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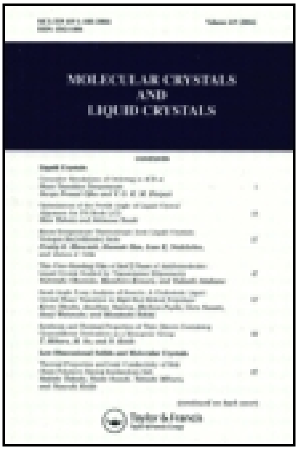

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Optical Transmission and Conductivity of Nematic Liquid Crystals Containing Dispersed Multiwall Nanotubes

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For nematic liquid crystals (LC) with small (0.01–0.15 wt%) concentration of multiwall nanotubes (NT) dispersed therein, optical transmission and electric conductivity were measured as a function of temperature. Characteristic changes in transmission at the nematic-isotropic phase transition temperature have been noted, suggesting that NT dispersed in the LC matrix behave in a manner similar to that of the conventional non-mesogenic dopants. This picture is supported by the electrical conductivity data. The electrical conductivity increased noticeably within ~ 0.01–0.1 wt% range of NT concentrations in the LC matrix, and a marked difference in the measured electrical conductivity values for the LC matrices of different polarity (e.g., cyanobiphenyl and azoxy) was observed.

Keywords: conductivity; nanotubes; nematic liquid crystals; non-mesogenic dopants; optical transmission; phase transition

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INTRODUCTION

Multi- and single-wall carbon nanotubes (MWNT and SWNT, respectively) are generally recognized as interesting objects related to nanoscience and nanotechnology [1]. A promising approach to studies and applications of nanotubes (NT) as small anisotropic particles is their combination with liquid crystals (LC) as anisotropic organic media existing in various phase states with different character and degree of orientational and translational ordering. Thus, an application has been recently proposed of LC as solvent hosts for controlling order of NT as nanometer-scale building blocks to be deposited onto a supporting substrate [2]. The ordered NT films were shown to be applicable for alignment of nematic LC, with specific arrangements and surface concentrations of NT required to achieve the proper effects [3]. Experimental evidence was presented [4] for the formation of a lyotropic nematic liquid crystalline phase of MWNT in aqueous dispersion [4]. Orientational ordering of NT dispersed in LC solvents has been reported [5,6], with eventual formation of a kind of LC phase formed by the nanotube molecules. An inverse effect was also reported, with substantial increases in the nematic-isotropic transition temperatures observed in a certain (rather narrow) NT concentration range [7], suggesting that the mixed LC + NT systems could be considered not just as dispersions, but as thermodynamically "true" solutions of NT in the LC solvent. The structural organization of nanotubes in the nematic LC matrix can be enhanced by application of the external fields in geometry similar to LC electrooptics [8,9]. A magnetically steered electrical switch device based on LC(E7)-SWNT dispersion was recently demonstrated [10].

In this article, we report the results of our spectral and electrical conductivity measurements of LC + MWNT dispersions. It is demonstrated that MWNTs clearly integrate into the LC matrix, and the dispersions obtained exhibit behaviour typical for nematic LC containing non-mesogenic dopants (NMD) both in the nematic phase and at the nematic to isotropic phase transition temperature.

MATERIALS AND METHODS

The MWNTs were prepared from ethylene using the chemical vapour deposition (CVD) method. FeAlMo0.07 was used as catalyst [11], and subsequent treatment by alkali and acid solutions was followed by filtering and repeated watering until the pH value of the filtrate became the same as that of the distilled water [11]. The MWNTs involved typically have the outer diameter d_e about 10–20 nm, while their length

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is about 5–10 microns (μm). The specific electric conductivity σ of the compressed powder of MWNTs was 10^3 S/m along the axis of compression.

The liquid crystal ZhK-1282 (NIOPIK, Russia) used in this work was a commercial mixture of several 4-alkyl- and alkoxy-4′-cyanobiphenyls and nematic cyclohexyl-containing esters. It displays nematic phase at room temperature with the nematic-isotropic phase transition at $t_{NI} \approx 62°C$. In conductivity experiments, we also used ZhK-440 (NIOPIK, Russia) – a mixture of nematic azoxy compounds with negative dielectric anisotropy.

The LC + NT composites were obtained by adding the appropriate weights of NT (0.01–0.15%) to the LC solvent in the isotropic state with their subsequent 20–30 min sonication using a UZDN-2T ultrasonic disperser, in accordance with procedure essentially similar to the previously described [12,13]. For further studies, samples were chosen that showed minimum number of macroscopic inclusions visible through an optical microscope.

The optical transmission spectra were measured in a 50 μm thick cell using a Hitachi 330 spectrophotometer. The dispersion was introduced between the cell walls by capillary forces [14] at a temperature above the nematic-isotropic transition. Before introduction of the LC + NT composites into the cell, the cell walls were rubbed in one direction in the same way as for obtaining the planar texture of cholesterics, and the resulting alignment was believed to be close to planar. The optical transmission values were measured, in parallel experiments under identical conditions, for the LC + NT dispersion (T) and the undoped liquid crystal (T_{LC}).

The electrical conductivity σ of the dispersed samples was measured in a three-electrode cell with sinusoidal voltage of 1 kHz frequency and 2 V amplitude applied to the cell. The thickness of layer was 160 μm, and the third electrode (guard ring) was grounded in order to eliminate the currents on the surface of a sample. The heating and cooling rate was 1 K/min.

RESULTS AND DISCUSSION

The optical transmission data are shown in Figure 1. The introduction of NT into the LC matrix results in substantial increase of the optical density at wavelengths above the absorption region of the liquid crystal solvent (see the Insert on Fig. 1). If the measured transmission of the LC + NT system is T, and the LC solvent transmission is T_{LC}, then $T_{LC} - T$ is a measure of the contribution of the dispersed nanotubes to the total value of $(1 - T)$ (i.e., absorption + reflectance/scattering)

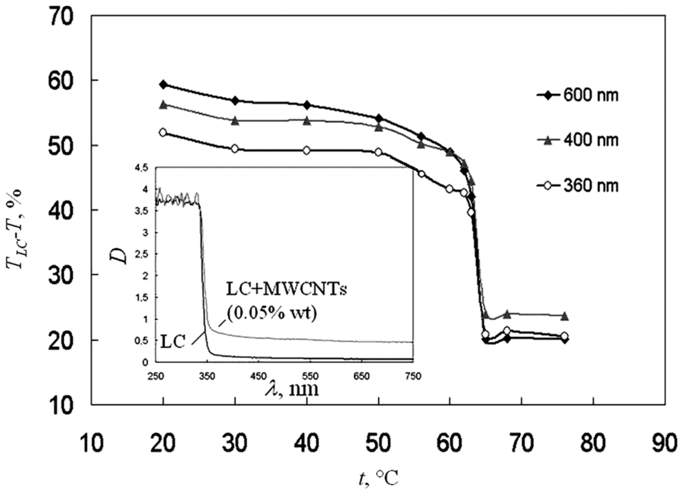

FIGURE 1 Difference between transmission values of the pure LC, T_{LC}, and the system of LC + MWNT (0.05% wt), T, as function of temperature, t. Insert shows optical transmission spectra of the pure LC solvent (ZhK-1282) and LC + MWNT (0.05% wt) composition at 50°C.

of the LC + NT composite at a given wavelength. Thus, the value of $(T_{LC} - T)$ might serve as a measure of the structural ordering of nanotubes in a composite. It is generally known that in conventional nematics the transmission in the nematic phase is always substantially lower than in the isotropic phase. In our experiments, well-defined stepwise changes in $(T_{LC} - T)$ at the nematic-isotropic transition were clearly observed for LC + NT dispersions (Fig. 1). These changes in $(T_{LC} - T)$ become more marked at higher wavelengths (i.e., when moving farther away from the LC absorption band). In the isotropic phase, the structural ordering is inessential, and $T_{LC} - T$ values are much smaller than in the nematic phase. This difference is a clear indication of liquid crystal-like organization of NT in the orientationally ordered nematic phase. Thus, the experimental data suggest that the dispersed nanotubes, as anisometric particles, form a joint orientationally ordered system with the molecules of the LC matrix. It can be concluded that the LC + NT systems studied were essentially similar to the LC + non-mesogenic dopant systems, which are generally considered homogeneous at the microscopic level.

The existence of strong interactions between nanotubes and LC matrix is also supported by the electrical conductivity data (Fig. 2). The electrical conductivity σ shows a noticeable rise (as compared

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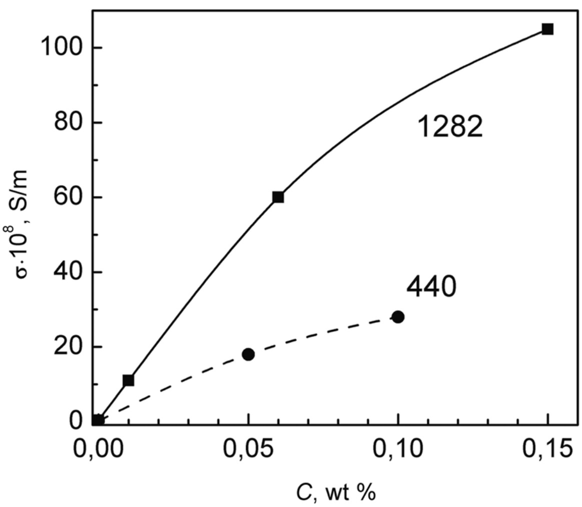

FIGURE 2 Electrical conductivity σ as function of nanotube concentration C (% wt) for LC + MWNT composites (measured on cooling at $t = 0.99t_{NI}$). LC matrices: ZhK-1282 ($\Delta\varepsilon > 0$) and ZhK-440 ($\Delta\varepsilon < 0$).

with the undoped LC) already at very low MWNT concentrations ($\sim$0.01–0.1 wt.%). The measured electrical conductivities σ are of the same order as reported in [8] for similar systems (MWNT dipersed in cyanobiphenyl LC) with unspecified small NT concentration. This result can be explained by the very high aspect ratio of the conductive filler and the existence of strong interactions between nanotubes and LC matrix, similarly as it was previously concluded for nanotube-polymer composites [15]. In fact, one can consider an effective NT concentration along the “least resistance” path of a charge carrier over the oriented nanotubes in the LC environment. It should be noted that for ZhK-440, with its negative $\Delta\varepsilon$, the conductivity values are lower by several times (since the LC environment does not favour NT orientation along the electric field), though the general picture remains similar.

The temperature dependencies of electrical conductivity in the LC + NT systems studied show a very distinct hysteresis behavior (Fig. 3). In these experiments, the composites were heated from room temperature to maximum 70°C and then cooled. The experimental data evidence that temperature affects the spatial arrangement of NT in the LC matrix. The characteristic discontinuities are clearly visible on the conductivity vs. temperature plots near the transition point $t_{NI} \approx 62$°C. Though these effects are not so evident as those

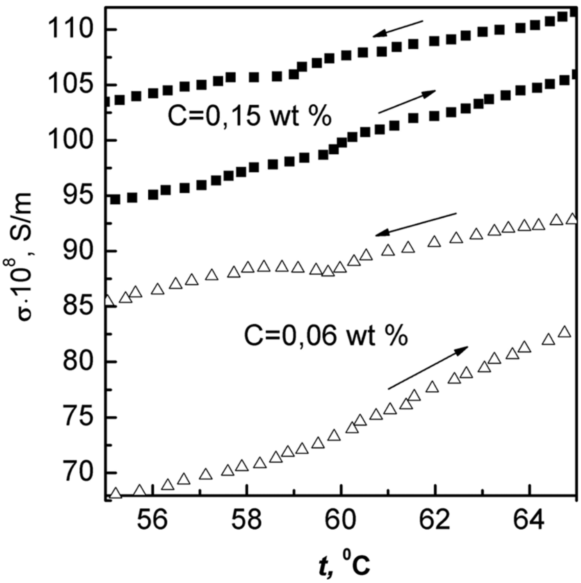

FIGURE 3 Electrical conductivity σ of LC + MWNT composites as function of temperature t, measured on heating (→) and cooling (←). The standard data deviations are of order of symbol size. LC matrix: ZhK-1282.

observed for spectral data in Figure 1, they are quite unambiguous and reproducible, also indicating high degree of incorporation of dispersed MWNTs into the liquid crystalline media.

CONCLUSIONS

The obtained data of optical transmission and electric conductivity measurements as function of temperature in multiwall nanotube-nematic liquid crystal systems suggest the existence of supramolecular organization in the studied LC + NT systems that is, in certain essential features, similar to LC systems containing non-mesogenic dopants. Existence of strong interactions between LC matrix and MWNTs is supported by high electrical conductivity values that depend strongly on concentration within ~0.01–0.1 wt.% range and substantially depend on the nature of the LC matrix. It can be expected that further studies along the lines of this approach, using different LC solvents and nanotubes of different type and dimensions, would provide a better insight into the structural features and conductivity mechanisms in the NT-containing blends and composites.

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REFERENCES

[1] Ajayan, P. M. (1999). *Chem. Rev.*, *99*, 1787.
[2] Patrick, D. L., Wilkinson, F. S., & Fergurgur, T. L. (2005). *Proc. SPIE*, *5936*, 59360A.
[3] Russel, J. M., Oh, S., LaRue, I., Zhou, O., & Samulski, E. T. (2006). *Thin Solid Films*, *509*, 53.
[4] Song, W., Kintoch, I. A., & Windle, A. H. (2003). *Science*, *302*, 1363.
[5] Lynch, M. D. & Patrick, D. L. (2002). *Nano Letters*, *2*, 1197.
[6] Song, W. & Windle, A. H. (2005). *Macromolecules*, *38*, 6181.
[7] Duran, H., Gazdecki, B., Yamashita, A., & Kyu, T. (2005). *Liq. Cryst.*, *32*, 815.
[8] Dierking, I., Scalia, G., Morales, P., & LeClere, D. (2004). *Advanced Materials*, *16*, 865.
[9] Dierking, I., Scalia, G., & Morales, P. (2005). *J. Appl. Phys.*, *97*, 044309.
[10] Dierking, I. & San, S. E. (2005). *Appl. Phys. Lett.*, *87*, 233507.
[11] Melezhyk, A. V., Sementsov, Yu. I., & Yanchenko, V. V. (2005). *Russian J. Appl. Chem.*, *78*, 924.
[12] Bezrodna, T., Chashechnikova, I., Dolgow, L., Puchkovska, G., Shaydyuk, Ye., Lebovka, N., Moraru, V., Baran, J., & Rataichak, H. (2005). *Liquid Crystals*, *32*, 1005.
[13] Chashechnikova, I., Dolgov, L., Gavrilko, T., Puchkovska, G., Shaydyuk, Ye., Lebovka, N., Moraru, V., Baran, J., & Ratajczak, H. (2005). *J. Mol. Struct.*, *744–747*, 563.
[14] Lisetski, L. N., Vashchenko, O. V., Panikarskaya, V. D., Sidletskiy, O. Ts., & Terenetskaya. I. P. (2003). *Proc. SPIE*, *5257*, 97.
[15] Jang, Q., Rastogi, S., Chen, D., Lippits, D., & Lemstra, P. J. (2006). *Carbon*, *44*, 778.

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