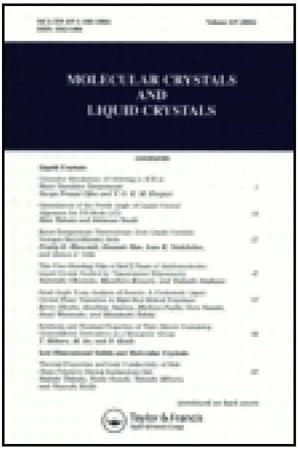
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Optical properties of Polymer Dispersed Liquid Crystals (PDLC) are determined by the used polymerisation method. We have previously performed a systematic study on UV curable mixtures in order to obtain a correlation between the characteristics of the UV irradiation i.e. intensity and exposure time, and the optical properties of PDLC samples. Here we report the results of a detailed investigation performed by using the UV lines of an Ar ion laser as light source to cure the standard mixture NOA65-E7. We observe that, due to the high intensity in a narrow wavelength region (333–363 nm), fast curing can be obtained leading to peculiar morphologies. We also demonstrate how is possible to exploit the laser curing technique to write switchable images in these materials.

Keywords: PDLC; Phase separation; Optical recording

INTRODUCTION

It has been recently shown that Polymer Dispersed Liquid Crystals (PDLC) can be successfully used to fabricate reflection and transmission gratings by means of holographic techniques. Besides use of the photorefractive effect recently reported in these materials [1-4], holographic gratings can be written during the curing process by means of laser light [5-7]. The aim of those researches is to obtain switchable devices to be used as optical interconnects or optical memories.

As it is well known, PDLC are composite materials in which nematic liquid crystals are phase-dispersed as droplets in a polymer matrix [8]. They can be switched from an opaque to a transparent state by means of the application of an external electric field. In fact, in absence of an applied field the symmetry axis of the liquid crystal droplets (i.e. droplet's director) is randomly oriented. In this case the refractive index mismatch between droplets and the polymer matrix produces a strong light scattering and the sample looks opaque. When an electric field of sufficient intensity is applied, the droplet directors are collectively aligned parallel to the field. If the value of the ordinary refractive index of the droplet is close to that of the matrix, as it is usual, this reorientation reduces the refractive index mismatch and the sample looks transparent.

One method used to fabricate a conventional PDLC is the photo-polymerisation induced phase separation (PIPS) [8]. In this process the mixture of liquid crystal and UV-curable resin, is irradiated by UV light so that liquid crystal and polymer are randomly phase-separated during the polymerisation of the matrix. If the UV curing light comes from two interfering laser beams, liquid crystal and polymer result to be microscopically and periodically phase-separated, giving rise to a periodic structure of planes in which phase separation follows the incident interference pattern [5].

In order to develop a technique to write holographic gratings during the curing process, we have firstly studied the phase separation process using an Ar-ion laser as curing source. Experimental results show that liquid crystal phase separation in the polymer matrix does not always lead to droplets formation. Anyway, our samples have the same optical properties of the ordinary PDLC.

EXPERIMENTAL

A detailed investigation of the curing process has been carried on for the standard mixture NOA65-E7 by using the UV lines (333-363 nm) of an Ar laser. The sample was fixed on a horizontal plane and irradiated by the laser beam. A lens and a diaphragm were used to adjust the beam spot size on the sample.

The experimental conditions are summarised in the following table:

Standard mixture	50%NOA65+50% E7
UV Intensity	I=(5-500)mW/cm^2
Curing Time	10 seconds
Film thickness	23μm
Substrates	ITOconductive glasses

Samples have been irradiated immediately after preparation, details on sample preparation have been given elsewhere [9]. The morphology of the films has been analyzed by Scanning Electron Microscope (SEM).

Measurements of the electro-optical response have also been performed. Both transmission versus voltage and threshold voltage for the transition to the transparent state have been measured for a voltage frequency of 3 kHz, using a He-Ne laser beam as probe.

RESULTS

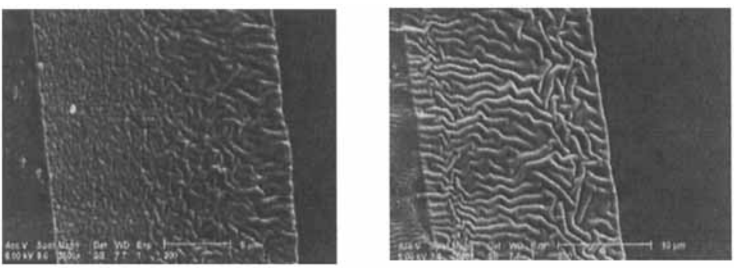
Figure 2 shows the morphology of the PDLC cured at 400 mW/cm^2. As can be seen, liquid crystal droplets are not present in the sample. The irradiated regions show highly interconnected channels dispersed in the polymeric matrix instead of the common droplet morphology. Channel dimensions increase far from these areas, where the curing process is driven by diffusion. A gradient of channel sizes is clearly visible in fig. 2a. They increase going from the left surface (place in front of the laser beam) to the right one.

It is interesting to notice that the pure polymer NOA 65 when irradiated by the same source, does not show the channel morphology observed in fig.2 (fig.3).

The channel morphology is present in all the analyzed samples, but it becomes less regular by lowering the curing intensity. In particular, the sample cured at the lowest intensity (5 mW/cm^2) exhibits some droplets dispersed in the volume as it is shown in fig.4.

The channels size always decreases by increasing the curing intensity.

The usual optical PDLC behavior has been observed in these samples. Switching from the opaque to the transparent state under the application of an external electric field has been demonstrated in all our samples. The threshold voltage depends on the curing intensity since it determines the liquid crystal channels dimensions. Figure 5 shows the electro-optics response of the sample cured at the lowest intensity. The threshold voltage, defined as the voltage necessary to reach 50% of the maximum transmission, is 25 V in this case.



(a) (b)

Fig.2 Morphology of the PDLC cured at 400 mW/cm^2. (a) irradiated region, (b) non irradiated region.

Fig.3 Morphology of the pure polymer NOA65.

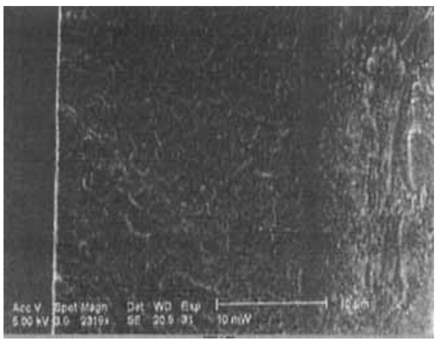


Fig.4 Sample cured at 5 mW/cm^2. Some droplets are visible in the volume.

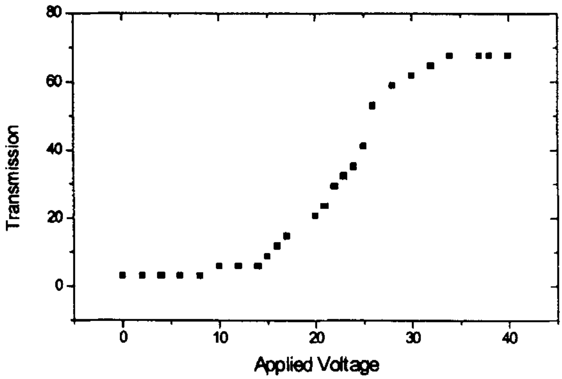


Fig.5 Electro-optic response of the sample cured at the lowest intensity.

IMAGE RECORDING

The laser curing technique has been also exploited to write permanent images on the analysed PDLCs. A laser beam passes through a mask before impinging on the sample to be cured. In this way, the spatial distribution of the curing intensity reproduces the image on the mask and a selective curing occurs, which fixes the image on the sample. In fact, the different morphology of the irradiated and of non-irradiated areas induces a different optical behaviour, depending on the size of the liquid crystal channels.

When the curing intensity is low, a high-scattering image on a transparent background is obtained, as expected with ordinary cured PDLCs (fig.6).

By increasing the laser intensity, the irradiated region becomes transparent. The image is still visible since, due to the high intensity, curing occurs also in the regions close to the irradiated one and a transparent image on a scattering background is obtained.

This kind of curing, which is driven by diffusion, occurs only if the curing intensity is high enough (of the order of 100 mW/cm^2) and if the sample is irradiated immediately after preparation so that NOA65 is still in the pre-polymeric phase and no spontaneous curing process has yet started. An example of the transparent image is shown in fig.7.

Opaque images can be switched to the transparent state by means of the application of an external electric field.

Fig.6 High-scattering image on a transparent background (low curing intensity).

Fig.7 Transparent image on a scattering background (high curing intensity)

DISCUSSION

The experimental results show that laser-cured PDLCs tend to develop an interconnected channel morphology, which is very different from the droplet morphology typical of UV cured samples. Channels are not observable in pure NOA65 samples that are cured in the same conditions, which confirms that their formation is due to the liquid crystal phase separation in the polymer matrix.

If the channels are liquid crystal domains, it is easy to understand why laser cured PDLCs show the ordinary electro-optical switching behaviour. Channels size decreases with increasing the curing intensity, leading to an increase of the threshold voltages, just as for ordinary PDLCs [8].

The observed morphology suggests that in the case of laser curing, liquid crystal phase separation occurs through spinodal decomposition (SD). Actually, SD leads to a peculiar morphological appearance which is different from the droplet morphology typical of the phase separation through nucleation and growth (NG), as reported in the following scheme [10].

SD	NG
• The two-phase structure is uniform and strongly interconnected. • The morphology is initially interconnected. It can then coarsen to form droplets. • The interface between phases is diffuse. Separated phases are generally non-spherical and interconnected.	• The two-phase structure is not uniform and not strongly interconnected. • The morphology is initially dispersed. Droplet sizes then increase by growth and coalescence. • The interface between phases is sharp. Minor phase tends to form spherical droplets and to be not interconnected.

PDLC samples obtained by using the same standard mixture and cured by means of a UV lamp have been already studied [9]. They show liquid crystal droplets of different size and distribution depending on the curing parameters. In that case, the UV light local intensity is of the order of some tens of mW/cm^2.

SEM analyses of the laser cured PDLC show that by increasing the laser intensity the liquid crystal channels net becomes more regular. Moreover, some droplet is visible in the sample cured at the lowest intensity (fig.3). Therefore, droplets formation seems to be favorite when the curing intensity is not too high. If intensity is of the order of some hundred of mW/cm^2 an interconnected channel structure is obtained. This structure is typical of SD.

Further investigation is necessary in order to figure out the role of local temperature rise in the sample during irradiation and how the speed of polymerization affects the phase separation process.

The dependence of channels size on laser intensity allows to explain why transparent images are obtainable on laser cured PDLCs. High laser intensity leads to very small channels, which are unable to scatter the visible light (see also fig.2a). Channels size increases near the irradiated region where curing is driven by diffusion and is slow. In this way, the background appears opaque and the image is transparent but visible.

By using lower intensities, channels are larger in the irradiated area which, as a consequence, becomes opaque. Moreover, diffusion curing does not occur, the background remains uncured and transparent so that an opaque image is visible on a clear background.

The usual alignment mechanism of liquid crystals under an applied field accounts for the ability to switch the image to a transparent state, thus erasing it for the time of field application.

CONCLUSIONS

In conclusion, we have demonstrated that using the UV lines of an Argon ion laser as a curing source for UV curable PDLCs, fast curing can be obtained leading to peculiar morphologies. Anyway, the usual electro-optical response of PDLCs has been demonstrated in all the analysed samples.

The observed morphology suggests that in some cases, phase separation can occur through spinodal decomposition, but further investigations are needed in order to understand how the local temperature rise and the speed of polymerisation, affect the process.

The laser curing technique has also been exploited to write permanent switchable images in the studied materials.

Acknowledgments

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