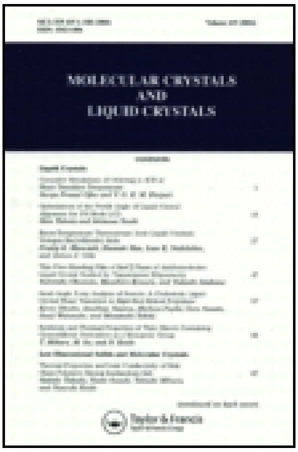


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

AFM Investigations of Banana-Shaped Mesogen Crystalline Phase in Thin Films

M. A. Zharova [a], N. V. Usol'tseva [a], I. V. Kholodkov [b], V. V. Rybkin [b] & S. G. Yudin [c]

[a] Ivanovo State University, Nanomaterials Research Institute, Ivanovo, Russia

[b] Ivanovo State University of Chemistry and Technology, Ivanovo, Russia

[c] A. V. Shubnikov Institute of Crystallography Russian Academy of Science, Moscow, Russia

Version of record first published: 16 Jun 2011

To cite this article: M. A. Zharova, N. V. Usol'tseva, I. V. Kholodkov, V. V. Rybkin & S. G. Yudin (2011): AFM Investigations of Banana-Shaped Mesogen Crystalline Phase in Thin Films, Molecular Crystals and Liquid Crystals, 546:1, 126/[1596]-133/[1603]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.571940

Mol. Cryst. Liq. Cryst., Vol. 546: pp. 126/[1596]–133/[1603], 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.571940

AFM Investigations of Banana-Shaped Mesogen Crystalline Phase in Thin Films

M. A. ZHAROVA,[1] N. V. USOL'TSEVA,[1]
I. V. KHOLODKOV,[2] V. V. RYBKIN,[2] AND
S. G. YUDIN[3]

[1]Ivanovo State University, Nanomaterials Research Institute,
Ivanovo, Russia
[2]Ivanovo State University of Chemistry and Technology,
Ivanovo, Russia
[3]A. V. Shubnikov Institute of Crystallography Russian
Academy of Science, Moscow, Russia

AFM investigations of surface relief of thermal treated thin films of modified banana-shaped compound–bis-{3,4,5-tri[4-(4′-nonyloxy-benzoyloxy)]benzoylamino}-1,3-phenylene (I)–in crystalline phase and films obtained by spin coating or Langmuir-Blodgett methods from chloroform solution without thermal treatment were carried out. It was determined that the thin films' surface topology of the compound I in the crystalline phase depends essentially on the way of the film preparation and filming process.

Keywords Atomic force microscopy; banana-shaped mesogen; chirality; Langmuir-Blodgett method

1. Introduction

Banana-shaped mesogens are relatively new class of liquid crystals. However the firsts rigid bent core compounds were synthesized by D. Vorländer *et al.* in Germany in 1929 [1]. Banana-shaped liquid crystals are interesting from many viewpoints. Since 1996 such compounds were studied in detail [2]. Banana-shaped liquid crystals are the first ferroelectric and antiferroelectric liquid crystals, which contain no chiral carbon. This is the most interesting aspect from the viewpoint of polarity. It turned out that because of the molecular structure peculiarities steric interaction leading to formation of helical filaments in smectic structures–a hint of spontaneous symmetry breaking appeared between banana-shaped achiral molecules [3–9].

Address correspondence to M. A. Zharova, Ivanovo State University, Nanomaterials Research Institute, Ermak str. 39, 153025, Ivanovo, Russia. Tel.: 007-4932-370808; Fax: 007-4932-324677; E-mail: Zharovama@mail.ru

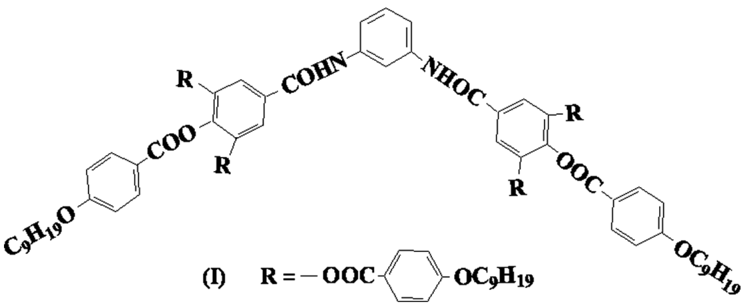


Figure 1. Molecular structure of compound **I**.

2. Results and Discussion

The object of the research is the modified banana-shaped mesogen–*bis*-{3,4,5-tri[4-(4′-nonyloxybenzoyloxy)]benzoylamino}-1,3-phenylene (**I**) (Fig. 1). Unlike the bent core banana-shaped mesogens investigated previously, in compound **I** not only the terminal groups but also the lateral substituents contain a benzene ring [10].

The data of the structure, mesomorphic, thermoelectrical and electrophysical properties of compound **I** were represented in detail in [11]. It was shown that this material possessed high temperature chiral mesophase with the following temperature sequence of phase transition on cooling: I • 284 ± 1°C SmCP(B2) • 280 ± 1°C Cr. α • 172 ± 3°C Cr. β • 73 ± 2°C Cr. γ. It was observed by optical polarization microscopy method that the chirality preservation effect becomes apparent in the crystalline phases (Cr. α, Cr. β and Cr. γ) forming on cooling of samples from isotropic liquid. It has been proved that thin crystalline films of compound **I** has polarity without prior polarization of the samples and shows pyroelectric effect at room temperature [11].

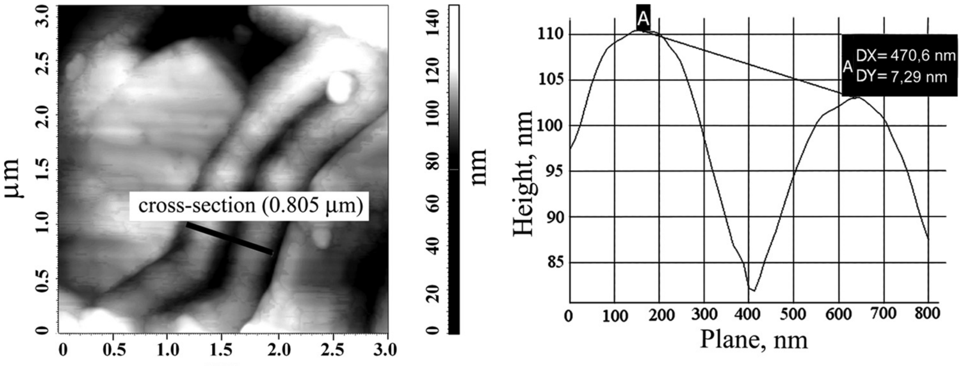
With the purpose of more in-depth study of structure peculiarity of thin crystalline films of this material we investigated thin films' surface topology by atomic force microscopy method (AFM). Atomic force microscope Solver 47 (NT–MDT) was used to study the film surface. The images were obtained by the semi-contact method at room temperature in air and under ambient conditions (cantilever resonance frequency: 150 kHz). Topography and phase contrasts were selected.

2.1. *Thermally Treated Film Samples of the Compound I*

In this case the sample preparation was done by filling the compound into a sandwich cell consisting of glass, heating to the clearing point (292.0°C), cooling down to room temperature and then removing the cover plate carefully. Heating and cooling rates were 2.0°C min^{-1}.

Areas with one-dimensional modulation in finger-like domains were discovered on film surface (Fig. 2a). The observed one-dimensional modulation is the evidence of helical superstructure presence. In Figure 2a the cross section is shown. Line measurements (cross section) of the finger-like domain were carried out (Fig. 2b). Compound **I** is chiral smectic therefore the distance between two maxima (A–A) equal to 470.6 nm (Fig. 2b) corresponds to the helical pitch dimension [12].

Partial frustration of films was observed when cover plates were removed. We tried to remove cover plate by mechanical shift in order to improve the film quality.

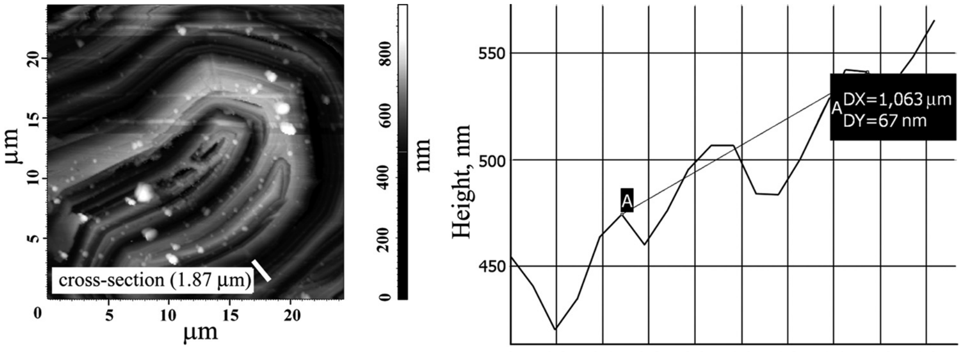


(a) (b)

Figure 2. AFM image (a) and line measurements (b) of surface area with one-dimensional modulation in finger-like domain of the film sample of compound **I**. The distance between two maxima (A–A) equal to 470.6 nm corresponds to the helical pitch dimension.

In this case glass plates were rubbed with abrasive. Mechanical shift of glass plate was made on cooling from isotropic liquid state in the mesophase existence temperature range according to glass plate orientation direction. Practically we untwisted the helical superstructure exposing the sample to shift deformation. AFM investigation results of these film samples are shown in Figures 3–5. The chirality character of periodic well-ordered layer structure is observed (Figs. 3 and 5). It is proved that the structure of thermally treated thin films in Cr γ-phase is really adequate to prior chiral mesophase structure.

More details can be seen by plotting the surface profile (cross section, see Fig. 3b). Set of steps corresponds to quantity of layers. Line measurements of a detail (cross section, see Fig. 3a) show a layer periodicity of about 500.0 nm (Fig. 3b). Besides, areas with a straight periodic streaky surface structure and disk-like domains were discovered (Fig. 4 and 5, correspondingly). The appearance



(a) (b)

Figure 3. AFM image of the area with chiral periodic well-ordered layer structure (a) and line measurements (b) of the cross-section indicated in (a).

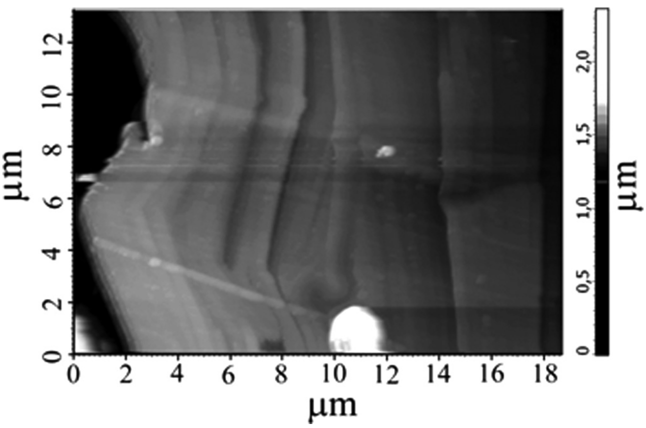


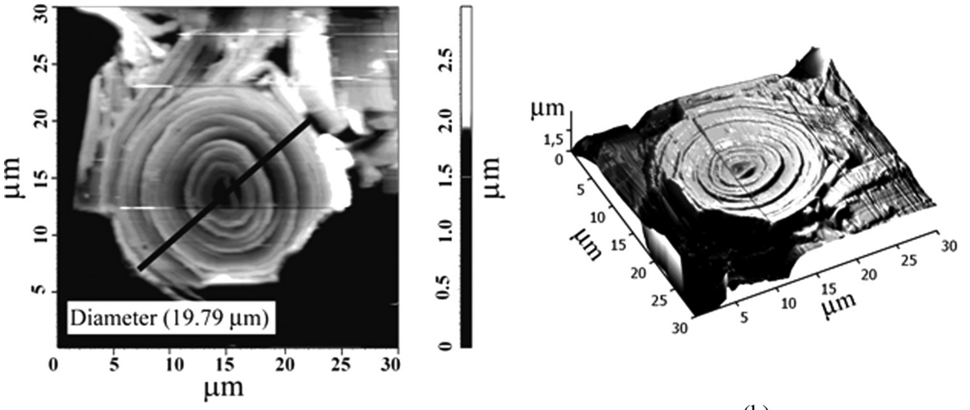
Figure 4. AFM image of the area with straight periodic streaky structure of the film sample of compound **I**.

of disk-like domains in Cr. γ phase was observed only at shift deformation of the samples. Chiral periodic well-ordered layer structure was shown in AFM images in plate (a) and 3D (b), too (Fig. 5).

2.2. *Film Samples of the Compound I Without Thermal Treatment*

At the first stage of our investigation we obtained the film samples from pure compound **I** exposing it to thermal treatment as indicated above. At the second stage the films were obtained from the solution of compound **I** in chloroform by spin coating or Langmuir-Blodgett methods.

2.2.1. *Spin Coating Method.* The solution of compound **I** in chloroform (0.01 weight %) was prepared using ultrasonic bath SONOREX SUPER and cast onto a not



(a)

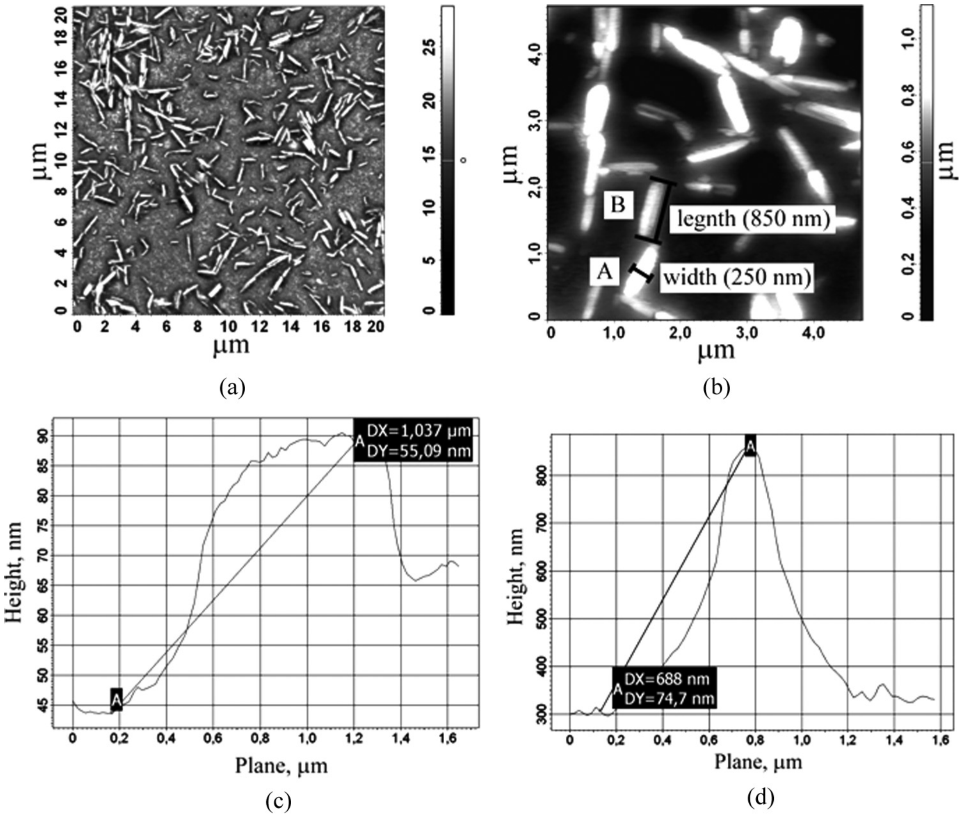
(b)

Figure 5. AFM image (a) and 3D image (b) of the area with disk-like domain. Diameter of the disk-like domain is approximately 20.0 µm.

rubbed glass plate by spin coating. After removing the solvent film surface was investigated by AFM.

The particles of regular rod-like form were revealed on the surface of film samples (Figs. 6a, b). The rod-like particles have the following sizes: 750.0 ÷ 950.0 nm, 200.0 ÷ 250.0 nm, 50.0 ÷ 100.0 nm (length, width and height, correspondingly) (Figs. 6b, c and d).

Interesting results were obtained when we used the solution of compound **I** in chloroform being in hermetically closed glass-stoppered flask during three months. There were no signs of sedimentation in this solution. The solution was cast onto a not rubbed glass plate covered with ITO by spin coating. The aggregates formed by rod-like particles are obviously observed (Figs. 7a, b). This fact demonstrates that side by side interaction of rod-like particles is stronger than the interaction of these particles with solvent molecules. Moreover, the defined orientation of "rods" long axes direction was observed in these aggregates (Fig. 7). The thickness of films obtained by spin coating method was about 1.0–2.0 μm.



(a) (b)

(c) (d)

Figure 6. Surface of the film samples of compound **I** deposited by spin coating method on a glass plate: (a) phase contrast (scan area–20.0 × 20.0 μm), (b) topography (scan area–4.8 × 4.8 μm), (c and d) line measurements of rod-like particles height from Figure 6b (indicated by A and B, correspondingly).

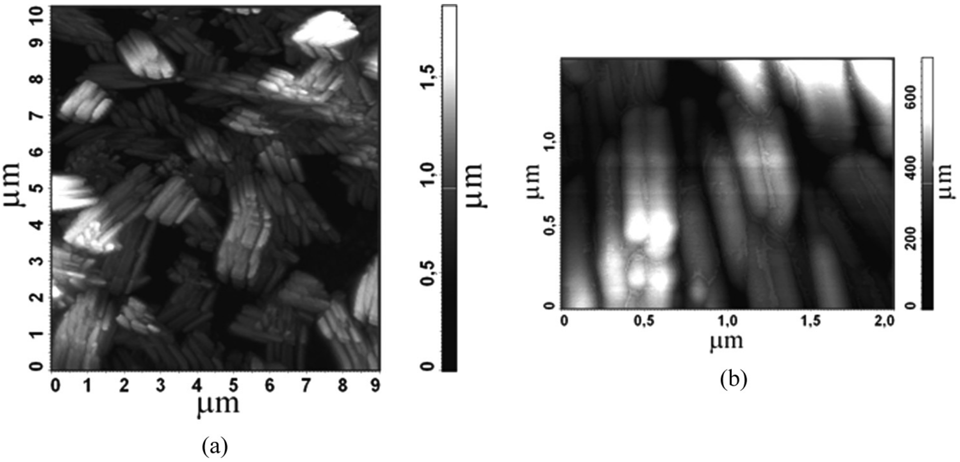


Figure 7. AFM images of the film sample deposited by spin coating on glass plate covered with ITO: (a) scan area–10.0 × 10.0 μm, (b) scan area–1.5 × 2.0 μm.

2.2.2. *Langmuir-Blodgett Method.* The next step in our work was to investigate thinner films of compound **I**. For this reason we tried to obtain layers at the air-solid substrate interface, *i.e.*, Langmuir-Blodgett (LB) films and research of their surface by AFM method. Moreover, floating layers behaviour of compound **I** on the water surface was studied. Figure 8 shows the π-A isotherm diagram, obtained during the compression (1) and expansion (2) processes. Langmuir and LB films were prepared on Langmuir trough [13]. The compound **I** was dissolved in chloroform to stock concentration of 0.01 weight %. Solution (1.6 ml) was coated on the water surface and floating layer was compressed and expensed at rate of 170.0 mm min^{-1} by barrier in automatic mode.

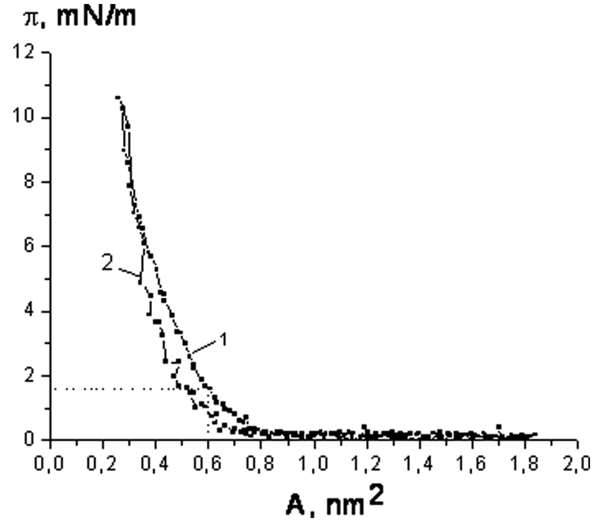
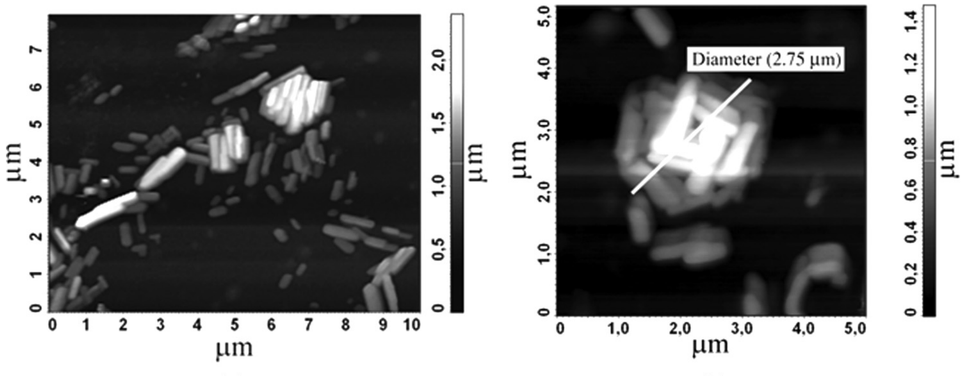


Figure 8. Isotherms of surface pressure dependence (π) from molecule area of Langmuir film formed from compound **I**: 1–isotherm of compression; 2–isotherm of expansion.



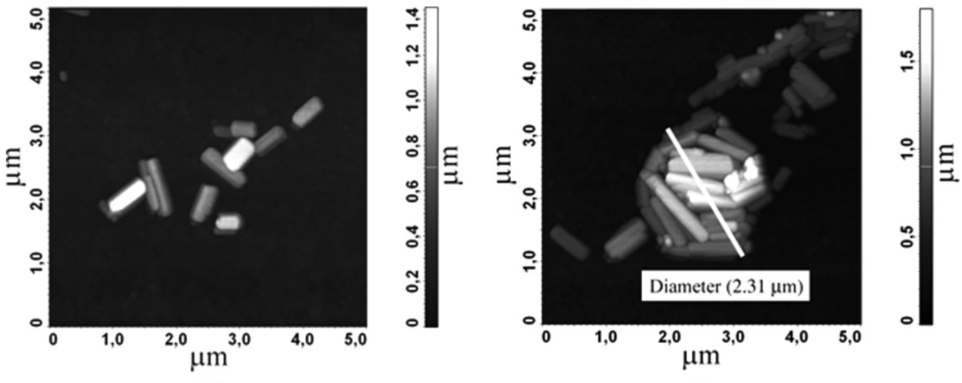
(a) (b)

Figure 9. AFM images of the film sample (thickness–1 floating layer) deposited by LB method on silicon plate covered with aluminium.

As shown in Figure 8 the areas of "gas phase" appeared before pressure less than 0.5 mN/m, areas of "liquid expanded" and "liquid condensed" phases appeared before pressure less than 10 mN/m, and collapse state area appeared over 10 mN/m. There is hysteresis of compression and expansion isotherms. This implies the instability of the floating layer and is connected with the fact that aggregation takes place on the water surface.

Langmuir films from water surface were transferred onto not rubbed silicon plates covered with aluminium or onto a rubbed glass plates covered with ITO. The last ones were rubbed by crocus. It was determined that compound **I** was unable to form the qualitative compressible monolayer at the air-water and air-solid substrate interfaces because of the aggregation.

Figures 9 and 10 show the AFM images of the film samples obtained by LB method. The same rod-like particles were detected. In Figures 9a and 10a prevailing direction of "rods" long axes orientation was observed in each aggregate. The aggregates consisting of "rods" rolled into a ball were revealed both in LB films on a



(a) (b)

Figure 10. AFM images of the film samples deposited by LB method on a rubbed glass plate covered with ITO: (a) thickness–1 floating layer, (b) thickness–3 floating layers.

silicon plate covered with aluminium and in LB films on a rubbed glass plate covered with ITO. Diameter of aggregates was 2.0–3.0 μm (Figs. 9b and 10b). We did not observe such aggregates in the films obtained by spin coating. We suppose that aggregates of similar form could be formed either on the water surface, or during the compression of surface layer, or during transfer of films onto plates.

3. Conclusion

Crystalline phase structure of thermally treated thin film samples of compound **I** and thin films without previous thermal treatment obtained by the spin coating or Langmuir-Blodgett methods was studied by AFM method. It is determined that the thin films' surface topology of the compound **I** in the crystalline phase essentially depends on the way of the film preparation and filming process.

In the thermally treated samples of the compound **I** the previous mesophase chirality preservation effect in the crystalline state was shown. Due to the fact that line measurements of the area (cross section) with one-dimensional modulation in finger-like domain were carried out, we can say that compound **I** is a chiral mesogen with fine helical pitch dimension (less than 1.0 μm).

Rod-like particles were detected on the films' surface obtained by the spin coating or Langmuir-Blodgett methods without previous thermal treatment. It was determined that rod-like particles had the tendency to aggregation with prevailing direction of "rods" long axes orientation in each aggregate.

Two types of aggregates were observed on LB films' surface: "rods" rolled into the "balls" and linear ones with prevailing parallel orientation of "rods" long axes direction. Since ball-like aggregates were not observed in films obtained by spin coating, we can suppose that its formation was related to the peculiarity of LB method.

References

[1] Vorländer, D., & Apel, A. (1929). *Ber. Dtsch. Chem. Ges.*, *2831*, 62.

[2] Pelzl, G., Wirth, I., & Weissflog, W. (2001). *Liq. Cryst.*, *969–972*, 28.

[3] Pelzl, G., Diele, S., Lischka, C., Wirth, I., & Weissflog, W. (1999). *Liq. Cryst.*, *26*, 135.

[4] Walba, D. M., Körblova, E., Shao, R., Maclennan, J. E., Link, D. R., Glaser, M. A., & Clark, N. A. (2000). *Science*, *2181–2184*, 288.

[5] Amarabatha Reddy, R., & Tschierske, Carsten. (2006). *Mater. Chem.*, *16*, 907–961.

[6] Eremin, A., Nemes, A., Stannarius, R., Pelzl, G., & Weissflog, W. (2008). *Soft Matter*, *4*, 2186–2191.

[7] Heppke, G., & Moro, D. (1998). *Science*, *1872–1873*, 279.

[8] Link, D. R., Natale, G., Shao, R., Maclennan, J. E., Clark, N. A., Körblova, E., Walba, D. M. (1997). *Science*, *1924–1927*, 278.

[9] Ros, M. B., Serrano, J. L., de la Fuente, M. R., & Folcia, C. L. (2005). *Mater. Chem.*, *15*, 5093.

[10] Zharova, M. A., Bykova, V. V., & Usol'tseva, N. V. (2007). (Rus). *Liquid Crystals and their Application*, *4*, 78.

[11] Zharova, M. A., Ungar, G., Zeng, X., Yablonsky, S. V., Yudin, S. G., & Usol'tseva, N. V. (2010). *Mol. Cryst. Liq. Cryst.*, *525*, 232–238.

[12] Chilaya, G. S. (1985). *Physical Properties and Application of Liquid Crystals with Induced Spiral Structure*, Tbilisi: Publishing house "Mecniereba", 88. (Rus).

[13] Yudin, S. G., Palto, S. P., Khavrichev, V. A., Mironenko, S. V., & Barnik, M. I. (1992). *Thin Solid Films*, *46*, 210–211.