

## PDF hosted at the Radboud Repository of the Radboud University Nijmegen

The following full text is a publisher's version.

For additional information about this publication click this link.

<http://hdl.handle.net/2066/72160>

Please be advised that this information was generated on 2020-10-21 and may be subject to change.

# Determination of liquid crystal orientation in holographic polymer dispersed liquid crystals by linear and nonlinear optics

M. Yemtsova,<sup>a)</sup> A. Kirilyuk, A. F. van Etteger, and Th. Rasing

*Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, Nijmegen 6525 ED, The Netherlands*

(Received 28 September 2007; accepted 18 June 2008; published online 13 October 2008)

The liquid crystal alignment imposed during the fabrication process of one-dimensional transmission gratings, holographically formed in a polymer dispersed liquid crystal, is determined by linear optical birefringence as well as rotational second harmonic generation. For a mixture consisting of nematic liquid crystal E7, a pentafunctional acrylate monomer, and a photoinitiator, the director orientation inside the liquid-crystal-rich layer is found to be approximately along the grating direction. We suggest that this molecular orientation is the consequence of the strong flow during the grating formation. © 2008 American Institute of Physics. [DOI: 10.1063/1.2969656]

## I. INTRODUCTION

Holographic polymer dispersed liquid crystals (HPDLCs) have been known for more than ten years and have many potential applications in the field of electro-optics<sup>1,2</sup> due to the electrically switchable large optical birefringence  $\Delta n = n_e - n_o$  of the liquid crystal (LC) part. A HPDLC is a stratified composite structure made of alternating LC-rich and polymer-rich planes. The morphology of this periodic structure can strongly vary depending on the materials used, the LC fraction in the initial mixture, and the exposure conditions.<sup>3-5</sup> Since the electro-optical properties depend strongly on the grating morphology, many fundamental studies have been performed on structure characterization<sup>1,6-8</sup> and, in particular, for the situation when the LC layer appears in the form of droplets surrounded by polymer chains.<sup>9-11</sup> Depending on the orientation of the LC molecules, a HPDLC can appear either as a medium with a periodically modulated refractive index or as an optically isotropic one (if the refractive index of the nematic matches that of the polymer). Hence, the ability to manipulate the LC orientation allows to gain control of light propagation. Besides, the performance of any LC electro-optical device depends critically on the LC alignment on the polymer surface, which is determined by the LC-polymer interface. Therefore, a challenge for manufacturing HPDLCs for practical applications is to be able to control the LC orientation in a predetermined way.

Based on the unequal diffraction efficiency for  $p$  and  $s$  polarizations, the anisotropic nature of HPDLC gratings has been recognized and investigated by different methods. For instance, Sutherland *et al.*<sup>12</sup> studied the temporal evolution of HPDLC reflective gratings made in prepolymer-LC mixtures designed for curing in visible light. They showed that the appearance of grating anisotropy during the grating formation nearly coincides with the moment of phase separation of the LC. In order to achieve LC alignment control inside the droplets through photoalignment, Cipparrone *et al.*<sup>13</sup> used two orthogonal, linearly polarized beams during the record-

ing process. The optical polarizing microscopy examination showed the presence of LC alignment inside the droplets parallel to the grating wave vector, which occurred during the illumination. Vardanyan *et al.*<sup>14</sup> also reported a LC alignment in ultraviolet light curable HPDLC materials. Based on the absence of droplets in scanning electron microscopy and a strong polarization dependence on the diffraction efficiency, a so-called polymer scaffolding model was proposed to describe the morphology. The authors suggested that the LC alignment is on average orthogonal to the holographic planes.<sup>14</sup>

In principle, the information on the LC orientation can be obtained from optical birefringence measurements. However, because in the present case we investigate a system with a large number of buried interfaces, the nondestructive and extremely interface sensitive optical second harmonic generation (SHG) technique was used as a complementary method for a more precise determination of the LC orientation inside the LC-rich layer. In addition, the birefringence results appear to be consistent with two different (mutually perpendicular) orientations of the LC molecules. The actual orientation could be determined by SHG. The high surface sensitivity of SHG originates from the fact that in the electric dipole approximation, second order optical processes are forbidden in the bulk of media with inversion symmetry. From the combined linear and nonlinear optical results we found that the molecules inside the LC-rich layers are aligned. This alignment is introduced during the fabrication process, and the director orientation is slightly tilted with respect to the grating direction. We suggest that the mechanism responsible for the observed molecular orientation is a strong flow alignment in the cell during the phase separation process.

## II. EXPERIMENTAL SECTION

The sample was a mixture of 33 wt % of the nematic LC E7 (Merck,  $T_{N-I} = 58$  °C,  $[n_e, n_o] = [1.747, 1.521]$  at 589 nm, 20 °C), 52 wt % of the dipentaerythrol hydroxyl pentaacrylate monomer, 12 wt % of the cross-linking monomer *N*-vinylpyrrolidinone (NVP), 2.85 wt % of the coinitiator *N*-phenylglycine (NPG), and 0.15 wt % of the photoinitiator

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: m.yemtsova@science.ru.nl

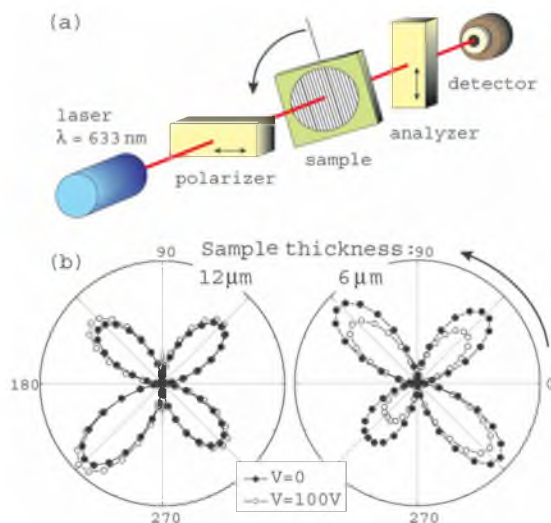


FIG. 1. (Color online) (a) Rotational optical birefringence setup for LC alignment determination inside the HPDLC structure. (b) Linear birefringence in 12- $\mu\text{m}$ -thick sample (left panel) and in 6- $\mu\text{m}$ -thick sample (right panel). Initial grating position corresponds to  $0^\circ$  on both graphs.

dye rose bengal (RB). The combination of the green sensitive photoinitiator RB and the coinitiator NPG generates free radicals that lead to free-radical addition polymerization. The cross-linking monomer NVP acts as a chain terminator and helps the LC to dissolve in the monomer. Further, the mixture of all the above chemicals was homogenized by ultrasonification in the dark for approximately 2 h, so a viscous solution appeared. The solution prepared was placed inside standard LC cells, with thicknesses of 12 and 6  $\mu\text{m}$ , respectively. When this homogeneous mixture is exposed to a periodically modulated light pattern, created by two coherent laser beams, a phase separation reaction takes place and a periodical structure with a period of the interference pattern forms. For the interference pattern we used the doubled output of a neodymium-doped yttrium lithium fluoride (Nd:YLF) laser at 532 nm. The laser intensity per beam was 50  $\text{mW}/\text{cm}^2$ , and the sample was exposed to this intensity for approximately 30 s, corresponding to a total energy density of 3  $\text{J}/\text{cm}^2$ . The two incident laser beams crossed at an angle of about  $24^\circ$ .

In order to investigate the LC alignment inside the HPDLC structure, we used linear optical birefringence and nonlinear optical SHG. The birefringence measurements were performed using a He-Ne laser by rotating the sample placed between crossed polarizers and by measuring the intensity of light reaching the detector. The characterization setup together with the initial grating orientation is shown in Fig. 1(a).

The nonlinear response in our gratings was generated by exciting the samples with the 800 nm light generated by a mode locked Ti:sapphire laser, which produces 150 fs pulses at a rate of 80 MHz. The experiment was performed in the transmission geometry at a normal incidence of light [Fig. 2(a)]. The samples were fixed and rotational anisotropy experiments were carried out by rotating the polarization of the incoming beam. The polarization state of light was set by using a Berek compensator. The light was focused onto a

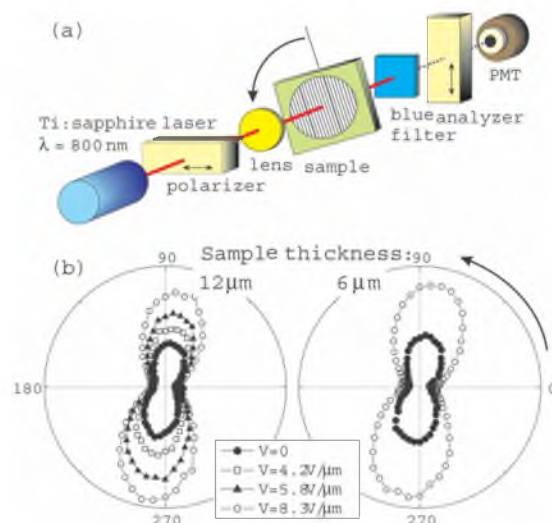


FIG. 2. (Color online) (a) Experimental arrangement used in SHG measurements, where PMT is a photomultiplier tube. (b) The SHG curves reflect the preferential orientation of the LC molecules in 12- $\mu\text{m}$ -thick (left panel) and 6- $\mu\text{m}$ -thick (right panel) samples.

spot with a diameter of about 100  $\mu\text{m}$  on the sample surface, and the average laser power was 5  $\text{mW}/\text{cm}^2$ . Any SHG-like signals coming from the laser or other optical components were filtered out by the transmission red filter RG 690. The SHG response generated by the sample was detected using a photomultiplier after color filtering with two BG39 filters and a spectrometer.

### III. RESULTS AND DISCUSSION

Upon exposing the samples to monochromatic laser radiation, a clear and strong diffraction pattern was observed. From the diffraction pattern we estimated the period of the HPDLC transmission grating to be 1.34  $\mu\text{m}$ . Our gratings are electrically switchable; the application of an external electric field with an amplitude of 16  $\text{V}/\mu\text{m}$  for the 6  $\mu\text{m}$  film along the light propagation direction leads to a drop in the detected intensity of about 25%, as shown in Fig. 1(b).

Figure 1(b) presents the results of the linear optical birefringence measurements for the 12 and 6  $\mu\text{m}$  thick films, respectively. These data reveal a mirror symmetry, which indicates that alignment of the LC layers is imposed to all samples during the fabrication process.

From these birefringence measurements we cannot unambiguously define the LC director orientation. However, our findings permit us to exclude several possible LC orientation geometries. First, the LC director cannot be oriented along the light propagation direction (along the  $z$  axis). This follows the fact that in that case the refractive index of light polarized in all directions perpendicular to the director is the same; hence, there can be no birefringence. Another impossible LC orientation is with the director parallel or perpendicular to the polarization plane of the incident light. In each case the incident light propagates according to a single index of refraction and again undergoes no change in polarization. Yet, there are at least two possible orientations that can result

in the observed birefringence symmetry. These are when the long molecular axis is oriented either parallel or perpendicular to the grating vector.

In order to resolve this ambiguity we used the nonlinear optical technique of SHG. Figure 2(b) depicts the SHG response as a function of rotation angle for the film thicknesses of 12 and 6  $\mu\text{m}$ , respectively. A strong anisotropy of the signal is evident.

Upon irradiation of a medium with a strong optical field (with electric field component  $\mathbf{E}$ ) such as those available in pulsed lasers, a nonlinear polarization  $\mathbf{P}$  is induced in the medium, which in the electric dipole approximation can be written as

$$\mathbf{P} = \epsilon_0 \cdot \chi^{(2)} \cdot \mathbf{E} \cdot \mathbf{E}, \quad (1)$$

where  $\chi^{(2)}$  denotes the second order susceptibility tensor of the medium. It follows directly from Eq. (1) that a second order polarization is forbidden in a medium with inversion symmetry. Only at surfaces and interfaces where the inversion symmetry is broken is the generation of a second-order polarization possible, which determines the interface specificity of the SHG technique. For a molecular system, the value of  $\chi^{(2)}$  observed in a particular experimental configuration depends on the molecular hyperpolarizability  $\beta$  of the molecules, their angular distribution function  $f(\Omega)$ , and their surface density  $N_a$ . Thus, one can write  $\chi^{(2)}$  in the following form:<sup>15</sup>

$$\chi_{lmn}^{(2)} = N_a \int T_{lmn}^{l'm'n'}(\Omega) \beta_{l'm'n'} f(\Omega) d\Omega. \quad (2)$$

Here  $T(\Omega)$  is the transformation matrix between the molecular ( $l', m', n' = 1, 2, 3$ ) and the laboratory frame ( $l, m, n = x, y, z$ ) expressed in terms of Euler angles  $\Omega = (\Theta, \Phi)$ . Due to the highly asymmetric rodlike shape of nematic LC molecules,  $\beta$  is mainly associated with the perturbation of the electronic density along the long molecular axis  $\hat{e}_3$ . Hence, in the first approximation, only the component of the molecular hyperpolarizability in this direction,  $\beta_{333}$ , has to be taken into account when the SHG signal from a LC layer is analyzed.<sup>16</sup> This significantly simplifies Eq. (2) and reduces it to

$$\chi_{zzz}^{(2)} = N_a \langle \cos^3 \Phi \rangle \beta_{333}, \quad (3)$$

where  $\Phi$  is the polar angle between  $e_3$  and the polymer interface normal. Therefore, the measured SHG response directly reflects the preferential orientation of the LC molecules.<sup>17,18</sup> Given these results, it may be concluded that the most probable orientation of the LC director is an angle of about  $8^\circ (\pm 3^\circ)$  with respect to the polymer layer boundary, as shown in Fig. 3. The polarization state of two linearly polarized beams used in the grating formation did not influence this orientation. We think that the flow of the LC molecules along the direction of the grating during the phase separation process mainly causes the observed perpendicular alignment. In order to explain the deviation from a perfect perpendicular orientation with respect to the polymer walls, additional studies have to be performed.

Finally, we checked the diffraction efficiency of all the prepared gratings with linearly polarized light. For light polarized perpendicular to the stratified layers ( $p$  polarization),

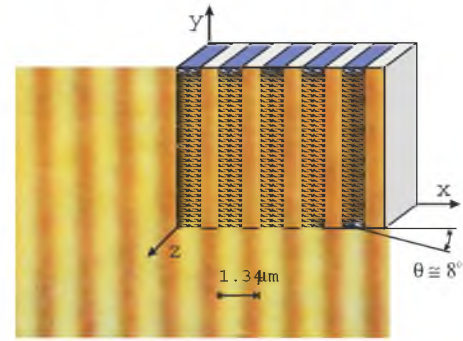


FIG. 3. (Color online) The polarizing optical micrograph of 12- $\mu\text{m}$ -thick holographically formed grating in a polymer dispersed LC sample. Inset: schematic representation of LC director orientation in LC-rich layers imposed during the fabrication process.

a strong diffraction pattern was observed. Conversely, when the polarization plane of light is parallel to them ( $s$  polarization), the intensity of the first order diffraction maximum drops by a factor of 10. Thus, in the first case light propagating through the LC layer feels the extraordinary refractive index  $n_e$ , which differs from the polymer one  $n_p$ , which causes the formation of a phase grating. In the second case the incident light sees the ordinary refractive index  $n_o$ , and because  $n_o \approx n_p$  the diffraction efficiency decreases. The lower efficiency for  $s$  polarized light was also reported by other researchers.<sup>9</sup> Consequently, the structure provides a switchable grating with a contrast ratio of 10. Unfortunately, the present structure requires rather high voltages and displays a slow response time (on the order of seconds), but this can potentially be improved.

## IV. CONCLUSIONS

In conclusion, we have shown that linear optical birefringence together with nonlinear optical SHG provides complementary information about LC molecular ordering in HPDLC structures. While the first provides information about the bulk properties of the material, the second one, being a higher order response, is more directly connected to the LC molecular ordering at the polymer surfaces in this multilayer system. Using these two methods we found that a LC alignment inside HPDLC films was imposed during the fabrication process, and the director orientation inside the LC-rich layer was approximately along the grating vector. A strong flow alignment is suggested as a mechanism responsible for the molecular orientation observed.

## ACKNOWLEDGMENTS

The authors acknowledge the support from the Dutch foundation for Fundamental Research on Matter (FOM). M. Yemtsova wishes to acknowledge S. V. Lazarenko for useful discussions.

<sup>1</sup>T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, and R. L. Sutherland, *Annu. Rev. Mater. Sci.* **30**, 83 (2000).

<sup>2</sup>G. P. Crawford, *Opt. Photonics News* **14**, 54 (2003).

<sup>3</sup>R. L. Sutherland, L. V. Natarajan, V. P. Tondiglia, and T. J. Bunning, *Chem. Mater.* **5**, 1533 (1993).

<sup>4</sup>M. Sarkar, N. L. Gill, J. B. Whitehead, and G. P. Crawford, *Macromolecules* **36**, 630 (2003).



- <sup>5</sup>R. L. Sutherland, V. P. Tondiglia, L. V. Natarajan, T. J. Bunning, and W. Adams, *Appl. Phys. Lett.* **64**, 1074 (1994).
- <sup>6</sup>R. A. Vaia, D. W. Tomlin, M. D. Schulte, and T. J. Bunning, *Polymer* **42**, 1055 (2001).
- <sup>7</sup>T. Kyu, D. Nwabunma, and H.-W. Chiu, *Phys. Rev. E* **63**, 061802 (2001).
- <sup>8</sup>M. Vilfan, B. Zalar, A. K. Fontecchio, M. Vilfan, M. J. Escuti, G. P. Crawford, and S. Žumer, *Phys. Rev. E* **66**, 021710 (2002).
- <sup>9</sup>M. Jazbinšek, I. Drevenšek Olenik, M. Zgonik, A. K. Fontecchio, and G. P. Crawford, *J. Appl. Phys.* **90**, 3831 (2001).
- <sup>10</sup>M. De Sarkar, J. Qi, and G. P. Crawford, *Polymer* **43**, 7335 (2002).
- <sup>11</sup>I. Drevenšek Olenik, M. Jazbinšek, M. E. Sousa, A. K. Fontecchio, G. P. Crawford, and M. Copic, *Phys. Rev. E* **69**, 051703 (2004).
- <sup>12</sup>R. L. Sutherland, V. P. Tondiglia, L. V. Natarajan, and T. J. Bunning, *Appl. Phys. Lett.* **79**, 1420 (2001).
- <sup>13</sup>G. Cipparrone, A. Mazzulla, and G. Russo, *Appl. Phys. Lett.* **78**, 1186 (2001).
- <sup>14</sup>K. K. Vardanyan, J. Qi, J. N. Eakin, M. De Sarkar, and G. P. Crawford, *Appl. Phys. Lett.* **81**, 4736 (2002).
- <sup>15</sup>Th. Rasing and I. Muševic, *Surfaces and Interfaces of Liquid Crystals* (Springer-Verlag, Berlin, 2004), Chap. 5, p. 113.
- <sup>16</sup>Y. R. Shen, *Liq. Cryst.* **5**, 635 (1989).
- <sup>17</sup>G. Berkovic, Th. Rasing, and Y. R. Shen, *J. Opt. Soc. Am. B* **4**, 945 (1987).
- <sup>18</sup>M. B. Feller, W. Chen, and Y. R. Shen, *Phys. Rev. A* **43**, 6778 (1991).