser beam is reported for a sample cured at an intensity of about 700 mW/cm^2. The three pictures refer to different values of an external d.c. applied voltage V. At small voltages (fig. 5A), the transparent area of the film is smaller than the size of the curing laser spot. This area was present in all the investigated samples, with spatial extension growing with the curing intensity. On increasing voltage, the

transparent region extends outside the directly illuminated area, with circular symmetry. However, points located farther become transparent at lower voltages than points located closer to the center of the Ar^+ beam because the reorientation field (voltage/film thickness) scales approximately as the inverse of the droplet size [1][2].

Accordingly, smaller droplets require higher fields to be reoriented and a continuous widening of the transparency area is observed on increasing V, proceeding from outer to inner regions (fig. 5B-C).

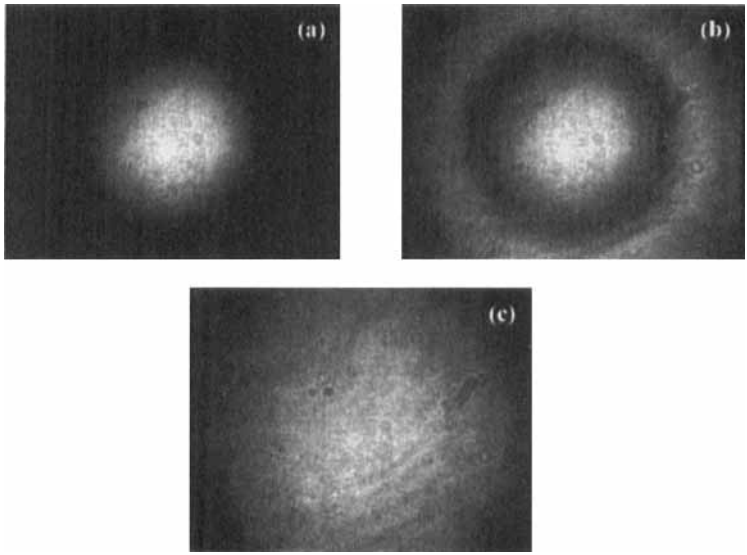

FIGURE 5 2D representation of the transmission properties of a PDLC film under different values of the applied voltage V. The curing intensity is 680 mW/cm^2. Figures 5(a)-(c) reports the 2D intensity distibution of the transmitted beam, corresponding to 10 V (a), 30V (b), and 80 V (c), as detected by a CCD camera.

This behavior makes it possible to control both the spatial extension and the intensity profile of the transmitted beam [4]. In addition, the application of a time-dependent voltage in the form of a

slow ramp leads to a continuous radial advance of the transparency wavefront, with a velocity dependent on the slope of the ramp. Similarly, application of a low-frequency sinusoidal electric field gives rise to a modulated reversible *iris* effect.

A similar electro-optical behavior was observed for samples cured at higher intensities. However, on increasing intensity the thermal effects on the droplet-size distribution become stronger and the temperature of the sample in the region of the tail of the gaussian incident beam increases. This favors the formation of a ring close to the border of the spot with a droplet-morphology characterized by very small radii. These droplets are small enough to require very high fields to be reoriented but, at the same time, are big enough to scatter the visible light. Accordingly, this ring remains opaque under any applied voltage lower than the maximum value allowed by our experimental set-up (100 V). Using higher curing intensities, however, the inner spot turn out to be brighter than that obtained at low curing intensities. For these reasons, in practical applications a compromise between the requirement of high transparency and reasonable reorienting fields is needed.

CONCLUSIONS

We have reported the morphological and electrooptical properties of PDLCs cured by high intensity laser radiation. The experimental results revealed the possibility of achieving LC ordering through freezing of the thermal convective motions activated by the photoinduced thermal gradients. This process, whose velocity is strongly dependent on the curing intensity, leads to a complex morphology in the direct illuminated region, which consists of *disordered* and *ordered* structural patterns. We have found that under certain experimental conditions it is possible to obtain macroscopically ordered channel structures along which the LC molecules are aligned. This feature is extremely interesting in view of the realization of an easy control of the LC orientation on a molecular scale without application of mechanical or electric/magnetic external fields. Outside the directly irradiated area, localized high-intensity curing generates a gradient of the droplet-size distribution as consequence of the non-uniform spatial-distribution of scattered intensity. The particular morphology of these samples reflect into a peculiar electrooptical behavior that could find application in optical devices.

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