Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Optical storage of hidden images in ultraviolet-cured polymer dispersed liquid crystals

L. Lucchetti; S. Di Bella; F. Simoni

To cite this Article Lucchetti, L. , Bella, S. Di and Simoni, F.(2002) 'Optical storage of hidden images in ultraviolet-cured polymer dispersed liquid crystals', Liquid Crystals, 29: 4, 515 — 519

To link to this Article: DOI: 10.1080/02678290110116204

URL: http://dx.doi.org/10.1080/02678290110116204

LIQUID CRYSTALS, 2002, VOL. 29, NO. 4, 515–519

Taylor & Francis
Taylor & Francis Group

Optical storage of hidden images in ultraviolet-cured polymer dispersed liquid crystals

L. LUCCHETTI*, S. DI BELLA and F. SIMONI
Dipartimento di Fisica e Ingegneria dei Materiali e del Territorio and Istituto
Nazionale per la Fisica della Materia,
Università di Ancona, via Brecce Bianche, 60131, Italy

(*Received 11 September 2001; accepted 7 November 2001*)

Among the different methods used to prepare polymer dispersed liquid crystals (PDLCs), polymerization induced phase separation can be successfully exploited to obtain optical recording of high resolution holographic gratings and binary images in these materials. In this paper we report a new method that allows hidden images to be obtained in PDLCs that are not detectable by light in the visible range. The possibility of storing invisible images during the curing process will be described and discussed. The binary images obtained can be detected by illuminating them with low power UV radiation, thus opening the way to interesting applications in the field of optical storage of reserved information.

1. Introduction

Materials capable of recording binary images and holographic gratings are becoming ever more attractive because of the possibility of developing novel optical devices. In particular, soft materials such as polymers and liquid crystals hold promise for a variety of applications in the field of optical data storage [1]. The investigation of media with optical properties that can be varied locally by light, permanently or in a reversible way, is in fact an area of intense research activity. High photosensitivity, high storage density, short switching and access time, reversibility and the possibility of non-destructive reading are the most common requirements. Organic media such as liquid crystals and polymers are at present among the most promising classes of materials which can fulfil these conditions. In recent years, polymer dispersed liquid crystals (PDLCs) have also been identified as suitable media for optical storage, and both diffraction gratings [2–10] and binary images [11] have been recorded by different methods, thereby achieving good spatial resolution and diffraction efficiency.

PDLCs are composite materials made from polymers and liquid crystals, and they show at the same time the properties of both materials [12]. They usually consist of a dispersion of liquid crystal droplets embedded in a polymeric matrix. Droplets are randomly distributed in the polymer and generally have a size close to the visible wavelength, thus producing a strong scattering of the incident light. A large variety of structures is possible, depending on the concentration, nature and properties of the polymer and the liquid crystal. PDLCs can be switched from the opaque to the transparent state by the application of an external electric field. In fact, in the absence of an applied field the symmetry axis of the droplets is randomly oriented and the refractive index mismatch between the droplets and the polymeric matrix produces strong light scattering. In this condition, samples are opaque. When an electric field of sufficient intensity is applied, the symmetry axes of the droplets are collectively aligned parallel to the field. If the ordinary refractive index of the droplets is close to that of the matrix, as usually happens, this reorientation reduces the refractive index mismatch to nearly zero and samples become transparent.

The mechanism of droplet formation is phase separation of the initial prepolymer/liquid crystal mixture. Phase separation can be accomplished through solution casting of the polymer and liquid crystal from a common solvent (solvent induced phase separation: SIPS), by cooling a thermoplastic/liquid crystal mixture below an upper critical solution temperature (thermal induced phase separation: TIPS), or by crosslinking a monomer or prepolymer within which the liquid crystal is soluble (polymerization induced phase separation: PIPS) [12]. The latter case can be effected thermally or optically. Among these methods, ultraviolet (UV) initiated crosslinking is by far the most common because of its use of low viscosity materials and simple processing. Moreover, the UV-initiated crosslinking technique allows the use of

---

*Author for correspondence;
e-mail: lucchetti@popcsi.unian.it

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110116204

PDLCs for optical recording of binary images and high resolution holographic gratings, since phase separation and consequent LC droplet formation occur in this case by light irradiation.

In this paper we report a new method that allows storage of binary images in PDLCs that are not detectable by light in the visible range, i.e. hidden binary images. The method we will describe is simple and inexpensive and could find intriguing applications in the optical storage of reserved information.

2. Writing of binary images in PDLCs

Binary images can be easily stored in PDLCs during the curing process by placing a mask in front of the UV curing source. In this way, the spatial distribution of the curing intensity reproduces the image on the mask and a selective curing occurs fixing the image on the sample. In order to achieve high quality images with useful spatial resolution, a highly collimated light beam is needed. Therefore the best curing source is the UV line of a laser.

We have recently exploited the laser curing technique to write permanent binary images in PDLCs. As described in [11], by changing the incident intensity we were able to write both opaque images on a transparent background and transparent images on a scattering background. This happens because of the well known dependence of the dimension of the domains of the liquid crystal on the curing intensity [13, 14]. High laser intensity leads to very small domains which are unable to scatter visible light. Their dimension increases on moving away from the irradiated region where the curing process is slower, and therefore the background looks opaque, thus making the image visible. By using lower intensities, LC domains in the irradiated area are larger and, as a consequence, this region looks opaque. Moreover, in this case curing does not occur outside the irradiated area, so that the background stays uncured and transparent.

One of the key points of the writing method described is the fact that, due to scattered light, the polymerization and phase separation processes extend outside the directly illuminated area. In fact [15], once the LC domains start to form in the illuminated area, the material begins to scatter laser light in all directions. The polymerization rate depends on the curing intensity I and it is higher where I is higher. As the intensity of the scattered light is inversely proportional to the square of the distance r from the centre of the irradiated spot, the polymerization rate in the sample changes with r depending on the local value of the intensity. In addition to the scattered intensity, diffusion phenomena involving migration of both excited photoinitiators and monomers from the central region of the beam to the outer region are expected to affect the polymerization rate, especially close to the direct beam where thermal gradients are stronger. However, diffusion of low molecular mass species through the polymer greatly depends on the viscosity which, on the other hand, depends on the degree of polymerization. As the starting isotropic mixture is rather viscous, and considering that the polymerization proceeds very quickly just in the region where the gradients are stronger, the latter effect plays a minor role in determining the rate of polymerization. In any case, the polymerization and consequent phase separation processes proceed outside the directly irradiated region more and more slowly with increasing r.

It is easy to imagine that if one could prevent curing from extending outside the directly irradiated area (i.e. outside the image), the transparent images obtained with high curing intensity could not be observable with visible light; that is they would be invisible to the human eye.

We now report a method of writing invisible images in PDLCs. The images obtained are undetectable under visible light illumination, but can be detected simply by irradiating the sample with low power near-UV radiation [16].

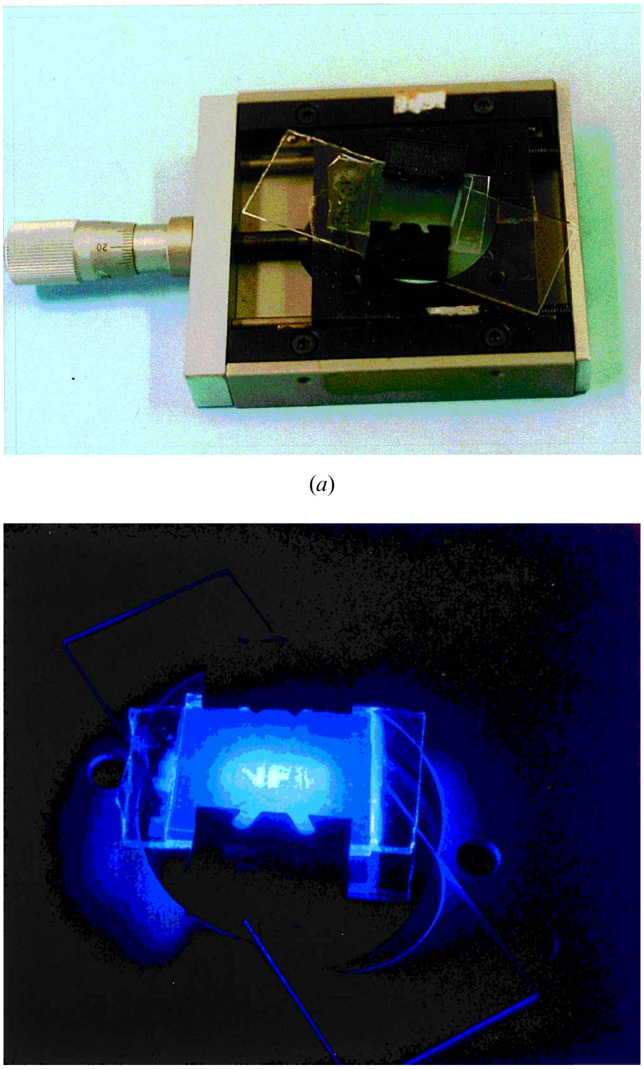
3. Experimental results and discussions

Samples have been prepared using cells consisting of two conductive glass plates ($3 \times 1.5 \times 0.1\,\mathrm{cm}^3$) filled by capillarity with a 1 : 1 weight ratio mixture of the nematic liquid crystal E7 (Merk) and the NOA65 (Norland) UV-curable commercial optical adhesive. The cell thickness was 23 μm. Samples were placed horizontally and irradiated by the UV lines of an Ar ion laser beam ($\lambda = 333$–363 nm) after its passage through a mask reproducing the image to be stored (the logo 'INFM' of the National Institute for the Physics of Matter). A description of the chemical reactions involved in the photopolymerization process for the NOA65-E7 mixture is reported in [17].

All samples were stored at room temperature for three days before being irradiated. Laser power and exposure times were varied between 300 and 500 mW and 10 and 60 s, respectively. Sample morphology was analysed by scanning electron microscopy (SEM) (sample preparation for the SEM analysis has been described in detail elsewhere [14]).

In all the cases analysed, samples looked completely transparent before and after irradiation. Only the illumination with light in the near UV range reveals the presence of the binary image, as shown in figure 1 in which a PDLC sample illuminated by ambient light (*a*) and low power near UV light (*b*) are shown. As can be seen in figure 1 (*b*), the stored image is sharp and well resolved with respect to the background. Increasing the laser power and the exposure time results in sharper images.

It is worth noting that the use of a low power UV source for decoding the hidden images is important from

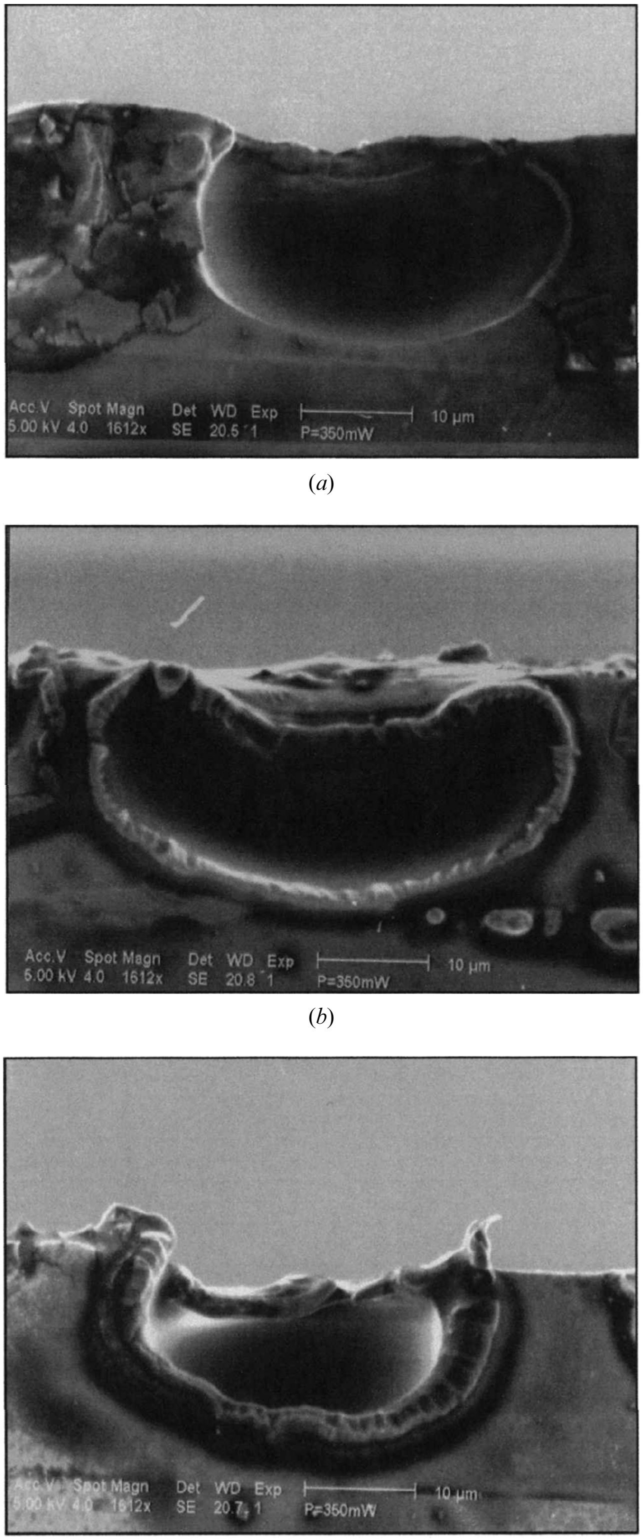

(*a*)

(*b*)

Figure 1. PDLC in which the image reproducing the logo 'INFM' has been stored. The sample is illuminated by ambient light (*a*) and by low power near UV light (*b*). The image is visible only in case (*b*).

the point of view of the lifetime of the image during multiple-read operations. In the case of figure 1, the UV 'reading' source was a very weak beam (less than 1 mW) from the Ar ion laser used to store the images.

The SEM investigation performed immediately before laser curing (i.e. three days after sample preparation) shows the presence over the whole volume of very large LC droplets whose diameter seems to be limited only by the sample thickness, figure 2 (*a*). Such a morphology is the result of a spontaneous curing process, which, being very slow, produces large LC domains. Samples are transparent due to the large dimensions of the droplets, which do not scatter visible light. Figures 2 (*b*)



(*a*)

(*b*)

(*c*)

Figure 2. SEM micrographs of PDLC samples before (*a*) and after laser irradiation (*b*, *c*). The only effect of the selective laser curing is the formation of small LC droplets on the borders of the large domains produced by spontaneous phase separation.

and 2(*c*) show the morphology of the PDLC samples after the selective laser curing. The curing power was 350 mW and the exposure time 10 s. The only effect of laser irradiation appears to be the formation of very small droplets at the borders of the larger ones produced during the spontaneous curing. The small droplet diameter hardly exceeds 500 nm.

It is reasonable to suppose that the presence of these small domains in the directly irradiated area makes the region opaque to near UV radiation, while maintaining it transparent to visible light. Moreover, spontaneous curing freezes the morphology in the non-irradiated area, thus preventing the previously described laser-induced formation of LC droplets of μm dimensions in this region. These droplets would make the background opaque and the image visible. The hidden images obtained have been shown to be stable for years and no degradation of the image sharpness has been observed.

Spontaneous phase separation takes place in our samples because of the presence of a photoinitiator in the prepolymer used. The time required for this process to occur can vary depending on prepolymer concentration, being of the order of a few days in the present case. It is well known that in a PDLC, the liquid crystal and the polymer are not in equilibrium since they are not completely separated. The true equilibrium state would consist of a region containing only the liquid crystal, and one containing only the polymer, but this final morphology is hindered by the increase in the polymer viscosity due to polymerization. Because of the slowness of spontaneous phase separation, polymer gelation occurs very slowly so that large liquid crystal regions, corresponding to a quasi-equilibrium configuration, have time to form. The resulting quasi-equilibrium morphology remains stable during the laser curing in our experimental conditions, thus maintaining transparency of the background of the images to visible light. In other words, storing the uncured PDLCs at room temperature for a few days before writing the image allows us to obtain precured samples whose morphology is affected by the subsequent laser curing only in regions that are directly irradiated. Therefore, this simple procedure allows freezing of the PDLC morphology outside the laser cured region, thus preventing the image's background from becoming opaque and revealing the presence of the image. In principle, precuring with a UV lamp should have the same effect with the advantage of being faster. However, this process was usable successfully with our materials only if the LC concentration did not exceed 40 wt-%. Just in this case in fact, samples remain transparent after the precuring and can be exploited for writing invisible images. If the LC content is higher than 40 wt-%, precuring produces opaque samples that are not useful for our purposes.

The method described for writing invisible images in conventional PDLCs is simple and inexpensive and offers the possibility of intriguing applications. For example, it can be exploited for the optical registration of reserved information, which could be decoded by means of a dedicated device comprising a low power UV source and a photocamera sensitive to this wavelength range. In this field, a possible application could be the use of the method presented to store a hidden personal code in a chip to be introduced into credit cards, cash dispensers, identity cards and so forth. The personal code can be stored as a hologram or as a binary image and would be read by a device of very simple conception.

Because of the well known optical properties of PDLCs [12], the hidden images described can in principle be switched between a state in which they are opaque to near UV light, and one in which they are transparent to light in the same wavelength range. Although no electro-optical measurements have been made, it is the authors' opinion that the application of a sufficiently high external voltage would allow switching of the images in the near UV range, and this could be another interesting feature for application purposes. The only limitation might be the value of the required voltage, since PDLCs containing NOA65 optical glue are easily damaged by external fields above the threshold of 10 V μm^{-1}.

4. Conclusions

We have reported on the possibility of writing hidden images in conventional UV curable PDLCs. The method presented exploits the well documented UV light-induced phase separation and so is simple and inexpensive. Nevertheless, it could open the door to very useful and important applications in the field of optical storage of reserved information.

References

[1] Lucchetti, L., and Simoni, F., 2000, *Riv. Nuovo Cimento*, **23,** 1.

[2] Sutherland, R. L., Tondiglia, V. P., Natarajan, L. V., Bunning, T. J., and Adams, W. W., 1994, *Appl. Phys. Lett.*, **64,** 1074.

[3] Sutherland, V. P., Natarajan, R. L., Tondiglia, L. V., Bunning, T. J., and Adams, W. W., 1995, *Proc. SPIE*, **2404,** 132.

[4] Tondiglia, V. P., Natarajan, L. V., Sutherland, R. L., Bunning, T. J., and Adams, W. W., 1995, *Opt. Lett.*, **20,** 1325.

[5] Natarajan, L. V., Sutherland, R. L., Tondiglia, V. P., Bunning, T. J., and Adams, W. W., 1996, *J. Nonlinear Opt. Phys. Mater.*, **5,** 89.

[6] Bunning, T. J., Natarajan, L. V., Tondiglia, V. P., Sutherland, R. L., Vezie, D. L., and Adams, W. W., 1995, *Polymer*, **36,** 2699.

[7] Sutherland, R. L., Natarajan, L. V., 1997, *Liq. Cryst.*, **7,** 1.

[8] Cipparrone, G., Mazzulla, A., Nicoletta, F.P., Lucchetti, L., and Simoni, F., 1998, *Opt. Commun.*, **150,** 297.

[9] Fuh, A., Tsai, M. S., Huang, C. Y., and Ko, T. C., 1996, *Opt. Quantum Electron.*, **28,** 1535.

[10] Fuh, A., Ko, T. C., Tsai, M. S., Huang, C. Y., and Chien, L. C., 1997, *J. appl. Phys.,* **83,** 679.

[11] Di Bella, S., Lucchetti, L., and Simoni, F., 1999, *Mol. Cryst. Liq. Cryst.*, **336,** 247–254.

[12] Simoni, F., 1997, *Non Linear Optical Properties of Liquid Crystals and Polymer Dispersed Liquid Crystals* (Singapore: World Scientific).

[13] Draize, P. S., 1995, *Liquid Crystals Dispersions* (Singapore: World Scientific).

[14] Di Bella, S., Lucchetti, L., and Simoni, F., 1998, *Mol. Cryst. liq. Cryst.*, **320,** 139.

[15] Lucchetta, D. E., Francescangeli, O., Lucchetti, L., and Simoni, F., *Liq. Cryst.* (in the press).

[16] Lucchetti, L., di Bella, S., and Simoni, F., 2000, Patent GE2 000 A000 031.

[17] Lucchetta, D. E., Lucchetti, L., Gobbi, L., Simoni, F., 2001, *Mol. Cryst. liq. Cryst.*, **360,** 93.