

Organo- and acid-modified laponites in lyotropic and thermotropic liquid crystals

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DPPC-based phospholipid model membranes with lyotropic lamellar structure and thermotropic liquid crystals of several chemical classes were loaded with particles of laponite (untreated, organomodified and acid-modified). DSC thermograms showed distinct difference between membranotropic action of the three types of laponite, which was related to peculiar interaction features on the molecular level. The general trends were qualitatively similar in thermotropic liquid crystals, evidenced by temperature-dependent optical transmission and polarizing optical microscopy.

Keywords: liquid crystals, nanoparticles, laponite, differential scanning calorimetry, polarizing optical microscopy.

Органно- та кислотно-модифіковані лапоніти в ліотропних і термотропних рідких кристалах. *Н.О.Касян, С.С.Міненко, О.М.Самойлов, Л.М.Лисецький*

Фосфоліпідні модельні мембрани на основі DPPC з ліотропною ламелярною структурою та термотропні рідкі кристали кількох хімічних класів були доповані частинками лапоніту (необробленого, органомодифікованого та кислотно-модифікованого). Термограми ДСК показали чітку різницю між мембранотропною дією трьох типів лапоніту, яка була пов'язана з особливостями взаємодії на молекулярному рівні. Загальна поведінка була якісно подібна до термотропних рідких кристалах, про що свідчать дані залежностей оптичного пропускання від температури та результати поляризаційної оптичної мікроскопії.

1. Introduction

The development of novel composite nanomaterials based on soft-matter systems with nanoparticles (NP) of various types dispersed therein is a rapidly expanding field of materials science and nanotechnology. Among various matrix systems used for this purpose, one should note liquid crystals, which, as anisotropic liquids, can incorporate nanoparticles into their ordered molecular structure, which opens wide possibilities for novel effects and possible applications [1–4]. From the viewpoint of nanophysics, of special interest is the case when the introduced nanoparticles are themselves characterized by anisotropy of their geometrical shape, with interaction of anisometric nanoparticles with anisotropic

LC structures being a challenging object of molecular physics. However, in most experimental works no attention was paid to the shape of nanoparticles, which were considered just as nearly spherical objects of a certain size. A theoretical study of anisometric nanoparticles in liquid crystals was reported in [5, 6], where interactions on molecular level were shown to affect phase transition temperatures and other properties of LC matrices. The most vivid example of anisometric nanoparticles is presented by carbon nanotubes, with their LC dispersions extensively studied (see, e.g., [7–9] and references therein). Alongside the rod-like carbon nanotubes, a different example can be given by disc-like nanoparticles of nanoclays, such as montmorillonite

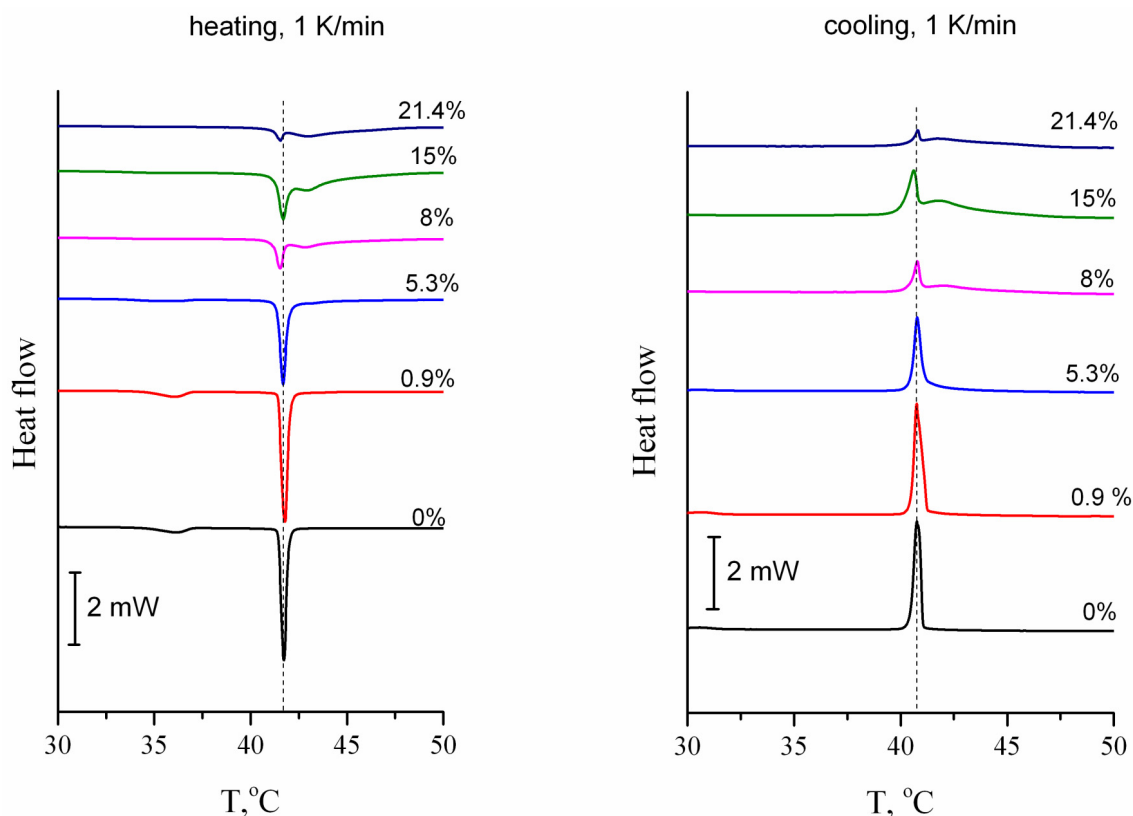


Fig.1. DSC thermograms of DPPC membranes containing Lap (laponite concentration is given in mass % with respect to the mass of lipid).

or laponite [10, 11]. Interestingly, the behavior of such discotic NPs in liquid crystals formed by rod-like molecules was either similar or complementary to the effects of CNTs [12, 13]; in particular, this applies to NP-induced effects on the nematic to isotropic phase transition [14].

A promising development of this approach would be the use of lyotropic liquid crystals as matrices for laponite nanoparticles. In this respect, model phospholipid membranes forming lyotropic LC phases with lamellar structures was a natural choice, since these systems are characterized by clear, reproducible and stable phase transitions easily recorded by differential scanning calorimetry (DSC) [15–17]. In a recent paper [18], the effects of laponite upon model membranes formed by lecithin were reported. By small angle X-ray scattering (SAXS) methods, the laponite discs were shown to incorporate between the lipid bilayers, which, however, did not expand the lamellar arrangement, but, on the contrary, reduced the interlayer repeat distance, presumably due to enhanced intermolecular interaction. Since a profound relationship has been established between the

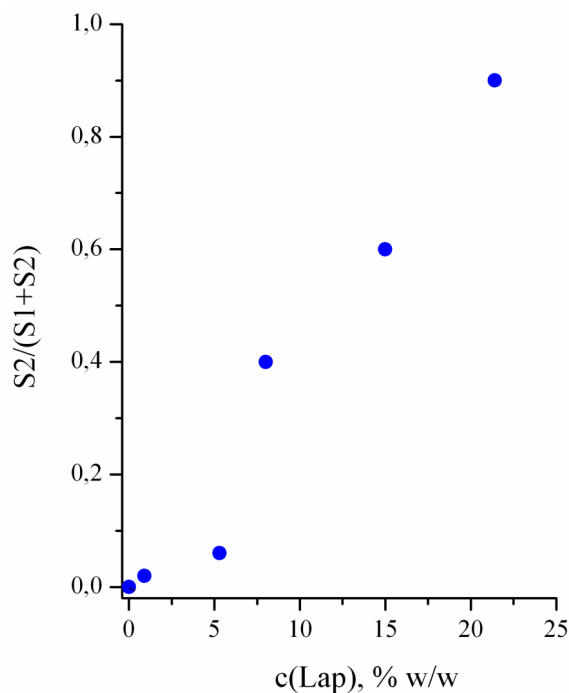


Fig. 2. The area under the high-temperature peak (S_2) with respect to the total area of the high- and low-temperature peaks ($S_2 + S_1$) as function of Lap concentration in the system.

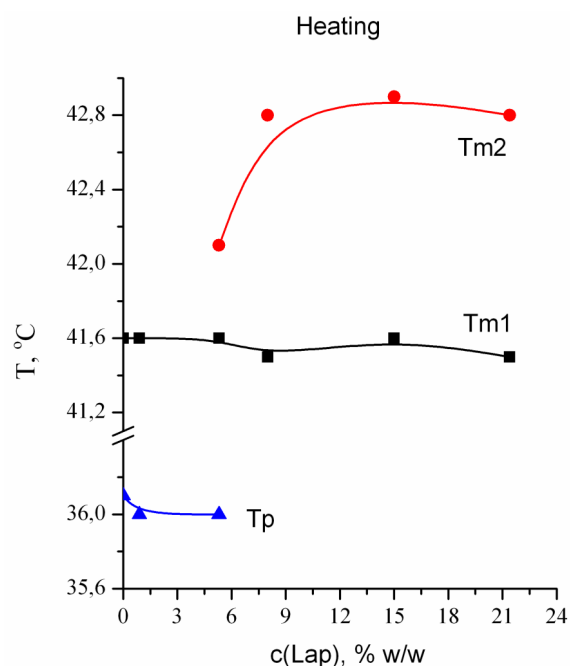


Fig. 3. Temperatures of pre-transition (T_p) and main phase transition (T_m) of DPPC membranes as function of Lap concentration. T_{m1} and T_{m2} are the low-temperature and high-temperature peaks which constitute the main phase transition in the presence of Lap.

effects of dopants on phospholipid membranes observed in SAXS and DSC experiments [19], it was natural to endeavor DSC studies of model phospholipid membranes containing laponite, using the general approach and ideology described in [20, 21].

2. Materials and methods

Three types of laponite samples were used: non-treated laponite of XLS grade (Lap), organomodified laponite prepared by "cold" method [14] (LapO), and acid-modified laponite treated with different amounts of H_2SO_4 and HCl (which presumably neutralized some functional groups on the laponite disc surface). The three samples were distinguished by the acidification degree in the order Lap2 > Lap5 > Lap6. All the laponite samples were obtained from Institute of Biocolloidal Chemistry, Kyiv, Ukraine.

The Lap powder was incubated in distilled water and ultrasonicated during 1–2 min. The exfoliated nanodiscs (diameter ~ 25 nm, thickness ~ 1 nm) formed transparent colorless suspensions. At higher concentrations of Lap, the viscosity of the suspension increased up to gel formation at > 5 %.

The phospholipid membranes were prepared using dipalmitoylphosphatidylcholine (DPPC) obtained from Aldrich. DPPC (~

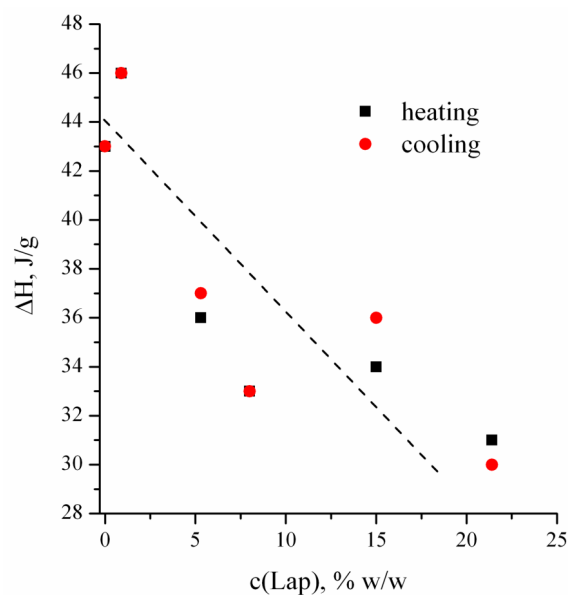


Fig. 4. The total enthalpy of the low- and high-temperature peaks of the main phase transition of DPPC membranes as function of Lap concentration.

20 mg) was added to distilled water or water dispersion of laponite (mass ratio DPPC: H_2O — 1:9, i.e., 10 % wt.% DPPC in water). Then the samples were incubated for 2–3 days with heating up to ~ 50°C and intensive mixing every 5–10 hours. Under these conditions, formation of multilamellar liposomes was expected [15, 20, 21]. DSC thermograms were obtained using a Mettler DSC1 calorimeter (Switzerland) in heating and cooling modes, scanning rate 1 K/min.

Polarizing optical microscopy studies were carried out using Micromed Polar 3 (Micromed).

Optical transmission spectra were measured in sandwich-type LC cells using a Shimadzu UV-2450 spectrophotometer (Shimadzu, Japan) within the spectral range of 300–900 nm. The measurements were carried out within a temperature range of 20–90°C both on heating and cooling, and the temperature values were changed in 0.2–0.5°C steps and stabilized using a flowing-water thermostat ($\pm 0.1^\circ C$).

3. Results and discussion

3.1 Lyotropic phases of phospholipid membranes

The obtained DSC thermograms are presented in Fig. 1. The initial sample (0 % Lap) shows two peaks of phase transitions — the pre-transition ($T_p = 36.1^\circ C$) and main transition ($T_m = 41.6^\circ C$). Increasing Lap

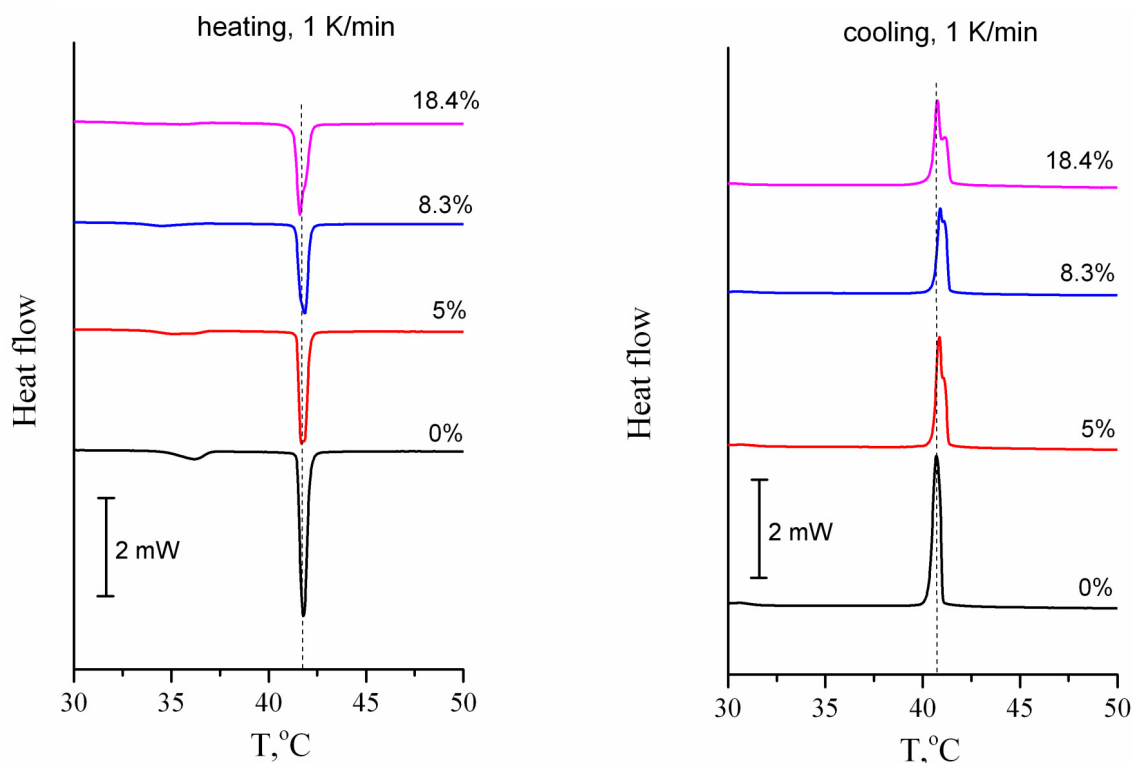


Fig.5. DSC thermograms of DPPC membranes containing LapO (laponite concentration is given in mass % with respect to the mass of lipid).

concentration leads to smearing and disappearance of the pre-transition and change in shape of the main transition peak. A high-temperature shoulder appears, resulting in an additional peak above 5 % of Lap. Its intensity (area under the peak, S_2) increases with higher Lap content, while intensity of the low-temperature peak (S_1) decreases (Fig. 2). So, we see re-distribution of the total transition enthalpy between these peaks, both under heating and cooling. It should be noted that the low-temperature peak T_{m1} remains nearly unchanged, while the second peak temperature T_{m2} increases up to 42.8°C at 8 % Lap (Fig. 3). The total enthalpy of both peaks is "decreased with concentration (Fig. 4) — by ~ 30 % at 20 % Lap.

These effects suggest that DPPC membranes and Lap nanodiscs interact on the molecular level. The appearance of the second peak can be explained in the following way. Water molecules are getting bound to the hydrophilic Lap. At low concentrations the Lap discs interact with molecules of free water. At higher Lap concentrations, a certain fraction of water molecules already bound to lipid molecules is transferred to the Lap hydration shell. Thus, Lap favors dehydration of DPPC, and, similarly to the

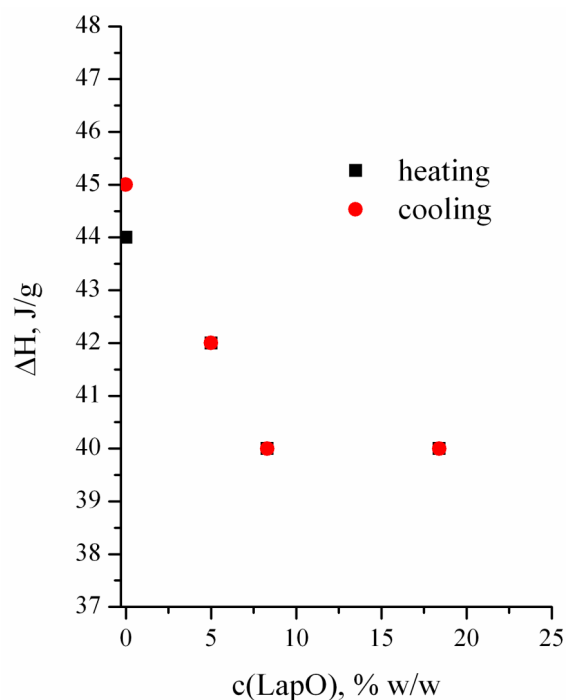


Fig. 6. Enthalpy of the main phase transition of DPPC membranes as function of LapO concentration.

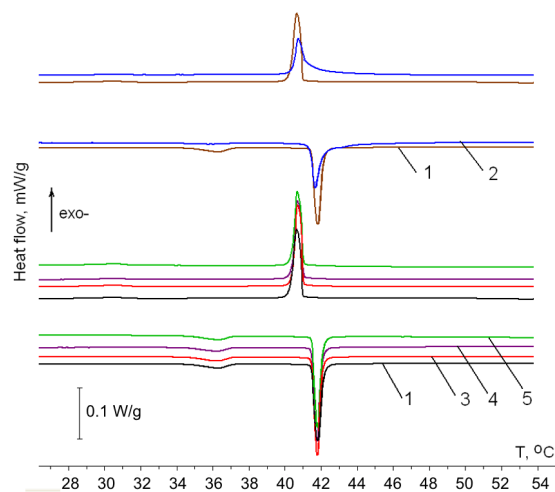


Fig. 7. DSC thermograms of DPPC membranes containing laponites: 1 — undoped DPPC, 2 — Lap1, 3 — Lap2, 4 — Lap5, 5 — Lap6. Concentration of laponites is 8.4mass % with respect to DPPC.

effects of DMSO and other cryoprotectants [21], this leads to an increase in the main phase transition temperature. The low-temperature peak (T_{m1} corresponds to the main phase transition temperature without Lap) is ascribed to fully hydrated lipids not interacting with Lap; the emerging second peak can be naturally ascribed to partially dehydrated lipids, which are thus indirectly interacting with Lap nanodiscs. This effect is enhanced at higher Lap concentrations, leading to the enthalpy re-distribution between the two peaks.

A similar set of data was obtained with organomodified laponite LapO under similar experimental conditions. The main difference was that LapO, unlike Lap, did not yield transparent samples when dispersed in water and did not form gels at higher concentrations; after ultrasonication, LapO particles showed a tendency to rather rapid sedimentation.

The DSC thermograms obtained with LapO are shown in Fig. 5.

It can be seen that introduction of LapO leads to smearing of the pre-transition peak, though it is less pronounced as compared with Lap. The main phase transition temperature remains practically unchanged, though at higher LapO concentrations (~ 18 %) a high-temperature shoulder appears. This is more obvious during cooling, where a second peak tends to emerge; we can say that the general behav-

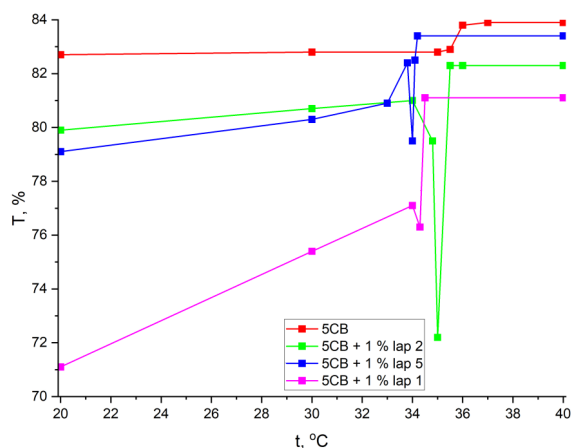


Fig. 8. Optical transmission vs. temperature for dispersions of untreated (Lap1) and acid-modified (Lap2, Lap5) laponite samples dispersed in nematic 5CB. Concentration of laponite — 1 %, measurement wavelength 700 nm, cell thickness — 20 μ m.

ior with LapO is similar to that with Lap, but the effects are noticeably weaker.

With higher concentrations of LapO, the enthalpy of the main phase transition is also decreased (Fig. 6), though this decrease is weaker than with Lap (Fig. 4). Thus, 20 % Lap lowers the enthalpy by ~ 30 %, while 18 % LapO — just by ~ 10 %.

The results obtained with LapO can be explained as follows — since a fraction of the LapO nanodisc area was covered by the organomodifying agent, the dehydration activity was weakened, and the effects of interaction with lipids were much less pronounced.

In one more set of experiments, a similar approach was applied to acid-modified laponite samples. The sample denoted as Lap1 was identical to Lap; the other three samples were distinguished by the acidification degree in the order Lap2 > Lap5 > Lap6. Water dispersions were prepared with 1 % laponite in deionized water incubated for 2–3 hours at room temperature and ultrasonicated for 2–3 min. Lap1, as Lap in the first series, readily formed a transparent suspension without traces of visible particles, while Lap2, Lap5 and Lap6 formed just a turbid suspension with a strong tendency to sedimentation.

Samples for DSC experiments were prepared in the same way as with Lap and LapO. The results of DSC measurements are shown in Fig. 7.

The model membrane samples with Lap2, Lap5 and Lap6 showed the same DSC pro-

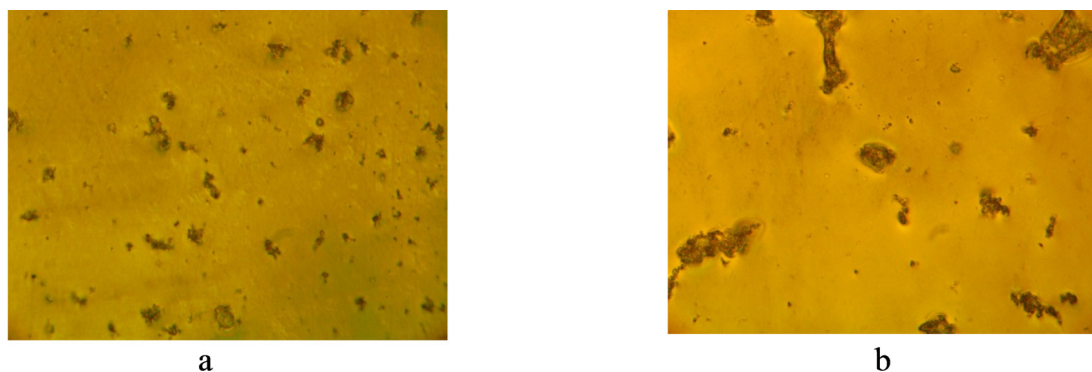


Fig.9. Microphotographs of nematic liquid crystal textures of 5CB+1% Lap. Cell thickness 20mkm, temperature 20°C, size of imaged area 500x500mkm, parallel polarizers, freshly prepared (a) and after 20min (b).

files (position and shape of the pre-transition and main transition peaks) as the pristine DPPC membrane without Lap. This obviously suggested the absence of any interaction between laponite discs and phospholipid membrane. Most probably the reason for such behavior was that acid-modified laponites were not exfoliated in the water phase due to their hydrophobicity. At the same time, DSC thermograms for Lap1 were quite similar to Lap studied in the first set of experiments.

3.2 Thermotropic liquid crystals

Thus, we have shown that different types of laponite can interact with the lyotropic phase of model phospholipid membranes in different ways. It was of certain interest to check how these features would be manifested in thermotropic liquid crystals.

As a first step, we took a standard nematic 4-pentyl-4'-cyanobiphenyl (5CB) and loaded it with 1 % laponite of each kind (Lap1, Lap2, Lap5). The procedure of sample preparation (by ultrasonication) was the same as described in our earlier works [13, 19]. The obtained temperature dependences of optical transmission are shown in Fig. 8.

In the case of undoped 5CB, in the nematic phase the optical transmission is practically independent of temperature, just at the temperature of the phase transition to the isotropic liquid ($N \rightarrow I$) a small jump is observed. However, the picture is changed when laponite is introduced to the system (Fig. 8). With Lap1, transmission in the nematic phase increases monotonously with temperature, and close to the isotropic transition we observe a small drop, and then a sharp rise of transmission, much larger than with undoped 5CB. This is naturally ascribed to incorporation of laponite nanoparticles as exfoliated discs into the

orientationally ordered nematic structure [9]. The effects of laponite samples upon 5CB are increasing in the order $Lap2 < Lap5 < Lap1$, which is in agreement with the same order obtained for laponite effects in phospholipid membranes described in the previous part of this work (Fig. 7). Thus, the non-modified Lap1 interacts with liquid crystals the most readily, while acid-modified laponites are quite poorly dispersed both in aqueous and organic media.

At the next stage of our studies, we used polarization optical microscopy (POM) to further examine the effects of dispersed laponite upon liquid crystal matrices. A freshly prepared Lap1 dispersion in 5CB showed rather homogeneous texture for several minutes (Fig. 9a). But then a sort of mechanical interaction of laponite particles with the matrix was observed. Aggregates growing in size appear, but they seem to result not from aggregation of laponite discs (like it occurs with carbon nanotubes), but from interaction of laponite with 5CB on molecular level (Fig. 9b).

Fig. 10 shows comparative microphotographs of the nematic mixture of 75 % 4CHCA + 25 % decanoic acid loaded with 1.5 % Lap. The image non-uniformity shows that the adding laponite to this matrix leads to rapid aggregation, which in turn violates the orientational order of the LC system. This is evidenced by both the similar picture in crossed and parallel polarizers (Fig. 10a, Fig. 10b), as well as the actual lack of influence of the phase transition (Fig. 10c, Fig. 10d) on the size and position of the aggregates in the system.

At Fig. 11, a somewhat different picture can be seen for the M5+Lap LC-systems, where the laponite particles are more uniformly distributed throughout the LC vol-

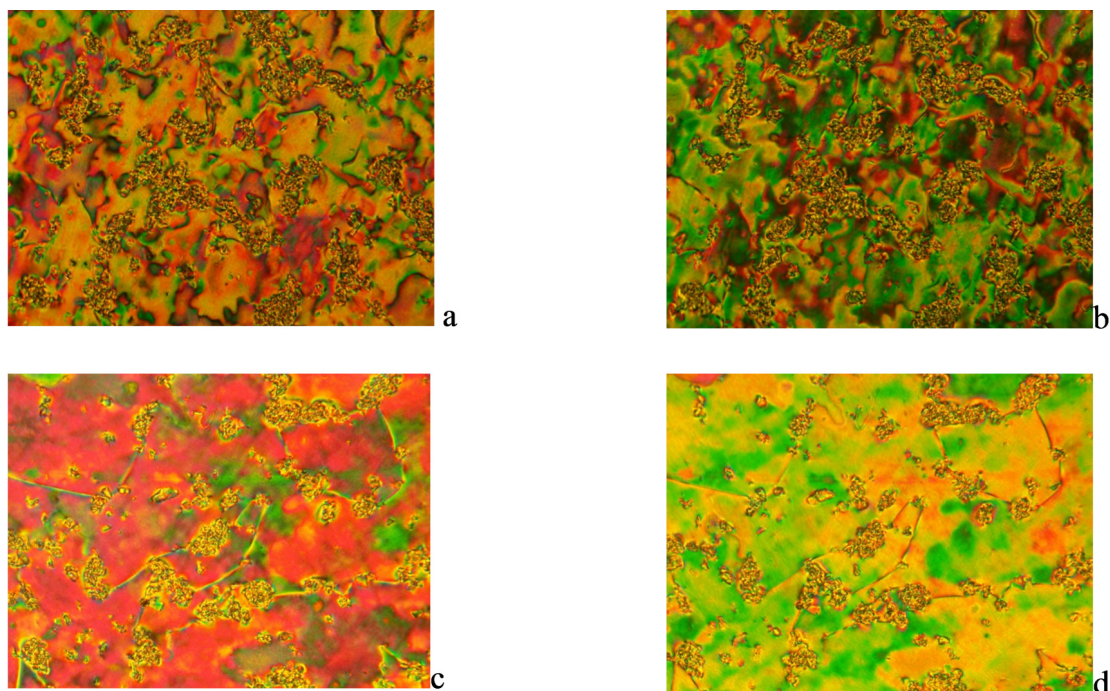


Fig. 10. Microphotographs of nematic liquid crystal textures of 75 % 4CHCA + 25 % decanoic acid loaded with 1.5 % Lap Cell thickness 20 μm , temperature 20°C, size of imaged area 500 \times 500 μm , parallel polarizers (a,c) crossed polarizers (b,d), freshly prepared (a,b) and after heating to the isotropic phase and cooling back to nematic (c,d).

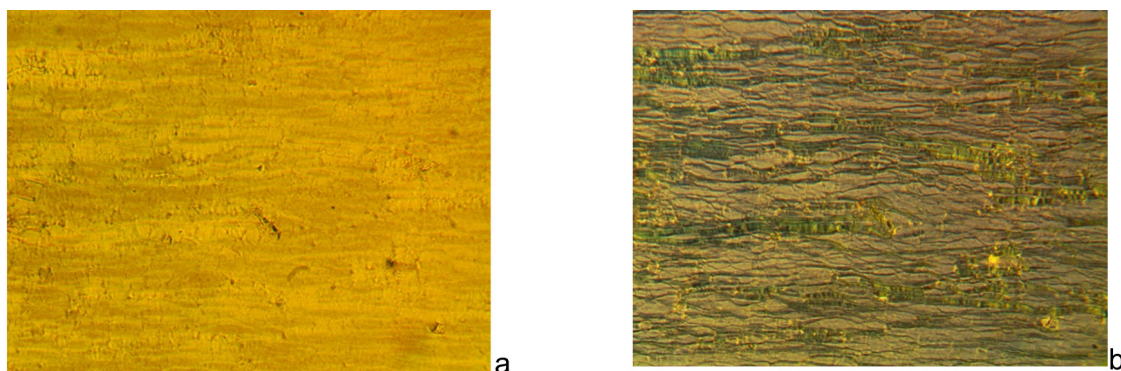


Fig.11. Microphotographs of liquid crystal textures of cholesteric mixture M5 loaded with 1.84% Lap. Cell thickness 20 μm , temperature 20°C, size of the imaged area 500 \times 500 μm , parallel polarizers (a), crossed polarizers (b).

ume, though they are more concentrated in the nodes of oily grooves, as was the case [22], which does not significantly influence the orientational arrangement of the system.

4. Conclusions

The interaction features of non-modified, organomodified and acid-modified laponite with liquid crystal hosts were shown to be different both in lyotropic liquid crystal phases of model phospholipid membranes and conventional thermotropic liquid crystals. The DSC data in phospholipid mem-

branes could serve as an indicator of the laponite modification degree. The results obtained by DSC correlate well with optical spectroscopy and microscopy data for laponite samples dispersed in thermotropic liquid crystals, with the acid-modified laponite showing the weakest affinity for these dispersion media.

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