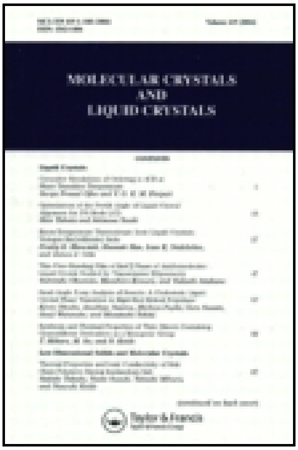

Molecular Crystals and Liquid Crystals

Highly Efficient Holographic PDLC Based on Acrylate Monomers with Low Functionality

H. Bensaid [a], U. Maschke [a], O. Sakhno [b] & J. Stumpe [b]

[a] Laboratoire de Chimie Macromoléculaire, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, Cedex, France

[b] Fraunhofer Institut für Angewandte Polymerforschung (IAP), Wissenschaftspark Golm, Geiselbergstraße, Potsdam, Germany

Version of record first published: 01 Jun 2009

To cite this article: H. Bensaid, U. Maschke, O. Sakhno & J. Stumpe (2009): Highly Efficient Holographic PDLC Based on Acrylate Monomers with Low Functionality, Molecular Crystals and Liquid Crystals, 502:1, 37-46

To link to this article: http://dx.doi.org/10.1080/15421400902813675

Mol. Cryst. Liq. Cryst., Vol. 502, pp. 37–46, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400902813675

Taylor & Francis
Taylor & Francis Group

Highly Efficient Holographic PDLC Based on Acrylate Monomers with Low Functionality

H. Bensaid[1], U. Maschke[1], O. Sakhno[2], and J. Stumpe[2]
[1]Laboratoire de Chimie Macromoléculaire, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, Cedex, France
[2]Fraunhofer Institut für Angewandte Polymerforschung (IAP), Wissenschaftspark Golm, Geiselbergstraße, Potsdam, Germany

The transmission holographic gratings were recorded by two coherent beams of Ar-laser ($\lambda = 514\,nm$) in the liquid crystal (LC) – prepolymer composition with prepolymeric component based on acrylic monomers of low functionality ($f \leq 3$). The diffraction efficiency of these gratings was studied as a function of recording conditions (exposure intensity and time) and applied voltage. In parallel, morphology of the obtained samples was investigated. It is shown that compositions based on acrylic monomers with $f \leq 3$ may yield holographic gratings with good characteristics (high diffraction efficiency, low scattering loss, good electrooptic performance), approaching those described for monomers with higher functionality. Besides, we observed difference in morphology of samples based on monomers with functionality 2 and 3; they show conventional and inverse morphology, respectively.

Keywords: diffraction efficiency; holographic polymer dispersed liquid crystal; morphology; phase separation

1. INTRODUCTION

In the beginning of 90th of past century polymer dispersed liquid crystals (PDLC) roused huge interest because of pronounced effect of

Mrs. H. Bensaid thank all group members of Laboratory of Polymer Photochemistry at Fraunhofer Institute for Applied Polymer Research in Potsdam (Germany) for daily support in an experimental work during her visit to this laboratory. The French group authors thank Dr. O. Yaroshchuk from Institute of Physics, NASU, Ukraine for fruitful discussions. Also, authors gratefully acknowledge the support of the C.N.R.S. and the Région Nord – Pas de Calais.

Address correspondence to U. Maschke, Laboratoire de Chimie Macromoléculaire, UMR CNRS N 8009, Bâtiment C6, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq, Cedex, France. E-mail: ulrich.maschke@univ-lille1.fr

electrically controlled light scattering [1,2]. PDLC are extensively studied as materials for light shutters, privacy windows and LCD [3].

A new wave of interest to these systems was excited by their use as materials for recording of diffraction gratings. At first, such gratings were recorded by using amplitude diffraction grating as a mask through which exciting light was directed to LC-prepolymer composition [4]. More recently, holographic principle was applied for creation of diffraction gratings in PDLC compositions [5,6]. The latter principle is especially useful, because parameters of holographic gratings can be readily changed by changing geometry of irradiation and parameters of recording beams.

In conventional PDLC formed by polymerization induced phase separation (PIPS), homogeneous mixture of photoreactive monomer and LC is uniformly irradiated with an actinic light. In contrast, in a course of holographic recording this mixture is subjected to spatially modulated light field (interference fringe pattern) formed by interfering coherent beams. Since the rates of polymerization and accompanying phase separation grow with the intensity of recording light, the photopolymerization preferentially initiates in the bright interference patterns. The polymer formed in these regions ejects LC which diffuses to the low intensity strips forming voids of different shapes and sizes or permanent layers.

Practical application of holographic PDLC (HPDLC) set strong demands, such as easiness of recording procedure, low scattering losses and controlling voltage. It is desirable to record holograms by relatively cheap lasers of visible range. The recording conditions shall be adjusted to obtain LC voids with a size sufficiently small to minimize scattering losses but, simultaneously, sufficiently high to minimize controlling voltage. This can be achieved by thorough optimization of polymer composition and exposure conditions. Big deal of work has been done in this direction since the discovering of HPDLC. It was shown that HPDLC can be recorded by coherent UV as well as visible light, including red one [7]. The LC and polymer materials, as well as their concentrations were optimized for HPDLC morphology of isolated LC voids [5,6,8] and permanent LC layers [9]. Special additives were found to improve electrooptic performance of HPDLC [6].

At the same time, problem of polymer compositions suiting in the best way for HPDLC is intensively discussed. There are two classes of compositions most suitable for photoinitiated PIPS. First class comprises thiol-ene mixtures undergoing step-growth polymerization under irradiation. The other class includes acrylate compositions capable to polymerize via chain-growth radical polymerization. Both of these classes are suitable for recording of HPDLC. The further improvement of

HPDLC is associated with structural optimization of these reactive compounds. The question of particular interest is the amount of reactive groups in monomers (or monomer functionality) at which the best phase separation conditions will be achieved. It was established that increase of monomer functionality in thiol–ene PDLCs results in substantial improvements, such as enhanced phase separation and reduced size of LC droplets [10]. The latter leads to a reduction of scattering losses. In case of acrylate monomers the situation is not so clear. It has been observed that in case of visible recording light, holograms with considerable diffraction efficiency η ($\eta > 50\%$) are formed in formulations with averaged functionality $f \geq 4$ [5]. At the same time, UV formulations require monomers with lower functionality ($f \leq 2$) [11,12].

In the present study we consider holographic recording with a visible light in acrylate monomers with $f < 4$. We utilize two monomers, tripropyleneglycoldiacrylate and glycerolpropoxy-triacrylate, earlier thoroughly optimized for the conventional PDLC [13,14]. The highly efficient holographic recording is realized in these acrylate compositions with the grating parameters similar to those described in literature for acrylate compositions with $f \geq 4$. Based on this we conclude that acrylate formulations with $f < 4$, same as formulations with $f \geq 4$, can be successfully used for the recording of HPDLC, if parameters of these compositions are well optimized.

2. EXPERIMENTAL SECTION

2.1. Materials and Film Preparation

The LC E7 was purchased from Merck KGaA (Darmstadt, Germany). It is an eutectic mixture exhibiting a nematic-isotropic transition at $T_{NI} = 61°C$, a glass transition at $T_g = -62°C$, $n_o = 1{,}5216$, and $n_e = 1{,}7462$ (at $\lambda = 589\,nm$).

The monomers tripropyleneglycoldiacrylate (TPGDA) and glycerolpropoxy-triacrylate (GPTA) were donated by Cray Valley (France). These monomers with functionality $f = 2$ (TPGDA) and $f = 3$ (GPTA) correspondingly form chemically crosslinked polyacrylates. Eosin was used as a conventional photoinitiator. A small amount of a co-initiator, the Meichler ketone, was added to the initial mixture.

The monomer/E7 blends containing x wt.% of monomer, and $(1\text{-}x)$ wt.% of LC E7 were stirred mechanically overnight at room temperature for homogenisation. A drop of the obtained mixture has been placed between two glass plates covered with ITO electrodes from the inner side. Teflon spacers with a thickness 12 μm were used to obtain an uniform thickness of the prepolymer/LC film. Then, the cell was exposed to the interference pattern formed by two interfering beams of Ar-laser generating light with $\lambda_r = 514\,nm$. The intensity ratio of the recording beams was approximately 1:1. A beam of He-Ne laser ($\lambda_t = 633\,nm$) was used as a probe beam to test the process of the gratings formation. The incident angle of testing beam was equal to the Bragg angle corresponding to the grating period used. The spatial period Λ of the gratings recorded was 1 μm, and the exposure time was typically 3–5 min. The samples were again post-cured for 10 min under a UV lamp (Philips, 20 W).

The gratings have been recorded at different intensities of recording beams: 17, 30 and 42 mW/cm^2 according to IR analyses preliminarily made, at these intensities high conversion rate of acrylate double bands $-C=C-$ was achieved. The power of the first order diffracted beam and zero order beam were measured in order to establish the diffraction efficiency of the grating.

2.2. Electro-Optical Measurements

Electro-optical properties were investigated by applying an ac sinusoidal electrical voltage, provided by a wave form generator at a frequency of 1 kHz and acquiring the transmitted and diffracted He-Ne probe beam by data acquisition system. The driving voltage value was varied from 0 up to 420 V. The decrease of the first order diffracted beam is accompanied by an equal but opposite change in the zero-order transmittance, indicating that the index modulation has been modified by the field.

2.3. Scanning Electron Microscopy (SEM)

Materials to be viewed under a scanning electron microscope (SEM) may require processing to produce a suitable sample. The two glass substrates were separated and immersed in ethanol for several hours, then dried in order to extract the LC. This preparation technique leads to the appearance of empty cavities that were once filled with LC. A Hitashi S-4700 microscope operating at low tension 3 kV, was used.

3. RESULTS AND DISCUSSION

The recorded holographic gratings were characterized by diffractive efficiency η defined according to formula (1):

$$\eta = \frac{I_d}{I_d + I_{tr}} \tag{1}$$

where I_d is the intensity of the 1st diffraction order (diffracted beam), and I_{tr} is the intensity of the zero diffracted order (transmitted beam).

The kinetics of holographic recording for various recording intensities I_{0r} was studied for both systems, on TPGDA and GPTA base. For example, Figure 1 shows the real time diffraction efficiency of gratings formed in the system based on bifunctional TPGDA monomer. It is obvious that diffraction efficiency η increases with the exposure time, reaching saturation. The grating recording time was in the range of 50–150 s and depends on intensity of recording beams. The maximal diffraction efficiency of the generated gratings was very high (85–98%). The grating recording kinetics in the system based on GPTA formulation was rather similar. The diffraction efficiency in saturation or maximum state exceeds 95%.

The non-monotonic behaviour of η(t) curves at high intensities has several reasons. First of all, this happens when the amplitude of the refractive index modulation exceeds the values corresponding to 100% of diffraction efficiency. In theory of diffraction gratings [15], the refractive index amplitude Δn determines value of diffraction efficiency:

$$\eta = \sin^2 \frac{\pi \Delta n d \cos 2\theta_B}{\lambda_t \cos \theta_B} \qquad (2)$$

where d is a film thickness, λ_t is a wavelength of testing beam, and θ_B is a Bragg angle for the wavelength used. If Δn grows above the value

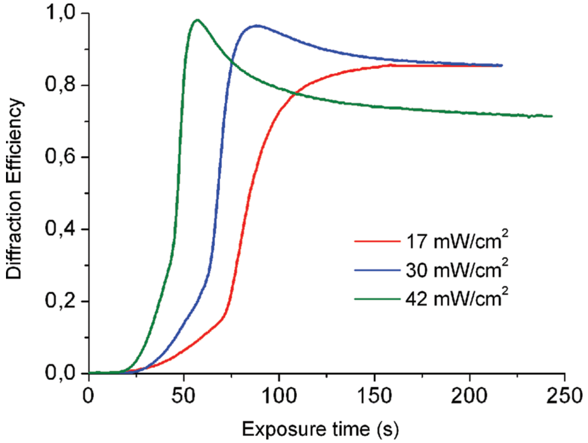

FIGURE 1 Diffraction efficiency of HPDLC film based on TPGDA composition (LC/monomer = 30/70 w/w) for *p*-polarization of reading beam as a function of exposure time. The curves are presented for three various laser intensities; $I_{0r} = 17$; 30 and 42 mW/cm^2.

at which argument of sine becomes equal to $\pi/2$, $\eta(\mathrm{t})$ gets down. The additional reason can be not perfect contrast of interference pattern, so that polymerization process also occurs in the interference minima, partially washing out the holographic grating. Using formula (2), were calculated refractive index amplitudes Δn corresponding to maximal values of η in Figure 1. These data are presented in Figure 2a.

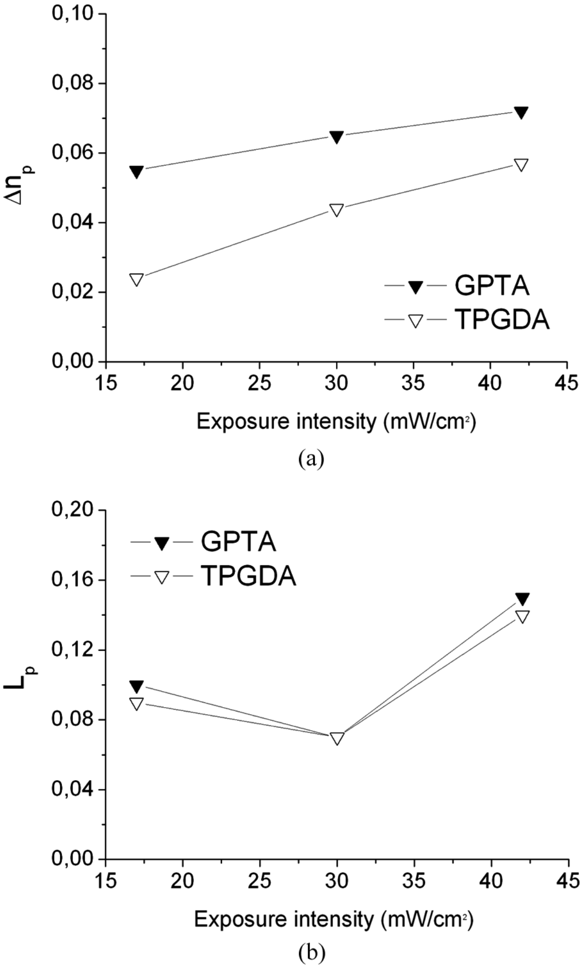

FIGURE 2 Refractive index modulation Δn (a) and optical losses (b) in holograms recorded in TPGDA and GPTA based compositions (LC/monomer = 30/70) as functions of intensity of recording beams. The curves correspond to p-polarization of reading beam. Recording time was 4 min.

It is evident that the refractive index modulation Δn obtained for both samples is high enough; Δn reaches almost 0.07 in GPTA based sample and 0.04 in TPGDA based sample at 30 mW/cm^2. Higher amplitude of Δn observed for sample on GPTA base might be explained by higher functionality of GPTA monomer (f = 3) comparing with TPGDA (f = 2). This leads to faster polymerization supporting better coalescence of LC.

The optical losses L due to the light scattering were estimated according to formula (3):

$$L = 1 - \frac{I_d + I_{tr} + I_r}{I_0} \tag{3}$$

where I_0 and I_r are the intensities of the incident testing beam ($\lambda_t = 633$ nm) and its reflected part, respectively.

The values of L estimated for different intensities of recording light are presented in Figure 2b. One can see that optical losses for TPGDA and GPTA based systems are quite similar. L shows some dependence on recording light intensity I_{0r} and varies in the range 7–15%. Some difference in L for the gratings formed at different intensities I_{0r} can be explained by the phase separation process and the system morphology. The scattering losses, in case of both systems, minimize at $I_{0r} = 30$ mW/cm^2. This intensity for the systems studied seems to be

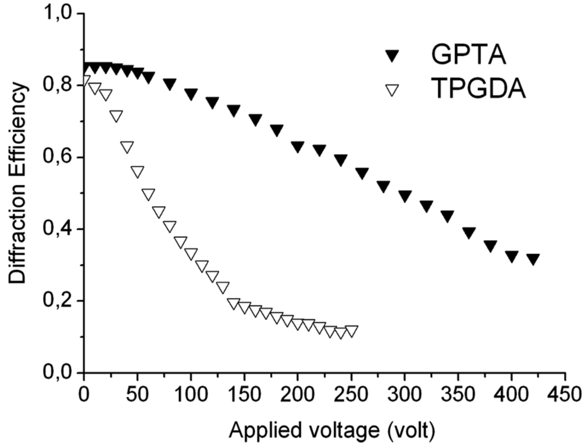

FIGURE 3 Diffraction efficiency as function of electric field applied to the gratings recorded in TPGDA and GPTA based compositions (LC/monomer = 30/70 w/w). $I_{0r} = 30$ mW/cm^2, $t_r = 4$ min. Thickness of HPDLC films was 12 μm.

close to optimization at which low scattering losses are combined with rather high diffraction efficiency (Fig. 1).

Figure 3 shows dependence of the diffraction efficiency η of the recorded HPDLC on the applied voltage U. The $\eta(U)$ curves

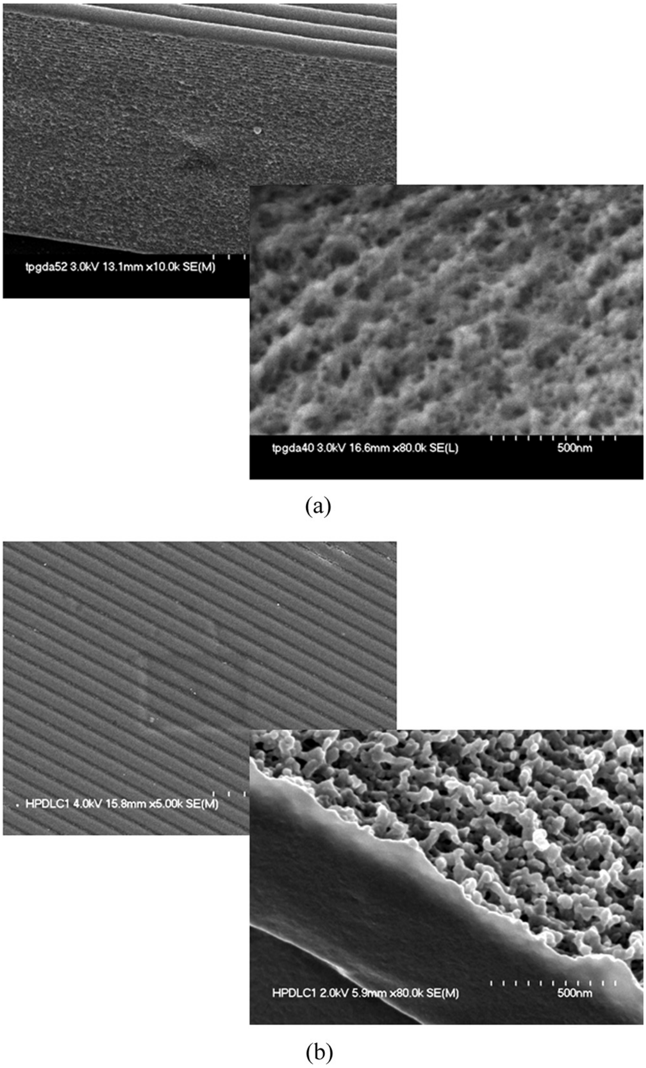

FIGURE 4 SEM images of HPDLC based on TPGDA (a) and GPTA (b) formulations (LC/monomer $= 30/70$, $I_{\text{rec}} = 30\,\text{mW/cm}^2$). Recording conditions: $I_{r0} = 30\,\text{mW/cm}^2$, $t_r = 4\,\text{min}$. Thickness of HPDLC films was $12\,\mu\text{m}$.

monotonically decrease. This implies that LC molecules orient along the electric field direction so that amplitude of the refractive index modulation Δn decreases. At high intensity of field, if $n_o \sim n_p$, η shall approach 0.

Figure 3 demonstrates that the falling rate of $\eta(U)$ curve for the sample based on TPGDA is much higher than for the sample on GPTA base. According to morphological studies (below), this is caused by bigger size of LC voids formed in TPGDA-LC composition that facilitate reorientation of LC in an electric field. Rather steep dependence of $\eta(U)$ curve and wide-range control of η(85–10%) makes TPGDA-LC composition promising for application. The holographic elements with electrically controlled diffraction efficiency are requested by many applications. Particularly, they can be utilized in reprogrammable interconnects, electro-optically adressable data storage devices and fiber optic switches.

The SEM images of the recorded gratings or, precisely speaking, images of polymer rests obtained after extraction of LC, are presented in Figure 4. The white sites correspond to polymer enriched sample areas, whereas the black ones were predominantly occupied by LC. The images of lower resolution obtained for both systems clearly show regular structural modulation typical for HPDLC. The high-resolution images show that network formed from GPTA monomer (Fig. 4b) is very clear with distinctive ball structure. Thus the HPDLC formed has a polymer ball morphology. In turn, the network formed from TPGDA is rather dense, while LC generally forms isolated voids. Thus morphology of this HPDLC is more similar to "Swiss cheese" rather than to polymer balls [1]. These structural peculiarities are quite similar to those described by other groups for holographic gratings based on monomers of weak functionality [16,17]. The difference in morphology of TPGDA and GPTA systems may explain difference in electro-optic behaviour displayed on Figure 3.

4. CONCLUSIONS

The transmission mode holographic gratings with high diffraction efficiency ($\eta \approx 95\%$) were recorded in PDLC compositions based on acrylic monomers with low functionality (TPGDA and GPTA monomers with, correspondingly, functionality 2 and 3, were utilized). These gratings are characterized by relatively low scattering losses (less than 10%) and switching with an electric field. The switching field is 20 V/μm for TPGDA based gratings and about 30 V/μm for the gratings based on GPTA. This difference can be explained by different morphologies of HPDLC, studied by SEM method. The obtained results show that highly efficient holographic recording can be realized in compositions based on polymeric formulations with $f < 4$, same as in the systems with polymers of higher functionalities.

REFERENCES

[1] Fergason, J. L. (1984). US Patent, 4, 435, 047.

[2] Doane, J. W., Vaz, N. A., & Chidichimo, G. (1985). *Int. Display Res. Conf. '85 Proc., 153*.

[3] Drzaic, P. S. (1995). *Liquid Crystal Dispersions*, World Scientific, Singapore.

[4] Lackner, A. M., Margerum, J. D., Ramos, E., & Lim, K. C. (1989). *SPIE*, *1080*, 53.

[5] Bunning, T. J., Natarajan, L. V., Tondiglia, V. P., & Sutherland, R. L. (2000). *Annu. Rev. Mater. Sci.*, *30*, 83.

[6] Crawford, G. P., Silverstein, L. D., & Fiske, T. G. (1996). *Society for Information Display Digest of Technical Papers XXVII*, 99.

[7] Ramsey, R. A. & Sharma, S. C. (2005). *Optics Letters*, *30*, 592.

[8] Bunning, T. J., Natarajan, L. V., Tondiglia, V., & Sutherland, R. L. (1996). *SPIE Proc.*, *2651*, 44.

[9] Abbate, G., Vita, F., Marino, A., Tkachenko, V., Slussarenko, S., Sakhno, O., & Stumpe, J. (2006). *Mol. Cryst. Liq. Cryst.*, *453*, 1.

[10] White, T., Natarajan, L. V., Tondiglia, V. P., Bunning, T. J., & Guymon, C. A. (2007). *Macromolecules*, *40*, 1112.

[11] De Sarkar, M., Gill, N. L., Whitehead, J. B., & Crawford, G. P. (2003). *Macromolecules*, *36*, 630.

[12] White, T. J., Natarajan, L. V., Bunning, T. J., & Guymon, C. A. (2007). *Liq. Cryst.*, *34*, 1377.

[13] Gyselinck, F., Maschke, U., Traisnel, A., & Coqueret, X. (2000). *Liq. Cryst.*, *27*, 421.

[14] Roussel, F., Buisine, J. M., Maschke, U., & Coqueret, X. (1998). *Liq. Cryst.*, *24*, 555.

[15] Kogelnik, H. (1969). *Bell. Syst. Tech. J.*, *48*, 2909.

[16] Park, M. S. & Kim, B. K. (2006). *Nanotechnology*, *17*, 2012.

[17] Liu, Y. J., Zhang, B., Jia, Y., & Xu, K. S. (2003). *Opt. Commun.*, *218*, 27.