CURED PMMA THIN FILMS FOR GREATLY IMPROVING THE ELECTRO-OPTICAL RESPONSE TIME IN NEMATIC LIQUID CRYSTAL PIXELS

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Comprehension of the interface/surface physical anchoring properties of nematic liquid crystals represents a constant challenge for many researchers in the field, while being also of great importance in the flat panel display industry, where controlling and enhancing the characteristics of optical devices based on these active materials is essential. Herein, we demonstrate the use of PMMA thin layers for highly improving the response (rise-up) time in a typical liquid crystal pixel. Experimental investigations show that these polymeric films strengthen the planar anchoring energy at the surface, providing a very fast reorientation of the nematic molecules when the applied electric field is switched off. Therefore, we are able to obtain particularly elevated refresh rates that are highly suitable for display applications.

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1. Introduction

Liquid crystals (LCs) are mesophase materials with physical properties between isotropic liquids and ordered solids, having characteristics from both these states of matter [1-4]. Liquid crystalline materials possess special physical properties such as the possibility to flow (specific to fluids), but also anisotropy of electrical, magnetical and optical properties (particular to solids) [1-6].

It immediately follows that this interesting class of materials has some unique combination of optical, electrical and mechanical properties [1-4, 7-9], being of considerable interest for both engineers and scientists [8-13]. The main technological application of the liquid crystals is in the field of the display devices [8, 9, 14-17].

The physical properties of LC displays are strongly determined by the orientational order imposed in the mesophase by the anisotropic interaction between the molecules, that compete with the surface anchoring effects and, eventually, with some electric fields [1-4, 8, 9]. The theoretical description of these interactions is of special interest to the scientific investigation from both theoretical [1-4, 17-20] and experimental points of view [8, 21-26]. In order to obtain a specific director distribution inside a liquid crystalline cell (or system), it is of the particular importance to initially and precisely describe the director distribution inside it. However, the theoretical study of the molecular arrangement of the liquid crystal molecules is a very complicated task, because of the complex calculus involved. Nevertheless, this can be significantly improved by computer simulations [14, 16, 27-33].

Understanding the interface properties of the nematic LCs represents a continuous challenge for many researchers in the field and is also relevant to controlling and enhancing the characteristics of optical devices based on these optical active materials [1, 2, 8, 9, 22-24]. In the last decades, much effort was devoted to obtaining appropriate polymeric substrates to be used as predetermined alignment materials for the liquid crystal molecules [34-40].

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In this manuscript we present the obtained results regarding the very fast on-off response times from nematic liquid crystal pixels when using an inside-cell deposited PMMA thin film substrate for controlling the initial planar anchoring energy of the LC molecules. The achieved electro-optical switching is fast enough and could be implemented in the flat panel (NLC display) industry.

2. Materials and methods

Flakes of poly(methyl methacrylate) (PMMA) (Sigma-Aldrich Chemistry) were dissolved in chloroform using a 8 hours ultrasonic bath. The resulting mixture had a concentration of 5% (weight ratio) and was used to obtain five thin film depositions on ITO covered glass (15 mm x 15 mm) by means of the spin coating technique.

Table 1. Samples and applied treatments.

Sample No.	Speed (rmp)	PMMA mixture	Treatment
1	200	1 ml	No Treatment
2	200	1 ml	Heated (100^{o})
3	200	1ml	Air plasma
4	200	1 ml	N_2 plasma
5	2000	2 ml	Planar Rubbing
6	no	no	Reference sample

Samples 1 and 6 were used as references in order to check the electro-optical behavior without any successive treatment and without any coating respectively. Sample 2 was heated to 100^{o}C for 20 minutes using an INSTEC mK1000 high precision Peltier stage and controller. Samples 3 and 4 were treated in a reflex plasma reactor [41] that uses a hallow cathode combined with a Penning trap in order to generate a high density plasma (~10^{16} electrons/m^3). First one was treated in air and the second one in a N_2 atmosphere, both at $1 \cdot 10^{-2}$ torr ($1.3 \cdot 10^{-2}$ mbarr). For the 5th sample we used a higher rotational speed during the spin coating process (in order to have a thinner uniform film). Afterwards we also applied to this sample a smooth unidirectional planar rubbing by means of a cotton bud.

Under the optical microscope, all these samples look roughly the same (no major differences have been observed), being uniform films.

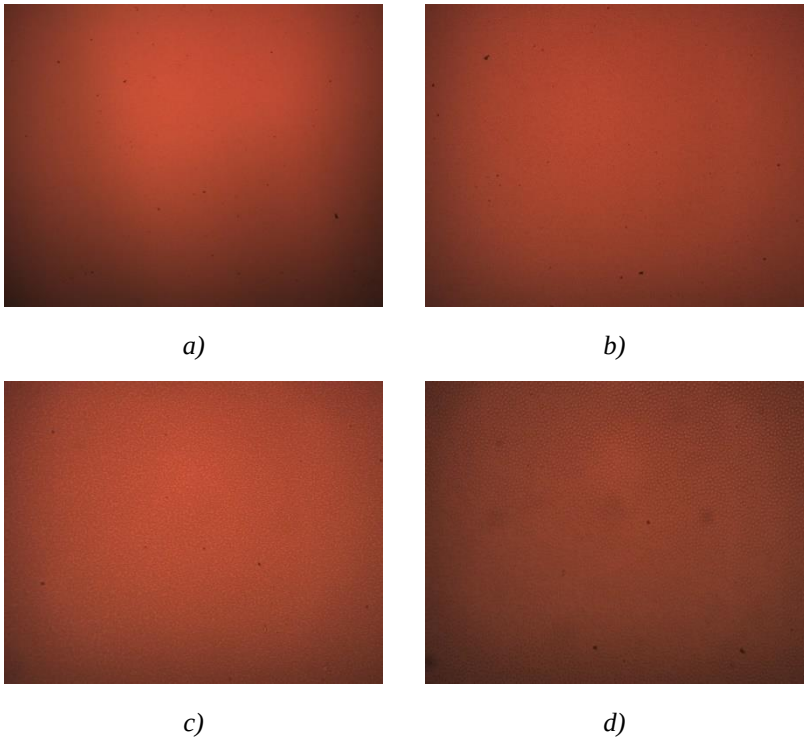


Fig. 1. Optical microscope images a)5x, b)10x, c)20x and d)50x for PMMA deposited sample 1.

These glass substrates (samples 1-6) coated with PMMA were subsequently used in the fabrication of liquid crystal cells (pixels). The cells are built using a second ITO deposited glass slide, which is sandwiched at a small distance from the PMMA glass plate by means of a 20 micron Mylar spacer. The volume between the plates was then filled by capillarity with the nematic liquid crystal E7 (from Merck).

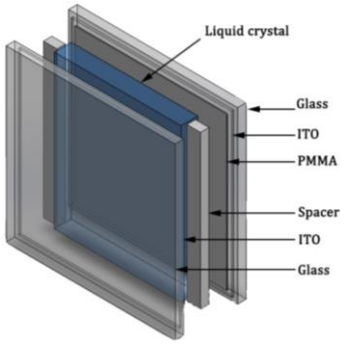


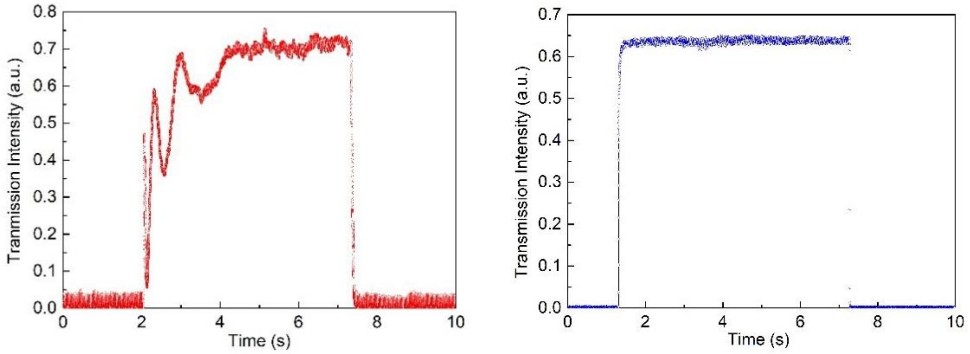
Fig. 2. Schematic representation of the fabricated liquid crystal sample cell (pixel).

The resulting liquid crystal cells were investigated on an electro-optical testing bench. The beam from a 633nm He-Ne continuous laser was directed through a polarizer, the LC pixel, an analyzer. At the end this effect was converted to an electric current by a fast photodiode. A rectangular shape electric field was applied to the electro-optical cells (+10V ; -10V), while the frequency was selected in the range 10 – 1000 Hz. Using crossed optical polarizors condition, we have then registered the electro-optic effect. The obtained signal was recorded on a 1 GHz Tektronix DPO 4032 oscilloscope.

3. Results and discussions

Taking advantage of the high dielectric anisotropy of nematic liquid crystalline materials all current LED (Light Emitting Diode) flat TV panels use the texture modification in thin films of a nematic material when applying an appropriate external voltage (DC or AC). When the field is off, a suitable method to illustrate the molecular configuration in a nematic film in an equilibrium arrangement dictated by the boundary glass surfaces is by means of the director *n*, that denotes an average of the molecular long axis orientations in the bulk. The application of the electric field between the two ITO glass slides alters the texture of the thin nematic layer. Considering the starting symmetric planar configuration of the sample (i.e. molecular director is parallel to the glass plates), the texture switches to homeotropic (i.e. perpendicular to the glass slides) only when the voltage exceeds a particular limit value (called Freedericksz threshold). An ideal homeotropic molecular arrangement yields the pixel uniaxial with respect to a linearly polarized light beam that crosses the sample perpendicular to its boundaries. When our sample is positioned between two crossed polarizers the light passes because of the planar alignment of the nematic director (we also choose a preferential direction for *n* to be at 45° with respect to one of the polarizers main axis). In contrast, a total homeotropic orientation of the NLC will give zero transmitted light through the pixel. Changing the applied voltage intensity one can play with the director pattern from maximum transmitted light (electric field off) to minimum transmitted light (when the electric field is on). Obviously, there exists a typical time, generally considered between a level of 10% up to 90% of the stable on and off textures. Switching off the voltage, because of the existing anchoring energies at the surfaces, the NLC system can relax with another distinctive time (90% to 10%). The characteristic time at field on (*t on*) is normally of the order of milliseconds (the positive dielectric anisotropy nematic molecules are rapidly reoriented). Meanwhile, at switching the field off (*t off*), the response time could be as large as seconds (the visco-elastic forces slowly reorganize the nematic molecules to the initially known boundary conditions). Therefore, for *t off* the refreshing frequency of the pixel cell would be less than 1 Hz, that is totally undesirable for a potential flat panel display application. To surmount this problem we herein demonstrate that the use of PMMA as coating for one side of the cell surface may induce very strong anchoring (and therefore fast reorientation of the NLC within the pixel).

By switching on a strong enough voltage across the sample (10V), the transmitted light is blocked. When switching off the voltage the NLC slowly relaxes back to the planar texture with a particular high characteristic time and with oscillations of the transmitted light intensity. Figures 3a and 3b depict this situation. We can observe the clear dissimilarity between the switch off time (Fig. 3a at the instant 2s) together with the electro-optic oscillations and the switch on characteristic time (Fig. 3a at the instant 7.5s) in a regular pixel (non PMMA - i.e. sample 6).



a) *b)*

Fig. 3. (a) Response times (t off and t on) for a regular NLC pixel (sample 6). (b) Response times (t off and t on) for a PMMA coated NLC pixel (sample 5).

We have that *t off* corresponds to the rise-up of the recorded curve (Transmission intensity increases) and *t on* corresponds to the fall down of the curve (when a dark pixel is obtained corresponding to zero transmission). Rise time value for a LC cell is considered to be the time it takes the LC to relax back and rearrange to the surface conditions and let the light pass through it (measured from 10% to 90% of the outgoing light). Figure 3b is obtained in the case of an electo-optical cell containing a thin PMMA film (sample 5). Here, one can observe that because of the strong anchoring induced by the PMMA layer the *t off* time is significantly smaller than in the case of a regular NLC sample.

In Figs. 4-8 below we present the response times (*t off*) in the case of all our samples.

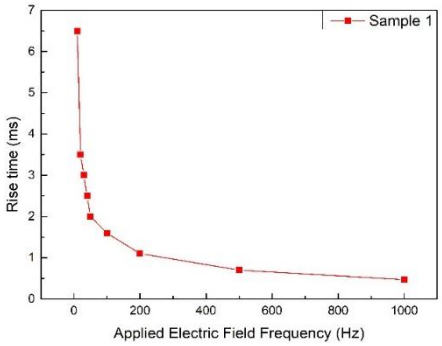


Fig. 4. Electro-optical response time (t off) for sample 1.

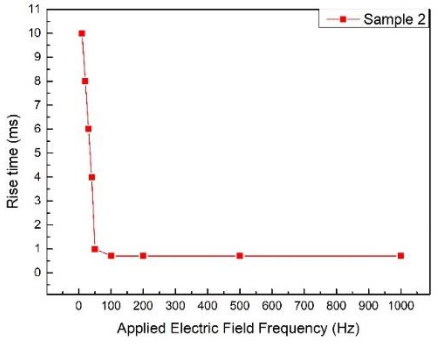


Fig. 5. Electro-optical response time (t off) for sample 2.

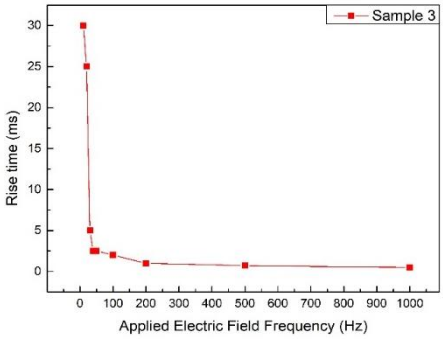


Fig. 6. Electro-optical response time (t off) for sample 3.

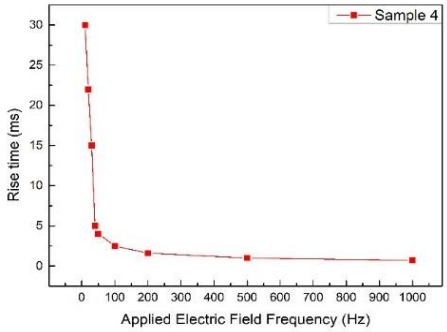


Fig. 7. Electro-optical response time (t off) for sample 4.

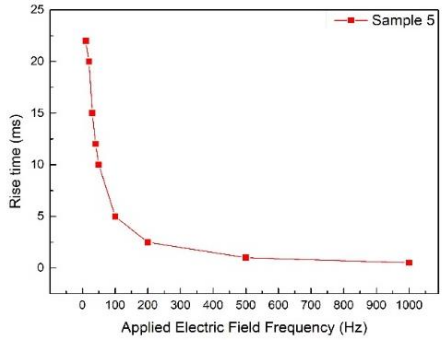


Fig. 8. Electro-optical response time (t off) for sample 5.

The experimental values can also be found in the table below and in Fig. 9 for a better comparison. The results for the *t off* are given in milliseconds (ms).

Table 2. Experimental data for the t off time measured for our samples.

v (Hz)	*S1 (ms)*	*S2 (ms)*	*S3 (ms)*	*S4 (ms)*	*S5 (ms)*
10	6.5	10	30	30	22
20	3.5	8	25	22	20
30	3	6	5	15	15
40	2.5	4	2.5	5	12
50	2	1	2.5	4	10
100	1.6	0.7	2	2.5	5
200	1.1	0.7	1	1.6	2.5
500	0.7	0.7	0.7	1	1
1000	0.5	0.7	0.5	0.7	0.5

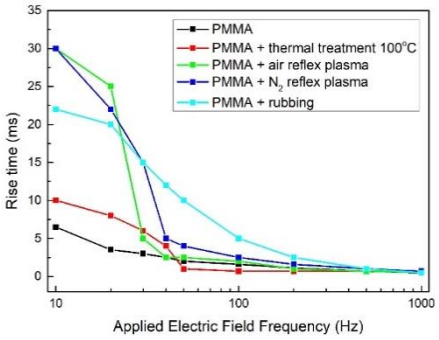


Fig. 9. Electro-optical rise time response (t off) of our PMMA NLC cells versus the applied electric field frequency.

We can clearly distinguish that for all our PMMA samples we obtain very good rise response times (*t off*) of the order of tens of ms (corresponding to circa 10-30Hz attainable optical refresh rate) for the low frequency of the applied electric field. For certain pixels (S1,S2,S3,S4) we can obtain great optical refresh rates (circa 200-300 Hz) for above 30Hz of the applied electric field making these materials suitable for application in the display industry. At higher voltage frequencies (500Hz) we are already obtaining remarkable values of the refresh rates (*t off* below 1ms – corresponding to over 1kHz controllable refresh rate for the pixel – far above the requirements for a flat panel LCD).

4. Conclusions

We conclude that the use of PMMA thin films as boundary planar conditions in standard nematic liquid crystal pixel cells highly improve the passive response time (rise up time) of the electro-optical effect. These results indicate this material (together with the subsequent treatments – plasma, thermal, rubbing) as a good candidate for immediate use in the flat panel LED LCD display industry.

References

[1] P. G. De Gennes, J. Prost, The Physics of Liquid Crystals, Clarendon Press, Oxford, 1993.
[2] S. Chandrasekhar, Liquid Crystals, Cambridge University Press, 1993.
[3] E. Priestly, Introduction to Liquid Crystals, Springer, 1976.
[4] P. J. Collings, M. Hird, Introduction to Liquid Crystals: Chemistry and Physics (Liquid Crystals Book Series), CRC Press, 1997.
[5] A. A. C. Toledo Hijo, G. J. Maximo, M. C. Costa, R. L. Cunha, J. F. B. Pereira, K. A. Kurnia, E. A. C. Batista, A. J. A. Meirelles, J. Phys. Chem. B **121**(14), 3177 (2017).
[6] N. Dalir, S. Javadian, J. Kakemam, A. Yousefi, Journal of Molecular Liquids **265**, 398 (2018).
[7] C. Berlic, L. Constantinescu, Revista de chimie **55**, 910 (2004).
[8] L. P. Jones, Alignment Properties of Liquid Crystals. In: J. Chen, W. Cranton, M. Fihn (eds) Handbook of Visual Display Technology. Springer, Berlin, Heidelberg, 2012.
[9] L. M. Blinov, V. G. Chigrinov, Electro-Optic Effects in Liquid Crystal Materials, Springer, New York, 1994.
[10] L. van 't Hag, S. L. Gras, C. E. Conn, C. J. Drummond, Chem Soc Rev. **46**(10), 2705 (2017), doi: 10.1039/c6cs00663a.
[11] A. L. Alexe-Ionescu, A. T. Ionescu, E. S. Barna et. al., Applied Physics Letters **84**(1), 40 (2004).
[12] H. Furue, Y. Ebato, A. Ninomiya, H. Sasaki, Mol. Cryst. Liq. Cryst. **646**(1),

99 (2017), DOI: 10.1080/15421406.2017.1284541.
[13] V. Barna, A. De Luca, C. Rosenblatt, Nanotechnology **19**(32), 325709 (2008).
[14] C. Berlic, V. Barna, Optics Express **18**(23), 23646 (2010).
[15] M. Kim H. S. Jin, S. J. Lee, Y. H. Shin, H. G. Ham D. K. Yang, P. J. Bos, J. H. Lee, S. H. Lee, Advanced Optical Materials **6**, 11 (2018).
[16] C. Berlic, V. Barna, Mol. Cryst. Liq. Cryst. **549**, 140 (2011).
[17] C. Miron, F. Simion, Materiale Plastice **41**(3), 185 (2004).
[18] C. Miron; D. Nedelcu, Materiale Plastice **41**(4), 215 (2004).
[19] C. Miron, Revista de Chimie **59**(2), 181 (2008).
[20] L. Georgescu, C. Berlic, C. Miron, Revista de Chimie **55**(5), 317 (2004).
[21] E. S. Barna, C. Iliescu, C. Miron, D. Nedelcu, V. Barna, C. Berlic, Materiale Plastice **41**(1), 36 (2004).
[22] A. L Alexe-Ionescu, A. T. Ionescu, E. S. Barna et al., Journal of Physical Chemistry B **108**(26), 8894 (2004).
[23] A. De Luca, V. Barna, S. Ferjani et al., Journal Of Nonlinear Optical Physics & Materials **18**(3), 349 (2009).
[24] M. D. Asiqur Rahman, H. Agha, T.-K.Truong, J. H Park, D. Suh, G. Scalia, Journal of Molecular Liquids **267**, 363 (2018).
[25] J.-H. Lee, J. T. Atherton, Timothy, V. Barna et al., Physical Review Letters **102**(16), Article Number: 167801, 2009.
[26] V. Barna, S. Ferjani, A. De Luca, et al., Applied Physics Letters **87**(22), Article Number: 221108, 2005.
[27] D. Frenkel, B. Smit, Understanding Molecular Simulation: From Algorithms to Applications, Academic Press, New York, 2001.
[28] D. P. Landau, K. Binder, A Guide to Monte Carlo Simulations in Statistical Physics, Cambridge University Press, Cambridge, 2000.
[29] P. Pasini, C. Zannoni, S. Žumer (Eds.), Computer Simulations of Liquid Crystals and Polymers, Kluver Academic Publishers, Dordrecht, 2005.
[30] M. P. Allen, D. J. Tildesley, Computer Simulation of Liquids, Oxford University Press, Oxford, 1989.
[31] C. Berlic, V. Barna, J. Optoelectron. Adv. M. **12**(6), 1427 (2010).
[32] C. Berlic, M. Moisescu, V. Barna, Digest Journal of Nanomaterials and Biostructures **7**(4), 1401 (2012).
[33] C. Berlic, E. Barna, C. Ciucu, J. Optoelectron. Adv. M. **9**, 3854 (2007).
[34] U. V. Mahilny, A I. Stankevich, A. A. Muravsky, A. A. Murauski, J. Phys. D: Appl. Phys. **42**, doi:10.1088/0022-3727/42/7/075303, 2009.
[35] C. Berlic, V. Barna, B. Manolescu, et al., Digest Journal of Nanomaterials and Biostructures **8**(4), 1845 (2013).
[36] V. Barna, C. Miron, C. Berlic, E.S. Barna, Materiale Plastice **40**(4), 168 (2003).
[37] C. Berlic, C. Miron, Romanian Reports in Physics **69**(4), 120 (2017).
[38] C. Berlic, V. Barna, Digest Journal of Nanomaterials and Biostructures **11**(1), 159 (2016).
[39] A. M. Parshin, V. Y. Zyryanov, V. F. Shabanov, Scientific reports **7**(1), 3042 (2017), doi:10.1038/s41598-017-03243-5
[40] A. Malik, B. Kandasubramanian, Polymer Reviews 1-38, doi: 10.1080/15583724.2018.1473424, 2018
[41] E. Barna, V. Covlea, H. Andrei, E. I. Toader, Fizika A (Zagreb) **9**(2), 87 (2000).