Mol. Cryst. Liq. Cryst., Vol. 527: pp. 130/[286]–136/[292], 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2010.486714

Liquid Crystal-Carbon Nanotubes Composites with the Induced Chirality: The Way Towards Enhancement of Electro-Optic Memory

S. TOMYLKO,[1,2] L. DOLGOV,[1] T. SEMIKINA,[1,3] AND O. YAROSHCHUK[1]

[1]Institute of Physics NASU, Kyiv, Ukraine
[2]Taras Shevchenko National University, Physical Faculty, Kyiv, Ukraine
[3]Institute of Semiconductors Physics, NASU, Kyiv, Ukraine

It is found that the effect of electro-optic memory earlier revealed in the liquid crystal (LC) – carbon nanotube (CNT) suspensions can be substantially enhanced by doping the LC with small amount of chiral agent. The induced chirality weakens homeotropic anchoring set by the aligning layers helping CNT network to maintain state of planar LC alignment realized in the electric field.

Keywords Carbon nanotubes; liquid crystal; memory effect

PACS 42.70.Df; 42.79.Kr; 77.22.Ch; 77.84.Lf; 81.07.De

1. Introduction

Recent years saw rapidly increasing interest to liquid crystals (LC) doped by carbon nanotubes (CNT). This interest is twofold. On the one hand, liquid crystal as an anisotropic liquid media is a unique host for CNT; the nanotubes ideally blend with LC, assume its orientational order and reorient together with the LC in an external field [1,2]. On the other hand, the dispersed CNT may essentially change viscoelastic [3], electrical [4,5] and electro-optical properties of LC [6,7] improving their characteristics for traditional applications (displays, shutters, LC lenses, etc.) and opening new application perspectives.

The LC-CNT composites exhibit number of amazing effects. One of them is the effect of electro-optic memory recently observed for the suspensions of multiwalled CNT in nematic LC with negative dielectric anisotropy [8,9]. The effect consists in irreversible electric switching of the suspension layer from dark to bright state when the layer is viewed between a pair of crossed polarizers. In the transmittance vs. voltage plot, it is detected as a residual transmittance T_m after the electric field is off.

The described effect is caused by homeotropic-to-planar alignment transition of LC-CNT composites under the electric field. The optical memory indicates that realized state of random planar alignment persists after the field switch-off. It is

Address correspondence to L. Dolgov, Institute of Physics, NASU, 46, Nauky Pr, Kyiv 03028, Ukraine. E-mail: dolgov@iop.kiev.ua

maintained by the CNT network formed in this alignment state of LC host. The network formation mechanism elucidated in [8,9] consists in the following. The electric field applied to the homeotropically aligned layer of LC-CNT suspension causes homeotropic-to-planar reorientation of the LC. At sufficiently high voltages, the homeotropic-to-planar reorientation of LC is accompanied by the intensive electro-hydrodynamic (EHD) flows disturbing the LC alignment and crushing big aggregates of CNT. The fine aggregates and single CNT appearing in a course of EHD dispergation form a fine CNT network. Since the network is formed in the state with planar LC alignment, it mimics an orientational ordering of LC hosts and maintains this ordering after the field is off.

The considered effect suggests new principle for displaying and storage of optical information in LC media. However, for these applications operation parameters of the memory type LC-CNT composites should be substantially improved. First of all, efficiency of the memory effect (i.e., switching contrast) should be essentially enhanced.

This paper describes effective way towards increasing of memory efficiency. The improvement is achieved by doping LC with a small amount of chiral dopant. This dopant causes additional force stabilizing planar alignment state realized in the electric field. Using this principle, efficiency of electro-optic memory was doubled.

2. Experimental

2.1. *Samples*

In these studies we used nematic mixture MLC6608 from Merck. This LC developed for a vertical alignment mode has dielectric anisotropy $\Delta\varepsilon = -4.2$ and clearing point at about 90°C. In contrast to nematic LC EBBA for which the memory effect was discovered [8], MLC6608 has nematic mesophase at ambient temperatures and thus is more convenient for experimental studies. Besides, it is more chemically stable and thus contains lower quantity of ions. It was also preliminarily checked that the MLC6608-CNT suspension clearly demonstrates the effect of electro-optic memory [9].

The LC was doped by chiral dopant (ChD) S811 from Merck ($c_{ch} = 0$–0.3 wt.%) and subsequently mixed with multiwalled CNTs (SpetsMash Ltd., Ukraine) by using ultrasonic mixer. The nanotubes were prepared from ethylene by the chemical vapor deposition method [10]. Typically, they had an outer diameter of about 15 nm and the length of about 5 μm. The samples with a zero concentration of chiral dopant were used as the reference one to elucidate influence of chiral dopant on the electro-optic performance.

The electro-optical cells were made from glass substrates containing patterned ITO electrodes and aligning layers of polyimide AL2021 (JSR, Japan) designed for homeotropic alignment. The polyimide layers were rubbed by a fleecy cloth in order to provide a uniform planar alignment of LC in the field-on state. The cells were assembled so that the rubbing directions of the opposite aligning layers were antiparallel. A cell gap was maintained by 16 μm glass spacers. The cells were filled by MLC6608/CNT composite using a capillary method.

2.2. *Methods*

The electro-optical measurements were carried out by using the experimental setup described in [11]. The cell was set between two crossed polarizers so that the angle between the polarizer axes and the rubbing direction was 45°. The sinusoidal voltage 0–60 V (at a frequency $f = 2$ kHz) was applied to the cell. The voltage was stepwise increased from 0 to 60 V and then decreased back to 0. The structure of the composites was monitored by observation of the filled cells placed between two crossed polarizers, both by naked eye and with an optical polarizing microscope. The microscope was conjugated with a digital camera making possible registration of the observed images.

3. Results and Discussion

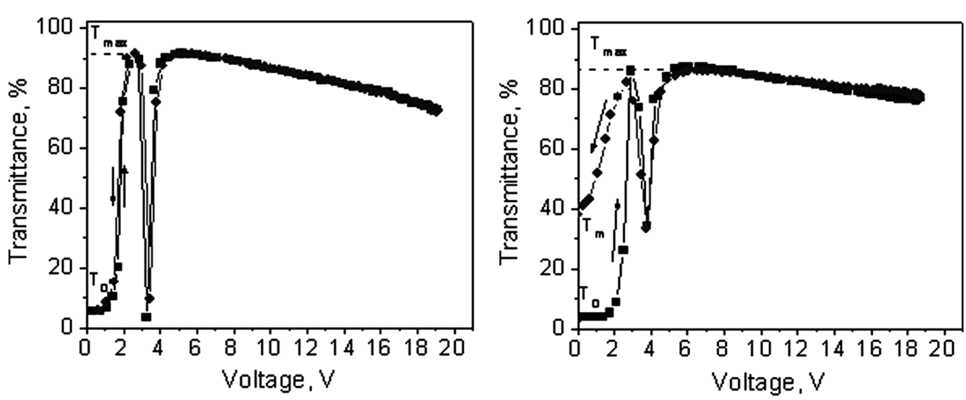
3.1. *Memory of LC-CNT Suspensions*

As was earlier established, MLC6608-CNT composites demonstrate memory effect starting from a very low concentration of CNT, c ($c > 0.01$ wt.%) [9]. To minimize probability of short-circuit in the cells, CNT concentration was kept at the low level ($c = 0.02$ wt.%) but above the limit needed for a clear memory effect.

The transmittance T vs. voltage U curves for the cell containing MLC6608-CNT suspension are presented in Figure 1b. For comparison, Figure 1a presents $T(U)$ curve for the reference sample containing neat LC MLC6608. The oscillations of $T(U)$ curves are caused by a phase incursion higher than $\pi/2$ appeared during the homeotropic-to-planar reorientation of LC in the electric field. In contrast to neat LC, MLC6608-CNT suspension demonstrates irreversible electro-optic response; instead of falling down to the initial value T_0, the sample transmittance keeps at the value $T_m >> T_0$ after the field is off. The efficiency of this process can be characterized by a memory parameter M:

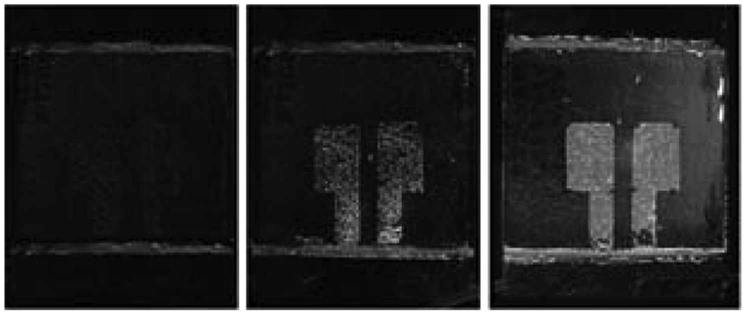
$$M = \frac{T_m - T_0}{T_{\max} - T_0} \times 100\%, \tag{1}$$

where $T_{\max}$ is a maximum value of transmittance (Fig. 1). For MLC6608-CNT sample, $M = 0.44$, while for the neat MLC6608 sample $M = 0$.



(a) (b)

Figure 1. The transmittance vs. applied voltage curves for the cells filled with LC MLC6608 (a) and MLC6608-CNT suspension (b). The arrows point directions of voltage ramping up and down.



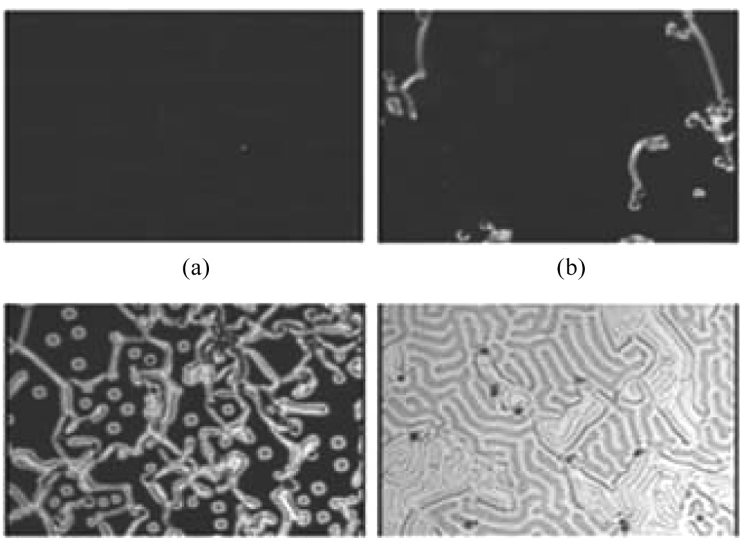
(a) (b) (c)

Figure 2. The cells filled with LC MLC6608 (a), MLC6608-CNT ($c = 0.02$ wt.%) (b) and MLC6608-ChD-CNT ($c = 0.02$ wt.%, $c_{ch} = 0.1$ wt.%) (c) suspensions viewed between a pare of crossed polarizers. The rectangular areas in the middle of the cells correspond to the pixels preliminarily subjected to cycle of electric field (30 V, 1 min).

The change in transmittance of MLC6608-CNT samples is clearly evident by a naked eye; the samples "bleach" in the areas subjected to the electric field cycle (Fig. 2b). In contrast, no any change in transmittance is visible in the reference samples based on the neat LC (Fig. 2a).

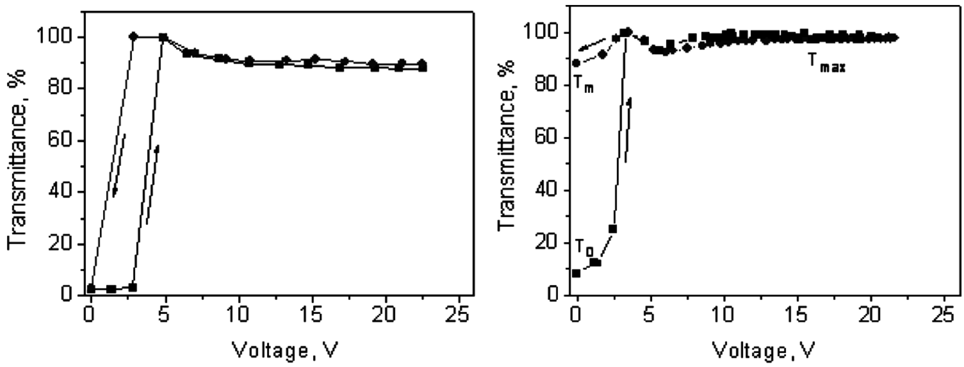
3.2. *Memory of LC-CNT Suspensions Doped by a Chiral Dopant*

The studies of these composites were carried out in two stages. The firs stage was aimed at optimization of chiral dopant concentration, c_{ch}. It is generally known that increase of c_{ch} strengthens twisting tensions in the LC. Figure 3 demonstrates that at



(c) (d)

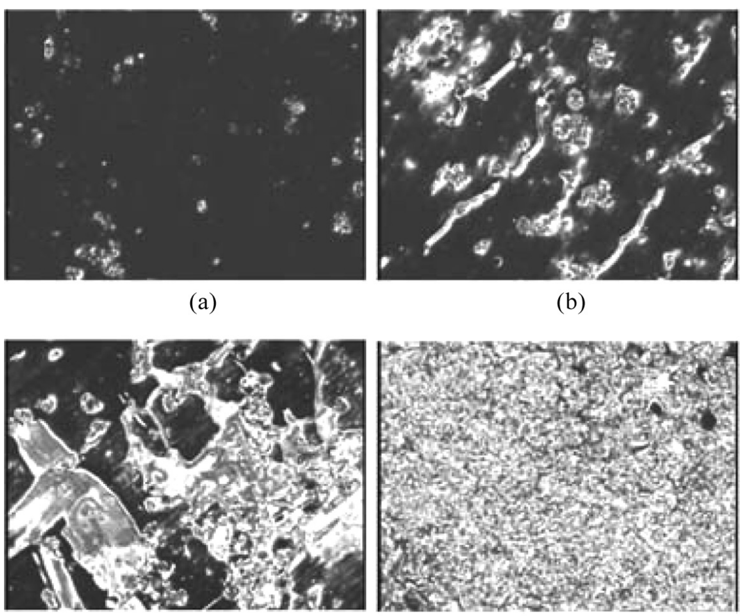
Figure 3. The cells filled with MLC6608-ChD compositions viewed in polarizing microscope (crossed polarizers view, ×100 magnification). The chiral dopant concentration is 0, 0.1, 0.15 and 0.2 wt.% in (a), (b), (c) and (d), respectively.



(a) (b)

Figure 4. The transmittance vs. applied voltage curves for the cells filled with MLC6608-ChD ($c_{ch} = 0.1$ wt.%) (a) and MLC6608-ChD-CNT ($c = 0.02$ wt.%, $c_{ch} = 0.1$ wt.%) (b) compositions. The arrows point directions of voltage ramping up and down.

$c_{ch} \leq 0.1$ wt.%, anchoring forces satisfactorily balance these twisting tensions maintaining homeotropic alignment. At $c_{ch} \geq 0.15$ wt.%, the anchoring forces can not restrain the twisting forces anymore that leads to formation of various helical structures; at $c_{ch} = 0.15$ wt.% the filamentary texture is formed which transforms in the fingerprint texture at higher concentrations. The maximal concentration



(a) (b) (c) (d)

Figure 5. Microphotographs of two cells filled with MLC6608-CNT ($c = 0.02$ wt.%) (a, c) and MLC6608-ChD-CNT ($c = 0.02$ wt.%, $c_{ch} = 0.1$ wt.%) (b, d) composition, respectively. The photos (a) and (b) show the cells before a field application, while the photos (c) and (d) show the same cells after the field application cycle (30 V, 1 min).

$c_{ch} = 0.1$ wt.%, at which a uniform homeotropic alignment was preserved, was selected for further preparation of LC-ChD-CNT samples.

The *T-U* characteristics for the LC-ChD-CNT sample and for the reference LC-ChD sample are given in Figure 4. As is evident, the LC-ChD sample demonstrates reversible response. In turn, transmittance of LC-ChD-CNT sample changes irreversibly showing high residual value in a zero field. The memory parameter estimated according to (1) is $M = 0.82$, i.e., the memory efficiency of LC-ChD-CNT sample is twice higher than that of the LC-CNT sample. The strengthening of the memory effect in the samples containing ChD can also be seen by a naked eye (Fig. 1). The observation in polarizing microscope demonstrates that the planar state has an islet structure in the LC-CNT samples, and a continuous structure in the LC-ChD-CNT samples (Fig. 5). This might explain the increased memory efficiency of LC-ChD-CNT samples.

The enhanced affinity of LC-ChD-CNT samples to planar alignment might be explained by the enhancement of forces resulting in a planar alignment. In the LC-ChD-CNT samples, the force associated with a CNT network is magnified by a twisting force, which eventually destroys homeotropic alignment. It worth mentioning that, in spite of the memory enhancement of LC-CNT samples, the twisting force by itself does not cause a memory effect (the case of LC-ChD samples, Fig. 4b). This suggests that the described memory effect is an intrinsic feature of CNT containing samples.

4. Conclusions

The efficiency of electro-optic memory of LC-CNT suspensions can be essentially (at least by a factor of 2) enhanced by doping this suspension by small amount of chiral agent. This realizes due to a twisting tensions caused by the chiral dopant, which, together with CNT network, support a planar alignment state of the LC formed in the electric field. It is shown that a chiral dopant concentration should be thoroughly optimized to realize a high switching contrast (high memory efficiency). The developed principle of the enhancement of electro-optic memory strengthens an application potential of this effect making it more suitable for the technologies of displaying and storage of optical information.

Acknowledgments

These studies were supported by NASci., Ukraine (grant VC 10-07-H) and "Dnipro" program of French-Ukrainian scientific cooperation (grant No. M/16-2009).

References

[1] Lynch, M. D., & Patrick, D. L. (2002). *Nano Lett.*, *2*, 1197.
[2] Dierking, I., Scalia, G., Morales, P., & LeClere, D. (2004). *Adv. Mat.*, *16*, 865.
[3] Jeon, S. Y., Shin, S. H., Lee, J. H., Lee, S. H., & Lee, Y. H. (2007). *Jpn. J. Appl. Phys.*, *46*, 7801.
[4] Lebovka, N., Dadakova, T., Lysetskiy, L., Melezhyk, O., Puchkovska, G., Gavrilko, T., Baran, J., & Drozd, M. (2008). *Journal of Molec. Struct.*, *877*, 135.
[5] Kovalchuk, A., Dolgov, L., & Yaroshchuk, O. (2008). *Semiconductor Physics, Quantum Electronics & Optoelectronics*, *11*, 337. (http://journal-spqeo.org.ua/n4_2008/v11n4-08-p337-341.pdf).

[6] Lee, W., Gau, J.-S., & Chen, H.-Y. (2005). *Appl. Phys. B*, *81*, 171.
[7] Lee, W., Chen, H.-Y., & Shih, Y.-C. (2008). *J. Soc. Info. Display*, *16*, 733.
[8] Dolgov, L., Yaroshchuk, O., & Lebovka, N. (2009). *Colloid J.*, *71*(5), 599.
[9] Dolgov, L., Yaroshchuk, O., & Lebovka, N. (2008). *Mol. Cryst. Liq. Cryst.*, *496*, 212.
[10] Melezhyk, A. V., Sementsov, Yu. I., & Yanchenko, V. V. (2005). *Appl. Chem.*, *78*, 938.
[11] Kovalchuk, O., Zakrevska, S., Yaroshchuk, O., & Maschke, U. (2001). *Mol. Cryst. Liq. Cryst.*, *368A*, 129.