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ANISOTROPIC ORGANIC MEDIA AS MODEL BIOEQUIVALENT SYSTEMS. I. LIQUID CRYSTALS CONTAINING DISPERSED MULTIWALL NANOTUBES UNDER ASPECTS OF ANISOTROPIC INTERMOLECULAR INTERACTIONS

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Dispersions of carbon nanotubes (NT) in liquid crystals have been considered as a model system for studies of anisotropic intermolecular interactions in condensed organic media. Electric conductivity data were obtained for nematic liquid crystals (LC) with small (0.01-0.15 wt %) concentrations of multiwall NT dispersed therein. The electric conductivity increased noticeably with NT concentration in the LC matrix, suggesting a percolation-like behaviour at NT content in the LC matrix below ~0.01 wt %. A marked difference in the measured electric conductivity values for the LC matrices of different polarity (e.g., cyanobiphenyl and azoxy) was observed. Assuming that supramolecular arrangement of NT dispersed in the LC matrix can be treated in a manner similar to the conventional non-mesogenic dopants, the observed behaviour is explained using our recent theoretical description of intermolecular interactions in anisotropic organic media formed by particles of essentially different size and anisometry.

KEY WORDS: nanotubes, nematic liquid crystals, non-mesogenic dopants, electric conductivity, intermolecular interactions, anisotropic organic media, bioequivalent systems.

Multi- and single-wall carbon nanotubes (MWNT and SWNT, respectively) are generally recognized as interesting objects related to nanoscience and nanotechnology [1]. Recent studies have also shown that nanotubes (NT) can also play a significant role in biophysics – e.g., they could be integrated with neuronal circuits, thus paving the way to artificial brain-related biomimetic systems [2]. Keeping in mind our ideas of liquid crystals as bioequivalent anisotropic media [3,4], we considered as a promising approach to study NT as small anisotropic particles in combination with liquid crystals (LC) as anisotropic organic media existing in various phase states with different character and degree of orientational and translational ordering. This approach has been recently used in areas other than biophysics – e.g., application of LC as solvent hosts for controlling order of NT as nanometer-scale building blocks to be deposited onto a supporting substrate [5]. 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 [6]. Experimental evidence was presented [7] for the formation of a lyotropic nematic liquid crystalline phase of MWNT in aqueous dispersion. Orientational ordering of NT dispersed in LC solvents has been reported [8,9], 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 [10], 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 [11].

In our recent paper [12], we reported data on optical transmission of MWNT dispersions in cyanobiphenyl liquid crystals. It was demonstrated that, at small (~0.1%) concentrations, MWNT could be clearly integrated into the LC matrix, with the dispersions obtained exhibiting behaviour typical for nematic LC containing non-mesogenic dopants (NMD) both in the nematic phase and at the nematic to isotropic phase transition temperature.

The idea of our present work was to study NT dispersions in two different nematic hosts with different polarity, i.e., with dielectric anisotropy of different signs ($\Delta\epsilon > 0$ and $\Delta\epsilon < 0$). It was assumed that in such systems the electric conductivity behaviour would be substantially different due to different molecular orientation mechanisms under electric fields.

MATERIALS AND METHODS

The MWNTs were prepared from ethylene using the chemical vapour deposition (CVD) method. FeAlMo0.07 was used as catalyst [13], 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 [13]. The MWNTs involved typically have the outer diameter d_o about 10-20 nm, while their length 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 $t_{NI} \approx 62^\circ\text{C}$. 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 [14,15]. For further studies, samples were chosen that showed minimum number of macroscopic inclusions visible through an optical microscope.

The electric conductivity σ of the dispersed samples was measured in a three-electrode cell with sinusoidal voltage of 1 kHz frequency and 2V 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 measured σ values showed a weak temperature dependence (an increase of $\sim 10\%$ in the temperature range of ~ 5 K below and above the nematic to isotropic transition temperature T_i [12]), so the values used in the σ vs. concentration plots (Fig.1) were taken at the constant reduced temperature $T/T_i = 0.99$.

RESULTS AND DISCUSSION

The electric conductivity σ (Fig.1) shows a very noticeable rise (as compared with the undoped LC) at ultra-low MWNT loading of LC, indicating an electrical percolation threshold at weight concentrations smaller than 0.01%. The measured values of σ are of the same order ($\sim 10^{-6}$ S/m) as reported in [11] for similar systems (MWNT dispersed in cyanobiphenyl LC) with unspecified small NT concentration.

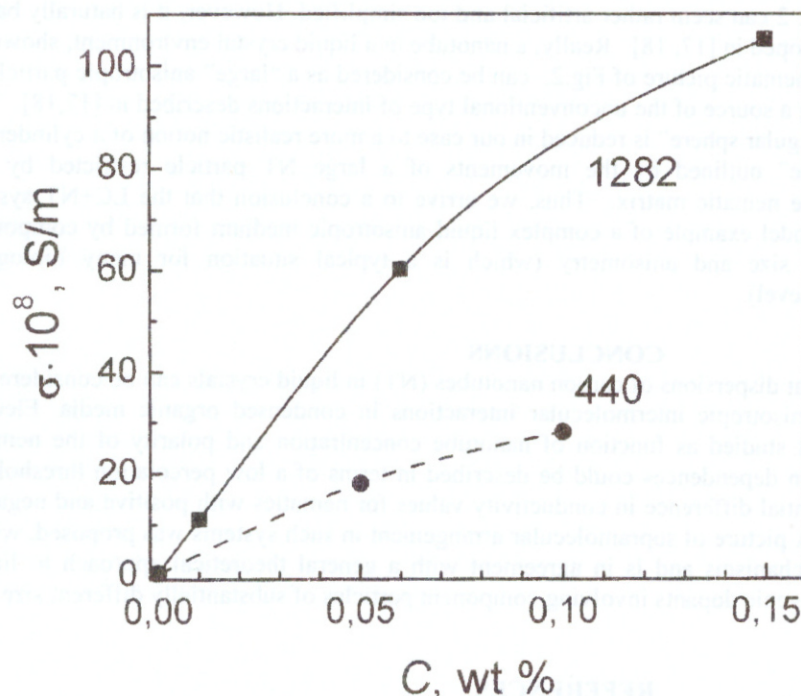


Fig.1. Electric conductivity σ as function of nanotube concentration C (% wt) for LC+ MWNT composites (measured on cooling at $T = 0.99 T_i$). LC matrices: ZhK-1282 ($\Delta\epsilon > 0$) and ZhK-440 ($\Delta\epsilon < 0$).

As compared with nanotube-polymer compositions [16], the observed strong increase in conductivity at much lower NT concentrations can be explained by the high aspect ratio of the conductive filler and the assumed existence of strong anisotropic interactions between nanotubes and orientationally ordered anisometric molecules

of the LC matrix. The presumed joint orientationally ordered arrangement formed in the LC+NT systems is schematically shown in Fig.2.

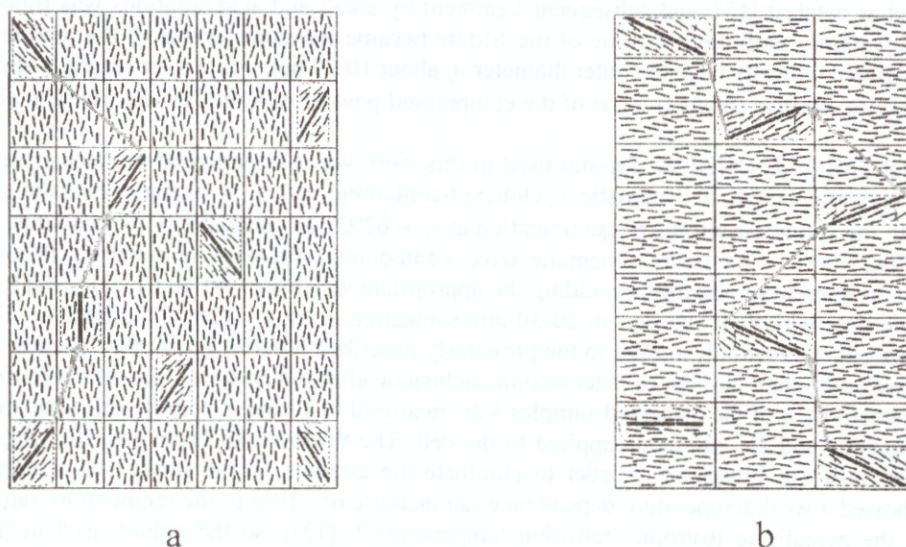


Fig.2. Schematic illustration of the molecular model used for explanation of the electric conductivity mechanism in NT+LC dispersions: $\Delta\epsilon > 0$ (a) and $\Delta\epsilon < 0$ (b).

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 with $\Delta\epsilon > 0$ (Fig. 2a). It should be noted that for ZhK-440, with its negative $\Delta\epsilon$, 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 (Fig.2b).

The picture illustrated by Fig. 2 can seem rather artificial and too simplified. However, it is naturally based on theoretical considerations developed in [17, 18]. Really, a nanotube in a liquid crystal environment, shown as a “cell”-forming element in the schematic picture of Fig.2, can be considered as a “large” anisotropic particle in a mixture with “small” ones, being a source of the unconventional type of interactions described in [17,18]. The over-generalized notion of the “singular sphere” is reduced in our case to a more realistic notion of a cylinder- or ellipsoid-shaped “singular volume” outlined by the movements of a large NT particle restricted by the orientational order imposed by the nematic matrix. Thus, we arrive to a conclusion that the LC+NT system studied can be considered as a model example of a complex liquid anisotropic medium formed by component particles of essentially different size and anisometry (which is a typical situation for many biological objects/tissues at the microscopic level).

CONCLUSIONS

The results obtained show that dispersions of carbon nanotubes (NT) in liquid crystals can be considered as a model system for studies of anisotropic intermolecular interactions in condensed organic media. Electric conductivity in such systems was studied as function of nanotube concentration and polarity of the nematic matrix. The obtained concentration dependences could be described in terms of a low percolation threshold at $<0.01\%$ NT content, and a substantial difference in conductivity values for nematics with positive and negative dielectric anisotropy was noted. A picture of supramolecular arrangement in such systems was proposed, which illustrates the charge transfer mechanisms and is in agreement with a general theoretical approach to liquid crystalline systems with non-mesogenic dopants involving component particles of substantially different size and anisometry.

REFERENCES

1. Ajayan P.M. // Chem.Rev. 1999, V.99, P.1787-1799.
2. Lovat V., Pantarotto D., Lagostena L., Cacciari B., Grandolfo M., Righi M., Spalluto G., Prato M., Ballerini L. // Nano Letters 2005, V.5, P.1107-1110.
3. Lisetski L.N., Malikov V.Ya., Sidletski O.Ts., Stadnik P.E. // Mol.Cryst.Liq.Cryst. 1998, V.324, P.243-249.
4. Lisetski L.N., Vashchenko O.V., Tolmachev A.V., Vodolazhskiy K.B. // Eur.Biophys.J. 2002, V.31, P.554-558.
5. Patrick D.L., Wilkinson F.S., Fergurgur T.L. // Proc.SPIE 2005, V.5936, 59360A (8p.)

6. Russell J.M., Oh S., LaRue I., Samulski E.T. // *Thin Solid Films* 2006, V.509, P.53-57.
7. Song W., Kintoch I.A., Windle A.H. // *Science* 2003, V.302, P.1363.
8. Lynch M.D., Patrick D.L. // *Nano Letters* 2002, V.2, P.1197-1201.
9. Song W., Windle A.H. // *Macromolecules* 2005, V.38, P.6181-6188.
10. Duran H., Gazdecki B., Yamashita A., Kyu T. // *Liq.Cryst.* 2005, V.32, P.815-821.
11. Dierking I., Scalia G., Morales P., LeClere D. // *Advanced Materials* 2004, V.16, P.865-869.
12. Lisetski L.N., Lebovka N.I., Sidletsky O.Ts., Panikarskaya V.D., Kasian N.A., Kositsyn S.S., Lisunova M.O., Melezhyk O.V. // *Functional Materials* 2007, V.14, No.2.
13. Melezhyk A.V., Sementsov Yu.I., Yanchenko V.V. // *Russian J.Appl.Chem.* 2005, V.78, P.924-930.
14. Bezrodna T., Chashechnikova I., Dolgow L., Puchkovska G., Shaydyuk Ye., Lebovka N., Morary V., Baran J., Rataichak H. // *Liq.Cryst.* 2005, V.32, P.1005-1012.
15. Chashechnikova I., Dolgov L., Gavrillko T., Puchkovska G., Shaydyuk Ye., Lebovka N., Moraru V., Baran J., Rataichak H. // *J.Mol.Struct.* 2005, V.744-747, P.563-571.
16. Zhang Q., Rastogi S., Chen D., Lippits D., Lemstra P.J. // *Carbon* 2006, V.44, P.778-785.
17. Shtifanyuk P.P., Dyomin A.V., Fedoryako A.P., Lisetski L.N., Yakovenko S.E. // *Functional Materials* 2004, V.11, P.661-670.
18. Shtifanyuk P.P., Dyomin A.V., Fedoryako A.P., Lisetski L.N., Yakovenko S.E. // *Biophysical Bulletin* 2005, No.1(15), P.49-52.

**АНИЗОТРОПНІ ОРГАНІЧНІ СЕРЕДОВИЩА ЯК МОДЕЛЬНІ БІОЕКВІВАЛЕНТНІ СИСТЕМИ.
І. РІДКІ КРИСТАЛИ З ДИСПЕРГОВАНИМИ БАГАТОСТІНКОВИМИ НАНОТРУБКАМИ
В АСПЕКТІ АНИЗОТРОПНИХ МІЖМОЛЕКУЛЯРНИХ ВЗАЄМОДІЙ**

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Дисперсії вуглецевих нанотрубок (НТ) в рідких кристалах розглядаються як модельна система для дослідження анізотропних міжмолекулярних взаємодій в конденсованих органічних середовищах. Отримано дані з електропровідності нематичних рідких кристалів (РК) з диспергованими в них малими концентраціями (0,01-0,15%) багатостінкових НТ. Електропровідність помітно зростала з концентрацією НТ в РК матриці, вказуючи на поведінку перколяційного типу при вмісті НТ в РК матриці менше за ~0,01%. Відзначено істотну відмінність вимірюваних значень електропровідності для РК матриць різної полярності (наприклад, ціанобіфеніли та азоксиполуки). Припускаючи, що надмолекулярне впорядкування НТ, диспергованих в РК, може розглядатися подібно до звичайних немезогенних домішок, спостережувана поведінка пояснюється за допомогою нашого нещодавно запропонованого теоретичного опису міжмолекулярних взаємодій в анізотропних органічних середовищах, утворених частинками істотно різного розміру та анізотрії.