JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 18, No. 11-12, November - December 2016, p. 928 - 937

Refractive and birefringent properties and order parameter of nematic liquid crystal at the direct and reverse nematic ↔ isotropic liquid phase transition

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Temperature dependences of the refractive indices, birefringence and molecular polarizability in large temperature interval and especially in the region of the direct *nematic mesophase – isotropic liquid* (for the heating process) and the reverse *isotropic liquid – nematic mesophase* (for the cooling process) phase transitions have been studied. Thermotropic monomorphic liquid crystalline material with enantiotropic nematic mesophase has been used. Temperature behavior of the order parameter has been determined. Peculiarities of the biphasic regions of the direct *crystal – nematic mesophase* and *nematic mesophase – isotropic liquid* and reverse *isotropic liquid – nematic mesophase* and *nematic mesophase - crystal* phase transitions have been investigated.

(Received September 15, 2015; accepted November 25, 2016)

Keywords: Liquid crystal, Refractive indices, Optical birefringence, Molecular polarizability, Order parameter, Phase transitions.

1. Introduction

Liquid crystals have both partially ordering properties of solid crystalline materials, and rheological properties of fluids. Therefore, liquid crystals exhibit unusual structural and physical properties. Important peculiarity of liquid crystals is availability of various physically anisotropic mesophases. Some of these mesophases are optically uniaxial and others are optically biaxial. Additionally, some of mesophases can be optically positive and others can be optically negative. Because of reach optical (thermo-optical, magneto-optical, electro-optical and acousto-optical) properties these materials have large possibilities of application in optoelectronic and microelectronic systems, in devices of recording and reading of optical information, thermography etc.]1-7].

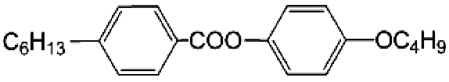
The optical properties of liquid crystals have aroused interest in past one-two decades [8-15]. Because of liquid crystals can use at different thermal regimes, within various temperature intervals and in different climatic conditions, information about temperature dependences of the optical properties and thermal behavior of optical parameters of these materials is very important. Such investigations have been carried out by various scientists for number of liquid crystalline materials in [8-21]. In these works, temperature behavior of the refractive index n, refractive indices of ordinary n_o and extraordinary n_e rays, and birefrincence Δn have been investigated. Using the data, connecting with these parameters, the principal polarizabilities α_o and α_e, effective geometry parameter α_{eg}, average polarizability α_{ave} and order parameter Q were determined. But in all of these works investigations of the optical properties and temperature behavior of the optical parameters have been carried out only for the heating processes and only for the direct *liquid crystalline mesophase – isotropic liquid* phase transitions. Unfortunately, information about temperature behavior of the above mentioned optical and polarizability parameters for the cooling processes and for the reverse isotropic liquid – liquid crystalline mesophase is absent in scientific literature. But liquid crystals can be used in the thermography and in the thermo-optical, electro-optical, magneto-optical and acousto-optical devices liquid crystalline materials as the reversible elements for the *heating – cooling – heating* processes and also at both the direct and reverse phase transitions. Therefore, information about temperature behavior of the optical parameters and polarizability for such processes is sufficiently important from fundamental and application points of view.

In the present work we report temperature behavior of the refractive and birefringence properties of thermotropic monomorphic liquid crystalline material with enantiotropic nematic mesophase for the *heating – cooling* processes and for the direct *nematic mesophase – isotropic liquid* (N–I) and reverse *isotropic liquid – nematic mesophase* (I–N) phase transitions. The molecular polarizability parameters and order parameter have been estimated. Besides, the thermo-morphologic properties of above mentioned liquid crystalline material at the direct (N–I) and reverse (I–N) phase transitions have been investigated in this work.

2. Experimental Details and Theoretical Background

2.1. Material

In this work, 4-buthoxyphenyl 4’-hexylbenzoate (BPHB) liquid crystal was object of our investigations. The structural formula of this material is given in Scheme 1.This material is thermotropic monomorphic nematogen, which has uniaxial molecular symmetry. BPHB displays enantiotropic nematic mesophase in large temperature interval, exhibits the thermotropic phase transitions, and is thermal stable and stable to moisture. In BPHB the *solid crystal – nematic mesophase – isotropic liquid – nematic mesophase – solid crystal* sequence of the phase transitions takes place.



Scheme 1. The structural formula of 4-buthoxyphenyl 4’-hexylbenzoate.

2.2. Methods

The thermotropic and thermo-morphologic properties, and temperatures of phase transitions in BPHB were studied using the polarizing optical microscopy (POM) technique. As is well known, the POM technique is sufficiently informative method for study of the mesomorphic, morphologic and thermotropic properties of liquid crystals, and is also very convenient for identification of liquid crystalline mesophases [10,22-26].

The study of the thermo-morphologic peculiarities of the biphasic regions of the phase transitions in BPHB has been carried out by the capillary temperature wedge (CTW) device. The CTW device was presented in [27-29]. This device provides the observation of all of the thermic states of liquid crystalline materials in the real scale of time. Besides, by the CTW device is possible the calculation of the phase transition temperatures and the temperature widths of the biphasic regions of these transitions with an accuracy not less than 10^{-3} K [28-30]. Temperature gradient of the temperature wedge was kept as $9.33 \cdot 10^{-4}$ K·μm^{-1}.

In this work, the temperature dependences of the refractive indexes n, n_e and n_o for BPHB have been measured by using the polithermic refractometry setup (PR). An accuracy of the refractive indices measurements by ATAGO Abbe’s refractometer with digital temperature control system was as 0,1%. Temperature of liquid crystal under investigation was controlled by the digital temperature controller with accuracy as ± 0.1 K.

For measurements of the refractive indices n_e and n_o, properties of the optical polarizers, and peculiarities of the uniform (homeotropic and planar) alignment of liquid crystal under investigation have been used. The planar and homeotropic alignments of nematic mesophase in BPHB have been obtained by treatment of the prisms of refractometer. For obtainment of the planar alignment (yielding n_o), a film of polyvinylalcohol has been deposited on the prisms and then was subsequently rubbed with velvet tissue.For obtainment of the homeotropic alignment (yielding n_e), the mixture of 1.0% lecithin in ethyl alcohol has been deposited on the prisms. Homogeneity of the homeotropic and planar alignment was controlled by study of the optical properties of aligned textures via POM technique. **,**

2.3. Theoretical Approach

Liquid crystals are partially ordered media, which exhibit optically anisotropic properties. The refractive properties of these materials are characterized by the mean refractive index n, and the refractive indices n_o and n_e for ordinary (the ordinary refractive index) and extraordinary (the extraordinary refractive index) rays, respectively. The mean refractive index n characterizes the optical isotropic properties of media; the refractive indices n_o and n_e and the birefringence Δn characterize the optical anisotropic properties of media. These optical parameters are mutually connected.

For the optically positive liquid crystals

$$\Delta n = n_e - n_o > 0 \tag{1}$$

takes place. The n, n_o, n_e and Δn are connected with one another as

$$n_o = n - \frac{1}{3}\Delta n \tag{2a}$$

$$n_e = n + \frac{2}{3}\Delta n \tag{2b}$$

Additionally, connection between n, n_o and n_e can be presented by

$$n = \frac{n_e^2 + 2n_o^2}{3} \tag{3}$$

As is known, behavior of the Δn, as behavior of other tensorial parameters, corresponds to behavior of the order parameter [9-12,31-35]. Therefore, a behavior of the order parameter in large number of liquid crystalline materials has been reported, using the Δn data [9-12,31-36]. Besides, as is pointed in [37], the anisotropy of any physical quantity can be a measure of the orientational order parameter in liquid crystalline mesophase. This parameter can be defined by the birefringence as [9,17,36,38-40]

$$Q(T) = \frac{\Delta n(T)}{\Delta n_0} \tag{4}$$

Here the Δn_0 is the birefringence of liquid crystalline material in the crystalline state (at T = 0). At this temperature $Q = 1$. Because of the Δn_0 is constant value for each liquid crystalline material, $Q \sim \Delta n$ correlation takes place.

On the other hand, the order parameter Q can be determined by means of Haller's approximation [41,42]. In accordance with this approximation the Q can be presented as

$$Q(T) = \left(1 - \frac{T}{T_C}\right)^{\beta} \tag{5}$$

Here T_C is the clearing temperature of liquid crystalline material and β is characteristic parameter of this material. In accordance with Eq. (4) and Eq. (5)

$$\Delta n(T) = \Delta n_0 \left(1 - \frac{T}{T_C}\right)^{\beta} \tag{6}$$

can be written. The Δn_0 value can be obtained by fitting the experimental data to a crystalline state of liquid crystal for $T = 0$. Accordingly, the degree parameter β of this material can be estimated by

$$\log \frac{\Delta n(T)}{\Delta n_0} = \beta \cdot \log\left(\frac{T_C - T}{T_C}\right) \tag{7}$$

Using the refractive indices data, is possible to determine some other physical parameters of liquid crystalline material such as the principal polarizabilities α_o and α_e, effective geometry parameter α_{eg}, average polarizability α_{ave} and polarizability anisotropy $\Delta\alpha$. In [8,12,29,32,33,43] temperature dependences of the refractive indices for various liquid crystals have been investigated and the α_o, α_e, α_{eg}, α_{ave} and $\Delta\alpha$ have been estimated, using both the isotropic internal field model (Vuks approach) and the anisotropic internal field model (Neugebauer's approach). In these works sufficiently good agreement between above mentioned values, estimated from these two independent methods, has been found.

In model, which is presented in [44,45], is accepted that the local field in crystals is the same in all directions, i.e. that this field is isotropic. In this case (so-called Vuks relations), the principal polarizabilities α_e and α_o can be estimated using the n_e and n_o refractive indices by [22,44-46]

$$\alpha_e = \frac{3}{4\pi N} \frac{n_e^2 - 1}{n^2 + 2} \tag{8}$$

$$\alpha_o = \frac{3}{4\pi N} \frac{n_o^2 - 1}{n^2 + 2} \tag{9}$$

Here N is number of liquid crystalline molecules per cm^3. From Eqs. (8) and (9), ratio between α_o and α_e can be determined by the n_o and n_e as

$$\frac{\alpha_0}{\alpha_e} = \frac{n_0^2 - 1}{n_e^2 - 1} \tag{10}$$

Using the α_o and α_e values, the average polarizability α_{ave} and the polarizability anisotropy $\Delta\alpha$ for the optically positive liquid crystal can be determined by

$$\alpha_{ave}^2 = \frac{\alpha_e^2 + 2\alpha_0^2}{3} \tag{11}$$

$$\Delta\alpha = \alpha_e - \alpha_o \tag{12}$$

accordingly. Additionally, using the n_o and n_e values, the effective geometry parameter α_{eg} can be determined for liquid crystals with the positive optical anisotropy by [8,14,15]

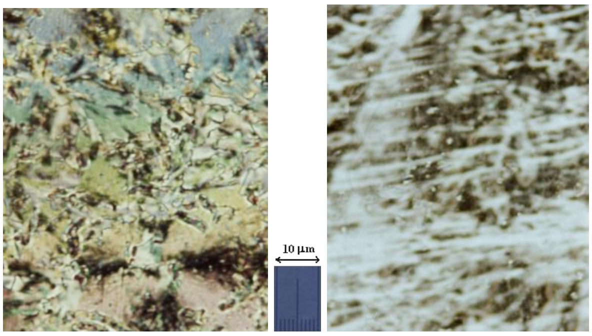
$$\alpha_{eg} = \frac{n_0}{n_e} \tag{13}$$

Thus, on the basis of the n, n_e, n_o and Δn can be obtain information about behavior of the order parameter Q, degree parameter β, polarizabilities α_0 and α_e, effective geometry parameter α_{eg}, average polarizability α_{ave} and polarizability anisotropy $\Delta\alpha$ in the thermal region of liquid crystalline mesophase and in region of the phase transition between various liquid crystalline mesophases and between liquid crystalline mesophase and isotropic liquid.

3. Results and Discussion

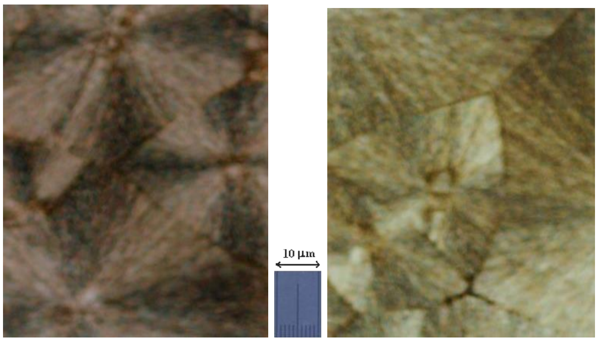
Nematic mesophase in BPHB displays by textures, which are presented in Fig. 1. Such type of textures is specific for thermotropic nematic mesophase [23,24,47]. As seen in Fig. 1, textures of this mesophase consist of the thread-like formations, inversion walls, singular points and separate regions with definite alignment. Such texture is typical for mesophase with the $D_{\infty h}$ symmetry.

Crystalline phase in BPHB displays by textures, which are presented in Fig. 2. As seen in this figures, these textures consist of so-colled "spherulite" formations. Such formations represent three dimensionally spatial figures, which consist radially arranged elongated color formations with sharp grain boundaries. The spherulite formations form as a germ growing from nematic or smectic A mesophases. This behavior can be observed for various types of liquid crystalline materials. By heating of the samples, spherulite formations melted to nematic mesophase (Fig. 3a); by cooling of the samples, these formations arose again in crystalline state (Fig. 3b).



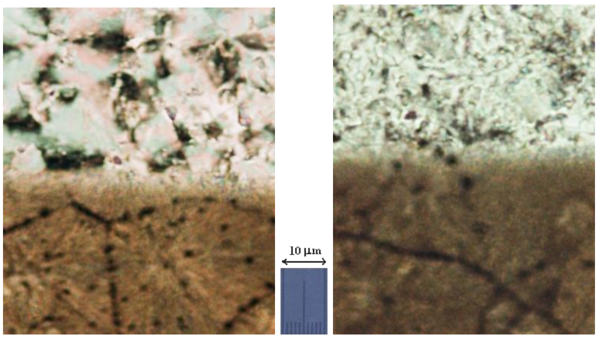
a b

Fig. 1. Typical textures of nematic mesophase in BPHB. Crossed polarizers; Magnification x100; – Temperature 340.0 K; b – temperature 343.3 K.



a *b*

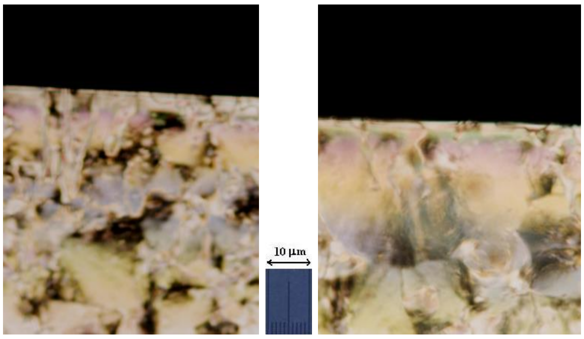
Fig. 2. Typical textures of crystalline mesophase with the spherulite formations.



a *b*

Fig. 3. Biphasic regions of the Cr–N (a) and N–Cr (b) phase transitions. Crossed polarizers; Magnification x100.

Investigations by the CTW device showed that the direct and reverse phase transitions between nematic mesophase and isotropic liquid are characterized by interesting texture transformations (Fig. 4). As is seen in this figure, the clear morphologic transitions between nematic mesophase and isotropic liquid take place. These morphologic transitions are characterized by narrow temperature width of the biphasic region. As seen in Fig. 4, texture of nematic mesophase in BPHB is stable up to the phase transition to isotropic liquid state and texture transformations are observed in sufficiently narrow temperature interval. Besides, as seen in Fig. 4, in the N–I and I–N phase transition regions alternation of the interference colors takes place. Availability of these colors is connected with temperature modulation of the refractive index and with appearance of layered structure in narrow temperature region.



a ***b***

Fig. 4. Biphasic regions of the N–I (a) and I–N (b) phase transitions. Crossed polarizers; Magnification x100.

Temperatures of the direct *crystal – nematic mesophase* (Cr–N) and *nematic mesophase – isotropic liquid* (N–I), and reverse *isotropic liquid – nematic mesophase* (I–N) and *nematic mesophase – solid crystal* (N–Cr) phase transitions in BPHB have been examined by observing of texture transformations, using the POM method. Results of this examination are tabulated in Table 1. As seen in this table, for the reverse I–N and N–Cr phase transitions the shift of transition temperatures to lower temperature takes place. This result indicates on the thermal hysteresis between the direct and reverse phase transitions in nematic mesophase of BPHB.

Table 1. Temperatures of phase transitions in nematic mesophase of BPHB.

Phase transition temperatures, K			
Cr–N	N–I	I–N	N–Cr
332.1	350.1	353.8	328.6

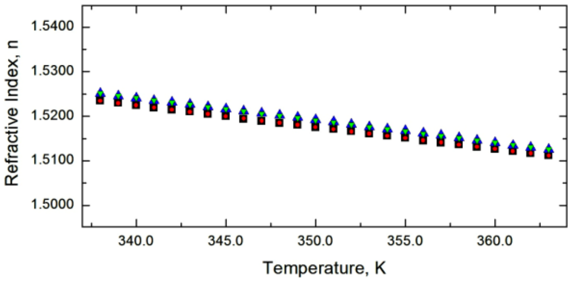


Fig. 5. Temperature dependences of the refractive index n. ▲ – experimental values for heating process); ▼ – fitting values for heating process; ■ – experimental values for cooling process; ● – fitting values for cooling process.

In this work temperature dependences of the *n* for the heating and cooling processes have been investigated (Fig. 5). As seen in Fig. 5, temperature dependences of the $n = n(T)$ exhibit the linear behavior for both the heating and cooling processes. These dependences can be described by the linear equation as $y = -5.00 \cdot 10^{-4} \cdot x + 1.69$ ($R = -5.00 \cdot 10^{-4} \cdot T + 1.69$). As seen in Fig. 5, the thermal hysteresis has not been observed for the $n = n(T)$ dependences. Besides, at the N–I and I–N phase transition regions any transformations of the *n* value are not take place for these dependences. This fact indicates that the optical isotropic properties of nematic mesophase in BPHB are stable in full nematic mesophase interval and at the direct and reverse phase transition between nematic mesophase and isotropic liquid.

Quite different behavior has been observed for the $n_o = n_0(T)$ and $n_e = n_e(T)$ dependences. As seen in Fig. 6, the refractive index n_e strongly depends on the temperature and decreases in nematic mesophase interval with an increase in temperature. The refractive index n_o shows weak temperature dependence in the mesophase region, but exhibits some increase near the clearing temperature. In the N–I phase transition region, a disappearance of the n_e and n_o refractive indices takes place. Such behavior of the n_e and n_o is connected with disappearance of the optical anisotropic properties of ordered structure and appearance of the optical isotropic properties of disordered structure at the clearing temperature. Then, in the isotropic liquid state the refractive index *n* slightly and linearly decreases with an increase in temperature, like various liquid crystalline materials for the N–I and *cholesteric mesophase – isotropic liquid* (Ch–I) phase transitions [12,21,31,39,48].

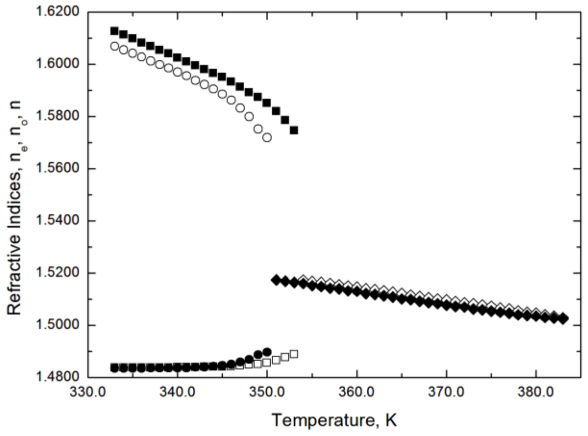


Fig. 6. Temperature dependences of the refractive indices. ■ – n_e *values for heating process;* □ – n_o *values for heating process;* ○ – n_e *values for cooling process;* ● – n_o *values for cooling process;* ◊ – n *values for heating process;* ♦ – n *values for cooling process.*

Temperature dependences of the n_e, n_o and *n* refractive indices for the cooling process from isotropic liquid state to nematic mesophase are also presented in Fig. 6. As seen in this figure, process transformation of the optical isotropic properties to the optical anisotropic properties and appearance of the n_e and n_o refractive indices are observed for the lower temperature than disappearance the n_e and n_o refractive indices and appearance of the mean refractive index *n*. I.e. for the $n_e = n_e(T)$, $n_o = n_o(T)$ and $n = n(T)$ dependences the thermal hysteresis is observed. Such hysteresis in the thermo-optical properties is connected with the thermal hysteresis of the thermo-morphologic properties of nematic mesophases in BPHB. The thermal hysteresis between the direct and reverse phase transition temperatures has been observed by various researchers for different physical parameters in large number of liquid crystals [18,47,49-62].

We would like to note that in this work the extrapolated average refractive index n_{ave} of isotropic liquid state into nematic mesophase has been determined. The results, which have been obtained by extrapolating, entirely coincide with results, which have been obtained by the refractometric method for non-aligned texture of nematic mesophase in BPHB (Fig. 6). I.e. the $n_{ave} = n$ equation has been obtained.

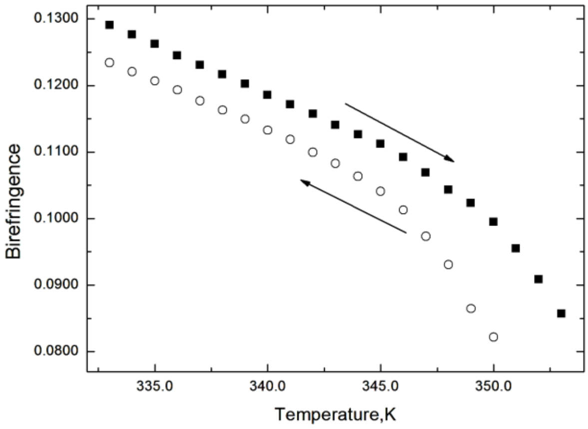


Fig. 7. Temperature dependences of the birefringence. ■ – Δn *values for heating process;* ○ – Δn *values for cooling process.*

The temperature dependences of the birefringence Δn provide obtainment more direct and fairly accurate dependences of the order parameter vs. temperature. Therefore, a behavior of the order parameter in large number of liquid crystalline materials has been reported, using the Δn data [8-10,12,17,32-36,63]. In our work the $\Delta n = \Delta n(T)$ dependences have been determined for the heating and cooling processes (Fig. 7). As is seen in Fig. 7, fluent decrease of the Δn with an increase of temperature in region of nematic mesophase in BPHB takes place. Such behavior of the Δn indicates on decreasing nematic molecular alignment in nematic mesophase. At the clearing point, when $n_e = n_0 = n$ takes place and, therefore the optical anisotropy of nematic mesophase disappears, the Δn value is zero. The situation with $\Delta n = 0$ in isotropic liquid state indicates that there is no pre-transitional effect in such state. For the cooling process, when temperature decreases, value of the Δn increases (Fig. 7). Such behavior of the birefringence testifies that nematic molecular alignment increases. The shift of the $\Delta n = \Delta n(T)$ dependences to the lower temperature for the cooling process is connected with the temperature shift of the reverse I–N phase transition temperatures.

In accordance with Eqs. (8) and (9), the α_e and α_o, and in accordance with Eq.11, the α_{ave} were determined for the heating and cooling processes. Results of such determination for nematic mesophase of BPHB are presented in Fig. 8. As seen in this figure, as the temperature increased, the α_e decreased and α_0 increased. A break in the $\alpha_e = \alpha_e(T)$ and $\alpha_0 = \alpha_0(T)$ dependences is observed at the N–I and I–N phase transitions. In the isotropic liquid state $\alpha_o = 0$ and $\alpha_e = 0$ takes place. This fact indicates on disappearance of the principal polarizabilities of liquid crystalline mesophase in the directions of the ordinary and extraordinary rays. As seen in Fig. 8, the α_{ave} parameter very slow changes with temperature. Such behavior of this parameter corresponds to temperature behavior of the optical isotropic parameter, i.e. behavior of the *n*.

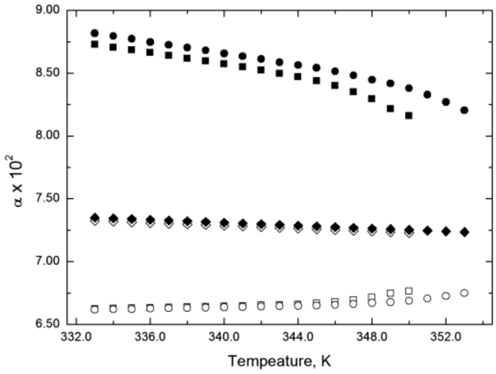


Fig. 8. Temperature dependences of the polarizabilities. ● – α_e values for heating process; ○ – α_o values for heating process; ■ – α_e values for cooling process; □ – α_o values for cooling process; ♦ – α_{ave} values for heating process; ◊ – α_{ave} values for cooling process.

In Fig. 9, temperature dependences of the α_{eg} parameter are presented. As is seen in this figure, is found that the α_{eg} fluently increases with an increase of temperature during the heating process. The value of the α_{eg} aspires to unity in isotropic liquid state. When the α_{eg} reaches unity, this means that there is not any orientational order in liquid crystalline material and that the value of the order parameter is therefore zero. Such behavior of the α_{eg} is connected with fact that differences between the n_e and n_o are decreased with an increase in temperature (Eq.13). In [64,65] is shown that the α_{eg} is connected with the propagation of light near the disclinations and other topological defects in liquid crystals, and also with the orientation of the director field. As is known, the topological disclinations and defects lead to a breach in the director field in liquid crystals. In [10,14,18,39,66] is shown that liquid crystals, which have higher values of the α_{eg}, exhibit lower deflection of the light. Therefore the α_{eg} is a measure of the degree of the light deflection.

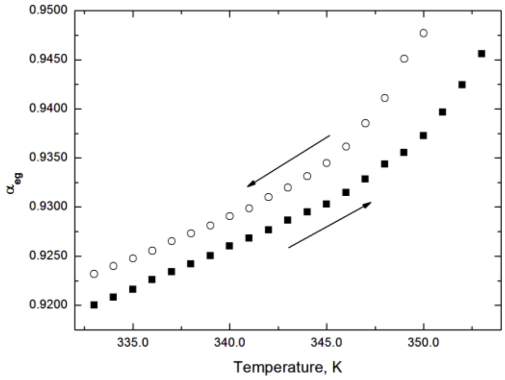


Fig. 9. Temperature dependences of the α_{eg}. ■ – values for heating process; ○ – values for cooling process.

Temperature behavior of the α_{eg} and the variation rate of the n_e and n_0 for the heating process was subject of investigation by various researches for different liquid crystalline materials in [8,11,20,21,67-69]. In our work temperature behavior of the α_{eg} parameter was also investigated for the cooling process (Fig. 9). During the cooling process, the α_{eg} parameter for nematic mesophase in BPHB exhibits opposite behavior, than that for the heating process. Namely, this parameter fluently decreases with a decrease of temperature from the I–N phase transition temperatures to nematic mesophase (Fig. 9). For examination of the α_{eg} behavior vs. the birefringence, the $\alpha_{eg} = \alpha_{eg}(\Delta n)$ dependences for the heating and cooling processes have been determined (Fig.

10). As is seen in Fig. 10, the α_{eg} parameter linearly decreases with increasing birefringence and linearly increases with decreasing birefringence. Such behavior of the α_{eg} indicates on an increase of the orientational order of nematic mesophase with a decrease of temperature and on a decrease of this order with an increase of temperature. We would like to emphasize, that the α_{eg} is connected with the order parameter as [66]

$$Q(T) = \frac{3n[1-\alpha_{eg}(T)]}{\Delta n_0[1+2\alpha_{eg}(T)]} \tag{14}$$

Taking into consideration Eqs. (7) and (17), can conclude that the calculation of the order parameter $Q(T)$ from the birefringence $\Delta n(T)$ data or from the effective geometry parameter $\alpha_{eg}(T)$ is identically equal to one another.

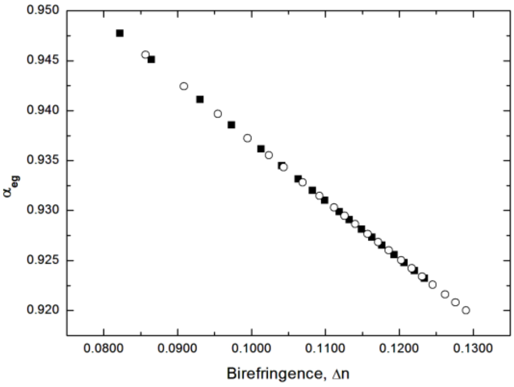


Fig. 10. The $\alpha_{eg} = \alpha_{eg}(\Delta n)$ dependences for the heating (○) and cooling (■) processes.

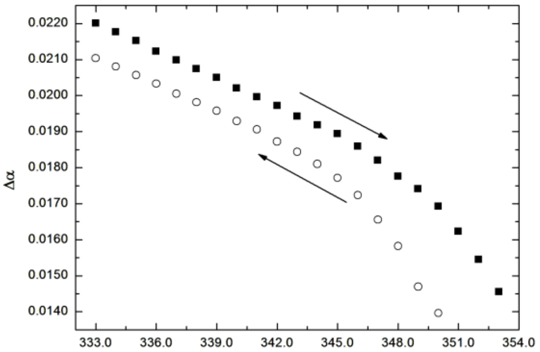


Fig. 11. Temperature dependences of the $\Delta\alpha$. ■ – values for heating process; ○ – values for cooling process.

In this work we also interested on temperature behavior of the polarizability anisotropy $\Delta\alpha$. The result is presented in Fig. 11. As seen in this figure, the $\Delta\alpha$ fluently decreased with an increase of temperature. By comparison Fig. 7 and Fig. 11, can see that character of the $\Delta\alpha = \Delta\alpha(T)$ dependences for the heating and cooling processes repeats character of the $\Delta n = \Delta n(T)$ dependences for these processes. Thus, can conclude that change in the optical anisotropy and the polarizability anisotropy values for nematic mesophase are correlated.

As is noted above, the birefringence Δn, as other tensorial parameters (e.g. the anisotropy of dielectric properties $\Delta\varepsilon$, anisotropy of diamagnetic properties $\Delta\chi$, anisotropy of viscosity $\Delta\gamma$ etc.), is considered as a measure of the order parameter in liquid crystalline mesophases The order parameter behaves in the same manner as the Δn (and accordingly as $\Delta\varepsilon$, $\Delta\chi$, $\Delta\gamma$ etc.) does. In Fig. 12, temperature dependences of the order parameter Q are presented. Behavior of the $Q = Q(T)$ in nematic mesophase for both the heating and cooling processes indicates on fluent change of the order of this mesophase by change of temperature. Similar behavior of the $Q(T)$ was observed for the heating process by various researchers for large number of nematic mesophase in various liquid crystals. Character of the $Q(T)$ changes by the cooling process is opposite such character by the heating process. But, as seen in Fig. 12, change of the order parameter value on 3.7% by the cooling process in compare with this value by the heating process takes place. As noted above, such differences in values of the *n*, Δn and *Q* by the heating and cooling processes are connected with distinction in character of structural transformation between *ordered structure* (nematic mesophase) → *disordered structure* (isotropic liquid) by the heating process and *disordered structure* (isotropic liquid) → *ordered structure* (nematic mesophase) by the cooling process. Furthermore, as seen in Figs. 7 and 12, character of the $\Delta n = \Delta n(T)$ and $Q = Q(\beta)$ dependences is typical for the first order phase transitions. Namely, for such transitions fluent decrease of the Δn and ΔQ with an increase of temperature, and jump of these parameters at the clearing point takes place.

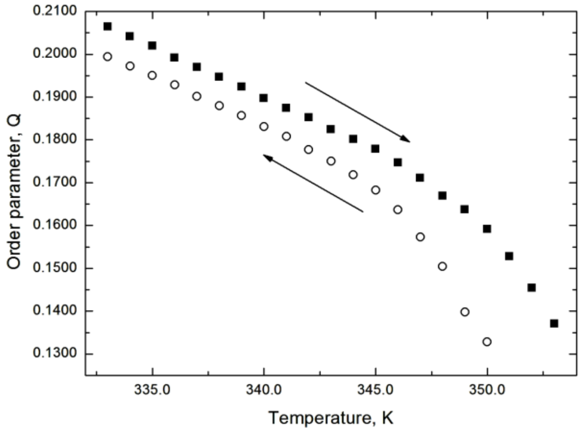


Fig. 12. Temperature dependences of the order parameter Q. ■ – $Q = Q(T)$ dependence for heating process; ○ – $Q = Q(T)$ dependence for cooling process.

As seen from Eqs. (5), (6) and (7), the degree of parameter β determines behavior of the order parameter. In Fig. 13, the $Q = Q(\beta)$ dependences are shown. As seen in this figure, nearly linear dependence of the parameter *β* vs. the order parameter *Q* is observed for nematic mesophase in BPHB for both the heating and cooling processes. Mutually $Q = Q(\beta)$ dependence was also presented in [69]. Taking into consideration Fig. 13 and the $Q = Q(\beta)$ dependence {Eqs. (5), (6) and (7)}, is interesting to see the temperature dependence of the *β*. In Fig. 14, temperature dependences of the parameter *β* are presented. The parameter *β* fluently decreases from 0.5500 to 0.3500 with an increase of temperature and increases from 0.5330 to 0.3360 with a decrease of temperature.

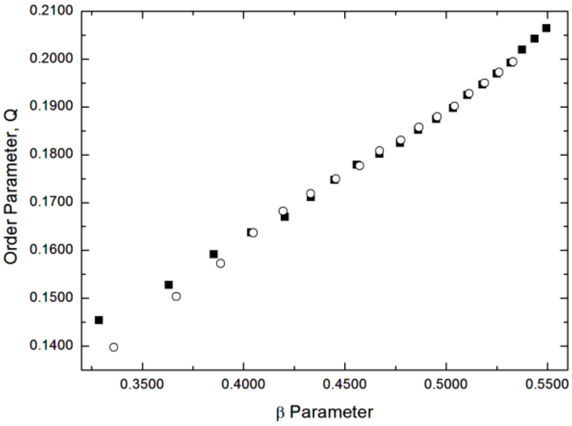


Fig. 13. The $Q = Q(\beta)$ *dependences for the heating (■) and cooling (○) processes.*

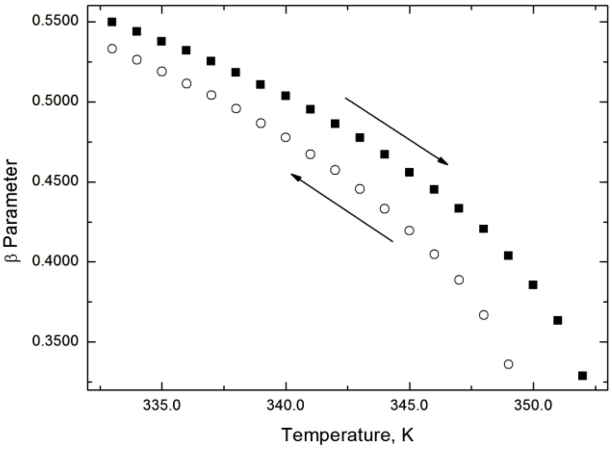


Fig. 14. Temperature dependences of the β parameter. ■ – values for heating process; ○ – values for cooling process.

We would like to emphasize that temperature dependent peculiarity of the parameter *β* was presented also in [13,33]. In these works is shown that with an increase of temperature, a decrease of the parameter β takes place for the heating process. In our work we have received that with an increase of temperature a decrease of the parameter *β* for the heating process and with a decrease of temperature an increase of the parameter *β* for the cooling process take place. Such behavior $\beta = \beta(T)$ corresponds to Eqs. (5), (6) and (7).

4. Summary

In this work the thermotropic and thermo-optical properties of nematic mesophase in 4-buthoxyphenyl 4'-hexylbenzoate (BPHB) liquid crystal have been investigated. Investigations have been carried out for the heating and cooling processes. As is showed in this work, in nematic mesophase of this liquid crystal the thermal hysteresis takes place. This hysteresis displays as differences between the direct and reverse phase transition temperatures and as the shift of the reverse I–N and N–Cr phase transitions to the lower temperatures (Table 1). This shift is as 3.7 K for the I–N and as 3.5 K for the N–Cr phase transitions. Investigations and determinations of the temperature dependences of the refractive index *n*, refractive indices of ordinary n_o and extraordinary n_e rays, birefringence Δn, principal polarizabilities α_o and α_e, effective geometry parameter α_{eg}, average polarizability α_{ave}, polarizability anisotropy $\Delta\alpha$, order parameter *Q* and degree parameter β showed also that the thermal hysteresis takes also place for these quantities. The thermal hysteresis is typical peculiarity for the first order phase transition between nematic mesophase and isotropic liquid. Such hysteresis for the first order phase transitions in liquid crystals was theoretically considered in [37,47,50-52,71,72] and was experimentally observed by various scientists for large number of liquid crystals in [18,47,49-62,73].

In this work differences between values of the n_o, n_e, Δn, α_o, α_e, effective geometry parameter α_{eg}, average polarizability α_{ave}, polarizability anisotropy $\Delta\alpha$, *Q* and β for the heating and cooling processes have been found. Differences between mentioned above quantities for the heating and cooling processes are connected with distinction in character of structural transformation between *ordered structure* (nematic mesophase) → *disordered structure* (isotropic liquid) by the heating process and *disordered structure* (isotropic liquid) → *ordered structure* (nematic mesophase) by the cooling process. These differences can be also connected with differences in intermolecular interactions during the heating and cooling processes.

By application of liquid crystals as working elements in technical and technological devices at the *heating – cooling* condition is necessary to takes into consideration availability of the thermal hysteresis in the thermotropic, thermo-morphologic and thermo-optical properties and differences in the *n*, n_e, n_o, Δn, α_e, α_o, *Q* and β values for the heating and cooling processes.

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