



Microstructure and optical properties of nematic and cholesteric liquid crystals doped with organo-modified platelets

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ABSTRACT

The nematic (5CB) and cholesteric (the mixture of 5CB with chiral M5) liquid crystals (LC) doped with organo-modified inorganic platelets Laponite® (LO) were studied by differential scanning calorimetry (DSC), X-ray diffraction (XRD), microscopic image analysis, and optical density measurements. Cetyl-trimethylammonium-bromide (CTAB) was used as an organo-modifier and "cold" and "hot" methods were applied for obtaining of LO_c and LO_h samples, respectively. The data of DSC and XRD for nematic 5CB + LO compositions evidenced the presence of strong interactions between 5CB molecules and LO platelets and the better exfoliation for LO_c as compared with LO_h platelets. Microscopic structure, optical density and selective reflection for cholesteric compositions evidenced the strong integration of LO_c platelets inside LC medium. The observed optical behavior reflects combination of initial perturbation of cholesteric matrix by LO_c particles and initiation of formation of topological defects at small concentration of LO_c, $C < 0.1\%$, as well as the partial trapping of LO_c by large scale oily streaks at higher concentrations, $C \geq 0.1\%$.

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1. Introduction

Liquid crystal (LC) colloids represent the suspensions of nano- or microparticles in a liquid crystalline hosts [1–3]. Mutual interactions for such colloids are expected: the particles can disturb the long-range orientational order inside LC medium whereas LC host can affect organisation inside the subsystem of dispersed particles. The suspensions of carbon nanotubes [4–6], clay platelets [7] and particles of other origin [8] in different LC media have been extensively studied. These functional materials demonstrated distinctive optical and electro-optic characteristics that can be useful for application in displays, optoelectronic and storage devices.

In recent years, great interest was attracted by LC colloids on the base of clay platelets (natural montmorillonite, MT, or synthetic Laponite®, L) particles [9–11]. These particles have a primary platelet thickness of approximately 1 nm and the diameter of 500–2000 nm for MT [12] and of 25 nm for L [13]. The primary platelets of MT or L have high negative surface charge that is counterbalanced by the positive charge of exchangeable sodium ions present in the interlayer. They are practically non-dispersible in organic media. However, covering of these platelets

with surfactant stabilizing layer (organic modification) allows obtaining LC colloids with good dispersion and long-term stability of media [14]. Small angle X-ray scattering (SAXS) has revealed that organically modified platelets of MT (MTO) and L (LO) can be well delaminated in a nematic liquid crystal 5CB (4-*n*-pentyl-4'-cyanobiphenyl, K15) [15–17]. It was demonstrated that suspensions consist of a mixture stacked and single platelets. For example, in 0.1% suspensions the stacks include ≈ 5 platelets for MTO and ≈ 2 platelets for LO [17]. The all particles in the suspensions (stacked and single platelets) form large-scale aggregates. The effects of LO on the isotropic–nematic phase transition temperature in the 5CB were ascribed to the surface anchoring and confinement effects [12]. In external magnetic fields the platelets of MTO in the nematic phase of 5CB can be aligned with their normals parallel to the field [18]. It was explained by a homeotropic anchoring of the liquid crystal at the clay particle surfaces. However, the effect of alignment was insignificant for smaller platelets such as LO.

Several works on the possibility of attractive application of LC colloids on the base of clay platelets have been also reported [19–21]. The reversible electro-optical memory effects have been observed in LCs doped with platelets of MTO [19]. The contrast between the light scattering and transparent memory states was higher for the organized platelets with better affinity for the liquid crystal. The effect of the widening of the blue phase range (by a factor of two) induced by LO

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platelets dispersed in a chiral liquid crystal CE8 have been observed [20]. The mechanism of stabilisation accounting for the integration of the trapped platelets on LC dislocations was discussed. The platelets of LO has been used to stabilize suspensions of carbon nanotubes (CNTs) in liquid crystalline media [21]. It was demonstrated that the LO platelets surround CNTs and hamper their aggregation.

The synthetic L platelets have a well-known chemical structure as well as reproducible properties as compared with those of natural MT clays. To obtain sufficiently homogeneous and stable dispersions in organic media, various methods for preparation of LO platelets using ionic surfactants have been proposed [22–24]. Typically, the preparation procedure includes temperature incubation of mixture of L and ionic surfactant in water [21,25] or in water/propanol solution [15,16] for a long time (several hours). Then the treated platelets are cleaned by repeated washing and dried to remove the water. The both surface and edge modification using different modifiers, incubation temperatures and other experimental conditions were reported. The incubation was done at room [15,16,26,27] and elevated (233–253 K) [14,21,22,25,28,29] temperatures. Note that details of preparation procedure and especially incubation time and temperature can be crucial in determination of the characteristics of LO platelets. The L is chemically unstable against degradation in water [30–33] and its properties can depend upon pH, concentration of L and temperature. The observed significant dissolution of L below the pH 9 was explained by leaching of magnesium Mg^{+2} ions [30]. The effects of leaching of Mg^{+2} ions depend also on concentration of L in aqueous suspension [32]. Increase in concentration of L as well as that of salt resulted in stabilizing effect against degradation [33]. The characteristics of LO platelets can greatly depend also upon the nature of a modifier. Among the most popular modifiers we can refer to primary *n*-alkyl and quaternary organic cations [34], dimethyldioctadecyl ammonium bromide [14–16], dimethyldioctadecyl ammonium chloride [22], hexadecyltributylphosphonium bromide [28], diethylamine and triethylamine [26], cetyl-trimethyl-ammonium bromide (CTAB) [21,25,27,29].

At the same time, there have been no detailed studies of effects of modifiers or preparation procedure and temperature of incubation on properties of LO platelets and LC colloids on their base. Even for very popular CTAB modifiers the mechanism of its adsorption on the surface of platelets is rather complex and still unclear [35,36]. CTAB can adsorb on the faces of L in an amount which exceeds the CEC (cation exchange capacity) value four times [35]. The disk morphology is retained for hybrid LO particle and its thickness increases up to 4 nm as compared with thickness of primary platelet (≈ 1 nm). Adsorption of CTAB increased the hydrophobicity of platelets, accelerated the gelation processes, and also decreased the sedimentation stability of suspensions [36]. Moreover, adsorption of CTAB induced the overcharging of laponite particles in aqueous suspension and an electrokinetic potential changed from negative to positive [37]. The observed behavior was explained by hydrophobic decoration of the surface of laponite by CTAB molecules.

In this work, we concentrate our attention on the behavior of LO platelets prepared using the CTAB modifier in nematic 5CB and 5CB + M5 mixtures. The “cold” LO_c and “hot” LO_h platelets were prepared by using thermal incubation at temperatures 298 K and 353 K, respectively. The platelets were dispersed LC media and studied by several complementary methods, differential scanning calorimetry (DSC), X-ray diffraction (XRD), optical transmission and microscopy. Effects of increasing the LO concentration on the measured characteristics were analyzed, and substantial differences were noted for LO samples prepared by different methods. The data of DSC and XRD for nematic 5CB + LO compositions evidenced the presence of strong interactions between 5CB molecules and LO_c or LO_h platelets and the better exfoliation for LO_c as compared with LO_h platelets. Impact of LO_h concentration on changes in microscopic structure, optical density and selective reflection was analyzed. The supporting information compares microscopic structure, optical density and selective reflection for cholesteric ZhK440 + M5 mixture with dispersed LO_c or LO_h platelets.

The rest of the paper is organized as follows. **Materials and methods** section presents the materials, technical details used for preparation of samples and methods. The experimental results and general discussion is presented in **Results and discussion** section. In **Conclusions and final remarks** section, we summarize the main results and conclude the paper.

2. Materials and methods

2.1. Preparation of organo-modified Laponite®

Laponite® RD (Rockwood Additives Ltd., UK), which is a synthetic hectorite, is a swelling layered substance of 2:1 structural type with molecular formula $Na_{0.7}(Si_8Mg_{5.5}Li_{0.4})O_{20}(OH)_4$. In dry state, it presents a white powder, in which the disc-like particles are packed into stacks. The thickness and diameter of these discs are about 1 nm and 25–30 nm, respectively [38]. The specific surface area and specific particle density are $S \approx 370$ m²/g (determined by nitrogen adsorption measurements) [39] and $\rho_l \approx 2650$ g/cm³ [40], respectively. Each sheet is composed of two tetrahedral silica sheets with one octahedral magnesia sheet between them. The edge of L particle contains predominantly MgOH groups from the octahedral magnesia sheets and their surface charge is positive below in acidic medium. The concentration of negative charges per unit weight of L, defined as a cation exchange capacity, is equal to CEC $\approx 0.75 \cdot 10^{-3}$ eq/g [40]. It corresponds to the surface charge density of individual disc of $q \approx 0.4$ e/unit cell.

The platelets of original L were modified by ion-exchange reactions with the surfactant CTAB ($C_{16}H_{33}-N(CH_3)_3Br$, Fluka, Germany) with 99.5% purity. CTAB has molar mass of $M_s = 364.45$ g/mol, length of the molecule of 2.33 nm, and critical micelle concentration (CMC) in water of ≈ 1 mM (0.0364% wt) [41].

In the aqueous suspension the surface coverage of L by adsorbed CTAB (fraction of L surface covered by CTAB molecules) in terms of cation exchange capacity, F_{CEC} can be evaluated as.

$$F_{CEC} = (CEC \times M_s)^{-1} C_s / C_l = 3.66 C_s / C_l \quad (1)$$

In initial stage the aqueous solution of CTAB (0.55% wt) and aqueous suspension of L (2% wt) were prepared at fixed pH 10. The mixtures were sonicated for 10 min using a UZDN-2T ultrasonic disperser at frequency of 22 kHz and the output power of 150 W. To prevent overheating, the sonication was done a cold-water bath, and the temperature never exceeded 30 °C.

Then the solution of CTAB was gradually added, by drops, to the suspension of L and the final suspension sonicated again for 10 min. The surface coverage of L by CTAB molecules in the final suspension was $F_{CEC} \approx 2$. Then the suspensions were divided into two parts and stirred vigorously for 6 h at $T = 293$ K (“cold” sample, LO_c) and $T = 353$ K (“hot” sample, LO_h). After temperature incubation, the suspensions were filtered using a disc filter funnel and centrifuged. Finally, the obtained LO_c and LO_h samples were freeze-dried (for 20 h) for preservation of their dispersion ability in organic media.

2.2. LC materials

The nematic liquid crystal 5CB of 99.5% purity was obtained from Chemical Reagents Plant, Ukraine. It was purified by column chromatography on silica gel using a mixture of petroleum ether and benzene as the eluent. After evaporation of the solvent, the material was recrystallized from hexane at -20 °C. As a chiral component, a mixture of cholesterol esters M5 (Chemical Reagents Plant, Ukraine) consisting of 30% cholesteryl formate ($C_{28}H_{46}O_2$), 5% cholesteryl butyrate ($C_{31}H_{52}O_2$) and 65% cholesteryl nonanoate $C_{36}H_{62}O_2$ was used. The studied cholesteric mixture 5CB + M5 contains 75% 5CB and 25% M5. Chemical structures and phase transition temperatures of the studied LC hosts are presented in Table 1.

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