

Spectrophotometry and electrical conductivity studies of multiwall nanotubes dispersed in nematic liquid crystals

L.N.Lisetski, N.I.Lebovka^{}, O.Ts.Sidletskiy, V.D.Panikarskaya, N.A.Kasian, S.S.Kositsyn, M.O.Lisunova^{*}, O.V.Melezhyk^{**}*

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine,
60 Lenin Av., Kharkiv 61001, Ukraine

^{*}F.Ovcharenko Institute of Biocolloid Chemistry, National Academy of
Sciences of Ukraine, 42 Vernadsky Ave., Kyiv 03142, Ukraine

^{**}TM Spetsmash Ltd, Kyiv, Ukraine

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Optical transmission and electric conductivity were measured as a function of temperature for thin layers of multiwall nanotubes (MWNTs) dispersed in a mixture of cyanobiphenyl nematic liquid crystals (LC) ZhK-1282. At MWNT concentrations of 0.01–0.15 wt.%, characteristic changes in transmission at the nematic-isotropic phase transition temperature evidence that MWNTs integrate into LC matrix in a manner similar to that of the conventional non-mesogenic dopants. The electrical conductivity shows a percolation-like behaviour at ultra-low MWNTs loading of LC matrix below concentration levels of ~0.01 wt.%, which reflects the high aspect ratio of the conductive filler and the existence of strong interactions between LC matrix and MWNTs.

Оптическое пропускание и электропроводность тонких слоев многостеночных нанотрубок (МСНТ), диспергированных в нематической жидкокристаллической смеси (ЖК) на основе цианобифенилов (ЖК-1282), были исследованы в зависимости от температуры. При концентрациях МСНТ 0,01–0,15 масс.% отмечены характерные изменения оптического пропускания при нематико-изотропном фазовом переходе, что свидетельствует об интегрировании МСНТ в ЖК матрицу аналогично традиционным немезогенным добавкам. Электропроводность проявляет поведение перколяционного типа при очень низких концентрациях МСНТ в ЖК матрице (менее ~0,01%), что отражает высокую степень анизотрии проводящего наполнителя и наличие сильного взаимодействия между МСНТ и ЖК матрицей.

Multi- and single-wall carbon nanotubes (MWNTs and SWNTs, respectively) show many unique electronic, thermal, optical, and mechanical properties and are generally recognized as interesting objects of nanoscience and nanotechnology [1]. The applications of nanotube-based fillers seems to be very promising for production of composite materials with attractive conductivity and tensile strength properties [2–5]. The MWNTs are reported to have a rather high electrical conduc-

tivity of about $1.85 \cdot 10^3$ S/cm along the long axis, which allows them to could conduct currents of enormously density exceeding 10^7 A·cm⁻² [6]. Owing to the high aspect ratio (100–1000) and specific surface area values, the conductive path can arise in such composites at very small concentration of nanotubes (~0.1–5 vol.%) [7, 8].

A promising approach to study and applications of nanotubes is their combination with liquid crystals (LC). An anisotropic liq-

uid crystal organic media can exist in various phases with different character and degree of orientational and translational ordering. The ability of LC solvents to align anisometric nanoparticles, such as organophilic clay minerals [9, 10] or polymeric [11] particles, was previously reported. The orientational organization is assumed to be controlled by the elastic interactions between nanoparticles and LC host [12]. The integration of SWNTs into a highly ordered hexagonal lyotropic LC matrix and increase of the degree of their alignment was demonstrated earlier [13]. Experimental evidence was presented for formation of a lyotropic nematic liquid crystalline phase by MWNTs dispersed in the aqueous medium [14]. The possibility of improving the orientational organization of SWNTs and MWNTs using thermotropic LC medium (5CB and E7, Merck) was also recently reported [15]. It was proposed to apply LCs as solvent hosts controlling ordering of the nanotubes as nanometer-scaled building blocks when they should be deposited on a supporting substrate [16]. Adding of carbon nanotubes into LC (E7) was found to increase the isotropic nematic transition temperature [17]. The structural organization of nanotubes in the nematic LC matrix can be enhanced by application of the external magnetic, electric or mechanic field [18, 19]. A magnetically steered electrical switch device based on LC(E7)-SWNT dispersion was recently demonstrated [20]. The SWCNT films were used to produce a novel optical device with planar orientation of nematic LC (Licristal K-15) [21]. The possibility of using of the LC precursors for synthesis of the high-aspect-ratio nanocarbons was recently shown [22].

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

The MWNTs were prepared from ethylene using the chemical vapour deposition (CVD) method, $\text{FeAlMo}_{0.07}$ was used as catalyst [23]. For purification of the MWNTs from mineral additives and for elimination of the catalyst effects, the samples were treated by concentrated alkali (NaOH) and acid (HCl) solutions, then filtered, and the excess acid was removed. The remaining black powder was watered repeatedly by the

distilled water until the pH value of the filtrate became the same as that of the distilled water. The residual mass content of the mineral additives was $<1\%$. The MWNTs involved typically have the outer diameter d_e about 12–20 nm, while their length is about tens of microns (μm), which results in the aspect ratio up to 100–1000. The inner MWNT diameter d_i varies from 1 to 3 nm, and MWNT specific surface area S is $190\text{ m}^2/\text{g}$ ($\pm 10\%$). The specific electric conductivity σ of the compressed powder of MWNTs (at 15 TPa) was 10^3 S/m along the axis of compression and appeared to be significantly lower than that of graphite ($\sigma = 10^3\text{--}10^6\text{ S/cm}$ [24]). The density of the MWNT walls was assumed to be the same as the density of pure graphite, $\rho_c = 2045\text{ kg/m}^3$. 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 $t_{NI} \approx 62^\circ\text{C}$ [25]. The LC+ MWNTs compositions were obtained by adding the appropriate weights of MWNTs (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 [9, 10]. Samples with minimum macroscopic inclusions visible through an optical microscope were selected among the obtained dispersions, and the subsequent procedures were similar to those conventionally used in spectrophotometry and conductivity studies of liquid crystalline systems.

The optical transmission spectra were measured in a $50\text{ }\mu\text{m}$ thick cell using a Hitachi 330 spectrophotometer. The dispersion was introduced between the cell walls by capillary forces [26] at a temperature above the nematic-isotropic transition. The cell walls (sapphire glasses) were pre-treated by immersion into 1 % water solution of polyvinyl alcohol and subsequent rubbing of the dried surface in one direction. In liquid crystal studies, such procedure has been widely used as a conventional way to obtain planar texture. The measured values of optical transmission values were obtained, in parallel experiments, for a LC+MWNT dispersion (T) and the undoped liquid crystal (T_{LC}). (It should be kept in mind that in standard physico-chemical measurements

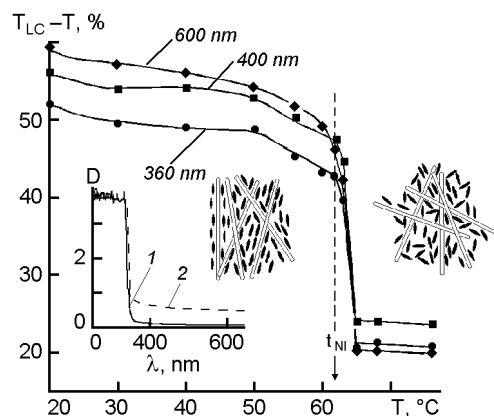


Fig. 1. Difference between transmission values of the pure LC, T_{LC} , and the system of LC+MWNTs, 0.05 wt. %, T , as function of temperature, t . Insert shows the optical transmission spectra of the pure LC solvent (ZhK-1282) and LC+MWNTs (0.05 wt.%) composition at 50°C.

the measured transmission values are automatically re-calculated by the instrument software into apparent optical density values $D = \lg(1/T)$. The conductivity of the dispersed samples was measured in a three-electrode cell (layer thickness 160 μm , the third electrode (guard ring) grounded in order to eliminate the currents on the sample surface) with sinusoidal voltage of 1 kHz frequency and 2 V amplitude applied to the cell. The σ values were calculated from the data on measured current through the sample accounting for the amplitude of the applied voltage and the cell thickness. The heating and cooling rate was 1 K/min.

The optical transmission data are shown in Fig. 1. The introduction of MWCNTs 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+MWCNTs 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 $(1 - T)$ (absorption + reflectance/scattering) at a given wavelength. This contribution, in a general case, should reflect the cumulative effects of absorption, scattering, and an eventual dichroism of the LC composite. Thus, the value of $(T_{LC} - T)$ might serve as a measure of the structural ordering in a composite. Fig. 1 shows $(T_{LC} - T)$ at several wavelengths as a function of temperature. The well-defined stepwise changes near the nematic-isotropic transition were clearly ob-

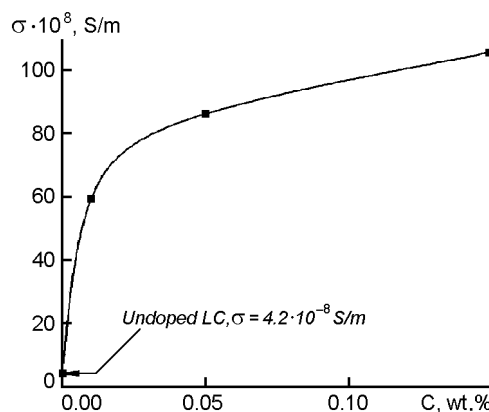


Fig. 2. Electrical conductivity σ versus fraction of nanotubes C wt. % for LC+MWCNT composites (measured on cooling at $t = 0.99t_{NI}$, $t_{NI} \approx 62^\circ\text{C}$).

served, and the difference in transmission between the MWNT-doped and undoped LC samples increased with the wavelength increasing farther from the LC absorption band. This behaviour unambiguously evidences a change in structural organization of the LC + MWNTs composite at the nematic-isotropic transition (Fig. 1). In the isotropic phase, the structural ordering is inessential, and $T_{LC} - T$ values are much smaller than in the isotropic phase. In the nematic phase, the $T_{LC} - T$ value increases considerably, which reflects the effects of spatial organization of MWNTs in the orientationally ordered phase. Thus, the experimental data suggest that the dispersed MWNTs are strongly integrated into the LC matrix and form a system of well-dispersed individual MWNTs or their relatively small aggregates in the LC medium. It can be concluded that the studied LC+MWNT systems were presumably similar to the LC+non-mesogenic dopant systems, which are generally considered homogeneous at the microscopic level [27].

The existence of strong interactions between MWNTs and LC matrix is also supported by the electrical conductivity data (Fig. 2). The electrical conductivity σ shows a very noticeable rise (as compared with the undoped LC) at ultra-low MWNTs loading of LC, indicating an electrical percolation threshold at weight concentrations smaller than 0.01 %. It should be noted that our conductivity values were of the same order of magnitude as those reported in [18] for similar systems (cyanobiphenyl LC+dispersed MWNTs for unspecified small concentrations). 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 [7, 8].

The electrical conductivities after the percolation threshold still remained by several orders lower than for pure nanotubes ($\sim 10^3$ S/m in our case). This effect probably reflects a decrease in the number of intersection contacts and increase in the energy barrier for the electron transfer required for "ballistic" conductivity between nanotube intersections in the LC environment. The temperature dependencies of electrical conductivity in LC+MWNTs 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 MWNTs in the LC matrix. The observed effects were more pronounced at smaller concentrations, i.e., in a closer vicinity to the eventual percolation threshold. The characteristic discontinuities (indicated by dashed lines in Fig. 3) are clearly visible on the conductivity vs. temperature plots near the transition point $t_{NI} \approx 62^\circ\text{C}$. Though these effects are not so evident as those observed for spectral data in Fig. 1, they are quite unambiguous and reproducible. The shape of these singularities on σ vs. temperature plots at the nematic to isotropic transition is quite similar to the picture commonly observed for liquid crystals [25, 28], which also supports our assumption that dispersed MWNTs (or their small anisometric aggregates) were really incorporated into the liquid crystalline structure.

Thus, in this paper we have presented results of optical transmission and electric conductivity studies of multiwall nanotube-nematic liquid crystal system. The obtained data support existence of organization in the studied LC+MWNT systems on the supramolecular level. The existence of strong interactions between LC matrix and MWNTs is supported a very low percolation threshold concentration of order 0.01 wt. %. It can be expected that further studies along the lines of this approach (experiments using different LC solvents and CNTs of different type and dimensions, as well as studies using more advanced spectroscopy techniques than simple optical transmission measurements) would provide a better insight into the structural features and con-

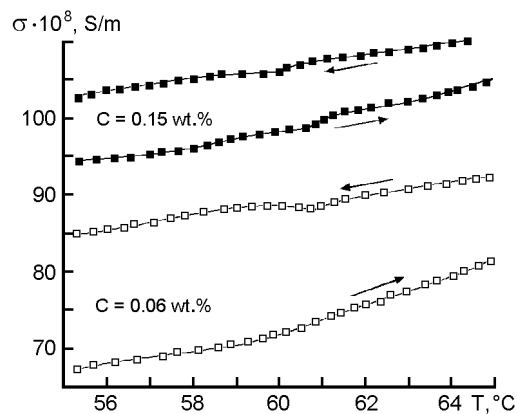


Fig. 3. Electrical conductivity σ of LC+MWNT composites vs. temperature t , measured on heating (\rightarrow) and cooling (\leftarrow). The standard data deviations are of order of symbol size.

ductivity mechanisms in the CNT-containing blends and composites.

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Спектрофотометрія та електропровідність багат шарових нанотрубок, диспергованих у нематичних рідких кристалах

**Л.М.Лисецький, М.І.Лебовка, О.Ц.Сідлецький,
В.Д.Панікарська, Н.О.Касян, С.С.Косіцин,
М.О.Лісунова, О.В.Мележик**

Оптичне пропускання та електропровідність тонких плівок багат шарових нанотрубок (БШНТ), диспергованих у нематичній рідкокристалічній суміші (РК) на основі ціанобіфенілів, досліджено в залежності від температури. При концентраціях БШНТ 0,01–0,15 мас.% відзначено характерні зміни оптичного пропускання при нематико-ізотропному фазовому переході, що свідчить про інтегрування БШНТ в РК матрицю аналогічно традиційним немезогенним домішкам. Електропровідність виявляє поведінку перколяційного типу при дуже низьких концентраціях БШНТ в РК матриці (менше ~0,01 %), що відображає високий ступінь анізотрії (аспектне відношення) електропровідного наповнювача та наявність сильної взаємодії між БШНТ та РК матрицею.