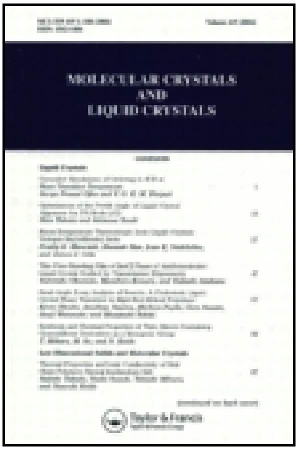

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Liquid Crystal Ordering by Freezing of Thermal Convective Motion in Polymer Dispersed Liquid Crystals

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Liquid Crystal Ordering by Freezing of Thermal Convective Motion in Polymer Dispersed Liquid Crystals

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This paper reports on the first observation of thermal convective motion in high-intensity photocured PDLC mixtures and demonstrates the possibility of LC ordering through the freezing of this thermal convective motion. The dependence of laser-cured PDLC films morphology on curing parameters such as light intensity, curing time, and sample temperature have also been studied. It is shown that the transition between ordered columnar and disordered turbulent motion is possible by increasing the laser beam intensity and that the flow patterns associated with both these regimes can be frozen by the photopolymerization process.

Keywords PDLC, morphology, electrooptical properties, UV laser curing

INTRODUCTION

Polymer dispersed liquid crystals (PDLCs) are composite materials in which nematic liquid crystals (NLC) are phase-dispersed as droplets in a polymer matrix [1]. The use of UV irradiation to initiate the free radical polymerization of unsaturated monomers is one of the best methods to prepare durable PDLC films with good mechanical and electrical properties. Incoherent radiation has generally been used to polymerize PDLC samples characterized by well-defined distribution functions of the liquid crystal (LC) droplets' size [2, 3] whereas coherent laser radiation has been recently proposed as a UV curing source to obtain holographic gratings in these materials [4, 5]. In spite of the large variety of innovative applications

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involving these materials, the laser-induced phase separation process has not been thoroughly investigated yet and only very few papers concerning this topic are available in the literature [6, 7]. In particular, the dependence of the phenomenon on the peculiarities of laser irradiation such as the high local intensity is completely unexplored. With the aim of providing new insights on this subject, we investigated the effects of light intensity, exposure time, and sample temperature on the morphology of PDLC mixtures. This study was performed with the use of different complementary techniques such as optical and scanning electron microscopy, electrooptical characterization, and X-ray diffraction (XRD). The experimental results show that the temperature gradient due to the high-intensity local irradiation originates a thermal convective motion, and the peculiar nature of the investigated samples makes it possible to freeze its kinetics during the time evolution.

In this paper, we report the first demonstration of the possibility of LC ordering by the freezing of thermal convective motion in high-intensity photocured PDLC mixtures. The most relevant consequence of this process is the formation of an ordered and stable columnar polymeric structure along which the LC molecules are forced to orient. This possibility leads to a macroscopic orientation of the LC director without any surface mechanical treatment. In this respect, these materials operate as self-ordering structures. This ordering is extremely interesting in view of achieving an easy control of the LC orientation on a molecular scale as well as in molecular micro-assembly without the application of mechanical or electric/magnetic external fields.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The PDLC samples were prepared using two conductive glasses (3×1.5 cm) filled by capillarity with a mixture (50 wt%) of the nematic liquid crystal E7 (Merk) and the NOA-65 UV (Norland) photocurable commercial optical adhesive. The cell thickness was 23 μm. The samples were fixed in a vertical position and irradiated with an Ar^+ ion laser beam ($\lambda = 333.6$–363.8 nm) impinging perpendicularly on the glass plates. The temperature was set at 30°C (±0.1°C), the exposure time was varied between 8 and 30 s and the light power varied in the range 6–400 mW. The diameter of the laser beam on the sample was 1.5 mm. It is worth noting that the conductive glasses used absorb more than 30% of the incident light in the explored wavelength range [8]. The light transmitted through the glass can excite the photoinitiators, thus originating a fast polymerization process. Because of the light scattered from the high-power direct beam, photopolymerization extends outside the directly illuminated area with circular symmetry. The dependence of the polymerization rate on the intensity I of the UV laser is described by [9] by $\sqrt{I}$, and the scattered intensity is proportional to $1/r^2$, where r is the distance from the irradiated spot. Accordingly, the polymerization rate changes with the distance from the center of the spot.

Concerning the morphology of the samples, the SEM analyses show an extremely interesting and unexpected behavior. It is known that the size of the liquid crystal domains in UV-cured PDLCs is closely connected to the intensity of the curing light. In particular, the domain size decreases with increasing UV intensity. In agreement with this, in the region outside the Ar^+ spot of the samples we always observed the classical PDLC morphology, consisting of droplets whose dimensions progressively increase on moving away from the illuminated area (Figure 1). However, this behavior was clearly detected outside the illuminated region where light scattering is the dominant effect [10]. On the contrary, in the irradiated area, a different behavior was observed. In fact, in addition to the change in size of the LC

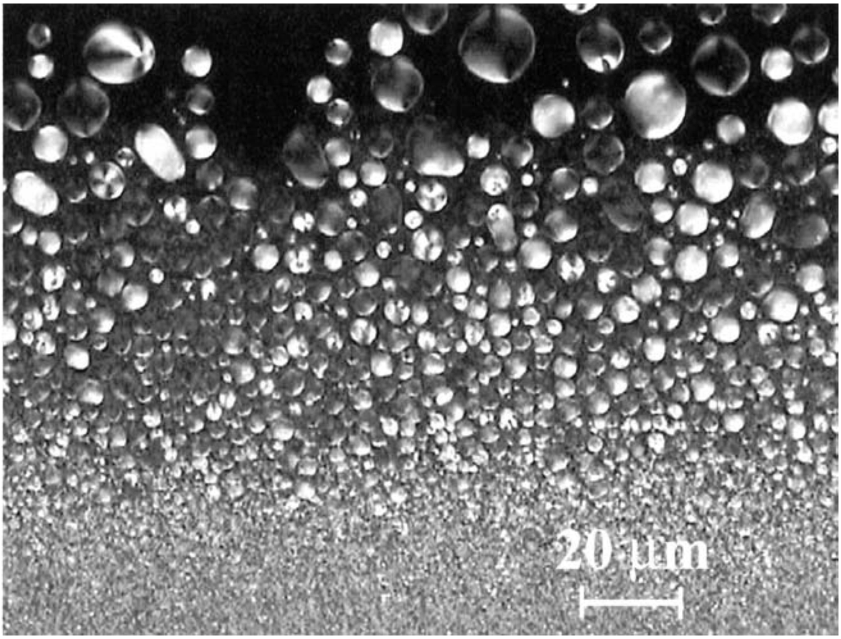

FIGURE 1 Optical micrograph showing the typical PDLC morphology outside the laser-spot area. The dimension of the liquid crystal droplets increases on moving away from this area.

domains, different curing intensities lead to completely different structures. In this area, the typical droplet-morphology of PDLCs cannot be observed because of the convective motions induced by the strong thermal gradient that is present in the illuminated region. On the contrary, depending on the light intensity two new principal morphologies were observed, as shown in Figure 2.

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 thermoconvective motion is *columnar* [11, 12]. The columnar motion is essentially due to the presence of a shallow heated surface layer near the irradiated surface as a direct consequence of the irradiation process. As the heating proceeds, this layer becomes unstable and breaks up to form the columnar motion [13, 14]. At this stage, the temperature difference over the whole depth of the sample differs from the theoretical classic criterion given by Rayleigh [11] in that the assumption of linear temperature profile throughout the entire fluid layer is not satisfied. As heating of the irradiated plate proceeds, however, the conditions envisaged by Rayleigh are approached and a linear temperature profile ultimately extends from the bottom surface to the top. At this stage *cellular* motion sets in, and the critical value of the temperature difference across the boundary glass surfaces can be described in the framework of Rayleigh's theory. However, in our experimental condition, due to the high velocity of propagation of the photoinduced polymeric network [10], the columnar motion can be observed only for low values of the laser intensity, whereas the cellular motion is inhibited by the photopolymerization process.

On raising the laser intensity, the viscosity of the mixture reduces and consequently the fluid velocity increases. When the intensity becomes greater than $\approx 5\ \mathrm{W/cm^2}$ the drastic reduction in viscosity leads to a fluid velocity above the threshold for the onset of *turbulent* motion. The thermoconvective motions are slowed down and finally quenched by the polymerization of the matrix, and the consequent structural patterns remain frozen in stable configurations. The latter consist of ordered polymeric *channel* structures in the case of columnar motion (Figure 2a) and of a typical *disordered* pattern in the case of turbulent motion (Figure 2b). For intermediate intensities the two patterns can be observed simultaneously. It is worth noting that on reducing the light intensity both the network turbulent pattern and the channel structure tend to increase in size. In both cases, the irradiated region is completely transparent to visible light. In the case of turbulent motion, this can be easily explained because of

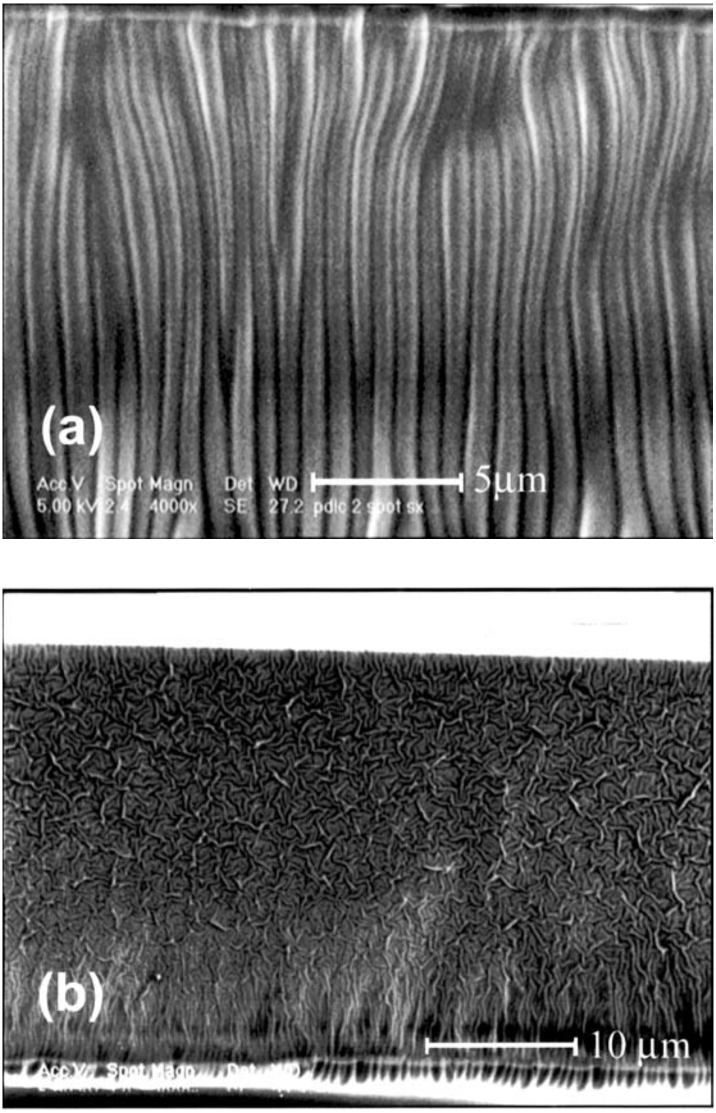

FIGURE 2 SEM micrographs showing the different PDLC morphologies observed in the illuminated regions: (a) ordered columnar, channel structure and (b) typical turbulent pattern.

the presence of very small LC domains that are unable to scatter visible light. In the other case, the reason for the transparency of the irradiated spot lies in the alignment of the liquid crystal molecules along the polymeric channel direction.

The measurements performed to study the morphology dependence on the exposure time revealed no appreciable differences in the irradiated area among samples cured at fixed intensity for different curing times (8–60 s). On the other hand, outside the irradiated area the effects due to different exposure times are very visible. In this region, the effect of the exposure time results in an increase in the dimension of the LC domains with increasing time. This result seems to be reasonable considering that, even in the case of low intensities, the polymerization rate is high enough for polymerization to take place in the irradiated regions within fractions of a second (i.e., less than the minimum investigated exposure time). On the other hand, the experimental technique used to produce the samples did not give good results with exposure times less than 8 s, especially at low intensities.

The LC orientation inside the illuminated region of the PDLC samples was studied by X-ray diffraction and optical microscopy. As a starting point the room temperature X-ray diffraction pattern of the E7 NLC was acquired, and it is shown in Figure 3. The sample was held in a 1 mm Lindemann glass capillary placed orthogonally to the incident beam along the vertical z direction. The measurement was performed in transmission mode. The slight anisotropy visible in the spectrum is due to the partial alignment of the LC induced by the capillary walls.

The wide angle diffuse ring is due to the short range liquid-like order and corresponds to about 4.5 Å. The small angle diffuse signal located on the meridional line is associated with the longitudinal molecular correlation and corresponds to a spacing of about 26.5 Å(comparable to the molecular length).

The XRD measurements on the PDLC samples were performed in the reflection mode after removing the upper glass substrate from the cell. Each sample was mounted with the lower glass substrate fixed to a horizontal stage, slightly tilted in the direction of the incident beam. Figure 4 shows a typical example of the low-angle XRD pattern measured for these samples. This last spectrum displays a diffuse ring at a scattering angle of $2\theta \cong 3.4°$, which in the real space corresponds to a spacing of $d \cong 26.5$ Å. As shown before, this is the value of the average molecular length of E7 in the nematic phase. Unoriented NLC would produce a uniform distribution of the scattered intensity, whereas the azimuthal intensity distribution of the ring is not uniform and exhibits a pronounced maximum at $\chi \cong 180$ deg (inset of Figure 4). This strong anisotropy reflects the preferential alignment of the LC molecules parallel to the vertical direction (i.e., along the polymeric channels).

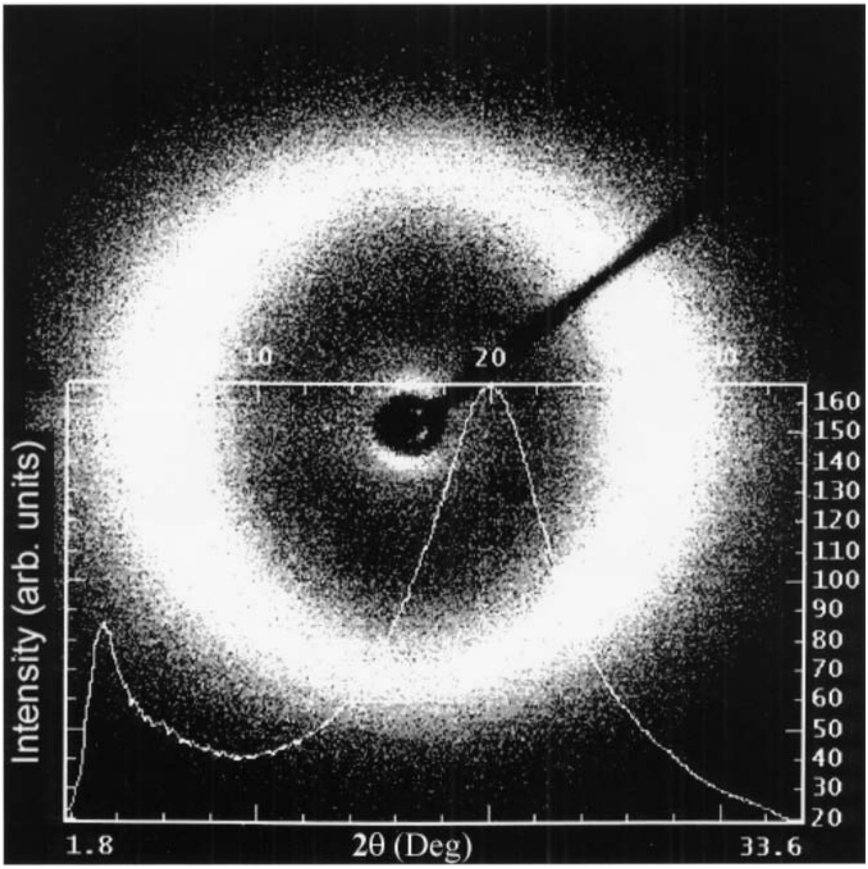

FIGURE 3 X-ray diffraction spectrum of the LC E7 in a confined cylindrical geometry.

Conoscopic measurements confirmed the XRD data, revealing the presence of well-ordered uniaxial structures perpendicular to the glass plates. The measurements were performed on the irradiated region after removal (by chemical etching) of the thin surface layer of LC molecules in close contact with the glass substrate. This interface layer (about 5 μm thick) is responsible for the surface radial orientation of the LC director, whose presence can be easily detected by orthoscopic measurements. For samples irradiated with laser powers between $\cong 12$ and 25 mW, the principal isogyres are very visible (Figure 5), and rotation of the microscope stage does not affect the shape of the cross arms. Moreover, in these conditions the melatope is always dark, thus indicating that no path

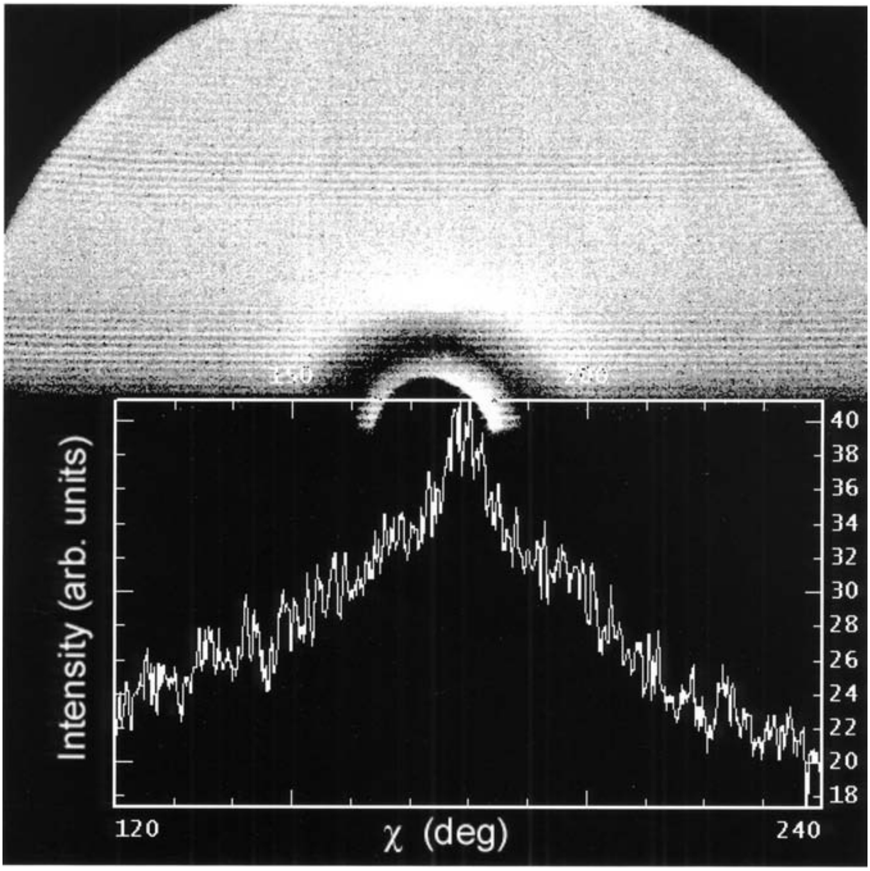

FIGURE 4 X-ray diffraction spectrum of the PDLC sample. Monochromatized CuKα radiation ($\lambda = 1.54$ Å) was used. The sample-detector distance was 30 cm. The inset reports the azimuthal profile of the diffuse ring at $2\theta = 3.4°$.

difference (or at least only a small difference) occurs between the light travelling along the optical axis and the light travelling close to it. The results of the conoscopic measurements are in agreement with the sample morphology as observed by SEM. In fact, when the channels are well defined (for laser powers up to $\cong 50$ mW in our experimental conditions) the LC molecules are well ordered and the conoscopic cross is symmetric and clearly defined. On the other hand, in the high power regime ($>$ 50 mW) the disordered network structure replaces the ordered channel configuration, which results in distortion of the conoscopic image. Similar analyses performed on samples without liquid crystal show the complete

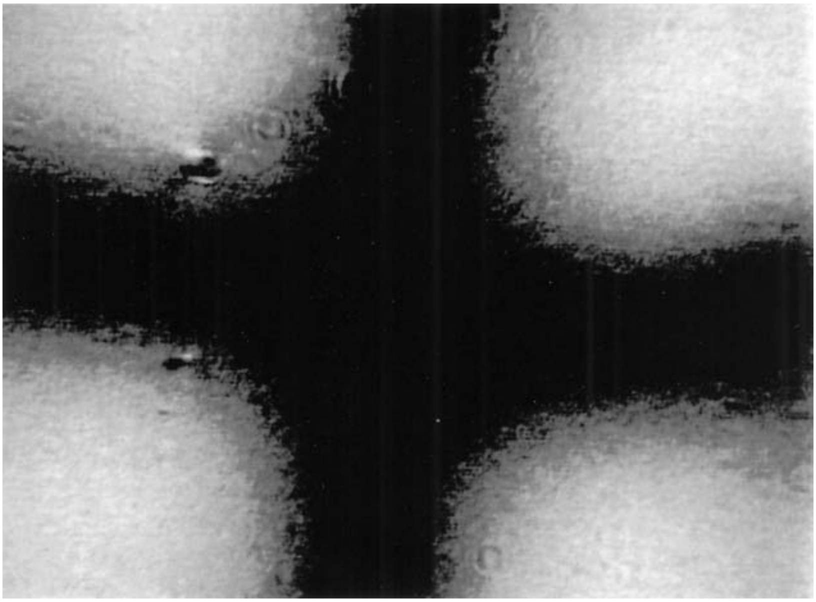

FIGURE 5 Typical conoscopic image recorded in samples irradiated with laser powers between 12 and 25 mW. The principal isogyres are very visible in the picture.

absence of the above described structures, thus indicating that the observation of these is directly connected to the presence of the liquid crystal and to its polymerization-induced orientation.

CONCLUSIONS

In conclusion, for the first time we have observed thermal convective motion in high-intensity photocured PDLC mixtures, and we have demonstrated the possibility of achieving LC ordering through the freezing of this thermal convective motion. This unique possibility is related to the peculiar nature of the investigated materials. We have found that under certain experimental conditions it is possible to obtain ordered channel structures along which the LC molecules align. This feature is very attractive in view of achieving an easy control of LC orientation on a molecular scale without the application of external electric or mechanical fields. An analytical description of the thermal convective motion in these materials is in progress.

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