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High Intensity UV Laser Curing of Polymer Dispersed Liquid Crystals

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As it is well known, the final morphology of PDLCs samples depends on a number of parameters among which light intensity, curing time and temperature are probably the most important once one has choose a particular mixture to cure. In this work, we show the influence of these different external curing parameters on the film morphology of PDLCs obtained by strong UV laser irradiation of the homogeneous prepolymer-liquid crystal mixture. In particular, we show that some of these parameters can affect the morphological uniformity of the samples and can give rise to a highly interconnected 'channel' pattern, while the classic 'droplets' morphology is almost completely lost.

Keywords: PDLC; Phase separation; Laser curing

INTRODUCTION

Polymer Dispersed Liquid Crystals (PDLCs) are composite materials in which a nematic liquid crystal is phase-separated, usually in form of nearly spherical droplets, in a polymer matrix [1]. One way for fabricating a conventional PDLC is the photo-polymerisation induced phase separation (PIPS). In particular, the use of ultraviolet (UV) radiation to initiate the free radical polymerisation of unsaturated monomers is one of the most common methods to obtain durable PDLC films with good mechanical and electrical properties. Generally, a diffuse incoherent light is exploited to induce the photo-polymerisation and, as a consequence, the phase separation process. This originates the well known droplet morphology with a droplet size

distribution which is strongly dependent on several external curing parameters, such as for example UV intensity and exposure time [2,3]. It has been shown in a previous paper [4] that by using a coherent UV beam as curing source, fast curing can be obtained leading to peculiar morphologies of the final film. In particular, the formation of interconnected channels as a result of the liquid crystal phase separation, instead of the conventional droplets nucleation, was reported and discussed.

In order to figure out the role of the laser–induced local temperature rise during irradiation and of the high polymerisation speed due to the high laser intensity on the observed "non conventional" PDLCs morphology, a detailed study has been performed on several samples cured at high intensity. In this work we show how light intensity, exposure time and temperature can affect the phase separation process and thus the morphology in laser cured samples. The used laser intensity varies in the range ($300 \div 20 \times 10^3$) mW/cm^2, which means that we recovered the curing conditions used in reference [4] for some of the analysed samples and we used much higher intensity values for the remaining ones.

EXPERIMENTAL

A detailed investigation of the laser curing process has been carried on for the standard mixture NOA65-E7 (50%-50% by weight). A (1.5x3.0) cm^2 sandwich cell made by two ITO coated glass plates 23 microns thick was filled by capillarity at a fixed temperature of 55°C with the E7 and pre-polymer mixture. Mylar spacers has been used to control the film thickness. The sample was fixed in vertical position and was irradiated by a laser beam with a spot diameter of 1.5 mm impinging perpendicularly to the glass plates. Sample morphology has been analyzed by Scanning Electron Microscope

(SEM). Details on sample preparation have been given elsewhere [5]. Fixing the sample temperature at T_0=30°C exposure time and light intensity have been varied according to the following table. The arrows connect the equal values of the energy density.

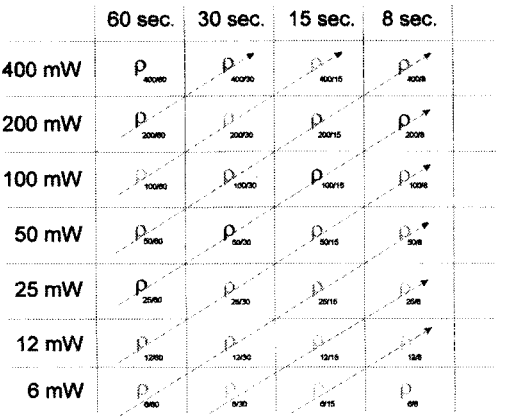

TABLE 1 Exposure time and curing power ranges. Arrows connect samples for which the energy density has the same values.

Measurements of the temperature reached by PDLC samples during the curing process, have been performed by means of a standard thermocouple fixed on the irradiated surface with a thermo conductive glue.

THE PHOTO-POLYMERISATION PROCESS

Concerning the details of the photo-polymerization process, we report the general reaction kinetic scheme for free radical addition reactions. Photo-activation of the initiator I forms free radical which can create an activated species A•. Reactions of this species with a monomer M completes the

initiation process. During the propagation stage reaction of the activated species with monomer causes rapid chain growth. The termination step ends the reaction.

Initiation

$$I \xrightarrow{h\nu} I\bullet$$

$$I\bullet + A \rightarrow A\bullet$$

$$A\bullet + M \rightarrow AM\bullet$$

Propagation

$$A(M)_n\bullet + M \rightarrow A(M)_{n+1}M\bullet$$

Termination

$$A(M)_m M\bullet + T \rightarrow A(M)_m MT$$

T is the molecule that ends the polymerization reaction.

The commercial optical adhesive Norland Optical Adhesive NOA-65, that we have used in all our experiments has usually the following general reaction scheme:

Initiation

$$I \xrightarrow{h\nu} I\bullet$$

$$I\bullet + HSR \rightarrow RS\bullet$$

$$RS\bullet + CH_2 = CHCH_2R' \rightarrow RSCH_2\dot{C}HCH_2R'$$

Propagation and Termination

$$RSCH_2\dot{C}HCH_2R' \xrightarrow{CH_2=CHCH_2R'} RSCH_2\underset{\displaystyle CH_2\dot{C}HCH_2R'}{\overset{|}{C}}HCH_2R'$$

$$RSCH_2\dot{C}HCH_2R' \xrightarrow{HSR} RSCH_2\underset{\displaystyle SR}{\overset{|}{C}}HCH_2R$$

The first two reactions are initiation steps. The third reaction represents the polymerization reaction, while the fourth reaction represents chain transfer.

Figure 1 shows the absorption spectrum of 1 mm thick conductive glasses used as substrate in our cells. It is easy to observe that about 30% of the laser light is absorbed in the range of 333.6-363.8 nm. The remaining 70% of transmitted light can excite the photo-initiators and cause a very fast polymerization process.

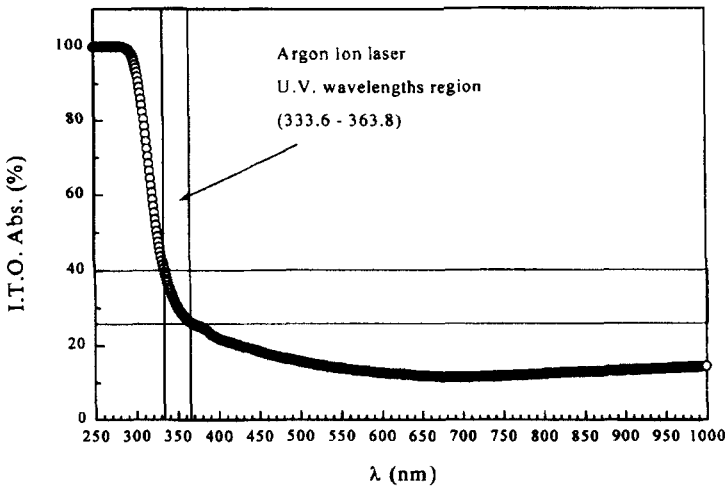

FIGURE 1 Absorption spectrum of ITO conductive glasses.

RESULTS

Figure 2 shows the cross section of the irradiated region of the PDLC cured at 400 mW (which corresponds to $20x10^3$ mW/cm^2) after 30 s irradiation, at different magnifications.

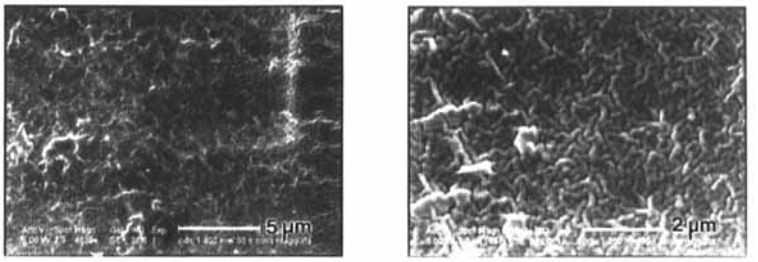

FIGURE 2 Cross section of the irradiated area of the PDLC cured at 400 mW with 30 s exposure time.

As can be seen, the morphology is very complex showing a highly interconnected polymer network with small liquid crystal domains randomly dispersed in the sample. Due to the small liquid crystal domains size, the irradiated region appears completely transparent to the visible light.

Moving away from this region, it is possible to observe a different morphology with a well defined channel pattern (fig. 3), which changes into the classical droplet morphology only very far from the irradiated area. By lowering the curing intensity, the channel pattern reported in figure 3 appears in the irradiated areas, while droplets are always present far from this region. The directly irradiated area of the sample looks completely transparent to the visible light, also in this case.

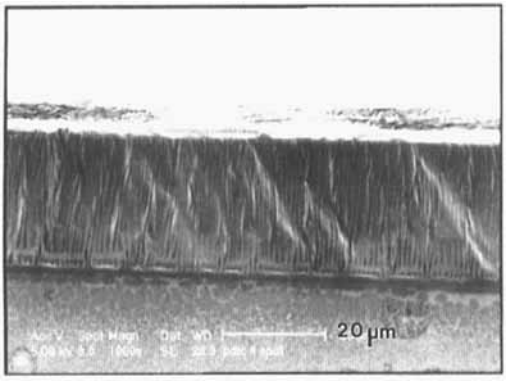

FIGURE 3 Typical channel pattern obtained by reducing the light intensity

As a general trend, all the observed structures tend to increase in size by decreasing the light intensity.

Preliminary measurements of the speed of polymerisation suggest that, because of the high velocity of the process, variations of the exposure time can affect just slightly the sample morphology inside the illuminated region, at least under the used experimental conditions. SEM observations support this hypothesis. On the other hand, our characterisation method does not easily allow the observation of PDLCs cured for even shorter times. Actually, the use of different exposure times has appreciable effects outside the illuminated area where light and heat diffusion are the most important effects. In particular, by increasing the curing time, all the observed structures tend to increase in size.

Because of these combined effects of the curing intensity and exposure time, equal values of the energy density can lead both to similar

morphologies with different domains size (especially in correspondence of non-illuminated regions) and to completely different morphologies.

In many samples it is also possible to observe a transition from a morphology typical of the "spinodal decomposition" process to a "nucleation and growth" phase separation moving away from the irradiated area, as shown in fig.4.

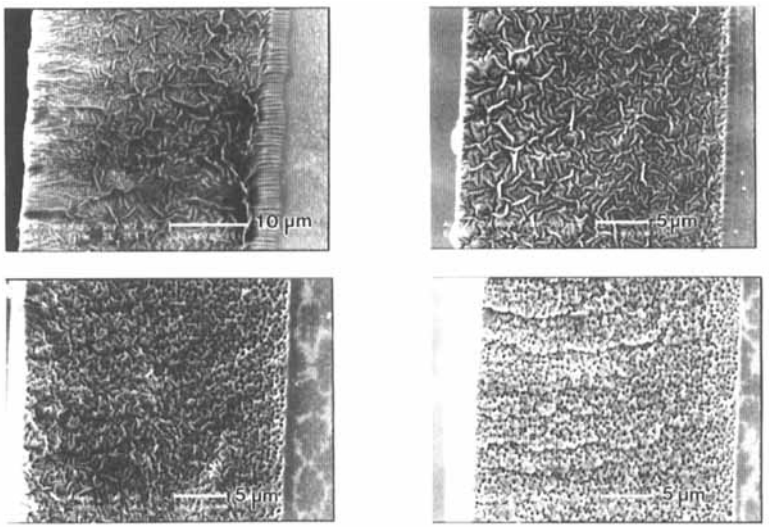

FIGURE 4 From left to right: transition from the morphology typical of spinodal decomposition to the one typical of nucleation and growth. UV intensity decreases from left to right.

Measurements of the temperature reached by the PDLC during the curing process for different laser intensities, are reported in fig.5 (t_0=60 sec).

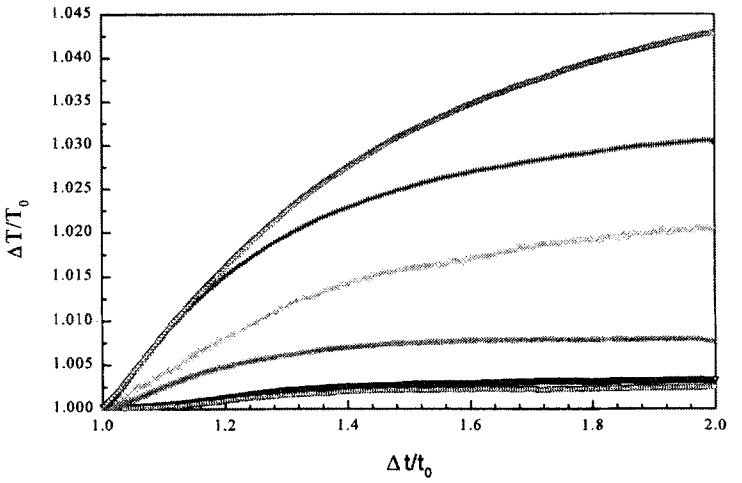

FIGURE 5 Temperature reached by PDLC samples vs exposure time. Laser power varies from 400 mW (upper curve) to 12 mW (lower curve).

As can be seen, sample temperature increases with time. Moreover, temperature rise is faster for samples cured at higher UV intensity. It is worth noting that the reported temperature values are certainly lower than those reached inside the sample. Work is currently in progress to improve the experimental technique for temperature measurements inside the samples.

DISCUSSION

Our experimental results show that the laser curing of PDLC samples always brings to non conventional film morphologies with an intensity dependent domain size.

The main differences between the conventional UV curing and the laser curing technique are the high temperature rise in the illuminated region connected to the local irradiation and the symmetrical light diffusion, which decreases moving away from the light spot, obtained by using laser light. This probably leads to the formation of strong thermal gradients in the directly irradiated area, which interfere in some way with the phase separation process and originate both the observed interconnected polymer networks and the channel pattern, instead of the classical droplet morphology. Outside this region, it is always possible to observe the classical transition between "spinodal decomposition" and "nucleation and growth" phase separations, which can be explained referring to the temperature dependence of the activation energies for nucleation and diffusion, as already reported in a previous paper [5].

The illuminated region appears completely transparent in all the analyzed samples. In PDLC cured at high intensity, the lack of scattering of the visible light is due to the small liquid crystal domains visible in fig. 1, as already observed in laser cured samples [4]. In samples irradiated with lower laser intensity the explanation seems to be more intriguing. In this case in fact, experimental evidences suggest that the observed strongly anisotropic channel pattern tends to arrange the LC molecules in a very ordered way along the channel direction. This liquid crystal alignment is responsible for the samples transparency, since in this case PDLCs should be optically homogenous just as if an external electric field aligned the liquid crystal molecules in the same direction thus reducing the refractive index mismatch to nearly zero values. Further investigations are in progress to confirm these preliminary hypothesis.

CONCLUSIONS

The morphology of high intensity laser cured PDLCs and its dependence on the curing parameters have been investigated. In particular, the connections between the non-conventional morphologies observed in the illuminated region of the samples and the peculiar features of the laser curing technique, have been analyzed. One of these non conventional structures can give rise to well defined polymer channels inside which liquid crystal molecules result to be all aligned in the same direction.

Acknowledgements

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