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Thermotropic and Thermo-optical Properties of Nematic Mesophase at Direct and Reverse Phase Transitions

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Abstract Comparative investigations of the thermo-optical, thermotropic, and thermo-morphologic properties of aligned and non-aligned textures in the nematic mesophase over a large temperature interval and in regions of direct and reverse phase transitions between the nematic mesophase and the isotropic liquid have been carried out. The character of the optical transmission and adsorption coefficient has been compared with that of the texture transformations. Nonlinearity of the thermo-optical and thermotropic behavior at the *nematic mesophase–isotropic liquid* and *isotropic liquid–nematic mesophase* phase transitions has been observed. Differences in the temperatures of phase transitions for the aligned and non-aligned textures of the nematic liquid crystals have been found.

Keywords Heterophase region · Nematic liquid crystal · Optical transmission · Phase transition · Thermo-optical properties

1 Introduction

Liquid crystals are remarkable materials because of their potential application in various thermo-optical, electro-optical, and magneto-optical devices. These materials have a large spectrum of various optical properties. Therefore, investigations of the optical properties of these materials are important topics from both fundamental and application points of view [1–4].

Investigations connected with the thermal behavior of physical properties, and especially with the optical properties of liquid crystalline materials, have attracted the

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attention of scientists. These materials are attractive for use as reversible elements in recording thermo-optical systems for permanent heating ↔ cooling processes [5–8]. Therefore, the investigation of the thermotropic and thermo-optical properties of liquid crystalline materials for thermal dynamic processes is an important topic from an application point of view. However, in most of the known investigations, the behavior of the optical parameters of liquid crystals has been studied only for the heating process. Additionally, the correlation between the optical behavior in oriented and non-oriented textures of liquid crystals, over a large temperature interval, is insufficiently investigated.

In this work comparative investigations of the thermo-morphologic, thermotropic, and thermo-optical properties in homeotropic aligned and non-aligned textures of nematic liquid crystals over a large temperature interval and in regions of the direct *nematic–isotropic liquid* (N–I) and reverse *isotropic liquid–nematic* (I–N) phase transitions have been carried out.

2 Materials and Methods

In this work *n*-(4-methoxybenzylidene)-4′-*n*-butylaniline (MBBA), the binary mixture of *n*-(4-methoxybenzylidene)-4′-*n*-butylaniline with *n*-(4-ethoxybenzylidene)-4′-*n*-butylaniline (MBBA + EBBA), and 4-cyano-4′-*n*-pentylbiphenyl (5CB) have been used as the investigated subjects. These liquid crystals are enantiotropic nematogens and have a nematic mesophase within a sufficiently large temperature interval. The samples used in this research were sandwich cells as plane capillaries. The thickness of the liquid crystal placed between the reference surfaces of the sandwich cell was determined as 20 μm. The liquid crystals were filled into the sandwich cells at room temperature.

In this work non-aligned and aligned textures of the nematic mesophase have been studied. Non-aligned textures have been obtained spontaneously in the sandwich cells with non-treated surfaces. Homeotropic aligned textures of the nematic mesophase have been obtained in sandwich cells with surfaces treated by a special orienting system. This system has been prepared as a homogeneous mixture of *n*-hexadecyl-*n*,*n*,*n*-trimethyl-ammonium bromide (CTAB), and bidistilled and deionized water with 0.10 mass% + 99.90 mass% composition. CTAB was obtained from AppliChem and had a high degree of purity.

The studies of the thermo-morphological properties of MBBA, MBBA + EBBA, and 5CB were carried out by means of a polarizing optical microscopy (POM) technique. Our set-up consisted of a trinoculer polarizing microscope, microphotographic system, optical filters, and λ-plates from Olympic Optical Co. and also an original heater-thermostat, differential Cu–Co thermocouples, a multimeter, a power supply, and a digital temperature controller. Investigations of the thermotropic properties and peculiarities of the biphasic regions of the phase transitions between the nematic mesophase and the isotropic liquid have been carried out by a capillary temperature wedge (CTW) device. The CTW device consists of a working element as the lengthy sandwich cell, a temperature control system, a heating and cooling system, and an observation and recording system [9,10]. This device allows one to determine the linear widths and to calculate the temperature widths of the biphasic regions of phase transitions with uncertainties of not less than 2×10^{-3} mm and 10^{-3} K, respectively [10,11].

The investigations of the temperature dependences of the optical transmission (OT) of the nematic mesophase were carried out using a special thermo-optical setup (TOS). The TOS consisted of a He–Ne laser light source, special heater-thermostat, digital temperature control system, differential Cu–Co thermocouples, polarizer, analyzer, the relative transmission object, power supply, multimeters, photodiode, video camera, and computer. The heating and cooling rate of the sandwich cell during the optical measurements was $0.7\,\text{K} \cdot \text{min}^{-1}$. The optical transmission values and corresponding temperatures were recorded by the video camera and transferred to the computer.

3 Results and Discussion

The aligned textures of MBBA, MBBA + EBBA, and 5CB were characterized by a high degree of homogeneity and exhibited the conoscopic picture with crossed isogyres by conoscopic observations (Fig. 1a). This picture characterizes the homeotropic state of optically uniaxial crystalline systems. The non-aligned samples of MBBA and MBBA + EBBA exhibit specific nematic textures. These textures consist of the schlieren and thread formations, disclinations, singularities, and inversion walls (Fig. 1b). The aligned and non-aligned textures of the liquid crystals under investigation were stable, reproducible, and appeared once again by the heating–cooling processes.

Investigations showed that the temperature dependences of the OT have a non-linear character and exhibit different behaviors for the aligned and non-aligned textures of MBBA, MBBA + EBBA, and 5CB for the nematic mesophase interval. As an example, the dependences of the OT versus temperature for the aligned and non-aligned textures of MBBA, MBBA + EBBA, and 5CB are given in Figs. 2, 3, and 4. As is seen in these figures, with an increase of temperature for the aligned texture, the OT remains constant, but for the non-aligned texture, a continuous increase of the OT takes place in the nematic mesophase interval. A further increase in temperature leads to a definite temperature region where abrupt changes of the OT for both

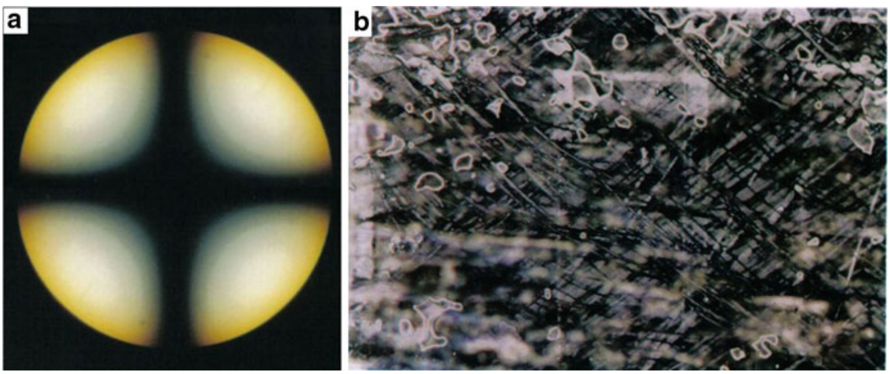

Fig. 1 Conoscopic picture of (a) aligned and (b) complicated texture of non-aligned sample

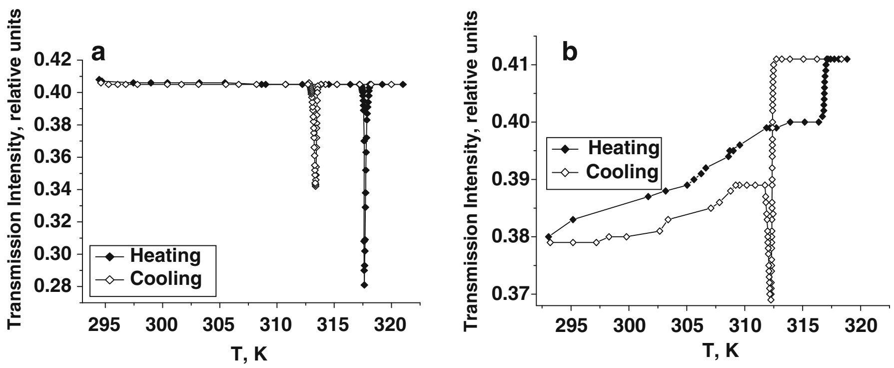

Fig. 2 Temperature dependences of the OT for (a) aligned and (b) non-aligned textures of MBBA [12]. These dependences were obtained with parallel polarizer and analyzer

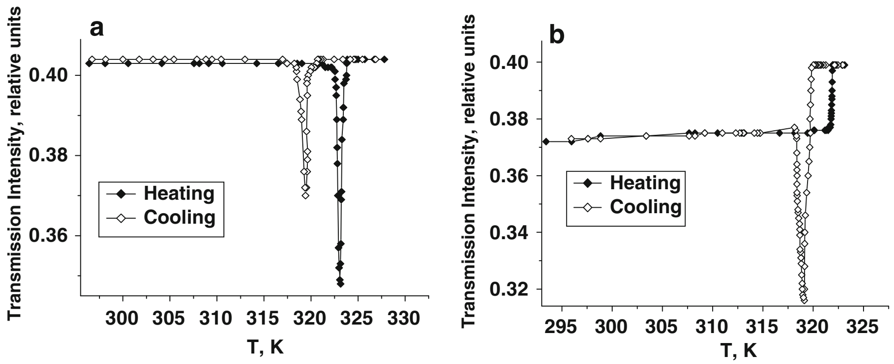

Fig. 3 Temperature dependences of the OT for (a) aligned and (b) non-aligned textures of MBBA + EBBA [12]. These dependences were obtained with parallel polarizer and analyzer

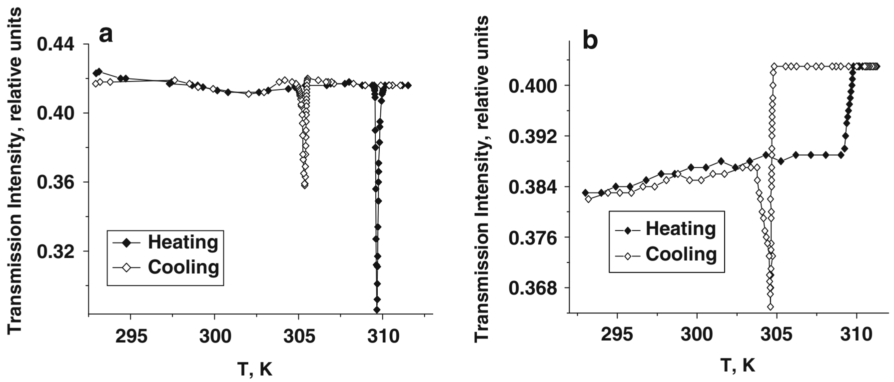

Fig. 4 Temperature dependences of the OT for (a) aligned [13] and (b) non-aligned textures of 5CB. These dependences were obtained with parallel polarizer and analyzer

aligned and non-aligned textures of MBBA, MBBA + EBBA, and 5CB take place. Then, further heating of the samples did not lead to changes of the OT for both the aligned and non-aligned textures. With a decrease in temperature, the reverse character of the temperature dependences of the OT has been observed for these textures.

The thermo-morphologic investigations showed that such a character of the OT for the aligned and non-aligned textures of MBBA, MBBA + EBBA, and 5CB is connected to the character of the texture transformations in these liquid crystals. Namely, on heating the sample with the aligned texture in the nematic mesophase temperature interval, no texture changes have been observed. However, on heating the sample with the non-aligned texture, smooth and continuous texture transformations have been observed for this interval. These investigations also showed that the abrupt changes of the OT for both aligned and non-aligned textures of MBBA, MBBA + EBBA, and 5CB take place in the heterophase region of the direct N–I phase transition by heating and in the heterophase region of the reverse I–N phase transition by cooling of the samples (Table 1). As is known, in the heterophase region with the low T^* and the high T^{**} temperature limits, a simultaneous coexistence of the low-temperature phase, i.e., the nematic mesophase, and the high-temperature phase, i.e., the isotropic liquid, takes place [14–19]. At temperatures higher than T^{**}, MBBA, MBBA + EBBA, and 5CB were in the isotropic liquid state. This corresponds to the final stage of the temperature dependences of the OT during heating and the first stage of these dependences during cooling of the samples (Figs. 2, 3, and 4). We would like to note that the OT intensity for MBBA, MBBA + EBBA, and 5CB in the isotropic liquid state was practically the same as that for the aligned texture. This is connected to the fact that the homeotropic oriented texture is optically isotropic for light rays which are orthogonal to the reference surfaces of the sandwich cell.

In this work we are also interested in the temperature dependences of the adsorption coefficient for the aligned and non-aligned textures. The intensity of the incident I_0 and transmitted I light is connected to the thickness of the liquid crystalline layer d and the adsorption coefficient α as

$$I = I_0 \exp(-\alpha d) \tag{1}$$

Table 1 Features of thermotropic properties for aligned and non-aligned textures of 5CB, MBBA, and MBBA + EBBA

Texture type	Liquid crystal type	Temperatures of the phase transitions (K)		Widths of heterophase regions (K)	
		N–I	I–N	N–I	I–N
Homeotropic aligned texture	5CB	309.66	305.36	0.69	1.38
	MBBA	317.21	313.81	0.88	0.98
	MBBA + EBBA	322.00	320.78	1.30	1.56
Non-aligned texture	5CB	309.25	304.77	0.55	1.01
	MBBA	316.63	312.35	0.52	0.96
	MBBA + EBBA	321.07	319.11	0.67	1.03

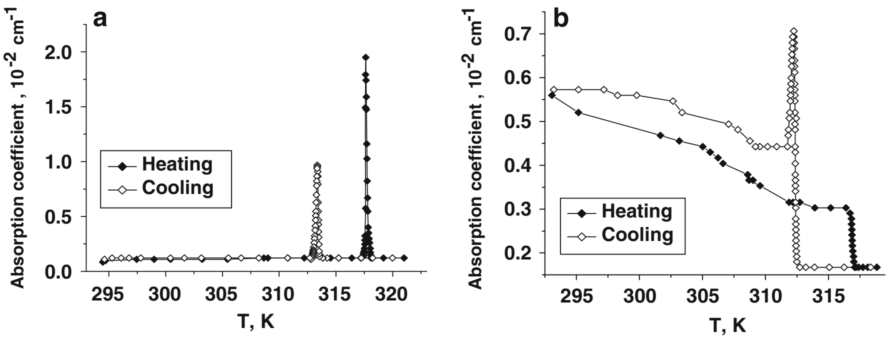

Fig. 5 Temperature dependences of the adsorption coefficient for (a) aligned and (b) non-aligned textures of MBBA

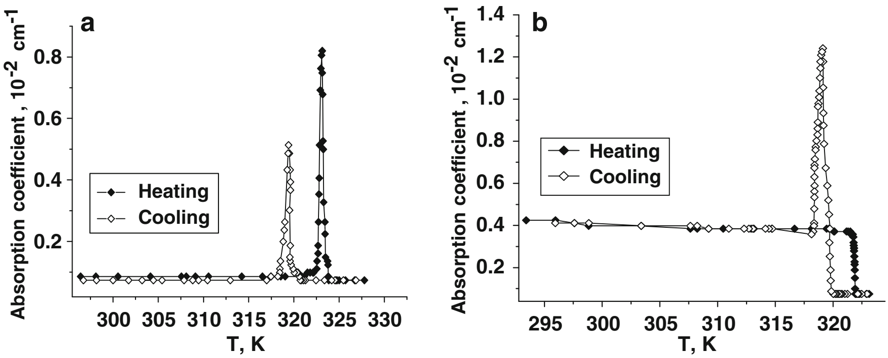

Fig. 6 Temperature dependences of the adsorption coefficient for (a) aligned and (b) non-aligned textures of MBBA + EBBA

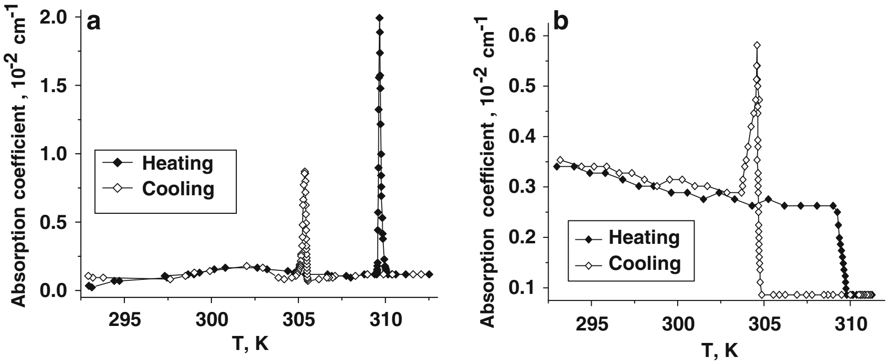

Fig. 7 Temperature dependences of the adsorption coefficient for (a) aligned and (b) non-aligned [13] textures of 5CB

Using Eq. 1, the temperature dependences of α have been calculated for MBBA, MBBA + EBBA, and 5CB. In Figs. 5, 6, and 7, the dependences of α versus temperature for MBBA, MBBA + EBBA, and 5CB are presented. As seen in Figs. 5a, 6a, and 7a, the values of α are minimal and remain constant in the nematic mesophase interval for the aligned texture. However, these values gradually change in the nematic mesophase interval for the non-aligned texture (Figs. 5b, 6b, and 7b). In the heterophase regions of the direct and reverse phase transitions, a non-linear abrupt change in α takes place for both aligned and non-aligned textures. Such a character of the temperature dependences of α corresponds to the character of the temperature dependences of the OT and the thermo-morphologic properties.

Investigations showed that the temperatures of the direct N–I and reverse I–N phase transitions and the widths of the heterophase regions of these transitions for the homeotropic aligned texture are different from the corresponding temperatures and widths of the heterophase regions for the non-aligned texture. Namely, the temperatures of the phase transitions for aligned textures are higher than those for the non-aligned texture and the temperature and linear widths of the heterophase regions for the aligned textures are larger than those for the non-aligned texture (Table 1). These differences are connected with those in the anchoring energy between liquid crystalline molecules and the reference surfaces of the sandwich cell for the homeotropic aligned and non-aligned textures [20–22]. Namely, the aligned textures, as noted above, have been obtained in the sandwich cells with the reference surfaces that were treated by the orienting system. However, the non-aligned textures have been formed spontaneously in sandwich cells with non-treated surfaces. In the case of the aligned texture, the anchoring energy between the liquid crystalline molecules and the surfaces of the sandwich cells is higher than that for the non-aligned texture. Therefore, it is clear that the greater anchoring energy leads to an increase of the thermal energy, which is necessary for carrying out of the phase transition between the nematic mesophase and the isotropic liquid [8,15,22,23]. Accordingly, an increase of the energy of interaction between liquid crystalline molecules and the reference surfaces leads to an increase of phase transition temperatures between the nematic mesophase and isotropic liquid and to an enlargement of the heterophase regions of these transitions.

4 Summary

The results obtained in this study may be briefly summarized as follows:

– The non-linear temperature behavior of the OT and adsorption coefficient and the abrupt changes of these parameters at the N–I and I–N phase transitions have been observed for the aligned and non-aligned textures of the nematic mesophase in MBBA, MBBA + EBBA, and 5CB. Full conformity between the thermo-morphologic, thermotropic, and thermo-optical properties has been found for both the aligned and non-aligned textures.
– Thermic hysteresis takes place for the N–I and I–N phase transitions for the aligned and non-aligned textures of the nematic mesophase in MBBA, MBBA + EBBA, and 5CB. This hysteresis is connected with the overheating and overcooling of liquid crystals. It was theoretically predicted in [15–19,24–26], is typical for first-order phase transitions between the liquid crystalline mesophase and the isotropic liquid, and was experimentally observed by various scientists for different liquid crystals [12,27–32].

– The temperatures of both the direct N–I and the reverse I–N phase transitions for the aligned homeotropic textures are higher than those for the non-aligned textures of the nematic mesophase in MBBA, MBBA + EBBA, and 5CB. The temperature widths of the heterophase regions of both the direct and the reverse phase transitions are larger than those for the non-aligned textures of the nematic mesophase in MBBA, MBBA + EBBA, and 5CB. These differences in the temperatures of the phase transitions and in the widths of the heterophase regions for the aligned and non-aligned textures are connected to those in the anchoring energy between the liquid crystalline molecules and the reference surfaces of the sandwich cells.
– The non-linear temperature behavior of the optical parameters (OT and adsorption coefficient) and the differences in the temperatures of the phase transitions between the nematic mesophase and isotropic liquid for the aligned and non-aligned textures are necessary to take into consideration by elaboration of liquid crystalline devices, which are used in various temperature regimes and for heating–cooling processes.

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