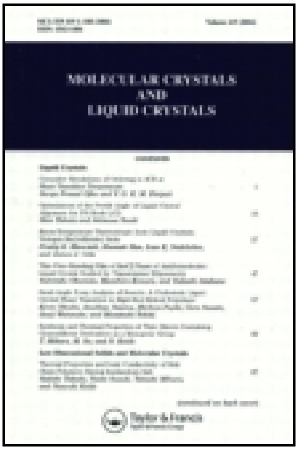

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Holographic Patterning of Composite Polymeric Materials for Photonic Applications

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Version of record first published: 22 Sep 2010

To cite this article: L. Criante, R. Castagna, F. Vita, D. E. Lucchetta, L. Gobbi & F. Simoni (2008): Holographic Patterning of Composite Polymeric Materials for Photonic Applications, Molecular Crystals and Liquid Crystals, 486:1, 21/[1063]-30/[1072]

To link to this article: http://dx.doi.org/10.1080/15421400801916462

Mol. Cryst. Liq. Cryst., Vol. 486, pp. 21/[1063]–30/[1072], 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801916462

Holographic Patterning of Composite Polymeric Materials for Photonic Applications

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We report the results of an extended investigation on holographic patterning of novel liquid crystal-polymer materials, developed with the aim of producing one- and two-dimensional periodic structures to be used in optical devices for data storage and processing. Characterization of reflection gratings recorded at 405 nm resulted in values of diffraction efficiency (>60%), sensitivity (up to 10^4 cm/J) and refractive index modulation ($\Delta n \sim 0.01$) that make these materials interesting for optical storage applications. Large-area two-dimensional periodic structures have been also patterned using a multibeam photolitigraphic technique. These planar photonic crystals have many possible uses, both in fundamental and applied physics.

Keywords: optical storage; photonic crystals; photopolymerisation

INTRODUCTION

It has been already pointed out that reflection gratings in polymeric materials have a great potential to become the single bit elements for a high density optical storage technique based on microholography [1]. In fact by using microholograms as bits in a conventional CD/DVD disk it is foreseen to achieve a disk capacity up to 1 TeraByte. This is consequence of the exploitation of the volume of the storage material and of the multiplexibility that is possible using holographic

This research has been supported by the EU as part of the STRP project MICROHOLAS, Contract No. 511437.

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techniques, while in the present technology only the surface of the storage material is exploited. To this aim the key issue is given by the material: several constrains must be achieved to fulfil all the requirements of a good storage material. These requirements are: sensitivity $S > 10^3\,\mathrm{cm/J}$ (affecting the recording speed); light-induced refractive index modulation $\Delta n \sim 0.01$ (linked to the obtained diffraction efficiency and affecting the potential multiplexing capabilities); low absorption and scattering losses allowing 80% transmission for thickness of $200 \div 300\,\mu\mathrm{m}$; polymer shrinkage $< 1\%$ (both mechanical and optical); finally high stability vs time and vs temperature is required.

One approach having highest chances to be successful to achieve the goal of fulfilling these requirements consists in using a composite polymeric mixture where the recording process is based on two phenomena at the same time: spatially modulated photopolymerisation and phase separation (consequent to polymerisation) between the different chemical components of the mixture. Actually this strategy is suggested by Holographic Polymer Dispersed Liquid Crystals (HPDLCs), where the photopolymerisation process induces also phase separation between liquid crystal and polymer. As a matter of fact this method is used to record gratings in HPDLC materials widely investigated for the realization of nano-structured electro-optical devices (electrically driven switchable gratings [2]) recorded through conventional holographic techniques [3]. By using two interfering beams that give rise to a spatially modulated light distribution it is possible to initiate a non-uniform polymerisation in a photosensitive pre-polymer-liquid crystal mixture. This spatially anisotropic polymerisation induces a counter-diffusion process of the mixture components leading to their phase-separation: the liquid crystal is forced to the dark regions as the monomers diffuse towards the bright regions. The result is a periodic structure due to alternating polymer-rich and liquid crystal-rich planes, giving rise to a strong refractive index modulation [4]. Most of the HPDLCs have been exploited for transmission gratings where it is not so difficult to get diffraction efficiency close to 100% or even to get overmodulated gratings. On the other hand the different reflection gratings are more tricky for at least two reasons. The first one is the different optical behaviour: in the two-coupled-wave approximation [5] the diffraction efficiencies η_r and η_t of lossless reflection and transmission gratings are respectively:

$$\eta_r = \tanh^2\left(\frac{\pi d \Delta n}{\lambda_B \cos\theta_B}\right) \tag{1}$$

and

$$\eta_t = \sin^2\left(\frac{\pi d \Delta n}{\lambda_B \cos\theta_B}\right), \tag{2}$$

where d is the sample thickness, Δn the refractive index modulation, λ_B the Bragg wavelength and θ_B the Bragg angle measured inside the sample. Comparing the two functional behaviours, one can note that the $\sin^2$ reaches its maximum for a lower Δn than $\tanh^2$, keeping fixed the other parameters. Moreover getting a high refractive index modulation is much more difficult in reflection gratings than in transmission gratings. In fact, the recording of reflection gratings requires beams impinging on both sides of the sample: this fact makes more critical the role of the material which strongly affects the interference pattern during the photopolymerisation process. Additionally the typical pitch of reflection gratings is much smaller than the one of transmission gratings (a few hundreds of nanometers vs $1 \div 2$ microns, respectively). This makes the holographic process much more critical and extremely sensitive to vibrations and other sources of noise. Nevertheless high quality reflection gratings have been recorded in these materials using different recording wavelengths [6]. In addition, these materials are also suitable to record two- and three-dimensional periodic structures [7,8].

In this paper we report the results of an investigation concerning holographic patterning of 1D and 2D periodic structures in HPDLCs. For what concerns the 1D case, we have studied reflection gratings recorded at 405 nm, which is the standard "blue light" wavelength used for optical storage. From this point of view we have considered these materials as "model" materials in the research of the optimum medium to realize microholographic optical disk. In fact, while they fulfil most of the requirements for the good holographic medium, the inclusion of liquid crystal make them very sensitive to temperature variation and not really suitable for the holographic disk. Thus their optical behaviour give hints to develop a material with similar properties but not including the liquid crystals. Following this strategy a novel class of polymeric materials for holographic storage has been recently patented [9].

Concerning the 2D structures we report the fabrication of high contrast and large area photonic crystals recorded in HPDLCs where a post-recording process allows washing out the liquid crystal in order to obtain a planar photonic film with any two-dimensional Bravais lattice. These films, easily placed in free standing geometry, have high potential for development of plastic photonic devices in waveguide geometry.

MATERIALS

The optimization of a HPDLC mixture sensitive to 405 nm is not a trivial work, even starting from visible sensitive mixtures. In fact it is not just a matter of changing the photo-initiator, but all the mixture must be modified. In order to clear this point it is useful to compare two HPDLC mixtures, the first one sensitive to 458 nm, the second one sensitive to the most interesting wavelength of 405 nm, as reported in Table 1.

In this case the change of the photoinitiator, from a mix of Genocure CQ (by Rahn.) and n-phenylglycine (NPG) to Irgacure 819 (by Ciba Specialty Chemicals), has the consequence of reducing the liquid crystal concentration from 25% to 16% and increasing the acrylate monomer concentration from 65% to 83%. Moreover, in the second case the use of the mono-functional monomer 1-vinyl-2-pyrrolidone (NVP) to dissolve the photoinitiators becomes unnecessary, due to the good solubility of the Irgacure 819 in the syrup. These features have been underlined to recall that changes of photoinitiator necessary to change the range of highest sensitivity require a further optimization of all the components of the mixture. The mixture is finally placed between two microscope glass slides using Mylar separator to fix the thickness.

For what concerns 2D photonic crystals recorded in HPDLCs, the used mixture is the more conventional one sensitive to green light (514 nm): acrylate monomer (M) dipentaerythritol hydroxy penta/hexa acrylate, nematic liquid crystal (LC) BL038, and the photoinitiator mix (PI) of Rose Bengal and NPG solved in NVP, with mass ratio M:LC:PI 65:25:10.

TABLE 1 Comparison Between Two HPDLC Mixtures

	Mixture sensitive to 458 nm	%	Mixture sensitive to 405 nm	%
Monomer	Dipentaerythritol hydroxy penta/hexa-acrylate	65	Dipentaerythritol hydroxy penta/hexa-acrylate	83
Liquid crystal	Cyano-biphenyl mixture BL038	25	Cyano-biphenyl mixture BL038	16
Reactive diluent	NVP	10	NVP	0
Photoinitiator(s)	Genocure CQ/NPG	0.6/1	Irgacure 819	1

CHARACTERISTICS OF 1D REFLECTION GRATINGS

The experimental setup used for writing 1D holographic reflection gratings has been reported elsewhere [10]. The recording source can be either an Argon Ion laser (recording at 514 nm or at 458 nm) or a low power (13 mW) diode laser when using the recording wavelength of 405 nm. The apparatus allows monitoring the rise of the grating during recording and checking its optical behaviour after the writing process using a spettrophotometric system. The sample transmittance is detected: the appearance of a minimum peak in the transmission spectrum is the clear signature of the growth of the grating. The measurement is performed by illuminating the grating with unpolarized broadband radiation. The transmission spectra are digitally recorded and displayed on line by the computer, with a time resolution of 0.4 s.

In Figure 1 it is shown a typical series of data obtained monitoring the recorded reflection grating at different times after a curing pulse of 0.2 s from the 405 nm laser. The sequence of the curves shows all the information that is possible to get from these data. The depth of the

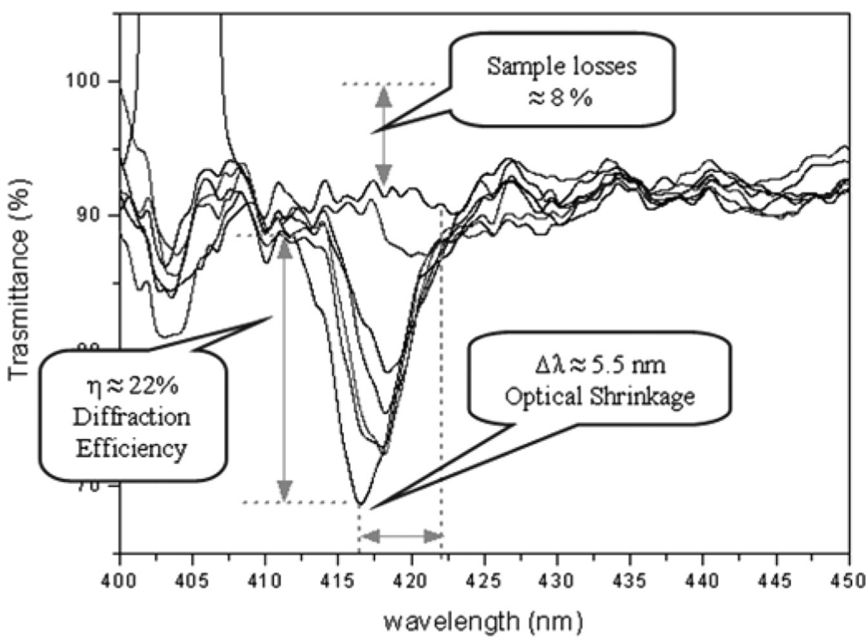

FIGURE 1 Real-time transmission spectra corresponding to the grating formation after a curing pulse of 0.2 s. Curves are taken each 0.4 s.

peak allows evaluating the diffraction efficiency η ($\sim$22%, see Fig. 2), hence the index modulation Δn ($\sim$0.005, calculated from Eq. (1)). The shift of the peak allows evaluating the shrinkage of the material ($\sim$1.4%, see Fig. 3), while the background level allows evaluating the overall sample losses due to absorption or scattering ($\sim$8%, including surface glass reflection).

We have to underline that all these data have been obtained with a very short curing pulse, in order to reproduce the experimental conditions for optical bit recording. In fact, longer exposure times give rise to deeper peaks, hence to a higher diffraction efficiency, which can easily reach 50%. However, the most interesting parameter for characterizing materials for holographic data storage is rather sensitivity (S) than diffraction efficiency, with S defined as

$$S = \frac{\sqrt{\eta}}{Itd}\ [\mathrm{cm/J}], \tag{3}$$

where I is the recording light intensity, t the exposure time and d the sample thickness. In this case we measured an extremely high sensitivity, $S = 1.3 \times 10^5\,\mathrm{cm/J}$, which makes this class of materials

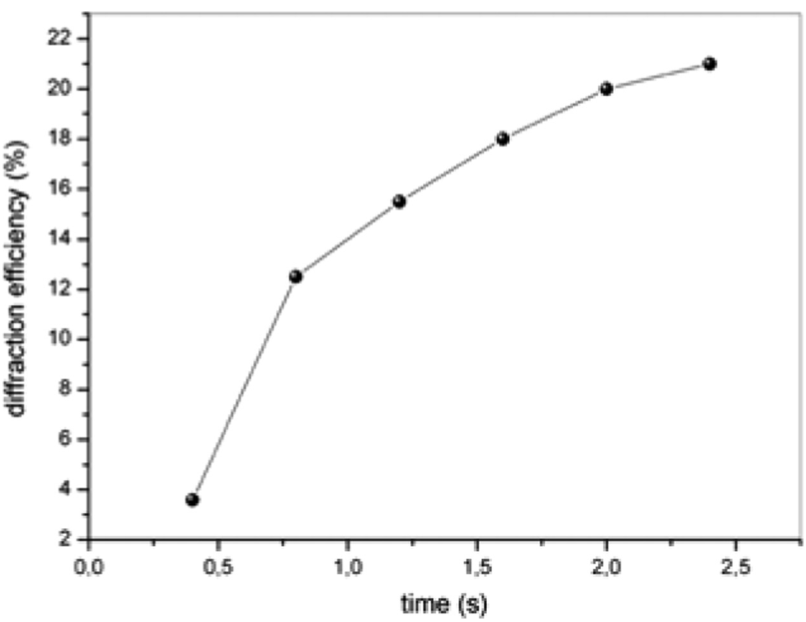

FIGURE 2 Diffraction efficiency vs time after a curing pulse of 0.2 s.

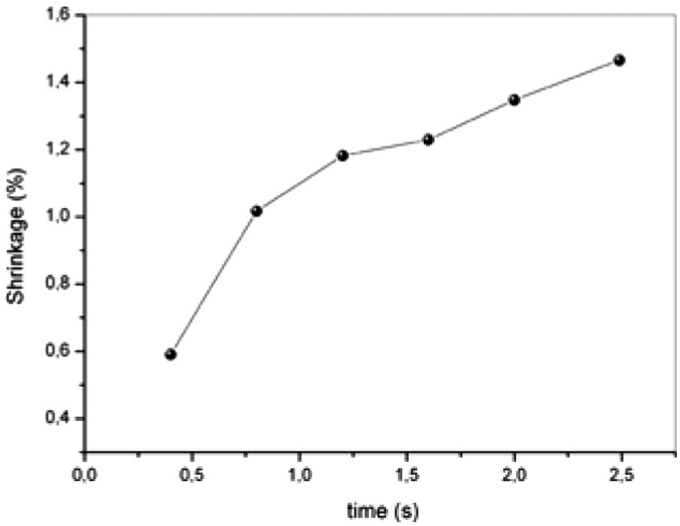

FIGURE 3 Shrinkage vs time after a curing pulse of 0.2 s.

interesting for optical recording since it allows low power and short recording time.

On the other hand shrinkage is low during recording, however it continues after recording even if the sample is placed in dark, reaching a value of about 2%, which represents still a limitation for holographic storage. The achieved spatial resolution of about 7000 lines/mm is very good and is only limited by the used geometry not by the material characteristics.

RECORDING OF 2D PERIODIC STRUCTURES

It is well known that multibeam interferometry can be used to obtain periodic patterns in two or three dimensions: it has been demonstrated that with three and four interfering beams it is possible to get all the different Bravais lattices in 2D and 3D, respectively [11,12]. In the case of three non-coplanar interfering beams, the resulting 2D spatial distribution of the light intensity is given by:

$$I(\mathbf{r}) = \sum_{i=1}^{3} E_i^2 + \sum_{i<j=1}^{3} 2E_iE_j(\mathbf{e}_i \cdot \mathbf{e}_j)\cos[(\mathbf{K}_i - \mathbf{K}_j) \cdot \mathbf{r}], \quad (4)$$

where E_i, $\mathbf{e}_i$, and $\mathbf{K}_i$ are the amplitudes, the polarization vectors, and the wave-vectors of each interfering laser beam respectively. Here we have neglected the relative phases of the beams because they only produce a translation of the interference pattern. The above expression clearly shows that the lattice geometry, i.e. the length and orientation of the cell lattice vectors, is completely determined by the set of K-vectors, hence by the beam incidence angles on the sample. On the other hand, the intensities of the beams and their mutual polarizations affect the light intensity distribution within the unit cell.

With this technique we have patterned square and triangular lattices in HPDLC mixtures, thus obtaining a correspondent distribution of the polymer rich and liquid crystal rich domains. With a second step, the liquid crystal has been washed out of the structure in order to get an higher index contrast between the polymeric structure and air. The organic solvent propylenglycolmethylether acetate (PMA) has been used for this purpose. We found PMA is able to remove the liquid crystal and all the non-polymerised material, apparently without affecting the polymerised structure. The complete removal of the LC has been verified by inspecting the sample under a polarizing microscope before and after the washing procedure.

An SEM picture of a sample of this kind is shown in Figure 4. The length of the lattice vectors for this triangular structure is about 1.8 μm, but samples with periodicity $<0.4\,\mu m$ have been fabricated. Higher spatial resolutions can be easily achieved by using shorter wavelengths. These types of samples have several interesting features. First of all, the holographic nature of the recording technique ensures that large areas, of the order of $\sim 1\,cm^2$ in our case, can be

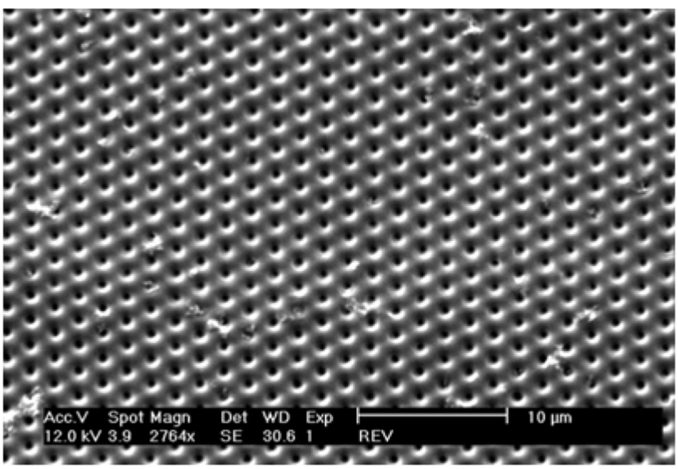

FIGURE 4 SEM image of a triangular lattice organic photonic crystal.

FIGURE 5 Diffraction pattern from a triangular lattice organic photonic crystal.

easily and immediately patterned with a very high degree of homogeneity. This is clearly visible observing the diffraction pattern generated by a single laser beam impinging normally to the photonic structure (Fig. 5).

Moreover, this technique allows the "in-depth" patterning of thick samples. In fact, we have recorded photonic structures in samples with a thickness ranging between 5 to 100 μm. We have also verified that the voids obtained after the LC removal were homogeneously extended over the whole sample thickness. Finally, we have demonstrated that these films can be peeled off from the substrate to be in a free standing geometry [13].

For these peculiar characteristics, these organic photonic crystals are ideal samples for studying the physical properties of polymeric materials in periodic morphologies (e.g. study of sound wave propagation, nonlinear optical propagation). Moreover, using these structures in a waveguide configuration it is possible to design photonic devices and sensor based on polymeric films.

CONCLUSIONS

In conclusion, we have reported our approach to the patterning of composite liquid crystal-polymer films by holographic lithography. On the one hand, we have shown how an optimized HPDLC mixture, sensitive to 405 nm, allows the recording of reflection gratings with high spatial frequency and high diffraction efficiency. Above all, the elevated sensitivity values reported suggest the use of HPDLCs as recording medium for holographic data storage applications. On the other hand, holographic lithography has been used on the same class of photosensitive materials for recording two-dimensional periodic structures characterized by high degree of homogeneity and easy processability. This kind of organic photonic crystals have many possible uses, both in fundamental and applied physics.

REFERENCES

[1] Orlic, S., Ch. Müller, A., Reinicke, R., Schön, M., Trefzer, H., & Eichler, J. (2001). *SPIE's International Technical Group Newsletter, Holography*, *12*, 3.
[2] Sutherland, R. L., Tondiglia, V. P., Natarajan, L. V., Bunning, T. J., & Adams, W. W. (1994). *Appl. Phys. Lett.*, *64*, 1074.
[3] Bunning, T. J., Natarajan, L. V., Tondiglia, V. P., & Sutherland, R. L. (2000). *Annu. Rev. Mater. Sci.*, *30*, 83.
[4] Sutherland, R. L., Natarajan, V. P., Tondiglia, T., & Bunning, J. (1993). *Chem. Mater.*, *5*, 1533.
[5] Kogelnik, H. (1969). *Bell Syst. Tech. J.*, *48*, 2909.
[6] Vita, F., Lucchetta, D. E., Castagna, R., Francescangeli, O., Criante, L., & Simoni, F. (2007). *J. Opt. Soc. Am. B*, *24*, 471.
[7] Escuti, M. J., Qi, J., & Crawford, G. P. (2003). *Appl. Phys. Lett.*, *83*, 1331.
[8] Sutherland, R. L., Tondiglia, V. P., Natarajan, L. V., Chandra, S., Tomlin, D., & Bunning, T. J. (2002). *Opt. Exp.*, *10*, 1074.
[9] Simoni, F., Castagna, R., Criante, L., Lucchetta, D. E., & Vita, F. Italian patent AN2007A000022.
[10] Criante, L., Vita, F., Castagna, R., Lucchetta, D. E., & Simoni, F. (2007). *Mol. Cryst. Liq. Cryst.*, *465*, 203.
[11] Escuti, M. J. & Crawford, G. P. (2004). *Opt. Eng.*, *43*, 1973.
[12] Cai, L. Z., Yang, X. L., & Wang, Y. R. (2002). *Opt. Lett.*, *27*, 900.
[13] Vita, F., Lucchetta, D. E., Castagna, R., Criante, L., & Simoni, F. (2007). *Appl. Phys. Lett.*, *91*, 103114.