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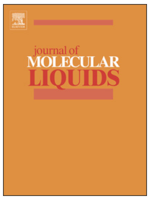

Change of thermo-morphologic and thermotropic properties in liquid crystals exhibiting multiple phase transitions

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ABSTRACT

Change of the thermo-morphologic and thermotropic properties of liquid crystals exhibiting multiple phase transitions vs. thickness of liquid crystalline layer have been investigated in this work. The sandwich-cells with 20 μm, 70 μm, 120 μm, 170 μm and 240 μm thicknesses were used. Liquid crystalline materials with smectic C, smectic A and nematic mesophases were objects of investigations. Change of the *crystal–smectic C*, *smectic C–smectic A*, *smectic A–nematic* and *nematic–isotropic liquid* phase transition temperatures, and transformation of texture from specific types to non-specific types with change of thickness of liquid crystalline layer have been found.

1. Introduction

Liquid crystals are materials having sufficiently sensitive and mobile structures, and are important objects for the thermography, optoelectronics, microelectronics and recording systems [1–6]. Availability of various thermotropic phase transitions is an important peculiarity of liquid crystals. By temperature changes at these transitions, transformations of the translational, positional and orientational orders, the change of spatial structure, point-like symmetry and physical properties take place. Accordingly, such changes lead to the change of the microscopic and macroscopic properties of liquid crystalline mesophases [7–12]. Special interest in physics, physical-chemistry and application of liquid crystalline materials have the *mesophase–mesophase* phase transitions, which occurred between ordered phases and *mesophase–isotropic liquid* phase transitions, which occurred between ordered and disordered phases. Therefore, topics, which are connected with experimental and theoretical studies of phase transitions in liquid crystals, have attracted the permanent attention of scientists [13–23].

Liquid crystals display the monomorphic and polymorphic properties, and exhibit various types of physically anisotropic optically uniaxial and optically biaxial mesophases. Such mesophases appear at different temperatures, take place within various temperature intervals and exhibit different types of phase transitions [25–29]. Therefore, liquid crystals can be use at different thermal regimes, within various temperature regions and in different climatic conditions.

On the other hand, in experimental studies of physical properties of liquid crystalline materials and also in technical devices, which are based on these materials, liquid crystals are placed between reference surfaces and must have definite thickness of liquid crystalline layer. But, because of interaction between liquid crystalline molecules and surfaces, character of surfaces and boundary conditions has effect on physical properties of liquid crystals [23–28]. Therefore, it is clear that thickness of liquid crystalline layer (i.e. distance between reference surfaces of the samples) must have an influence on the thermotropic and thermo-morphologic properties of phase transitions, and also on character of the biphasic regions of these transitions. Besides, is well known that the thickness of liquid crystalline displays and multimatrix elements is sufficiently important parameter, which determines the electro-optical, magneto-optical, thermo-optical and acousto-optical effects in liquid crystalline materials. These problems have been partially investigated theoretically in some works [25,29,30]. Unfortunately, influence of boundary conditions on the thermotropic and thermo-morphologic properties of liquid crystalline materials have been experimentally investigated insufficiently.

We are interested in influence of thickness of liquid crystalline layer, which is placed between reference surfaces of the sandwich-cells, on the thermo-morphologic and thermotropic properties of liquid crystals exhibiting multiple phase transitions. The results of these investigations are presented in this work.

2. Experimental

2.1. Methods

Investigations of the thermotropic and thermo-morphologic properties of liquid crystals under investigations have been carried out by the

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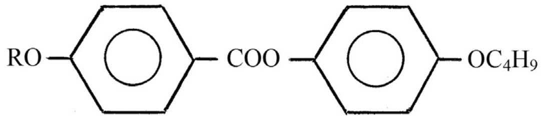

Fig. 1. The molecular structure of liquid crystals, examined in this study. **LC1:** R = C_8H_{17}; **LC2**: R = C_9H_{19}.

polarizing optical microscopy (POM) technique using the trinocular polarizing conoscopic/orthoscopic microscope, compensators, optical filters and λ-plates from Olympus Optical Co., Ltd., and also special heater-thermostat with digital temperature control system, multimeters and power supply. Registration of microphotographs and conoscopic images has been carried out by digital microphotographic system from Olympus Optical Co.

The thermo-morphologic properties of the heterophase regions of phase transitions have been studied by method of the temperature wedge [31], which was modified by us as the capillary temperature wedge (CTW) device [32,33]. The CTW device was used for study of the thermotropic and thermo-morphologic properties of various liquid crystalline materials and determination of the temperature and linear width of the heterophase regions of phase transitions in [28,34,35]. This device provides the observation of all of the thermal states of liquid crystalline materials in the real scale of time and in a wide temperature range, and provides also the calculation of the phase transition temperatures and the temperature widths of the heterophase regions with an accuracy not less than 10^{-2} K [28,32–35].

The crystallo-optics and crystallo-physics methods have been also used in this study [36–38]. These methods allow determining number and orientation of the optical axes, value and optical sign of the birefringence, peculiarities of defects and disclinations etc. in materials with optically anisotropic properties.

2.2. Materials and samples

In this work, two homologs 4-octyloxyphenyl esters of 4′-buthoxybenzoic acid (**LC1**) and 4-nonyloxyphenyl esters of 4′-buthoxybenzoic acid (**LC2**) of the 4-alkyloxyphenyl esters of 4′-alkyloxybenzoic acid liquid crystalline compound's series, which were purchased from Soyuzkhim Reactive Inc. (Russia), have been investigated. These materials have the calamitic molecular form, are polymorphic liquid crystals, display smectic C (SmC), smectic A (SmA) and nematic (N) mesophases, exhibit the thermotropic phase transitions and are thermal stable and stable to moisture. The structural formula of these materials is given in Fig. 1. As seen in this figure, molecules of **LC1** and **LC2** have axial symmetry.

The purity of **LC1** and **LC2** was estimated to be 99.70% by the liquid chromatography [39].

The samples used in this study were the sandwich-cells with fixed thickness. The reference surfaces of the sandwich-cells were optical glass slides. The spacer was placed between glass surfaces and fixed the thickness of liquid crystalline layer. The thicknesses of liquid crystalline layer have been examines by the POM technique and the digital micrometer with an accuracy as ±0.1 μm. The thicknesses of the liquid crystalline layer in the sandwich-cells were fixed as 20 μm, 70 μm, 120 μm, 170 μm and 240 μm. **LC1** and **LC2** have been filled into the sandwich-cells by the capillary forces at the isotropic liquid state.

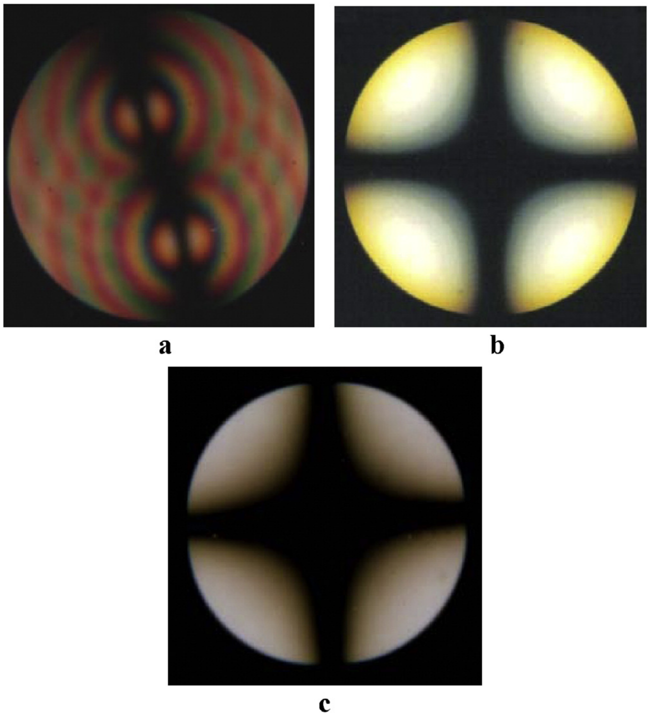

Fig. 3. Conoscopic images of aligned mesophases in **LC1** and **LC2**. a — SmC mesophase; b — SmA mesophase; c — N mesophase.

3. Results and discussion

In **LC1** and **LC2** the sequence of the phase transitions is as following: *solid crystal* (Cr) → SmC *mesophase* → SmA *mesophase* → N *mesophase* → *isotropic liquid* (I). Investigations showed that in regions of the Cr–SmC, SmC–SmA, SmA–N and N–I phase transitions are not sharp boundaries. This fact indicates that for these transitions the heterophase regions take place. Schematic presentation of the phase transition regions in **LC1** and **LC2** is given in Fig. 2.

Investigations showed also that aligned textures of **LC1** and **LC2** display the conoscopic images, which are presented in Fig. 3. The conoscopic image in Fig. 3a consists of the isogyres, isochromates and two melatopes; the conoscopic images in Fig. 3b and c consist of the isogyres and one apiece melatope. Melatope on the conoscopic image indicates on the place of exist of the optical axis from the sample. As is known, image in Fig. 3a is typical for the biaxial solid crystals and liquid crystals [36,37,40,41]. This image corresponds to SmC mesophase in **LC1** and **LC2**. Images in Fig. 3b and c are typical for the uniaxial solid crystals and liquid crystals [36,37,40,41]. As seen from comparison of Fig. 3b and c, the conoscopic image in Fig. 3b corresponds to more uniform alignment than that in Fig. 3c. This peculiarity is typical for SmA and N mesophases in liquid crystals exhibiting multiple phase transitions

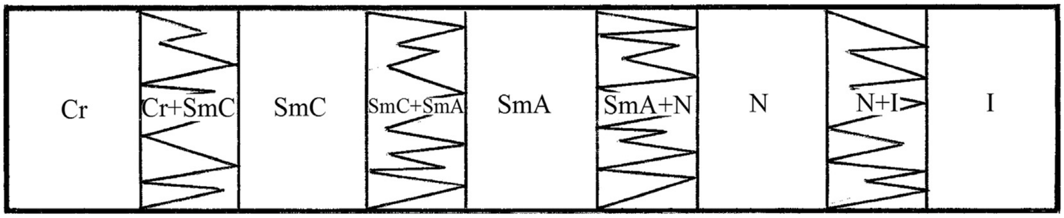

Fig. 2. Schematic representation of the phase transition regions in **LC1** and **LC2**.