Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoinduced Alignment of Nematic Liquid Crystal on the Polymer Surface Microrelief

Alexander Parfenov [a b c], Nobuyuki Tamaoki [a b] & Satomi Ohni-shi [a b]

[a] Diagnostic Instrumentation and Analysis Laboratory, 205 Research Blvd, Starkville, MS, 39759, USA

[b] National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki, 305, Japan

[c] Lebedev Physics Institute, Leninsky 53, Moscow, Russia E-mail:

Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2001, Vol. 359, pp.167-175
Reprints available directly from the publisher
Photocopying permitted by license only

Photoinduced Alignment of Nematic Liquid Crystal on the Polymer Surface Microrelief

ALEXANDER PARFENOV*, NOBUYUKI TAMAOKI
and SATOMI OHNI-SHI

Diagnostic Instrumentation and Analysis Laboratory, 205 Research Blvd, Starkville, MS 39759, USA; National Institute of Materials and Chemical Research, 1–1 Higashi, Tsukuba, Ibaraki 305, Japan

Polymer film surface modified in the holographic process under the laser illumination was used for nematic liquid crystal (LC) alignment. Azobenzene - containing polyurethanes were taken for a material of the film. A relief grating inscribed by laser illumination onto the surface of these polymers induced a reorientation of LC director from initial homeotropic alignment. Possible applications of described processes include command-surface creation for liquid crystal displays, reversible and adaptable in real-time liquid crystal structures for laser beam targeting and aiming, etc.

Keywords: liquid crystal; alignment; polymer; relief

INTRODUCTION

Alignment of liquid crystal (LC) films on the surfaces of polymer films treated with a light is a subject under intensive investigation[1-4] mostly due to practical importance for liquid crystal displays production. It is well known that nematic liquid crystals exhibit the alignment along the grooves of a grat-

* author for correspondence. e-mail: parfenov@neur.lpi.msk.su. on leave from Lebedev Physics Institute. Leninsky 53, Moscow, Russia

ing relief [5]. Recently new technological methods were applied to align liquid crystals on a patterned surfaces, including surface relief [6-8]. On the other hand the simple procedure was found [9-12] to form the geometrical relief on the surface of the azo dyes-containing polymers via holographic recording. In this paper we report the results on the LC alignment on the polymer surfaces with such a relief.

MATERIALS, PREPARATION OF SAMPLES.

The alignment of 5CB (Merck) nematic liquid crystals was performed on the photomodified surface of polymer. The film preparation technique and some parameters (including transmission spectrum) of the polymer were published earlier [12]. The thickness of polymer films was taken in a range of 0.1 - 0.5 μ m. Experimental cell contains LC between two glasses - first was coated by the mentioned polymer and second - treated with surfactant to create conditions for hometropic alignment on this glass. The LC filled a gap between glasses by capillary flow in isotropic phase (ca 37-40 °C). The thickness of LC layer was measured as of 5-10 μm.

The LC alignment was observed on the polymer films with the surface relief and (for a comparison) on bare and homogeneously illuminated films. The relief was created in a holographic process with spatial period of 500-1500 nm. The process of a polymer photomodification [12] gave the depth of the film thickness modulation reaching 100 nm. The depth of surface relief was determined optically (through diffraction efficiency) and with atomic force microscope.

The images of the surface relief on the films were taken in contact mode using silicon nitride tips on Nanoscope III atomic force microscope (Digital Instruments). A sample of the observed relief is shown in Figure 1. One can see the spectrum of scan containing the single spatial frequency and the quite sinusoidal shape of grating. This means that the process of the relief creating/writing depends quite linearly on the light exposure. The same linearity is also confirmed to some extent by nearly quadratic dependence of diffraction efficiency η on the exposure presented in FIGURE 2.

Unexposed samples and samples with holographic recording show no differences in their absorption spectra [12]. This fact indicates that the polymer

retained its essential structure in holographic process and the products of the photodestruction are unlikely involved in the LC alignment.

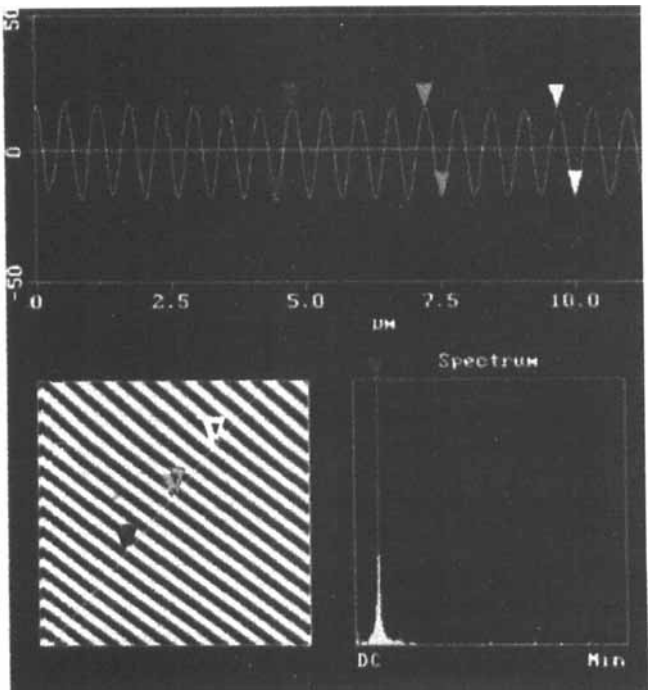

FIGURE 1 The surface relief (near 30-36 nm in depth) produced under holographic exposure with argon laser for a few minutes at intensity near 20 mW/cm^2 (measured with AFM). Period of grating is near 600 nm. On the left side is AFT scan. On the right - the spatial spectrum of this scan, showing the dominance of the single spatial component.

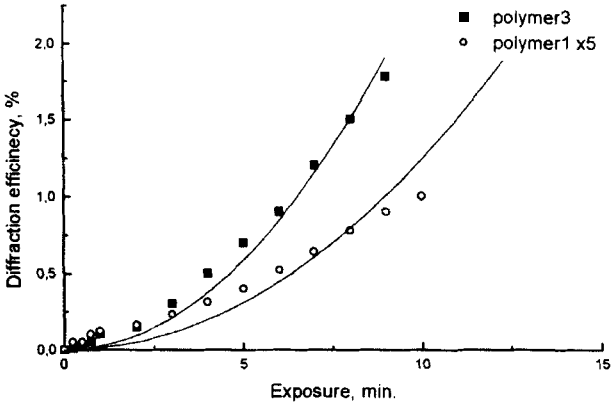

FIGURE 2 Diffraction efficiency of written gratings vs exposure (light intensity 20 mW/cm^2 @488 nm) for two polymer films of 300 nm thickness : polymer 3 - poly-Orange Tom-1 Isophoronedisocyanate; polymer 1 - poly-Orange Tom-1 Toluendiisocyanate (diffraction efficiency is enlarged 5 times for the last one for better presentation).

LIQUID CRYSTAL ALIGNMENT ON THE INSCRIBED GRATINGS.

Alignment of LC was observed under the polarization microscope. The LC alignment was hometropic on the untreated surface of polymer. At the same time on the inscribed gratings LC demonstrates the inclination of the director of molecules along the grooves of grating as it is illustrated by the Figure 3.

As there was no diffraction observed for LC-grating structure it states the uniform alignment within the grating area. The angle ϑ of the inclination was of 30° estimated from the color change (from black to green) observed in under the polarization microscope. Figure 4 shows the LC layer contacting the polymer film with the inscribed grating (diameter of the grating area is 3 mm – it was restricted mostly by available optics and power of the laser to record the relief).

LC director alignment along the grooves of inscribed grating was determined via rotation of the cell in oblique readout light. The optical contrast

exceeded 50:1 in the experimental cells (excluding points soiled or scratched during film preparation). Alignment on the inscribed gratings was permanent for at least several hours. The reason why the director was realigned within the grating region probably is in additional anchoring energy induced by this grating relief. This can be verified by an estimation of the surface energy as well as by its comparison with energy of LC deformation (as additional anchoring to the surface causes this deformation).

Estimation of azimuthal anchoring energy based on the "Neel walls" technique [13,14]: $E_\phi = 2dK/w^2$, where w is a width of the Neel wall (approximately 30 microns measured for our experimental cells as shown enlarged in inset to Figure 3) gave the value of $0.2 \cdot 10^{-6}$ J/m^2. The surface energy induced by grating is $2Ku^2(\pi/\Lambda)^3$, where u is amplitude of relief and Λ is period of inscribed grating. Calculations gave its value of $0.3 \cdot 10^{-6}$ J/m^2 for $u \sim 30$ nm and $\Lambda \sim 600$ nm. Estimation of energy of LC volume deformation (as a result of stronger surface anchoring at the relief) $E \sim K\vartheta^2/d$ gives $0.3 \cdot 10^{-6}$ J/m^2 (for elastic coefficient $K \sim 10^{-11}$ N, thickness $d \sim 10$ μm) for mentioned experimental value $\vartheta \sim 0.2$). As we see these estimations give close values, which says in the favor of steric mechanism of liquid crystal alignment.

FIGURE 3 Illustration of the LC director alignment along the grooves of the holographic grating written onto the polymer surface

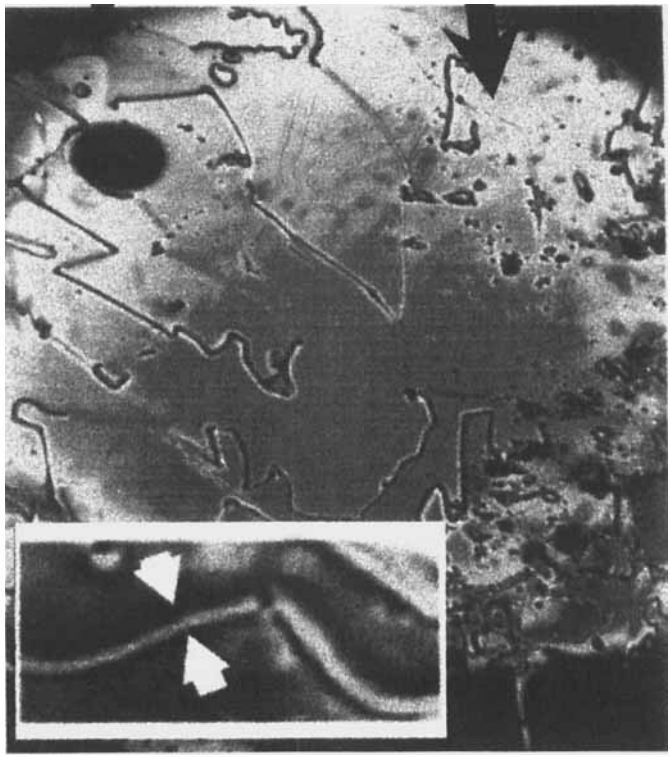

FIGURE 4 The photograph of nematic LC aligned on the surface of the polymer 3 with the grating written by circularly polarized light (inset shows a defect region used to determine surface energy). Black arrow points exposed area (grating area), while dark periphery is unexposed blank polymer.

We have made efforts excluding others sources of LC alignment different from the surface relief. First of all we have considered possible alignment of LC mediated by azo-groups alignment on the surface of polymer. The last

alignment is possible and occurs under polarized light. We performed experiments when the alignment on azo-groups could be excluded, when influence of these groups was diminished and when there was pure alignment of such groups. We tested the LC alignment on the samples with the same relief, but these samples have been protected with PVCi overcoat film of 100 nm in thickness. This coating suppresses an ability of oriented side-group to interact with LC but keeps the surface relief. These samples retained the ability to align the LC homogeneously. The coated samples demonstrated longer lifetime (approximately 24 hours) compare with bare polymer surface relief. Measurements of surface anchoring energy [15] became therefore possible and gave the value of $0.6 \cdot 10^{-6}$ J/m^2 for the surface with the relief and $0.5 \cdot 10^{-6}$ J/m^2 for the surface with PVCi but without relief. Thus this experiments also shown the extra anchoring energy due to the relief on the polymer. Several gratings were written with circular polarized laser light, which excluded polymer azo-groups alignment by linearly polarized light. These gratings were able to align the LC on them. The other verifying experiments included the alignment on the surface of the polymer under spatially uniform linearly polarized illumination when the shorter relaxation time of LC orientation was shown (this alignment probably could be indebted to the alignment of azo-group in the polymer film). The LC molecules returned in a few minutes to the initial homeotropic state after the illumination interruption. The saturated value of the LC inclination angle in this case was set in 1-2 minutes after the illumination start achieving approximately 10° at the intensity of 3-10 mW/cm^2. These three above verifying experiments say in favor of the surface relief mechanism of the LC alignment observed in the main experiment with the grating.

CONCLUSIONS

Permanent LC alignment exists on the surface relief grating recorded via holographic process on azo-group containing polymer films. The verifying experiments and estimations say in a favor of LC alignment by the surface relief. The surface relief can be created not exclusively by means of holography. It can be written also in a projection scheme (as a photolithography setup) and the polymer layer could be transformed into a large polymer micro-circuit combining both LC aligning elements and elements for light guid-

ance, modulation etc. The polymer photomodification process is in the compliance with a waveguide technology [16] (to make light coupling and modulating elements), hence different combination of the polymer waveguides and LC elements can be constructed on this base. The process of a relief formation seems to be reversible as the gratings can be rewritten optically [12, 17] (opposite to the permanent lithographic relief made onto ITO or polyimide coating on glass surfaces). This promises new opportunities for LC technology in a part of readjustment of LC elements and devices.

As LC and polymer are close in their refractive indices there is no reflection on their interface. The short life time realized for the investigated samples (a few hours due to the polymer solubility in LC and 24 hours in the same overcoated samples) can be extended as the gratings can be inscribed onto a number of the azo-dyes substituted polymers [10, 11]. Hence it should be possible to apply these results to the more stable LC-polymer pair (variant to protect relief by the over-coating could be also fruitful).

When this work was being prepared for publication the results of research on the similar subject has appeared [18]

Acknowledgements.
A. Parfenov thanks Association for Super-Advanced Electronics Technologies (ASET), New Energy Development Organization (NEDO), Electrotechnical Laboratory and Mississippi State University for support. Dr. H.Yokoyama suggested using our previous results with the polymers for liquid crystal technique and his considerations were of great importance for the revision of this work. Dr. R. Sun generously helped in measurements of surface anchoring energy.

References

[1] W.M. Gibbons, P.J. Shannon, S.T. Sun and B.J Swetlin, *Nature* **351** No.6321, pp.49–50 (1991).
[2] A. G. Dyadyusha, T. Ya. Marusii, Yu. A. Reznikov, *JETP Letters* **56** n 1, p. 18 (1992).
[3] V. Chigrinov, V. Kozinkov, M. Schadt and K. Schmitt, *Jap. J. Appl. Phys.*Pt. 1, **31** No. 7, p.2155(1992).
[4] K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, *Langmuir,* **4,** 1214 (1988). See also series of publications by H. Tomita, K. Kudo, K. Ichimura – "Command surfaces", e.g., *Liquid Crystals* **20,** No.2, pp.171–176 (1996).
[5] D.W. Berreman, *Mol. Cryst. Liq. Cryst.*, **23** p.215 (1973).
[6] V.K. Gupta and N.L. Abbot, *Science,* **276** pp. 1533–1536 (1997).
[7] G.P. Bryan-Brown, C.V. Brown, I.C. Sage, V.C. Hui, *Nature,* **392** pp.365–367 (1998).
[8] C.J. Newsome, M. O'Neill, R.J. Farley, G.P. Bryan-Brown, *Appl. Phys. Lett.*, **72** No.17, pp.2078–2080 (1998).
[9] S. Hvilsted, F. Andruzzi, C. Kulinna, H. W. Siesler, P. S. Ramanujam, *Macromolecules* **28** p.2172 (1995).
[10] D.Y. Kim, Lian Li, X. L. Jiang, V. Shivshankar, J. Kumar, S. K. Tripathy, *Macromolecules* **28** No.26, pp. 8835–8839 (1995).
[11] C.J. Barret, A.L Natansohn, P.L. Rochon *J. Phys. Chem.* **100**, No.21, pp. 8836–8842 (1996).
[12] K. Harada, M. Itoh, H. Matsuda, S. Ohnishi, A. Parfenov, N. Tamaoki, T. Yatagai *J. Phys. D.: Appl. Phys.*, **31,** 463–471 (1998).

[13] X.T. Li, D.H. Pei, S. Kobayashi, Y. Iimura, *Jpn. J. Appl. Phys.*, **36,** pp.L432–434 (1997).
[14] Y. Iimura, S. Kobayashi, T. Hashimoto, T. Sugiyama, K. Katoh *IEICE Trans. Electron.*, **E79-C,** No.8, pp. 1040–1046 (1996).
[15] H. Yokoyama and H.A. Van Spring, *J. Appl. Phys.*, **57,** pp. 4520–4526 (1985).
[16] K. Harada, M. Itoh, H. Matsuda, S. Ohnishi, N. Tamaoki, A. Parfenov and T. Yatagai *OSA TOPS,* **14** Spatial light modulators, ed. G. Burdge and S. Esener, pp. 132–137 (1997).
[17] X.L. Jiang, L. Li, J. Kumar, D.Y. Kim, S.K. Tripathy, *Appl. Phys. Lett.,* **72** No.20, pp. 2502–2504 (1998).
[18] Xiang Tong, A. Natansohn, Paul Rochon, *Appl. Phys. Letters* **74** pp.3791–3793 (1999).