Aggregates of multiwalled carbon nanotubes in nematic liquid crystal dispersions: experimental evidence and a physical picture

S.S.Minenko, L.N.Lisetski, A.I.Goncharuk[*]*, N.I.Lebovka*[*]*,*
V.V.Ponevchinsky[**]*, M.S.Soskin*[**]

Institute for Scintillation Materials, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine
[*]F.Ovcharenko Institute of Biocolloidal Chemistry,
National Academy of Sciences of Ukraine,
42 Vernadsky Prosp., 03142 Kyiv, Ukraine
[**]Institute of Physics, National Academy of Sciences of Ukraine,
46 Prospekt Nauky, 03039 Kyiv, Ukraine

Formation of aggregates of multiwalled carbon nanotubes dispersed in nematic 5CB was studied using different methods (microscopy, optical transmission, electric conductivity, differential scanning calorimetry, and methods of singular optics). Monitoring of the aggregate formation on the time scale of several hours has been realized, and a physical model of the aggregation process has been proposed. It is assumed that the aggregates formed consist of a "skeleton" formed by nanotubes arranged in a stochastic fractal structure and a "shell" ("coat") of incorporated and adjacent nematic molecules. The aggregates of this type ("S-aggregates") can be considered as large quasi-macroscopic particles in the nematic matrix. The experimental results obtained by different methods appear to be in agreement with each other and the proposed physical picture.

Образование агрегатов многостеночных углеродных нанотрубок, диспергированных в нематическом жидком кристалле 5СВ, исследовано различными методами (микроскопия, оптическое пропускание, электропроводность, дифференциальная сканирующая калориметрия и методы сингулярной оптики). Реализован мониторинг формирования агрегатов на временном масштабе нескольких часов и предложена физическая модель, описывающая их образование. Предполагается, что агрегаты состоят из "скелета" из нанотрубок, упорядоченных в стохастическую фрактальную структуру, и оболочки ("шубы") из инкорпорированных и прилегающих молекул нематика. Агрегаты этого типа ("S-агрегаты") можно рассматривать как квазимакроскопические частицы в нематической матрице. Экспериментальные данные, полученные различными методами, согласуются между собой и с предлагаемой физической картиной.

1. Introduction

Since their discovery [1], carbon nanotubes (NT) have been a subject of intense studies [2, 3]. An important direction of NT studies and applications was related to preparation of composite materials based on NT dispersions in various condensed organic media, such as polymers [3] and liquid crystals (LC). In the latter case, first application-related works were made by Wei Lee e.a. [4, 5], and the first paper where a physical picture of orientation of NTs by a nematic LC matrix was explicitly stated was presented by Lynch and Patrick [6].

Numerous experimental studies of LC+NT dispersions were largely summa-

rized in several reviews [7–10]. As for theoretical treatment, much less attention has been paid, and we can only note papers where calculations of NT+LC molecule interactions were made (using quantum chemistry [11] and molecular dynamics with Lennard-Jones type atom-atom potentials [12]), as well as semi-phenomenological approaches relating orientational order parameter of the nematic matrix and dispersed NTs [13, 14].

Among experimental data on LC+NT dispersions, one should note a concept of "percolation"-type behavior describing concentration dependence of electric conductivity [15], as well as data on optical transmittance, Raman scattering, and electrooptic effects typical for nematics obtained in different LC matrices [16, 17].

From these results, the picture of orientation of NTs by the LC matrix seems to be sufficiently clear. In many papers [18–20], explanatory drawings are included, depicting NTs and NLC molecules in a joint supramolecular arrangement. According to these pictures, NTs can be really considered as a sort of non-mesogenic dopants of large size and anisometry, with no specific features and a conventional scheme of the Freedericks transition [21]. One can just mention a too large NT length leading to shunting of a LC cell [22].

At the level of qualitative molecular models, the most detailed and comprehensive description seems to have been offered by Basu and Iannacchione [23–25]. Their vision of supramolecular arrangement in NLC+NT dispersions is based on the picture of a multiwalled carbon nanotube as a relatively large cylinder-shaped object aligning anisometric nematic molecules of much smaller size at the scale of several molecular layers. In this supramolecular structure of the nearest molecular environment induced by the nanotube, the local orientational order parameter of the nematic is clearly increased; however, on the macroscopic scale the nematic-isotropic phase transition is not increased, but even slightly decreased. This most probably reflects the fact that director orientations of the ordered "micro-domains" are not correlated on the macroscopic scale, and the resulting contribution on the nematic order parameter tends to be negative.

This picture, however, seems to adequately describe only the NLC+NT dispersions at very low NT concentrations (< 0.01 %) or during a short time interval after ultrasonication when emerging processes of NT aggregation do not significantly affect the picture. We can refer to several publications [26–28] where this aspect has been considered (though explicit data on the effects of concentration/time related aggregation seem to have remained in the "know-how" subtext implications).

In our approach, we treat the aggregate formation in NLC+NT dispersions not as a spurious phenomenon that should be avoided (using lower concentrations, more efficient sonication, chemical treatment of NTs, etc.), but as a natural behavior of a complex multi-component anisotropic liquid system. Taking dispersions of multiwalled carbon nanotubes in the well-known nematic 5CB as a basis for our studies, we used five different experimental methods to monitor the dynamics of NT aggregate formations and proposed a tentative theoretical model to describe the whole complex of the obtained results.

2. Materials and methods

As a nematic host, we used 4-pentyl-4'-cyanobiphenyl (5CB) — a typical LC substance with dielectric anisotropy $\Delta\varepsilon > 0$ and nematic range 22–35°C (Chemical Reagents Plant, Kharkiv, Ukraine). The multi-walled NTs (TMSpetsmash Ltd., Kyiv, Ukraine) were prepared from ethylene using the chemical vapour deposition (CVD) method as described in [29, 17]. The NTs involved typically had the outer diameter d_e about 10–20 nm, while their length ranged from 5 to 10 μm.

The optical microscopy images were obtained using OI-3 UHL 4.2 microscope (LOMO, Russia). The microscope detector unit was interfaced with a digital camera and a personal computer. The images were taken with 400 enlargement, the layer thickness was 50 μm.

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; the resulting alignment was believed to be close to planar.

The home-made cell, used for measurement of electrophysical characteristics, included a grounded guard ring, which reduced the influence of the edge effects. The cell was a capacitor with metal plates, covered by a polyvinyl alcohol film rubbed in one direction for ensuring the planar texture. The cell thickness (50 μm) was set by a Teflon spacer. Before the measurements,
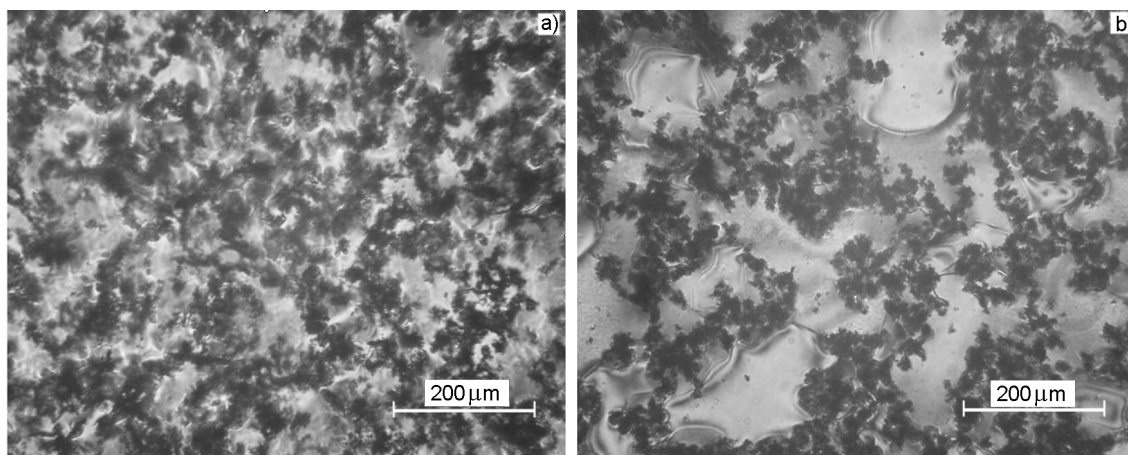
Fig. 1. Microphotographs of 5CB + 0.1 % NT dispersion samples before (a) and after (b) incubation for 8 h. The number and size of aggregates is obviously increased.

the cell parts were washed in hexane and dried at 390 K. After assembling, the cell was connected to E7-12 LCR-meter (KA-LIBR, Belarus), to make sure that tgδ of the empty cell did not exceed 0.0001.

For conductivity and capacitance measurements, the ac voltage of 0.25 V and 1 MHz was used, which should not affect the LC director field. The experimental set-up provided application of DC bias voltage up to 40 V to the cell. The external DC voltage could align the molecules, thus leading to re-orientation of the nematic director and corresponding changes in dielectric properties and conductivity.

Differential scanning calorimetry (DSC) measurements in the temperature range around the nematic-isotropic transition (35°C) were carried out using a Mettler TA 3000 thermoanalytical system at 1 K/min scanning rate both on heating and cooling.

Experiments using methods of singular optics were carried out essentially as described in [34].

In all the experiments carried out by the above-listed methods, the 5CB+NT dispersions were first studied just after preparation (sonication), and then measurements under the same conditions were repeated after these dispersions had been incubated for several hours (i.e., when the formation process of NT aggregates was expected to be sufficiently developed (at least partially completed)).

Results and discussion

Fig. 1 shows the microscopic picture of the dispersion 5CB + 0.01 % NT just after sonication (a) and after incubation for 6 hours at 25°C (b). It can be seen that NT
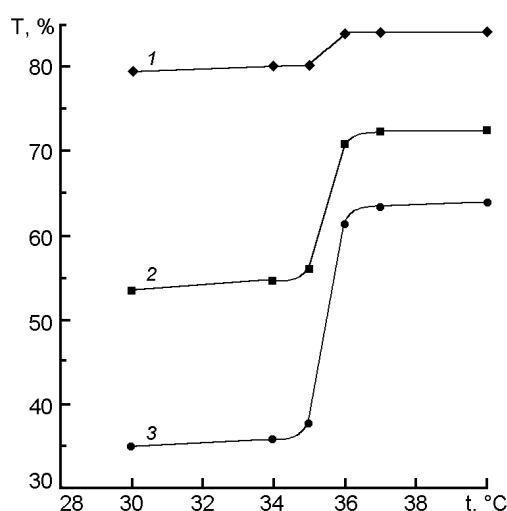

Fig. 2. Optical transmittance in the vicinity of isotropic-nematic transition temperature for undoped 5CB (*1*) and 5CB + 0.1 % NT dispersion (just after sonication (*2*) and after incubation for 8 h (*3*).

aggregates have been substantially grown, both in relative and absolute size; the area fraction occupied by the aggregates after incubation can be estimated as 35–40 % of the total area. The corresponding changes in optical transmission (measured in parallel experiments using the same dispersion samples) are shown in Fig. 2. The characteristic "jump" of optical transmission at the nematic-isotropic transition [15, 17] becomes noticeably smaller after incubation. This reflects a decrease in the general anisotropy of the composite system, which can be due to formation of NT aggregates (considered as "non-anisometric" objects embedded into the anisotropic phase formed by anisometric
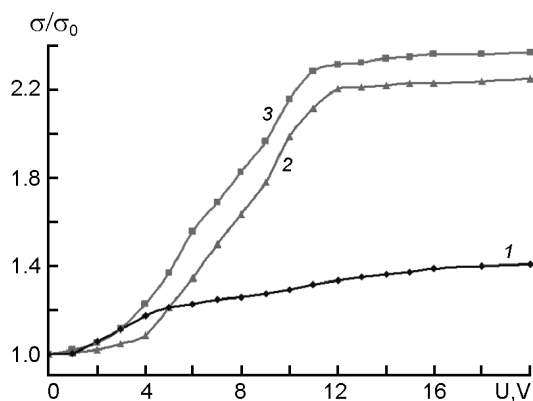
Fig. 3. Changes in relative electrical conductivity σ/σ_0 versus the dc voltage U applied to the measurement cell containing pure nematic 5CB (*1*) and 5CB doped by MWCNT (0.1 % wt) for "fresh" (*2*) and "incubated"(*3*) (8 hours) suspensions, $T = 298$ K.

Fig. 4. Relative changes in electrical conductivity σ/σ_0 versus the dc voltage U applied to the measurement cell containing undoped nematic 5CB (*1*) and 5CB doped with 0.1 % MWCNT (*2*), and 0.1 % MWCNT + 0.1 % organomodified MMT (*3*). Insert shows the threshold voltages U_{th} for samples *1–3*.

particles (5CB molecules and individual NTs). Such behavior is similar to that noted earlier for EBBA+NT dispersions [30].

Fig. 3 shows changes in electrical conductivity upon application of dc voltage to the "fresh" and incubated 5CB + 0.01 % NT dispersion samples. The introduction of NTs leads to a significant increase in conductivity, with the relative increase in conductivity above a certain "threshold" voltage becoming noticeably larger. This can be explained by the mechanism of Freedericks transition typical for nematics with $\Delta\varepsilon > 0$ [31], when the planar alignment of both 5CB molecules and nanotubes incorporated into the orientationally ordered nematic structure is changed into the homeotropic alignment (with long axes of anisometric particles aligned along the electric field) [17]. After incubation and resulting large-scale formation of NT aggregates, the after-threshold conductivity values become smaller (reflecting a decrease in the general anisotropy of the system), and the threshold voltage (and the onset voltage of the conductivity rise) is increased. This can mean that the NT aggregates formed hinder the reorientation of 5CB molecules (and nanotubes incorporated into the oriented nematic structure).

At this stage, we recalled some earlier experiments made under the same conditions, when we studied 5CB+NT dispersions into which we added, at the stage of preparation of the dispersion, certain amounts of organomodified montmorillonite (MMT) [31]. The preparation of LC+MMT dispersions means, at the level of molecular physics, exfoliation of the organoclay plate-like
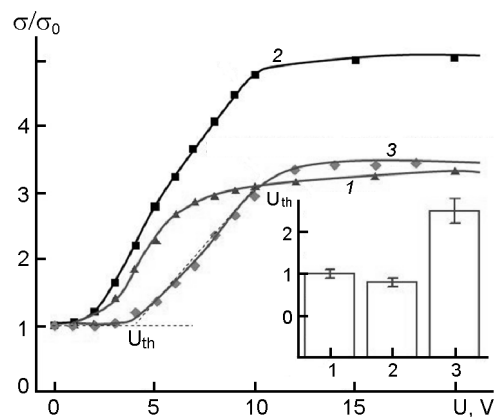
particles and their incorporation into the orientationally ordered nematic structure. To make the comparison easier, we present here some of these results (Fig. 4). It can be noted that introduction of MMT particles into the 5CB+NT dispersion leads to changes in the conductivity behaviour at Freedericks transition that are similar to those induced by NT aggregate formation (the after-threshold conductivity values become smaller, and the threshold/onset voltage is increased). The idea of NT aggregates as newly-formed particles, with their three-dimensional shape more plate-like than elongated, and probably of fractal nature [30], does naturally arise.

Considering NT aggregates in LC media, one can imagine two limiting cases of their eventual structure. One of them, with strong interaction between NTs, are, in fact, residual bundles or clusters of not fully dispersed nanotubes structured parallel to each other. The other type could emerge as a result of "secondary" interaction of the dispersed individual nanotubes in the LC medium. This interaction can be described as proposed in [33]. The case illustrated by Fig. 3b of this paper involves fractal clusters of rods formed by diffusion-limited cluster aggregation, with isotropic distribution of rod orientations. If the volume fraction is low, the fractal structure implies the existence of voids in the suspension of relatively large size. In further narration, we will denote the structures of this type formed by nanotubes as "S-aggregates".
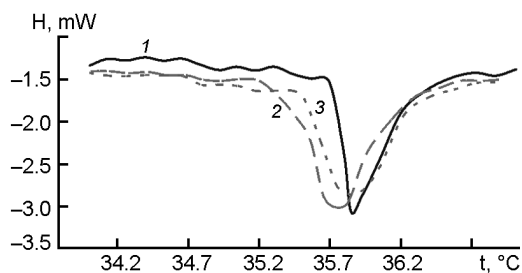
Fig. 5. Heat flow H versus temperature T in DSC experiments (heating) with pure 5CB (*1*) and 5CB filled by MWCNT (0.1 wt. %) for "fresh" (*2*) and "incubated" (*3*) (for 8 h at 298 K) suspensions.

Fig. 6. Heat flow H versus temperature T in DSC experiments (cooling) with pure 5CB (*1*) and 5CB filled by MWCNT (0.1 wt. %) for "fresh" (*2*) and "incubated" (*3*) (for 8 h at 298 K) suspensions.

One can image an S-aggregate as a fractal structure formed by nanotubes with voids filled with captured nematic molecules. In a simplified model, the intersecting individual nanotubes form stochastic fractal structures based on simple geometrical figures. If the nanotube length is a, and its aspect ratio is r, one can calculate the volume V_s of a three-dimensional "skeleton", as well as the total volume V_n of the nanotubes forming the skeleton. At aspect ratios of ~100, the V_s/V_n ratio can be of the order of several hundred. The ramified S-aggregates capture surrounding LC molecules, and their microsize volume can be by 2–2.5 orders greater than the total volume of the nanoparticles involved. This means that at NT concentrations of ~0.1 %, the volume fraction of S-aggregates in the nematic matrix can reach 25–30 % and more, which is clearly reflected in the microscopic images. Thus, we obtain a heterogeneous system comprising S-aggregates with incorporated and adjacent nematic molecules and the "bulk" nematic phase with dispersed "uncaptured" nanotubes.

It could be expected that behavior of nematic molecules "inside" and "outside" the S-aggregates in the nematic-isotropic phase transition would be different, and these features would affect the shape of corresponding DSC peaks. The obtained DSC thermograms for pure 5CB and 5CB + 0.1 % NT dispersion before and after incubation are shown in Figs. 5,6.

On heating, the nematic-isotropic transition temperature T_i of the "fresh" dispersion is slightly (by 0.1–0.2°C) lowered, and the peak is slightly broadened. This behavior is close to that observed in [23–25], suggesting that the few already formed aggregates practically do not contribute. After incubation, the peak broadens further, and this broadening goes essentially to higher temperatures; the broadened peak seems to cover T_i values of both pure 5CB and
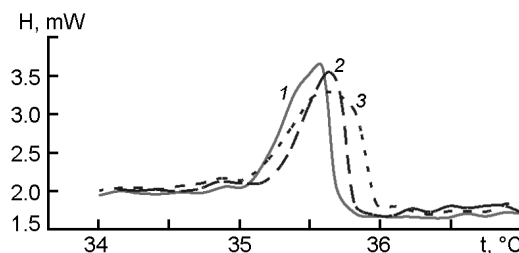
"fresh" dispersion. This may indicate that "captured" 5CB molecules undergo the transition with a certain lag.

On cooling, T_i of pure 5CB is lower by 0.2–0.3° than on heating (which is typical for all nematics). With incubated dispersions, the isotropic-nematic transition begins earlier than with pure 5CB, and the apparent T_i is close to that on heating. One may assume that 5CB molecules in the "captured" state are oriented more readily — the "skeleton" favors the nematic ordering. With "fresh" dispersions the picture is similar, but less pronounced. In another set of experiments, using methods of singular optics as described in [34] it was shown that such anisotropic microsized shells initiate strong speckled scattering with induced optical singularities, which is clearly enhanced after incubation. The details of these experiments will be published elsewhere.

4. Conclusions

Formation of aggregates of multiwalled carbon nanotubes dispersed in nematic 5CB was studied using five different experimental techniques (microscopy, optical transmission, electric conductivity, differential scanning calorimetry, and methods of singular optics). It is assumed that these aggregates consist of a "skeleton" formed by nanotubes arranged in a stochastic fractal structure and a "shell" ("coat") of the incorporated and adjacent nematic molecules. These aggregates can be considered as large quasi-macroscopic particles in the nematic matrix. The experimental results obtained by different methods appear to be in agreement with each other and the proposed physical picture.

Next steps toward deeper understanding of the process of NT aggregate formation and development of a molecular theory of this new class of anisotropic colloidal systems require further experimental data, including the effects of nanotube concentra-

tion, aspect ratio, percolation phenomena, molecular structure of anisotropic dispersion media, etc. These studies are now under way in our laboratories and will be presented in further publications.

References

1. S.Iijima, *Nature*, **354**, 56 (1991).

2. P.M.Ajayan, *Chem. Rev.*, **99**, 1787 (1999).

3. A.Khare, S.Bose, *J. Minerals and Mater. Character. and Engin.*, **4**, 31 (2005).

4. W.Lee, C.-S.Chiu, *Opt. Lett.*, **26**, 521 (2001).

5. W.Lee, S.-L.Yeh, C.C.Chang, C.C.Lee, *Optics Express*, **9**, 791 (2001).

6. M.D.Lynch, D.L.Patrick, *Nano Lett.*, **2**, 1197 (2002).

7. C.Zakri, *Liq. Cryst. Today*, **16**, 1 (2007).

8. J.P.F.Lagerwall, G.Scalia, *J. Mater. Chem.*, **18**, 2890 (2008).

9. M.Rahman, W.Lee, *J. Phys. D:Appl. Phys.*, **42**, 063001 (2009).

10. L.Dolgov, O.Kovalchuk, N.Lebovka et al., Carbon Nanotubes, ed. J.M.Marulanda, in: Tech Education and Publishing, Vukovar, Croatia (2010), p.451.

11. K.A.Park, S.M.Lee, S.H.Lee, Y.H.Lee, *J. Phys. Chem. C*, **111**, 1620 (2007).

12. W.Gwizdala, K.Gorny, Z.Gburski, *J. Mol. Struct.*, **887**, 148 (2008).

13. P.Van der Schoot, V.Popa-Nita, S.Kralj, *J. Phys. Chem. B*, **112**, 4512 (2008).

14. V.Popa-Nita, S.Kralj, *J. Chem. Phys.*, **132**, 024902 (2010).

15. L.Lysetskiy, V.Panikarskaya, O.Sidletskiy et al., *Mol. Cryst. Liq. Cryst.*, **478**, 127 (2007).

16. N.Lebovka, T.Dadakova, L.Lysetskiy et al., *J. Mol. Struct.*, **887**, 135 (2008).

17. L.N.Lisetski, S.S.Minenko, A.P.Fedoryako, N.I.Lebovka, *Physica E*, **41**, 431 (2009).

18. I.Dierking, G.Scalia, P.Morales, *J. Appl. Phys.*, **97**, 044309 (2005).

19. I.Dierking, S.Eren San, *Appl. Phys. Lett.*, **87**, 233507 (2005).

20. J.Lydon, *Liq. Cryst. Today*, **15**, 1 (2006).

21. I.Dierking, K.Casson, R.Hampson, *Jap. J. Appl. Phys.*, **47**, 6390 (2008).

22. H.J.Shah, A.K.Fontecchio, D.Mattia, Y.Gogotsi, *J. Appl. Phys.*, **103**, 064314 (2008).

23. R.Basu, G.S.Iannacchione, *J. Appl. Phys.*, **106**, 124312 (2009).

24. R.Basu, G.S.Iannacchione, *Appl. Phys. Lett.*, **95**, 173113 (2009).

25. R.Basu, G.S.Iannacchione, *Phys. Rev. E*, **81**, 051705 (2010).

26. S.J.Jeong, K.A.Park, S.H.Jeong et al., *Nano Lett.*, **7**, 2178 (2007).

27. O.Trushkevych, N.Collings, T.Hasan et al., *J. Phys. D:Appl. Phys.*, **41**, 125106 (2008).

28. O.Trushkevych, F.Golden, M.Pivnenko et al., *Electron. Lett.*, **46**, 693 (2010).

29. A.V.Melezhyk, Yu.I.Sementsov, V.V.Yanchenko, *Russian Zh. Prikl. Chimii*, **78**, 924 (2005).

30. A.I.Goncharuk, N.I.Lebovka, L.N.Lisetski, S.S.Minenko, *J. Phys. D:Appl. Phys.*, **42**, 165411 (2009).

31. P.de Gennes, J.Prost, Physics of Liquid Crystals, Chapter 3.2.3., Clarendon Press, Oxford (1993), p.123.

32. S.S.Minenko, A.I.Kocherzhyn, L.N.Lisetski, N.I.Lebovka, *Functional Materials*, **16**, 319 (2009).

33. M.J.Solomon, P.T.Spicer, *Soft Matter*, **6**, 1391 (2010).

34. V.V.Ponevchinskiy, A.I.Goncharuk, V.I.Vasilyev, N.I.Lebovka, M.S.Soskin, *Zh. Eksp. Teor. Fiz. Lett.*, **91**, 259 (2010).

Агрегати багатостінкових вуглецевих нанотрубок у нематичних рідких кристалах: експериментальні свідчення та фізична картина

С.С.Міненко, Л.М.Лисецький, А.І.Гончарук, М.І.Лебовка, В.В.Поневчинський, М.С.Соскін

Утворення агрегатів багатостінкових вуглецевих нанотрубок, диспергованих у нематичному рідкому кристалі 5СВ, досліджено різними методами (мікроскопія, оптичне пропускання, електропровідність, диференціальна скануюча калориметрія і методи сингулярної оптики). Здійснено моніторінг формування агрегатів у часовому масштабі декількох годин та запропоновано фізичну модель, яка описує їх утворення. Припускається, що агрегати складаються зі "скелета" із нанотрубок, упорядкованих у стохастичну фрактальну структуру, та оболонки ("шуби") з інкорпорованих та прилеглих молекул нематика. Агрегати цього типу ("S-агрегати") можна розглядати як квазі-макроскопічні частинки у нематичній матриці. Експериментальні результати, отримані різними методами, узгоджуються між собою та з пропонованою фізичною картиною.