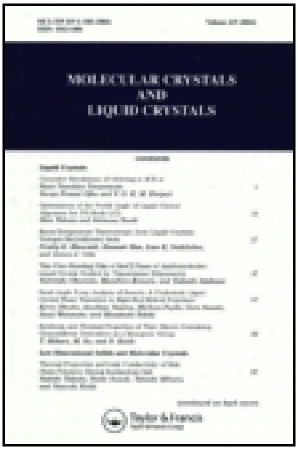

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Dispersions of Carbon Nanotubes in Cholesteric Liquid Crystals

L. N. Lisetski [a] , S. S. Minenko [a] , A. V. Zhukov [a] , P. P. Shtifanyuk [a] & N. I. Lebovka [b]

[a] Institute for Scintillation Materials, STC "Institute for Single Crystals", NAS of Ukraine, Kharkov, Ukraine

[b] Institute for Biocolloidal Chemistry, NAS of Ukraine, Kyiv, Ukraine

Version of record first published: 05 Oct 2009

To cite this article: L. N. Lisetski, S. S. Minenko, A. V. Zhukov, P. P. Shtifanyuk & N. I. Lebovka (2009): Dispersions of Carbon Nanotubes in Cholesteric Liquid Crystals, Molecular Crystals and Liquid Crystals, 510:1, 43/[1177]-50/[1184]

To link to this article: http://dx.doi.org/10.1080/15421400903058056

Mol. Cryst. Liq. Cryst., Vol. 510, pp. 43/[1177]–50/[1184], 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903058056

Dispersions of Carbon Nanotubes in Cholesteric Liquid Crystals

L. N. Lisetski[1], S. S. Minenko[1], A. V. Zhukov[1], P. P. Shtifanyuk[1], and N. I. Lebovka[2]
[1]Institute for Scintillation Materials, STC "Institute for Single Crystals", NAS of Ukraine, Kharkov, Ukraine
[2]Institute for Biocolloidal Chemistry, NAS of Ukraine, Kyiv, Ukraine

Dispersions were studied of multiwall carbon nanotubes in cholesteric liquid crystals of three types: nematics with chiral dopant, mixtures of cholesterol derivatives, and similar mixtures close to smectic-A transition. In the first two cases, no appreciable effects of nanotubes upon selective reflection spectra were noted, while optical transmission increased significantly at the isotropic phase transition. Aromatic and steroid matrices differed significantly in this respect, though in both cases the nanotubes were apparently oriented along the directors of quasi-nematic layers. In the third case, nanotubes slightly but clearly affected the measured selective reflection peaks, suggesting suppression of the smectic-A phase formation.

Keywords: cholesteric liquid crystals; helical pitch; multiwall carbon nanotubes; optical transmission; selective reflection; smectic-A

INTRODUCTION

Dispersions of carbon nanotubes (NTs) in liquid crystals (LC) were a subject of great interest in a number of recent studies. Orientational ordering of single- and multiwalled carbon nanotubes (MWCNTs) in nematic liquid crystal solvents was first reported in [1]. This effect was used for the controlled surface assembling of the organized blocks of NTs and other nanoscale particles [2]. Thus, LC can be used as templates, as their orientational order can be transferred to CNTs dispersed in them; this technique may thus play a decisive role in the future development of CNT technology. It was also found that carbon

Address correspondence to L. N. Lisetski, Institute for Scintillation Materials, STC "Institute for Single Crystals", NAS of Ukraine, 60 Lenin Ave., Kharkov 61001, Ukraine. E-mail: lisetski@isc.kharkov.com

NTs, dispersed in nematic matrices, followed the host molecules in re-orientation processes induced by electric [3,4] or magnetic [5] fields. From the other side, effects of nanotubes on LC phase behavior [6], as well as alignment of LC molecules on the glass substrates [7], were reported.

Doping of LC mixtures by NTs can be promising for liquid crystal display technologies. It was shown that minute additions of carbon NTs could substantially reduce the transient currents in nematic cells under DC electric fields [8,9]. Here, the carbon NTs presumably play the role of traps for the charge carriers, thus hindering the ion transport [10]. This, in turn, leads to suppression of the field screening, which largely eliminates the image sticking on LC displays. Also, the carbon NT dopants caused a decrease in rotational viscosity of the nematic matrix, resulting in shorter response times of LC electrooptic cells [11]. In another effect, NT aggregates dispersed in a nematic started to elongate above the certain threshold field strength, expanding up to four times their original size and restoring the initial morphology after removal of the electric field; this effect is thought to be useful for shortening of the response times in LC displays and improvement of the image quality [12].

In all these works involving the combination of carbon nanotubes (CNTs) and liquid crystals, only nematic liquid crystals were used. Alongside with the above-noted thermotropic nematics, lyotropic nematics were also shown to be a promising medium which can be used to align and at the same time disperse CNTs [13,14]. As for introduction of CNTs into mesophases of more complex structure than nematics, only a few examples can be given. Thus, CNT dispersion in a hexagonal columnar lyotropic phase was reported [15], and an attempt was made of CNT-doping of chiral smectics [16]. In this latter case, effects of CNTs upon smectic ordering were mostly disruptive, though many subtle features could be noted.

In this study, the anisotropic media used for dispersing carbon nanotubes represented one more type of liquid crystals with complex character of long-range molecular ordering – cholesteric liquid crystals (CLC). The relatively easily measured CLC parameters that could be expected to be affected by introduction of CNTs were the helical pitch (estimated from selective reflection peaks) and changes in optical transmission at the cholesteric-isotropic transition point outside selective reflection and absorption bands. The latter method has been used recently for studies of nematics with dispersed multiwall carbon nanotubes (MWCNTs) [17,18]. Three different types of cholesteric matrices were used – induced cholesterics (i.e., nematics with optically active dopants), steroid cholesterics (based on mixtures of cholesterol esters), and cholesterol ester mixtures exhibiting helix unwinding at temperatures close to cholesteric-smectic A transition point.

MATERIALS AND METHODS

Three different cholesteric hosts were used: (1) an induced cholesteric composed of 70% of nematic ZhK-1282 (a commercial mixture of several 4-alkyl- and 4-alkoxy-4′-cyanobiphenyls and nematic cyclohexyl-containing esters, NIOPIK, Russia) and 30% of chiral dopant 4-(2-methylbutyl)-4′-cyanobiphenyl (CB-15, Merck, Germany); (2) a mixture of 80% COC (cholesteryl oleyl carbonate, Aldrich, USA) and 20% CC (cholesteryl chloride, Chemical Reagents Plant, Kharkov, Ukraine); 3) a mixture of 60% cholesteryl nonanoate, 20% cholesteryl caprynate and 20% cholesteryl caprylate (Chemical Reagents Plant, Kharkov, Ukraine), designated below as Matrix M4.

The MWNTs were prepared from ethylene using the chemical vapour deposition (CVD) method. FeAlMo0.07 was used as catalyst [19], and subsequent treatment by concentrated alkali (NaOH) and acid (HCl) solutions was followed by filtering and repeated watering until the pH value of the filtrate became the same as that of the distilled water [19]. The residual mass content of the mineral additives was <1%. The MWCNTs involved typically had the outer diameter d_e about 10–20 nm, while their length ranged from 5 to 10 μm. Further details can be found in [18].

The MWCNTs+LC composites were obtained by adding the appropriate weights of NTs (0.005–0.1%) to the LC solvent in the isotropic state with subsequent 20–30 min sonication of the mixture using a UZDN-2 T ultrasonic disperser, in accordance with procedure essentially similar to the previously described [20,21].

The optical transmission spectra were measured in a 50 μm thick cell using a Hitachi 330 spectrophotometer. The studied dispersion was introduced between the cell walls by the capillary forces at a temperature above the cholesteric-isotropic transition point.

Before introduction of the MWCNTs+LC composites into the cell, the cell walls were treated with polyvinyl alcohol water solution and, after drying, rubbed in one direction to obtain the planar texture. The presence of clearly distinguished peaks of the selective reflection bands suggested sufficient perfection of the obtained planar alignment.

All optical transmission values were determined at 700 nm. This wavelength was chosen as optimal because it was well above the absorption region and selective reflection bands of the studied CLC solvents. The parallel experiments were done under identical conditions for the CLC+MWCNT dispersion (T) and the undoped liquid crystal (T_o).

RESULTS AND DISCUSSION

The cholesteric-isotropic (or nematic-isotropic) transition commonly results in a step-wise increase in the optical transmittance T. An example of such behaviour is presented for ZhK1282+CB15 system (Fig. 1). The presence of NTs in a LC matrix even enhances such transitional behaviour, and the optical transmittance jump can be substantial within the studied concentration range of MWCNTs.

The measured transmittance values are influenced both by molecular ordering of the LC host and the structural ordering of MWCNTs inside suspension. To separate the effects of these two factors, we introduced a somewhat artificial parameter $T_o - T$ – the difference between transmittances of the undoped LC matrix (T_0) and the same matrix with dispersed NTs (T). This parameter can serve as a measure of contribution of the dispersed NTs to the total value of $(1 - T)$ (i.e., absorption + reflectance/scattering) of a composite at the given wavelength. Thus, the value of $(T_o - T)$ can be used for characterization of the structural ordering and integration of NTs in a composite [17,18]. The dependence of $(T_o - T)$ on temperature for the ZhK1282+CB15 with nanotubes is shown in Figure 2.

Similar optical transmission measurements were carried out for COC+CC (80:20) cholesteric mixture (Fig. 3). The introduction of MWCNTs made much more pronounced the transmission jump at

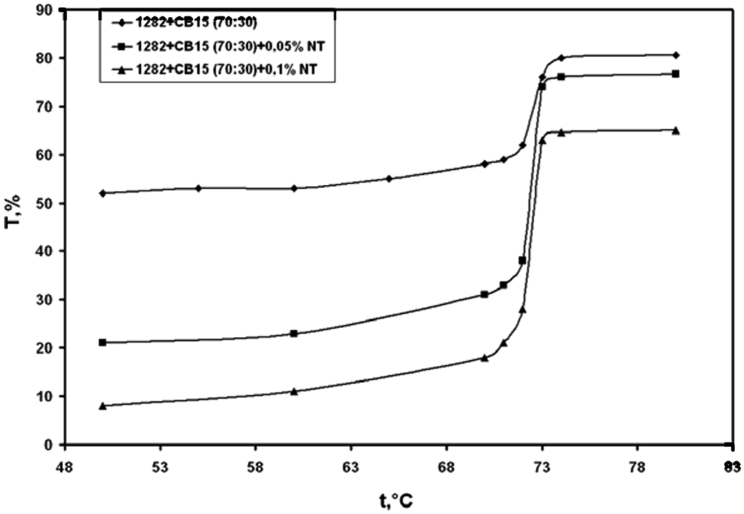

FIGURE 1 Optical transmittance as function of temperature for dispersions of MWCNT in the induced cholesteric ZhK-1282+CB15.

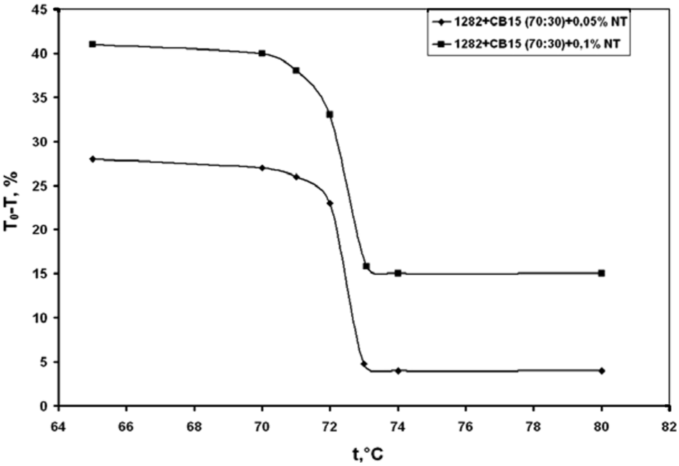

FIGURE 2 Difference in transmittances of the cholesteric matrix ZhK-1282+ CB15 (T_o) and its composite with MWCNTs (T) as function of temperature.

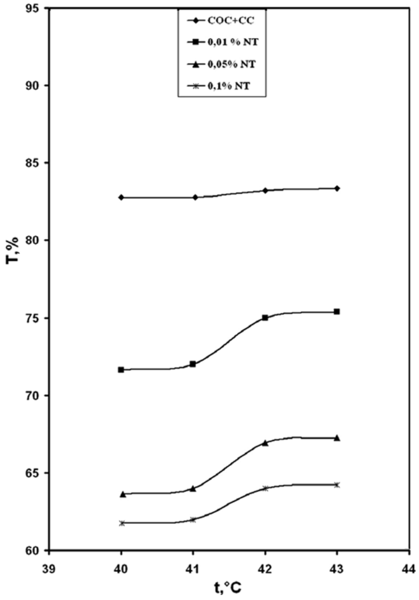

FIGURE 3 Optical transmittance as function of temperature for dispersions of MWCNT in the cholesteric mixture containing 70% cholesteryl oleyl carbonate (COC) and 30% cholesteryl chloride (CC).

the isotropic transition, which was but very small in the initial cholesteric.

Figure 4 shows comparative plots of optical transmission vs. temperature for the two cholesteric mixtures studied, i.e., COC+CC and ZhK1282+CB15. As in Figure 2, the difference ($T_o - T$) between transmittances of the same matrix in the initial state and containing dispersed nanotubes is used. To account for the difference of isotropic transition temperatures, the temperatures are given with respect to the isotropic transition point t_i.

In both cases, the transmission jumps evidence orientation of the nanotubes by the liquid crystalline matrix. However, in the case of cyanobiphenyl-based induced cholesteric, this effect was much more pronounced, which could be related with strong interaction of nanotubes with aromatic rings of the host molecules.

It should be noted that introduction of MWCNTs into both cholesteric matrices did not lead to any noticeable change in selective transmission properties, either in the shape of selective reflection bands or position of λ_{max}. Thus, the cholesteric helix remained essentially unaffected by nanotubes. Taking into account that optical transmission behavior outside the absorption and selective reflection bands is essentially similar for the ZhK1282+CB15 induced cholesteric and previously studied cyanobiphenyl nematics [17,18], it can be assumed

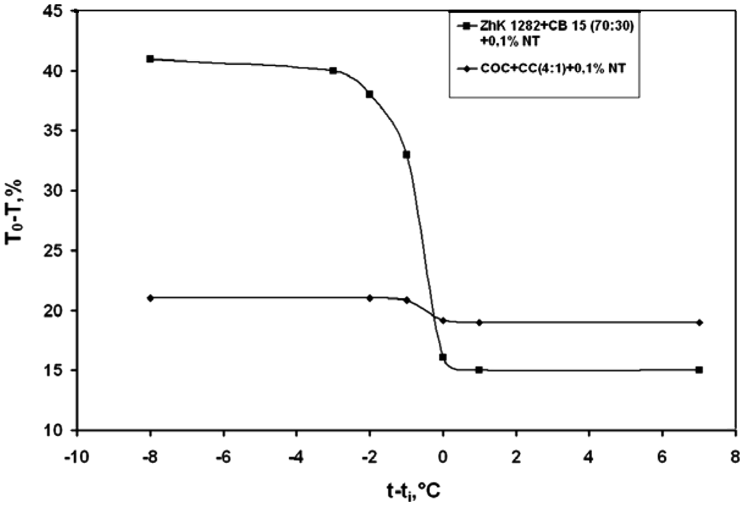

FIGURE 4 Difference in transmittances of the cholesteric matrices ZhK1282+CB15 and COC+CC (T_o) and their composites with 0.1% MWCNTs (T) as function of as function of relative temperature $t - t_i$.

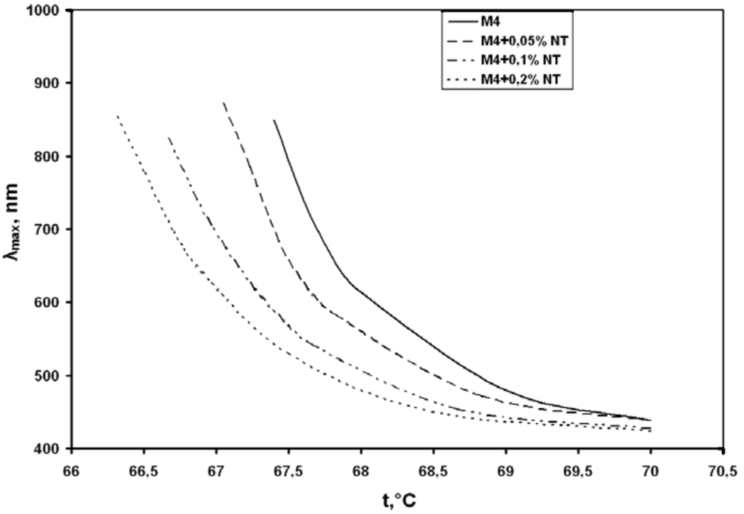

FIGURE 5 Wavelength of maximum selective reflection for cholesteric mixture M4 as function of temperature in the vicinity of the cholesteric to smectic-A transition point.

that MWCNTs dispersed in the cholesteric matrix are aligned in the planes of quasi-nematic layers, i.e., perpendicular to the helical axis.

The picture becomes somewhat different when we use cholesteric matrix M4, which exhibits smectic-A phase at temperatures below the cholesteric range. The unwinding of the cholesteric helix in approaching the cholesteric to smectic-A transition is reflected in the characteristic increase in λ_{max} with decreasing temperature (Fig. 5). Upon introduction of MWCNTs, $\lambda_{max}(t)$ plots are shifted towards lower temperatures, reflecting corresponding decreases in the cholesteric to smectic-A transition temperatures. This implies that MWCNTs, which are aligned by the orientationally ordered nematic mesophase (or quasinematic layers of the cholesteric mesophase), disrupt translational order of the smectic-A mesophase, lowering its thermal stability.

CONCLUSIONS

For the first time, effects of dispersed multiwall carbon nanotubes upon optical properties of cholesteric liquid crystals of different types were studied. The behavior of optical transmission at the cholesteric-isotropic transition outside absorption or selective reflection bands was essentially similar to that noted earlier for nematics, and no effects of MWCNTs upon helical twisting characteristics were noted, suggesting that nanotubes were aligned in the planes of quasinematic layers. On the other hand, introduction of MWCNTs led to lowering of the temperature range of cholesteric to smectic-A transition, suggesting that nanotubes caused disruption of the translational order.

REFERENCES

[1] Lynch, M. D. & Patrick, D. L. (2002). *Nano Letters*, *2*, 1197.

[2] Patrick, D. L., Wilkinson, F. S., & Fergurgur, T. L. (2005). *Proc. SPIE*, *5936*, 59360A.

[3] Dierking, I., Scalia, G., & Morales, P. (2005). *J. Appl. Phys.*, *97*, 044309.

[4] Dierking, I., Scalia, G., Morales, P., & LeClere, D. (2004). *Advanced Materials*, *16*, 865.

[5] Dierking, I., & Eren San, S. (2005). *Appl. Phys. Lett.*, *87*, 233507.

[6] Duran, H. Gazdecki, B., Yamashita, A., & Kyu, T. (2005). *Liquid Cryst.*, *32*, 815.

[7] Russell, J. M., Oh, S., LaRue, I., Zhou, O., & Samulski, E. T. (2006). *Thin Solid Films*, *509*, 53.

[8] Yang, K.-X. & Lee, W. (2007). *Mol. Cryst. Liq. Cryst.*, *475*, 201.

[9] Lee, W. & Chen, H.-Y. (2007). *Japanese J. Appl. Phys.*, *46*, 2962.

[10] Baik, I.-S., Jeon, S. Y., Lee, S. H., Park, K. A., Jeong, S. H., An, K. H., & Lee, Y. H. (2005). *Appl. Phys. Lett.*, *87*, 263110.

[11] Chen, H.-Y., Lee, W., & Clark, N. A. (2007). *Appl. Phys. Lett.*, *90*, 033510.

[12] Jeong, S. J., Park, K. A., Jeong, S. H., Jeong, H. J., An, K. H., Nah, C. W., Pribat, D., Lee, S. H., & Lee, Y. H. (2007). *Nano Letters*, *7*, 2178.

[13] Lagerwall, J. P. F., Scalia, G., Haluska, M., Dettlaff-Weglikowska, U., Giesselmann, F., & Roth, S. (2006). *Phys. Status Solidi B*, *246*, 3046.

[14] Lagerwall, J. P. F., Scalia, G., Haluska, M., Dettlaff-Weglikowska, U., Giesselmann, F., & Roth, S. (2007). *Adv. Mater.*, *19*, 359.

[15] Weiss, V., Thiruvengadathan, R., & Regev, O. (2006). *Langmuir*, *22*, 854.

[16] Lagerwall, J. P. F., Dabrowski, R., & Scalia, G. (2007). *J. Non-Cryst. Solids*, *353*, 4411.

[17] Lysetskiy, L., Panikarskaya, V., Sidletskiy, O., Kasian, N., Kositsyn, S., Shtifanyuk, P., Lebovka, N., Lisunova, M., & Melezhyk, O. (2007). *Mol. Cryst. Liq. Cryst.*, *478*, 127.

[18] Lisetski, L. N., Lebovka, N. I., Sidletskiy, O. Ts., Pankarskaya, V. D., Kasian, N. A., Kositsyn, S. S., Lisunova, M. O., & Melezhyk, O.V. (2007). *Functional Materials*, *14*, 233.

[19] Melezhyk, A.V., Sementsov, Yu. I., & Yanchenko, V. V. (2005). *Russian J. Appl. Chem.*, *78*, 924.

[20] Lebovka, N., Dadakova, T., Lysetskiy, L., Melezhyk, O., Puchkovska, G., Gavrilko, T., Baran, J., & Drozd, M. (2008). *J. Mol. Struct.*, *887*, 135.

[21] Bezrodna, T., Chashechnikova, I., Dolgow, L., Puchkovska, G., Shaydyuk, Ye., Lebovka, N., Moraru, V., Baran, J., & Rataichak, H. (2005). *Liquid Crystals*, *32*, 1005.