Nonlinear thermotropic and thermo-optical behaviour of planar oriented textures in nematic liquid crystals at phase transitions

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Thermotropic, thermo-morphologic and thermo-optical properties of the planar oriented nematic liquid crystals have been investigated for large temperature interval and especially for the direct *nematic – isotropic liquid* and the reverse *isotropic liquid – nematic* phase transition regions. Temperature dependences of the optical transmission, absorption coefficient and optical birefringence for both heating and cooling processes were obtained. Nonlinear thermotropic and thermo-optical behaviour and temperature hysteresis for the optical transmission, absorption coefficient and optical birefringence at the phase transitions has been found.

Keywords: Liquid crystals; Nematic; Phase transitions; Texture; Optical transmission; Optical birefringence.

1. INTRODUCTION

Liquid crystals have mobile structures which are very sensitive to various external effects and boundary conditions. These materials display anisotropies in the optical, electrical and magnetic properties, exhibit unusual physical properties and are attractive and perspective materials for application in special liquid crystalline devices [1-4]. Oriented textures of liquid crystals are the active elements of these devices. Liquid crystalline devices usually work at different thermal regimes, within various temperature intervals and in different climatic conditions. Besides, liquid crystals are attractive for application as reversible materials in the recording thermo-optical systems for heating $\longleftrightarrow$ cooling processes. Therefore studies of the thermotropic and thermo-optical properties of liquid crystals, which can be switched at *mesophase–isotropic liquid* and *isotropic liquid–mesophase* phase transition temperatures, are important topics from both fundamental and application points of view.

In this work we are interested in the connection between thermo-morphologic, thermotropic and thermo-optical properties of the planar oriented nematic mesophase for a large temperature interval. Our objective was to study the character of temperature dependences of the optical transmission (OT) and the absorption coefficient (AC) in monomorphic nematogens for the direct *nematic mesophase–isotropic liquid* and the reverse *isotropic liquid–nematic mesophase* phase transitions, to determine the character of temperature dependences of the optical birefringence (Δn) and to calculate the widths of the biphasic regions of these transitions.

2. EXPERIMENTAL

The liquid crystals, used in this study, were n-(4-methoxybenzylidene)-4'-n-butylaniline (MBBA) and the binary mixture of n-(4-methoxybenzylidene)-4'-n-butylaniline with n-(4-ethoxybenzylidene)-4'-n-butylaniline (MBBA+EBBA). These materials are classic nematogens and exhibit enantiotropic nematic mesophase in sufficiently large temperature interval. The samples used in this work were the sandwich-cells. Reference surfaces of the samples were the optical glass plates. The sandwich-cell was constructed by two glass surfaces, spacer and glue. The thickness of liquid crystalline layer was determined as 20μm. The glass reference surfaces were preliminary carefully cleaned using alcohol and acetone. Then, they were washed in an ultrasonic bath by the bidistilled and deionized water and dried in a drying oven at 313 K during 2 hours.

The temperature dependences of the OT have been investigated using the special thermo-optical set-up. Our set-up consists of the light source as He-Ne laser, special heater-thermostat, the 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 during the optical measurements was 0.7 Kmin–1. For investigations of the OT character, the sample with planar orientation was placed between crossed polarizes that make 450 with the nematic direction and perpendicularly to the incident light. The OT values and the corresponding temperatures have been registered by the video-camera and temperature control system.

Investigations of the thermotropic properties and peculiarities of the biphasic regions of the *nematic–isotropic liquid* (N–I) and *isotropic liquid–nematic* (I–N) phase transitions have been carried out by means of the capillary temperature wedge (CTW) method. This method allows to obtain simultaneously all thermal states of the liquid crystal, to study the thermotropic properties, to determine the phase transition temperatures and to calculate the linear and temperature widths of the biphasic regions of the transitions with an accuracy not less than ±2.010–3 mm and ±10–3 K, respectively [5-7].

The studies of the thermo-morphologic properties of MBBA and MBBA+EBBA have been carried out by means of the polarizing optical microscopy (POM) with using of the optical filters, λ – plates and Berek compensator. Our set-up consists of the trinocular polarizing microscope, microphotographic system, special heater-thermostat and digital temperature control system.

In this study the sandwich-cells with the planar orientation of liquid crystal were used. The rubbing method has been applied for creation of the planar orientation of nematic mesophase in MBBA and MBBA+EBBA [8-10]. Homogeneity of the planar orientation has been examined by the

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TABLE 3: CFeatures of the direct and reverse phase transitions for the planar oriented and non-oriented textures of MBBA and MBBA+EBBA.

Type of liquid crystal	Type of textures	Phase transition temperatures, K		Temperature widths of biphasic regions, K	
		N–I	I–N	N–I	I–N
MBBA	Non-oriented	316.6	312.4	0.526	0.956
	Planar	317.6	314.7	0.990	1.371
MBBA+EBBA	Non-oriented	321.1	319.1	0.669	1.030
	Planar	324.5	321.4	1.789	1.942

POM and estimated by the optical polarization (OP) degree. The value of the OP degree has been determined as

$$P = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \tag{1}$$

Here I_{max} is maximum and *Imin* is minimum intensity of the OT for the samples which were placed between crossed polarizers.

3. RESULTS AND DISCUSSIONS

Investigations showed that the planar oriented samples of MBBA and MBBA+EBBA exhibit interesting thermomorphologic behaviour. Namely, any changes of the planar texture have not been observed by heating of the sandwich-cell within sufficiently large temperature interval. The value of the OP degree within this temperature interval was stable. Then, the sharp texture transformations and destruction of the planar orientation at 317.6 K for MBBA and at 324.5 K for MBBA+EBBA have been observed. The texture transformations and destruction of the planar orientation took place in definite and sufficiently narrow temperature intervals. These intervals are the biphasic regions of the direct N–I phase transition, where simultaneous coexistence of nematic mesophase and isotropic liquid has been observed for MBBA and MBBA+EBBA. An abrupt decrease of the OP in these biphasic regions has been also observed. The temperature widths of the biphasic regions of the direct N–I phase transition were calculated by the CTW method. These widths were as Δ TNI (MBBA)= 0.990 K for MBBA and Δ TNI (MBBA+EBBA) = 0.880 K for MBBA+EBBA (Table 1). At the temperatures higher than 318.6 K for MBBA and higher than 325.4 K for MBBA+EBBA, the samples were in isotropic liquids states. In this states the isotropic background was observed by means of the polarizing microscope.

By cooling the sandwich-cells from isotropic liquid to nematic mesophase an appearance of the biphasic regions of the reverse I–N phase transition at 312.8 K for MBBA and at 321.4 K for MBBA+EBBA have been observed. The temperature widths of the biphasic regions of the reverse I–N phase transition were also calculated by the CTW method. These widths were ΔTIN (MBBA) = 1.371 K for MBBA and ΔTIN (MBBA+EBBA) = 1.770 K for MBBA+EBBA. Then, by cooling of the sandwich-cell and at the temperatures lower than 314.2 K for MBBA and 323.2 K for MBBA+EBBA the planar textures were occurred again.

In this work we are also interested in temperature behaviour of the OT and connection between the thermomorphologic and thermo-optical properties in the planar oriented textures of MBBA and MBBA+EBBA. Investigations showed that MBBA and MBBA+EBBA display similar temperature behaviour of the OT (Fig.1). Namely, the OT was not generally changed by increasing temperature in definite temperature interval. This temperature interval corresponds to an interval where the planar orientation of nematic mesophase in MBBA and MBBA+EBBA is kept. Then, by heating of the samples in narrow temperature intervals the jump-like changes of the OT for MBBA and MBBA+EBBA have been observed. These temperature intervals were as 0.990 K for MBBA and as 0.880 K for MBBA+EBBA (Table 1 and Fig. 1). I.e. the jump-like changes of the OT up to a minimum values took place in the biphasic regions of the N–I phase transition. These temperature regions with the minimum values of the OT in MBBA and MBBA+EBBA correspond to isotropic liquid state. The minimum values of the OT were kept by the following heating.

By cooling the liquid crystals from state with the minimum value of the OT, the jump-like changes and sharp increase of the OT in sufficiently narrow temperature interval have been observed (Fig.1). These temperature intervals were as 1.371 K for MBBA and as 1.770 K for MBBA+EBBA (Table 1 and Fig.1), i.e. these intervals correspond to the biphasic region of the I–N phase transition. Then, by further cooling the liquid crystals in definite temperature regions an increase of the OT to the maximum value has been observed. These temperature regions correspond to nematic mesophase in the planar orientation.

In this work the temperature dependences of the AC for the planar oriented nematic mesophase in MBBA and MBBA+EBBA have been determined. For the planar oriented samples, which have been placed between crossed polarizers that make 450 with the nematic direction, the intensity of the incident *I0* and transmitted *I* lights is connected with the AC and thickness of the liquid crystalline layer as

$$I = I_0 e^{-\alpha d} \tag{2}$$

Here *a* is the absorption coefficient and *d* is the thickness of liquid crystalline layer.

Using Eq.(2) the temperature dependences of the α for the heating and cooling MBBA and MBBA+EBBA have been calculated (Fig.2). As it is seen in Fig.2, the α has minimum value in nematic mesophase and this value keeps practically as constant in the nematic mesophase temperature interval. But the α has maximum value in isotropic liquid and this value keeps practically as constant in isotropic liquid temperature interval. In the biphasic regions, the jump-like changes and abrupt increase of the α take place.

Thus, the changes of the thermo-morphologic and thermotropic properties of MBBA and MBBA+EBBA in the planar orientation for the N–I and I–N correspond to the behaviour of the thermo-optical properties for these transitions. Besides, the nonlinear temperature behaviour of the OT and AC takes place in the biphasic regions of these phase transitions.

As it is seen in Figs. 1,2 and Table 1, the temperatures of the direct and the reverse phase transitions in the planar oriented nematic mesophase of both MBBA and MBBA+EBBA do not coincide to each other. Namely, the differences between temperatures of the direct and reverse phase transitions were as 4.8 K for MBBA and 3.1 K for MBBA+EBBA. Investigation showed also that temperature width of the biphasic regions for the N–I phase transition was narrower than this width for the I–N phase transition. These results show that for the phase transition between nematic mesophase and isotropic liquid in planar oriented textures the thermic hysteresis takes place. We would like to note that nonlinear behaviour of the optical parameters and the thermic hysteresis for these parameters at the phase transition between mesophase and isotropic liquid were also observed for thermotropic mesogen in [11-13] and for polymer liquid crystals in [14-16].

As it is known from theoretical studies [17-20], the phase transitions between nematic mesophase and isotropic liquid are the first order transitions. These transitions are characterized by an existence of the biphasic region with temperature limits as T^* and T^{**} and also by an availability of the thermic hysteresis. T^* is low temperature limit and T^{**} is high temperature limit of the biphasic region. The $\Delta T = T^{**} - T^*$ value determines the temperature width of the biphasic region. Such type of the thermic hysteresis and existence of the biphasic regions for phase transitions between nematic mesophase and isotropic liquid for various liquid crystals were also observed by various scientists in [21-26]. Thus, the results, obtained in this research, are in good conformity with the theoretical studies.

We would like to note that temperatures of the direct N–I and reverse I–N phase transitions and the widths of the biphasic regions of these transitions for the planar oriented nematic mesophase are different from corresponding temperatures and widths of the biphasic regions for the non-oriented nematic mesophase (Table 1). These differences in temperatures of the phase transitions are connected with differences in the anchoring energy between liquid crystalline molecules and reference surfaces of the sandwich-cell for the planar oriented and non-oriented cases. Namely, the non-oriented textures were obtained in the sandwich-cells with non-elaborated reference surfaces, but the planar oriented textures were obtained in the sandwich-cell with surfaces, which were treated by the rubbing method. The anchoring energy between liquid crystalline molecules and the surfaces for the case of elaborated surfaces is higher than this energy for the case of non-elaborated surfaces. Therefore, it is clear that an increase of the anchoring energy leads accordingly to an increase of the thermal energy, which is necessary to carry out the phase transition between nematic mesophase and isotropic liquid.

We are also interested in temperature behaviour of the Δn in MBBA and MBBA+EBBA (Fig. 3). The Δn have been calculated by Eq.3:

$$I = I_0 \sin^2 \frac{\pi d \Delta n}{\lambda} \tag{3}$$

Here, d is the thickness of liquid crystalline layer in the sandwich-cell and λ is the wave length of the light source.

As it is seen in Fig.3, the Δn values keep stable in temperature interval of nematic mesophase by the heating of the sandwich-cell. By drawing near to the N–I phase transition a sharp decrease of the Δn in definite temperature interval was observed. Besides, as the calculation showed, the values of the OP also sharply decrease in this temperature interval**.** By comparison of the thermo-morphologic properties with the temperature behaviour of the OT and Δn (Fig.1 with Fig.3) it is seen that the sharp increase of the Δn values takes place in the biphasic region of the N–I phase transition. Besides, a decrease of the Δn values to the zero takes place in isotropic liquid state. We would like to note that, because of the thermic hysteresis, formation of the planar texture and appearance of the birefringent properties by cooling of samples were observed by temperature lower than that, where a destruction of the planar texture and disappearance of the Δn took place (Table 1).

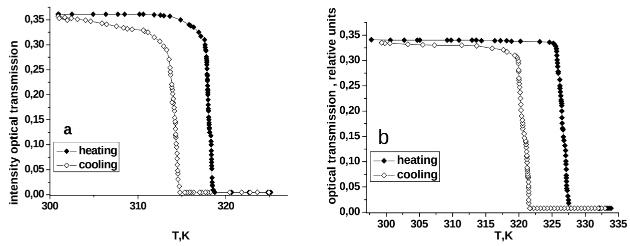

FIG. 1: Temperature dependences of the optical transmission for MBBA (a) and MBBA+EBBA (b).

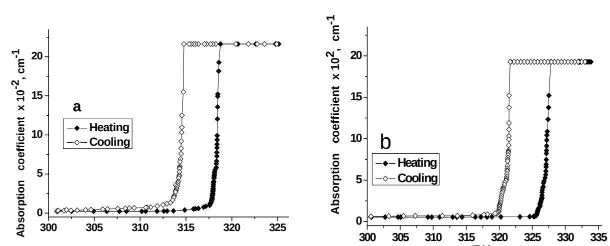

FIG. 2: Temperature dependences of the absorption coefficient for MBBA (a) and MBBA+EBBA (b).

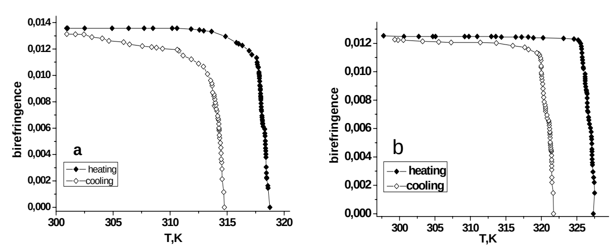

FIG. 3: Temperature dependences of the optical birefringence for MBBA (a) and MBBA+EBBA (b).

In conclusion we would like to note that, the character of temperature dependences of the Δn by the heating and cooling of MBBA and MBBA+EBBA corresponds to the character of temperature transformation of the macroscopic order parameter of nematic mesophase at the first order phase transition between nematic mesophase and isotropic liquid [9,18,20]. Besides, character of the Δn in the planar oriented nematic mesophase of MBBA and MBBA+EBBA for the *nematic* $\longleftrightarrow$ *isotropic liquid* phase transition region is in good conformity with the theoretically predicted character of the temperature dependences of the orientational order parameter $Q = Q\ (T)$ at the first order transition between nematic mesophase and isotropic liquid [9,18,20,27].

4. SUMMARY

The results obtained in this study can be summarized as follows:

– The temperature behaviour of the optical transmission, absorption coefficient, optical birefringence and the temperature transformations of the planar oriented textures of nematic mesophase in MBBA and MBBA+EBBA were investigated.

– A complete conformity between thermotropic, thermomorphologic and thermo-optical properties of the planar oriented nematic mesophase in MBBA and MBBA+EBBA was found. The temperature behaviour of the optical transmission, adsorption coefficient and optical birefringence corresponds to character of texture transformation in the liquid crystals for both the heating and cooling processes.

– The nonlinear behaviour of the optical transmission and absorption coefficient by the heating and cooling of the planar oriented nematic mesophase in MBBA and MBBA+EBBA for the biphasic regions of the direct N–I and reverse I–N phase transitions have been observed. The temperature hysteresis of the optical transmission and adsorption coefficient at the direct and reverse phase transitions has been found.

– The differences in temperatures of the phase transitions between nematic mesophase and isotropic liquid and in temperature widths of the biphasic regions of these transitions for the planar oriented and non-oriented textures have been found. These differences are connected with differences in the anchoring energy between liquid crystalline molecules and reference surfaces of the sandwich-cells for the oriented and non-oriented textures of nematic mesophase.

– Character of the temperature dependences of the optical birefringence in the planar oriented nematic mesophase of MBBA and MBBA+EBBA is in good correspondence with the theoretically predicted character of the temperature dependences of the orientational order parameter $Q = Q\ (T)$ in the phase transition region at the first order transition between nematic mesophase and isotropic liquid [9,18.20,27].

5. ACKNOWLEDGEMENT

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[1] P. Yeh and C. Gu, Optics of Liquid Crystal Displays, Wiley-Interscience, New York, 1999.
[2] E. Lueder, Liquid Crystal Displays: Addressing, Schemes and Electro-Optical Effects, Wiley, New York, 2001.
[3] G. Crawford, Flexible Flat Panel Displays, Wiley, New York, 2005.
[4] D. K. Yang and S.-T. Wu, Fundamentals of Liquid Crystal Devices, Wiley, New York, 2006.
[5] A. Nesrullajev, DSc Dissertation, Institute of Physics, Academy of Sciences, Baku, 1992.
[6] A. Nesrullajev, S. Salihoðlu and H. Yurtseven, Intern. J. Modern Phys. B. **12** 213 (1998).
[7] S. Yıldız and A. Nesrullajev, Physica A **385** 25 (2007).
[8] J. Cognard, Alignment of Nematic Liquid Crystals and Their Mixtures, Gordon and Breach Sci. Publ., London-New York-Paris, 1982.
[9] A.S. Sonin, Introduction to the Physics of Liquid Crystals, Science Publ., Moscow, 1983.
[10] H. Yokoyama, in: P.J. Collings, J.S. Patel (Eds.), Handbook of Liquid Crystals, Oxford University Press, New York-Oxford, 1997, pp.179-235.
[11] N. Avcı, A. Nesrullajev and ł. Oktik, Journ. Optoelectr. Adv. Mater. **9** 415 (2007).
[12] M. Sharma, C. Kaur, J. Kumar and K. Chandramani Singh, J. Phys.: Condens Matter. **13** 7249 (2001).
[13] S. Yıldız, . Pekcan, A.N. Berker and H. zbek, Phys. Rev. E. **69** 031705 (2004).
[14] Y. Hotta and T. Yamaoka, Chem. Mater. **7** 1793 (1995).
[15] C.E. Hoppe, M.J. Galante, P.A. Oyanguren and R.J.J. Williams, Mater. Sci. Eng. C **24** 591 (2004).
[16] A. Jannesari, S.R. Ghaffarian and A. Molaei, Reactive & Functional Polym. **66** 1250 (2006).
[17] M.A. Anisimov, V.I. Labko, G.L. Nikolaenko and I.K. Yudin, JETF (Sov.) **45** 111 (1987).
[18] J.C. Toledano and P. Toledano, The Landau Theory of Phase Transition, World Scientific, Singapore, 1987.
[19] M.A. Anisimov, Mol. Cryst. Liq. Cryst. A**162** 1 (1988).
[20] S. Singh, Phys. Repts. 324 107 (2000).
[21] G.A. Oweimgreen and M.A. Morsy, Thermochim. Acta **325** 111 (1999).
[22] G.A. Oweimgreen and M.A. Morsy, Thermochim. Acta **326** 37 (2000).
[23] G.S. Chilaya, Z.M. Elashvili, M.A. Gogadze, S.P. Tavzarashvili, K.D. Vinokur and S.A.Pikin, Liq. Cryst. **5** 1195 (1989).
[24] A. Nesrullajev and B. Bilgin Eran, Mater. Chem. Phys. **93** 21 (2005).
[25] S. Hosaka, K. Tozaki, H. Hayashi and H.Inaba, Physics B **337** 138 (2003).
[26] H.K. Cammenga, K. Gehrich and S.M. Sarge, Thermochim. Acta **446** 36 (2006).
[27] A. Nesrullajev, H. Yurtseven and N. Kazanci, Liquid Crystals: Structures, Properties, Applications, Ege University Publ., Izmir, 2000.